Studies of Hydrogen Bonding in Protonic Ionic Liquids and Their Binary Mixtures

by

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DECLARATION

The work described in this thesis was carried out in QUILL, within the School of Chemistry and Chemical Engineering at the Queen’s University of Belfast, or ITQB NOVA, University of Lisbon or ISIS Rutherford Appleton Laboratories, between November 2013 and November 2016. This thesis has not been submitted for any other degree or institution and is the original work upon my own research, except where acknowledged by reference.

Isabel Vázquez Fernández
January, 2018
This thesis is dedicated to my mum, Manuela

and to the memory of my supervisor

Prof. Kenneth R. Seddon, OBE
“I learned that courage was not the absence of fear, but the triumph over it.”
From “Long walk to freedom”
Nelson Mandela (1994)

“Begin at the beginning,” the King said, very gravely, "and go on till you come to the end: then stop.”
From “Alice in Wonderland”
Lewis Carroll (1865)
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ABSTRACT

It is nearly thirty years since the first report of hydrogen-bonding in room-temperature ionic liquids, which was met by an immediate chorus of derision. Today, it is universally accepted, but still has not received the degree of attention that it deserves.

The focus of this thesis was the study of hydrogen-bonding in protonic ionic liquids and their binary mixtures. To achieve it, several high purity alkylammonium nitrate ionic liquids were synthesised and characterised by elemental analysis, Karl Fisher titration, $^1$H and $^{13}$C NMR, DSC and TGA. The study was focussed on two aspects, firstly the comparison of the homologous $[\text{N}_n\text{O}_0\text{O}_n][\text{NO}_3]$ series ($n = 2, 3, \text{or} 4$) and secondly the related series $[\text{N}_0\text{O}_2\text{O}_2][\text{NO}_3]$, $[\text{N}_0\text{O}_2\text{O}_2][\text{NO}_3]$, and $[\text{N}_2\text{O}_2\text{O}_2][\text{NO}_3]$ (where there is no hydrogen-bonding in the last salt). This is the first systematic study of mixtures of protonic alkylammonium nitrate salts.

Physicochemical properties, such as density, dynamic viscosity and ionic conductivity, were determined to investigate how hydrogen bonds influence the macroscopic features of these pure compounds and their binary mixtures, in a collaboration with a research group at ITQB (Lisbon). In addition, a mathematical model based on a neural network was performed to establish the relationship between physical properties and the intrinsic characteristics of these systems, such as temperature, composition and molecular weight, in a collaboration with a research group from Complutense University of Madrid.

All these ionic liquids: ethylammonium nitrate, propylammonium nitrate, butylammonium nitrate, diethylammonium nitrate, triethylammonium nitrate, and tetraethylammonium nitrate, their binary mixtures and their deuteriated analogues were investigated by the vibrational spectroscopic methods - infrared, and Raman spectroscopies, and inelastic neutron scattering - and the results were supported by theoretical calculations performed at ISIS Rutherford Appleton Laboratories. The selective deuteriation of the pure salts, and their deuteriated binary mixtures, was an important tool to determine the manner in which the hydrogen bonding networks were organised.

In a preliminary study, the temperature dependence of the proton dynamics of pure methylammonium nitrate and its deuteriated analogue were evaluated by quasi-elastic neutron scattering (QENS), collected at ISIS Rutherford Appleton Laboratories. The results reported here suggest that a jump diffusional model accurately represents its molecular motion.
This thesis reports, for the first time, the actual hydrogen bond frequencies at low wavenumber for a series of protonic ionic liquids. This work, and its future extensions, thus may have a significant impact on our understanding of the relationship between the chemical structure of ionic liquids and the physicochemical properties.
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ABBREVIATIONS

ANN Artificial neural network
DSC Differential scanning calorimetry
DWF Debye-Waller factor
EISF Elastic incoherent structure factor
FWHM Full width at half maximum
HNN Hidden neuron number
HWHM half width at half maximum
ILL Institut Laue Langevin
INS Inelastic neutron scattering
IR Infrared
ITQB Instituto de Tecnologia Química e Biológica
MD Molecular dynamic
MPE Mean prediction error
MPL Multilayer perceptron
MSD Mean-Square Displacement
NMR Nuclear magnetic resonance
QENS Quasi-elastic neutron scattering
TGA Thermal gravimetric analysis
XRD X-ray diffraction
1 Introduction
1.1 Ionic liquids

1.1.1 A little history

Ethylammonium nitrate was the first recognised low melting salt (melting point 12 °C); it was synthesised by Walden, in 1914, who identified it as the first of a new class of liquids [1]. Ethanolammonium nitrate was reported in 1888 [2], but it was not recognised as anything more than a routine compound. Over 100 years after Walden's paper, alkylammonium nitrates are still being studied by many scientists.

Conventionally, ionic liquids were defined as salts (made of ions, cations and anions) that are liquid at a temperature lower than 100 °C [3]. Over the years, there have been many alternative names used for ionic liquids, such as, 'low temperature molten salts', 'liquid organic salts' 'ambient temperature molten salts', 'ionic fluids' and 'room temperature molten salts'. Although the term most widely used was 'molten salts' (or simply 'melts'), there are some fundamental features to distinguish between 'ionic liquids' and 'molten salts'. The strong ion-ion interactions in ionic liquids are not necessarily present in molten salts [4]. However, it has been recommended the term 'ionic liquids' be applied to both 'room temperature ionic liquids' and 'molten salts', and simply defined as 'liquids which contain only ions'.

Twenty years after the synthesis of ethylammonium nitrate, Graenacher showed that 1-ethylpyridinium chloride cause the dissolution of cellulose [5]. The new cellulose solution was suitable for various chemical reactions, such as etherification or esterification, as the cellulose was present in a very reactive form. Hurley and Wier published a patent in 1948 describing the use of a mixture of aluminium(III) chloride and ethylpyridinium bromide, which is liquid at room temperature, as an electrolyte for the electrodeposition of aluminium [6]. In 1964, Gordon suggested for the first time the use of tetraalkylammonium nitrates as media for organic reactions [7], and in the early 70s, tetraalkylammonium salts were proposed for electrochemical [8] and homogenous catalytic [9] applications. Ionic liquids were taking off.

The Osteryoung group studied the use of a melt of aluminium(III) chloride and ethylpyridinium bromide for alkylation in the Friedel-Crafts reaction [10] and described an aluminium(III) chloride / 1-butylpyridinium chloride salt liquid system, in a wide range of compositions [11]. Poole and coworkers proposed ethylammonium nitrate as a stationary phase in gas-liquid chromatography [12]. Magnuson introduced, for the first time, the use of ionic liquid with biological systems: ionic liquid-enzyme [13]. In 1996, Seddon proposed the use of ionic liquids for clean technology [14], and since then, there has been an explosion of academic research using ionic liquids in a variety of scientific and engineering disciplines. There are many good reasons for that. The number of possible combinations of cation and anion to obtain an ionic liquid is...
extremely large, $10^6$, if compared with the number of existing organic solvents available. Commonly used cations and anions are listed in [15]. Ionic liquids have sometimes been considered as “green solvents”, particularly due to their extremely low volatility [16]. However, this is only one aspect of a green solvent, and factors such as toxicity and biodegradability must also be considered; ionic liquids can be designed to be green but are not intrinsically green. Compared to conventional organic solvents, ionic liquids offer several advantages for synthesis and extraction processes that even, in some cases, would be impossible because of the limited range of miscibility and solubility of organic solvents [3].

**Figure 1.1** Representative cations and anions of the most commonly used in ionic liquids [15].

### 1.1.2 Current ionic liquid applications

There are many reviews and books about ionic liquids, so this section merely summarises some recent works which have been published. Ionic liquids are emerging as important materials in many other disciplines: lubrication [17], drug delivery [18], solar cells [19].

The first publicised industrial ionic liquid application was in 2002. The BASIL process, produces a protonic ionic liquid, 1-methylimidazolium chloride, [Hmim]Cl [20]. By replacing triethylamine with 1-methylimidazole, the formation of 1-methylimidazolium chloride, an ionic liquid, avoided the formation of
triethylammonium chloride, which is a dense insoluble paste difficult to handle and separate. Following this announcement, a broad range of industrial applications has been reported [21]. Since this review was published almost ten years ago, ionic liquids have entirely established in all the disciplines (see Figure 1.2).

![Figure 1.2 Commercial applications of ionic liquids [21].](image)

The use of ionic liquids is in high demand. The reduction of the ozone layer has concerned many scientists since almost all countries in the world signed the Montreal Protocol to ban the gases that destroy atmospheric ozone [22]. Almost three decades of uncertainty had passed when, in October 2015, the Antarctic ozone hole set a record of seriousness.

![Figure 1.3 A view of the total ozone over the Antarctic pole (left to right) in August 2014, October 2015 and June 2016. The purple and blue colours are where there is the least ozone, and the yellows and reds are where there is more ozone [23].](image)
The current situation is that the Antarctic hole has been reduced to 4 million square kilometres, roughly the area of the European Union (excluding the UK) according to recent research (see Figure 1.3) [24]. Although there is evidence that the main cause of the ozone hole is chlorinated organic compounds (chlorofluorocarbons, CFC), Shindell et al. [25] states: “Greenhouse gases warm the Earth’s surface but cool the stratosphere radioactively, and therefore affect ozone depletion.” It is essential, therefore, to reduce the greenhouse effect by reducing greenhouse gases, such as carbon dioxide.

Although some strategies for reducing carbon dioxide emissions, usually involving reacting CO$_2$ with organic molecules to generate high value-added products, have been proposed, these are unlikely to have significant impact on CO$_2$ level in the atmosphere. A more promising strategy for trapping carbon dioxide is named “carbon dioxide capture and storage” (CCS) [26]. CCS is a technology aimed at reducing greenhouse gases emissions generated by the treatment of fossil feedstock during industrial processes, which involves capture, transport and long-term storage of CO$_2$. For many years, this strategy has been exploited by chemical or physical sorption (depending on the interaction between CO$_2$ and the sorbent) in solids, liquids or membranes, Figure 1.4.

![Figure 1.4 Strategies for post-combustion of CO$_2$ capture using physisorption or chemisorption [26].](image-url)
The most common physical sorbents are activated carbons, organic liquids, porous organic polymers, zeolite 13X unmodified periodic mesoporous silica, and traditional metal organic frameworks. However, their use requires extremely conditions of pressure and temperature due to the weak interaction between the sorbate and the sorbent and the low selectivity toward CO\(_2\) [26]. In 1999, Blanchard et al. [27] proposed for the first time the use of 1-butyl-3-methylimidazolium hexafluorophosphate ([C\(_4\)mim][PF\(_6\)]) for solubility measurements of CO\(_2\). Since then, there has been an explosion of academic research that has concluded that the absorption of CO\(_2\) is too low to use in a large-scale industrial process. The reason is that during physisorption, no chemical reaction takes place, as there are no chemical interaction sites in these ionic liquids. Davis and coworkers [28] published the first functionalised ionic liquid for CO\(_2\) chemisorption capture, based on an imidazolium cation covalently tethered to a primary amine moiety. This was found to capture 0.5 mol of CO\(_2\) per mole of ionic liquid under ambient pressure, Figure 1.5.

Subsequently, there have been many publications exploring CO\(_2\) chemisorption with other functionalised ionic liquids [29], but none of these systems have been commercialised.

Replacing organic solvents, which are usually highly volatile, with ionic liquids has been proposed for greener industrial processes [30]. However, there are still many issues to be resolved:

- Many ionic liquids, and their by-products are toxic.
- Many ionic liquids are not biodegradable.
- Many ionic liquids are expensive.

In addition, the commercial production of many ionic liquids is not green [31] because quite often the synthesis of “clean” ionic liquids include a series of reactions.
where organic solvents are involved. The term “green” should be reconsidered and applied only to an ionic liquid if the ionic liquid itself, and the process used to generate it, are green, and if all the twelve principles of green chemistry are applied to the entire process [32]. Scale is also an important factor to be considered. It is not the same amount of waste associated with laboratory-scale ionic liquid preparations as for those that are produced by industrial-scale syntheses.

![Diagram](image)

**Figure 1.6** SWOT analysis of the preparation of 1-alkyl-3-methylimidazoliun halide salts and their subsequent purification [32].

In order to assess the relationship between the amount of the desired product and the waste generated in each process, several methods have been used, such as: atom economy [33], and the E-factor [34]. Deetlefs and Seddon [32] also applied a SWOT analysis to estimate the green credentials of several series of ionic liquids. SWOT (strengths, weaknesses, opportunities, threats) is a tool commonly used for the analysis of strategic plans. It gives an overview of the advantages and disadvantages of a given process, taking into account both the present and the future consequences. For instance, **Figure 1.6** shows SWOT analysis of the preparation of 1-alkyl-3-methylimidazoliun halide salts and their subsequent purification. Examination of the SWOT analysis indicated that, although the procedure is dirty, there are some strengths, such as: simple, and well-established process, and can be performed in most common laboratories with no need for expensive or specialised equipment. The atom economy is 100%, but the E-factor is poor as both separation and purification generate large amounts of waste solvent. It has been proved that, by the combination of SWOT analysis, atom economy and E-factor, we have a critical point of view and an easier overall vision about the greenness of the preparation and purification of 1-alkyl-3-methylimidazoliun halide salts [32].
Hulsbosch et al. [35] have suggested a way to improve the green character of ionic liquids by using renewable compounds as ionic liquid precursors: sugars from cellulose, aromatic aldehydes from lignin, amino acids and amino alcohols from proteins, chitin, starch and other polysaccharides, and a diverse group of other compounds such as fatty acids from vegetable or algae-derived oils. On the basis of their structure, green character, thermal stability and other characteristics, these bio-based ionic liquids were compared with the conventional ionic liquids and confirmed to be useable in the selected processes as metal-ion separations, organocatalysts or reaction media, Figure 1.7.

![Image](image.png)

**Figure 1.7** Scheme of a cycle proposed by Hulsbosch et al. [35]. Ionic liquids are synthesised from renewable and available feedstocks and then used in different industrial areas.

Many research groups are working on different environmentally-friendly pathways to obtain ionic liquids. Imidazolium ionic liquids are known to dissolve biomass and represent a universal platform for biomass treatment. However, the high cost of these ionic liquids limited their large-scale industrial application. To replace them, protonated trialkylammonium ionic liquids have been synthesised from aromatic aldehydes derived from lignin and hemicellulose [36]. These polymers represent abundant and inexpensive waste streams from several biomass-processing industries including textiles, pulp/paper, and the major by-products of lignocellulosic biofuel production. Reductive amination of the aromatic aldehydes added to a treatment with phosphoric acid provided three ionic liquids in excellent yields without the need of any purification process: $N$-ethyl-$N$-(furan-2-ylmethyl)ethanammonium hydrogenphosphate $[\text{FurEt}_2\text{NH}]\text{[H}_2\text{PO}_4\text{]}$, $4$-$((\text{diethylamino})\text{methyl})\text{-2-methoxyphenol hydrogenphosphate [VanEt}_2\text{NH}]\text{[H}_2\text{PO}_4\text{]}$, and $N$-ethyl-$N$-
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(4-methoxybenzyl)ethanammonium hydrogenphosphate \([p\text{-AnisEt}_2\text{NH}][\text{H}_2\text{PO}_4]\). Structures of these three ionic liquids are shown in Figure 1.8.

![Figure 1.8 Lignin and hemicellulose ionic liquids evaluated in this study (1) \([\text{FurEt}_2\text{NH}][\text{H}_2\text{PO}_4]\), (2)\([\text{VanEt}_2\text{NH}][\text{H}_2\text{PO}_4]\) and (3) \([p\text{-AnisEt}_2\text{NH}][\text{H}_2\text{PO}_4]\) [36].](image)

Compositional analysis and molecular modelling data suggested high lignin removal efficiency and these results indicate that biomass-derived ionic liquids are very effective in biomass pre-treatment [36].

![Figure 1.9 Hypothetical biorefinery process using ionic liquids derived from lignocellulosic biomass [36].](image)

Some combinations of cations and anions exhibit extremely high electrochemical and thermal stability, low volatility, and ionic conductivity, which
allows the design of optimised electrolytes for batteries, actuators, super-capacitors, thermo-electrochemical cells, and dye sensitised solar cells [37]. Lithium-ion batteries are nowadays considered one of the most important energy storage devices, and now are the subject of many papers. Kitagawa et al. [38] reported for the first time the dynamics of lithium ion-doped ionic liquids in the micropores of metal-organic frameworks in terms of the self-diffusion. This system enabled the study of the conductive mechanism of lithium ions.

CuS is a promising option for lithium-ion batteries, biosensors, photothermal conversion, gas sensors, catalysts, solar cell devices, and superionic materials, because of its properties as a semiconductor, and its relatively cheap price, as well as its low toxicity and high abundance. Nevertheless, CuS also presents a low area capacitance, low energy densities, and slow rate capabilities. It might be possible to modify these properties by controlling the structure and the composition of CuS materials using ionic liquids [39]. Zheng et al. [40] reported the use of [C₄mim]₂[Cu₂Cl₆] (where [C₄mim]⁺ = 1-butyl-3-methylimidazolium), as a copper source in the synthesis of CuS for high performance supercapacitors.

Platinum and palladium are usually present together in many ores. Due to similarities in hydrometallurgical properties, purification of these metals is tedious, but essential for high technology purposes, from aerospace to automotive catalytic converters [41]. The work of Chainet et al. [42] demonstrated an efficient separation process for Pt(IV) and Pd(II) using 1-octyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide (bistriflamide; [NTf₂]) or trihexyltetradecylphosphonium bromide, ([C₆mim][NTf₂] or [P₆₆₆₁₄]Br, respectively).

Kelley and Rogers [43] described the isolation of uranyl dicyanamide compounds. Due to the lack of experimental data on soft donor complexes of actinides and the difficulties of working with actinides and lanthanides, the isolation and characterisation of this compounds is a challenge. By using 1-ethyl-3-methylimidazolium dicyanamide ([C₃mim][N(CN)₂]) and N-butyl-N-methyl/pyrrolidinium dicyanamide ([C₄mpyr][N(CN)₂]), they studied the nature of f-element bonds to moderately soft donor atoms, such as nitrogen. The knowledge may help to separate the trivalent actinides and lanthanides, which appear together in spent nuclear fuel.

Studies of f-element speciation in ionic liquids have provided insight, allowing the design of ionic liquids, such as carboxyl-functionalised phosphonium salts, to target f-elements for specific separation [44].

A recently published paper shows that a combination of Au@Fe₃O₄ nanospheres covered with a room temperature ionic liquid increases the sensitivity of
detection of highly toxic As(III). The catalytic properties of the Au nanoparticles combined with the good adsorption capacity of Fe₃O₄ nanospheres toward As(III), helped by the good conductivity of 1-butyl-2,3-dimethylimidazolium bis[(trifluoromethyl)sulfonyl]amide, [C₄dmim][NTf₂], permit this system to show excellent performance for the detection of arsenic in water. Arsenic recovery was found between 90% and 110% by adding free As to the water [45].

The examples chosen above are not exhaustive, but serve to illustrate the diversity in application for ionic liquids.

1.1.3 Classification of ionic liquids

Ionic liquids are usually classified by their chemical structure, as is common for the organic solvents. However, in the case of ionic liquids, as there are so many potential combinations of anion and cation (Figure 1.1), it is often useful to create subcategories, which are related by common structural features. For many years, protic [46] and aprotic [47] ionic liquids were considered the two most common ionic liquids types, based on the classification of molecular solvent by Parker [48]: proton-donating (protic) and non-proton-donating (aprotic). A relevant distinction between protic ionic liquids and aprotic ionic liquids is the characteristic positive charge on the cation. In the case of aprotic ionic liquids, this positive charge is permanent and the cation does not dissociate. For protic ionic liquids the cation is in equilibrium with the neutral base and a proton. Where the anion is significantly basic, the ionic liquid dissociates (but not necessary completely) into a neutral base derived from the cation and a neutral acid derived from the anion. This dynamic will depend on the acid and base pair. It led to a debate, whether they should be consider ionic liquids or not [16]. Nevertheless, this classification is not as complete as it would seem. Recently, Davis and coworkers [49] reported an intermediate case of ionic liquids containing two different cations: one protic, and one aprotic. These showed features of both aprotic and protic ionic liquids. They have rich hydrogen bond and a Brønsted acid–base character similar to some protic ionic liquids, but very low apparent vapour pressures, usually seen in aprotic ionic liquids.

Several other types of ionic liquids are described in the literature, based on distinct structural features: chiral ionic liquids (show a chiral centre) [50], fluorous ionic liquids (a fluorocarbon moiety) [51], magnetic ionic liquids (content a paramagnetic atom/group) [52], solvate ionic liquids (coordinated ion) [53], or polymerised ionic liquids [54]. There are also aryl alkyl ionic liquids [55] and amino acid ionic liquids [56] seen in the literature. Those are classified according to the functionality present in either the cation or anion.
Within this thesis we introduce the term “protonic” and “aprotic” ionic liquids. We found the terms protic and aprotic too restrictive for the broad range of known ionic liquids. For example, 1-ethyl-3-methylimidazolium is conventionally described as aprotic. However, in the presence of strong base, the 2-proton dissociates to yield the free neutral carbene. This is a very different type of behaviour that is found for cations containing protonated amines. Thus, we introduce the term protonic ionic liquids to distinguish strongly acidic cations (i.e. those which contain readily dissociable protons) from protic ionic liquids, which contain very weakly acidic protons. By analogy an aprotic ionic liquid contains non-dissociable protons, and aprotic ionic liquid contain no protons at all.

1.1.4 Protonic ionic liquids
Protonic ionic liquids are of increasing importance in science and technology. They are formed by the transfer of a proton from a Brønsted acid, HA, to a Brønsted base, B. Protonic ionic liquids have at least one proton available for the formation of hydrogen bonding:

\[ B + HA \rightleftharpoons [BH]^+ + A^- \]  \hspace{1cm} (1.1)

They have very different properties from their aprotic analogues due to the presence of the exchangeable proton. As ionic liquids are entirely comprised of ions, in principle, the equilibrium shown in Equation (1.1) must lie substantially towards the right (e.g. the ionised forms) in order for this fluid to be considered a pure ionic liquid [16]. Otherwise, it would just be a mixture of free acid, free base, and salt. The presence of more than 1% of the neutral acid and base species would be considered a significant impurity. However, the degree to which the proton transfer occurs has not been quantified.

Canongia Lopes et al. [57] studied the relationship between the acid–base reactions implicit in the definition of protonic ionic liquids and their solutions, and the existence of reactive azeotropy. Their work suggested that the corresponding equilibrium constants are probably much lower than those expected based solely on the aqueous solution acidity data.

Even though, the importance of protonic ionic liquids has increased and there have been several papers in last few years, aprotic ionic liquids have received much more attention. In the field of lithium-batteries, almost all research has been focussed on aprotic ionic liquids as an alternative to the common electrolytic cells. However, recent studies have shown that protonic ionic liquids might be competitive with the commonly used aprotic ionic liquids, Figure 1.10 [37,58].
Amongst the advantages of protonic ionic liquids are their low cost and facile synthesis. Hence, detailed knowledge of protonic ionic liquids at a molecular structure level becomes a priority, as understanding is essential for the development of almost any successful application. In this regard, molecular dynamics simulations are important in order to complement experimental research, and provide a description of dynamic and structural properties [59]. A direct comparison between the simulation and experimental results allows the accuracy of the molecular dynamic simulations to be evaluated. Triolo and coworkers [59] performed several room-temperature simulations of solutions of lithium nitrate in ethylammonium nitrate.

Controlling the purity of an ionic liquid is essential, as it dominates the properties of the system [60]. The presence of residual water and chloride ion change the physical properties of ionic liquid dramatically. Recent interest in ionic liquid-water mixtures has been focussed, at least in part, by the desire to understand the changes in ionic liquid properties observed after contamination with water [61]. Computational models have predicted that at low concentration of water, the ionic liquids’ structure will still be relatively retained, while at higher water content, the fluid becomes an aqueous solution of a salt [62]. Despite the fact that the behaviour of individual protonic ionic liquids has been studied thoroughly [47a,63], there have been no significant studies of series of related protonic ionic liquids.

Ideally, the proton transfer in protonic ionic liquids is complete [46]; therefore, the only species present are cations and anions. There are several techniques to determinate how good is the transfer, and the Walden plot is the most common [64]. The Walden plot relates to the log of the equivalent conductivity, versus the log of the fluidity (inverse viscosity); therefore, it is necessary to know the density, viscosity and ionic conductivity of the systems. The position of the ideal line is fixed by using KCl solutions at high dilution. According to Angell’s classification [65], they could be “good”
ionic liquids (i.e. they are highly dissociated), or “poor” ionic liquids (i.e. they may have some association of the ions and/or incomplete proton transfer from the acid to the base). **Figure 1.11.**

![Figure 1.11 Walden plot of log₁₀ of molar conductivity against log₁₀ of fluidity [65b].](image)

Some protonic ionic liquids are classified as a “poor” ionic liquid according to the classification scheme by Angell *et al.* [65a]. This fact can be explained considering the “Madelung energy”. An ionic liquid system where ions are uniformly surrounded by ions of the opposite charge has a Madelung energy comparable to an ideal ionic crystal energy. The more ideal the quasi-lattice is, the larger the Madelung energy of the liquid. Madelung energy is the main factor responsible for the low vapour pressure that defines the properties of ionic liquids. To vaporise, the ionic liquids must overcome the Madelung energy as well as the dipole-dipole interaction, so “good” ionic liquids are known to possess low vapour pressure. Protonic ionic liquids formed by weak acids will not form uniform charge distribution, thus their position in the Walden plot will not fall close to the ideal line and their vapour pressure will not be very low [65a,66]. Also, if there is some energetic feature involved, like a strong hydrogen bond, that intervenes in the formation of the Coulomb screen, the Madelung energy will be reduced and the vapour pressure will increase [65b]. The ionicity of ionic liquids have been widely studied by the groups of Watanabe [67] and MacFarlane [68], *inter alia.*
1.2 Hydrogen bonds

The idea of attractive and repulsive molecular interactions in gases was observed in the second half of the nineteenth century, leading to the formulation of van der Waal's law in 1881 [69]. A few years later, a separate study of vapour pressure by Raoult (1887-1888) [70] and osmotic pressure by van't Hoff (Nobel prize 1901) [71] evidenced the deviation from ideal behaviour in liquids, which very often was found stronger than in gas phase. The degree of association was very dependent on the functionality of the molecules involved. For example, alcohols and phenols formed aggregate complexes that were not present in hydrocarbons [72]. In 1903, Alfred Werner suggested that an ammonium salt has a configuration in which the proton lies between the ammonia and the anion, linking them with the symbol, (H$_3$N⋯H)X. Nevertheless, it was not until 1920 when two young scientists, Latimer and Rodebush, assured that the cause of the unique properties of water was due to a novel concept [73].

1.2.1 My name is bond, hydrogen bond [74]

Among chemical bonds (ionic, covalent and metallic) and van der Waals forces, there are other intermolecular interactions of intermediate energies. Normally, those energies involved are less than 160 kJ mol$^{-1}$. The six recognised intermolecular forces are: repulsion forces, orientation forces, polarisation forces, dispersion (London) forces, Mulliken charge transfer forces, and hydrogen bonds [75]. Out of the six, the first five are isotropic and the last one is anisotropic. Hydrogen bonds are the most important of all, being strongly directional interactions. They may be so strong that they are considered to be covalent (i.e., in [HF$_2$]) [76], or so weak as to be easily confused with van der Waals forces [76-77].

The definition of a hydrogen bond was a controversial topic due to the existence of a number of different views, and the wide range of effects and energies observed. The earliest views of Latimer and Rodebush [73] did not mention a “hydrogen bond” explicitly, but they stated that a “hydrogen nucleus held between two octets constitutes a weak bond” in their paper:

“Water [...] shows tendencies both to add and give up hydrogen, which are nearly balanced. Then [...] a free pair of electrons on another water molecule might be able to exert sufficient force on a hydrogen held by a pair of electrons on another water molecule to bind the two molecules together [...]. Indeed the liquid may be made up of large aggregates of molecules, continually breaking up and reforming under the influence of thermal agitation. [...] Such an explanation amounts to saying that the hydrogen nucleus held between two octets constitutes a weak ‘bond’.”
The first use of the term found in the literature was in Lewis’ book in 1923 [78]:

“It seems to me that the most important addition to my theory of valence lies in the suggestion of what has become known as the hydrogen bond.”

In 1928, the term “hydrogen bond” was later used by Pauling [79], but is not until 1941, when he gave a simple definition describing its nature [80]:

“It has been recognized in recent years that under certain conditions an atom of hydrogen is attracted by rather strong forces to two atoms, instead of only one, so that it may be considered to be acting as a bond between them. This is called the hydrogen bond. It is now recognized that [...] the hydrogen bond is largely ionic in character and is formed only between the most electronegative atoms. [...] Although the hydrogen bond is not a strong bond (its bond energy [...] being only about 5 kcal/mole.), it has great significance in determining the properties of substances.”

Nevertheless, the best empirical definition for those interactions was defined by Pimentel and McClellan in 1960 as [81]:

“A H bond [A – H–B] exists between a functional group A – H and an atom or group of atoms B in the same or a different molecule when:
(a) there is evidence of bond formation (association or chelation)
(b) there is evidence that this new bond liking A – H and B especially involves the hydrogen atom already bonded to A.”

Pimentel and McClellan considered essential to separate both conditions (a) and (b) due to the necessity of different measurement to prove specifically each of them [72].

These classical definitions are not actually strict definitions, and they leave the concept of a hydrogen bond rather vague. Although it might be possible to rationalise the existence of a hydrogen bond from a series of experimental measurements, it was not possible either to predict or to prove the existence of a hydrogen bond in many cases. The definition left uncertain the role of bond polarity that the true hydrogen bonds should have, and the fact that not all the attractive interactions where a proton is involved entail hydrogen bonds. Nor did the definition include any chemical detail of the atoms involved, or any restrictions regarding the environment of these atoms. This lacuna created a need for a more detailed definition, such as the one proposed by Gilli and Gilli [72]:

“The H-bond is a three-centre-four-electron (3c–4e) shared-proton interaction having the general form R–D–H ⇌ A–R’, where D is the proton donor (an electronegative atom, such as F, O, N, C, S, Cl, Br, and I) and :A the proton acceptor or lone-electron-pair carrier (a second electronegative atom of the π-bond of a multiple bond ). The H-bond
can also be seen as a single proton sharing two lone-electron pairs from two adjacent electronegative atoms or groups: \( R-D\cdots H\cdots A-R' \).

This definition considers that the hydrogen bond is not a bond in the sense of commonly recognised chemical bonds. The hydrogen bond may be considered as a dual (or multiple) bond made by a single proton with two or more electron pairs located on the surrounding "ligands". Thus, the proton acceptor does not need to be a particularly electronegative atom or anion, just to possess an accessible concentration of negative charge [76]. Today, it is known that the hydrogen bond is a very complex concept to be treated carefully, and only a very flexible and wide definition can justify and explain this phenomenon. If one considered a bond, as was described earlier, from a modern point of view, Steiner proposed [76]:

"An \( X-H\cdots A \) interaction is called a "hydrogen bond", if 1. it constitutes a local bond, and 2. \( X-H \) acts as proton donor to \( A \)"

The atoms \( X \) and \( A \) do not need to be very electronegative. The requirements are: \( X \) has to be slightly polar and the negative charge of \( A \) has to be sterically accessible. The hydrogen bond can be considered as the first step in a proton transfer reaction, in which strength can vary tremendously from strong to weak bonds.

### 1.2.2 Further terminology

In order to classify hydrogen bonds, it is necessary to initially focus on one or several parameters. Intermolecular or intramolecular hydrogen bonds, interaction energies, the covalent or ionic nature of the force, steric accessibility, and physical state are some terms commonly used.

There is a particular ambiguity in the terms attractive and repulsive. They can be used to label forces or energies. In this case, those concepts will be used for attractive and repulsive forces. Energies will be defined as stabilising \((E < 0)\) or destabilising \((E > 0)\) interactions. Since repulsive and attractive forces are always present in any molecular system (intermolecular or intramolecular), the overall net attraction or repulsion depend on the sum of the interactions. Focussing on the intermolecular forces, the energy profile for weak interactions (such as van der Waals) would be as represented in Figure 1.12.
Figure 1.12 Potential energy profiles for intermolecular forces, for a) repulsive forces, b) attractive forces (van der Waals are shown), and c) the sum of repulsive and attractive forces (a + b) [75].

For stronger interactions, such as hydrogen bonds, the resultant potential well is deeper, steeper, and better defined, as in Figure 1.13 [76]

Figure 1.13 A schematic of a hydrogen bond potential energy curve [76], where $d_0$ is the equilibrium length of the hydrogen bond.

At the equilibrium length of the hydrogen bond, $d = d_0$, there is no net force acting on the atoms. If $d < d_0$, the repulsive forces are dominant, and the system will move toward a low energy configurations. Similarly, for distances where $d > d_0$, there is an attractive force moving the system towards equilibrium [76]. Although Figure 1.13 focusses on the hydrogen bond potentials, every interaction (no matter how weak) will have a similar characteristic profile.

Since intramolecular hydrogen bonds occur when the donor and the acceptor are on the same molecule, and do not involve molecular association, changes induced
in the physical properties, if any, are minimal. The behaviour of intramolecular hydrogen bonded systems is similar to that with no hydrogen bonds, except that the hydrogen bond can lock the structure into a unique low energy structure. Due to this fact, the path to understand the nature and effect of hydrogen bonds is to investigate experimentally and theoretically the hydrogen bond itself [75].

Thus, the hydrogen bond represents a complex balance of interactions. Its total energy can be factorised into contributions from electrostatic ($E_{el}$), polarisation ($E_{pol}$), charge transfer ($E_{ct}$), dispersion ($E_{dis}$), and exchange repulsion ($E_{er}$). The relative contributions of these energies change depending on the chemical composition of the donor-acceptor pair and their contact geometry. The electrostatics energy ($E_{el}$) is usually the most important term in “normal” hydrogen bonds, although charge transfer ($E_{ct}$), and van der Waals contributions are always present too. The energy of the network of hydrogen bonds cannot be calculated accurately by summing the term from isolated molecules [76]. Most importantly, unless at 0 K, the nature of the hydrogen bond is intrinsically dynamic, and the study of its dynamics (quasielastic neutron scattering, QENS) is a field in its own right.

1.2.3 How can we see them?
It is relatively easy to define what is meant by a hydrogen bond; it is much harder to observe hydrogen bonds experimentally.

The first sight of hydrogen bonds was noted in solubility studies in 1891 [82]. Nernst described a weak interaction that involved the atom of hydrogen (dimeric association) in molecules that present hydroxyl groups [82-83]. Latimer and Rodebush studied the dielectric constant of some liquids. They could not explain why if a high dielectric constant is due to the orientation of the dipoles in an electric field, the compounds with hydrogen, presented higher dielectric constants. For instance, hydrogen chloride should have a higher dielectric constant than water and hydrogen fluoride, but it did not happen. In fact, the vapour and liquid phases of hydrogen chloride have a much lower dielectric constant, and nor does it seem to be associated [73]. After this, hydrogen bonds were also studied by the many other "classical" techniques available at the beginning of the twentieth century. Vapour density and vapour pressure, dielectric constant, partition or distribution, molecular weight, molar volume, electrical and thermal conductivity, refractive index, and acoustic behaviour are a few of the physical properties that suggest the presence of hydrogen bonds, but do not prove it.

In the 1930s, infrared and Raman spectroscopic techniques received more attention. Rodebush, in 1936, published a paper about the similarities and differences
between hydrogen bonding and coordination [84]. He concluded that the hydrogen bond is much weaker than the coordination of metal ions. He also stressed that fifteen years after the introduction of the term “hydrogen bond”, X-ray studies of Pauling and the disappearance of the O-H vibrational frequency in the IR in possibly hydrogen bonded interactions, definitively prove the existence of hydrogen bonds. They did not detect the hydrogen bond itself. Just the presence of the hydrogen bond. Afterwards, nuclear magnetic resonance and neutron technique became an essential tool to identify the position of the atom in molecular interactions, complementing X-ray studies.

Nowadays, the uncertainty in establishing hydrogen bonds makes it particularly challenging to define what constitutes a hydrogen bond, giving rise many specialised definitions of hydrogen bonds based on particular properties. The classification by Jeffrey, including geometry, energy, IR and NMR spectroscopies, is shown in Table 1.1 [15,85].

### Table 1.1 Properties of hydrogen bonds [15,85].

<table>
<thead>
<tr>
<th></th>
<th>Strong</th>
<th>Moderate</th>
<th>Weak</th>
<th>Weak ionic dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Covalent</td>
<td>Ionic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H···Y (Å)</td>
<td>1.2–1.5</td>
<td>1.5–2.2</td>
<td>&gt;2.2</td>
<td></td>
</tr>
<tr>
<td>Lengthening H···Y (Å)</td>
<td>0.08–0.025</td>
<td>0.02–0.08</td>
<td>&lt;0.02</td>
<td></td>
</tr>
<tr>
<td>X-H vs. H···Y</td>
<td>X-H ≈ H···Y</td>
<td>X-H &lt; H···Y</td>
<td>X-H &lt; H···Y</td>
<td></td>
</tr>
<tr>
<td>X Y length</td>
<td>2.2–2.5</td>
<td>2.5–3.2</td>
<td>&gt;3.2</td>
<td></td>
</tr>
<tr>
<td>Directionality</td>
<td>Strong</td>
<td>Moderate</td>
<td>Weak</td>
<td></td>
</tr>
<tr>
<td>Bond angles (°)</td>
<td>170–180</td>
<td>&gt;130</td>
<td>&gt;90</td>
<td></td>
</tr>
<tr>
<td>Bond energy (kJ mol⁻¹)</td>
<td>63–167</td>
<td>17–63</td>
<td>&lt;17</td>
<td></td>
</tr>
<tr>
<td>Bond energy (kcal mol⁻¹)</td>
<td>15–40</td>
<td>4–15</td>
<td>&lt;4</td>
<td></td>
</tr>
<tr>
<td>IR shift (cm⁻¹)</td>
<td>25%</td>
<td>10–25%</td>
<td>&lt;10%</td>
<td></td>
</tr>
<tr>
<td>¹H shift (ppm)</td>
<td>14–22</td>
<td>&lt;14</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The presence of hydrogen bonds has a direct consequence in [81]:

- **Geometrical effects:**
  - The X-H···Y bonds show a preference for a collinearity of the X-H donor and the Y acceptor group (the X-H···Y angle tends to be close to 180°), which distinguishes hydrogen bonds from van der Waals interactions [83].
  - The X-H distance is short, compared with the sum of the van der Waals radii.

- **Order of magnitude in energies [76]:**
  - There are numerous effect from the near and the remote environments that may considerably increase or decrease the hydrogen bond energies.
Normally, the reported values for hydrogen bonds lie within the 1-167 kJ mol\(^{-1}\) energy range [77].

- **Vibrational spectra** [86]:
  - The stretching mode of X-H is shifted to lower frequencies (blue shift) and the intensity increases.
  - The bending mode of X-H is shifted to higher frequencies.
  - The band width of the H····Y stretching mode is broader.
  - New frequency modes associated with stretching and bending of the H····Y bond itself are below 500 cm\(^{-1}\), which is studied further in this thesis.

- **Nuclear magnetic resonance spectroscopy**:
  - The hydrogen bond shifts are usually as large as the chemical shifts of the gases.
  - The hydrogen bond shifts are all negative, towards lower fields, implying a decrease in diamagnetic shielding.
  - The association shifts of the substances forming strong hydrogen bonds, HF and H\(_2\)O, are distinctly larger than the shifts of the other substances.

### 1.3 Nomenclature

Throughout this manuscript, \([\text{N}wxyz]^+\) represents a substituted ammonium cation, using a long-established convention for quaternary alkylammonium salts: \(w\), \(x\), \(y\), and \(z\) represent the number of carbon atoms for each of the alkyl chains; a subscript 0 thus represents a proton, and the subscript D represents deuterium. Hence, \([\text{N}0002]^+\) represents the ethylammonium cation, \([\text{NEtH}_3]^+\).

### 1.4 Hydrogen bonds in ionic liquids

It is nearly thirty years since the first report about hydrogen-bonding in room-temperature ionic liquids [87], which was met by an immediate chorus of derision. Since 1986, a large number of papers have shown clear evidence for the presence of hydrogen bonds between anions and cations of ionic liquids, and between solutes and the components of ionic liquids (e.g. [88]).

Today it is universally accepted, but still has not received the attention that it deserves. Properties of ionic liquids can only be explained by understanding the intermolecular forces: the Coulomb forces, hydrogen bonding and dispersion forces [89], but some authors consider that the nature of these interactions is entirely electrostatic and pay no attention to hydrogen bonds [90]. One of the recent strong points of disagreement is the C(2)-H····anion interaction in imidazolium ionic liquids.
Ludwig and coworkers [91], with a combination of FTIR measurements in the far-infrared region and *ab initio* calculations, described the cohesion energies between cations and anions. They claimed that the bands with the lowest frequencies can be assigned to the bending and stretching vibrational modes of hydrogen bonds. Tsuzuki *et al.* [90b,92] suggested that the nature of the C(2)-H···anion interaction is completely different to a conventional hydrogen bond. This new interpretation is in strong contradiction to the common view that the C-H bonds of the imidazolium ring are involved in hydrogen bonding and that the C(2)-H vibrational band is further red-shifted compared to that of C(4,5)-H which indicate a stronger interaction with the anion [93].

By alkyl substitution in a series of 1,3-dialkylimidazolium cations combined with different hydrophobic anions (trifluoromethanesulfonate, [OTf]−; bis[(trifluoromethyl)sulfonyl]amide, [NTf2]−; and trifluoroethanoate, [CF3CO2]−) the C(2)-H···anion hydrogen-bond interaction was expected to lower the melting point and to decrease the viscosity, since the ability to form hydrogen bonds have been significantly reduced. However, the opposite behaviour was observed [94]. Hunt [95] hypothesised that the effects due to a loss in hydrogen bonding were outweighed by those due to a loss in entropy. The reduction in entropy means a greater ordering within the liquid that would explain the raised melting point and increasing viscosity. Therefore, according to her finding, hydrogen bonds stabilise imidazolium ionic liquids. Hydrogen bonds have been mostly studied in aprotic ionic liquids. The strong anion–cation interaction in ionic liquids is reflected in the extremely low vapour pressures and high enthalpies of vaporisation [46,96]. Spectroscopic studies, such as Raman, NMR, mid-infrared spectroscopies, or X-ray and neutron diffraction, have proved that imidazolium ionic liquids report shorter C-H···anion distances, red-shifted C-H frequencies and downfield shifted C-H proton chemical shift [94,97]. Ludwig and coworkers [98] studied low vibrational modes for polymethylated imidazolium ionic liquids, and they quantified the hydrogen bond contributions relative to the overall interaction. The hydrogen-bonding forces represent between 10-16%, and their influence has been demonstrated on melting points, viscosity and enthalpies of vaporisation. Their work also concluded that hydrogen bonds represent defects in the Coulombic system, giving rise to more fluid liquids rather than more rigid ionic liquids [99], which agrees with Hunt [95].

Hydrogen bonding in protonic ionic liquids is less well studied that in aprotic systems. Apart from being cheaper and easier to synthesise, the key properties that differentiate protonic ionic liquids from the rest are the proton transfer from the acid to
the base. The hydrogen bond then can be considered as a point intermediate in the transfer in ionic liquids [72,76].

The commonly studied hydrogen bond is between two neutral molecules, as is the case for water, or of a neutral species and a charged ion. Hydrogen bonds are commonly found in biological systems, as in the human mitochondrial DNA polymerase, where base pair hydrogen bonding contributes at least a third of the energy underlying nucleoside incorporation efficiency and specificity [100]. In the case of protonic ionic liquids, hydrogen bonds occur between two ionic species. Hunt has named these as “doubly ionic hydrogen bonds” [15].

The most extensively studied protonic ionic liquid is definitely ethylammonium nitrate, \([\text{N}_0\text{O}_0\text{O}_2]\)[NO₃]. Its similar behaviour and properties to water have captured the attention of many scientists. Ethylammonium nitrate, as water, has a strong ability to promote aggregation of surfactants as well as possessing a high cohesive energy density [46]. Both ethylammonium nitrate and water possess both hydrogen-bond acceptor and donor sites. It has been suggested that the hydrogen bonds between ammonium cations and nitrate anions induce a network structure which in some respects recall the three-dimensional hydrogen-bonded network of the water [101]. Far-infrared spectroscopy, supported by DFT calculations, has also proved that the intermolecular vibrational bands of the three protonic ionic liquids: \([\text{N}_0\text{O}_0\text{O}_1]\)[NO₃], \([\text{N}_0\text{O}_0\text{O}_2]\)[NO₃], \([\text{N}_0\text{O}_0\text{O}_3]\)[NO₃]) show the same structure as the measured connectivity bands of water [102]. **Figure 1.14** shows the network structure of ethylammonium nitrate and water.

![Figure 1.14](image)

**Figure 1.14** Three-dimensional structures of ethylammonium nitrate \([\text{N}_0\text{O}_0\text{O}_2]\)[NO₃]) and water obtained from DFT calculations.

Protonic ionic liquids, in a similar way to water, present unique properties not seen in other ionic liquids. That makes this group of ionic liquids ideal candidates to study hydrogen bonding. Intermolecular interactions between molecules and ions, as hydrogen bonds, present in the frequency range between 100 and 500 cm⁻¹, can be
studied by several experimental spectroscopic methods. The variety of methods includes optical heterodyne-detected Raman, Raman-induced Kerr-effect, terahertz spectroscopy (THz), dielectric relaxation, low-energy neutron scattering, as well as far-infrared (FIR) spectroscopy [103]. The interpretation of the complex spectra at very low frequencies requires theoretical calculations to aid the assignments. In order to support the assignments, Ludwig and coworkers compared the infrared spectra of trimethylammonium nitrate, [N\textsubscript{0111}]\textsubscript{3}NO\textsubscript{3}, and tetramethylammonium nitrate, [N\textsubscript{1111}]\textsubscript{3}NO\textsubscript{3}, the former possessing a three-dimensional hydrogen-bonding network (cf. Figure 1.14), the latter possessing no recognisable hydrogen bonds [104]. Bands at 100 cm\textsuperscript{-1} were observed for both ionic liquids, and an additional band at 170 cm\textsuperscript{-1} was observed only in the spectrum of [N\textsubscript{0111}]\textsubscript{3}NO\textsubscript{3}. This latter band was assign by the authors to be an N-H\cdots-O hydrogen bond between the cation and the anion. The former band was assigned as non-specific lattice modes. The same authors have frequently assigned bands at ca. 100 cm\textsuperscript{-1} to hydrogen-bonded modes, in relation to ionic liquids [105]. [N\textsubscript{01111}]\textsubscript{3}NO\textsubscript{3} and [N\textsubscript{11111}]\textsubscript{3}NO\textsubscript{3} are not isostructural, and the cations have different symmetries (C\textsubscript{3v} and T\textsubscript{d}, respectively). It is extremely dangerous to argue the assignment of the band at 170 cm\textsuperscript{-1} by comparing the spectra from both ionic liquids when there are so many uncontrolled variables.

1.5 Previous results from QUILL

The starting point for the work in this thesis was the PhD thesis of (now) Dr. Simona Stana [106]. She studied a number of series of protonic alkylammonium nitrates, with varying alkyl chain lengths, and varying number and strength of hydrogen bonding capabilities. The ionic liquids that she prepared and characterised are detailed in Table 1.2.

Table 1.2 The ionic liquids, alkylammonium nitrates, prepared and characterised by Dr. Stana are indicated by orange squares (X represents salts where crystal structures have been determined) [106].

<table>
<thead>
<tr>
<th>(n)</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{N}_n\text{nnn}]\text{NO}_3)</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>
The nitrate anion was chosen because of its highly symmetrical structure, $D_{3h}$. The low molecular weights of the nitrate anion and the short chain ammonium cation made these systems particularly accessible for \textit{ab initio} DFT calculations.

By varying the sites available for hydrogen bonding, it was possible to systematically observe and evaluate the nature of this interaction surrounded by a different environment. The physical and chemical features were studied by NMR spectroscopy, thermal analysis (DSC and TGA), X-ray crystallography, and vibrational spectroscopies (infrared, Raman, and Inelastic neutron scattering). She concluded that:

(a) The salts were fully ionised in the liquid state, as deduced by NMR spectroscopic studies, and were thus ionic liquids.

(b) The phase transitions of the ionic liquids, including melting points, glass transitions temperatures, and solid-solid transformations, were determined by DSC, and the thermal stability (typically stable up to 250 °C) was determined by TGA. This high thermal stability reinforced the conclusion from the NMR studies that the salts were fully ionised.

(c) The crystal structures of eight of these alkylammonium nitrates were determined (mark with X in the Table 1.2). All suggested the presence of strong interionic hydrogen bonds, characterised by short N-H···O distances.

(d) There were few significant changes in the infrared and Raman spectra studies of series of ionic liquids for chain lengths longer than butyl, even when the chain length was increased to dodecyl.

(e) The assignment of the stretching frequencies of the hydrogen bonds, for the three series of alkylammonium nitrates, were around 170 and 250 cm$^{-1}$, based on inelastic neutron scattering data. However, these conclusions were tenuous as there were no supporting detailed theoretical studies, and as one of the key compounds has since proven to be impure (see Chapter 5). Moreover, the assignments were unduly influenced by the reports of Ludwig and coworkers.

So Stana's study established some extremely interesting phenomena, which left some crucial open questions. Most importantly, she did not produce definitive assignments of the N-H···O hydrogen bond stretching frequencies, although many of the spectra in the thesis are of extremely high quality.
1.6  Aim of this work

As seen above, the presence of hydrogen bonds in ionic liquids, although originally controversial, is now well established. Despite this, the following areas contain many unanswered questions:

a) The hydrogen bonds at low frequency have never been directly observed spectroscopically.

b) The effect of hydrogen bonds upon the physical properties of ionic liquids is not understood.

c) There are only a very few studies of binary mixtures of ionic liquids, especially of protonic ionic liquids.

The aim of this thesis is to establish the nature of hydrogen bonding in protonic ionic liquids, and the manner in which the hydrogen bonding determines the physical properties of both pure ionic liquids, and their binary mixtures.
2 Synthesis and Characterisation
This chapter describes the experimental syntheses of a series of alkylammonium nitrate ionic liquids. They have been characterised by elemental analysis, nuclear magnetic resonance spectroscopy (NMR), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), and (where possible) X-ray crystallography.

2.1 Experimental

The freeze-drier and the glovebox, frequently used in this Section, are detailed in Appendices B1 and B2. Synthesis of pure alkylammonium nitrites

The syntheses were carried out in the fume hood because of the odour of amines and acid compounds. Starting materials are found in Table 2.1. The amount of water was checked by Karl Fischer titrations. Samples were connected to the freeze-drier until the amount of water was found constant.

Table 2.1 Masses, yield, colour and physical state of series of alkylammonium nitrates.

<table>
<thead>
<tr>
<th>n</th>
<th>Conc./% (w/w)</th>
<th>Conc. /% (w/w)</th>
<th>Mw</th>
<th>mg</th>
<th>mg</th>
<th>m/g</th>
<th>No. of moles</th>
<th>m/g</th>
<th>No. of moles</th>
<th>Yield /%</th>
<th>Colour</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N0 2 n</td>
<td>HNO3*</td>
<td>[N0 0 0 n][NO3]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>70</td>
<td>45.08</td>
<td>51.8</td>
<td>0.804</td>
<td>78</td>
<td>0.804</td>
<td>97</td>
<td>colourless</td>
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<td></td>
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<td>41.1</td>
<td>0.423</td>
<td>92</td>
<td>pale yellow</td>
<td>liquid</td>
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<tr>
<td>4</td>
<td>99.5</td>
<td>73.14</td>
<td>25.8</td>
<td>0.352</td>
<td>29.2</td>
<td>0.300</td>
<td>97</td>
<td>white</td>
<td>liquid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N0 n n</td>
<td>HNO3*</td>
<td>[N0 0 n n][NO3]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>2</td>
<td>99</td>
<td>73.14</td>
<td>27.4</td>
<td>0.371</td>
<td>35.9</td>
<td>0.371</td>
<td>97</td>
<td>yellow</td>
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<td></td>
</tr>
<tr>
<td>Nn n n</td>
<td>HNO3*</td>
<td>[N0 n n n][NO3]</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>2</td>
<td>98</td>
<td>101.19</td>
<td>30.8</td>
<td>0.301</td>
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<td>0.301</td>
<td>98</td>
<td>white</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>[Nn n n n][OH]</td>
<td>HNO3*</td>
<td>[N0 n n n][NO3]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>35</td>
<td>147.26</td>
<td>116.56</td>
<td>0.277</td>
<td>26.9</td>
<td>0.277</td>
<td>70</td>
<td>white</td>
<td>solid</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* HNO3 (65 % wt in aqueous solution, 1.16 g cm⁻³)

2.1.1 Synthesis of ethylammonium nitrate, [N0 0 2][NO3]

\[
\overset{\text{NH}_2}{\text{HNO}_3} \rightarrow \left[ \overset{\text{NH}_3}{\text{H}_3\text{O}^+} \right] \left[ \text{NO}_3^- \right]
\]

Nitric acid (65 wt % aqueous solution; 77.96 g; 804 mmol) was added dropwise from a dropping funnel to a frozen solution (-196 °C) of ethylamine (70 wt % aqueous solution; 51.80 g; 804 mmol) in a round-bottomed flask (500 cm³) under dinitrogen. After all the acid had been added, the reaction flask was allowed to warm to room temperature (20 °C), while stirring magnetically. After two hours of vigorous stirring, the round-bottomed flask was connected to the freeze-drier (Appendix B1) for five
days at 0.021 mbar pressure at room temperature, to remove the water, to produce a clear yellow, viscous liquid (84.24 g, 780 mmol, 97% yield), which was immediately transferred into the glovebox (Appendix B2).

2.1.1.2 Synthesis of propylammonium nitrate, \([N_0003][NO_3]\)

\[
\text{NH}_2 + \text{HNO}_3 \rightarrow \left[\text{NH}_3\right][\text{NO}_3]
\]

Propylammonium nitrate ionic liquid has been synthesised by acid-base reaction of the corresponding propylamine (98 wt % in aqueous solution, 25.55 g, 423 mmol) and nitric acid (65 wt % in aqueous solution; 41.0626 g, 423 mmol). They were mixed together by adding nitric acid dropwise from a dropping funnel to a frozen propylamine (cooled with liquid nitrogen (-196 °C) in a round-bottomed flask of 250 cm³. After four hours of magnetic stirring at room temperature (20 °C), the flask was placed in the freeze-drier for six days (0.021 mbar pressure at room temperature) to remove the water. The viscous colourless liquid, \([N_0003][NO_3]\) (47.98 g, 393 mmol, 92% yield) was placed into the glovebox.

2.1.1.3 Synthesis of butylammonium nitrate, \([N_0004][NO_3]\)

\[
\text{NH}_2 + \text{HNO}_3 \rightarrow \left[\text{NH}_3\right][\text{NO}_3]
\]

To a solution of butylamine (99.5 wt % in aqueous solution, 25.8484 g, 352 mmol) was added acid nitric (65 wt % in aqueous solution; 29.2123 g, 352 mmol). The exothermicity of the reaction was controlled by the slow addition of the acid (dropwise using a dropping funnel) and by keeping the reaction temperature at -196 °C. After two hours of magnetic stirring at room temperature, the round-bottomed flask was deposed in freeze-drier (0.021 mbar pressure at room temperature) for six days to remove the water. The white solid product, \([N_0004][NO_3]\) (46.77 g, 343 mmol, 97% yield) was placed into the glovebox to keep in an inert atmosphere.

2.1.1.4 Synthesis of diethylammonium nitrate, \([N_0022][NO_3]\)

\[
\text{NH}_2 + \text{HNO}_3 \rightarrow \left[\text{NH}_3\right][\text{NO}_3]
\]

Diethylamine (99 wt % in aqueous solution, 27.4041 g, 371 mmol) and nitric acid (65 wt % in aqueous solution; 35.9577 g, 371 mmol) were mixed together in a round-bottomed flask of 250 cm³. Nitric acid was added dropwise from a dropping funnel to a frozen solution of diethylamine (-196 °C). When addition was completed, the reaction was left to warm up to room temperature with a magnetic stirring (three
hours). Water was removed by the freeze drying at 0.021 mbar pressure at room temperature (7 days). The white solid product, \([N_{0222}][NO_3]\) (49.02 g, 359 mmol, 97% yield) was immediately transferred to the glovebox.

### 2.1.1.5 Synthesis of triethylammonium nitrate, \([N_{0222}][NO_3]\)

\[
\text{\(\text{N} + \text{HNO}_3 \rightarrow \text{[N][NO}_3\text{]}\)}
\]

Nitric acid (65 wt % in aqueous solution; 29.2123 g, 300 mmol) was added dropwise from a dropping funnel to a solution of triethylamine (99 wt % in aqueous solution, 30.7972 g, 301 mmol) in a round-bottomed flask of 250 cm³. The process was cooled to -196 °C with liquid nitrogen. The solution was vigorously stirring for two hours at room temperature, and then, the round-bottomed flask was connected to freeze drier to remove the water (six days). The yellow product, \([N_{0222}][NO_3]\) (49.47 g, 301 mmol, 98% yield) was placed into the glovebox.

### 2.1.1.6 Synthesis of tetraethylammonium nitrate, \([N_{2222}][NO_3]\)

\[
\text{[N][OH]} + \text{HNO}_3 \rightarrow \text{[N][NO}_3\text{]}
\]

The synthesis of tetraethylammonium nitrate was similar to the already presented in previous reactions. Tetraethylammonium hydroxide (35 wt % in aqueous solution, 116.56 g, 277 mmol) and nitric acid (65 wt % in aqueous solution; 26.8568 g, 277 mmol) were mixed in a round-bottomed flask of 500 cm³. The acid was added dropwise to the base due to the exothermicity nature of the reaction. Low temperature was assured by using liquid nitrogen (-196 °C). After three hours of stirring with a magnetic stirring at room temperature, it was placed in the freeze-drier to remove the water. The white solid product \([N_{2222}][NO_3]\) (37.11 g, 192 mmol, 70% yield) was placed into the glovebox.

### 2.1.2 Characterisation of pure alkylammonium nitrates

#### 2.1.2.1 Elemental analysis and Karl Fischer titration

Elemental analysis (or CHN) analysis is essential to characterise and/or prove the elemental composition of an organic sample. Elemental analyses of the protonic ionic liquids have been performed. Results are detailed in Table 2.2. Karl Fischer titration results are shown in Table 2.3. A description of the instruments and the methods could be found in Appendices B3 and B4, respectively.
Table 2.2 Elemental analysis of alkylammonium nitrates.

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{N}_0\text{0}][\text{NO}_3])</td>
<td>22.22</td>
<td>21.86</td>
<td>7.46</td>
<td>7.28</td>
<td>25.91</td>
<td>24.68</td>
</tr>
<tr>
<td>([\text{N}_0\text{0}][\text{NO}_3])</td>
<td>29.51</td>
<td>29.09</td>
<td>8.25</td>
<td>8.53</td>
<td>22.94</td>
<td>21.83</td>
</tr>
<tr>
<td>([\text{N}_0\text{0}][\text{NO}_3])</td>
<td>35.29</td>
<td>34.89</td>
<td>8.88</td>
<td>8.99</td>
<td>20.58</td>
<td>20.31</td>
</tr>
<tr>
<td>([\text{N}_0\text{2}][\text{NO}_3])</td>
<td>35.29</td>
<td>35.66</td>
<td>8.88</td>
<td>8.96</td>
<td>20.58</td>
<td>20.29</td>
</tr>
<tr>
<td>([\text{N}_0\text{2}][\text{NO}_3])</td>
<td>43.89</td>
<td>43.37</td>
<td>9.82</td>
<td>9.84</td>
<td>17.06</td>
<td>16.61</td>
</tr>
<tr>
<td>([\text{N}_2\text{22}][\text{NO}_3])</td>
<td>49.98</td>
<td>49.88</td>
<td>10.48</td>
<td>10.26</td>
<td>14.57</td>
<td>14.27</td>
</tr>
</tbody>
</table>

Table 2.3 Karl Fischer titration results.

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Water content / ppm</th>
<th>(\chi_{\text{water}}\times 10^4 / \chi_{\text{ionic liquid}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{N}_0\text{0}][\text{NO}_3])</td>
<td>1996</td>
<td>120</td>
</tr>
<tr>
<td>([\text{N}_0\text{0}][\text{NO}_3])</td>
<td>247</td>
<td>17</td>
</tr>
<tr>
<td>([\text{N}_0\text{0}][\text{NO}_3])</td>
<td>196</td>
<td>15</td>
</tr>
<tr>
<td>([\text{N}_0\text{2}][\text{NO}_3])</td>
<td>299</td>
<td>23</td>
</tr>
<tr>
<td>([\text{N}_2\text{2}][\text{NO}_3])</td>
<td>518</td>
<td>47</td>
</tr>
<tr>
<td>([\text{N}_2\text{2}][\text{NO}_3])</td>
<td>545</td>
<td>58</td>
</tr>
</tbody>
</table>

2.1.2.2 \(^1\text{H} \text{ and } ^{13}\text{C NMR spectroscopy}\)

NMR studies were used to evaluate the purity of the ionic liquids (see Appendix B5). \(^1\text{H} \text{ and } ^{13}\text{C NMR spectra of the six alkylammonium nitrates were recorded at room temperature (see Tables 2.4-2.5). NMR spectra are illustrated in Figures 2.1-2.12.}

![Figure 2.1](image-url)
Figure 2.2 $^{13}$C($^1$H) NMR spectrum of neat $[\text{N}_0\text{O}_0\text{O}_3][\text{NO}_3]$ (100.6 MHz; 21 °C; d$_6$-dmso internal capillary, marked with asterisk).

Figure 2.3 $^1$H NMR spectrum of neat $[\text{N}_0\text{O}_0\text{O}_3][\text{NO}_3]$ (400 MHz; 21 °C; d$_6$-dmso internal capillary, marked with asterisk).
Figure 2.4 $^{13}\text{C}[^{1}\text{H}]$ NMR spectrum of neat $[\text{N}_0.0.3][\text{NO}_3]$ (100.6 MHz; 21 °C; $d_6$-dmso internal capillary, marked with asterisk).

Figure 2.5 $^1\text{H}$ NMR spectrum of neat $[\text{N}_0.0.3][\text{NO}_3]$ (400 MHz; 21 °C; $d_6$-dmso, marked with asterisk).
Figure 2.6 $^{13}$C($^1$H) NMR spectrum of neat $[\text{N}_0\text{O}_0\text{O}_4][\text{NO}_3]$ (100.6 MHz; 21 °C; d$_6$-dmso, marked with asterisk).

Figure 2.7 $^1$H NMR spectrum of neat $[\text{N}_0\text{O}_2\text{O}_3][\text{NO}_3]$ (400 MHz; 21 °C; d$_6$-dmso, marked with asterisk).
Figure 2.8 $^{13}$C($^1$H) NMR spectrum of neat $[N_0.222][NO_3]$ (100.6 MHz; 21 °C; $d_6$-dmso, marked with asterisk).

Figure 2.9 $^1$H NMR spectrum of neat $[N_0.222][NO_3]$ (400 MHz; 21 °C; $d_6$-dmso, marked with asterisk).
Figure 2.10 $^{13}$C$\ (^1H\}$ NMR spectrum of neat [N$_2$H$_2$][NO$_3$] (100.6 MHz; 21 °C; $d_6$-dms, marked with asterisk).

Figure 2.11 $^1$H NMR spectrum of neat [N$_2$H$_2$][NO$_3$] (400 MHz; 21 °C; $d_6$-dms, marked with asterisk).
Figure 2.12 $^{13}$C($^1$H) NMR spectrum of neat [N$_2$2 2 2][NO$_3$] (100.6 MHz; 21 °C; d$_6$-dmso, marked with asterisk).

Table 2.4 $^1$H NMR data (400 MHz; 21 °C; d$_6$-dmso; $\delta$ / ppm) for pure alkylammonium nitrates.

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>$\delta$ / ppm $^a$</th>
<th>$\delta$ / ppm $^a$</th>
<th>$\delta$ / ppm $^a$</th>
<th>$\delta$ / ppm $^a$</th>
<th>NH$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[N$_0$0 0 2][NO$_3$] $^b$</td>
<td>2.95 (2H, q, J= 7.2)</td>
<td>1.13 (3H, t, J= 7.3)</td>
<td>7.37 (3H, s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[N$_0$0 0 3][NO$_3$] $^b$</td>
<td>2.76 (2H, t, J= 6.3)</td>
<td>1.53 (2H, m, J= 7.5)</td>
<td>7.85 (3H, s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[N$_0$0 0 4][NO$_3$] $^c$</td>
<td>2.79 (2H, t, J= 7.6)</td>
<td>1.50 (2H, m, J= 7.5)</td>
<td>1.30 (3H, m, J= 7.5)</td>
<td>0.86 (3H, t, J=7.4)</td>
<td>7.82 (3H, s)</td>
</tr>
<tr>
<td>[N$_0$2 2 2][NO$_3$] $^c$</td>
<td>3.94 (4H, q, J= 7.5)</td>
<td>1.15 (6H, t, J= 7.3)</td>
<td>8.43 (2H, s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[N$_0$2 2 2][NO$_3$] $^c$</td>
<td>3.12 (6H, q, J= 7.2)</td>
<td>1.18 (9H, t, J= 7.3)</td>
<td>9.07 (3H, s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[N$_2$2 2 2][NO$_3$] $^c$</td>
<td>3.22 (8H, q, J= 7.2)</td>
<td>1.16 (12H, q, J= 7.3)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Units of $J$ are Hz. $^b$ Neat ionic liquids. $^c$ Dissolved in d$_6$-dmso.

Table 2.5 $^{13}$C NMR data (100.6 MHz; 21 °C; d$_6$-dmso; $\delta$ / ppm) for pure alkylammonium nitrates.

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>$^c$</th>
<th>$^c$</th>
<th>$^c$</th>
<th>$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[N$_0$0 0 2][NO$_3$] $^a$</td>
<td>34.88</td>
<td>12.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[N$_0$0 0 3][NO$_3$] $^a$</td>
<td>41.23</td>
<td>20.80</td>
<td>10.95</td>
<td></td>
</tr>
<tr>
<td>[N$_0$0 0 4][NO$_3$] $^b$</td>
<td>39.12</td>
<td>29.48</td>
<td>19.50</td>
<td>13.86</td>
</tr>
<tr>
<td>[N$_0$2 2 2][NO$_3$] $^b$</td>
<td>41.94</td>
<td>11.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[N$_0$2 2 2][NO$_3$] $^b$</td>
<td>46.27</td>
<td>9.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[N$_2$2 2 2][NO$_3$] $^b$</td>
<td>51.86</td>
<td>7.51</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Neat ionic liquids. $^b$ Dissolved in d$_6$-dmso.
2.1.2.3 Thermal analyses
Thermal studies such as thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) reveal important information about the stability and thermal behaviour of these ionic liquids. A description of the instruments and the TGA and DSC methods can be found in Appendices B6 and B7, respectively.

2.1.2.3.1 THERMAL GRAVIMETRIC ANALYSES (TGA)

The decomposition temperatures of the series of alkylammonium salts were measured using aluminium pans under a dinitrogen atmosphere at a heating rate of 10 °C min⁻¹. The TGA traces are illustrated in Figures 2.13-2.18.

![Figure 2.13 TGA traces for [N₉₀₀₂][NO₃] at heating rate of 10 °C min⁻¹.](image)
Figure 2.14 TGA traces for $[\text{NiO}_0\text{O}_3]\text{[NO}_3]$ at heating rate of 10 °C min$^{-1}$.

Figure 2.15 TGA traces for $[\text{NiO}_4\text{O}_4]\text{[NO}_3]$ at heating rate of 10 °C min$^{-1}$. 
Figure 2.16 TGA thermogram of [N₂O₂][NO₃] at heating rate of 10 °C min⁻¹.

Figure 2.17 TGA traces for [N₂O₂][NO₃] at heating rate of 10 °C min⁻¹.
Figure 2.18 TGA traces for \([\text{N}_2\text{O}_2\text{NO}_3]\) at heating rate of 10 °C min\(^{-1}\).

Table 2.6 Decomposition temperatures (\(T_d\)) of alkylammonium nitrate.

<table>
<thead>
<tr>
<th>Ionic liquids</th>
<th>(T_d) (exp)/ °C</th>
<th>(T_d) / °C [106]</th>
<th>(T_d) (lit)/ °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{N}_0\text{O}_0\text{O}_2])[NO(_3)]</td>
<td>200.74</td>
<td>227</td>
<td>242 [46] (^a)</td>
</tr>
<tr>
<td>([\text{N}_0\text{O}_0\text{O}_3])[NO(_3)]</td>
<td>182.53</td>
<td>177</td>
<td>-</td>
</tr>
<tr>
<td>([\text{N}_0\text{O}_0\text{O}_4])[NO(_3)]</td>
<td>182.11</td>
<td>180</td>
<td>-</td>
</tr>
<tr>
<td>([\text{N}_0\text{O}_2\text{O}_2])[NO(_3)]</td>
<td>148.66</td>
<td>183</td>
<td>-</td>
</tr>
<tr>
<td>([\text{N}_2\text{O}_2\text{O}_2])[NO(_3)]</td>
<td>154.43</td>
<td>156</td>
<td>-</td>
</tr>
<tr>
<td>([\text{N}_2\text{O}_2\text{O}_2])[NO(_3)]</td>
<td>252.06</td>
<td>234</td>
<td>180 [46]</td>
</tr>
</tbody>
</table>

\(^a\) The values are discussed in Section 2.2.4

2.1.2.3.2 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The glass temperature, the solid-solid transitions, the melting point and freezing temperature for the alkylammonium series were determined by DSC (see Table 2.7). All the samples were measured in the same condition of 5 K min\(^{-1}\) over three cycles. Here is reported the second cycle, as same pattern was observed for all of them. Dinitrogen gas was purged through the cell with a flow rate of ca. 20 cm\(^3\) min\(^{-1}\). DSC traces are illustrated in Figures 2.19-2.24.
Figure 2.19 DSC trace of $[N_{0.0.2}][NO_3]$ at a standard heating and cooling rate of $5^\circ C$ min$^{-1}$.

Figure 2.20 DSC trace for $[N_{0.0.3}][NO_3]$ at a standard heating and cooling rate of $5^\circ C$ min$^{-1}$. 
Figure 2.21 DSC trace for $\left[N_0\left(0.4\right)\left[\text{NO}_3\right]\right]$ at a standard heating and cooling rate of $5^\circ\text{C/min}$.

Figure 2.22 DSC trace for $\left[N_0\left(0.2\right)\left[\text{NO}_3\right]\right]$ at a standard heating and cooling rate of $5^\circ\text{C/min}$. 
Figure 2.23 DSC trace for \([\text{N}_2\text{H}_2\text{NO}_3]\) at a standard heating and cooling rate of 5°C min\(^{-1}\).

Figure 2.24 DSC trace for \([\text{N}_2\text{H}_2\text{NO}_3]\) at a standard heating and cooling rate of 5°C min\(^{-1}\).
Table 2.7 The glass transition temperatures, the solid-solid phase transitions, the melting points for the alkylammonium series.

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Glass transitions $T_g$/°C</th>
<th>Solid-solid transitions $T_{sol}$/°C</th>
<th>Melting $T_m$/°C</th>
<th>$\Delta H$/kJ mol$^{-1}$</th>
<th>$\Delta H_fusion$/kJ mol$^{-1}$</th>
<th>$T_m$ lit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{N}_0\text{002}]\text{NO}_3$</td>
<td>13.6</td>
<td>7</td>
<td>9 [46]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{N}_0\text{003}]\text{NO}_3$</td>
<td>6.5</td>
<td>8</td>
<td>4.0 [107]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{N}_0\text{004}]\text{NO}_3$</td>
<td>-48.3</td>
<td>2</td>
<td>39.3</td>
<td>2</td>
<td>42.2</td>
<td>9</td>
</tr>
<tr>
<td>$[\text{N}_0\text{223}]\text{NO}_3$</td>
<td>61.1</td>
<td>7</td>
<td>99.3</td>
<td>6</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$[\text{N}_0\text{222}]\text{NO}_3$</td>
<td>10.4</td>
<td>10</td>
<td>116.0</td>
<td>11</td>
<td>113-114 [46]</td>
<td></td>
</tr>
<tr>
<td>$[\text{N}_2\text{222}]\text{NO}_3$</td>
<td>15.6</td>
<td>22</td>
<td>92.1</td>
<td>14</td>
<td>115 [108]</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.8 The freezing points for the alkylammonium series.

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Crystallisation $T_c$/°C</th>
<th>$\Delta H$/kJ mol$^{-1}$</th>
<th>$T_c$</th>
<th>$\Delta H$</th>
<th>$T_c$</th>
<th>$\Delta H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{N}_0\text{002}]\text{NO}_3$</td>
<td>-14.5</td>
<td>7</td>
<td>7</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{N}_0\text{003}]\text{NO}_3$</td>
<td>-20.7</td>
<td>7</td>
<td>7</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{N}_0\text{004}]\text{NO}_3$</td>
<td>2.5</td>
<td>7</td>
<td>7</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{N}_0\text{222}]\text{NO}_3$</td>
<td>55.1</td>
<td>7</td>
<td>70.3</td>
<td>7</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>$[\text{N}_0\text{222}]\text{NO}_3$</td>
<td>-11.9</td>
<td>1</td>
<td>-10.7</td>
<td>2</td>
<td>-5.8</td>
<td>5</td>
</tr>
<tr>
<td>$[\text{N}_2\text{222}]\text{NO}_3$</td>
<td>75.7</td>
<td>4</td>
<td>78.8</td>
<td>3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.1.2.4 X-ray crystallography

Diffraction data of $[\text{N}_0\text{004}]\text{NO}_3$, and $[\text{N}_0\text{002}]\text{NO}_3$, were collected by Nockemann and reported by Stana [106] (see Appendix B8). The crystallographic structure of diethylammonium nitrate, $[\text{N}_0\text{022}]\text{NO}_3$, will be used to simulate their vibrational properties, for extended comparison with experimental measurement in Chapter 5. Figures were drawn using Mercury 3.8 software. Although these two structures are reported in Stana’s PhD thesis [106], the data and structures in the thesis did not correspond to the experimental .cif files. The following structures have been recreated from the original .cif files and, do not correspond to the information elsewhere [106]. The R factor is the usual measure of experimental precision quoted for a crystal-structure. Roughly speaking, structures with R factors lower than 0.05 (or, equivalently, 5%) are high quality; anything above 0.10 may have significant inaccuracies in bonds lengths and angles. The R factors were found 0.04, and 0.042 for $[\text{N}_0\text{004}]\text{NO}_3$ and $[\text{N}_0\text{022}]\text{NO}_3$, respectively.
2.1.2.4.1 \([\text{N}_0\text{O}_0\text{O}_4][\text{NO}_3]\)

**Crystal data of \([\text{N}_0\text{O}_0\text{O}_4][\text{NO}_3]\) at 293K:** \(M = 136.014\), monoclinic, space group P1 21/c, \(a = 7.5101(3)\) Å, \(b = 10.5203(4)\) Å, \(c = 9.4867(3)\) Å, \(\alpha = 90^\circ\), \(\beta = 108.436(2)^\circ\), \(\gamma = 90^\circ\), \(V = 711.06\) Å\(^3\), \(Z = 4\), \(D_{\text{calc}} = 1.272\) mg mm\(^{-3}\).

Butylammonium nitrate, \([\text{N}_0\text{O}_0\text{O}_4][\text{NO}_3]\) adopts a monoclinic lattice, with four identical “ion pairs” per unit cell (see Figure 2.25).

![Figure 2.25 Unit cell of \([\text{N}_0\text{O}_0\text{O}_4][\text{NO}_3]\).](image)

In the full structure, each cation is surrounded by three anions, creating a three-dimensional network of hydrogen bonds, with one of them being bifurcated. Similarly, each anion is surrounded by three cations, again with one of the hydrogen bonds being bifurcated (Figure 2.26).

![Figure 2.26 Hydrogen bond interactions around the cation and anion in \([\text{N}_0\text{O}_0\text{O}_4][\text{NO}_3]\); distances are given in Å units.](image)
Hydrogen bonds formed around the cation vary in strength. According to the classification of Hunt [15], hydrogen bonds which fall in the range of 1.5-2.2 Å and $\angle XHY > 130^\circ$ are considered as moderate (Table 2.1). From Figure 2.26 and Table 2.9, it can be seen that all the simple hydrogen bonds (2, 3, and 4) in the structure of $\left[NO_3\right]^{-}$ are moderate, and one branch of the bifurcated hydrogen bond (1) is weak.

**Table 2.9** Bond distances and angles for $\left[N_0004\right]\left[NO_3\right]$.

<table>
<thead>
<tr>
<th>Hydrogen bonds</th>
<th>$d(H\cdots O)$ / Å</th>
<th>$\angle NHO$ / °</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.755</td>
<td>133.81</td>
</tr>
<tr>
<td>2</td>
<td>2.017</td>
<td>155.55</td>
</tr>
<tr>
<td>3</td>
<td>2.054</td>
<td>157.93</td>
</tr>
<tr>
<td>4</td>
<td>1.992</td>
<td>167.29</td>
</tr>
</tbody>
</table>

The extended hydrogen bonded network breaks the symmetry of the anions to different extents. The symmetry breaking is characterised in Table 2.10.

**Table 2.10** Bond distances and angles for the anion of $\left[N_0004\right]\left[NO_3\right]$.

<table>
<thead>
<tr>
<th>$d(NO)$ / Å</th>
<th>$\angle ONO$ / °</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-O$_1$</td>
<td>1.261</td>
</tr>
<tr>
<td>N-O$_2$</td>
<td>1.270</td>
</tr>
<tr>
<td>N-O$_3$</td>
<td>1.239</td>
</tr>
</tbody>
</table>

From Table 2.10, the average value of the angle around the plane anion is 120° and all of the N-O distances are slightly different, with one of them being particularly shorter than the other two. The absolute symmetry of the anion in the solid state has been lowered from D$_{3h}$ to C$_1$, but approximates to a local symmetry of C$_{2v}$. Butylammonium nitrate, $\left[N_0004\right]\left[NO_3\right]$, therefore contains a network of hydrogen bonds, with every hydrogen-bond donor and every hydrogen-bond acceptor contributing to that network.

The crystalline solid morphology is represented in Figure 2.27, where a repetitive sequence of layers, with polar and non-polar regions, can be seen formed of cations and anions.
The alkyl chains adopt a distinctive conformation in the non-polar layer, with sequences of alternating alkyl ammonium chains, arranged parallel and ‘head to tail’. Therefore the polar layer is formed by hydrogen bonds with the ammonium ‘heads’ being intercalated through the alkyl ‘tails’. The layered structure is held together by contributions from the hydrogen-bonded network and from the weak van der Waals interaction between the alkyl chains.

2.1.2.4.2 \([\text{N}_0\text{O}_2\text{S}]\text{[NO}_3\text{]}\)

**Crystal data of \([\text{N}_0\text{O}_2\text{S}]\text{[NO}_3\text{]}\) at 273:** \(M = 136.14, \) monoclinic, space group P1, \(a = 5.2927 (3),\) \(b = 6.2918(3),\) \(c = 11.1237(6),\) \(\alpha = 90.002(3)^\circ,\) \(\beta = 90.028(3)^\circ,\) \(\gamma = 90.007(3)^\circ,\) \(V = 370.43 \ \text{Å}^3,\) \(Z = 4,\) \(D_{\text{calc}} = 0.610 \ \text{mg mm}^{-3}.\)

This compound adopts a monoclinic lattice with two pairs of ions in the unit cell (see **Figure 2.28**).
The cation is surrounded by two anions forming two bifurcated hydrogen bonds, and the anion, similarly, is surrounded by two cations Figure 2.29. The result of this hydrogen-bonded network is an environment where both the hydrogen-donor and hydrogen-acceptor sites are occupied. The hydrogen bond distances are from 1.966 Å to 2.452 Å, which correspond to moderate hydrogen bonds under the Hunt classification [15]. The hydrogen bond parameters are given in Table 2.11.

Table 2.11 Bond distances and angles for \([\text{N}_{0.22}]\text{[NO}_3\text{]}\).

<table>
<thead>
<tr>
<th>Hydrogen bonds</th>
<th>(d(\text{H} \cdots \text{O}) / \text{Å})</th>
<th>(\angle \text{HNO} / ^\circ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.966</td>
<td>169.35</td>
</tr>
<tr>
<td>2</td>
<td>2.452</td>
<td>133.48</td>
</tr>
</tbody>
</table>

The presence of the hydrogen bonds slightly deforms the anion from \(D_{3h}\) to a lower symmetry, \(C_{2v}\), where the two N-O groups involved in stronger hydrogen interactions have a longer distance than the N-O group involved in weaker hydrogen bonds. The deformation parameters of the anion are shown in Table 2.12.

Table 2.12 Bond distances and angles for the anion of \([\text{N}_{0.22}]\text{[NO}_3\text{]}\).

<table>
<thead>
<tr>
<th>(d(\text{NO}) / \text{Å})</th>
<th>(\angle \text{ONO} / ^\circ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-O_1</td>
<td>1.251</td>
</tr>
<tr>
<td>N-O_2</td>
<td>1.251</td>
</tr>
<tr>
<td>N-O_3</td>
<td>1.242</td>
</tr>
</tbody>
</table>

Figure 2.29 Hydrogen bond interactions around the cation and anion in \([\text{N}_{0.22}]\text{[NO}_3\text{]}\).

The developed hydrogen-bonded network determines a packing conformation with alternating layers, of polar domains and non-polar domains. The non-polar domains are formed of intercalated alkyl chains. The polar domains are staggered between the alkyl chains, forming in this way alternating layers (see Figure 2.30).
2.1.3 Preparation of mixtures of alkylammonium nitrates

Binary mixtures were prepared in a dinitrogen-filled glovebox to prevent water vapour uptake, using an analytical high-precision (±10 μg) balance, by adding known masses of the each component into stoppered bottles. Two main binary systems were tackled here:

Firstly, equimolar mixtures of two monoalkylammonium nitrate ionic liquids (three hydrogen bond donor groups in the cation), viz: ethylammonium nitrate ([N\(_{0\,0\,2}\)][NO\(_3\)]), propylammonium nitrate ([N\(_{0\,0\,3}\)][NO\(_3\)]), and butylammonium nitrate ([N\(_{0\,0\,4}\)][NO\(_3\)]).

In order to study possible deviations from ideality, the selected mixtures were compared with systems with equivalent numbers of carbon atoms in the cation (henceforth simply referred as composite cations, and denoted by enclosure in curly brackets, {...}): {[N\(_{0\,0\,2}\)]\(_{0.75}\)[N\(_{0\,0\,4}\)]\(_{0.25}\)}[NO\(_3\)] and {[N\(_{0\,0\,2}\)]\(_{0.5}\)[N\(_{0\,0\,3}\)]\(_{0.5}\)}[NO\(_3\)] (2.5 equivalent carbons); {[N\(_{0\,0\,2}\)]\(_{0.25}\)[N\(_{0\,0\,4}\)]\(_{0.75}\)}[NO\(_3\)], {[N\(_{0\,0\,3}\)]\(_{0.5}\)[N\(_{0\,0\,4}\)]\(_{0.5}\)}[NO\(_3\)] (3.5 equivalent carbons) (see Figure 2.31 (a)).

Secondly, homologous binary series, all containing [N\(_{0\,0\,2}\)][NO\(_3\)] mixed with similar cations with different numbers of hydrogen-bond donor groups, were prepared. The second component was selected from: diethylammonium nitrate, [N\(_{0\,2\,2}\)][NO\(_3\)] (two hydrogen-bond donors); triethylammonium nitrate, [N\(_{2\,2\,2}\)][NO\(_3\)] (one hydrogen-bond donor); and tetraethylammonium nitrate, [N\(_{2\,2\,2}\)][NO\(_3\)] (no hydrogen bond donors) cf. Figure 2.31 (b). The latter salt is an aprotic ionic liquid, and was studied for comparison purposes. The hydrogen bond patterns for each cation are shown in Figure 2.31.
Figure 2.31 Structure, name and acronym of (a) pure monoalkylammonium nitrate ionic liquids and their mixtures, and (b) pure di-, tri-, and tetra-ethylammonium nitrate and their mixtures with ethylammonium nitrate.
Since the binary mixtures of ionic liquids studied here have three constituents (each ionic liquid has a specific alkylammonium cation, but all have the nitrate anion in common), the adopted nomenclature is based on the number of constituents: \([A]_x[B]_{1-x}[/Y]\) \([109]\). In these examples, \(x\) is the mole fraction of the salt \([A]/[Y]\) in the mixture, while \((1-x)\) is the corresponding mole fraction of \([B]/[Y]\) (see Figure 2.31).

### 2.1.3.1 Binary mixtures of monoalkylammonium nitrates \([N_{0,0,0,0}][NO_3]\) series \((n = 2, 3, 4)\)

The masses and molar composition for the monoalkylammonium nitrates binary mixtures are shown in Table 2.13.

**Table 2.13** Masses and composition for the mixtures of monoalkylammonium nitrates \([N_{0,0,0,0}][NO_3]\) series \((n = 2, 3, 4)\).

<table>
<thead>
<tr>
<th>([N_{0,0,0,2}][N_{0,0,0,4}]/{1-x})[NO_3]</th>
<th>([N_{0,0,0,2}][NO_3]/g)</th>
<th>([N_{0,0,0,4}][NO_3]/g)</th>
<th>Real mol fraction of ([N_{0,0,0,2}][NO_3])</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x = 0.75)</td>
<td>4.20103</td>
<td>1.76256</td>
<td>0.7500</td>
</tr>
<tr>
<td>(x = 0.50)</td>
<td>2.03691</td>
<td>2.56172</td>
<td>0.4999</td>
</tr>
<tr>
<td>(x = 0.25)</td>
<td>1.28901</td>
<td>4.86909</td>
<td>0.2499</td>
</tr>
<tr>
<td>([N_{0,0,0,3}][N_{0,0,0,4}]/{1-x})[NO_3]</td>
<td>([N_{0,0,0,3}][NO_3]/g)</td>
<td>([N_{0,0,0,4}][NO_3]/g)</td>
<td>Real mol fraction of ([N_{0,0,0,3}][NO_3])</td>
</tr>
<tr>
<td>(x = 0.50)</td>
<td>2.21873</td>
<td>2.50155</td>
<td>0.5004</td>
</tr>
<tr>
<td>([N_{0,0,0,3}][N_{0,0,0,4}]/{1-x})[NO_3]</td>
<td>([N_{0,0,0,3}][NO_3]/g)</td>
<td>([N_{0,0,0,4}][NO_3]/g)</td>
<td>Real mol fraction of ([N_{0,0,0,3}][NO_3])</td>
</tr>
<tr>
<td>(x = 0.50)</td>
<td>2.59120</td>
<td>2.88170</td>
<td>0.5005</td>
</tr>
</tbody>
</table>

2.1.3.1.1 Mixtures of Ethylammonium Nitrate and Butylammonium Nitrate.

\[
\text{[\text{NH}_3][\text{NO}_3]} + \text{[\text{NH}_3][\text{NO}_3]} - \text{[\text{NH}_3][\text{NO}_3]} \rightarrow \text{[\text{NH}_3][\text{NO}_3]} (1-x) \text{[\text{NO}_3]}
\]

\([N_{0,0,0,2}][NO_3]\) and \([N_{0,0,0,4}][NO_3]\) were mixed together in three molar concentration ratios:

- \([N_{0,0,0,2}][NO_3]]_{0.75}[N_{0,0,0,4}]]_{0.25}[NO_3]\); For this mixture, 4.20103 g of \([N_{0,0,0,2}][NO_3]\) (liquid) were added to 1.76256 g of \([N_{0,0,0,4}][NO_3]\) (solid) in a plastic cylinder, forming a liquid solution that was stirred for six hours stirring at room temperature.

- \([N_{0,0,0,2}][NO_3]]_{0.5}[N_{0,0,0,4}]]_{0.5}[NO_3]\); For this mixture 2.03691 g of \([N_{0,0,0,2}][NO_3]\) (liquid) were added to 2.56172 g of \([N_{0,0,0,4}][NO_3]\) (solid) in the cylinder, giving rise a homogenous liquid. Good mixing was assured by magnetic stirring at room temperature for twelve hours.

- \([N_{0,0,0,2}][NO_3]]_{0.25}[N_{0,0,0,4}]]_{0.75}[NO_3]\); For this mixture, 1.28901 g of \([N_{0,0,0,2}][NO_3]\) (liquid) were added to 4.86909 g of \([N_{0,0,0,4}][NO_3]\) (solid) in a plastic cylinder,
forming a very viscous solution that was stirred for twelve hours at room temperature.

### 2.1.3.1.2 Mixture of Ethylammonium Nitrate and Propylammonium Nitrate.

\[
\left[ \text{NH}_3\right]\text{[NO}_3\left\rangle \right] + \left[ \text{NH}_3\right]\text{[NO}_3\left\rangle \right] \rightarrow \left[ \text{NH}_3\right]\text{[NO}_3\left\rangle \right]_x \left(1-x\right)\text{[NO}_3\left\rangle \right]
\]

\[
\left[\text{NO}_3\right]_2\text{[NO}_3\] and \left[\text{NO}_3\right]_3\text{[NO}_3\] were mixed together in equimolar proportion. For this mixture 2.2187 g of \left[\text{NO}_3\right]_2\text{[NO}_3\] (liquid) were added to 2.5015 g of \left[\text{NO}_3\right]_3\text{[NO}_3\] (solid) in the cylinder, giving rise a homogenous liquid. Good mixing was assured by magnetic stirring at room temperature for twelve hours.

### 2.1.3.1.3 Mixture of Propylammonium Nitrate and Butylammonium Nitrate.

\[
\left[ \text{NH}_3\right]\text{[NO}_3\left\rangle + \left[ \text{NH}_3\right]\text{[NO}_3\left\rangle \rightarrow \left[ \text{NH}_3\right]\text{[NO}_3\left\rangle \right]_x \left(1-x\right)\text{[NO}_3\right]
\]

\[
\left[\text{NO}_3\right]_3\text{[NO}_3\] and \left[\text{NO}_3\right]_4\text{[NO}_3\] were mixed together in equimolar proportion. For this mixture 2.5912 g of \left[\text{NO}_3\right]_3\text{[NO}_3\] (liquid) were added to 2.8817 g of \left[\text{NO}_3\right]_4\text{[NO}_3\] (solid) in the cylinder, giving rise a homogenous liquid. Good mixing was assured by magnetic stirring at room temperature for twelve hours.

### 2.1.3.2 Binary mixtures of \(\text{[NO}_0\text{.0}_2\text{]}\text{[NO}_3\] with di-, tri- or tetra-ethylammonium nitrate

The binary systems, composed of di-, tri- or tetra- ethylammonium nitrate mixed with ethylammonium nitrate, were prepared in two different series, where the molar concentration (\(x\)) ranged either from \(x = 0.05\) until solidification, or from \(x = 0.1\) until solidification, both having molar concentration increments in steps of \(x = 0.1\). This procedure allowed us to track possible systematic errors.

### 2.1.3.2.1 Mixture of Ethylammonium Nitrate and Diethylammonium Nitrate.

\[
\left[ \text{NH}_3\right]\text{[NO}_3\left\rangle + \left[ \text{NH}_2\text{H}\right]\text{[NO}_3\left\rangle \rightarrow \left[ \text{NH}_3\right]\text{[NO}_3\left\rangle \right]_x \left(1-x\right)\text{[NO}_3\right]
\]

\[
\left[\text{NO}_3\right]_2\text{[NO}_3\] and \left[\text{NO}_3\right]_2\text{[NO}_3\] were used to prepare binary mixtures. As \left[\text{NO}_3\right]_2\text{[NO}_3\] is a solid ionic liquid with melting point of 369.15 K, the molar composition studied for the binary mixtures was from 0.05 to 0.35 of \left[\text{NO}_3\right]_2\text{[NO}_3\], which was defined by the solubility limit. Masses and molar composition for the mixtures \{\left[\text{NO}_3\right]_2\text{[NO}_3\],\left(1-x\right)\text{[NO}_3\right]\} are shown in Table 2.14.
Table 2.14 Masses and molar composition for the mixtures {[N₂O₂]₂[N₂O₂]/[r-x][NO₃].

<table>
<thead>
<tr>
<th>{[N₂O₂]₂[N₂O₂]/[r-x][NO₃]}</th>
<th>[N₂O₂]₂[NO₃] / g</th>
<th>[N₂O₂]₂[NO₃] / g</th>
<th>Real mol fraction of [N₂O₂]₂[NO₃]</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0.05</td>
<td>0.33120</td>
<td>5.00450</td>
<td>0.04992</td>
</tr>
<tr>
<td>x = 0.10</td>
<td>0.69900</td>
<td>5.00540</td>
<td>0.09981</td>
</tr>
<tr>
<td>x = 0.15</td>
<td>1.08771</td>
<td>4.89579</td>
<td>0.14995</td>
</tr>
<tr>
<td>x = 0.20</td>
<td>1.52886</td>
<td>4.85734</td>
<td>0.19994</td>
</tr>
<tr>
<td>x = 0.25</td>
<td>1.83969</td>
<td>4.38071</td>
<td>0.25005</td>
</tr>
<tr>
<td>x = 0.30</td>
<td>2.21301</td>
<td>4.10299</td>
<td>0.29983</td>
</tr>
<tr>
<td>x = 0.35</td>
<td>2.77118</td>
<td>3.97922</td>
<td>0.35605</td>
</tr>
</tbody>
</table>

2.1.3.2.2 Mixture of ethylammonium nitrate and triethylammonium nitrate.

\[
\text{NH}_3\left[\text{NO}_3\right] + \text{N}_3\left[\text{H}_3\right]\left[\text{NO}_3\right] \rightarrow \text{NH}_3\left[\text{NO}_3\right]_x + \text{N}_3\left[\text{H}_3\right]\left[\text{NO}_3\right]_{(1-x)}
\]

[N₂O₂]₂[NO₃] and [N₂₂₂]₂[NO₃] were used to prepare binary mixtures. As [N₂₂₂]₂[NO₃] is a solid ionic liquid, a starting molar composition of [N₂₂₂]₂[NO₃] = 0.05 was selected, which was then increased as in Section 2.1.3.2.1 up to [N₂₂₂]₂[NO₃] = 0.55, which was defined by the solubility limit. Masses and molar composition for the mixtures {[N₂₂₂]₂[N₂O₂]/[r-x][NO₃] are shown in Table 2.15.

Table 2.15 Masses and molar composition for the mixtures {[N₂₂₂]₂[N₂O₂]/[r-x][NO₃].

<table>
<thead>
<tr>
<th>{[N₂₂₂]₂[N₂O₂]/[r-x][NO₃]}</th>
<th>[N₂₂₂]₂[NO₃] / g</th>
<th>[N₂O₂]₂[NO₃] / g</th>
<th>Real mol fraction of [N₂₂₂]₂[NO₃]</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0.05</td>
<td>0.39940</td>
<td>5.00450</td>
<td>0.04992</td>
</tr>
<tr>
<td>x = 0.10</td>
<td>0.84550</td>
<td>5.01740</td>
<td>0.09986</td>
</tr>
<tr>
<td>x = 0.15</td>
<td>1.30100</td>
<td>4.85340</td>
<td>0.15009</td>
</tr>
<tr>
<td>x = 0.20</td>
<td>1.71640</td>
<td>4.54450</td>
<td>0.19913</td>
</tr>
<tr>
<td>x = 0.25</td>
<td>2.51821</td>
<td>4.97319</td>
<td>0.25001</td>
</tr>
<tr>
<td>x = 0.30</td>
<td>2.79676</td>
<td>4.31024</td>
<td>0.29931</td>
</tr>
<tr>
<td>x = 0.35</td>
<td>2.75609</td>
<td>3.36811</td>
<td>0.35010</td>
</tr>
<tr>
<td>x = 0.40</td>
<td>2.03561</td>
<td>2.00321</td>
<td>0.40082</td>
</tr>
<tr>
<td>x = 0.45</td>
<td>2.54302</td>
<td>2.03948</td>
<td>0.45081</td>
</tr>
<tr>
<td>x = 0.50</td>
<td>3.20878</td>
<td>2.11564</td>
<td>0.50038</td>
</tr>
<tr>
<td>x = 0.55</td>
<td>3.69958</td>
<td>1.99557</td>
<td>0.54964</td>
</tr>
</tbody>
</table>

2.1.3.2.3 Mixture of ethylammonium nitrate and tetraethylammonium nitrate.

\[
\text{NH}_3\left[\text{NO}_3\right] + \text{N}_4\left[\text{H}_4\right]\left[\text{NO}_3\right] \rightarrow \text{NH}_3\left[\text{NO}_3\right]_x + \text{N}_4\left[\text{H}_4\right]\left[\text{NO}_3\right]_{(1-x)}
\]

[N₂O₂] and [N₂₂₂]₂[NO₃] were used to prepare binary mixtures following the procedure previously described up to [N₂₂₂]₂[NO₃] = 0.35. Masses and molar composition for the mixtures {{N₂₂₂}₄[N₂₀₂]/(r-x)[NO₃] are shown in Table 2.16.
Table 2.16 Masses and molar composition for the mixtures \{[N_{2.2.2.2}]_x[N_{0.0.0.2}]_{(1-x)}[NO_3] \}

<table>
<thead>
<tr>
<th>x</th>
<th>[N_{2.2.2.2}][NO_3] / g</th>
<th>[N_{0.0.0.2}][NO_3] / g</th>
<th>Real mol fraction of [N_{2.2.2.2}][NO_3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.47080</td>
<td>5.01430</td>
<td>0.05015</td>
</tr>
<tr>
<td>0.10</td>
<td>0.98810</td>
<td>5.00000</td>
<td>0.10001</td>
</tr>
<tr>
<td>0.15</td>
<td>1.50239</td>
<td>4.78691</td>
<td>0.15000</td>
</tr>
<tr>
<td>0.20</td>
<td>1.97348</td>
<td>4.43502</td>
<td>0.19994</td>
</tr>
<tr>
<td>0.25</td>
<td>4.03532</td>
<td>2.47918</td>
<td>0.25675</td>
</tr>
<tr>
<td>0.30</td>
<td>2.63786</td>
<td>3.46924</td>
<td>0.29949</td>
</tr>
<tr>
<td>0.35</td>
<td>3.10556</td>
<td>3.24284</td>
<td>0.35000</td>
</tr>
</tbody>
</table>

2.2 Results and discussion

2.2.1 Synthesis

The synthesis of alkylammonium nitrates consists of an acid-base reaction between an amine and nitric acid, Equation (2.1):

\[ N_{xyz} + HNO_3 \rightarrow [N_{0xy}z][NO_3] \]  \hspace{1cm} (2.1)

Tetraethylammonium nitrate, \([N_{2.2.2.2}][NO_3]\), was prepared by an analogous procedure, in which aqueous tetraethylammonium hydroxide was treated with concentrated nitric acid, Equation (2.2):

\[ [N_{2.2.2.2}][OH] + HNO_3 \rightarrow [N_{2.2.2.2}][NO_3] + H_2O \]  \hspace{1cm} (2.2)

As all the reactions were highly exothermic, it was needed to cool to -196 °C using liquid nitrogen. The yield of the ionic liquid was found to be no less than 92%, except for \([N_{2.2.2.2}][NO_3]\), which indicates a good optimisation of the reaction process.

For an ionic liquid to be considered pure, less than 1% of neutral, acid or base species must be present [16]. For this to be possible, the proton from the acid to the base must be efficiently transferred. There are several means to establish the degree of proton transfer. For instance, the principle method is based on the aqueous pK_a values of the amines (see Table 2.17). The pK_a of the nitric acid is -1.3 at \(T = 25\ \degree C\), determined experimentally by NMR and Raman [97c]. Angell discussed the criteria for essentially complete proton transfer, and concluded that the minimum pK_a difference between the acid and the base is 5. As can be seen from Table 2.17, all the amines used in this work should form stable protonated cations.
Table 2.17 \( pK_a \) values of alkylamine determined experimentally and predicted.

<table>
<thead>
<tr>
<th>( \text{N}_2 \text{O} \text{N}_2 \text{N}_2 )</th>
<th>( pK_a \text{ exp.} )</th>
<th>( pK_a \text{ cal.} )</th>
<th>( T / ^\circ C )</th>
<th>( \Delta pK_a )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>10.8</td>
<td>-</td>
<td>20</td>
<td>12.1</td>
<td>[110]</td>
</tr>
<tr>
<td>3</td>
<td>10.7</td>
<td>-</td>
<td>20</td>
<td>12.0</td>
<td>[110]</td>
</tr>
<tr>
<td>4</td>
<td>10.8</td>
<td>-</td>
<td>20</td>
<td>12.0</td>
<td>[110]</td>
</tr>
</tbody>
</table>

\( \text{N}_2 \text{N}_2 \text{N}_2 \) | \( pK_a \text{ exp.} \) | \( pK_a = 11.1 + 0.1 - (0.1 \times n) \) | \( T / ^\circ C \) | \( \Delta pK_a \) | Ref. |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>11.0</td>
<td>11.2</td>
<td>18</td>
<td>12.5</td>
<td>[110]</td>
</tr>
</tbody>
</table>

\( \text{N}_2 \text{N}_2 \text{N}_2 \) | \( pK_a \text{ exp.} \) | \( pK_a = 10.5 + 0.2 - (0.2 \times n) \) | \( T / ^\circ C \) | \( \Delta pK_a \) | Ref. |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>9.9</td>
<td>10.7</td>
<td>25</td>
<td>12</td>
<td>[110]</td>
</tr>
</tbody>
</table>

The freeze-drier was used to remove any excess of water in the ionic liquids, because of the explosive nature of the nitrates. During the freeze-drying, or lyophilisation, process, the ice changes directly to vapour, without passing through a liquid phase due to the powerful vacuum system.

### 2.2.2 Elemental analysis and Karl Fischer titration

The elemental analysis of the ionic liquids shows acceptable deviation from the theoretical values for the %C and %H composition, from 0.002 to 0.1% (see Table 2.2). In the case of %N, the deviation varies from 0.03% to 0.7%, as is normal for the analysis of the ammonium salts, due to incomplete nitrogen combustion.

Even though these systems are correctly regarded as highly hygroscopic, coulometric Karl Fischer titrations revealed water content between 200 and 550 ppm, with the exception of ethylammonium nitrate, which has a water content approaching 2000 ppm (see Table 2.3).

### 2.2.3 \( ^1H \) and \( ^{13}C \) NMR spectroscopy

The \( ^1H \) NMR experiment is the most common NMR experiment. The hydrogen nucleus is very sensitive and usually yields sharp signals. Even though its chemical shift range is narrow, its sharp signals make proton NMR very useful. All the ionic liquid spectra were recorded in \( d_6 \)-dmso. In the case of \( [\text{N}_2 \text{O} \text{N}_2 \text{N}_2] \text{[NO}_3] \) and \( [\text{N}_0 \text{O} \text{O} \text{O}_2] \text{[NO}_3] \), both liquids, \( d_6 \)-dmso was introduced in a quartz capillary, to avoid possible hydrogen-bonding interactions with the samples. As \( [\text{N}_0 \text{O} \text{O}_4] \text{[NO}_3] \), \( [\text{N}_0 \text{O}_2 \text{O}_2] \text{[NO}_3] \), \( [\text{N}_2 \text{O}_2 \text{O}_2] \text{[NO}_3] \) and \( [\text{N}_2 \text{O}_2 \text{O}_2] \text{[NO}_3] \) are all solid at room temperature, they could not be examined as neat liquids; hence, \( d_6 \)-dmso was used as a solvent (despite its ability to disrupt hydrogen bonds). However, the presence of \( d_6 \)-dmso did not disrupt from using the spectra in order to check the purity of the material.

Since ethylammonium nitrate, \( [\text{N}_0 \text{O} \text{O}_2] \text{[NO}_3] \), contains three types of hydrogen atoms, \( [\text{C}_2 \text{H}_5 \text{C}_2 \text{H}_2 \text{N}_2 \text{H}_3] \text{[NO}_3] \), the spectrum shows three sets of peaks with distinctive and sharp signals for the methylene and methyl protons, but a broad peak for the
acidic protons (which indicates a complex interaction due to the rapid exchange of the proton).

Regarding the assignment of the peaks (see Figure 2.1):

\[ \delta(\text{NH}_3) = 7.37 \text{ ppm (integration = 3H; broad singlet)} \]
\[ \delta(\text{CH}_2) = 2.95 \text{ ppm (integration = 2H; quartet)} \]
\[ \delta(\text{CH}_3) = 1.13 \text{ ppm (integration = 3H; triplet)} \]

Coupling patterns emerge because of the magnetic field of vicinal (adjacent) protons influencing the field that the proton experiences. The proximity of "\( n \)" equivalent proton on neighbouring carbon atoms causes the signals to be split into \( n+1 \) lines. The coupling constants, \( ^3J \), measure the interaction between a pair of protons (in frequency units, Hz) were found 7.3 Hz and 7.2 Hz for \(-\text{CH}_3\) and \(-\text{CH}_2\) respectively.

The \(^{13}\text{C} \) NMR spectrum for ethylammonium nitrate (see Figure 2.2) shows two sharp and distinctive peaks, as \([\text{CH}_3\text{CH}_2\text{NH}_3]^{+}\text{NO}_3^{-}\) has two types of carbon. As the external magnetic field experienced by the carbon is affected by the electronegativity of the atoms surrounded to them, the peak at about 35 ppm (the larger chemical shift) is due to the methylene group, because it has a more electronegative environment.

The complete analysis of the \(^1\text{H} \) and \(^{13}\text{C} \) NMR shifts for all the series of alkylammonium nitrates is shown in Table 2.4 and Table 2.5, respectively. The quality of the spectra (see Figures 2.1-2.12) demonstrate the high purity of all the samples. The alkylammonium nitrate products are highly hydroscopic. Despite this, \(^1\text{H} \) NMR and IR spectroscopy, as well as Karl Fischer measurements, demonstrated that the samples were effectively water-free. The compounds were stored in a glovebox when not in use.

2.2.4 Thermal analysis
A good thermal stability of the samples for study is required, and they were investigated by TGA and DSC.

2.2.4.1 Thermal gravimetric analyses (TGA)
The samples size used was between 5 and 10 mg. All the alkylammonium nitrates samples were prepared in an aluminium pan in a glove box (under dinitrogen conditions). The measurements were carried out strictly under the same conditions, to facilitate their comparison. The onset of the weight loss in each trace was used to determine the decomposition temperature \( (T_d) \). Universal Analysis 2000 software was used to determine the onset temperature.

The TGA traces for all six ionic liquids were reported in Figures 2.13-2.18 and decomposition temperatures are listed in Table 2.6. These alkylammonium salts
decompose in one step, as can be clearly seen by the curve shape. The decomposition is complete and corresponds to a dissociation of the ionic liquids back into their volatile precursor amines and acid. Decomposition occurs above 145 °C for all the salts. The absence of water was confirmed by the lack of weight loss around 100 °C in the TGA. The most stable compound is \([\text{N}_0\text{O}_0\text{O}_2][\text{NO}_3]\) which decomposes at 201 °C and the least stable is \([\text{N}_0\text{O}_2\text{O}_2][\text{NO}_3]\), which decomposes at 149 °C. As the alkyl chain length increases, the salts decompose at lower temperature, being the decomposition temperature for \([\text{N}_0\text{O}_0\text{O}_3][\text{NO}_3]\), and \([\text{N}_0\text{O}_0\text{O}_4][\text{NO}_3]\) similar (Table 2.6).

\[
T_d[\text{N}_0\text{O}_0\text{O}_2][\text{NO}_3] > T_d[\text{N}_0\text{O}_0\text{O}_3][\text{NO}_3] \approx T_d[\text{N}_0\text{O}_0\text{O}_4][\text{NO}_3]
\]

2.2.4.2 Differential scanning calorimetry (DSC)

Differential scanning calorimetry is used to measure the characteristic thermal transitions of a sample, such as: the glass transition temperature, the solid-solid phase transitions, the melting point, and the freezing point. Every process has an associated change of enthalpy. For instance, the heat of fusion is the amount of energy required during a phase change from solid to liquid. The enthalpy changes were calculated from the area under the appropriate DSC curve, and can be either exothermic or endothermic. From a practical point of view, the transition temperature measured is dependent on the rate of the thermal ramp. Thus, all the DSCs were recorded at the same scan rate, 5 °C min\(^{-1}\). The uncertainty associated with each determination is ±0.3 °C (Glass transition, \(T_g\)), ±0.2 °C (Solid-solid transitions, \(T_{ssd}\)), ±0.2 °C (Melting transition, \(T_m\)) and ±0.3 °C (Crystallisation, \(T_c\)). The uncertainty associated with the determination of the enthalpies using the present technique and samples was estimated to be ±3 kJ mol\(^{-1}\).

The DSC traces for all six ionic liquids were reported in Figures 2.19-2.24 and Tables 2.7 and 2.8. The DSC trace for \([\text{N}_0\text{O}_0\text{O}_2][\text{NO}_3]\) (see Figure 2.19) shows a melting temperature (\(T_m\)) of 13.6 °C and a heat of fusion of 7 kJ mol\(^{-1}\). The thermogram of \([\text{N}_0\text{O}_0\text{O}_3][\text{NO}_3]\) (see Figure 2.20) is very similar that of \([\text{N}_0\text{O}_0\text{O}_2][\text{NO}_3]\) with \(T_m = 6.5\) °C and the enthalpy of 8 kJ mol\(^{-1}\); the compound freezes at about -21 °C. These two salts crystallise very energetically, with the characteristic loop on the crystallisation peak. The case of \([\text{N}_0\text{O}_0\text{O}_4][\text{NO}_3]\) (see Figure 2.21) is different. Apart from fusion (42.2 °C) and crystallisation (2.5 °C) phenomena, glass and solid-solid transitions before melting, have been observed. Glass transitions (\(T_g\)) is observed at -48.3 °C. A solid-solid phase transition is recorded at 39.3 °C, which indicates that the \([\text{N}_0\text{O}_0\text{O}_4][\text{NO}_3]\) transform from one crystal to another crystal structure before melting. \([\text{N}_0\text{O}_0\text{O}_2][\text{NO}_3]\) (see Figure 2.22) shows two highly energetic crystallisation peaks (55.0 °C, with \(\Delta H_c\) of 7 KJ mol\(^{-1}\), and 70.3 °C, with \(\Delta H_c\) of 7 KJ mol\(^{-1}\). The solid-solid
transition occurs at 61°C and melting is observed at about 99 °C. As an ethyl chain has very few conformations which it can adopt, the probability is the low temperature forms have different configurations of the two ethyl groups relative to each other.

The salt \([N_{0.22.2}][NO_3]\) (see Figure 2.23) behaves rather differently. The DSC trace of the cooling rate shows multiple crystallisation transformations, three of them below 0 °C with low enthalpies. At 79 °C another crystallisation peaks is observed with high energetic enthalpy 10 KJ mol\(^{-1}\). The solid-solid transition occurs at 10.4°C and melting is observed at about 116 °C, which means that is forming a large plastic phase domain, from 10 °C to 116 °C.

The ionic liquid \([N_{2.2.2}][NO_3]\), with no proton available to form hydrogen bond, shows a melting temperature of 92 °C. The presence of the four alkyl chains attached gave a symmetric structural configuration which give rise to relatively high the melting temperature and highly enthalpies energy (14 KJ mol\(^{-1}\)).

### 2.2.5 X-ray crystallography

#### 2.2.5.1 \([N_{0.0.0.4}][NO_3]\)

The comparison of the simulated powder diffraction pattern with the experimental (taken from Stana [106]) shows a good agreement. The powder diffraction pattern confirms the layer distribution structure of \([N_{0.0.0.4}][NO_3]\) (see Figure 2.32). Hence, the single crystal structure is representative of the bulk of sample. There is no evidence of polymorphism present in \([N_{0.0.0.4}][NO_3]\).

![Figure 2.32 The powder diffraction spectra of \([N_{0.0.4}][NO_3]\) (a) determined experimentally and (b) predicted.](image)
In the experimental XRD studies of $\left[N_{0.022}\right]\left[NO_3\right]$ in Stana [106], there were significant differences between the experimentally measured powder diffraction pattern at RT, see Figure 2.33(a), and the simulated diffraction pattern at 120 K, see Figure 2.33(b). This is possibly due to the different temperatures at which they were recorded [106]. In addition, there is a broad shoulder at $2\theta = 15^\circ$ due to a hydrated impurity. It was assumed, therefore, that Stana’s sample had absorbed water to form a crystalline hydrate. Hence, a fresh sample was prepared and its powder diffraction pattern was re-recorded (see Figure 2.34 and Section 2.1.1.4). By comparing Figure 2.33(a) and Figure 2.34(a), it can be seen that the powder XRD of the freshly prepared sample for this thesis does not contain hydrated impurity [106].

In Figure 2.34, the crystal structures remain the same from low temperature to room temperature confirmed by the Rietfeld refinement of the room-temperature powder XRD data and single crystal data at 120 K.
Figure 2.34 Powder diffraction patterns of [N\textsubscript{0.222}][NO\textsubscript{3}] (a) determined experimentally using powder XRD at room temperature, (b) determined using a single-crystal XRD instrument in a capillary at room temperature, (c) determined using a single-crystal XRD instrument at 120 K, and (d) simulated spectrum using mercury software at 120K.

The change in lattice constants from room temperature, \(a = 5.4618\ \text{Å}, b = 6.1545\ \text{Å},\) and \(c = 11.4764\ \text{Å},\) to the single-crystal at 120K, \(a = 5.2927\ \text{Å (3.2%)}, b = 6.2918\ \text{Å (2.2%) and c = 11.1237\ \text{Å (3.1%)},}\) are within 3%. The visible differences between the room-temperature and the low-temperature data are only due to the thermal expansion, indicating a considerable softness of this material. The differences in the peak intensities and width can be attributed to the Debye-Waller factor and disorder effects of both cationic and anionic counterparts, respectively. The calculated structure as shown in the uppermost panel, is confirming that the agreement between the calculated and the low temperature is very good.

Small differences are found in the region characteristic of the small range order, where the configuration of the alkyl chain is more disordered in the bulk sample than in the analysed crystal. The sharp peak at \(2\theta = 16^\circ\) corresponds to the distance between two polar layers, \(d = 6.3\ \text{Å}\) and the peaks at \(2\theta = 20^\circ\) to \(24^\circ\) correspond to distances between 5.5 Å and 4.9 Å, distances related to the order of alkyl chains in the alternating layers.
2.3 Conclusions

The six protonic alkylammonium nitrates synthesised by proton transfer were obtained with a yield higher than 70% after the freeze-drying process. The water content was found between 200 and 550 ppm, with the exception of ethylammonium nitrate. This has a water content approaching 2000 ppm, which is common for these hygroscopic materials. Storage under a dinitrogen atmosphere was essential to prevent further water uptake. The elemental analysis of the ionic liquids shows acceptable low deviation from the theoretical values.

The \(^1\)H and \(^{13}\)C NMR analysis for the series of alkylammonium nitrates shown in Table 2.4 and Table 2.5, respectively, and the quality of the spectra (see Figures 2.1-2.12) demonstrate the high purity of the samples. The thermal stability of the ionic liquids were checked by TGA and DSC. The most stable compound was found to be \([\text{N}_0\text{O}_0\text{O}_2]\)[NO\(_3\)], which decomposes above 201 °C; the least stable is \([\text{N}_0\text{O}_2\text{O}_2]\)[NO\(_3\)], which decomposes above 149 °C. The six compounds showed physical appearances, from liquid (ethylammonium nitrate) to solid (tetraethylammonium nitrate) that are influenced by a number of factors, such as the formation of hydrogen bonds. For instance, the absence of the solid-solid phase transitions before melting may decrease drastically the melting temperature [112].

The crystal data of butylammonium nitrate, \([\text{N}_0\text{O}_4]\)[NO\(_3\)], and diethylammonium nitrate, \([\text{N}_0\text{O}_2\text{O}_2]\)[NO\(_3\)] reveal that both materials contain a network of hydrogen bonds, with every hydrogen-bond donor and every hydrogen-bond acceptor contributing to that network. It can be seen that there are three moderate hydrogen bonds, with one branch of the bifurcated hydrogen bond weak (under the Hunt classification [15]) in the structure of \([\text{N}_0\text{O}_4]\)[NO\(_3\)]. For \([\text{N}_0\text{O}_2\text{O}_2]\)[NO\(_3\)], the two hydrogen bond formed are classified as moderate, with distances from 1.966 Å to 2.452 Å.

All the alkylammonium mixtures were prepared by weight, just prior to the measurements, in a dinitrogen-filled glovebox to prevent water vapour uptake. To ensure proper mixing, each vial was stirred using a magnetic stirrer and in an automated shaker.
3 Thermophysical Behaviour
This chapter is centred on the thermophysical characterisation of different families of alkylammonium nitrate ionic liquids and their binary mixtures, namely the determination at atmospheric pressure of densities, electric conductivities and viscosities in the $288.15 < T/K < 353.15$ range. Initially, measurements will focus on ethylammonium, propylammonium and butylammonium nitrate systems, and their binary mixtures. These will be followed by studies involving binary mixtures composed of ethylammonium nitrate (with three hydrogen bond donor groups) and different homologous ionic liquids with differing numbers of hydrogen bond donor groups: diethylammonium nitrate (two hydrogen bond donors), triethylammonium nitrate (one hydrogen bond donor) and tetraethylammonium nitrate (no hydrogen bond donors). Finally, the behaviour of mixtures with different numbers of equivalent carbon atoms in the alkylammonium cations will be analysed.

3.1 Introduction

The hydrogen bonding rôle in protonic ionic liquids has been frequently addressed [113]. In a study of protonic monoalkylammonium ionic liquids, Atkin and coworkers suggested a clear relationship between hydrogen bond strength and several physical properties. They claimed that when the hydrogen bond is enhanced, glass transitions, melting points, and viscosity increase while ionic conductivity decreases. They also suggested that protonic ionic liquids containing strong linear hydrogen bonds have more “solid-like” behaviour, whereas those containing weaker, bent hydrogen bonds present a more “liquid-like” character [113b].

Despite the fact that the behaviour of individual protonic ionic liquids have been studied thoroughly, [47a,63] further research on this topic is still necessary. Kirchner suggested that oversimplifications and generalisations of the rôle of the hydrogen bond in ionic liquids should be avoided [114]. Even though conventionally strong hydrogen bonding leads to a strong lattice, it has been emphasised that, in specific cases, the elimination of a hydrogen bond leads to an increase in the viscosity and melting point temperatures of protonic ionic liquids instead of a decrease [95,115].

These intriguing observations launched a vigorous debate as described previously in Section 1.4, and motivated several authors to question the impact of hydrogen bonding in respect to other intermolecular interactions [95,102,104,116].

The fundamental motivation of this current chapter is to deepen our understanding of the behaviour of alkylammonium nitrates and their mixtures, including some long-known protonic ionic liquids.
Where the pure ionic liquids were liquids at room temperature, the physical properties were measured. If the pure ionic liquid was a solid at room temperature, its properties were extrapolated from those of its binary mixtures (vide infra).

Two main aspects of binary systems have been tackled here. Firstly, the thermophysical properties of monoalkylammonium nitrate ionic liquids and their mixtures with three hydrogen bond donor groups in the cation, viz: ethylammonium nitrate ([N\textsubscript{0002}][NO\textsubscript{3}]), propylammonium nitrate ([N\textsubscript{0003}][NO\textsubscript{3}]), and butylammonium nitrate ([N\textsubscript{0004}][NO\textsubscript{3}]), have been determined (see Figure 2.31).

In order to study possible deviations from ideality, the thermophysical behaviour (viz., density, ionic conductivity and dynamic viscosity) of selected mixtures have been compared with mixtures with equivalent numbers of carbon atoms in the cation: {[N\textsubscript{0002}0.75,N\textsubscript{0004}0.25][NO\textsubscript{3}]} and {[N\textsubscript{0002}0.5,N\textsubscript{0003}0.5][NO\textsubscript{3}]} (2.5 equivalent carbons); {[N\textsubscript{0002}0.25,N\textsubscript{0004}0.75][NO\textsubscript{3}]}, {[N\textsubscript{0003}0.5,N\textsubscript{0004}0.5][NO\textsubscript{3}]} (3.5 equivalent carbons). In addition, the mixture {[N\textsubscript{0002}0.5,N\textsubscript{0004}0.5][NO\textsubscript{3}]} (3 equivalent carbons) was also studied and compared with the pure [N\textsubscript{0003}][NO\textsubscript{3}].

Secondly, homologous binary mixtures based on [N\textsubscript{0002}][NO\textsubscript{3}] (three hydrogen bonds) have been studied, in which it is combined with similar cations with different numbers of hydrogen-bond donor groups, cf. Figure 2.31: diethylammonium nitrate, [N\textsubscript{0022}][NO\textsubscript{3}] (two hydrogen-bond donors); triethylammonium nitrate, [N\textsubscript{0222}][NO\textsubscript{3}] (one hydrogen-bond donor); and tetraethylammonium nitrate, [N\textsubscript{2222}][NO\textsubscript{3}] (no hydrogen bond donors). The latter salt is an aprotic ionic liquid, and was studied for comparison purposes (see Figure 3.1).

Figure 3.1 Scheme of the structures of alkylammonium nitrates with increasing number of chains.

The thermophysical responses of these systems were measured over a relatively large temperature range. The results were correlated to the overall ionicity of the systems, using representations of the corresponding Walden plots [117].
3.2 Physicochemical properties

3.2.1 Density

The density is the mass per unit volume of a material, which is a measure of the degree of compactness of a substance. The density of a material depends on how the ions are packed together, and hence, the size, shape and the ion-ion interaction.

Regarding the influence of the size and the shape, the density of protonic ionic liquids has been widely studied [46]. It has been shown that the density decreases as the alkyl chain length increases and temperature increases. It is apparent that primary amines are likely to have higher densities than secondary or tertiary ones. Heterocyclic amine cations make ionic liquids denser than alkylammonium cations. Replacing one methyl group by one hydroxyl group in the alkyl chain of the anion or cation increases the density, probably because of the formation of hydrogen-bonding.

For alkyl- and alkoxylimidazolium complexes, small chains have a similar behaviour but the density is higher in alkoxy chains. For large chains, there are considerable differences in their densities [46]. Kolbeck et al. [118] analysed nine bis{(trifluoromethyl)sulfonylamide} ([NTf$_2$])-based and twelve 1-methyl-3-octylimidazolium ([C$_6$C$_1$im]$^+$)-based ionic liquids. This selection of ionic liquids was chosen to probe the influence of the cations and anions on density.

Regarding the dependence of density on the temperature, it decreases with increasing temperature, for pure ionic liquids, as was expected.

The mixture of two components, in these case ionic liquids, can lead to ideal or non-ideal mixing. If the mixture behaves ideally, the excess molar volume, $V^e$, will be 0 and there is a linear change in the molar volume of the mixture between the molar volumes of the two pure components. The excess volume can be calculated from the density of the pure ionic liquids and from the mixture at defined compositions. Rebelo et al. [119] analysed the volumes of mixing of the mixtures of $\{[C_nC_1im][C_mC_1][NTf_2], [C_nC_1im][PF_6][NTf_2], [C_nC_1im][BF_4][NTf_2]\}$ and $\{[C_nC_1im][BF_4][PF_6]\}$ (with $n$ and $m$ ranging from 2 to 10). In all cases, the behaviour was almost linear. $V^e$ for all of these mixtures was small and less than 0.1% of the overall volume. Therefore, both experimental evidence and theoretical studies reveal a quasi-ideal behaviour, which increases as the size differences between the cations rise. This behaviour is common for most of the studied mixtures of two distinct ionic liquids.

3.2.2 Dynamic viscosity

The viscosity of a fluid is a measure of its resistance to gradual deformation by shear stress or tensile stress. The viscosity is dependent on ion-ion interactions in the ionic
liquid, such as van der Waals, hydrogen-bonding or Coulombic. When the interactions are larger, the viscosity is higher. A previous study of aprotic ionic liquids [120], showed that increasing the length of alkyl chains increases the viscosity because of stronger van der Waals interactions, meanwhile fluorination of the anion/cation decreases the viscosity by eliminating hydrogen bonding. It is consistent with what has been seen for protonic ionic liquids [46].

Rheology is also used to evaluate the ionicity of ionic liquids, using a method based also on the Walden rule. The rheological properties of five pure ionic liquids have been studied recently [121]: ethylammonium nitrate, propylammonium nitrate, ethanolammonium nitrate, ethylammonium methanoate, and dimethylethylammonium methanoate. The Walden plot shows that those ionic liquids are completely dissociated and, hence the presence of neutral species is low or practically non-existent. For all of these ionic liquids, the viscosity decreases with temperature. Moreover, the viscosity at constant temperature decreases in the order: 

\[
\text{[N}_0\text{0}_0\text{0}_0\text{C}_2\text{OH}][\text{NO}_3] > \text{[N}_0\text{0}_0\text{0}_3][\text{NO}_3] > \text{[N}_0\text{0}_0\text{2}_0][\text{NO}_3] > \text{[N}_0\text{0}_2\text{1}_1][\text{HCO}_2] > \text{[N}_0\text{2}_1\text{1}_1][\text{HCO}_2] 
\]

Hydrogen bonding is an important intermolecular force in these systems and the order obtained is consistent with this fact. \([\text{N}_0\text{0}_0\text{1}_1]^+\) can only form one hydrogen bond; as a result, \([\text{N}_0\text{2}_1\text{1}_1][\text{HCO}_2]\) has the lowest viscosity. On the other side, \([\text{N}_0\text{0}_0\text{C}_2\text{OH}][\text{NO}_3]\) has the denser hydrogen bond network and the highest viscosity. In \([\text{N}_0\text{0}_0\text{3}_0][\text{NO}_3]\), the -OH in \([\text{N}_0\text{0}_0\text{C}_2\text{OH}][\text{NO}_3]\) is replaced by a -CH\(_3\) and the level of hydrogen-bonding decreases. By replacing nitrate in \([\text{N}_0\text{0}_0\text{2}_0][\text{NO}_3]\) with formate in \([\text{N}_0\text{0}_0\text{2}_0][\text{HCO}_2]\), the hydrogen bonding capacity of the anion is lower, and this weakens the hydrogen bond network.

The high viscosity of ionic liquids is an important limitation in their application, as it reduces transport capabilities and retards the chemical processes in these solvents. This can be minimised by mixing with molecular solvents, and investigating the effect to of it. Studies of density, viscosity and conductivity of binary mixtures containing pyrrolidinium nitrate (protonic ionic liquids) and propylene carbonate as a function of the temperature from 283.15-353.15 K in the whole composition range [122]. All compositions obey the Walden rule. \([\text{Hpyrr}][\text{NO}_3]\) seems to be regrouped in the zone which correspond to the "good" ionic liquids zone, however, in the presence of propylene carbonate (PC), the ionicity of these mixtures change from "good" to "poor".

### 3.2.3 Ionic conductivity

The conductivity of a liquid is a measure of its ability to conduct electricity. Ionic conductivity depends on the mobility of the ions, which depends on the viscosity and
the number of charge carried. Any ionic association causes a decrease in ionic conductivity, as it decreases the number of available ions [46]. Greaves et al. [46] studied the conductivity for alkylammonium protonic ionic liquids. It was shown that the conductivity decreases as the alkyl chain length increases. The longer the chain, the smaller the change.

For the conductivity of mixtures, it is not clear what would constitute ideal behaviour, and therefore what constitutes excess conductivity. Pure ionic liquid and ionic liquid mixture conductivity has been widely studied [109]. Macfarlane et al. [123] found positive deviation of the molar conductivity for a simple linear combination for mixtures of \([\text{C}_2\text{C}_1\text{im}]\text{NTf}_2\) and \([\text{C}_2\text{C}_1\text{im}]\text{OTf}\), showing higher conductivity values than simple ionic liquids for all the composition range studied. \([\text{C}_2\text{C}_1\text{im}]\text{BF}_4\) and \([\text{C}_2\text{C}_1\text{im}]\text{N(CN)}_2\) also presented a positive deviation, but in this case, none of the data exceeded the pure compound values. For \([\text{C}_2\text{C}_1\text{im}]\text{BF}_4\) and \([\text{C}_2\text{C}_1\text{im}]\text{Br}\), the conductivity seemed to be less than that expected from simple linear mixing, with no minima or maxima. Nonetheless, for other mixtures, a different behaviour has been found. Some show the typical trend over almost the whole composition range till, suddenly, the conductivity drops for one of the pure compounds. This may be due to the fact that conductivity depends on charge density and viscosity. These two factors affect the conductivity in opposing ways, and it changes when the composition, if the mixture is different. Depending on which is stronger for each range of concentration, the conductivity will increase or decrease.

### 3.3 Experimental

#### 3.3.1 Densimeter

Density was measured at atmospheric pressure with an Anton Paar DMA 5000 digital vibrating tube densimeter (see Figure 3.2) from 288.15 K up to 353.15 K.

The calibration of the densimeter was periodically checked by measuring the densities of atmospheric air and Millipore-water, according to the manufacturer recommendations. Temperature stability during measurements was always better than ±2 mK, and the reported density data undertook a correction for the viscosity effect using the internal calibration of the densimeter. The repeatability of this densimeter is known to be very good (±1 µg cm\(^{-3}\)). However taking into account sample handling, the repeatability here is nearly 500 µg cm\(^{-3}\), mainly due to the high hygroscopicity of the ionic liquids.
3.3.2 Viscometer
Measurements of dynamic viscosity were performed at atmospheric pressure using an automated SVM 3000 Anton Paar rotational Stabinger viscometer-densimeter (see Figure 3.3). In this equipment, the precision of the dynamic viscosity measurements is ±0.5%. However, it is known that small amounts of water result in a significant decrease in the viscosity of ionic liquids [124]. Using different batches, deviations smaller than 2% were obtained for the large majority of samples, but some exceptional cases suggest a higher lack of precision (±6%). It is important to stress that, for each sample, the viscosity measurements were repeated three times, and the data here always agreed within a 1% deviation.

Figure 3.2 DMA 5000 Anton Paar densimeter.

Figure 3.3 SVM 3000 Anton Paar rotational Stabinger viscometer-densimeter.
3.3.3 Conductivity meter

Ionic conductivity measurements of the ionic liquid systems were performed at atmospheric pressure using a CDM210 Radiometer Analytical conductivity meter (see Figure 3.4). The measurements were carried out using a jacketed glass cell with a volume of 1.5 cm$^3$ containing a magnetic stirrer. A water bath, controlled to ±0.01 °C, was used to thermostat the cell, whose temperature was measured by means of a platinum resistance thermometer coupled to a previously calibrated Keithley 199 System DMM/Scanner. This conductivity meter uses an alternating current of 12 V and a frequency of 2.93 kHz for the range of conductivities measured. The use of high-frequency (above 600 Hz) alternating currents, and the fact that the electrodes are platinum coated, avoids polarisation phenomena at the surface of the cell electrodes. The conductivity meter was previously calibrated at each temperature with certified 0.01 D, 0.1 D and 1 D aqueous KCl standard solutions supplied by Radiometer Analytical [125]. This calibration was also checked using different aprotonic ionic liquids [126]. The repeatability of measurements is estimated to be less than 1%. Using different batches, the uncertainty of the ionic conductivity measurements ranged within this value for the vast majority of samples, however we obtained a deviation slightly higher for some measurements (±6%).

![Figure 3.4 CDM210 Radiometer Analytical conductimeter.](image)

3.4 Results and discussion

The samples for this chapter were prepared as described in Section 2.1.3
3.4.1 Monoalkylammonium nitrates

The density, dynamic viscosity and ionic conductivity data of pure protonic ionic liquids: [N\text{\textsubscript{0.002}}][NO\text{\textsubscript{3}}], [N\text{\textsubscript{0.003}}][NO\text{\textsubscript{3}}] and [N\text{\textsubscript{0.004}}][NO\text{\textsubscript{3}}] are depicted in Figure 3.5. Experimental data are shown in Tables 3.1-3.3.

**Figure 3.5** Experimental density, $\rho$, viscosity, $\eta$, and conductivity, $\sigma$, of pure [N\text{\textsubscript{0.002}}][NO\text{\textsubscript{3}}], [N\text{\textsubscript{0.003}}][NO\text{\textsubscript{3}}] and [N\text{\textsubscript{0.004}}][NO\text{\textsubscript{3}}] as well as their selected binary mixtures versus temperature, and (a2, b2 and c2) versus the number of carbons in the cation/composite cation at constant temperature.
Table 3.1 Experimental density, $\rho$, of pure $[\text{N}_0\text{O}_2\text{O}_2][\text{NO}_3]$, $[\text{N}_0\text{O}_3\text{O}_3][\text{NO}_3]$ and $[\text{N}_0\text{O}_4\text{O}_4][\text{NO}_3]$. The $[\text{NO}_3]$ anions omitted from the table heading.

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</tr>
<tr>
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<td>1.1412</td>
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<td>1.1830</td>
<td>1.1220</td>
<td>1.0761</td>
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<tr>
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<td>1.1406</td>
<td>1.0952</td>
<td>348.15</td>
<td>1.1824</td>
<td>1.1214</td>
<td>1.0755</td>
</tr>
<tr>
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<td>1.1400</td>
<td>1.0946</td>
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<td>1.1818</td>
<td>1.1208</td>
<td>1.0749</td>
</tr>
<tr>
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<td>1.2007</td>
<td>1.1394</td>
<td>1.0939</td>
<td>350.15</td>
<td>1.1813</td>
<td>1.1203</td>
<td>1.0744</td>
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<tr>
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<td>1.1807</td>
<td>1.1197</td>
<td>1.0738</td>
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<tr>
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<td>1.1382</td>
<td>1.0927</td>
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<td>1.1801</td>
<td>1.1191</td>
<td>1.0732</td>
</tr>
<tr>
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<td>1.1989</td>
<td>1.1376</td>
<td>1.0921</td>
<td>353.15</td>
<td>1.1795</td>
<td>1.1186</td>
<td>1.0726</td>
</tr>
</tbody>
</table>
Table 3.2 Experimental dynamic viscosity, $\eta$, of pure $[\text{N}_0\text{O}_2\text{NO}_3]$, $[\text{N}_0\text{O}_3\text{NO}_3]$ and $[\text{N}_0\text{O}_4\text{NO}_3]$.

<table>
<thead>
<tr>
<th>$T$ / K</th>
<th>$[\text{N}_0\text{O}_2\text{NO}_3]$ / mPa s</th>
<th>$[\text{N}_0\text{O}_3\text{NO}_3]$</th>
<th>$[\text{N}_0\text{O}_4\text{NO}_3]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>288.15</td>
<td>52.6</td>
<td>117</td>
<td>-</td>
</tr>
<tr>
<td>293.15</td>
<td>43.5</td>
<td>93</td>
<td>-</td>
</tr>
<tr>
<td>298.15</td>
<td>36.5</td>
<td>75</td>
<td>-</td>
</tr>
<tr>
<td>303.15</td>
<td>31</td>
<td>61.5</td>
<td>-</td>
</tr>
<tr>
<td>308.15</td>
<td>26.5</td>
<td>51</td>
<td>-</td>
</tr>
<tr>
<td>313.15</td>
<td>22.8</td>
<td>42.9</td>
<td>-</td>
</tr>
<tr>
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<td>20</td>
<td>36.2</td>
<td>48.2</td>
</tr>
<tr>
<td>323.15</td>
<td>17.6</td>
<td>31</td>
<td>40.7</td>
</tr>
<tr>
<td>328.15</td>
<td>15.6</td>
<td>26.8</td>
<td>34.7</td>
</tr>
<tr>
<td>333.15</td>
<td>13.8</td>
<td>23.4</td>
<td>30.5</td>
</tr>
<tr>
<td>338.15</td>
<td>12.5</td>
<td>20.5</td>
<td>26</td>
</tr>
<tr>
<td>343.15</td>
<td>11.2</td>
<td>18.2</td>
<td>22.7</td>
</tr>
<tr>
<td>348.15</td>
<td>10.2</td>
<td>16.2</td>
<td>20.2</td>
</tr>
<tr>
<td>353.15</td>
<td>9.21</td>
<td>14.6</td>
<td>17.8</td>
</tr>
</tbody>
</table>

Table 3.3 Experimental ionic conductivity, $\sigma$, of pure $[\text{N}_0\text{O}_2\text{NO}_3]$, $[\text{N}_0\text{O}_3\text{NO}_3]$ and $[\text{N}_0\text{O}_4\text{NO}_3]$.

<table>
<thead>
<tr>
<th>$T$ / K</th>
<th>$[\text{N}_0\text{O}_2\text{NO}_3]$ / mS cm$^{-1}$</th>
<th>$[\text{N}_0\text{O}_3\text{NO}_3]$</th>
<th>$[\text{N}_0\text{O}_4\text{NO}_3]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>288.15</td>
<td>16.2</td>
<td>5.34</td>
<td>-</td>
</tr>
<tr>
<td>293.15</td>
<td>19.3</td>
<td>6.6</td>
<td>-</td>
</tr>
<tr>
<td>298.15</td>
<td>22.5</td>
<td>8.01</td>
<td>-</td>
</tr>
<tr>
<td>303.15</td>
<td>26</td>
<td>9.62</td>
<td>-</td>
</tr>
<tr>
<td>308.15</td>
<td>29.7</td>
<td>11.3</td>
<td>-</td>
</tr>
<tr>
<td>313.15</td>
<td>33.7</td>
<td>13.2</td>
<td>-</td>
</tr>
<tr>
<td>313.20</td>
<td>-</td>
<td>-</td>
<td>7.24</td>
</tr>
<tr>
<td>315.70</td>
<td>-</td>
<td>-</td>
<td>7.99</td>
</tr>
<tr>
<td>318.15</td>
<td>37.8</td>
<td>15.3</td>
<td>-</td>
</tr>
<tr>
<td>318.20</td>
<td>-</td>
<td>-</td>
<td>8.48</td>
</tr>
<tr>
<td>320.70</td>
<td>-</td>
<td>-</td>
<td>9.31</td>
</tr>
<tr>
<td>323.15</td>
<td>42.2</td>
<td>17.5</td>
<td>-</td>
</tr>
<tr>
<td>323.20</td>
<td>-</td>
<td>-</td>
<td>9.83</td>
</tr>
</tbody>
</table>

The three pure monoalkylammonium ionic liquids have been previously prepared, and very limited density, viscosity and conductivity data published [127]. These are compared with data reported here in **Table 3.4.**
Table 3.4 Comparison between our values of density, $\rho$, dynamic viscosity, $\eta$, and ionic conductivity, $\sigma$, for pure $\left[ N_0 0 0 2 \right][NO_3]$, $\left[ N_0 0 0 3 \right][NO_3]$ and $\left[ N_0 0 0 4 \right][NO_3]$ and the ones available in literature. The $[NO_3]$ anions omitted from the table.

<table>
<thead>
<tr>
<th></th>
<th>$\rho$ / cm$^3$mol$^{-1}$</th>
<th>$\eta$ / mPa s</th>
<th>$\sigma$ / mS cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\left[ N_0 0 0 2 \right]^*$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>298.15</td>
<td>1.2124</td>
<td>1.122 [127b]</td>
<td>36.5</td>
</tr>
<tr>
<td>300.15</td>
<td>1.2112</td>
<td>1.216 [127a]</td>
<td></td>
</tr>
<tr>
<td>$\left[ N_0 0 0 3 \right]^*$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>298.15</td>
<td>1.1509</td>
<td>1.157 [127b]</td>
<td>75.1</td>
</tr>
<tr>
<td>$\left[ N_0 0 0 4 \right]^*$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>313.15</td>
<td>1.0964</td>
<td>1.09217 [127c]</td>
<td></td>
</tr>
</tbody>
</table>

The small differences indicate a higher purity for the samples prepared for this thesis (as the presence of water as an impurity lowers both the density and the viscosity of an ionic liquid, the higher values represent the purest materials). Figure 3.5 also shows a comparison of these pure protonic ionic liquids with mixtures containing equivalent number of carbons in the cation: $\left[ N_0 0 0 2 \right]_{0.75}\left[ N_0 0 0 4 \right]_{0.25}[NO_3]$ and $\left[ N_0 0 0 2 \right]_{0.5}\left[ N_0 0 0 3 \right]_{0.5}[NO_3]$; $\left[ N_0 0 0 2 \right]_{0.25}\left[ N_0 0 0 4 \right]_{0.75}[NO_3]$, $\left[ N_0 0 0 3 \right]_{0.5}\left[ N_0 0 0 4 \right]_{0.5}[NO_3]$ and $\left[ N_0 0 0 2 \right]_{0.5}\left[ N_0 0 0 4 \right]_{0.5}[NO_3]$. Numerical experimental data for the binary mixtures are given in Tables 3.5-3.7.

Density, dynamic viscosity, and ionic conductivity data were fitted with the commonly used Equations (3.1), (3.2) and (3.3) [128]

\[
\ln(\rho / g \, cm^{-3}) = A_2 T^2 + A_1 T + A_0 \tag{3.1}
\]

\[
\ln(\eta / mPa \, s) = \ln(A_\eta) + \frac{B_\eta}{T - T_{0\eta}} \tag{3.2}
\]

\[
\sigma / mS \, cm^{-1} = A_\sigma \exp\left(\frac{-B_\sigma}{T - T_{0\sigma}}\right) \tag{3.3}
\]

where $A_2, A_1, A_0, A_\eta, B_\eta, T_{0\eta}, A_\sigma, B_\sigma$ and $T_{0\sigma}$ are fitting parameters and $T$ is the absolute temperature. All fitting parameters and corresponding standard deviations of each fitting are presented in Table 3.8. A second order polynomial equation was used to fit the data since the standard deviation of the linear fitting is greater than the repeatability of the density measurements. As expected, the lengthening of the alkyl chain of the pure compounds induces a decrease either in density or ionic conductivity, and an increase in dynamic viscosity, as can be seen in Figure 3.5. If one considers the number of equivalent carbons in the composite cations of the monoalkylammonium nitrate mixtures, these trends are maintained.
Table 3.5 Experimental density, $\rho$, of binary mixtures composed of monoalkylammonium nitrate ionic liquids.

<table>
<thead>
<tr>
<th>T / K</th>
<th>$n = 2.5$</th>
<th>$n = 3$</th>
<th>$n = 3.5$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>${[N_{0,0,0,2}]<em>{0.75}[N</em>{0,0,0,3}]_{0.25}]$[NO$_3$]</td>
<td>${[N_{0,0,0,2}]<em>{0.5}[N</em>{0,0,0,3}]_{0.5}]$[NO$_3$]</td>
<td>${[N_{0,0,0,3}]<em>{0.25}[N</em>{0,0,0,4}]_{0.75}]$[NO$_3$]</td>
</tr>
<tr>
<td>293.15</td>
<td>1.1805</td>
<td>1.1816</td>
<td>1.154</td>
</tr>
<tr>
<td>298.15</td>
<td>1.1774</td>
<td>1.1785</td>
<td>1.1509</td>
</tr>
<tr>
<td>303.15</td>
<td>1.1743</td>
<td>1.1754</td>
<td>1.1478</td>
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<tr>
<td>308.15</td>
<td>1.1712</td>
<td>1.1724</td>
<td>1.1448</td>
</tr>
<tr>
<td>313.15</td>
<td>1.1682</td>
<td>1.1693</td>
<td>1.1418</td>
</tr>
<tr>
<td>318.15</td>
<td>1.1652</td>
<td>1.1663</td>
<td>1.1388</td>
</tr>
<tr>
<td>323.15</td>
<td>1.1622</td>
<td>1.1634</td>
<td>1.1359</td>
</tr>
<tr>
<td>328.15</td>
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</tr>
<tr>
<td>333.15</td>
<td>1.1563</td>
<td>1.1575</td>
<td>1.13</td>
</tr>
<tr>
<td>338.15</td>
<td>1.1534</td>
<td>1.1546</td>
<td>1.1271</td>
</tr>
<tr>
<td>343.15</td>
<td>1.1506</td>
<td>1.1517</td>
<td>1.1243</td>
</tr>
<tr>
<td>348.15</td>
<td>1.1477</td>
<td>1.1488</td>
<td>1.1214</td>
</tr>
<tr>
<td>353.15</td>
<td>1.1448</td>
<td>1.146</td>
<td>1.1186</td>
</tr>
</tbody>
</table>

$n$ = number of equivalent carbons in the cation
Table 3.6 Experimental dynamic viscosity, $\eta$, of binary mixtures composed of monoalkylammonium nitrate ionic liquids.

<table>
<thead>
<tr>
<th>$T / K$</th>
<th>$n = 2.5$</th>
<th>$n = 3$</th>
<th>$n = 3.5$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>${[N_{0002}]<em>{0.75}[N</em>{0004}]_{0.25}]NO_3$</td>
<td>${[N_{0002}]<em>{0.5}[N</em>{0003}]_{0.5}]NO_3$</td>
<td>${[N_{0002}]<em>{0.25}[N</em>{0004}]_{0.75}]NO_3$</td>
</tr>
<tr>
<td>293.15</td>
<td>62</td>
<td>64.5</td>
<td>82.3</td>
</tr>
<tr>
<td>298.15</td>
<td>50.6</td>
<td>53</td>
<td>66.6</td>
</tr>
<tr>
<td>303.15</td>
<td>42.1</td>
<td>44.1</td>
<td>54.7</td>
</tr>
<tr>
<td>308.15</td>
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<td>37.1</td>
<td>45.6</td>
</tr>
<tr>
<td>313.15</td>
<td>30.6</td>
<td>31.6</td>
<td>38.5</td>
</tr>
<tr>
<td>318.15</td>
<td>26</td>
<td>27.1</td>
<td>32.7</td>
</tr>
<tr>
<td>323.15</td>
<td>22.6</td>
<td>23.5</td>
<td>28.1</td>
</tr>
<tr>
<td>328.15</td>
<td>19.8</td>
<td>20.5</td>
<td>24.4</td>
</tr>
<tr>
<td>333.15</td>
<td>17.6</td>
<td>18.1</td>
<td>21.3</td>
</tr>
<tr>
<td>338.15</td>
<td>15.5</td>
<td>16</td>
<td>18.7</td>
</tr>
<tr>
<td>343.15</td>
<td>13.8</td>
<td>14.3</td>
<td>16.6</td>
</tr>
<tr>
<td>348.15</td>
<td>12.4</td>
<td>12.8</td>
<td>14.8</td>
</tr>
<tr>
<td>353.15</td>
<td>11.3</td>
<td>11.5</td>
<td>13.3</td>
</tr>
</tbody>
</table>

$n$ = number of equivalent carbons in the cation
Table 3.7 Experimental ionic conductivity, $\sigma$, of binary mixtures composed of monoalkylammonium nitrate ionic liquids.

<table>
<thead>
<tr>
<th>T / K</th>
<th>$n = 2.5$</th>
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<th>$n = 3.5$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$[[N_{0002}]<em>{0.75}[N</em>{0004}]_{0.25}][NO_3]$</td>
<td>$[[N_{0002}]<em>{0.5}[N</em>{0003}]_{0.5}][NO_3]$</td>
<td>$[[N_{0002}]<em>{0.25}[N</em>{0004}]_{0.75}][NO_3]$</td>
</tr>
<tr>
<td>288.15</td>
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<td>6.46</td>
</tr>
<tr>
<td>293.15</td>
<td>12</td>
<td>12</td>
<td>7.92</td>
</tr>
<tr>
<td>298.15</td>
<td>14.3</td>
<td>14.2</td>
<td>9.51</td>
</tr>
<tr>
<td>303.15</td>
<td>16.8</td>
<td>16.7</td>
<td>11.3</td>
</tr>
<tr>
<td>308.15</td>
<td>19.5</td>
<td>19.3</td>
<td>13.3</td>
</tr>
<tr>
<td>313.15</td>
<td>22.4</td>
<td>22.2</td>
<td>15.4</td>
</tr>
<tr>
<td>318.15</td>
<td>25.5</td>
<td>25.3</td>
<td>17.7</td>
</tr>
<tr>
<td>323.15</td>
<td>28.8</td>
<td>28.5</td>
<td>20.2</td>
</tr>
</tbody>
</table>

$n =$ number of equivalent carbons in the cation
Table 3.8 Fitting parameters for experimental density, $\rho$, dynamic viscosity, $\eta$, and ionic conductivity, $\sigma$, respectively used in Equations (3.1), (3.2) and (3.3) of this thesis, with the corresponding standard deviation (SD) of the overall fitting.

<table>
<thead>
<tr>
<th>Pure compounds</th>
<th>([\text{N}_2\text{O}_2][\text{NO}_2])</th>
<th>([\text{N}_2\text{O}_3][\text{NO}_2])</th>
<th>([\text{N}_2\text{O}_4][\text{NO}_2])</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fitting parameter</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_2 / 10^7$</td>
<td>3.34</td>
<td>3.1</td>
<td>2.8</td>
</tr>
<tr>
<td>$A_1 / 10^4$</td>
<td>-7.18</td>
<td>-7.2</td>
<td>-7.34</td>
</tr>
<tr>
<td>$A_0 / 10$</td>
<td>3.77</td>
<td>3.28</td>
<td>2.95</td>
</tr>
<tr>
<td>SD / $10^5$</td>
<td>1.29</td>
<td>1.7</td>
<td>0.23</td>
</tr>
<tr>
<td>eq. (1)</td>
<td> </td>
<td> </td>
<td> </td>
</tr>
<tr>
<td>$A_\eta$</td>
<td>0.2199</td>
<td>0.2082</td>
<td>0.2203</td>
</tr>
<tr>
<td>$B_\eta$</td>
<td>765.2</td>
<td>836</td>
<td>836.7</td>
</tr>
<tr>
<td>$T_{0\eta}$</td>
<td>148.5</td>
<td>156.1</td>
<td>162.9</td>
</tr>
<tr>
<td>SD / $10^2$</td>
<td>3.63</td>
<td>5.33</td>
<td>18.19</td>
</tr>
<tr>
<td>eq. (2)</td>
<td> </td>
<td> </td>
<td> </td>
</tr>
<tr>
<td>$A_\sigma$</td>
<td>1473</td>
<td>1449.5</td>
<td>1428.7</td>
</tr>
<tr>
<td>$B_\sigma$</td>
<td>587.6</td>
<td>729.8</td>
<td>864.1</td>
</tr>
<tr>
<td>$T_{0\sigma}$</td>
<td>157.7</td>
<td>157.8</td>
<td>149.4</td>
</tr>
<tr>
<td>SD / $10^2$</td>
<td>4.5</td>
<td>2.34</td>
<td>7.71</td>
</tr>
<tr>
<td>eq. (3)</td>
<td> </td>
<td> </td>
<td> </td>
</tr>
</tbody>
</table>
Table 3.9 Fitting parameters for experimental density, \( \rho \), dynamic viscosity, \( \eta \), and ionic conductivity, \( \sigma \), respectively used in Equations (3.1), (3.2), and (3.3) of this thesis, with the corresponding standard deviation (SD) of the overall fitting.

<table>
<thead>
<tr>
<th>Fitting parameter</th>
<th>Binary mixtures</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( n = 2.5 )</td>
<td>( n = 3 )</td>
<td>( n = 3.5 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( A_2 / 10^7 )</td>
<td>3.16</td>
<td>2.96</td>
<td>3.01</td>
<td>3.33</td>
<td>2.92</td>
</tr>
<tr>
<td>( A_1 / 10^4 )</td>
<td>-7.15</td>
<td>-7.01</td>
<td>-7.13</td>
<td>-7.56</td>
<td>-7.26</td>
</tr>
<tr>
<td>( A_0 / 10 )</td>
<td>3.48</td>
<td>3.47</td>
<td>3.26</td>
<td>3.15</td>
<td>3.1</td>
</tr>
<tr>
<td>( SD / 10^3 )</td>
<td>0.89</td>
<td>1.06</td>
<td>1.15</td>
<td>1.23</td>
<td>0.66</td>
</tr>
<tr>
<td>eq. (1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( A_\eta )</td>
<td>0.1886</td>
<td>0.189</td>
<td>0.1968</td>
<td>0.2102</td>
<td>0.2062</td>
</tr>
<tr>
<td>( B_\eta )</td>
<td>835.5</td>
<td>835.6</td>
<td>836</td>
<td>837.9</td>
<td>837.8</td>
</tr>
<tr>
<td>( T_{0\eta} )</td>
<td>148.8</td>
<td>149.9</td>
<td>154.6</td>
<td>158.2</td>
<td>157.8</td>
</tr>
<tr>
<td>( SD / 10^2 )</td>
<td>2.79</td>
<td>0.96</td>
<td>4.63</td>
<td>6.19</td>
<td>5.14</td>
</tr>
<tr>
<td>eq. (2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>( A_\sigma )</td>
<td>1465.1</td>
<td>1465.1</td>
<td>1451.7</td>
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<td>1441.2</td>
</tr>
<tr>
<td>( B_\sigma )</td>
<td>652.9</td>
<td>653</td>
<td>712.5</td>
<td>788.3</td>
<td>786.6</td>
</tr>
<tr>
<td>( T_{0\sigma} )</td>
<td>157</td>
<td>157.3</td>
<td>156.4</td>
<td>153.6</td>
<td>154.4</td>
</tr>
<tr>
<td>( SD / 10^2 )</td>
<td>1.41</td>
<td>3.19</td>
<td>2.33</td>
<td>1.39</td>
<td>0.86</td>
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<td>eq. (3)</td>
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</tbody>
</table>
The density values of the binary mixture \([N_0.002][N_0.004][NO_3]\) (3 carbons in the composite cation) perfectly match with the ones for pure \([N_0.003][NO_3]\), once the deviation between these series is below the uncertainty in the density measurements (see Table 3.5 and Figure 3.5). The viscosity and conductivity values differ by 12 and 19 %, respectively (see Tables 3.6 and 3.7 and Figure 3.5). This result seems to indicate a non-ideal behaviour of both viscosity and conductivity. It is also important to highlight that the latter result is the only one based on the direct comparison between a mixture and a pure compound. Comparing the mixtures \([N_0.002][N_0.004][NO_3]\) with \([N_0.003][N_0.004][NO_3]\) (3.5 carbons in the composite cation) and \([N_0.002][N_0.004][NO_3]\) with \([N_0.002][N_0.004][NO_3]\) (2.5 carbons in the composite cation) we observed a maximum deviation percentage of the experimental data of 0.1, 4.6 and 2.3 % for density, viscosity and conductivity, respectively. The deviation values obtained are within the uncertainty on the properties measurements which indicate a quasi-ideal behaviour of these mixtures.

The isobaric thermal expansion coefficient, \(\alpha_p\), was calculated using Equation (3.4) which is obtained from the first derivative of Equation (3.1)

\[
\alpha_p = -\frac{\partial \ln(\rho)}{\partial T} = (2A_2T + A_1)
\]

(3.4)

The values of \(\alpha_p\) (cf. Figure 3.6) are within 4.8-5.6 x 10\(^{-4}\) K\(^{-1}\) usual range for ionic liquids found in literature [128b], and increase with the alkyl chain length of the cation or composite cation.

**Figure 3.6** Isobaric thermal expansion coefficients (a), \(\alpha_p\), of pure \([N_0.002][NO_3]\), \([N_0.003][NO_3]\) and \([N_0.004][NO_3]\) as well as their selected binary mixtures versus temperature, and (b) versus the number of carbons in the cation/composite cation at constant temperature.
The molar volumes \((V_m)\) at 298.15 K of \([\text{N}\_0\_0\_2]\text{[NO}_3\text{]}, \ [\text{N}\_0\_0\_3]\text{[NO}_3\text{]}\) and \([\text{N}\_0\_0\_4]\text{[NO}_3\text{]}\) and their binary mixtures are depicted in Table 3.10 and Table 3.11. The average increase per CH\(_2\) group in this family of ionic liquids and mixtures is 16.97 cm\(^3\) mol\(^{-1}\). These values are perfectly consistent with the recognised increase of 17.2±0.3 cm\(^3\) mol\(^{-1}\) per each CH\(_2\) increment in the cation (or anion) at 298.15 K [128b]. The excess molar volume \((V^E)\) of the binary monoalkylammonium nitrate mixtures was calculated, Equation (3.5), as the difference between the molar volume of the mixture and molar volume of the hypothetical ideal mixture:

\[
V^E = V_{mix} - (V_1 x_1 + V_2 x_2)
\]  

(3.5)

where \(V_{mix}, V_1\) and \(V_2\) are the molar volumes of the mixture and of the two pure components, respectively, while \(x_1\) and \(x_2\) are the corresponding molar fractions. For solids, hypothetical liquid molar volumes have been used, which can be interpreted as the values of supercooled \([\text{N}\_0\_0\_2]\text{[NO}_3\text{]}, [\text{N}\_0\_0\_3]\text{[NO}_3\text{]},\) and \([\text{N}\_2\_2\_2\_2]\text{[NO}_3\text{]}\) salts. Discussions over ideal solutions in mixtures of ionic liquids and their excess volume of mixing have been presented elsewhere [129], and more recently discussed in a critical review by Welton and co-workers [109]. However, to the best of our knowledge, this is the first work reporting \(V^E\) values of protonic ionic liquids mixtures solely composed of ammonium cations and nitrate anions. The obtained \(V^E\) values range between -0.1 < \(V^E\) / cm\(^3\) mol\(^{-1}\) < 0.1. The almost zero \(V^E\) values presented here clearly suggest a quasi-ideal behaviour for all binary mixtures in accordance with the data for binary mixtures containing the imidazolium cation combined with different anions [129].

**Table 3.10** Molar volume \((V_m)\) of protic monoalkylammonium ionic liquids at 298.15 K.

<table>
<thead>
<tr>
<th>Pure compounds</th>
<th>([\text{N}_0_0_2]\text{[NO}_3\text{]})</th>
<th>([\text{N}_0_0_3]\text{[NO}_3\text{]})</th>
<th>([\text{N}_0_0_4]\text{[NO}_3\text{]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(V_m) / cm(^3) mol(^{-1})</td>
<td>89.16</td>
<td>106.04</td>
<td>123.07 (\text{[a]})</td>
</tr>
<tr>
<td>Number of carbons ((n))</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>(\Delta V_m/ (n-2)) / cm(^3) mol(^{-1})</td>
<td>-</td>
<td>16.89</td>
<td>16.96</td>
</tr>
</tbody>
</table>

\(\text{(a) Assuming a linear extrapolated density value at 298.15 K; } \frac{\Delta V_m}{n-2} / \text{cm}^3\text{mol}^{-1}\text{ gives the increase in } V_m \text{ per methylene group added to the alkyl side chain of the cation.}\)
Table 3.11 Molar volume ($V_m$) and the selected binary mixtures of monoalkylammonium nitrates at 298.15 K.

<table>
<thead>
<tr>
<th>$V_m$ / cm$^3$ mol$^{-1}$</th>
<th>Mixtures</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>([NO$_3$]$1$[N$_0$0$0$2]$0.75$[N$_0$0$0$4]$0.25$][NO$_3$]</td>
</tr>
<tr>
<td>97.74</td>
<td>97.64</td>
</tr>
</tbody>
</table>

| Num. carbons ($n$) | ([NO$_3$]$1$[N$_0$0$0$2]$0.75$[N$_0$0$0$4]$0.25$][NO$_3$] | ([NO$_3$]$1$[N$_0$0$0$2]$0.5$[N$_0$0$0$3]$0.5$][NO$_3$] | ([NO$_3$]$1$[N$_0$0$0$2]$0.25$[N$_0$0$0$4]$0.75$][NO$_3$] | ([NO$_3$]$1$[N$_0$0$0$3]$0.5$[N$_0$0$0$4]$0.5$][NO$_3$] |
| 2.5                  | 2.5       | 3      | 3.5    | 3.5    |

| $\Delta V_m / (n-2)$ / cm$^3$ mol$^{-1}$ | ([NO$_3$]$1$[N$_0$0$0$2]$0.75$[N$_0$0$0$4]$0.25$][NO$_3$] | ([NO$_3$]$1$[N$_0$0$0$2]$0.5$[N$_0$0$0$3]$0.5$][NO$_3$] | ([NO$_3$]$1$[N$_0$0$0$2]$0.25$[N$_0$0$0$4]$0.75$][NO$_3$] | ([NO$_3$]$1$[N$_0$0$0$3]$0.5$[N$_0$0$0$4]$0.5$][NO$_3$] |
| 16.94                 | 16.90     | 17.17  | 16.98  | 16.92  |
3.4.2 Binary mixtures of $[\text{N}_0\text{O}_0\text{O}_2]\text{[NO}_3\text{]}$ with di-, tri- or tetra ethylammonium nitrates

The experimental data for binary mixtures of ethylammonium nitrate, $[\text{N}_0\text{O}_0\text{O}_2]\text{[NO}_3\text{]}$, with nitrates of the analogous diethyl-, triethyl- and tetraethylammonium cations: $[\text{N}_0\text{O}_2\text{O}_2]\text{[NO}_3\text{]}$, $[\text{N}_0\text{O}_2\text{O}_2\text{O}_2]\text{[NO}_3\text{]}$ and $[\text{N}_2\text{O}_2\text{O}_2\text{O}_2]\text{[NO}_3\text{]}$, are presented in Figure 3.7. For greater insight, instead of plotting density, viscosity or conductivity versus temperature, they are now plotted versus the mole fraction ($x$) of the di-, tri- or tetra-ethylammonium ionic liquid, in steps of approximately 0.05 mole fraction (the upper limit being determined by solidification).

![Figure 3.7](image)

Figure 3.7 Experimental density, $\rho$, dynamic viscosity, $\eta$, and ionic conductivity, $\sigma$, of (1) $([\text{N}_0\text{O}_2\text{O}_2], [\text{N}_0\text{O}_0\text{O}_2][\text{NO}_3])$, (2) $([\text{N}_0\text{O}_2\text{O}_2\text{O}_2], [\text{N}_0\text{O}_0\text{O}_2][\text{NO}_3])$ and (3) $([\text{N}_0\text{O}_2\text{O}_2\text{O}_2], [\text{N}_0\text{O}_0\text{O}_2][\text{NO}_3])$. The red line of each plot is only a guide to the eye.

The density and dynamic viscosity were measured from 293.15 to 353.15 K, whilst ionic conductivity was measured from 293.15 to 323.15 K. The full data sets are presented in Tables 3.12-3.20.
Table 3.12 Experimental density data, $\rho$, for binary mixtures composed of ethylammonium nitrate with diethylammonium nitrate.

<table>
<thead>
<tr>
<th>$x$</th>
<th>0</th>
<th>0.0499</th>
<th>0.0998</th>
<th>0.1499</th>
<th>0.1999</th>
<th>0.2501</th>
<th>0.2998</th>
<th>0.3501</th>
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</thead>
<tbody>
<tr>
<td>$T/K$</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
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<td>1.1981</td>
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<td>1.1821</td>
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<tr>
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<tr>
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<td>1.2000</td>
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<td>1.1832</td>
<td>1.1760</td>
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<td>1.1629</td>
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<tr>
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<td>1.1969</td>
<td>1.1888</td>
<td>1.1802</td>
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<td>1.1253</td>
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Table 3.13 Experimental viscosity data, $\eta$, for binary mixtures composed of ethylammonium nitrate with diethylammonium nitrate.

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<td>10.5</td>
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</table>
Table 3.14 Experimental conductivity data, $\sigma$, for binary mixtures composed of ethylammonium nitrate with diethylammonium nitrate.

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<th>$T / K$</th>
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<th>0.0998</th>
<th>0.1499</th>
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<th>0.2501</th>
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<td>35.9</td>
<td>35.9</td>
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</table>

Table 3.15 Experimental density data, $\rho$, for binary mixtures composed of ethylammonium nitrate with triethylammonium nitrate.

<table>
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<th>$T / K$</th>
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<th>0.0999</th>
<th>0.1499</th>
<th>0.1997</th>
<th>0.25</th>
<th>0.2993</th>
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Table 3.16 Experimental viscosity data, $\eta$, for binary mixtures composed of ethylammonium nitrate with triethylammonium nitrate.

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Table 3.17 Experimental conductivity data, $\sigma$, for binary mixtures composed of ethylammonium nitrate with triethylammonium nitrate.

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Table 3.18 Experimental density data, \( \rho \), for binary mixtures composed of ethylammonium nitrate with tetraethylammonium nitrate.

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Table 3.19 Experimental viscosity data, \( \eta \), for binary mixtures composed of ethylammonium nitrate with tetraethylammonium nitrate.

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<td>16.9</td>
<td>18.4</td>
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</table>
Table 3.20: Experimental conductivity data, $\sigma$, for binary mixtures composed of ethylammonium nitrate with tetraethylammonium nitrate.

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<thead>
<tr>
<th>$x$</th>
<th>$T$ / K</th>
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<td>1.25</td>
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</table>

As seen in Figure 3.7 (a1, b1 and c1) and Tables 3.12-3.14, the experimental data for $\{[N_{2222}]_x[N_{0002}]_{(1-x)}][NO_3]$ follow the expected trend with temperature: density and viscosity values decrease with temperature, while conductivity values increase. Of more interest, for a given temperature, the values of density or ionic conductivity decline when the mole ratio of $[N_{0002}][NO_3]$ increases in the binary mixture. In surprising contrast, the viscosity remains effectively constant when the mole fraction of $[N_{0002}][NO_3]$ increases, Figure 3.7 (b1) and Table 3.13. It is worth emphasising that $[N_{0002}][NO_3]$ is solid at room temperature, with a melting point at 373.15 K. Hence, the liquid density was not available, and the direct calculation of the $V^E$ for the mixtures of $\{[N_{0002}]_x[N_{0002}]_{(1-x)}][NO_3]$ is simply not feasible.

To overcome this, a calculation method based on the relation of known variables: $V_m$ of $[N_{0002}][NO_3]$, $V_m$ of the binary mixture ($V_{mix}$), and the corresponding molar concentration of each component, was used. It was assumed that the $V^E$ for a given mixture can be described by a parabolic function with a downward concavity:

$$V^E \equiv Ax(1 - x) \quad (3.6)$$

where $A$ is a fitting parameter. Taking into account Equation (3.6), it is possible to rearrange Equation (3.5) to give:

$$V_{mix} = V_1 x + V_2 (1 - x) + Ax(1 - x) \quad (3.7)$$

where $V_1$ and $V_2$ are the molar volumes of the component added to $[N_{0002}][NO_3]$, and the molar volume of $[N_{0002}][NO_3]$, respectively.
By rearranging Equation (3.7), Equation (3.8) is obtained:

\[ \frac{V_{\text{mix}} - V_2}{x} = (V_1 - V_2) + A(1 - x) \quad (3.8) \]

Thus, Equation (3.8), describes a linear function where \((V_1 - V_2)\) and \(A\) are the intercept and slope, respectively, while \((1 - x)\) is the dependent variable. The \(V_m\) values for \([\text{N}_0\text{O}_2\text{N}]\) can be found in Tables 3.21-3.23.

**Table 3.21** Calculated excess molar volumes, \(V^E\), of the binary mixture \([\text{N}_0\text{O}_2\text{N}][\text{N}_0\text{O}_2\text{N}][1-x][\text{NO}_3]\), and the respective molar volume, \(V_m\).

<table>
<thead>
<tr>
<th>(x) / K</th>
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<th>0.0998</th>
<th>0.1499</th>
<th>0.1999</th>
<th>0.2501</th>
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<td>0.40</td>
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<td>0.63</td>
<td>0.55</td>
<td>0.75</td>
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<td>0.62</td>
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<td>0.36</td>
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<td>0.48</td>
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</tr>
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<td>0.36</td>
<td>0.42</td>
<td>0.57</td>
<td>0.47</td>
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<td>125.8</td>
</tr>
<tr>
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<td>0.21</td>
<td>0.35</td>
<td>0.41</td>
<td>0.56</td>
<td>0.46</td>
<td>0.66</td>
<td>126.1</td>
</tr>
<tr>
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<td>0.48</td>
<td>0.35</td>
<td>0.58</td>
<td>127.5</td>
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</table>

**Table 3.22** Calculated excess molar volumes, \(V^E\), of the binary mixture \([\text{N}_0\text{O}_2\text{N}][\text{N}_0\text{O}_2\text{N}][1-x][\text{NO}_3]\), and the respective molar volume, \(V_m\).

<table>
<thead>
<tr>
<th>(x) / K</th>
<th>0.0499</th>
<th>0.0999</th>
<th>0.1499</th>
<th>0.1997</th>
<th>0.25</th>
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<td>151.8</td>
</tr>
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<td>0.68</td>
<td>1.07</td>
<td>1.05</td>
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<td>1.73</td>
<td>1.89</td>
<td>-</td>
<td>153.2</td>
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</tbody>
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Interestingly, the calculated values of $V_m$ for $[\text{N}_{0.022}]\text{[NO}_3\text{]}$ (which has the same molecular weight), having a deviation less than 0.58 \% over the entire temperature range. At 298.15 K, this indicates an increase of 17.02 cm$^3$ mol$^{-1}$ per each CH$_2$ in the cation, which is in agreement with the literature value of 17.2±0.3 cm$^3$ mol$^{-1}$ [128b]. The corresponding $V^E$ values of the binary mixture \{[N$_{0.022}$][N$_{0.002}$](1-x)][NO$_3$] \}, also presented in Table 3.21 deviate from 0.12 to 0.75 cm$^3$ mol$^{-1}$ from the ideal molar volume. These values are slightly higher values than those observed for the monoalkylammonium mixtures but, still, suggest a quasi-ideal behaviour. One particular aspect of the system \{[N$_{0.222}$][N$_{0.002}$](1-x)][NO$_3$] \} is the formation of bubbles at high temperatures and higher values of $x$, which precludes the correct measurement of the physical properties under those conditions. Like the results for \{[N$_{0.022}$][N$_{0.002}$](1-x)][NO$_3$] \}, those for \{[N$_{0.222}$][N$_{0.002}$](1-x)][NO$_3$] \} follow the expected universal trend with temperature. In contrast, \{[N$_{0.222}$][N$_{0.002}$](1-x)][NO$_3$] \}, Figure 3.7 (b2) and Table 3.16, shows that the viscosity behaviour of these mixtures presents a clearer dependency on $x$. The effect on conductivity, Figure 3.7 (b3), is also more pronounced. Using the Equations (3.6) and (3.8) the resulting $V_m$ values of \{[N$_{0.222}$][N$_{0.002}$](1-x)][NO$_3$] \}, reported in Table 3.22, are lower than expected. Compared with \{[N$_{0.022}$][N$_{0.002}$](1-x)][NO$_3$] \}, the increase in $V_m$ per CH$_2$ group is only 13.4 cm$^3$ mol$^{-1}$ at 298.15 K, instead of 17.2 cm$^3$ mol$^{-1}$. Moreover, the $V^E$ presents a maximum of 2.08 cm$^3$ mol$^{-1}$, which suggests a deviation from ideality. Figure 3.7 (a3, b3 and c3) show the experimental data for \{[N$_{2.222}$][N$_{0.002}$](1-x)][NO$_3$] \} mixtures. The effect of increasing the mol ratio of [N$_{2.222}$][NO$_3$] on the physical properties of this mixture is more pronounced than for the other two systems. Using

### Table 3.23

Calculated excess molar volumes, $V^E$, of the binary mixture \{[N$_{2.222}$][N$_{0.002}$](1-x)][NO$_3$] \}, and the respective molar volume, $V_m$.

<table>
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<th>$x$</th>
<th>(T / K)</th>
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<th>0.1000</th>
<th>0.1500</th>
<th>0.2001</th>
<th>0.2567</th>
<th>0.2995</th>
<th>0.3500</th>
<th>(V_m / \text{cm}^3 \text{mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>0.60</td>
<td>0.60</td>
<td>0.59</td>
<td>0.59</td>
<td>0.58</td>
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<td>0.55</td>
</tr>
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<td>0.57</td>
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<td>0.55</td>
</tr>
<tr>
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</tr>
<tr>
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<tr>
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<tr>
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<td>0.55</td>
<td>0.55</td>
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</tr>
</tbody>
</table>
Equations (3.6)-(3.8), the calculated value of $V_m$ at 298.15 K is 172.7 cm$^3$ mol$^{-1}$. This value for $[\text{N}_2\text{N}_2\text{N}_2\text{N}_2][\text{NO}_3]$ represents an increase of 11.6 cm$^3$ mol$^{-1}$ per CH$_2$ group relative to $[\text{N}_0\text{N}_0\text{N}_0\text{N}_2][\text{NO}_3]$. The exchange of the fourth ethyl group for a proton in the triethylammonium cation produces an even more pronounced deviation from ideality, with $V^e$ values that approach 2.8 cm$^3$ mol$^{-1}$.

3.4.3 An overall picture

The experimental data for the mixtures depicted in Figure 3.7 clearly show that, for a given mole fraction, density, dynamic viscosity and ionic conductivity values change more dramatically as the number of ethyl chains in the cation increases. Figure 3.8 illustrates the relationship between molar volume, dynamic viscosity and ionic conductivity values and the number of carbon atoms in the cation or composite cation.

The molar volume behaviour shows a remarkable insensitivity to the chemical composition of the cations (less than 2.5% difference for the various systems), and depends only on the total number of carbon atoms in the cation or composite cation, Figure 3.8 (a). However, the analysis of the viscosity and ionic conductivity data is not straightforward, and the results indicate a different behaviour for each system studied Figure 3.8 (b) and (c).

The increase in viscosity as the number of carbon atoms in the cation increases is more pronounced for the monoalkylammonium nitrate (pure and binary mixtures) and for $([\text{N}_2\text{N}_2\text{N}_2\text{N}_2]_x[\text{N}_0\text{N}_0\text{N}_0\text{N}_2]_{1-x})[\text{NO}_3]$. This result contrasts with a smaller increase for the system $([\text{N}_0\text{N}_0\text{N}_0\text{N}_2]_x[\text{N}_0\text{N}_0\text{N}_0\text{N}_2]_{1-x})[\text{NO}_3]$ atoms in the cation of the ionic liquid, these results prove that there are some structural features that are playing an important rôle in the distinct behaviours of the studied systems.

It has been demonstrated that excess properties are prone to increase with the difference of the aliphatic chain length between two components [130]. More recently, such a trend was also confirmed for the excess molar volume in binary mixtures of ionic liquids [119,131]. Moreover, the excess volumes in binary mixtures of ionic liquids are usually below 1 cm$^3$ mol$^{-1}$. 

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Figure 3.8 Experimental (a) molar volume, $V_m$, (b) dynamic viscosity, $\eta$, and (c) ionic conductivity, $\sigma$, of pure and binary mixtures ionic liquids at 313.15 K versus the number of carbons in the cation/composite cation.
Under the assumption that the $V^E$ is described by a parabolic function centred at a mole fraction of 0.5, the pseudo-liquid molar volume of the pure compounds $[\text{N}_{0\ 0\ 2\ 2}]\text{[NO}_3\text{]}$, $[\text{N}_{0\ 2\ 2\ 2}]\text{[NO}_3\text{]}$, $[\text{N}_{2\ 2\ 2\ 2}]\text{[NO}_3\text{]}$ (impossible to measure due to their high melting point) have been calculated, Figure 3.9 (a), along with the corresponding $V^E$ values of the binary mixtures composed of the above mentioned ionic liquids with $[\text{N}_{0\ 0\ 0\ 2}]\text{[NO}_3\text{]}$, Figure 3.9 (b).

**Figure 3.9** (a) Molar volume, $V_m$, of the systems composed of ethylammonium nitrate with di-, tri- and tetra-ethylammonium nitrate – the dashed line describes the ideal molar volume taking into account the calculated molar volume of di-, tri- and tetra-ethylammonium nitrate; (b) excess molar volume, $V^E$ of the systems mentioned above. $x$ is the mol fraction of the di-, tri-, tetra-alkylammonium compound.
These results indicate a trend with the maximum $V_E$ changing from $0.75\ \text{cm}^3\ \text{mol}^{-1}$ for {[N$_{0\ 0\ 2\ 2}$][N$_{0\ 0\ 0\ 2}$][NO$_3$]} to $2.8\ \text{cm}^3\ \text{mol}^{-1}$ for {[N$_{2\ 2\ 2\ 2}$][N$_{0\ 0\ 0\ 2}$][t-x]][NO$_3$], Figure 3.9 (b).

Another result that is worth comparing is the increase in the molar volume of the pure compounds by both lengthening the alkyl chain of the monoalkylammonium nitrate, and by successively replacing the proton by ethyl groups in the ammonium cation. The molar volume increment from {[N$_{0\ 0\ 0\ 2}$][NO$_3$]} to {[N$_{0\ 0\ 0\ 3}$][NO$_3$]} and {[N$_{0\ 0\ 0\ 4}$][NO$_3$]} follows the usual trend for ionic liquids. This also happens when changing from {[N$_{0\ 0\ 0\ 2}$][NO$_3$]} to {[N$_{0\ 0\ 2\ 2}$][NO$_3$]}. However, more intriguingly, this increment is much smaller when increasing the number of ethyl groups within the cation for more highly substituted systems. Thus, for {[N$_{0\ 0\ 0\ 2}$][NO$_3$]} and {[N$_{2\ 2\ 2\ 2}$][NO$_3$]}, the steric hindrance at the central nitrogen atom significantly increases with the addition of the fourth ethyl group (see also Section 2.2.4.2).

Furthermore, the pronounced increase of the equimolar excess molar volume, $V_{E1/2}$, is linearly related to the difference in the number of alkyl substituent groups attached to the nitrogen atom, $\Delta L$, of mixtures composed of ethylammonium nitrate with propyl- or butylammonium nitrate ($\Delta L = 0$), and with di-, tri- and tetra-ethylammonium nitrate ($\Delta L = 1$, 2 and 3) as shown in Figure 3.10.

**Figure 3.10** Equimolar excess molar volume, $V_{E1/2}$, versus the difference in the number of alkyl substituent groups attached to the nitrogen atom, $\Delta L$, of mixtures composed of ethylammonium nitrate with propyl- or butylammonium nitrate ($\Delta L = 0$), and with di-, tri- and tetra-ethylammonium nitrate ($\Delta L = 1$, 2 and 3, respectively).

One way to study the ionicity of ionic liquids is by comparison with an ideal electrolyte (fully dissociated potassium chloride ions in a dilute aqueous solution) in the well-known Walden plot (see Section 1.1.4) [117a,117b].
By relating the molar conductivity with the fluidity of the ionic liquid, it is possible to measure the ionicity, giving the deviation from the “ideal line”. According to the classification proposed by Xu and Angell [117c], [\text{[NO}_2\text{][NO}_3\text{]}], [\text{[NO}_3\text{][NO}_3\text{]}], [\text{[NO}_4\text{][NO}_3\text{]}], and their binary mixtures, can be classified as “good” ionic liquids based on their position on the Walden plot, see Figure 3.11.

![Walden plot](image-url)

**Figure 3.11** Walden plots for (a) pure [\text{[NO}_2\text{][NO}_3\text{]}], [\text{[NO}_3\text{][NO}_3\text{]}], and [\text{[NO}_4\text{][NO}_3\text{]}] as well as their selected binary mixtures, and (b) for the mixtures {\text{[NO}_0\text{0}_2\text{2}\text{][NO}_0\text{0}_2\text{2}\text{][NO}_3\text{]}}, {\text{[NO}_0\text{2}\text{2}\text{][NO}_0\text{0}_2\text{2}\text{][NO}_3\text{]}}, and {\text{[NO}_0\text{2}\text{2}\text{][NO}_0\text{0}_2\text{2}\text{][NO}_3\text{]}}, and their selected binary mixtures.
Similar behaviour has been observed for several alkylammonium bistriflamide salts [132], and for ionic liquids based on the imidazolium cation combined with a range of anions [133]. Excluding the two mixtures with the highest concentrations of [N₂₂₂₂][NO₃], the ionicity appears to decrease when temperature increases. A similar trend has been reported for other ionic liquids, such as ionic liquids based on pyrroldinium [134], or even Group 1 cations combined with oligoether carboxylate anions [53]. Nevertheless, a linear relationship should not be taken for granted, given that data for other ammonium bistriflamides [135] suggest an ionicity minimum for a given temperature. The Walden plot for pure monoalkylammonium nitrate ionic liquids and their mixtures, Figure 3.11 (a), also shows a direct relationship between ionicity and the alkyl chain length of the cation or composite cation. On the other hand, and somewhat surprisingly, the ionicity of the homologous mixtures di-, tri- and tetraethylammonium nitrate with [N₀₀₀₂][NO₃], cf. Figure 3.11 (b) remains essentially independent of the mol fraction or degree of alkylation of the first component. This behaviour might be directly related to a change in the initial network of the pure ethylammonium nitrates, due to specific interactions between the two components present in the mixture, as had already been demonstrated for mixtures of ionic liquids with inorganic salts [126]. Furthermore, a constancy of ionicity was observed for mixtures of 1-alkyl-3-methylimidazolium ethanoate with nucleobases, where the invariable ionicity was related to the hydrogen bonding network formed in these mixtures [136].

3.5 Conclusions

The thermophysical properties of three monoalkylammonium nitrate ionic liquids [N₀₀₀₂][NO₃], [N₀₀₀₃][NO₃] and [N₀₀₀₄][NO₃], and their binary mixtures in selected concentrations (all having three hydrogen-bond donors in the cation) were studied. The measured thermophysical data follow the expected trends. The dynamic viscosity values increased with the length of the alkyl chain, and with the number of carbons present in the cation or composite cation. In contrast, density and ionic conductivity followed the opposite trend. Moreover, small excess properties for all binary mixtures were obtained. These results confirm that ideal behaviour is a good model for an approximate description of these binary ionic liquid mixtures.

In addition, binary mixtures, composed of [N₀₀₀₂][NO₃] and an increasing mole fraction of homologous ionic liquids with decreasing numbers of hydrogen-bond donors in the cation: [N₀₀₂₂][NO₃], [N₀₂₂₂][NO₃] and [N₂₂₂₂][NO₃], were also investigated. The results show that, besides the expected influence of increasing the number of carbon atoms in an ionic liquid cation, there are other interactions affecting
the thermophysical properties of these ionic liquid mixtures. This can be seen by direct comparison of the binary mixtures, where a divergent trend in both dynamic viscosity and ionic conductivity is revealed as the number of carbon atoms in the composite cation increases. In contrast, with the results of monoalkylammonium nitrate mixtures, the $V^E$ data also reveal a clear deviation from ideal behaviour as the number of ethyl chains is increased on the ethylammonium cation. Furthermore, there is also an unexpected change in the (pseudo-liquid) molar volume increase of $[\text{N}_2\text{O}_2\text{N}_2][\text{NO}_3]$, $[\text{N}_2\text{O}_2\text{N}_2][\text{NO}_3]$ and $[\text{N}_2\text{O}_2\text{N}_2][\text{NO}_3]$ when removing hydrogen-bond donors from the cation.

Some alkylammonium nitrates, such as ethylammonium or propylammonium nitrates can be used as a strength-adjusting solvents with miscible organic solvents (e.g. methanol, ethanol, or acetonitrile). This facilities the elution of a larger range of hydrogen-bond acid compounds from column packing. However, the mixing behaviour of these salts can be ideal to non-ideal depending on the constituents, as seen in this Chapter. Hence, mixtures of monoalkylammonium nitrates, in which excess molar volumes were found quasi-ideal, are possible alternatives for chromatography purposes.

As the result of our studies, we came to the conclusion that the use of monoalkylammonium ionic liquids in chromatography might be a very interesting alternative for this technology applied so far. Also, this work reinforces the complicated behaviour of simple and binary protonic ionic liquids and the need for further studies into the hydrogen-bond networks in these, and related systems.
4 IR and Raman Spectroscopic Studies
The objective of this work is to identify, unambiguously, for the first time, the interionic hydrogen bond in ionic liquids. The technique of choice was inelastic neutron scattering (INS) spectroscopy, which (unlike the complementary techniques of infrared and Raman spectroscopies) exhibits no selection rules, and is particularly sensitive to protons in the region 1000-0 cm$^{-1}$). To optimise our chance of success, infrared and Raman spectroscopies of a series of alkylammonium nitrates and their binary mixtures were also studied and are described in this chapter. INS studies are described in Chapter 5.

Key to our strategy was the synthesis of the deuteriated analogues, $[\text{N}D\text{D}D\text{D}]\text{[NO}_3\text{]}$, $[\text{N}D\text{D}r\text{n}]\text{[NO}_3\text{]}$ and $[\text{N}D\text{r}r\text{n}]\text{[NO}_3\text{]}$, as the position of the $D\cdot\cdot\cdot O$ stretching frequencies occurs at significantly lower frequency than for $H\cdot\cdot\cdot O$. The salts, $[\text{N}D\text{D}z\text{z}]\text{[NO}_3\text{]}$ and $[\text{N}oz\text{z}]\text{[NO}_3\text{]}$, for which we have a substantial body of structural, spectroscopic and theoretical data, will be the starting point of the sequence of alkylammonium salts studied.

4.1 Introduction

When matter is exposed to electromagnetic radiation, it can be transmitted, absorbed, reflected, dispersed, or photoluminescence may occur. The latter term is used to designate different effects, such as fluorescence, phosphorescence and Raman scattering. There are many ways to measure this vibrational effect of the radiation to a material, although not all of the methods are applicable to all systems. The various methods are classified into two broad groups:

- Those in which a photon of the correct energy to excite a vibrational transition is absorbed or emitted. Infrared spectroscopy falls into this category.
- Those in which a particle is inelastically scattered by a material, such that the particle’s energy changes by an amount equal to the vibrational transition energy. For the second group, the particle can be a photon (Raman scattering), an atom (helium atom scattering), an electron (high-resolution electron energy loss spectroscopy and inelastic electron tunnelling spectroscopy), or a neutron (inelastic neutron scattering (INS) spectroscopy) [137].

4.1.1 Group theoretical treatment of vibrational analysis [138]

Molecular vibrations encompass motions from the simple coupled motion of two atoms of a diatomic molecule to the much complex motions of every atom in a large molecule. Molecules with $N$ atoms have $3N$ degrees of freedom, three of which represent translational motion in perpendicular directions (the $x$-, $y$-, and $z$-axes) and
three that represent rotational motion about same axes. The remaining $3N-6$ degrees of freedom give the number of vibrational modes. In the special case of a linear molecule, there are only two rotational modes and hence, $3N-5$ degrees of freedom. A molecule can vibrate in many ways, and each way is called a *vibrational mode*.

Assignment of vibrational modes is a complex procedure and the difficulty increases with the number of atoms of the molecule. However, the task assignment is controlled by two phenomena: the different selection rules which apply to IR and Raman spectroscopies, and the use of group theory to analyse molecular vibrations.

### 4.1.2 Terminology and types of fundamental vibrations

There are two types of molecular vibrations:

- **Stretching**: the bond length change, but the bond angle remains unchanged.
  - Symmetrical stretching ($v_s$)
  - Asymmetrical stretching ($v_{as}$)

- **Bending**: involve a change in bond angle, while maintaining a constant distance between atoms. These vibrations are also called *deformations*.
  - In-plane bending (scissoring) ($\delta$)
  - In-plane bending (rocking) ($\rho$)
  - Out-of-plane bending (wagging) ($\omega$)
  - Out-of-plane bending (twisting) ($\tau$)

For a specific hydrogen bonded system, $X-H\cdots Y$, the vibrational modes observed at high frequencies are shown in **Figure 4.1** [81]. The A-H bond is a conventional sigma bond, weakened by the hydrogen bond, H\cdots B, which has vibrations at much lower frequencies.
The A-H stretching mode, \( \nu \), is characteristic of the A-H··B system; the stronger the H··B hydrogen bond, the weaker the A-H covalent bond [81]. Its broadening is caused by the superposition of many sharper bands. The effect of the hydrogen bonds on vibrational spectra can be seen by the change in the stretching and bending modes. In many systems these shifts, \( \Delta \nu \), are of the order of 10% of the stretching frequency. The size of the shift, \( \Delta \nu \), is also related to the chemical and physical properties of the hydrogen bonded systems. The shape of the mode and its harmonics are broadened when a hydrogen bond is formed. The half-width, \( \nu_{1/2} \), is approximately \( \frac{3}{4} \Delta \nu \). The intensity of the band in the IR spectra increases significantly when a hydrogen bonded is formed [81].

The R-A-H in-plane bending modes, \( \delta \) and \( \rho \) (see Figure 4.1), are usually found between 1700-1000 cm\(^{-1}\), and are shifted to a frequency above the frequency of the mode in the absence of the hydrogen bond. The relative magnitude of this shift is normally smaller than that for the stretching mode. Unlike \( \nu \), the bending modes display no spectacular changes in the width of the bands upon hydrogen bond formation [81].

The R-A-H out-of-plane bending modes, \( \omega \) and \( \tau \) (see Figure 4.1), are usually at frequencies below 900 cm\(^{-1}\), characterised by restricted rotations around some bond, may be active upon hydrogen formation. Also, hydrogen bond forces might restrict certain rotational and translational degrees, and form an equal number of new vibrational degrees of freedom [81].

4.1.3 Infrared studies
Infrared spectroscopy is a technique based on the vibrations of atoms of a molecule. The absorption of radiation causes excitation of vibrations of the atoms of a molecule or the crystal lattice and causes bands in the spectra. Conventionally, bands in the infrared spectra are plotted on a wavenumber scale (\( \tilde{\nu} \) in cm\(^{-1}\)), which is linear in energy, rather than wavelength (which is not). The energy at which any peak in an
absorption spectrum appears corresponds to the frequency of a vibration of a part of a molecule.

The infrared range of the electromagnetic spectrum is divided into three regions, named in relation to the visible spectrum: near, mid and far-infrared. The limits of these three regions are not agreed upon and can vary. The main consideration that determines which wavelengths are included in each of these regions is the type of detector technology used for gathering infrared light.

- **Near-infrared**: \((\tilde{v} \text{ ranges from } 14000 \text{ to } 4000 \text{ cm}^{-1})\) lying adjacent to the visible region.
- **Mid-infrared**: \((\tilde{v} \text{ ranges from } 4000 \text{ to } 400 \text{ cm}^{-1})\) excites mainly fundamental vibrations.
- **Far-infrared**: \((\tilde{v} \text{ ranges from } 400 \text{ to } 10 \text{ cm}^{-1})\) is the lowest-energy region which excites mainly low energy vibrations, such as hydrogen bonds, metal-halogen vibrations, or lattice modes.

For a molecule to show infrared absorptions, an electric dipole moment of the molecule must change during the movement. In molecules such as H\(_2\), O\(_2\), or N\(_2\), the dipole moment does not change during the vibration or rotation, and hence, these types of compounds do not absorb infrared radiation.

The atoms of a molecule are never stationary. In a simple diatomic molecule A-B, such as CO or HCl, the wavenumber of absorbance, \(\tilde{v}\), can be calculated by the model of the harmonic oscillator, **Equation (4.1)**.

\[
\tilde{v} = \frac{1}{2} \pi \left(\frac{k}{\mu}\right)^{1/2}
\]  

**Equation (4.1)**

From **Equation (4.1)**, it can be seen that the frequency can be obtained from the square root of the ratio between the force constant \(k\), and the reduced mass, \(\mu\). The reduced mass is defined by **Equation (4.2)**.

\[
\mu = \frac{m_A \ast m_B}{m_A + m_B}
\]  

**Equation (4.2)**

Note that the force constant is a criterion for the strength of the chemical bond in the molecule A-B. Therefore, the stronger the chemical bond (electronic effect) and the smaller the reduced mass \(\mu\) (mass effect), the higher the wavenumber of the absorption band. **Equation (4.1)** can be applied also for some structurally complex molecules, as long as the coupling between the atoms can be neglected [139].
There are different factors that may affect the position of the absorption band:

- **Electronic effects:** The force constant increases with the bond order:
  \[ k_{C-X} < k_{C=O} < k_{C=\equiv}, \]
  however, the neighbour atoms of the bond can reduce the electron density, thus, the force constant and bonding strength, resulting in a smaller vibrational frequency.

- **Mass effects:** For a given bond type, the mass of the atoms is reflecting in the frequency of vibration. Thus, the frequency will be different for different isotopes. The smaller the mass of the atoms, the higher the vibrational frequency. For example, for C-H and C-D stretching frequencies:
  \[ \tilde{v}(C-H) \approx 3000 \text{ cm}^{-1}; \tilde{v}(C-D) \approx 2120 \text{ cm}^{-1}. \]

For molecules, the quantum mechanical formalism must be applied, as they consider the quantised nature of the vibration energies. For every molecule, discrete energy levels exist, and the only possible transitions allowed are between consecutive energy levels, see Equation (4.3).

\[ E_n = \hbar \nu \left( \nu + \frac{1}{2} \right) \] \hspace{1cm} (4.3)

in which \( \nu \) is the vibrational quantum number. According to this selection rule, transitions are only allowed with \( \Delta \nu = \pm 1 \). Most molecules nearly exclusively occupy the ground state, \( \nu = 0 \), at ambient temperatures. Hence, the experimentally observed infrared absorption band of a diatomic molecule is caused by the transition \( \nu=0 \rightarrow \nu=1 \), which is known as a *fundamental vibration*.

This harmonic oscillator model is incomplete for the description of real molecules. The anharmonic oscillator model allows for two important effects:

- As two atoms approach each other, the Coulombic repulsion will increase very rapidly.
- If a sufficiently large vibrational energy is reached, the molecule will dissociate (break apart). This is called the dissociation energy.

Consequently, the simple harmonic oscillator was replaced by the anharmonic oscillator model. This leads to a shape of the potential curve which is asymmetric and the right part of which converges to the dissociation energy (see Figure 4.2). The curve of the energy of both is similar at low energy levels. The energy level is not equidistant in the anharmonic oscillator model, and the distance decrease with increasing vibrational quantum number, \( \nu \).
Group theory predicts that some vibrational modes may be degenerate, so that more than one mode may occur at a given vibrational frequency, whilst others might be completely forbidden. Therefore, the number of fundamental absorption bands observable may be less than $3N-6$. However, the selection rule for the harmonic oscillator is not strictly obeyed, since the oscillator is anharmonic (see Figure 4.2). Transitions with $\Delta \nu = \pm 1, \pm 2, \pm 3, \text{ etc.}$ additionally occur, although with lower intensity: these are named overtones or higher harmonics [139-140]. In addition, combination bands will also be observed. This fact leads to additional peaks and more complicated infrared spectra. The intensity of fundamental bands in IR spectra is proportional to $(d\mu_D/dQ)^2$, where $\mu_D$, is the dipole moment and $Q$, is the normal coordinate of the vibration. Overtones and combination bands are usually much weaker than the fundamental modes from which they derived.

### 4.1.4 Raman studies

Raman spectroscopy is a complementary vibrational technique to Infrared spectroscopy. When a beam of monochromatic light of wavenumber, $\tilde{v}_0$, interacts with a sample, most of the incident light is transmitted without change (Rayleigh scattering). The analysis of the spectra of the scattered light shows that, in addition to Rayleigh scattering, there are also discrete components with altered wavenumbers positioned symmetrically about the Rayleigh line. This is called the Raman effect or Raman scattering (see Figure 4.3). In other words, during the inelastic photon interaction with the sample, the molecules are excited to virtual energy levels, very unstable, and the excited molecules relax back very rapidly to a lower state, more energetically stable, with emission of a photon. The scattering event occurs in $10^{-14}$ second or less [141]. If the reemitted photon is elastically scattered, it has the same
energy as the incident radiation, and gives the Rayleigh scattering phenomena, or if it is inelastically scattered, its energy is different from the incident radiation, to give the Raman scattering phenomena (see Figure 4.3).

Figure 4.3 Schematic diagram of the energy transitions involved in Rayleigh scattering (a) and Raman scattering (b,c). Raman scattering, gaining (anti-Stokes scattering, blue-shifted) or losing (Stokes scattering, red-shifted) an amount of energy equal to that vibrational mode. The Stokes lines are significantly stronger than the anti-Stokes [142].

Raman spectra are acquired by irradiating a sample with a powerful laser source of monochromatic radiation. During irradiation, the spectrum of the scattered radiation is measured at 90° with a suitable spectrometer (see Figure 4.4).

Figure 4.4 Schematic representation of a Raman spectrometer.
The intensity of Rayleigh scattering is around $10^7$ times that of Stokes scattering. Hence, the key point of Raman spectroscopy is to detect the Raman scattering by filtering out the strong Rayleigh scattering. In order to reduce the intensity of the Rayleigh scattering, multiple monochromators are applied to selectively transmit the needed wave range.

As seen in Section 4.1.3, the prerequisite for IR activity is a change in the dipole moment of the molecule during a given normal mode of vibration. Hence, some molecular vibrations that do not generate a vibrating electrical dipole are IR inactive. However, the selection rules of Raman spectroscopy require a change in the polarisability of the vibration [143], which means that bands observable in IR may be invisible in Raman, and vice versa. In addition, one of the greatest strengths of both techniques is their ability to study samples in all phases of matter.

Although not so sensitive as IR spectroscopy, Raman spectroscopy has other advantages [138]:

- Sample preparation for Raman spectroscopy can be made in standard glass tubes, making samples handling far simpler for Raman than for IR.
- Low frequency bands are far more easily measured.

However, it should be noted that, if the sample is coloured, it may absorb the laser beam, and cause sample decomposition. In addition, if the sample contains fluorescent impurities, or if it is fluorescent itself, then this radiation can swamp the Raman signal.

For the Raman spectral band to occur with a significant intensity, the vibrational mode must cause a change in the polarisability of the molecule [143]. The intensity of any band in Raman is given by Equation (4.4)

$$I_{\text{Raman}} = K I_L (\tilde{v}_0 - \tilde{v}_\lambda)^4 \left(\frac{d\alpha}{dQ}\right)^2$$

(4.4)

where $I_L$ is the power of the laser at the sample, $(\tilde{v}_0 - \tilde{v}_\lambda)$ is the wavenumber at which the band is measured, and $(d\alpha/dQ)$ is the change in the polarisability with the normal coordinate of the vibration. $K$, is the constant of proportionality, which is dependent on the efficiency at which Raman-scattered light is collected, among some other factors [138].

**4.1.5 The importance of deuteriation**

When an atom is replaced by an isotope of larger mass, $\mu$ increases, leading to a smaller $\tilde{v}$ and a downshift (smaller wavenumber) in the vibrational spectrum of the
molecule, according to **Equation (4.1)**. Taking the diatomic molecule HCl, if the hydrogen is replaced by its isotope deuterium, \( \mu \) is almost doubled and therefore \( \tilde{\nu} \) will be decreased by approximately \( \sqrt{2} \). Therefore, deuterium substitution in a molecule leads to an isotopic ratio of ca.1.4 for the frequencies corresponding to the hydrogen/deuterium vibrations. Consequently, there will also be a decrease in the band width and the integration of the band in the vibrational spectra of the deuteriated molecule [144]. In the Infrared spectrum of 2-hydroxybenzyl alcohol, the two O-H stretching bands at 3420 cm\(^{-1}\) and 3140 cm\(^{-1}\) in the hydrogen form of the compound disappear essentially completely from the deuterated compound, and the corresponding O-D stretching bands appear at around 2550 cm\(^{-1}\) and 2350 cm\(^{-1}\), respectively. The wavenumber ratios \( \tilde{\nu}_{OH}/\tilde{\nu}_{OD} \) for the two pairs of bands have a value of 1.34 [144].

Poylaniline is a stable and environmentally friendly polymer. In order to determine the exact mechanism of conductivity of this polymer, Quillard *et al.* [145] carried out comparative infrared and Raman spectroscopy studies of polyaniline and deuteriated polyaniline. The Raman spectra of both showed that the bands assigned to the C-C vibrations are only slightly downshifted, as expected, because they should not be significantly affected by deuteration. In contrast, the C-H bending vibrations (1192 cm\(^{-1}\) and 1166 cm\(^{-1}\)) and the N-H stretching mode (1515 cm\(^{-1}\)) are strongly affected by deuteration. In the deuteriated polyaniline, these bands are found at 876 cm\(^{-1}\) and 856 cm\(^{-1}\) for C-D bending and 1085 cm\(^{-1}\) for N-D stretching. Thus, the shift of the C-H stretching and N-H mode is in agreement with the expected isotope shift based on the square root of the C-D/C-H mass ratio (1.36 for both bending vibrations and 1.39 for the stretching mode).

The attractive optoelectronic properties of conducting polymers can be effectively modified by deuteration. Selective substitutions of deuterium on the backbone or side-chains of poly(3-hexylthiophene)s result in distinct optoelectronic responses (see **Figure 4.5**). The weak intermolecular interactions induced by the main-chain deuteration changed the film crystallinity and morphology, reducing the short-circuit current. However, side-chain deuteration did not significantly modify the film morphology but caused a decreased electronic coupling, giving rise to a reduction in the open circuit voltage [146]. The effects of deuteration on different photovoltaic processes, in this case, help to understand the structure-performance relationship by combining multiple analysis techniques.
4.1.5.1 Deuteriation effects in hydrogen-bonded systems

An extremely strong H/D isotope effect observed in hydrogen bonded $X-H\ldots Y$ systems is connected with a rich diversity of the potential energy shape for the proton/deuteron motion, which can be explained by the anharmonicity of the proton/deuteron vibrations and the tunnelling effect [147].

It is commonly accepted that the deuterated bridges are weaker than protonated ones, but this should not be taken as a general rule. In the case of harmonic or close to harmonic potentials with a single minimum, the deuterated bridges are slightly stronger than protonated ones. The zero point energy level of protonic vibrations lies above those levels for the deuterium analogues, as shown in Figure 4.6 (a). Despite the fact that they are located close to the centre of the potential curve, the amplitude of protonic vibrations is greater than those of the deuterons.

Figure 4.6 (b) shows the case of anharmonic vibrations: the zero point energy level of vibrations on the X atom is shifted towards the proton acceptor atom Y, which leads...
to a strengthening of the protonated bridge. In contrast, a deuteriated bridge is a little more stable. Nevertheless, the most important fact here is the difference in the amplitude of bending vibrations, which is undoubtedly weaker in the X-D bending vibrations (see Figure 4.7) [147].

![Figure 4.7](image)

**Figure 4.7** Illustration of the deuteriation effect on the bending vibrations. The amplitude of X–D vibration is less than its protonated analogue.

### 4.1.5.2 Deuteriation effects in hydrogen-bonded systems of ionic liquids

The contribution of hydrogen bonds to the ordering and dynamics of ionic liquids has been the subject of debate and numerous studies. The measurement of deuterium isotope effects on ionic liquids using IR and Raman spectrosopies [148], and NMR methods [149], is a useful tool to determine the evidence for this interaction.

In 1952, the infrared spectra of some solid secondary and tertiary amine hydrohalides, and also measurements on their deuteriated analogues, were studied by Stone et al. [150]. In the case of the secondary amine salts (containing the -NH$_2^+$ ion), there were two N-H stretching vibration bands, the symmetric and antisymmetric vibrations, at about 2920 cm$^{-1}$ and 2800 cm$^{-1}$ respectively, which decreased in intensity upon deuteriation. Two new bands then appeared, near 2200 cm$^{-1}$ and 2120 cm$^{-1}$. Near 1600 cm$^{-1}$, there was also a sharp band of the secondary amine hydrohalides, which was replaced by another around 1200 cm$^{-1}$ after deuteriation. This band was assigned to a NH$_2$ deformation mode. These authors also found that there were other prominent bands near 2500 cm$^{-1}$ and 2400 cm$^{-1}$, which decrease in intensity after deuteriation. They did not conclude what these bands were due to, but they knew these bands must be connected in some way with the -NH$_2^+$ group, as there was a regular relation between these bands and those assigned to the stretching vibrations of this group. For the tertiary amine hydrohalides, only the assignment of the -NH$_3^+$ stretching mode was recorded. The frequency ratio for the isotopic species is between 1.25 and 1.30. These results agree with earlier suggestions.

In 1984, Hagemann and Bill [151] reported Raman studies upon [N$_{0.002}$X, (X=Cl, or Br) and several deuteriated analogues. The deuteriation was carried out on the alkyl protons [CD$_3$CH$_2$N$_{0.00}$]X, [CH$_3$CD$_2$N$_{0.00}$]X, and on the ammonium protons, [N$_{0.00.0}$]X as well as the deuteriation of both sites, [CH$_3$CD$_2$N$_{0.00.0}$]X. The NH$_3$ torsion vibrations seem to be the most sensitive with respect to changes in the strength of hydrogen bonds.
Focussing on more complex structure of ionic liquids, imidazolium ionic liquids have been also studied for many years. The majority of these investigations have also identified hydrogen bonds between the anion and the imidazolium cation protons. Deuteriation is critical to gain a better understanding of the interactions forces that compose these ionic liquids. The first vibrational analysis of the 3-ethyl-1-methylimidazolium chloride - aluminium(III) chloride system was reported by Tait and Osteryoung [152] in 1984. They found that the IR spectra of the imidazolium salt in acidic and neutral form were the same, but that in basic environments, which contain an excess of Cl\textsuperscript{-} anions, some bands changed in intensity and a new broad band appeared in the C-H stretching region. They suggested that chloride may form a hydrogen bond with the C(2)-H hydrogen of the imidazolium ring [152]. Results from IR studies of these systems were re-evaluated by Dieter et al. [153] in 1988. These authors also reported the spectra of protonated versus deuteriated samples, in different sites of the ring, to confirm the assignments and look for other possible interactions (see Figure 4.8). In order to achieve this goal, they also replaced the C(2)-H with methyl.

Figure 4.8 Infrared spectra of (a) protonated, (b) deuteriated in C(2) position and (c) deuteriated C(2), C(4) and C(5), for two different mole fractions of AlCl\textsubscript{3} (basic (--) or acidic (—)) for [C\textsubscript{2}mim]Cl-AlCl\textsubscript{3}.
The \([\text{C}_2\text{mim}]\text{Cl}\)-\(\text{AlCl}_3\) ionic liquids exhibit acid-base chemistry depending on the mole fraction of \(\text{AlCl}_3\). When the mole fraction of \(\text{AlCl}_3\) used in preparing the ionic liquid is less than 0.5, it contains an excess of Cl\(^-\), which acts as a Lewis base, and is basic. For compositions with mole fractions of \(\text{AlCl}_3\) over 0.50, the ionic liquid is considered acidic, because it contains an excess of \([\text{Al}_2\text{Cl}_7]\)^-, which acts as a Lewis acid. At a mole fraction of \(\text{AlCl}_3\) of 0.50, the ionic liquid is neutral, with \([\text{Al}_2\text{Cl}_7]\)^- as the only detectable anion. The IR spectra of different mole fractions of \(\text{AlCl}_3\) 0.33, 0.40, and 0.50 ionic liquids showed a broad band around 3049 cm\(^{-1}\) as the ionic liquid become more basic, and as more Cl\(^-\) is present. They called this band the Cl\(^-\) interaction band. To determine which C-H stretching frequencies shift to form the Cl\(^-\) interaction band, they deuteriated first the C(2)-H and then the C(2)-H, C(4)-H, and C(5)-H positions. Their spectral studies showed that Cl\(^-\) interacts with imidazolium cation to cause similar shifts in the frequencies of the C(2)-H, C(4)-H, and C(5)-H hydrogen stretches, and not just confined to C(2)-H.

Others evidence of hydrogen bonds in ionic liquids have been obtained by \(^{35/37}\text{Cl}\) NMR spectroscopy though deuteriation effects [154]. Shift of \(^{35/37}\text{Cl}(H,D)\) values obtained for the model system 1-butyl-3-methylimidazolium chloride (\([\text{C}_4\text{mim}]\text{Cl}\)) upon deuteration of the imidazolium the C(2)-H and then the C(2)-H, C(4)-H, and C(5)-H positions, of nearly 1 and 2 ppm, respectively, indicate the existence of Cl-H hydrogen bonds between the anion and cation (see Figure 4.9).

![Figure 4.9](image_url)

Figure 4.9 Structure and \(^{35}\text{Cl}\) NMR spectra of protonated (black), deuteriated in C(2)-H position (blue), and C(2)-H, C(4)-H, and C(5)-H positions (red), of \([\text{C}_4\text{mim}]\text{Cl}\).

These studies, amongst others, evidence the importance of the use of deuterium isotope effects to investigate hydrogen-bonding in ionic liquids, and this will be one of the key points in this thesis.
4.1.6 Infrared and Raman studies in ionic liquids, and their computational simulations

Infrared and Raman spectroscopies have been used to study the nature of ionic liquids, such as molecular conformations, at different temperatures and pressure [140], as well as the role that hydrogen bonds play in the cation-anion interactions [15]. Many inorganic anions possess highly symmetrical structures, leading to much simpler vibrational fingerprints than organic cations.

In a zeroth order approximation, the vibrational spectrum of the ionic liquid would be the sum of the spectra of the anions and the cations. However, for a real ionic liquid, the interactions between the anions and the cations induce changes in the vibrational patterns of each. These induced changes are a reflection of the strengths of these interactions, which can influence the local symmetry (and hence selection rules) and the bond strengths (and hence frequencies) of the ions. For these reasons, it is convenient to consider the spectroscopic studies according firstly to the nature of the cation, and then according to the nature of the anion.

Together with experimental data, quantum mechanical methods are now commonly used to calculate vibrational frequencies. Despite the advantages of that, strong ionic interactions between cation and anion may imply that experimental and calculated vibrations do not exactly match in all the cases.

4.1.6.1 Imidazolium salts

The imidazolium cation has been discussed in more detail than other cations which form ionic liquids, despite the intrinsically complicated electronic structure of the imidazolium ring. Historically, the pyridinium and imidazolium salts dominated the field of ionic liquids from the 1940s to the 1990s. The lower melting points of the imidazolium salts meant that they attracted the most attention, with the first vibrational study being published by Tait and Osteryoung [152]. Their work showed the IR vibrational analysis of 1-butylpyridinium chloride - AlCl₃ and 1-ethyl-3-methylimidazolium chloride - AlCl₃ ionic liquids as a function of Lewis acidity, in order to examine the nature of the ionic interaction more closely. This paper reported for the first time that the main difference in IR spectra between basic and acidic forms of both mixtures occurs in the C−H stretching region. Vibrational spectra also enabled the study of molecular conformations in ionic liquids. An X-ray diffraction study of [C₄mim]Cl suggested that it possessed two crystalline phases, each with a different conformation of the butyl chain, with different assignment of bands for each crystal in the Raman spectra [155]. The two sets of characteristic Raman bands, which are
mutually exclusive with each other, coexist in the spectrum of liquid [C₄mim]Cl, which indicates that there is a mixture of conformers in the ionic liquid (see Figure 4.10).

![Figure 4.10](image_url)

**Figure 4.10** Raman spectra of (a) Crystal 1, (b) Crystal 2, and (c) liquid [C₄mim]Cl. Arrows point out characteristic Raman bands of Crystal 1 and 2 [155].

At the same time, Holbrey et al. [97c] reported the crystal structures of these two polymorphs of [C₄mim]Cl (see Figure 4.11) and compared them with that of [C₄mim]Br using X-ray diffraction. Their results showed that the structure of the [C₄mim]^+ cation in one of the conformers of [C₄mim]Cl was the same as that in [C₄mim]Br.

![Figure 4.11](image_url)

**Figure 4.11** Scheme of two cations from the orthorhombic (I, blue) and monoclinic (II, green) polymorphs of [C₄mim][Cl] showing in Fisher projection, the conformation of the C(7)–C(8) bond of the butyl chain.

A vibrational analysis of this system was carried out by Ozawa et al. [156] showing that two characteristic Raman bands of crystalline [C₄mim]Cl and three of crystalline [C₄mim]Br can be used as marker bands of the rotational isomerism around the C(7)-C(8) bond of the butyl group. In order to confirm that the Raman spectral differences obtained truly reflect the structural variation of the [C₄mim]^+ cation, and
not the difference in the crystal environment, they carried out a DFT calculation of the [C₄mim]⁺ cation in both conformers. The calculation reproduced the Raman spectral patterns remarkably well, not only the peak positions but also the intensities of those characteristic bands. This group also compared the Raman spectra of [C₄mim]Cl and [C₄mim]Br with [C₄mim][BF₄]. In the Raman spectrum of liquid [C₄mim][BF₄], both sets of marker bands (two due to one conformer of [C₄mim]Cl and another two from [C₄mim]Br) are simultaneously observed, proving that at least two rotational isomers of the [C₄mim]⁺ cation coexist in the ionic liquid state. Berg et al. [97e] calculated vibrational frequencies of [C₄mim]⁺ and demonstrated that similar analysis using Raman can be obtained by ab initio MP2 calculations using Gaussian 03. Once verified, the same method was used to assign the peaks in the previously unreported [C₆mim]Cl and [C₆mim][PF₆] liquids, and also to determine the presence of any conformers in the [C₆mim]⁺ cation. The results showed that the Raman spectral bands identified as characteristic for the conformer of the 1-butyl-3-methylimidazolium cation by Ozawa et al. [156], were also characteristic for the conformers of the 1-hexyl-3-methylimidazolium cation. A few years after that paper, same author, Berg, published a review of Raman spectroscopy and ab initio calculations on ionic liquids. The results obtained indicated that the neglect of the presence of cation-anion interactions was a reasonable approximation for successful prediction of the Raman spectra. Grondin et al. [157] calculated harmonic and also anharmonic frequencies of [C₄mim]⁺ and [C₆mim]⁺. Detailed tables of vibrational frequencies calculated for [Cₙmim]⁺ (n = alkyl chain) can be found in a recently published review [140].

The hydrogen-bond donor in the imidazolium cation is the C-H group; this can be either on the aromatic ring, or a C-H from the alkyl groups of the side chains. The high-frequency range, 2800-3200 cm⁻¹, exhibits a complex pattern of overlapping bands, corresponding to these C-H stretching modes. Further research showed that this can be separated into two groups: bands 2800-3000 cm⁻¹, belonging to CH modes of alkyl chains attached to the imidazolium ring, and bands 3000-3200 cm⁻¹, belonging to CH of the imidazolium ring (see Figure 4.12). The 800-1600 cm⁻¹ range exhibits bands related to the imidazolium ring vibrations. The 400-800 cm⁻¹ range, which also contains ring vibrations, provides insight into the conformations of the alkyl chains (see Figure 4.10). As the authors suggested, this is a clear proof that this spectral range is a signature of ionic interactions [140,158].
Figure 4.12 IR (red) and Raman (black) spectra in the high frequency range for [C₄mim][CF₃SO₃] and [C₄mim][PF₆] [140].

For ionic liquids that contain the same cation, there are considerable differences in the ring C-H stretching modes for both the Raman and IR spectra (see Figure 4.12). For example, the band at 3125 cm⁻¹ in the [C₄mim][PF₆] salts is shifted to 3115 cm⁻¹ in the [C₄mim][CF₃SO₃] salts, as the C(2)-H bond of the cation is weakened by hydrogen bonding to the triflate anion. Of course, the selection rules, and hence the band intensities, are different in both techniques, and so the maximum information can be garnered by studying the system with both Raman and IR spectroscopies. However, the work of Tait and Osteryoung [152] has shown that it is possible, with very pure samples, to make a full assignment in this region with just infrared data.

It is worth stressing, however, that hydrogen bonds in ionic liquids are rarely simple. They are a combination of heteronuclear, bifurcated and chelated components. Anions can form interactions with multiple hydrogen atoms, on the same or different cations simultaneously. The structural characteristic of the anion, and their ability to form hydrogen bonds can be evaluated and classified: [O₂CMe] > [Me₂PO₄] > [MeSO₃] > Cl⁻ > [NO₃] ≈ [MeSO₄] > [N(CN)₂] > [OTf] ≈ [BF₄] > [NTf₂] > [PF₆] > [SbF₆] [15]. Thus, this is also the series of expected shifts in the C-H stretching frequencies of the cation. Historically, many of the literature assignments are dubious (see Section 1.4 and Section 4.1.5.2.), but now (particularly with the aid of modern computational chemistry) assignment in this region are reasonably straightforward.
4.1.6.2 Ammonium salts

The vibrational frequencies of the tetrahedral, $T_d$, [NH$_4$]$^+$ cation, in its halide salts were first reviewed by Herzberg in 1945 [159]. The free ammonium ion has four vibrational modes, classified as: $v_1(A_1)$, symmetric stretching at 3033 cm$^{-1}$; $v_2(E)$, angular deformation at 1685 cm$^{-1}$; $v_3(T_2)$, antisymmetric stretching at 3134 cm$^{-1}$ and $v_4(T_2)$, angular deformation at 1397 cm$^{-1}$, with all modes Raman active, but only $v_3$ and $v_4$ IR active.

The preparation of simple ammonium ionic liquids via acid-base neutralisation from cheap amines and acids has been used for many purposes. A large variety of these ionic liquids can be prepared by alkylation of one, two, three or four hydrogen atoms bound to the nitrogen atom. Unlike, mono, di- and tri-ammonium salts, detailed assignments of the cation vibrational modes with the help of quantum chemistry calculation just appeared recently for tetraalkylammonium compounds [160].

Clearly, the tetraalkylammonium cation does not have N-H bonds available as hydrogen bonds donors. Thus, the high frequency region of the vibrational spectra (from 3200-2800 cm$^{-1}$) will be mostly dominated by C-H stretching modes of the cation. Indeed, there is little evidence that tetraalkylammonium cations are involved in significant hydrogen bonding in any known salts [161]. An indication of the weakness of these interactions between tetraalkylammonium cations and their anions can be seen by comparison of the calculated frequencies for the isolated anions and cations with the experimental spectroscopic data for [N$_{1113}$][NTf$_2$] and [N$_{1116}$][NTf$_2$] salts [160]. [NTf$_2$]$^-$ molecular motions are very strong and are present in the frequency ranges between 800-150 cm$^{-1}$ and 1350-1050 cm$^{-1}$. The dynamics of the cations gives absorptions in three spectral ranges: 3050-2850 cm$^{-1}$, 1550-1350 cm$^{-1}$, and 1030-750 cm$^{-1}$. While the cationic absorptions in the two highest range are due to C-H bending and stretching, the vibrations between 1030-750 cm$^{-1}$ correspond to more complex vibrations. The cation vibrations outside those range have negligible intensity [160]. As tetraalkylammonium salts contain four alkyl chains, there are a huge number of possible conformations for each cation. Thus, unlike the case of the alkylimidazolium salts, computations of conformational isomerism is not fruitful, as experimentally there are many overlapping frequencies.

4.1.6.3 Nitrate salts

For the studies in this thesis, nitrate salts were selected over, say, halide salts as they have their own internal vibrations, which will be sensitive to the formation of hydrogen bonds. They also are strong hydrogen bonds acceptors, and in the free state have a
very high symmetry \( (D_{3h}) \), making the experimental spectra very sensitive to small changes in the environment.

Upon interaction between the cation and anion, the three N-O bonds become non-equivalent. The isolated ion has a planar trigonal structure, belonging to \( D_{3h} \), with the excess negative charge equally distributed among the three equivalent oxygen atoms and all three N-O bonds having the same partial double bond character [162], with the same N-O distances and 120° planar structure. The fundamental vibrations of the free ion were assigned from dilute aqueous solutions and classified by \( D_{3h} \) symmetry as [162a,163]:

\[
\Gamma_{D_{3h}}: A_1^* + A_2^* + 2E'
\]  \( (4.5) \)

The four vibrational modes of the trigonal, planar nitrate ion are the two non-degenerate modes: symmetric stretch (\( \nu_s \)) and the out-of-plane deformation (\( \omega_{oop} \)), and the two doubly degenerate modes: asymmetric stretch (\( \nu_{as} \)), and in-plane bending (\( \rho_{ip} \)) modes. Under \( D_{3h} \) symmetry, there is no overlap between infrared and Raman activity. Thus, the symmetric stretch, \( \nu_s \), does not generate a change in the dipole moment, and is therefore only Raman active, and the out-of-plane deformation mode, \( \omega_{oop} \), does not cause a change in the polarisability vector, and is therefore only infrared active (Figure 4.13).

![Figure 4.13 Vibrational modes of nitrate anion, \( D_{3h} \) symmetry.](image)

When the solid, or molten salts of Group 1 nitrates such as lithium nitrate, potassium and caesium nitrate, were analysed, it was clear that the nitrate ion exists in a lower symmetry environment than \( D_{3h} \), as more bands are observed experimentally than expected. Thus, the symmetric stretch, \( \nu_s \), only Raman active in \( D_{3h} \) symmetry, becomes infrared active as well, and the degeneracy of the asymmetric stretch, \( \nu_{as} \), is removed. Also, the Raman forbidden fundamental, is observed in the Raman spectra of some of the molten nitrates [162b]. All these observations indicate that the nitrate ion in the Group 1 salts, molten and even solid-state, has a lower
symmetry than expected. The symmetry is lowered mostly to $C_{2v}$ symmetry, as seen for solid and molten KNO$_3$ [163-164]. The fundamental vibrational N-O frequencies are classified on the $C_{2v}$ symmetry as $A$ and $B$ and are all IR allowed: six infrared bands are expected. The bands arising from the doubly degenerate, $E'$, $\nu_{as}$ and $\rho_{ip}$, are split as seen, and the infrared inactive $A_{1}'$ mode of the free nitrate becomes active giving a total of six infrared bands. If the symmetry is reduced further to $C_{2v}$ symmetry, the number of the infrared bands will be the same as on $C_{2v}$ symmetry, classified as $4A'+2A''$, and all will be Raman active too.

Solid KNO$_3$, purchased from Sigma-Aldrich has been analysed by IR and Raman spectroscopy at QUILL [106], to evaluate the nitrate vibrational modes in the high frequency range (see Figure 4.14).

The specific frequencies of solid KNO$_3$, with $C_{2v}$ symmetry, are shown in Table 4.1. These frequencies are a guideline for the assignment of frequencies of the anion in the alkylammonium nitrates ionic liquids.
Table 4.1 Vibrational modes of [NO$_3$]$^-$ in water for D$_{3h}$ [162b] and C$_{2v}$ symmetry [163, 106].

<table>
<thead>
<tr>
<th></th>
<th>D$_{3h}$</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A$^1$ (Raman)</td>
<td>A$^2$ (IR)</td>
<td>E$^+(R+IR)$</td>
<td>E$^+(R+IR)$</td>
</tr>
<tr>
<td>[NO$_3$]$^-$ (in water) [162b]</td>
<td>V$_s$</td>
<td>$\omega_{oopp}$</td>
<td>V$_{as}$</td>
<td>$\rho_p$</td>
</tr>
<tr>
<td></td>
<td>1050</td>
<td>820</td>
<td>1390</td>
<td>720</td>
</tr>
<tr>
<td>C$_{2v}$</td>
<td>A$^1$ (R+IR)</td>
<td>A$^1$ (R+IR)</td>
<td>B$^2$ (R+IR)</td>
<td>A$^1$ (R+IR)</td>
</tr>
<tr>
<td>KNO$_3$ (solid) [106]</td>
<td>1042, 1050</td>
<td>820</td>
<td>1341</td>
<td>1356</td>
</tr>
<tr>
<td>KNO$_3$ (in water) [163]</td>
<td>1040</td>
<td>828</td>
<td>1340-1400</td>
<td>723</td>
</tr>
</tbody>
</table>

* The symmetric stretch, $\nu_s$, has a low intensity in the IR, giving a combination band (possibly $\nu_s + \rho_p$) around 1800 cm$^{-1}$.

### 4.1.6.4 Alkylammonium nitrates

The structure of the simplest alkylammonium nitrate, [N$_{0.0.0.1}$][NO$_3$], has been studied, theoretically and experimentally, by Bodo et al. [165]. Raman, as well as X-ray powder analysis at different temperatures, have been performed for this ionic liquid. The assignment of the vibrational bands was helped by MD simulations for small clusters of this salt, ([N$_{0.0.0.1}$][NO$_3$])$_n$ for $n$ up to 8. The structures were optimised by quantum chemical calculations. The agreement between theoretical and experimental spectra allow a good interpretation of the hydrogen bonds. In their work, C-H stretching modes are localised in the region 2800-3050 cm$^{-1}$, together with the N-H stretching bands, which are broad bands in the region 3100-3300 cm$^{-1}$. Two distinct broad bands were observed in the reported experimental Raman spectra due to NH vibrations: one at 3100-3150 cm$^{-1}$ and another at 3250 cm$^{-1}$. They concluded that these spectral features were due to one of the three N-H donor sites having a weaker hydrogen bond to the nitrate ion than the other two. Thus, there exist two different absorption peaks in the spectra in the N-H region due to two different hydrogen bonds with different strengths. The distinction between the bands become less clear at higher temperatures [165]. Further details of these systems will be discussed in Section 4.3.
4.1.7 Theoretical calculations: CASTEP
The vibrational frequencies of $[\text{N}_2\text{O}_2\text{N}][\text{NO}_3]$ were calculated using the comprehensive $ab\text{}initio$ simulation code, called CASTEP. This program is based on density functional theory and incorporates concepts such as: a plane-wave basis set, pseudo-potential descriptions, exchange-correlation functionals, and geometry-optimisation. The physical properties of materials that can be calculated using CASTEP. Also, it uses a supercell approach, which enables the calculations of the lattice dynamics, from which can be derived the vibrational spectra. CASTEP is a commercial software and has been completely written by researchers at the Universities of York, Durham, St. Andrews, Cambridge and Rutherford Labs [166]. More details can be found in Section 4.2.4. This programme has been mostly used for inorganic complexes [167], nanomaterials [168], and metal-organic frameworks (MOF) [169]. The only example of CASTEP being used in ionic liquids was to analyse the experimental results of a scanning transmission electron microscopy image carried out for $[\text{C}_2\text{mim}][\text{TFSI}]$ and $[\text{C}_8\text{mim}]\text{Br}$ [170].

4.2 Experimental
4.2.1 Preparation of deuteriated alkylammonium nitrates
Deuteriated ionic liquids were prepared from their protonated analogues by heating in D$_2$O at 40 °C overnight and subsequent evaporation of the solvent by freeze-drying. The process was repeated until there were no N-H bands detected by infrared spectroscopy (typically 4-5 times). The quantitative nature of the deuteriation was demonstrated by IR and Raman spectroscopy, which showed the disappearance of the $\nu$(N-H) bands and the appearance of the $\nu$(N-D) bands (see Sections 4.4 and 4.5)
4.2.2 IR spectrometer (Appendix B9)
Data were recorded at RT, in the range of 4000-650 cm\(^{-1}\), by accumulating at least 8 scans with a resolution of 4 cm\(^{-1}\). Samples were analysed by placing a small amount onto the ATR accessory, with dinitrogen flowing over it using a glass conical funnel attached to the dinitrogen gas tube. The funnel was kept as close as possible to the sample, to minimise the exposure of the sample to moisture.

4.2.3 Raman spectrophotometer (Appendix B10)
A 785 nm laser was used, with a spectral range from 3500-500 cm\(^{-1}\) Raman shift. The samples were sealed in the glove box in a standard glass cuvette and analysed. For each sample, at least sixteen scans were obtained in less than five minutes.

4.2.4 CASTEP code
First-principles electronic-structure calculations of \([N\text{O}_2\text{NO}_3]\) were performed within density functional theory (DFT) as implemented in the CASTEP code [166]. Plane-wave basis sets and optimised norm-conserving pseudo-potentials [171] generated with the Perdew-Burke-Ernzerhof (PBE) [172] functional within the generalised-gradient approximation (GGA) have been used for all calculations. The frequencies obtained with GGA functionals scales around 1.000. This is due to the fact that GGA functionals somehow wrongly describe the potential energy surfaces / their curvatures. In that way GGA effectively compensated the errors due to anharmonicity to a large extent. Dispersion corrections to the PBE functional (PBE+D) were included following the methodology of Tkatchenko and Scheffler (TS) [173]. Semi empirical dispersion corrections (although its use is not critical in the present case) are formally needed as density functional theory, in principle, cannot describe van der Walls forces due to its inability to deal with long-range electron correlation effects. A plane-wave cut-off of 800 eV and a Brillouin-zone (BZ) sampling of 4x2x4 k-points (8 points when symmetry-reduced) were found to be sufficient to converge energy and atomic forces below 2.5x10\(^{-3}\) eV/ion and 1.0x10\(^{-3}\) eV/Å, respectively. Self-consistent single-point energy minimisations used a tolerance of 2.5x10\(^{-9}\) eV. Full-geometry optimisations were performed with a force tolerance of 1.0x10\(^{-3}\)eV/Å using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm as implemented on CASTEP. Phonon frequencies and eigenvectors of the resulting minimum-energy structures were calculated at \(\Gamma\) point via diagonalisation of dynamical matrices computed using density-functional perturbation theory (DFPT) and linear-response methods using ACLIMAX [174]. The spectra of \([N\text{O}_2\text{NO}_3]\) have been computed and optimised on ISIS cluster, at the Rutherford Institute, by Dr Sanghamitra Mukhopadhyay. A CIF file generated from solving the crystallographic
structure was used to generate lattice dynamics of the initial model, and then was fully optimised with PBE-TS.

4.2.5 Jmol [175]

Jmol is a program that allows the visualisation of unit cells, space groups and symmetry operators, and the measurement of angles and distances. A key feature of Jmol is its ability to localise and display hydrogen bonds, and to visualise the actual vibrational modes for the chemical structure under study. This feature is crucial for the assignment of the vibrational bands obtained from the theoretical calculation. In a pocket at the back of the thesis, the main vibrational modes of \([\text{N}_0\text{O}_2\text{D}_2]\text{[NO}_3\text{]}\) and \([\text{N}_0\text{D}_2\text{D}_2][\text{NO}_3]\) are recorded on a CD-ROM.

4.3 Results and discussion of pure ionic liquids and their deuteriated analogues

4.3.1 Analysis of diethylammonium nitrate, \([\text{N}_0\text{O}_2\text{D}_2][\text{NO}_3]\)

4.3.1.1 Empirical results for \([\text{N}_0\text{O}_2\text{D}_2][\text{NO}_3]\)

The high frequency vibrational modes of both ions are easily identified by both techniques, IR and Raman spectroscopies. As discussed earlier (Section 2.1.2.4.2.), in the lattice of \([\text{N}_0\text{O}_2\text{D}_2][\text{NO}_3]\), both hydrogen donor sites form two bifurcated hydrogen bonds, the strongest at 1.966 Å, and the weakest at 2.452 Å. Thus, two sets of distinct broad features of N-H motions can be spotted from the IR spectra at 3200-2800 cm\(^{-1}\), and the two NH bending modes near 1600 cm\(^{-1}\) are easily identified by IR spectroscopy [81] (see Figure 4.16). These bands are at frequencies modified by the H\(\cdots\)O hydrogen bonding interactions visible in the low frequency range of the INS spectra, Chapter 5. The assignments of the cation will be discussed, together with those of its deuteriated analogue, in the following sections. For the anion, the vibrational modes are summarised in Table 4.2.

Table 4.2 Experimentally observed bands\(^a\) for the nitrate ion in \([\text{N}_0\text{O}_2\text{D}_2][\text{NO}_3]\) and their comparison with the literature [106].

<table>
<thead>
<tr>
<th>Mode assignment</th>
<th>Raman</th>
<th>IR</th>
<th>KNO(_3) (solid) [106]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Wavenumber / cm(^{-1})</td>
</tr>
<tr>
<td>(\nu_{as})</td>
<td>-</td>
<td>1307 (s)</td>
<td>1356, 1341</td>
</tr>
<tr>
<td>(\nu_{s})</td>
<td>1055 (w), 1047 (s)</td>
<td>1057 (w), 1049 (w)</td>
<td>1050, 1042</td>
</tr>
<tr>
<td>(\omega_{oop})</td>
<td>-</td>
<td>826 (s)</td>
<td>820</td>
</tr>
<tr>
<td>(\rho_{in})</td>
<td>719 (w), 712 (w)</td>
<td>715 (w), 711 (w)</td>
<td>718, 710</td>
</tr>
</tbody>
</table>

\(^a\) (w): weak intensity band, (s): strong intensity band.
As can be seen from Figure 4.16 and Table 4.2, the assignments for the nitrate anion are unambiguous and consistent with those found in the literature for solid potassium nitrate and the aqueous nitrate ion. The splitting of the bands due to $\nu_{as}$, $\nu_{s}$, and $\rho_{in}$ in solid $[\text{NO}_2\text{NO}_2\text{NO}_3]$, compared to the equivalent bands in K[NO$_3$] and [NO$_3$]$\text{aq}$, originates with the symmetry breaking induced by the hydrogen bonding in the lattice.

![Vibrational spectra of [NO$_2$NO$_2$NO$_3$]: (a) infrared (red) and (b) Raman (blue).](image)

**Figure 4.16** Vibrational spectra of $[\text{NO}_2\text{NO}_2\text{NO}_3]$: (a) infrared (red) and (b) Raman (blue).

### 4.3.1.2 Empirical results for $[\text{ND}_2\text{NO}_2\text{NO}_3]$  

For $[\text{ND}_2\text{NO}_2\text{NO}_3]$, the NH$_2$ symmetric ($\nu_{s}$) and asymmetric ($\nu_{as}$) overlap with the CH$_2$ and CH$_3$ stretching modes $\nu$(CH$_n$) (see Figure 4.16). By comparison with the spectra of $[\text{ND}_2\text{NO}_2\text{NO}_3]$ (see Figure 4.17), this overlap is eliminated, as the $\nu$(ND$_2$) bands are shifted to a different region (ca. 2200 cm$^{-1}$). The two ND$_2$ bending bands, also affected by deuteriation, appear at about 1150 cm$^{-1}$ (shifted by a factor of 1.3).
Figure 4.17 Vibrational infrared spectra for (a) \([\text{ND}_2\text{D}][\text{NO}_3]\), and (b) \([\text{ND}_2\text{D}][\text{NO}_3]\) and Raman spectra for (c) \([\text{ND}_2\text{D}][\text{NO}_3]\) and (d) \([\text{ND}_2\text{D}][\text{NO}_3]\).

Table 4.3 Experimentally observed bands (FT-IR and FT-R) for the cation for \([\text{ND}_2\text{D}][\text{NO}_3]\) and \([\text{ND}_2\text{D}][\text{NO}_3]\)

<table>
<thead>
<tr>
<th>Mode assignment</th>
<th>([\text{ND}_2\text{D}][\text{NO}_3])</th>
<th>([\text{ND}_2\text{D}][\text{NO}_3])</th>
<th>(v_{\text{OH}}/v_{\text{OD}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v(\text{NH}_2))</td>
<td>2959, 2923</td>
<td>2854, 2805</td>
<td>-</td>
</tr>
<tr>
<td>(v(\text{ND}_2))</td>
<td>-</td>
<td>-</td>
<td>2185, 2163</td>
</tr>
<tr>
<td>(\delta(\text{NH}_2))</td>
<td>-</td>
<td>1615</td>
<td>-</td>
</tr>
<tr>
<td>(\delta(\text{ND}_2))</td>
<td>-</td>
<td>-</td>
<td>1180</td>
</tr>
<tr>
<td>(\omega(\text{NH}_2))</td>
<td>1482</td>
<td>1483</td>
<td>-</td>
</tr>
<tr>
<td>(\omega(\text{ND}_2))</td>
<td>-</td>
<td>-</td>
<td>1146</td>
</tr>
</tbody>
</table>

4.3.1.3 Theoretical calculations: Castep code.

The calculated infrared and Raman spectra using the Castep software for \([\text{ND}_2\text{D}][\text{NO}_3]\) and \([\text{ND}_2\text{D}][\text{NO}_3]\) are compared with the empirical data in Figure 4.18. The theoretical spectra gives excellent agreement with experiment on the whole, but not in the N-H stretching region. This is the effect of dynamics and anharmonicity, which cannot be well described with a static, quasi-harmonic approximation [176]. The calculations for the Raman spectra predict very well, but not perfectly, the C-H
stretching frequencies, while the calculations for IR and experimental at ca. 3000 cm$^{-1}$ predict the N-H. The spectral signatures of deuteriation are clear in the IR and Raman calculations, and support the experimental findings. However, as in the case for N-H, the N-D bands in the theoretical calculations are sharp and well defined, and in the experimental shows a broad signal. Comparison of the experimental results and the theoretical predictions is presented in Table 4.4.

![Vibrational spectra for $[\text{NO}_3]$ and $[\text{ND}_3]$](image)

**Figure 4.18** Vibrational spectra for $[\text{NO}_3]$ and $[\text{ND}_3]$: (a) IR CASTEP calculations, (b) empirical IR, (c) Raman CASTEP calculations, and (d) empirical Raman.
Table 4.4 Collection of experimentally observed and calculated CASTEP infrared and Raman vibrational bands for [N\textsubscript{0 2 2}][NO\textsubscript{3}] and [N\textsubscript{D 2 2}][NO\textsubscript{3}].

<table>
<thead>
<tr>
<th>Mode assignment</th>
<th>[N\textsubscript{0 2 2}][NO\textsubscript{3}]</th>
<th>[N\textsubscript{D 2 2}][NO\textsubscript{3}]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Wavenumber / cm(^{-1})</strong></td>
<td><strong>Wavenumber / cm(^{-1})</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Raman</strong></td>
<td><strong>IR</strong></td>
</tr>
<tr>
<td>(\nu(\text{CH}_2))</td>
<td>3000, 2998, 2982</td>
<td>3050, 2990, 2970</td>
</tr>
<tr>
<td>(\nu(\text{NH}_2))</td>
<td>2959, 2923</td>
<td>2854, 2805</td>
</tr>
<tr>
<td>(\nu(\text{ND}_2))</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\omega(\text{NH}_2))</td>
<td>2923</td>
<td>2805</td>
</tr>
<tr>
<td>(\omega(\text{ND}_2))</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\delta(\text{NH}_2))</td>
<td>-</td>
<td>1615</td>
</tr>
<tr>
<td>(\delta(\text{ND}_2))</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\omega(\text{NH}_3))</td>
<td>1482</td>
<td>1483</td>
</tr>
<tr>
<td>(\omega(\text{ND}_3))</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Complex motion region:</td>
<td>1482-1442</td>
<td>1482-1459</td>
</tr>
<tr>
<td>(\nu_{as}(\text{NO}_3))</td>
<td>-</td>
<td>1308</td>
</tr>
<tr>
<td>(\rho(\text{CH}_3))</td>
<td>1162</td>
<td>1158</td>
</tr>
<tr>
<td>(\gamma(\text{C-C}))</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\nu(\text{NO}_3))</td>
<td>1055, 1047</td>
<td>1057, 1049</td>
</tr>
<tr>
<td>(\nu(\text{C-N}))</td>
<td>859, 867</td>
<td>-</td>
</tr>
<tr>
<td>(\omega_{\text{vap}}(\text{NO}_3))</td>
<td>-</td>
<td>826</td>
</tr>
<tr>
<td>(\rho(\text{NH}), \rho(\text{CH}_3))</td>
<td>-</td>
<td>790</td>
</tr>
<tr>
<td>(\rho_{as}(\text{NO}_3))</td>
<td>719, 712</td>
<td>715, 711</td>
</tr>
</tbody>
</table>
**Region 3050-1700 cm\(^{-1}\).** By analysing the IR spectra of \([\text{N}_2\text{H}_2][\text{NO}_3]\), one can observe a broad band covering the spectrum from the range 3050-2800 cm\(^{-1}\). The large contribution from the \(\nu\)(N-H) modes partially masks the weak \(\nu\)(C-H) bands. There are three broad components with the centres of gravity found at 3000 cm\(^{-1}\), 2998 cm\(^{-1}\), and 2982 cm\(^{-1}\). According to the calculations, the highest frequencies (3074-2967 cm\(^{-1}\)) correspond to symmetric and asymmetric stretches of the C-H vibrational modes, while N-H symmetric stretches, \(\nu_s\)(NH\(_2\)), can be found at 2939 cm\(^{-1}\) and 2934 cm\(^{-1}\) and N-H asymmetric stretches, \(\nu_{as}\)(NH\(_2\)), at 2899, and 2898 cm\(^{-1}\), which are shifted to lower frequencies upon deuteriation. The theoretical calculations predict a large intensity for these bands. However, in the experiment, this intensity is distributed over the entire range of modes, resulting in a broader, weaker band. Around 2484-2393 cm\(^{-1}\) there are two small peaks of low intensity due to adventitious carbon dioxide in the system. By analysing the Raman spectrum of \([\text{N}_2\text{H}_2][\text{NO}_3]\), the \(\nu\)(C-H) stretching distributed over 3000, 2998, and 2982 cm\(^{-1}\) can be clearly identified. The spectrum reveals three relatively sharp set of bands, also present in the deuteriated experimental analogue. The experimental wavenumbers calculated for both the protonated and deuteriated samples show the same red shift with respect to the calculated.

**Region 1700-650 cm\(^{-1}\).** An excellent agreement between the experimental and theoretical spectra has been achieved for IR and Raman spectra, giving rise to a precise assignment for the vibrational modes in this region. A very significant influence of the long-range dipole coupling has been found in the IR, showing a broadening of some of the experimental bands and introducing the band shape asymmetry, which is not observed in the Raman spectrum, which is free of these effects. The long-range dipole coupling not only affects the wavenumber of the absorption bands, but it very significantly affects their intensities.

By analysing the IR spectra, there is a small peak around 1752 cm\(^{-1}\) in both protonated and deuteriated, possibly due to adventitious water, as it is not visible in the calculations. Although the sample was dry and kept in the glove box, there is a minimum unavoidable air exposure during the measurement. The NH\(_2\) scissoring mode at 1615 cm\(^{-1}\) is easy to identify, however, and it appears to be red shifted in the calculated spectrum. At 1483 cm\(^{-1}\), there is a band visible in IR and Raman, which disappears upon deuteriation in both cases, and also disappear from the calculations. This is due to NH\(_2\) wagging. The set of bands covering the range of 1490-1345 cm\(^{-1}\), is composed of many complex motions, mainly of CH\(_2\) scissoring. There are also overtones of the NO\(_3\) deformation and NH\(_2\) bending modes. In addition, at 1308 cm\(^{-1}\),
a strong NO$_3$ asymmetric stretch is seen in the IR spectrum. The peaks in the range of 1250-1047 cm$^{-1}$ are mainly due to CH bending. The very intense Raman peak around 1047 cm$^{-1}$, also visible (but weaker) in the IR, is the NO$_3$ symmetric stretching motion. The two pair of bands, at about 859 and 719 cm$^{-1}$, can be assigned respectively, to $\nu_6$(NO$_3$), and $\rho_{\text{NO}}$(NO$_3$). At 790 cm$^{-1}$, the contribution of NH$_2$ and CH$_n$ bending motions gives a prominent IR signal that disappears upon deuteration, which is replicated in the CASTEP calculations. It should be noticed that in the frequencies, where there is a contribution of several motions and NH is involved (according to CASTEP), mainly in the IR, there are several bands that disappear after deuteration (Figure 4.19). The $\nu_{\text{OH}}/\nu_{\text{OD}}$ ratios for these bands are detailed in Table 4.5.

**Table 4.5** Experimentally observed bands (IR and Raman) for [N$_{0222}$][NO$_3$] and [N$_{0222}$][NO$_3$]

<table>
<thead>
<tr>
<th>Bands</th>
<th>IR ($\nu$ / cm$^{-1}$)</th>
<th>$\nu_{\text{OH}}/\nu_{\text{OD}}$</th>
<th>Raman ($\nu$ / cm$^{-1}$)</th>
<th>$\nu_{\text{OH}}/\nu_{\text{OD}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[N$_{0222}$][NO$_3$]</td>
<td>[N$_{0222}$][NO$_3$]</td>
<td>[N$_{0222}$][NO$_3$]</td>
<td>[N$_{0222}$][NO$_3$]</td>
</tr>
<tr>
<td>1</td>
<td>1615</td>
<td>1180</td>
<td>1.36</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>1483</td>
<td>1138</td>
<td>1.30</td>
<td>1482</td>
</tr>
<tr>
<td>3</td>
<td>1332</td>
<td>996</td>
<td>1.34</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>790</td>
<td>(607)$^a$</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Calculated on the basis of 1.30 ratio for $\nu_{\text{OH}}/\nu_{\text{OD}}$; frequency below observed range.
4.3.1.4 An overall picture

The spectral analyses of \([\text{N}_0\text{D}_2\text{D}_2][\text{NO}_3]\) and \([\text{N}_0\text{D}_2\text{D}_2][\text{NO}_3]\) are fully supported by the density functional theory calculations, which indicates that the isotopic substitution was performed successfully. A summary of the main features is shown in Figure 4.20. The assignment of diethylammonium nitrates has been used as an archetype for the assignment of a series of alkylammonium nitrates which are studied in the following Sections 4.3.2-4.3.7.

![Figure 4.20 An overall picture of experimental and theoretical calculations for \([\text{N}_0\text{D}_2\text{D}_2][\text{NO}_3]\) and \([\text{N}_0\text{D}_2\text{D}_2][\text{NO}_3]\). IR (red), Raman (blue), and theoretical calculations (grey). Significant bands have been highlighted.](image)

The low frequency region (below 500 cm\(^{-1}\)) will be discussed in detail in Chapter 5.

4.3.2 Analysis of ethylammonium nitrate, \([\text{N}_0\text{D}_2\text{D}_2][\text{NO}_3]\)

The main vibrational bands for ethylammonium nitrate are labelled in Figure 4.21. By analysing the IR spectra, one can observe a broad band in the range 3255-2888 cm\(^{-1}\). As found for \([\text{N}_0\text{D}_2\text{D}_2][\text{NO}_3]\), see Section 4.3.1 and Figure 4.16, the large contribution from the \(\nu(\text{N-H})\) modes partially masks the weak \(\nu(\text{C-H})\) bands. The N-H symmetric stretch was identified at ca. 3100 cm\(^{-1}\) by infrared. Upon deuteriation, these bands are shifted to a lower frequencies, giving rise to three broad bands at 2369, 2280, and 2201 cm\(^{-1}\) for \([\text{N}_0\text{D}_2\text{D}_2][\text{NO}_3]\), observed by IR and two bands active in the Raman
spectrum at 2358 and 2213 cm\(^{-1}\) (see Figure 4.22 and Table 4.6). The ratio between the assignments of \(\tilde{v}_{OH}/\tilde{v}_{OD}\) is 1.39, which is reasonable according to the literature.

**Figure 4.21** Vibrational spectra of \([\text{ND}_3\text{NO}_3]\): (a) infrared (red) and (b) Raman (blue).

**Figure 4.22** Infrared spectra (red) for (a) \([\text{ND}_3\text{D}_2\text{NO}_3]\), and (b) \([\text{ND}_3\text{D}_2\text{NO}_3]\) and Raman spectra (blue) for (c) \([\text{ND}_3\text{D}_2\text{NO}_3]\) and (d) \([\text{ND}_3\text{D}_2\text{NO}_3]\).
Table 4.6 Experimentally observed bands (IR and R) and the ratios, $\bar{v}_{OH}/\bar{v}_{OD}$ for [N\textsubscript{002}][NO\textsubscript{3}] and [N\textsubscript{DD2}][NO\textsubscript{3}]

<table>
<thead>
<tr>
<th>Mode assignment (^a)</th>
<th>[N\textsubscript{002}][NO\textsubscript{3}]</th>
<th>[N\textsubscript{DD2}][NO\textsubscript{3}]</th>
<th>$\bar{v}<em>{OH}/\bar{v}</em>{OD}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raman (cm\textsuperscript{-1})</td>
<td>IR (cm\textsuperscript{-1})</td>
<td>Raman (R)</td>
</tr>
<tr>
<td>$\nu$(CH\textsubscript{3})</td>
<td>2993, 2957 2895</td>
<td>2991, 2948 2888</td>
<td>2993, 2957 2895</td>
</tr>
<tr>
<td>$\nu$(NH\textsubscript{3})</td>
<td>3277, 3076 3255, 3166 3070</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\nu$(ND\textsubscript{3})</td>
<td>-</td>
<td>2358, 2213 2369, 2280, 2201</td>
<td>Raman: 1.39</td>
</tr>
<tr>
<td>$\delta$(NH\textsubscript{3})</td>
<td>1619</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\delta$(ND\textsubscript{3})</td>
<td>1157</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\omega$(NH\textsubscript{3})</td>
<td>1515</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\omega$(ND\textsubscript{3})</td>
<td>1157</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\nu_{as}$(NO\textsubscript{3})</td>
<td>1296</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\rho$(CH\textsubscript{3})</td>
<td>1197</td>
<td>1219-1193 1197</td>
<td>-</td>
</tr>
<tr>
<td>$\nu$(NO\textsubscript{3})</td>
<td>1041</td>
<td>1041 1041</td>
<td>-</td>
</tr>
<tr>
<td>$\delta$(NH\textsubscript{3}), $\delta$(C-N), $\nu$(C-C)</td>
<td>989</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\delta$(ND\textsubscript{3})</td>
<td>809</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\nu$(C-N)</td>
<td>873</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\omega$(as NO\textsubscript{3})</td>
<td>825</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\rho$(NH\textsubscript{3}), $\rho$(CH\textsubscript{3})</td>
<td>793</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\rho$(ND\textsubscript{3})</td>
<td>719</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\) The numbers (1-4) relate to the assignment in Figure 4.23. \(^b\) Calculated on the basis of 1.30 ratio for $\bar{v}_{OH}/\bar{v}_{OD}$; frequency below observed range.

By analysing the Raman spectrum of [N\textsubscript{002}][NO\textsubscript{3}], the $\nu$(C-H) stretching is distributed over 2993, 2957, and 2895 cm\textsuperscript{-1}, and is unaltered upon deuteration. In the IR, however, these bands are extremely weak (see Figure 4.22). At about 1619 cm\textsuperscript{-1} and 1515 cm\textsuperscript{-1}, there are two bands related to the NH\textsubscript{3} bend (scissoring and
wagging, respectively). Upon deuteriation, these bands are shifted to approximately 1245 cm\(^{-1}\), which is covered by the broadness of NO\(_3\) symmetric stretch, and 1157 cm\(^{-1}\), respectively. The split of the NH\(_3\) bend signal, is possibly due to the bending of more than one type of hydrogen bonds formed. The NO\(_3\) symmetric out-of-plane stretch is found at 1296 cm\(^{-1}\) in a broad peak, found in the fingerprint region. The strong and sharp Raman peak at 1041 cm\(^{-1}\) is the NO\(_3\) symmetric stretch motion. The two IR bands at 825 cm\(^{-1}\) and 719 cm\(^{-1}\) are due to NO\(_3\) deformation (out-of-plane) and bending (in-plane) of the NO\(_3\), respectively. The peak that lies at 873 cm\(^{-1}\) in the Raman is due to C\(_n\)–N symmetric stretching. At 793 cm\(^{-1}\), the contribution of NH\(_3\) and CH\(_n\) bending motions gives a prominent IR signal that disappears upon deuteriation. As has been seen for [N\(_0\) \(\text{D}_2\)\][$\text{NO}_3$], where there is a contribution of several motions and NH is involved, mainly in the IR, there are several bands that disappear after deuteriation (numbered by 3, and 4 of the Figure 4.23).

![Figure 4.23](image)

Figure 4.23 Expansion of the infrared spectra for (a) [N\(_0\) \(\text{D}_2\)\][$\text{NO}_3$], and (b) [N\(_0\) \(\text{D}_2\)\][$\text{NO}_3$] and Raman spectra for (c) [N\(_0\) \(\text{D}_2\)\][$\text{NO}_3$] and (d) [N\(_0\) \(\text{D}_2\)\][$\text{NO}_3$]. The numbers assigned to the bands are related to the assignments in Table 4.6.

### 4.3.3 Analysis of propylammonium nitrate, [N\(_0\) \(\text{D}_2\)\][$\text{NO}_3$]

The main vibrational bands for propylammonium nitrate are labelled in Figure 4.24. In the IR spectrum, one can observe a broad band in the range 3254-2882 cm\(^{-1}\). As in the previous cases (see Sections 4.3.1 and 4.3.2), the large contribution from the
ν(N-H) modes partially masks the weak ν(C-H) bands. The N-H symmetric stretch was identified as a broad peak at ca. 3170 cm⁻¹. Upon deuteriation, this broad band is shifted in both IR and Raman, and resolves into a broad band with three features at 2353, 2282, and 2196 cm⁻¹ (see Figure 4.25 and Table 4.7). The ratio between the assignments of \( \tilde{\nu}_{OH} / \tilde{\nu}_{OD} \) is 1.39.

**Figure 4.24** Vibrational spectra for [N\(_0\)\(_0\)\(_0\)3][NO\(_3\)] (a) infrared (red) and (b) Raman (blue).

**Figure 4.25** Vibrational infrared spectra (red) for (a) [N\(_0\)\(_0\)\(_0\)3][NO\(_3\)], and (b) [N\(_0\)\(_0\)\(_0\)3][NO\(_3\)] and Raman spectra (blue) for (c) [N\(_0\)\(_0\)\(_0\)3][NO\(_3\)] and (d) [N\(_0\)\(_0\)\(_0\)3][NO\(_3\)].
Table 4.7 Experimentally observed bands (IR and R) and ratios $\tilde{v}_{OH}/\tilde{v}_{OD}$ for [N$_{3}$O]NO$_{3}$ and [N$_{3}$D]$^2$O$_{3}$NO$_{3}$

<table>
<thead>
<tr>
<th>Mode assignment $^a$</th>
<th>[N$<em>{3}$O]NO$</em>{3}$</th>
<th>[N$<em>{3}$D]$^2$O$</em>{3}$NO$_{3}$</th>
<th>$\tilde{v}<em>{OH}/\tilde{v}</em>{OD}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wavenumber / cm$^{-1}$</td>
<td>Raman IR</td>
<td>Raman</td>
</tr>
<tr>
<td>$\nu$(CH$_n$)</td>
<td>2993, 2957, 2895</td>
<td>2970, 2940, 2882</td>
<td>2993, 2957, 2895</td>
</tr>
<tr>
<td>$\nu$(NH$_3$)</td>
<td>3265, 3076</td>
<td>3254, 3170, 3077</td>
<td>-</td>
</tr>
<tr>
<td>$\nu$(ND$_3$)</td>
<td>-</td>
<td>-</td>
<td>2349, 2213</td>
</tr>
<tr>
<td>$\delta$(NH$_3$)</td>
<td>3</td>
<td>-</td>
<td>1617</td>
</tr>
<tr>
<td>$\delta$(ND$_3$)</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\omega$(NH$_3$)</td>
<td>2</td>
<td>-</td>
<td>1520</td>
</tr>
<tr>
<td>$\omega$(ND$_3$)</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\nu_{as}$(NO$_3$)</td>
<td>1315, 1295</td>
<td>1315</td>
<td>1297</td>
</tr>
<tr>
<td>$\rho$(CH$_3$)</td>
<td>1183, 1183</td>
<td>1183</td>
<td>1183</td>
</tr>
<tr>
<td>$\delta$(NH$_3$), $\delta$(C-N), $\nu$(C-C)</td>
<td>955, 953</td>
<td>957, 960</td>
<td>-</td>
</tr>
<tr>
<td>$\nu$(C-N)</td>
<td>3</td>
<td>871</td>
<td>867</td>
</tr>
<tr>
<td>$\omega_{oop}$(NO$_3$)</td>
<td>831, 825</td>
<td>-</td>
<td>826</td>
</tr>
<tr>
<td>$\rho$(NH$_3$), $\rho$(CH$_3$)</td>
<td>767, 766, 753</td>
<td>779</td>
<td>774</td>
</tr>
<tr>
<td>$\rho$(NO$_3$)</td>
<td>719, 718</td>
<td>718</td>
<td>715, 734</td>
</tr>
</tbody>
</table>

$^a$ The numbers (1-3) relate to the assignment in Figure 4.26. $^b$ Calculated on the basis of 1.30 ratio for $\tilde{v}_{OH}/\tilde{v}_{OD}$; frequency below observed range.

In the Raman spectrum of [N$_{3}$O]NO$_{3}$, the $\nu$(C-H) stretching is distributed over 2993, 2957, and 2895 cm$^{-1}$, which is unaltered upon deuteriation. As expected, these bands in the IR are extremely weak (see Figure 4.25). At about 1620 cm$^{-1}$ and 1520 cm$^{-1}$, there are two strong bands in the IR related to the N-H bend (scissoring and wagging, respectively). Upon deuteriation, these bands are shifted to approximately 1234 cm$^{-1}$, which is under covered by the broadness of NO$_3$ asymmetric stretch, as in the case of [N$_{3}$O]NO$_{3}$, and 1157 cm$^{-1}$, respectively. NO$_3$ asymmetric stretch is found at 1296 cm$^{-1}$ in a broad peak, composed also for a region of many complex motion, mainly due to CH$_n$ scissoring. In this case, NO$_3$ asymmetric stretch is also
active by Raman, which did not occur for the previous alkylammonium nitrates studied. The strong and sharp Raman peak at 1045 cm\(^{-1}\) is the NO\(_3\) symmetric stretch motion. The two IR bands at 828 cm\(^{-1}\) and 719 cm\(^{-1}\) are due to NO\(_3\) deformation (out-of-plane) and bending (in-plane) of the NO\(_3\), respectively. The peak that lie at 871 cm\(^{-1}\) (3) will be discussed in Section 4.3.5. Figure 4.26 shows an expansion of the infrared and Raman spectra for [N\(_{0\,0\,0\,3}\)][NO\(_3\)], and its deuteriated analogue.

![Figure 4.26](image)

**Figure 4.26** Expansion of the infrared spectra for (a) [N\(_{0\,D\,D\,3}\)][NO\(_3\)], and (b) [N\(_{0\,0\,0\,3}\)][NO\(_3\)] and Raman spectra for (c) [N\(_{D\,D\,3}\)][NO\(_3\)] and (d) [N\(_{0\,0\,3}\)][NO\(_3\)]. The numbers assigned to the bands are related to the assignments in Table 4.7.

### 4.3.4 Analysis of butylammonium nitrate, [N\(_{0\,0\,4}\)][NO\(_3\)]

The main vibrational bands for butylammonium nitrate are labelled in Figure 4.27. By analysing the IR spectra of [N\(_{0\,2\,2}\)][NO\(_3\)], one can observe a broad band covering the spectrum from the range 3267-2877 cm\(^{-1}\). As in the previous cases (see Sections 4.3.1-4.3.4), the large contribution from the \(\nu(N-H)\) modes partially masks the weak \(\nu(C-H)\) bands. The N-H symmetric stretch was identified as a broad peak at ca. 3171 cm\(^{-1}\). Upon deuteriation, this broad band is shifted in both IR and Raman, and resolves into a broad band with three features at 2351, 2287, and 2198 cm\(^{-1}\) (see Figure 4.28 and Table 4.8). The ratio between the assignments of \(\tilde{\nu}_{OH}/\tilde{\nu}_{OD}\) is 1.39 as for propylammonium and ethylammonium nitrates.
Figure 4.27 Vibrational spectra of [N\textsubscript{0.0.4}][NO\textsubscript{3}] (a) infrared (red) and (b) Raman (blue).

Figure 4.28 Infrared spectra (red) for (a) [N\textsubscript{0.0.4}][NO\textsubscript{3}], and (b) [N\textsubscript{0.0.4}][NO\textsubscript{3}] and Raman spectra (blue) for (c) [N\textsubscript{0.0.4}][NO\textsubscript{3}] and (d) [N\textsubscript{0.0.4}][NO\textsubscript{3}].
Table 4.8 Experimentally observed bands (FT-IR and FT-R) and $\tilde{v}_{OH}/\tilde{v}_{OD}$ for $[\text{N}_0\text{O}_0\text{O}_4]\text{[NO}_3]$ and $[\text{N}_4\text{D}_0\text{D}_0\text{D}_0]\text{[NO}_3]$.

<table>
<thead>
<tr>
<th>Mode assignment</th>
<th>[N$_0$O$_0$O$_4$]NO$_3$</th>
<th>[N$_4$D$_0$D$_0$D$_0$]NO$_3$</th>
<th>$\tilde{v}<em>{OH}/\tilde{v}</em>{OD}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raman</td>
<td>IR</td>
<td>Raman</td>
</tr>
<tr>
<td>$\tilde{v}$(CH$_3$)</td>
<td>2973, 2925, 2877</td>
<td>2962, 2939, 2876</td>
<td>2972, 2925, 2877</td>
</tr>
<tr>
<td>$\tilde{v}$(NH$_3$)</td>
<td>3265, 3077</td>
<td>3267, 3164, 3055</td>
<td>-</td>
</tr>
<tr>
<td>$\tilde{v}$(ND$_3$)</td>
<td>-</td>
<td>-</td>
<td>2349, 2214</td>
</tr>
<tr>
<td>$\delta$(NH$_3$)</td>
<td>1645, 1619</td>
<td>1632, 1615</td>
<td>-</td>
</tr>
<tr>
<td>$\delta$(ND$_3$)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\omega$(NH$_3$)</td>
<td>-</td>
<td>1512</td>
<td>-</td>
</tr>
<tr>
<td>$\omega$(ND$_3$)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\nu$(NO$_3$)</td>
<td>1306</td>
<td>1317</td>
<td>1312</td>
</tr>
<tr>
<td>$\rho$(CH$_3$)</td>
<td>1173</td>
<td>1169</td>
<td>1165</td>
</tr>
<tr>
<td>$\nu$(NO$_3$)</td>
<td>1039</td>
<td>1039</td>
<td>1039</td>
</tr>
<tr>
<td>$\delta$(NH$_3$), $\delta$(C-N), $\nu$(C-C)</td>
<td>941</td>
<td>942</td>
<td>-</td>
</tr>
<tr>
<td>$\nu$(C-N)</td>
<td>900</td>
<td>916</td>
<td>-</td>
</tr>
<tr>
<td>$\omega_{oop}$(NO$_3$)</td>
<td>-</td>
<td>825</td>
<td>-</td>
</tr>
<tr>
<td>$\rho$(NH$_3$), $\rho$(CH$_3$)</td>
<td>767</td>
<td>743</td>
<td>779</td>
</tr>
<tr>
<td>$\rho$(NO$_3$)</td>
<td>721, 715</td>
<td>717</td>
<td>718</td>
</tr>
</tbody>
</table>

* The numbers (1-2) relate to the assignment in Figure 4.29.

In the Raman spectrum of $[\text{N}_0\text{O}_0\text{O}_4]\text{[NO}_3]$, the $\nu$(C-H) stretching is distributed over 2973, 2925, and 2877 cm$^{-1}$, which is unaltered upon deuteriation. As expected, these bands in the IR are extremely weak (see Figure 4.25). The N-H scissoring bend is splitting in two bands at 1645 cm$^{-1}$ and 1619 cm$^{-1}$ active by IR and Raman. At 1512 cm$^{-1}$, there is a strong band in the IR related to the N-H wagging bend. Upon deuteriation, the N-H scissoring bend band is shifted to approximately 1248 cm$^{-1}$, as a small shoulder in the broadness of NO$_3$ symmetric stretch, and the N-H wagging bend to 1151 cm$^{-1}$. NO$_3$ asymmetric stretch is found at 1317 cm$^{-1}$ in a broad peak, composed also for a region of many complex motion, mainly due to CH$_n$ scissoring.
In this case, NO₃ asymmetric stretch is also active by Raman, which occur for the propylammonium nitrate. The strong and sharp Raman peak at 1039 cm⁻¹ is the NO₃ symmetric stretch motion. The two IR bands at 825 cm⁻¹ and 717 cm⁻¹ are due to NO₃ deformation (out-of-plane) and bending (in-plane), respectively. The NO₃ bending (in-plane) is splitting in two peaks at 721 cm⁻¹ in the Raman spectrum, and 715 cm⁻¹. Figure 4.29 shows an expansion of the infrared and Raman spectra for [N₀₀₀₄][NO₃] and its deuteriated analogue, where the bands related to N-H have been highlighted.

![Figure 4.29 Expansion of the infrared spectra for (a) [N₀₀₀₂][NO₃] and (b) [N₀₀₀₄][NO₃] and Raman spectra for (c) [N₀₀₀₄][NO₃] and (d) [N₀₀₀₄][NO₃]. The numbers assigned to the bands are related to the assignments in Table 4.8.](image)

### 4.3.5 Comparison with literature

Bodo et al. [177] examined [N₀₀₀₂][NO₃], [N₀₀₀₃][NO₃] and [N₀₀₀₄][NO₃] by Raman spectroscopy and ab initio DFT calculations, and found an excellent agreement between experiment and theory. The theoretical calculations involved geometric optimisation of clusters of the different ionic liquids, guiding the interpretation and assignment of almost all the spectral features. Their vibrational analyses are shown in Tables 4.9-4.11.
Table 4.9 Comparison between Raman experimental frequencies modes from this work and those from Bodo et al. [177] for \([\text{NO}_3]^{-}\).

<table>
<thead>
<tr>
<th>Mode assignment</th>
<th>([\text{NO}_3]^{-})</th>
<th>This work</th>
<th>Literature [177]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wavenumber / cm(^{-1})</td>
<td>Experimental</td>
<td>Theoretical</td>
</tr>
<tr>
<td>(\nu(\text{NH}_3))</td>
<td>3277, 3076</td>
<td>3300-2900</td>
<td>3300-2900</td>
</tr>
<tr>
<td>(\delta(\text{NH}_3))</td>
<td>1619</td>
<td>1660-1600</td>
<td>1660-1600</td>
</tr>
<tr>
<td>(\nu(\text{NO}_3))</td>
<td>1041</td>
<td>1044</td>
<td>1083</td>
</tr>
<tr>
<td>(\omega_{\text{oop}}(\text{NO}_3))</td>
<td>825</td>
<td>830-825</td>
<td>878</td>
</tr>
<tr>
<td>(\rho_{\text{in}}(\text{NO}_3))</td>
<td>719</td>
<td>719</td>
<td>715</td>
</tr>
</tbody>
</table>

Table 4.10 Comparison between Raman experimental frequencies modes from this work and those from Bodo et al. [177] for \([\text{N}_2\text{O}_3]^{-}\).

<table>
<thead>
<tr>
<th>Mode assignment</th>
<th>([\text{N}_2\text{O}_3]^{-})</th>
<th>This work</th>
<th>Literature [177]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wavenumber / cm(^{-1})</td>
<td>Experimental</td>
<td>Theoretical</td>
</tr>
<tr>
<td>(\nu(\text{NH}_3))</td>
<td>3265, 3077</td>
<td>3200-3100</td>
<td>3200-3100</td>
</tr>
<tr>
<td>(\delta(\text{NH}_3))</td>
<td>1617</td>
<td>1660-1600</td>
<td>1660-1600</td>
</tr>
<tr>
<td>(\nu(\text{NO}_3))</td>
<td>1045</td>
<td>1044</td>
<td>1082</td>
</tr>
<tr>
<td>(\omega_{\text{oop}}(\text{NO}_3))</td>
<td>831</td>
<td>830-825</td>
<td>867</td>
</tr>
<tr>
<td>(\rho_{\text{in}}(\text{NO}_3))</td>
<td>719</td>
<td>718</td>
<td>711</td>
</tr>
</tbody>
</table>

Table 4.11 Comparison between Raman experimental frequencies modes from this work and those from Bodo et al. [177] for \([\text{N}_4\text{O}_3]^{-}\).

<table>
<thead>
<tr>
<th>Mode assignment</th>
<th>([\text{N}_4\text{O}_3]^{-})</th>
<th>This work</th>
<th>Literature [177]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wavenumber / cm(^{-1})</td>
<td>Experimental</td>
<td>Theoretical</td>
</tr>
<tr>
<td>(\nu(\text{NH}_3))</td>
<td>3265, 3077</td>
<td>3200-3100</td>
<td>3200-3100</td>
</tr>
<tr>
<td>(\delta(\text{NH}_3))</td>
<td>1645,1619</td>
<td>1660-1600</td>
<td>1660-1600</td>
</tr>
<tr>
<td>(\nu(\text{NO}_3))</td>
<td>1039</td>
<td>1044</td>
<td>1086</td>
</tr>
<tr>
<td>(\omega_{\text{oop}}(\text{NO}_3))</td>
<td>825</td>
<td>830-825</td>
<td>887</td>
</tr>
<tr>
<td>(\rho_{\text{in}}(\text{NO}_3))</td>
<td>721, 715</td>
<td>718</td>
<td>717-700</td>
</tr>
</tbody>
</table>
The comparison of all the experimental data (theirs and mine) with the theoretical calculations for each of the three ionic liquids was consistent, each following the same pattern. Bodo et al. [177] often cite ranges of frequencies, while here specific values are reported, but these are very broad bands where the maxima are difficult to precisely determine. Their assignments of the bands were based on \textit{ab initio} DFT simulations that use an empirical model of the interactions followed by an optimisation based on Monte Carlo sampling, with the OPLS force field [178]. For [N\textsubscript{0002}][NO\textsubscript{3}], they used ωB97X-D/6-311+G(d,p) level for the clusters up to 6 ionic couples and for [N\textsubscript{0003}][NO\textsubscript{3}] and [N\textsubscript{0004}][NO\textsubscript{3}], ωB97X-D/6-31+G(d) level to the clusters with 4 and 6 ionic couples, respectively. Although these simulations were used as a tool for assessing ionic liquid bulk properties a few years ago, there are still some limitations. Their calculations of clusters of ionic liquids, instead of only an ion pair, is an improvement. However, there is still some concern about the harmonic vibrational frequencies, which means that some scaling factors are needed for better agreement between theory and practice. Also, to make these simulations in a reasonable time, the system may only contain a few hundred atoms. In this thesis, the electronic-structure calculations were performed within density functional theory as implemented in the CASTEP code, which allowed simulation of the vibrational modes in 3D at the corresponding frequencies in a structural viewer called Jmol [175]. Also, the shift of the N-H bands upon deuteriation helped us to differentiate between C-H and N-H bands.

According to Bodo et al. [177], a series of peaks for [N\textsubscript{0002}][NO\textsubscript{3}] between 3100 cm\textsuperscript{-1} and 3250 cm\textsuperscript{-1} frequencies are clearly visible in both experiment and theory. This bands are due to N-H stretching modes that are involved in weaker hydrogen bonds, compared to those that produce the band at 2900 cm\textsuperscript{-1}. They claimed that in the real ionic liquid, as well as the theoretical calculations there is, probably, a mixture of different hydrogen bonds strength. As a consequence, the signals due to the N-H stretching modes are spread over a large range of frequencies from 3300 cm\textsuperscript{-1} and 2900 cm\textsuperscript{-1}. The coexistence of hydrogen bonding with different strength is not unlikely, and has already been found previously in a study of solid methylammonium nitrate by the same authors [165], as well as in this work for [N\textsubscript{0002}][NO\textsubscript{3}]. In [165], two different hydrogen bonds exist in the solid crystal of [N\textsubscript{0001}][NO\textsubscript{3}]. For [N\textsubscript{0003}][NO\textsubscript{3}] and [N\textsubscript{0004}][NO\textsubscript{3}], the theoretical assignment was similar to that for [N\textsubscript{0002}][NO\textsubscript{3}], with small differences due to the different environment of the alkyl chain surrounded the hydrogen bond network [165]. The experimental Raman spectra for [N\textsubscript{0003}][NO\textsubscript{3}] and [N\textsubscript{0004}][NO\textsubscript{3}], showed analogous effects to
[N$_{0\ 0\ 2}$][NO$_3$], They all show the coexistence of strong and weak hydrogen bonds due to the broad and unstructured bands founded between 3100-3200 cm$^{-1}$.

Protonic alkylammonium nitrates, [N$_{0\ 0\ 0\ n}$][NO$_3$], with varying alkyl chain lengths up to $n = 18$, were also studied by infrared and Raman spectroscopies by Stana [106]. Above 1800 cm$^{-1}$, the vibrations of the two ions, the [NO$_3^-$] and [RNH$_3^+$] of [N$_{0\ 0\ 0\ n}$][NO$_3$], were affected in only minor ways by the increase in the length of the alkyl chain, whereas in the lower frequency region, 1800-600 cm$^{-1}$, obviously major differences were observed. This is expected, as the inductive effect will have little influence on the N-H stretching frequencies for chains longer than butyl. This was also observed by Bodo [165,177].

With increasing alkyl chain length of the cation, the bending of the N-O peak became less visible: this mode is best defined when the length of the alkyl chain, varies from $n = 1$ to $n = 4$ [106]. One interesting feature highlighted by Bodo et al. [112,165,177] for this series was found in the range 900-800 cm$^{-1}$. The Raman spectra for different phases of [N$_{0\ 0\ 0\ 3}$][NO$_3$] [179], along with the ab initio DFT calculations, indicate that the bands at 868 and 828 cm$^{-1}$ are signatures of the gauche and anti conformers, respectively, of the propyl chain, as there is a mixture of conformers in the liquid phase. The same effect was found in our study for [N$_{0\ 0\ 2}$][NO$_3$] (see Section 4.3.4), and indeed in literature studies of 1,3-dialkylimidazolium cations (see Section 4.1.6).

4.3.6 Analysis of triethylammonium nitrate, [N$_{0\ 2\ 2}$][NO$_3$]

Although there are a few vibrational studies of alkylammonium nitrates which investigate the influence of alkyl chain length [112,165,177], there are no literature results concerning the effect on the hydrogen bonds. A physicochemical study of diethylammonium, triethylammonium, and tetraethylammonium nitrates, and their binary mixtures, was discussed in Chapter 3, and published elsewhere [180]. As an extension of this study, the compounds and their mixtures were also studied by infrared and Raman spectroscopies.

The main vibrational bands for triethylammonium nitrate are labelled in Figure 4.30. A priori, analysing the spectra, fewer peaks than for [N$_{0\ 0\ 2}$][NO$_3$] and [N$_{0\ 0\ 2}$][NO$_3$] were observed. This arises for two reasons: firstly, the [N$_{0\ 2\ 2}$]$^+$ cation has a higher symmetry, and also has a different hydrogen bonding pattern. By IR spectroscopy, a broad band is observed in the range 3100-2700 cm$^{-1}$. As found for [N$_{0\ 0\ 2}$][NO$_3$], see Section 4.3.1 and Figure 4.16, the large contribution from the v(N-H) modes partially masks the weak v(C-H) bands. The N-H stretching was identified at ca. 2800 cm$^{-1}$. Upon deuteration, this band was shifted to lower
frequencies, giving rise to one band at 2098 cm\(^{-1}\) for \([\text{N}_2\text{D}_2\text{D}_2][\text{NO}_3]\), observed by IR and one broad band active in the Raman spectrum at 2075 cm\(^{-1}\). Around 2300 cm\(^{-1}\) there is a small peak due to adventitious carbon dioxide in the system (see Figure 4.31 and Table 4.12). The ratio between the assignments of \(\tilde{v}_{OH}/\tilde{v}_{OD}\) is 1.38, which is reasonable according to \([\text{N}_0\text{D}_2\text{D}_2][\text{NO}_3]\).

**Figure 4.30** Vibrational spectra of \([\text{N}_2\text{D}_2\text{D}_2][\text{NO}_3]\) (a) infrared (red) and (b) Raman (blue) spectroscopy.

**Figure 4.31** Vibrational infrared spectra (red) for (a) \([\text{N}_2\text{D}_2\text{D}_2][\text{NO}_3]\), and (b) \([\text{N}_2\text{D}_2\text{D}_2][\text{NO}_3]\) and Raman spectra (blue) for (c) \([\text{N}_2\text{D}_2\text{D}_2][\text{NO}_3]\) and (d) \([\text{N}_2\text{D}_2\text{D}_2][\text{NO}_3]\).
Table 4.12 Experimentally observed bands (IR and Raman) and $\tilde{v}_{OH}/\tilde{v}_{OD}$ for $[\text{N}_2\text{O}_2\text{O}_3]$ and $[\text{N}_2\text{O}_2\text{O}_3]$.

<table>
<thead>
<tr>
<th>Mode assignment</th>
<th>$[\text{N}_0\text{O}_2\text{O}_3][\text{NO}_3]$</th>
<th>$[\text{N}_2\text{O}_2\text{O}_3][\text{NO}_3]$</th>
<th>$\tilde{v}<em>{OH}/\tilde{v}</em>{OD}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raman</td>
<td>IR</td>
<td>Raman</td>
</tr>
<tr>
<td>$\nu(\text{CH}_3)$</td>
<td>2991, 2957, 2897</td>
<td>2983, 2948, 2887</td>
<td>2991, 2957, 2897</td>
</tr>
<tr>
<td>$\nu(\text{NH})$</td>
<td>2790</td>
<td>2818</td>
<td>-</td>
</tr>
<tr>
<td>$\nu(\text{ND})$</td>
<td>-</td>
<td>-</td>
<td>2075</td>
</tr>
<tr>
<td>Complex motion region</td>
<td>1463</td>
<td>1477-1306</td>
<td>1461</td>
</tr>
<tr>
<td>$\nu_2(\text{NO}_3)$</td>
<td>-</td>
<td>1306</td>
<td>-</td>
</tr>
<tr>
<td>$\rho(\text{CH}_3)$</td>
<td>-</td>
<td>1192, 1168</td>
<td>-</td>
</tr>
<tr>
<td>$\nu_3(\text{NO}_3)$</td>
<td>1083, 1045</td>
<td>1069, 1038</td>
<td>1081, 1045</td>
</tr>
<tr>
<td>$\nu(\text{C-N})$</td>
<td>-</td>
<td>-</td>
<td>853</td>
</tr>
<tr>
<td>$\delta_{\text{as}}(\text{NO}_3)$</td>
<td>-</td>
<td>829</td>
<td>-</td>
</tr>
<tr>
<td>$\delta(\text{NH})$, $\delta(\text{C-N})$, $\nu(\text{C-C})$</td>
<td>-</td>
<td>804</td>
<td>-</td>
</tr>
<tr>
<td>$\rho(\text{NH})$, $\rho(\text{CH}_3)$</td>
<td>755</td>
<td>750</td>
<td>757</td>
</tr>
<tr>
<td>$\rho_{\text{as}}(\text{NO}_3)$</td>
<td>717</td>
<td>715</td>
<td>719</td>
</tr>
</tbody>
</table>

By Raman spectrum of $[\text{N}_0\text{O}_2\text{O}_3][\text{NO}_3]$, the $\nu(\text{C-H})$ stretching is distributed over 2991, 2957, and 2897 cm$^{-1}$, and is unaltered upon deuteration. As $[\text{N}_0\text{O}_2\text{O}_3][\text{NO}_3]$, the $\nu(\text{C-H})$ stretching are found at higher frequencies than N-H symmetric stretch, despite of the monoalkylammonium nitrates studied before, $[\text{N}_0\text{O}_2\text{O}_3][\text{NO}_3]$, $[\text{N}_0\text{O}_3\text{O}_3][\text{NO}_3]$ and $[\text{N}_0\text{O}_4\text{O}_4][\text{NO}_3]$. There is no bands related to the N-H bend in the IR spectrum around 1600 cm$^{-1}$. The NO$_3$ symmetric out-of-plane stretch is found only in IR in a broad peak at 1306 cm$^{-1}$. The NO$_3$ symmetric stretch motion is split in two bands active by IR and Raman. The two IR bands at 829 cm$^{-1}$ and 715 cm$^{-1}$ are due to NO$_3$ deformation (out-of-plane) and bending (in-plane) of the NO$_3$, respectively.

4.3.7 Analysis of tetraethylammonium nitrate, $[\text{N}_2\text{O}_2\text{O}_3][\text{NO}_3]$

The main vibrational bands for tetraethylammonium nitrate are illustrated in Figure 4.32 and detailed in Table 4.13.
Figure 4.32 Vibrational spectra of $[\text{N}_2\text{H}_2\text{H}_2\text{H}_2][\text{NO}_3]$ (a) infrared (red) and (b) Raman (blue) spectroscopy.

Table 4.13 Experimentally observed bands (IR and Raman) for $[\text{N}_2\text{H}_2\text{H}_2\text{H}_2][\text{NO}_3]$.

<table>
<thead>
<tr>
<th>Mode assignment</th>
<th>$[\text{N}_2\text{H}_2\text{H}_2\text{H}_2][\text{NO}_3]$</th>
<th>Wavenumber / cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raman</td>
<td>IR</td>
</tr>
<tr>
<td>$\nu$(CH$_3$)</td>
<td>3005, 2959, 2909</td>
<td>3001, 2985, 2957</td>
</tr>
<tr>
<td>$\nu_{as}$(NO$_3$)</td>
<td>-</td>
<td>1326</td>
</tr>
<tr>
<td>p(CH$_3$)</td>
<td>1181, 1121</td>
<td>1189, 1173</td>
</tr>
<tr>
<td>$\nu_s$(NO$_3$)</td>
<td>1045</td>
<td>1051</td>
</tr>
<tr>
<td>$\delta$(C-N), $\nu$(C-C)</td>
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<td>999</td>
</tr>
<tr>
<td>$\nu_s$(C-N)</td>
<td>907</td>
<td>894</td>
</tr>
<tr>
<td>$\omega_{oop}$(NO$_3$)</td>
<td>-</td>
<td>831</td>
</tr>
<tr>
<td>p(CH$_3$)</td>
<td>797</td>
<td>790</td>
</tr>
<tr>
<td>$\rho$(NO$_3$)</td>
<td>677</td>
<td>677</td>
</tr>
</tbody>
</table>

One can observe that there are weak signals due to $\nu$(C-H) bands, and that the broad bands due to $\nu$(N-H) modes for the protonic ionic liquids are not visible in this
case. In the Raman spectrum of \([\text{N}_2\text{N}_2\text{N}_2][\text{NO}_3]\), the \(\nu(\text{C-H})\) stretching, is well defined, and distributed over 3005, 2959, and 2909 cm\(^{-1}\). As the symmetry of the cation, \(T_d\), is higher than that of the protonic cations, there are fewer bands present. In addition, there is no hydrogen bonding present to lower the symmetry of the nitrate anion, which should have pure \(D_{3h}\) symmetry. As a consequence, the \([\text{NO}_3^-]\) asymmetric stretch is sharper than in the previous cases. The \([\text{NO}_3^-]\) symmetric stretch motion is found at 1045 cm\(^{-1}\). The two bands at 831 cm\(^{-1}\) and 677 cm\(^{-1}\) are due to \(\text{NO}_3^-\) deformation (out-of-plane) and bending (in-plane) of the \(\text{NO}_3^-\), respectively.

4.3.8 Comparison of \([\text{N}_0\text{N}_0\text{N}_0\text{N}_2][\text{NO}_3]\), \([\text{N}_0\text{N}_0\text{N}_2\text{N}_2][\text{NO}_3]\), \([\text{N}_0\text{N}_2\text{N}_2\text{N}_2][\text{NO}_3]\), and \([\text{N}_2\text{N}_2\text{N}_2\text{N}_2][\text{NO}_3]\)

The comparison of the main vibrational frequencies for \([\text{N}_0\text{N}_0\text{N}_0\text{N}_2][\text{NO}_3]\), \([\text{N}_0\text{N}_0\text{N}_2\text{N}_2][\text{NO}_3]\), \([\text{N}_0\text{N}_2\text{N}_2\text{N}_2][\text{NO}_3]\), and \([\text{N}_2\text{N}_2\text{N}_2\text{N}_2][\text{NO}_3]\) are shown in Table 4.14. By increasing the number of alkyl chains, the vibrational frequencies for \(\nu(\text{N-H})\) are shifted to lower frequencies, which means that stronger hydrogen bonding are formed by adding alkyl chains. Same trend is seen for \(\delta(\text{N-H})\) and \(\omega(\text{N-H})\) for \([\text{N}_0\text{N}_0\text{N}_0\text{N}_2][\text{NO}_3]\) and \([\text{N}_0\text{N}_0\text{N}_2\text{N}_2][\text{NO}_3]\).

By decreasing the number of acid protons in the cation, the asymmetric stretch \((\nu_{\text{as}})\) and the out-of-plane deformation \((\omega_{\text{oop}})\) modes of nitrate ion are shifted up to higher frequencies. The bending in-plane mode \((\rho_{\text{ip}})\) is shifted to lower frequencies. Although the symmetric stretch \((\nu_s)\) for \([\text{N}_0\text{N}_0\text{N}_2\text{N}_2][\text{NO}_3]\), and \([\text{N}_2\text{N}_2\text{N}_2\text{N}_2][\text{NO}_3]\) showed two components, the strongest vibrational band remained practically at the same wavenumber for all the alkylammonium nitrates (ca. 1040 cm\(^{-1}\)).

**Table 4.14** Comparison between (IR and Raman) frequencies modes for \([\text{N}_0\text{N}_0\text{N}_0\text{N}_2][\text{NO}_3]\), \([\text{N}_0\text{N}_0\text{N}_2\text{N}_2][\text{NO}_3]\), \([\text{N}_0\text{N}_2\text{N}_2\text{N}_2][\text{NO}_3]\), and \([\text{N}_2\text{N}_2\text{N}_2\text{N}_2][\text{NO}_3]\).
4.4 Results and discussion for monoalkylammonium mixtures

The same mixtures that were studied by physicochemical properties have been also studied by IR and Raman spectroscopies.

4.4.1 Infrared studies

4.4.1.1 Protonated and deuteriated equimolar mixture of [N\textsubscript{0}002][NO\textsubscript{3}] and [N\textsubscript{0}003][NO\textsubscript{3}]

The NH\textsubscript{3} stretching and bending vibrational bands for pure [N\textsubscript{0}002][NO\textsubscript{3}] and [N\textsubscript{0}003][NO\textsubscript{3}], their equimolar binary mixture, ([N\textsubscript{0}002]0.5[N\textsubscript{0}003]0.5)[NO\textsubscript{3}], and their deuteriated analogues in the range from 3500-650 cm\textsuperscript{-1} are shown in Figure 4.33. The vibrational frequencies for nitrate anion for the same compounds are detailed in Table 4.15 and Table 4.16. As expected, the vibrational frequencies of the mixtures lie between the pure components from which they were made. However, as the N-H stretching frequencies for ethylammonium and propylammonium are very similar, it is not surprising that their mixtures show no unusual features. Similarly, the vibrational modes of the nitrate anion do not present significant variations for the six ionic liquids.

Figure 4.33 Infrared spectra of deuteriated (dotted line): (a) [N\textsubscript{0}D\textsubscript{3}][NO\textsubscript{3}] (brown), (b) ([N\textsubscript{0}D\textsubscript{3}]0.5[N\textsubscript{0}003]0.5)[NO\textsubscript{3}] (green), (c) [N\textsubscript{0}D\textsubscript{3}][NO\textsubscript{3}] (orange) and protonated (solid line): (d) [N\textsubscript{0}003][NO\textsubscript{3}] (brown), (e) ([N\textsubscript{0}002]0.5[N\textsubscript{0}003]0.5)[NO\textsubscript{3}] (green), (f) [N\textsubscript{0}002][NO\textsubscript{3}] (orange).
Table 4.15 Comparison between infrared frequencies modes for \([\text{N}_0\text{D}_0\text{D}_2][\text{NO}_3],[\text{N}_0\text{D}_0\text{D}_2]_0.5[\text{N}_0\text{D}_0\text{D}_3]_0.5[\text{NO}_3]\), and \([\text{N}_0\text{D}_0\text{D}_3][\text{NO}_3]\).

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<th>Mode assignment</th>
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<td>(\delta(\text{NH}_3))</td>
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<tr>
<td>(\omega(\text{NH}_3))</td>
<td>1515</td>
</tr>
<tr>
<td>(\nu_{as}(\text{NO}_3))</td>
<td>1296</td>
</tr>
<tr>
<td>(\nu_{s}(\text{NO}_3))</td>
<td>1041</td>
</tr>
<tr>
<td>(\omega_{dop}(\text{NO}_3))</td>
<td>825</td>
</tr>
<tr>
<td>(\rho(\text{NO}_3))</td>
<td>719</td>
</tr>
</tbody>
</table>

Table 4.16 Comparison between infrared frequencies modes for \([\text{N}_0\text{D}_0\text{D}_3][\text{NO}_3],[\text{N}_0\text{D}_0\text{D}_2]_0.5[\text{N}_0\text{D}_0\text{D}_3]_0.5[\text{NO}_3]\), and \([\text{N}_0\text{D}_0\text{D}_3][\text{NO}_3]\).

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<tr>
<td>(\omega(\text{ND}_3))</td>
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</tr>
<tr>
<td>(\nu_{as}(\text{NO}_3))</td>
<td>1296</td>
</tr>
<tr>
<td>(\nu_{s}(\text{NO}_3))</td>
<td>1041</td>
</tr>
<tr>
<td>(\omega_{dop}(\text{NO}_3))</td>
<td>825</td>
</tr>
<tr>
<td>(\rho(\text{NO}_3))</td>
<td>719</td>
</tr>
</tbody>
</table>

\(^{a}\) Calculated on the basis of the ratio 1.30 \(v_{\text{OH}}/v_{\text{OD}}\); frequency below observed range.

4.4.1.2 Protonated and deuterated equimolar mixture of \([\text{N}_0\text{D}_0\text{D}_3][\text{NO}_3]\) and \([\text{N}_0\text{D}_0\text{D}_2][\text{NO}_3]\)

The \(\text{NH}_3\) stretching and bending vibrational bands for pure \([\text{N}_0\text{D}_0\text{D}_2][\text{NO}_3]\) and \([\text{N}_0\text{D}_0\text{D}_3][\text{NO}_3]\), their equimolar binary mixture, \([\text{N}_0\text{D}_0\text{D}_2]_0.5[\text{N}_0\text{D}_0\text{D}_3]_0.5[\text{NO}_3]\), and their deuterated analogues in the range from 3500-650 cm\(^{-1}\) are shown in Figure 4.34. The vibrational frequencies for nitrate anion for the same compounds are detailed in Table 4.17-Table 4.18. As in Section 4.4.1.1, the vibrational frequencies of the mixtures lie between those of the terminal components. The vibrational modes of the nitrate anion again do not present significant variations for the six ionic liquids.

An interesting feature of the deuterated mixture, \([\text{N}_0\text{D}_0\text{D}_3]_0.5[\text{N}_0\text{D}_0\text{D}_4]_0.5[\text{NO}_3]\), which was not observed for \([\text{N}_0\text{D}_0\text{D}_2]_0.5[\text{N}_0\text{D}_0\text{D}_3]_0.5[\text{NO}_3]\), is that the bands due to \(\nu(\text{ND}_3)\), and \(\nu_{as}(\text{NO}_3)\) are better resolved, and with different relative intensities, than for the pure components. The reason for this is not obvious.
Figure 4.34 Infrared spectra of deuteriated (dotted line): (a) [ND₃][NO₃] (blue), (b) ([ND₃][NO₃])₀.₅[ND₄][NO₃] (red), (c) [ND₄][NO₃] (brown) and protonated (solid line): (d) [N₃][NO₃] (blue), (e) ([N₃][NO₃])₀.₅[N₄][NO₃] (red), (f) [N₄][NO₃] (brown).

Table 4.17 Comparison between infrared frequencies for [N₃][NO₃], ([N₃][NO₃])₀.₅[N₄][NO₃], and [N₄][NO₃].

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<th>Mode assignment</th>
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<td></td>
<td>[N₃][NO₃]</td>
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<tr>
<td>v(NH₃)</td>
<td>3254, 3170, 3077</td>
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<td>δ(NH₃)</td>
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<tr>
<td>ω(NH₃)</td>
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<td>νas(NO₃)</td>
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<td>νs(NO₃)</td>
<td>1038</td>
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<tr>
<td>θ_{oop}(NO₃)</td>
<td>825</td>
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<tr>
<td>ρ_{in}(NO₃)</td>
<td>718</td>
</tr>
</tbody>
</table>

Table 4.18 Comparison between infrared frequencies for [ND₃][NO₃], ([ND₃][NO₃])₀.₅[ND₄][NO₃], and [ND₄][NO₃].

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<tr>
<th>Mode assignment</th>
<th>Wavenumber / cm⁻¹</th>
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<td>[ND₃][NO₃]</td>
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<td>δ(ND₃)</td>
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<td>ω(ND₃)</td>
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</tr>
<tr>
<td>νas(NO₃)</td>
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<tr>
<td>νs(NO₃)</td>
<td>1040</td>
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<tr>
<td>θ_{oop}(NO₃)</td>
<td>826</td>
</tr>
<tr>
<td>ρ_{in}(NO₃)</td>
<td>715, 734</td>
</tr>
</tbody>
</table>

a Calculated on the basis of 1.30 ratio for v_{OH}$/v_{OD}$; frequency below observed range.
4.4.1.3 Protonated and deuteriated mixture of \([\text{N}_0\text{O}_0\text{O}_2][\text{NO}_3]\) and \([\text{N}_0\text{O}_0\text{O}_4][\text{NO}_3]\)

As the major differences between the studied monoalkylammonium ionic liquids would be found between \([\text{N}_0\text{O}_0\text{O}_2][\text{NO}_3]\) and \([\text{N}_0\text{O}_0\text{O}_4][\text{NO}_3]\), it was anticipated that studying their mixtures would be the most interesting. Hence, here, 3:1, 1:1, and 1:3 mole ratio mixtures were studied.

4.4.1.3.1 Protonated Mixtures

As anticipated, the \(\nu(\text{NH}_3)\) symmetric \((\nu_s)\) and asymmetric \((\nu_a)\) for the mixtures shifted to lower frequencies moving from pure \([\text{N}_0\text{O}_0\text{O}_2][\text{NO}_3]\), as the concentration of \([\text{N}_0\text{O}_0\text{O}_4][\text{NO}_3]\) increased (see Figure 4.35 and Table 4.19). Also, the \(\nu(\text{CH}_2)\) and \(\nu(\text{CH}_3)\) stretching modes \(\nu(\text{CH}_n)\) are more visible at higher concentration of \([\text{N}_0\text{O}_0\text{O}_4][\text{NO}_3]\) as there are more \(\text{CH}_n\) groups per molecular unit. The two sets of \(\text{N-H}\) bending motions are both visible and can be found in the same frequency range as the pure compounds. \(\text{NO}_3\) asymmetric stretching for all the mixtures are at the same frequency as that of \([\text{N}_0\text{O}_0\text{O}_2][\text{NO}_3]\), at 1296 cm\(^{-1}\). Consequently, in the region 1000-700 cm\(^{-1}\), which contains the \(\text{C-N}\) and \(\text{C-C}\) stretching modes as well as the \(\text{CH}_n\) bending modes, the number of bands increases as the concentration of \([\text{N}_0\text{O}_0\text{O}_4][\text{NO}_3]\) increases.

![Figure 4.35 Infrared spectra for (a) \([\text{N}_0\text{O}_0\text{O}_2][\text{NO}_3]\) (blue), (b) \([\text{N}_0\text{O}_0\text{O}_2][\text{NO}_0\text{O}_4][\text{NO}_3]\) (light blue), (c) \([\text{N}_0\text{O}_0\text{O}_2][\text{NO}_0\text{O}_4][\text{NO}_3]\) (grey), (d) \([\text{N}_0\text{O}_0\text{O}_2][\text{NO}_0\text{O}_4][\text{NO}_3]\) (brown), and (e) \([\text{N}_0\text{O}_0\text{O}_2][\text{NO}_3]\) (orange).](image)
### Table 4.19 Comparison of infrared frequencies for \([\text{N}_0\text{N}_0\text{N}_0\text{2}]\)[NO₃], \([\text{N}_0\text{N}_0\text{N}_0\text{2}]\text{[N}_0\text{N}_0\text{O}_2]\text{[NO}_3\text{]}\), \([\text{N}_0\text{N}_0\text{N}_0\text{2}]\text{[N}_0\text{N}_0\text{N}_0\text{3}]\)[NO₃], \([\text{N}_0\text{N}_0\text{N}_0\text{2}]\text{[N}_0\text{N}_0\text{O}_2]\text{[NO}_3\text{]}\) and \([\text{N}_0\text{N}_0\text{N}_0\text{4}]\)[NO₃].

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<td>([\text{N}_0\text{N}_0\text{N}_0\text{4}])[NO₃]</td>
<td>([\text{N}_0\text{N}_0\text{N}_0\text{4}])[NO₃]</td>
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<td>(\nu(\text{NH}_3))</td>
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<td>3252, 3170, 3070</td>
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<td>(\delta(\text{NH}_3))</td>
<td>1619</td>
<td>1619</td>
</tr>
<tr>
<td>(\omega(\text{NH}_3))</td>
<td>1515</td>
<td>1515</td>
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<td>(\nu_d(\text{NO}_3))</td>
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<td>(\omega_{\text{op}}(\text{NO}_3))</td>
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<td>825</td>
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<tr>
<td>(\rho_{\text{in}}(\text{NO}_3))</td>
<td>719</td>
<td>719</td>
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</table>

4.4.1.3.2 Deuteriated Mixtures

The ND₃ stretching modes, \(\nu(\text{ND}_3)\), for the mixtures have been slightly shifted to lower frequencies by increasing the concentration of \([\text{N}_0\text{N}_0\text{N}_0\text{4}]\)[NO₃] (see Figure 4.36 and Table 4.20).

**Figure 4.36** Infrared spectra for (a) \([\text{N}_0\text{D}_0\text{D}_0\text{4}]\)[NO₃] (blue), (b) \([\text{N}_0\text{D}_0\text{D}_0\text{4}]\text{[N}_0\text{D}_0\text{D}_0\text{4}]\text{[NO}_3\text{]}\) (light blue), (c) \([\text{N}_0\text{D}_0\text{D}_0\text{2}]\text{[N}_0\text{D}_0\text{D}_0\text{4}]\text{[NO}_3\text{]}\) (grey), (d) \([\text{N}_0\text{D}_0\text{D}_0\text{2}]\text{[N}_0\text{D}_0\text{D}_0\text{4}]\text{[NO}_3\text{]}\) (brown), and (e) \([\text{N}_0\text{D}_0\text{D}_0\text{4}]\)[NO₃] (orange).
As for the protonated mixtures, demonstrates that, within the experiments error, there is a linear correlation between the N-D stretching frequencies and the mole fraction of \([\text{ND}_4\text{D}_4][\text{NO}_3]\) in the mixtures. The ND₃ bending mode, \(\delta(\text{ND}_3)\) is masked by the broadness of the NO₃ asymmetric stretching band, as seen for both pure \([\text{ND}_2\text{D}_2][\text{NO}_3]\) and \([\text{ND}_4\text{D}_4][\text{NO}_3]\). The wagging mode of the ND₃, \(\omega(\text{ND}_3)\), is also slightly shifted to lower frequencies.

**Table 4.20** Comparison of infrared frequencies for \([\text{ND}_2\text{D}_2][\text{NO}_3]\), \([\text{ND}_2\text{D}_2]_{0.75}[\text{ND}_4\text{D}_4]_{0.25}[\text{NO}_3]\), \([\text{ND}_2\text{D}_2]_{0.5}[\text{ND}_4\text{D}_4]_{0.5}[\text{NO}_3]\), \([\text{ND}_2\text{D}_2]_{0.25}[\text{ND}_4\text{D}_4]_{0.75}[\text{NO}_3]\) and \([\text{ND}_4\text{D}_4][\text{NO}_3]\).

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<th>([\text{ND}_2\text{D}<em>2]</em>{0.5}[\text{ND}_4\text{D}<em>4]</em>{0.5}[\text{NO}_3])</th>
<th>([\text{ND}_2\text{D}<em>2]</em>{0.25}[\text{ND}_4\text{D}<em>4]</em>{0.75}[\text{NO}_3])</th>
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<td>(\rho_{in}(\text{NO}_3))</td>
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<td>718</td>
<td>718</td>
<td>718</td>
<td>719</td>
</tr>
</tbody>
</table>

\(^a\) Calculated on the basis of 1.30 ratio for \(v_{\text{OH}}/v_{\text{OD}}\); frequency below observed range.

### 4.4.1.4 The concept of equivalent mixtures

As seen in **Section 3.4.1**, in order to study possible deviations, equimolar mixtures have been compared with mixtures with equivalent numbers of carbon atoms \(n\), the total number of carbon atoms in the equivalent formula) in the cation (composite cations; see **Figure 4.37**).

\[
\begin{align*}
\text{[NO}_0\text{D}_3]\text{[NO}_3] \\
\text{([NO}_0\text{D}_3]_{0.5}[\text{NO}_0\text{D}_3]_{0.5}\text{[NO}_3]
\text{([NO}_0\text{D}_2]_{0.5}[\text{NO}_0\text{D}_3]_{0.5}\text{[NO}_3]
\text{([NO}_0\text{D}_2]_{0.25}[\text{NO}_0\text{D}_3]_{0.75}\text{[NO}_3]
\text{([NO}_0\text{D}_2]_{0.5}[\text{NO}_0\text{D}_3]_{0.5}\text{[NO}_3] \\
\text{([NO}_0\text{D}_2]_{0.25}[\text{NO}_0\text{D}_3]_{0.75}\text{[NO}_3]
\end{align*}
\]

\(n = 3\)

\(n = 2.5\)

\(n = 3.5\)

**Figure 4.37** Scheme for the equivalent mixtures studied.
Thus, for \{[N_0\ 0\ 0\ 2][N_0\ 0\ 0\ 3][\text{NO}_3]\} and \{[N_0\ 0\ 0\ 2][0.75[N_0\ 0\ 0\ 4][0.25][\text{NO}_3]\}, n = 2.5 (see Figure 4.38); for \{[N_0\ 0\ 0\ 3][\text{NO}_3]\} and \{[N_0\ 0\ 0\ 2][0.75[N_0\ 0\ 0\ 4][0.5][\text{NO}_3]\}, n = 3 (see Figure 4.39); for \{[N_0\ 0\ 0\ 3][0.5[N_0\ 0\ 0\ 4][0.5]][\text{NO}_3]\} and \{[N_0\ 0\ 0\ 2][0.25[N_0\ 0\ 0\ 4][0.75][\text{NO}_3]\}, n = 3.5 (see Figure 4.40).

As can be seen in Figures 4.38-4.40 the region 3500-2500 cm\(^{-1}\) is dominated by NH\(_3\) stretching modes, and is very similar in all the cases. Again, from 2500-1500 cm\(^{-1}\), the spectra do not change appreciably and, as anticipated, the major differences are found below 1100 cm\(^{-1}\), which is where the C-N and C-C stretching modes, as well as CH\(_n\) bending modes occur. Logically, the selected mixtures have different vibrational pattern specifically in this region, the most bands correspond to the highest values of \(n\).

![Figure 4.38](image_url) Comparison of infrared spectra for \{[N_0\ 0\ 0\ 2][0.5[N_0\ 0\ 0\ 3][\text{NO}_3]\} (green) and \{[N_0\ 0\ 0\ 2][0.75[N_0\ 0\ 0\ 4][0.25][\text{NO}_3]\} (brown); \(n = 2.5\).
Figure 4.39 Comparison of infrared spectrum for $\left[\text{N}_0 \text{O}_3\right]\text{[NO}_3\text{]}$ (brown) and $\left[\text{N}_0 \text{O}_4\right]\text{[NO}_3\text{]}$ (grey); $n = 3$.

Figure 4.40 Comparison of infrared spectrum for $\left[\text{N}_0 \text{O}_3\right]_{0.5}\left[\text{N}_0 \text{O}_4\right]_{0.5}\text{[NO}_3\text{]}$ (purple) and $\left[\text{N}_0 \text{O}_2\right]_{0.25}\left[\text{N}_0 \text{O}_4\right]_{0.75}\text{[NO}_3\text{]}$ (red); $n = 3.5$. 
4.4.2 Raman studies

Although the same features were observed for infrared and Raman spectroscopies for all the mixtures, this section will highlight the shift of the $\nu$(ND$_3$) bands with respect to $\nu$(NH$_3$). For the equimolar mixture of [N$_{0\ 0\ 0\ 2}$][NO$_3$] and [N$_{0\ 0\ 0\ 3}$][NO$_3$], $\nu_{OH}/\nu_{OD}$ is shifted by a factor of 1.39 (see Figure 4.41). For the equimolar mixture of [N$_{0\ 0\ 0\ 3}$][NO$_3$] and [N$_{0\ 0\ 0\ 4}$][NO$_3$], $\nu_{OH}/\nu_{OD}$ is also shifted by a factor of 1.39 (see Figure 4.42). The antisymmetric stretching of the nitrate anion produces a weak Raman band at around 1300 cm$^{-1}$. The strongest band, assigned to the NO$_3$ symmetric stretching is localised at around 1041 cm$^{-1}$ for all the ionic liquids. The in-plane bending of the nitrate anion for the mixtures does not show any splitting due to degeneracy loss and occurs around 719 cm$^{-1}$.

4.4.2.1 Protonated and deuteriated equimolar mixture of [N$_{0\ 0\ 0\ 2}$][NO$_3$] and [N$_{0\ 0\ 0\ 3}$][NO$_3$]

![Figure 4.41 Raman spectra of deuteriated (dotted line): (a) [N$_{0\ D\ D\ 3}$][NO$_3$] (brown), (b) ([N$_{D\ D\ D\ 2}$]$_{0.5}$[N$_{D\ D\ D\ 3}$]$_{0.5}$[NO$_3$] (green), (c) [N$_{D\ D\ D\ 3}$][NO$_3$] (orange) and protonated (solid line): (d) [N$_{0\ 0\ 0\ 3}$][NO$_3$] (brown), (e) ([N$_{0\ 0\ 0\ 2}$]$_{0.5}$[N$_{0\ 0\ 0\ 3}$]$_{0.5}$)[NO$_3$] (green), (f) [N$_{0\ 0\ 0\ 2}$][NO$_3$] (orange).](image-url)
4.4.2.2 Protonated and deuteriated equimolar mixture of $[\text{N}_0\text{D}_0\text{D}_0\text{3}][\text{NO}_3]$ and $[\text{N}_0\text{D}_0\text{D}_0\text{4}][\text{NO}_3]$

![Raman spectra of deuteriated (dotted line): (a) $[\text{N}_0\text{D}_0\text{D}_0\text{4}][\text{NO}_3]$ (blue), (b) $[[\text{N}_0\text{D}_0\text{D}_0\text{3}][\text{N}_0\text{D}_0\text{D}_0\text{4}][\text{NO}_3]$ (red), (c) $[\text{N}_0\text{D}_0\text{D}_0\text{3}][\text{NO}_3]$ (brown) and protonated (solid line): (d) $[\text{N}_0\text{D}_0\text{D}_0\text{4}][\text{NO}_3]$ (blue), (e) $[[\text{N}_0\text{D}_0\text{D}_0\text{3}][\text{N}_0\text{D}_0\text{D}_0\text{4}][\text{NO}_3]$ (red), (f) $[\text{N}_0\text{D}_0\text{D}_0\text{3}][\text{NO}_3]$ (brown).](image)

4.4.2.3 Protonated and deuteriated mixture of $[\text{N}_0\text{D}_0\text{D}_0\text{2}][\text{NO}_3]$ and $[\text{N}_0\text{D}_0\text{D}_0\text{4}][\text{NO}_3]$

As for infrared, (Section 4.4.1.3), the monoalkylammonium ionic liquids $[\text{N}_0\text{D}_0\text{D}_0\text{2}][\text{NO}_3]$ and $[\text{N}_0\text{D}_0\text{D}_0\text{4}][\text{NO}_3]$ were mixed together giving rise 3:1 and 1:1 mole ratio mixtures (see Figure 4.43). Their deuteriated analogues were also studied (see Figure 4.44).

4.4.2.3.1 PROTONATED MIXTURES

The Raman spectra of the mixtures were unsurprisingly similar to those of the pure materials, as seen in Figure 4.43. The $\nu(\text{CH}_2)$ and $\nu(\text{CH}_3)$ stretching modes, $\nu(\text{CH}_n)$, found around 2900 cm$^{-1}$ are better defined for $[\text{N}_0\text{D}_0\text{D}_0\text{4}][\text{NO}_3]$. The NO$_3$ symmetric stretching is localised at 1040 cm$^{-1}$ for all the ionic liquids. The in-plane bending modes of the nitrates are found at 720 cm$^{-1}$. 


4.4.2.3.2 Deuterated Mixtures

**Figure 4.43** Raman spectra for (a) $[N_{0002}][NO_3]$ (blue), (b) $\{[N_{0002}0.5][N_{0004}0.5][NO_3]\}$ (grey), (c) $\{[N_{0002}0.75][N_{0004}0.25][NO_3]\}$ (brown), and (d) $[N_{0004}][NO_3]$ (orange).

**Figure 4.44** Raman spectra for (a) $[N_{0002}][NO_3]$ (blue), (b) $\{[N_{0002}0.5][N_{0004}0.5][NO_3]\}$ (grey), (c) $\{[N_{0002}0.75][N_{0004}0.25][NO_3]\}$ (brown), and (d) $[N_{0004}][NO_3]$ (orange).
Again, the similarity of the spectra for the deuteriated mixtures of $[\text{ND}_{3}]\text{NO}_3$ and $[\text{ND}_{4}]\text{NO}_3$ is as expected (see Figure 4.44). It seems that the structural properties of these liquids are very similar.

### 4.4.2.4 Analysis of pure ionic liquids and their equivalent mixtures

![Figure 4.45 Comparison of Raman spectrum for $([\text{NO}_3]_0.5[\text{NO}_3]_0.5)[\text{NO}_3]$ (green) and $([\text{NO}_3]_0.75[\text{NO}_3]_0.25)[\text{NO}_3]$ (purple); $n = 2.5$.](image)

![Figure 4.46 Comparison of Raman spectrum for $[\text{NO}_3]$ (brown) and $([\text{NO}_3]_0.5[\text{NO}_3]_0.5)[\text{NO}_3]$ (pink); $n = 3$.](image)
As can be seen in Figure 4.45 and Figure 4.46, the region 3500-2500 cm\(^{-1}\) is dominated by CH\(_n\), stretching modes, and is very similar in all the cases. As has been seen by infrared (Section 4.4.1.4), from 2500-1100 cm\(^{-1}\), the spectra do not change appreciably and, as before, the major differences are found below 1100 cm\(^{-1}\), which is where the C-N and C-C stretching modes, as well as CH\(_n\) bending modes, occur. Logically, the selected mixtures have different vibrational patterns specifically in this region, the number of bands increasing with \(n\).

### 4.5 Results and discussion for binary mixtures of \([\text{N}_0\text{D}_0\text{D}_2][\text{NO}_3]\)

with di-, tri-, or tetra-ethylammonium nitrates

Unlike in the previous sections, the number of hydrogen bonds donors on the cation in these mixtures is different.

#### 4.5.1 Infrared studies

##### 4.5.1.1 Binary mixtures of \([\text{N}_0\text{D}_0\text{D}_2][\text{NO}_3]\) and \([\text{N}_0\text{D}_0\text{D}_2][\text{NO}_3]\)

The comparisons of the N-H frequencies for the binary mixtures of \([\text{N}_0\text{D}_0\text{D}_2][\text{NO}_3]\) and \([\text{N}_0\text{D}_0\text{D}_2][\text{NO}_3]\), and their deuteriated analogues, are shown in Figure 4.47 and Figure 4.48. A detailed assignment of the main vibrational bands can be found in Table 4.21 and Table 4.22. One should note that N-H frequency modes for \([\text{N}_0\text{D}_0\text{D}_2][\text{NO}_3]\) appear at lower frequencies than the CH\(_n\) vibrations, unlike for \([\text{N}_0\text{D}_0\text{D}_2][\text{NO}_3]\) (see Sections 4.3.1 and 4.3.2). As the solubility limits for this mixture do not allow to go further than \{\([\text{N}_0\text{D}_0\text{D}_2]\)\(0.3\)[\([\text{N}_0\text{D}_0\text{D}_2]\)\(0.7\)][\([\text{NO}_3]\)], the study of equimolar mixture, which would give more information, was not possible. This is unfortunate, as this is an interesting system, and the data would have been very useful. The vibrational frequencies for the nitrate anion, \(\nu_{as}(\text{NO}_3)\), \(\nu_{s}(\text{NO}_3)\), \(\omega_{oop}(\text{NO}_3)\), and \(\rho_{a}(\text{NO}_3)\), for the mixtures remain at the same frequencies as those for \([\text{N}_0\text{D}_0\text{D}_2][\text{NO}_3]\), although again the full range of concentrations was not available.

The N-D frequencies for the deuteriated binary mixtures are slightly shifted to lower frequencies with increasing concentration of \([\text{N}_0\text{D}_0\text{D}_2][\text{NO}_3]\). Again, the vibrational frequencies for nitrate anion, for the mixtures remain at the same frequencies than those for \([\text{N}_0\text{D}_0\text{D}_2][\text{NO}_3]\).
Figure 4.47 Infrared spectra of: (a) \([\text{N}_0 \text{D}_2] [\text{NO}_3] \), (b) \([(\text{N}_0 \text{D}_2].0.1, [\text{N}_0 \text{D}_2].0.9)] [\text{NO}_3] \), (c) \([(\text{N}_0 \text{D}_2].0.1, [\text{N}_0 \text{D}_2].0)] [\text{NO}_3] \), (d) \([(\text{N}_0 \text{D}_2].2, [\text{N}_0 \text{D}_2].0.8)] [\text{NO}_3] \), (e) \([(\text{N}_0 \text{D}_2].2, [\text{N}_0 \text{D}_2].0.7)] [\text{NO}_3] \), and (f) \([\text{N}_0 \text{D}_2].2)] [\text{NO}_3] \).

Table 4.21 Comparison between infrared frequencies modes for \([\text{N}_0 \text{D}_2] [\text{NO}_3] \), \([(\text{N}_0 \text{D}_2].0.1, [\text{N}_0 \text{D}_2].0.9)] [\text{NO}_3] \), \([(\text{N}_0 \text{D}_2].2, [\text{N}_0 \text{D}_2].0.7)] [\text{NO}_3] \), and \([\text{N}_0 \text{D}_2].2)] [\text{NO}_3] \).

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<td>(\rho_{\text{in}}(\text{NO}_3))</td>
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Table 4.22 Comparison between infrared frequencies modes for \([\text{N}_0 \text{D}_2] [\text{NO}_3] \), \([(\text{N}_0 \text{D}_2].0.1, [\text{N}_0 \text{D}_2].0.9)] [\text{NO}_3] \), \([(\text{N}_0 \text{D}_2].2, [\text{N}_0 \text{D}_2].0.7)] [\text{NO}_3] \), and \([\text{N}_0 \text{D}_2].2)] [\text{NO}_3] \).

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<td>(\omega_{\text{oop}}(\text{NO}_3))</td>
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</tr>
<tr>
<td>(\rho_{\text{in}}(\text{NO}_3))</td>
<td>719</td>
</tr>
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</table>

* Calculated on the basis of 1.30 ratio for \(\nu_{\text{OH}}/\nu_{\text{OD}}\); frequency below observed range.
Figure 4.48 Infrared spectra of: (a) [N\textsubscript{D}D\textsubscript{2}][NO\textsubscript{3}], (b) ([N\textsubscript{D}D\textsubscript{2}]\textsubscript{0.1}[N\textsubscript{D}D\textsubscript{2}]\textsubscript{0.9})[NO\textsubscript{3}], (c) ([N\textsubscript{D}D\textsubscript{2}]\textsubscript{0.2}[N\textsubscript{D}D\textsubscript{2}]\textsubscript{0.8})[NO\textsubscript{3}], (d) ([N\textsubscript{D}D\textsubscript{2}]\textsubscript{0.3}[N\textsubscript{D}D\textsubscript{2}]\textsubscript{0.7})[NO\textsubscript{3}], and (e) [N\textsubscript{D}D\textsubscript{2}][NO\textsubscript{3}].

### 4.5.1.2 Binary mixtures of [N\textsubscript{0}0\textsubscript{2}][NO\textsubscript{3}] and [N\textsubscript{0}22\textsubscript{2}][NO\textsubscript{3}]

As seen in Section 4.5.1.1 for the dialkylammonium mixtures, the solubility limits for this mixture do not allow to go further than ([N\textsubscript{0}22\textsubscript{2}]\textsubscript{0.5}[N\textsubscript{0}0\textsubscript{2}]\textsubscript{0.5})[NO\textsubscript{3}]. The comparisons of the N-H frequencies for the binary mixtures for [N\textsubscript{0}0\textsubscript{2}][NO\textsubscript{3}], and [N\textsubscript{0}22\textsubscript{2}][NO\textsubscript{3}] and their deuteriated analogues, are shown in Figure 4.49 and Figure 4.50. The assignment of the main vibrational bands can be found in Table 4.23 and Table 4.24.

Again, the N-H vibrational modes of the mixtures are quite similar to those of [N\textsubscript{0}0\textsubscript{2}][NO\textsubscript{3}] with small deviations to lower frequencies. N-D modes for the mixtures give broader signals than for [N\textsubscript{D}D\textsubscript{2}][NO\textsubscript{3}]. The vibrational mode for the NO\textsubscript{3} asymmetric stretch remains at same frequencies for all the mixtures, as expected.

The NO\textsubscript{3} asymmetric stretch for the deuteriated mixtures varies from 1296 cm\textsuperscript{-1} to 1310 cm\textsuperscript{-1}, getting closer to the vibrational frequency of NO\textsubscript{3} asymmetric stretching for [N\textsubscript{0}22\textsubscript{2}][NO\textsubscript{3}], placed at 1311 cm\textsuperscript{-1}. The \(\nu_6\)(NO\textsubscript{3}), \(\omega_{oo0}(\text{NO}_3)\), and \(\rho_{\alpha}(\text{NO}_3)\) for the protonated and deuteriated mixtures remain at the same frequencies as those for [N\textsubscript{0}0\textsubscript{2}][NO\textsubscript{3}], and [N\textsubscript{0}22\textsubscript{2}][NO\textsubscript{3}]. The splitting of the band, \(\nu_5\)(NO\textsubscript{3}), for [N\textsubscript{0}22\textsubscript{2}][NO\textsubscript{3}] is not observed in any of the mixtures.
Figure 4.49 Infrared spectra of: (a) [N0 0 0][NO3], (b) [N0 2 2 2][N0 0 0 0][NO3], (c) [N0 2 2 2][N0 0 0 0][NO3], (d) [N0 2 2 2][N0 0 0 0][NO3], and (e) [N0 2 2 2][NO3].

Figure 4.50 Infrared spectra of: (a) [ND 0 0 0][NO3], (b) [N0 2 2 2][N0 0 0 0][NO3], (c) [N0 2 2 2][N0 0 0 0][NO3], (d) [N0 2 2 2][N0 0 0 0][NO3], and (e) [N0 2 2 2][NO3].
The comparison of the N-H frequencies for the binary mixtures for [N\textsubscript{0002}][NO\textsubscript{3}] and [N\textsubscript{2222}][NO\textsubscript{3}] and their deuteriated analogues, are shown in Figure 4.51 and Figure 4.52. A detailed assignment of the main vibrational bands can be found in Table 4.25 and Table 4.26.
Figure 4.51 Infrared spectra of: (a) [N\textsubscript{0 0 0 2}][NO\textsubscript{3}], (b) ([N\textsubscript{2 2 2 2}:0.1[N\textsubscript{0 0 0 2}:0.9]][NO\textsubscript{3}], (c) ([N\textsubscript{2 2 2 2}:0.3[N\textsubscript{0 0 0 2}:0.8]][NO\textsubscript{3}], (d) ([N\textsubscript{2 2 2 2}:0.3[N\textsubscript{0 0 0 2}:0.7]][NO\textsubscript{3}], and (e) [N\textsubscript{2 2 2 2}][NO\textsubscript{3}].

Figure 4.52 Infrared spectra of: (a) [N\textsubscript{D D 2}][NO\textsubscript{3}], (b) ([N\textsubscript{2 2 2 2}:0.1[ND\textsubscript{0 D 2}:0.9]][NO\textsubscript{3}], (c) ([N\textsubscript{2 2 2 2}:0.3[ND\textsubscript{0 D 2}:0.8]][NO\textsubscript{3}], and (d) ([N\textsubscript{2 2 2 2}:0.3[ND\textsubscript{0 D 2}:0.7]][NO\textsubscript{3}].
As anticipated, the N-H vibrational modes of the mixtures are very similar to those of \([\text{N}_0\,\text{D}_0\,\text{O}_2]\,[\text{NO}_3]\), although there is a broader range of frequencies than found for the pure material. An analogous effect was found for the deuteriated analogues. The bending modes, \(\delta(\text{NH}_3)\) and \(\omega(\text{NH}_3)\), are shifted to higher frequencies, indicating that the binary mixtures present weaker hydrogen bonding interactions than \([\text{N}_0\,\text{D}_0\,\text{O}_2]\,[\text{NO}_3]\). This is understood in terms of the \([\text{N}_2\,\text{D}_2\,\text{O}_2]\) cation, which is not capable of forming hydrogen bonds, sterically obstructing the average approach of \([\text{N}_0\,\text{D}_0\,\text{O}_2]\) to the nitrate anion. This is most noticeable, of course, when comparing the nitrate frequencies in the pure compounds; there is a shift to higher frequency of 30 cm\(^{-1}\) for the NO\(_3\) asymmetrical stretching mode.

| Mode assignment | \([\text{N}_0\,\text{D}_0\,\text{O}_2]\)\(^+\) | \([\text{N}_2\,\text{D}_2\,\text{O}_2]\,\text{D}_1\,[\text{N}_0\,\text{D}_0\,\text{O}_2]\,\text{O}_3\)\(^+\) | \([\text{N}_2\,\text{D}_2\,\text{O}_2]\,\text{D}_3\,[\text{N}_0\,\text{D}_0\,\text{O}_2]\,\text{O}_7\)\(^+\) | \([\text{N}_2\,\text{D}_2\,\text{O}_2]\)\(^+\) |
|-----------------|----------------|----------------|----------------|
| \(\nu(\text{NH}_3)\) | 3255, 3166, 3070 | 3263, 3162, 3065 | 3268, 3159, 3066 | - |
| \(\delta(\text{NH}_3)\) | 1619 | 1626 | 1630 | - |
| \(\omega(\text{NH}_3)\) | 1515 | 1520 | 1524 | - |
| \(\nu_D(\text{NO}_3)\) | 1296 | 1295 | 1294 | 1326 |
| \(\nu_e(\text{NO}_3)\) | 1041 | 1040 | 1038 | 1051 |
| \(\omega_{oo}(\text{NO}_3)\) | 825 | 826 | 827 | 831 |
| \(\rho_{ee}(\text{NO}_3)\) | 719 | 717 | 716 | 677 |

Table 4.25 Comparison between infrared frequencies modes for \([\text{N}_0\,\text{D}_0\,\text{O}_2]\,[\text{NO}_3]\), \([\text{N}_2\,\text{D}_2\,\text{O}_2]\,\text{D}_1\,[\text{N}_0\,\text{D}_0\,\text{O}_2]\,\text{O}_3\), \([\text{N}_2\,\text{D}_2\,\text{O}_2]\,\text{D}_3\,[\text{N}_0\,\text{D}_0\,\text{O}_2]\,\text{O}_7\), and \([\text{N}_2\,\text{D}_2\,\text{O}_2]\)\(^+\)\([\text{NO}_3]\)\(^-\).  

| Mode assignment | \([\text{N}_0\,\text{D}_0\,\text{D}_2]\)\(^+\) | \([\text{N}_2\,\text{D}_2\,\text{D}_2]\,\text{D}_1\,[\text{N}_0\,\text{D}_0\,\text{D}_2]\,\text{O}_3\) | \([\text{N}_2\,\text{D}_2\,\text{D}_2]\,\text{D}_3\,[\text{N}_0\,\text{D}_0\,\text{D}_2]\,\text{O}_7\) |
|-----------------|----------------|----------------|
| \(\nu(\text{ND}_3)\) | 2369, 2280, 2201 | 2372, 2276, 2174 | 2379, 2269, 2178 |
| \(\delta(\text{ND}_3)\) | 1245 \(^a\) | 1250 | 1253 |
| \(\omega(\text{ND}_3)\) | 1157 | 1160 | 1171 |
| \(\nu_D(\text{NO}_3)\) | 1296 | 1300 | 1313 |
| \(\nu_e(\text{NO}_3)\) | 1041 | 1038 | 1038 |
| \(\omega_{oo}(\text{NO}_3)\) | 825 | 826 | 827 |
| \(\rho_{ee}(\text{NO}_3)\) | 719 | 716 | 715 |

\(^a\) Calculated on the basis of 1.30 ratio for \(\nu_{OD}/\nu_{OD}^-\); frequency below observed range.
4.5.2 Raman studies

Raman studies for the mixtures of ethylammonium nitrate with diethylammonium nitrate, triethylammonium nitrate and tetraethylammonium nitrate, and their deuteriated analogues are shown in Figures 4.53-4.57. As has been seen for the mixtures of monoalkylammonium nitrates, Raman spectroscopic does not provide new insight into N-H vibrational modes. The only feature that can be spotted is the N-D bands upon deuteriation, which have been shifted to lower frequencies.

4.5.2.1 Binary mixtures of $[\text{N}_0\text{O}_2][\text{NO}_3]$ and $[\text{N}_0\text{O}_2][\text{NO}_3]$

![Raman spectra](image)

**Figure 4.53** Raman spectra of: (a) $[\text{N}_0\text{O}_2][\text{NO}_3]$, (b) $([\text{N}_0\text{O}_2]_0.1[\text{N}_0\text{O}_2]_0.9)[\text{NO}_3]$, (c) $([\text{N}_0\text{O}_2]_0.2[\text{N}_0\text{O}_2]_0.8)[\text{NO}_3]$, (d) $([\text{N}_0\text{O}_2]_0.3[\text{N}_0\text{O}_2]_0.7)[\text{NO}_3]$, and (e) $[\text{N}_0\text{O}_2][\text{NO}_3]$.
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4.5.2.2 Binary mixtures of \([\text{ND}_3]\text{[NO}_3\text{]}\) and \([\text{ND}_{2}\text{D}_2]\text{[NO}_3\text{]}\)

Figure 4.54 Raman spectra of: (a) \([\text{ND}_3]\text{[NO}_3\text{]}\), (b) \([\text{ND}_{2}\text{D}_2]\text{[NO}_3\text{]}\), (c) \([\text{ND}_{2}\text{D}_2]\text{[NO}_3\text{]}\), (d) \([\text{ND}_{2}\text{D}_2]\text{[NO}_3\text{]}\), and (e) \([\text{ND}_{2}\text{D}_2]\text{[NO}_3\text{]}\).

Figure 4.55 Raman spectra of: (a) \([\text{NO}_2\text{D}_2]\text{[NO}_3\text{]}\), (b) \([\text{NO}_2\text{D}_2]\text{[NO}_3\text{]}\), (c) \([\text{NO}_2\text{D}_2]\text{[NO}_3\text{]}\), (d) \([\text{NO}_2\text{D}_2]\text{[NO}_3\text{]}\), and (e) \([\text{NO}_2\text{D}_2]\text{[NO}_3\text{]}\).
**4.5.2.3 Binary mixtures of \([N_9002][NO_3]\) and \([N_{2222}][NO_3]\)**

Figure 4.56 Raman spectra of: (a) \([N_0D_0D_2][NO_3]\), (b) \([N_0D_0D_2][NO_3]\), (c) \([N_0D_0D_2][NO_3]\), (d) \([N_0D_0D_2][NO_3]\), and (e) \([N_2222][NO_3]\).

Figure 4.57 Raman spectra of: (a) \([N_0002][NO_3]\), (b) \([N_0002][NO_3]\), (c) \([N_0002][NO_3]\), (d) \([N_0002][NO_3]\), and (e) \([N_2222][NO_3]\).
4.6 Conclusions

4.6.1 Pure ionic liquids
Diethylammonium nitrate (two cationic hydrogen atoms available to form hydrogen bonds) has been analysed from DFT perspective, alongside vibrational spectroscopy to assess the nature of the hydrogen bonds. This ionic liquid has been compared with triethylammonium nitrate (one hydrogen-bond donor per cation) and tetraethylammonium nitrate (with no hydrogen-bond donor), as well as ethylammonium nitrate (three hydrogen-bond donors per cation). In parallel, ethylammonium nitrate has been compared to propylammonium nitrate and butylammonium nitrate. Selective binary mixtures of these six ionic liquids were also studied. Deuteriated analogues of all the samples studied were also spectroscopically analysed; only the acidic cationic protons were exchanged.

For diethylammonium nitrate, for which the most structural data were available, and its deuteriated derivate, the agreement between the calculated vibrational frequencies and the empirical infrared and Raman data is excellent. This established, unambiguously, the frequencies of the principal vibrational modes of the ionic liquid, which were reinforced by the observed deuterium shift (see Tables 4.2-4.4).

All the other salts examined were studied and analysed using the same methodology. Assignments for diethylammonium nitrate were used as a template for the analysis of the other ionic liquids, and all the assignments were self-consistent, and are detailed in Tables 4.9-4.11, and 4.14. Where the data were available in the literature, they were in general in good agreement with the assignments in this Chapter.

It is, perhaps, useful to compare the utility of the Raman and infrared studies. The Raman spectra showed distinctive signals for the vibrations of the highly symmetric $D_3h$ anion, and strong well-defined signals for the C-H stretching frequencies. In contrast, infrared spectroscopy clearly identified the N-H and N-D stretching and bending modes for pure ionic liquids and their binary mixtures, but the C-H modes were very weak. Thus, the two techniques were truly complementary, and the full analysis was only possible by using data from both.

In all the systems studied, the N-H stretching modes are found within the range 3200-2800 cm$^{-1}$ and the N-H bending modes at about 1600 cm$^{-1}$ and 1500 cm$^{-1}$, which agree well with the literature. However, there is an unfortunate manner in which the N-H stretching frequencies are discussed in the literature. There is a tendency to refer to these frequencies as the hydrogen-bond frequencies, which is a misrepresentation.
The frequencies are certainly lowered by formation of hydrogen bonds between the N-H cationic donor sites and the O-N anionic acceptor sites:

\[ \text{N-H} \cdots \text{O} \]

but the hydrogen bond itself is not synonymous with the N-H bond: the hydrogen bond is the \( \text{H} \cdots \text{O} \) bond. Of course, the valence bond two-electron one-centre representation of bonds is a vast oversimplification, and the N-H and \( \text{H} \cdots \text{O} \) bond will be mixed by delocalisation, nevertheless is still useful to discuss these as individual vibrational entities. Hence, the real hydrogen bond is the \( \text{H} \cdots \text{O} \) interaction, which is much weaker than the N-H covalent bond, and it is expected to lie below 500 cm\(^{-1}\). Apart from these already recognised N-H modes, other N-H contributions together with other interactions have been spotted from several bands in the range 1500-700 cm\(^{-1}\).

In contrast to the analysis of the diethylammonium nitrate, the monoalkylammonium nitrates exhibit N-H frequencies at higher values than those of the C-H modes, suggesting that they form weaker hydrogen bonds (see Table 4.27). In addition, increasing the length of the alkyl chain does not appear to have a significant effect on the N-H stretching frequencies.

Comparing \([\text{N}_0\text{0\text{0\text{2}}}][\text{NO}_3]\), \([\text{N}_0\text{0\text{2\text{2}}}][\text{NO}_3]\), and \([\text{N}_0\text{2\text{2\text{2}}}][\text{NO}_3]\) shows (see Table 4.27) that the hydrogen bond become stronger (\( \nu(\text{NH}_n) \) become smaller) the fewer the number of N-H sites on the cation. This can be explained by considering the partial charge of the N-H protons in the cation. At a zeroth order of approximation, in triethylammonium nitrate, the positive charge is localised on one proton. For diethylammonium nitrate, the positive charge is split between the two N-H protons, and in the case of monoethylammonium, the charge is split between the three N-H protons. Thus, at this oversimplified level, the observed experimental frequencies match the same pattern as the simple prediction. Of course, in reality, the charges are delocalised over the whole cation but, nevertheless, the same sequence appears to be observed.

Table 4.27 N-H frequencies modes of \([\text{N}_0\text{0\text{0\text{2}}}][\text{NO}_3]\), \([\text{N}_0\text{0\text{2\text{2}}}][\text{NO}_3]\), \([\text{N}_0\text{2\text{2\text{2}}}][\text{NO}_3]\), \([\text{N}_0\text{0\text{3}}}][\text{NO}_3]\), \([\text{N}_0\text{0\text{4}}][\text{NO}_3]\)

<table>
<thead>
<tr>
<th>Mode assignment</th>
<th>( \nu(\text{NH}_n) )</th>
<th>( \nu(\text{NH}_n) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{N}_0\text{0\text{0\text{2}}}][\text{NO}_3])</td>
<td>3255, 3166, 3070</td>
<td>2854, 2805</td>
</tr>
<tr>
<td>([\text{N}_0\text{0\text{2\text{2}}}][\text{NO}_3])</td>
<td>3070</td>
<td>2818</td>
</tr>
<tr>
<td>([\text{N}_0\text{2\text{2\text{2}}}][\text{NO}_3])</td>
<td>3254, 3170, 3077</td>
<td>3267, 3164 3055</td>
</tr>
</tbody>
</table>
Increasing the number of N-H hydrogen atoms also leads to bifurcated intermolecular bonds, which will tend to form weaker hydrogen bonds. Hence, the N-H vibrational bands will appear in the spectra at higher wavenumbers. This behaviour is reflected in all the spectra studied.

4.6.2 Binary mixtures

Mixtures of monoalkylammonium nitrates do not reveal much information as the N-H environment for the three ionic liquids is very similar. The study of binary mixtures composed of \([\text{N}_0 \text{0} \text{0} \text{0} \text{2}][\text{NO}_3]\) and an increasing concentration of a homologue ionic liquid with decreasing hydrogen bond donors in the cation do not present major frequency differences for mixtures of \(\{\text{N}_0 \text{0} \text{0} \text{2} \text{2}\}_x[\text{N}_0 \text{0} \text{0} \text{0} \text{2}(1-x)][\text{NO}_3]\) or \(\{\text{N}_0 \text{2} \text{2} \text{2}\}_x[\text{N}_0 \text{0} \text{0} \text{2}(1-x)][\text{NO}_3]\). Larger frequency shifts have been found for \(\{\text{N}_2 \text{2} \text{2} \text{2}\}_x[\text{N}_0 \text{0} \text{0} \text{2}(1-x)][\text{NO}_3]\) mixtures.
5 Inelastic Neutron Scattering
Hydrogen bonds in ionic liquids have been usually studied in the low frequency range by vibrational spectroscopy techniques, such as terahertz time-domain far-infrared spectroscopy [181], dielectric relaxation [182], Raman spectroscopy [183] and the optical Kerr effect [103a]. The low frequency range (<500 cm\(^{-1}\)) is the region in which one would anticipate observing anion-cation interionic interactions. The novelty of this thesis is the use of the inelastic neutron scattering technique (INS) [103c], which may provide unambiguous assignments of the actual hydrogen bonding. There are very few studies of ionic liquids by INS in the literature [184], and not a single one where hydrogen bonding has been probed.

5.1 Introduction
The neutron is a subatomic particle with zero charge, mass close to that of a proton, and a magnetic moment (spin \(\frac{1}{2}\)). Neutrons have wave-particle duality, and hence can be diffracted. The de Broglie wavelength of a thermal neutron (ca. 1-5 \(\text{Å}\)) is similar to interatomic and intermolecular distances, and its energy (30-700 cm\(^{-1}\)) is comparable to vibrational energies. This is why neutron scattering experiments display structural and dynamic information of the material under study.

Neutrons are scattered by nuclei, while photons (X-ray) and electrons are scattered by electrons. When a neutron passes through a sample and is scattered with no loss of energy, the scattering is called elastic. When the neutron exchanges energy with the sample, the scattering is inelastic. This is the type of scattering that provides spectroscopic information, and is described in this chapter. The interaction between neutrons and the nuclei of the atom (elastic or inelastic) is generated by two mechanisms of scattering: coherent and incoherent scattering. Coherent scattering occurs when the scattered waves from different nuclei interfere. Coherent elastic scattering is measured in diffraction experiments, as it is an indication of the relative positions of the atoms.

The scattering of neutrons where the target contains molecules or ions which act independently of each other (i.e., where there are no clear phase relationship between different elements of the scattered beam) is referred to as incoherent scattering. Therefore, the coherent/incoherent scattering is the manifestation of the wave-particle duality of neutrons. Some interactions will enhance the neutron wave behaviour while others will stress the neutron particle nature.

The scattering of the neutron by a single nucleus can be described in terms of its cross section, \(\sigma\), which is a measure of the effectiveness of the interaction. It is measured in barns (1 barn = \(10^{-28}\) m\(^2\)). In neutron experiments, the scattering function, \(S(Q, \omega)\), Equation (5.1), is measured in a scattering experiment, and consists of a
mixture of coherent and incoherent components (if an independence of the scattering from the neutron or the nuclear spin is assumed).

\[ S(Q, \omega) = S_{\text{coherent}}(Q, \omega) + S_{\text{incoherent}}(Q, \omega) \quad (5.1) \]

where, \( Q (\text{Å}^{-1}) \) is transfer of momentum, and \( \omega (\text{cm}^{-1}) \), the energy. Although the energy is strictly \( \tilde{\nu} \ h c \), the symbol used in the literature for the energy in neutron scattering is \( \omega \), with the spectroscopic wavenumber unit (cm\(^{-1}\)).

- **Energy:** Although the SI unit of energy is the Joule, in neutron scattering it is conventional to use meV or THz units. However, in molecular spectroscopy, the wavenumber, cm\(^{-1}\), is the common energy unit and this has been used in this thesis:
  \[ 1 \text{ meV} = 0.2418 \text{ THz} = 1.602 \times 10^{-22} \text{ J} = 8.066 \text{ cm}^{-1} \]

- **Momentum:** Although the SI of length is the metre and the units of momentum are g m s\(^{-1}\), it is conventional in neutron scattering to express length in Ångstrom units: 1 Å = 10\(^{-10}\) m. Thus, the units for neutron wavelength are Å, and for the neutron wave vector are Å\(^{-1}\).

Systems containing hydrogen atoms are well-known for their high incoherent cross section, and neutrons interact with protons behaving as particles. Inelastic neutron scattering is sensitive to the hydrogen motions due to their high incoherent cross sections, which is an order of magnitude larger than any other nucleus (see Table 5.1). The direct consequence of this fact is that in typical molecules, the dynamics of a single hydrogen atom will appear more intensely than the vibrations of other atoms. The difference between hydrogen and deuterium is of particular significance.

**Table 5.1** Neutron cross-sections for selected elements [103c].

<table>
<thead>
<tr>
<th>Element (Relative atomic mass)</th>
<th>( \sigma_{\text{incoh}} ) / barn</th>
<th>( \sigma_{\text{coh}} ) / barn</th>
<th>( \sigma_{\text{total}} ) / barn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen (1.0079)</td>
<td>80.3</td>
<td>1.8</td>
<td>82.1</td>
</tr>
<tr>
<td>Deuterium (2.0141)</td>
<td>2.0</td>
<td>5.6</td>
<td>7.6</td>
</tr>
<tr>
<td>Carbon (12.011)</td>
<td>0.001</td>
<td>5.6</td>
<td>5.007</td>
</tr>
<tr>
<td>Nitrogen (14.007)</td>
<td>0.5</td>
<td>11.0</td>
<td>11.5</td>
</tr>
<tr>
<td>Oxygen (15.999)</td>
<td>0.001</td>
<td>4.0</td>
<td>4.001</td>
</tr>
</tbody>
</table>
To summarise, the important role of the high incoherent cross section of hydrogen atoms is the main reason why this technique is an outstanding tool for the study of hydrogen bonds in alkylammonium nitrates.

5.1.1 Inelastic neutron scattering vs other spectroscopies techniques

As it was seen in Chapter 4, different selection rules allow the observation of different active modes by IR or Raman spectroscopies. However, some vibrations are silent in both spectroscopies. The higher the molecular symmetry, the fewer modes that are visible. An example of this is the study of $C_{60}, (I_h)$ where 70% of the vibrational motions are optically inactive [185]. Inelastic neutron scattering and Raman spectroscopy are conceptually similar. Both measure the change in the energy of the radiation from a sample, reflection of the excitation in the material under study. The most obvious difference is that for inelastic neutron scattering, the neutron interacts with the nuclei of the atoms in the sample, whereas for Raman spectroscopy, the photons interact with the electrons. INS can be used to probe a wide variety of different physical phenomena, such as hopping or diffusional motions of atoms, the rotational motion of molecules, molecular vibrations, magnetic and quantum excitations, recoil in quantum fluids, or electronic transitions.

Inelastic neutron scattering has several advantages compared to the most common vibrational spectroscopies: infrared and Raman spectroscopies.

- **INS spectra are accurately modelled**: INS intensities are related to the atomic displacements of the scattered atom, which can be easily calculated from *ab initio* computational methods. The manipulation of INS data is straightforward.
- **INS spectra are especially sensitive to hydrogen atoms**: IR and Raman spectroscopies are usually more sensitive to heavier atoms, because of the number of electrons.
- **INS does not have optical selection rules**: All vibrations are active, thus, measurable. The measured INS intensity is proportional to the concentration of the element in the sample.
- **Neutrons are penetrating, photons are not**: Neutrons penetrate deeply into the sample though the walls of the container, normally aluminium.
- **Low spectral range**: The lower energy range (below 400 cm$^{-1}$) is both accessible and exhibits strong bands, a region which is experimentally more difficult for IR and Raman spectroscopies.
Also, the spectral broadening in IR and Raman spectroscopy caused by extensive intermolecular hydrogen bonding is absent in INS because neutrons interact only with the nuclei [185]. In this work samples were measured at 4K for INS to suppress the natural motions of the atoms.

The disadvantages of inelastic neutron scattering are that neutron sources are very expensive, spectra may have too many peaks, and they show low resolution at high frequencies.

5.1.2 Energy and momentum transfer

Before proving deeply inelastic neutron scattering, a few concepts should be defined, such as the energy, $E$, and the momentum of a neutron, $k$. The expression for the de Broglie energy, $E$, is shown in Equation (5.2)

$$E = \hbar \omega = \tilde{v} \hbar c = \frac{m_n |v|^2}{2}$$  \hspace{1cm} (5.2)

where $\hbar$ is the Planck constant/2π, $\omega$ is the angular frequency, $\tilde{v}$ is the wavenumber, $c$ is the speed of light, $m_n$ is the neutron mass, and $v$ is the neutron velocity. As seen in Section 5.1.1, the energy is represented by $\omega$. The momentum of a neutron, $k$, is given by Equation (5.4).

$$\lambda = \frac{h}{k} = \frac{h}{m_n v}$$  \hspace{1cm} (5.3)

$$\frac{2\pi}{\lambda} = \frac{m_n v}{\hbar} = k$$  \hspace{1cm} (5.4)

In optical methods, such as Raman and infrared spectroscopies, the term momentum is commonly ignored, because the momentum of a photon is very small. Thus, a photon does not have significant momentum to exchange with the sample, and can only probe the zero region of momentum transfer. This has important implications.

A good example of the utility of INS is the study of polyethylene, which exhibits a large number of crystalline microstructures within an amorphous matrix. Vibrational spectroscopies have played an important role in the study and characterisation of these materials, since they are sensitive to both regions: crystalline and amorphous. The infrared, Raman and INS spectra of polyethylene below 2000 cm$^{-1}$ are shown in Figure 5.1 [185].
As the crystal is centrosymmetric, there is no coincidence between peaks in infrared and Raman. However, all the peaks that are not active in the infrared or Raman are clearly identified by INS, since it provides information about all the values of the momentum, \( k \), not just at zero as for infrared and Raman. Also, below 600 cm\(^{-1}\) the C-C-C in-plane and out-of-plane bending, as well as the 12 lattice modes are only visible by INS.

Thus, to obtain a complete description of the vibrational modes, all three forms of vibrational spectroscopy are needed. The same philosophy has been adopted for the studies reported in this thesis.

### 5.1.3 The theory behind of inelastic neutron scattering

The theory of neutron scattering can be studied at different levels of sophistication. As our concern is the information obtained from the experimental data, rather than the physics behind the mathematical equations, it has not been a focus to illustrate the derivations of such equations. Instead, a summary of the INS technique has been given, and further details can be found in Appendix C1. An inelastic collision between the neutron and the nuclei of the atom in the sample involves a significant transfer of momentum, \( Q (\text{Å}^{-1}) \) and energy to the irradiated sample. **Equation (5.5)** gives the intensity of each molecular vibrational transition, \( I_i \) [186]:

\[
I_i \propto Q^2 U_i^2 \exp\left(-Q^2 U_{\text{total}}^2\right) \sigma
\]
where, for each vibrational mode, \( i \), \( U_i \) stands for the amplitude of vibration of the atoms in this mode, and \( U_{\text{total}} \) is the total amplitude of the vibrations of all the atoms. The exponential term, \( \exp(-Q^2U_{\text{total}}^2) \), is the well-known Debye-Waller factor [187]. To reduce the impact of the Debye-Waller factor on the observed intensities, the samples are cooled to ca. 4 K in all the INS experiments described here.

5.1.4 The effect of deuteriation

As has been seen in Chapter 4, the N-D stretching frequencies in the deuteriated samples are shifted downfield by \( \sqrt{2} \) compared to the N-H stretching frequencies of the protonated samples. As seen in Table 5.1, the total cross section of a proton is about ten times larger than that of a deuteron. Hence, vibrations involving deuterium appear ten times weaker than those involving a proton, sometimes apparently disappearing from the spectrum [188]. This is well illustrated in a spectroscopic study of benzoic acid, \( \text{C}_6\text{H}_5\text{COOH} \), were Plazanet et al. [188] selectively deuteriated both the ring and the carboxylic acid protons, to form \( \text{C}_6\text{D}_5\text{COOH} \), and then fully deuteriated, \( \text{C}_6\text{D}_5\text{COOD} \). Here, the bands due to O-D and D···O were very low intensity, and not always observed.

Inelastic neutron scattering (INS) has four key advantages compared to the classical spectroscopies:

- The assignment of modes that involve hydrogen bonds are relatively straightforward.
- The identification of hydrogen atoms which are not involved in hydrogen bonds is also straightforward.
- The spectra are well defined, which leads to easier interpretation of the rest of the bands.
- The effect of deuteriation is invaluable for definitive assignments.

In order to obtain the best spectra and assignments possible, the simplest systems were selected for study, both to reduce the number of skeletal vibrations (which might overlap with bands of interest) and to increase the relative intensities of the H···O and D···O vibrations.

5.1.5 Use of inelastic neutron scattering to study hydrogen bonds

Inelastic neutron scattering has been very often used to study hydrogen bonds in inorganic salts [189], biological systems [190], and also in disordered systems where diffraction techniques failed to localise the hydrogen atoms [191]. The use of INS to investigate the phase changes in proton-conducting materials such as sulfates [192], arsenates [193] and selenates [191b] has been one important application of this technique. Although the attention has been mainly focussed on structural elucidation
of alkanes, cycloalkanes, alkynes, or organic molecules [194], the hydrogen bonds of water in different environments, such as mineral lattices or biological systems, have also been studied successfully by neutrons [195].

The dynamics of the hydrogen atom in the hydrogen bond, X-H···Y, are controlled by the potential surface between the heavy atoms X and Y. Due to the high cross section of the hydrogen, and hence the strong bands, these dynamics are accessible by INS spectroscopy.

It is usual to consider the vibration of the hydrogen atom in hydrogen bonds by comparison with the vibrations that existed before the bonds are formed. For example, the internal deformation of an alcohol group, such as in-plane deformation ($\theta$) and libration ($\phi$) (see Figure 5.2), become in-plane deformation and out-of-plane deformation upon hydrogen bond formation.

![Figure 5.2 Internal deformations of an alcohol group, the in-plane deformation ($\theta$) and libration, ($\phi$) [185].](image)

For instance, in the reaction of an alcohol with aldehyde:

$$R\cdot O\cdot H + O=\overset{C}{\underset{R_1}{\overset{H}{\bigcdot}}} \rightarrow R\cdot O\cdot H\cdots O=\overset{C}{\underset{R_1}{\overset{H}{\bigcdot}}}$$

The diffusional motion of the two molecules is now described as $\nu$(H···O) with typical values of 200 cm$^{-1}$, which is the actual frequency of the hydrogen bonds. The rest of the vibrational bands have, of course, also changed. Thus, the $\nu$(O-H) stretch of R-O-H, which is usually observed at about 3200 cm$^{-1}$, is now observed around 2900 cm$^{-1}$ upon the formation of a weak hydrogen bond. This Chapter is focussed on identifying the H···O. As these hydrogen bonds are between anions and cations, they should be stronger than those observed, for example, between neutral alcohols and aldehydes. Thus, it is anticipated, that the hydrogen bonds in these alkylated ammonium nitrates will occur in the region between 500 and 200 cm$^{-1}$.

Most of the important biological and physical properties of water, which is essential for life, are related to the formation of hydrogen bonds. A molecule of water can be a proton acceptor and a proton donor not only to itself, also to other different molecules. Consequently, the effects of confinement of the molecular properties of water have attracted a lot of interest in the past few decades. Understanding the
behaviour of the hydrogen bond upon confinement is important for problems ranging from oil recovery and geochemical applications to biophysical interactions [185]. In weakly bonding environments, the water molecules are disordered and diffraction techniques are ineffective to determine the hydrogen bonds positions. INS can provide information in this case.

5.1.6 Hydrogen bond frequencies. Where?
To the best of our knowledge, here is presented the first spectroscopic observation of hydrogen bonding (H–O) in protonic ionic liquids by INS studies. There have been numerous studies of the cation-anion interactions in ionic liquids. These specific interactions have been mainly probed by methods, such as terahertz time-domain far-infrared spectroscopy [181], dielectric relaxation [182], Raman spectroscopy [183] and the optical Kerr effect [103a]. Since 2008, Ludwig and coworkers [91,93c,98-99,102,104-105,196] have studied a wide number of ionic liquids by far-infrared spectroscopy (see Table 5.2).

In their first study, four imidazolium ionic liquids were measured: [C2mim][SCN], [C2mim][N(CN)2], [C2mim][EtSO4], and [C2mim][NTf2]. The FTIR experimental results were supported by ab initio calculated frequencies of clusters of ionic liquids. According to these authors, the bands between 120 cm⁻¹ and 50 cm⁻¹ can be clearly assigned to the bending and stretching modes of the cation-anion interaction of the ‘C-H(2)···A’ hydrogen bonds in these ionic liquids, see Figure 5.3 [91].

![Figure 5.3 FIR spectra of [C2mim][SCN], [C2mim][N(CN)2], [C2mim][EtSO4], and [C2mim][NTf2] ionic liquids, at 273K [91].](image-url)
Table 5.2 FIR assignment for the stretching and bending hydrogen bonds modes of ionic liquids.

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Stretching mode</th>
<th>Bending mode</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wavenumber / cm(^{-1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{C}_2\text{mim}][\text{SCN}])</td>
<td>117.6</td>
<td>50</td>
<td>[91]</td>
</tr>
<tr>
<td>([\text{C}_2\text{mim}][\text{N(CN)}_2])</td>
<td>113.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{C}_2\text{mim}][\text{EtSO}_4])</td>
<td>106.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{C}_2\text{mim}][\text{NTf}_2])</td>
<td>83.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{C}<em>2\text{C}</em>{1}\text{mim}][\text{NTf}_2])</td>
<td>&lt; 150</td>
<td></td>
<td>[93c]</td>
</tr>
<tr>
<td>([\text{C}<em>2\text{C}</em>{1}\text{mim}][\text{BF}_4])</td>
<td>83.5</td>
<td>78</td>
<td>[99]</td>
</tr>
<tr>
<td>([\text{C}_2\text{mim}][\text{NO}_3])</td>
<td>93.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{N}_{0003}][\text{NO}_3])</td>
<td>118.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{N}_{0003}][\text{NO}_3])</td>
<td>159.4/224.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{C}<em>4\text{C}</em>{1}\text{mim}][\text{BF}_4])</td>
<td>Asymmetric: 199-224</td>
<td>60-78</td>
<td>[102]</td>
</tr>
<tr>
<td>([\text{C}<em>4\text{C}</em>{1}\text{mim}][\text{BF}_4])</td>
<td>Symmetric modes: 134-159</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{C}_4\text{mim}][\text{NO}_3])</td>
<td>83.5</td>
<td>62.3</td>
<td>[105a]</td>
</tr>
<tr>
<td>([\text{C}_4\text{mim}][\text{NO}_3])</td>
<td>93.5</td>
<td>85.7</td>
<td></td>
</tr>
<tr>
<td>([\text{HC}_1\text{mim}][\text{NO}_3])</td>
<td>118.9</td>
<td>96.7</td>
<td></td>
</tr>
<tr>
<td>([\text{Hmim}][\text{NO}_3])</td>
<td>159.4/224.9</td>
<td>100.7</td>
<td></td>
</tr>
<tr>
<td>([\text{C}_2\text{mim}][\text{SCN}])</td>
<td>Around 120</td>
<td>50-60</td>
<td>[196a]</td>
</tr>
<tr>
<td>([\text{C}_2\text{mim}][\text{N(CN)}_2])</td>
<td>111</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{C}_2\text{mim}][\text{EtSO}_4])</td>
<td>116</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{C}_2\text{mim}][\text{NTf}_2])</td>
<td>119</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{C}_2\text{mim}][\text{NTf}_2])</td>
<td>136</td>
<td></td>
<td></td>
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<tr>
<td>([\text{N}_{0111}][\text{NO}_3])</td>
<td>170</td>
<td></td>
<td>[104]</td>
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<tr>
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<td>No hydrogen atom available to form hydrogen bonds</td>
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<tr>
<td>([\text{C}_2\text{mim}][\text{N(CN)}_2])</td>
<td>111</td>
<td></td>
<td>[196b]</td>
</tr>
<tr>
<td>([\text{C}_2\text{mim}][\text{SCN}])</td>
<td>116</td>
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<td>([\text{C}_2\text{mim}][\text{NO}_3])</td>
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<tr>
<td>([\text{C}_2\text{mim}][\text{CH}_3\text{COO}])</td>
<td>136</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) The same ionic liquids that in ref [91] were studied by THz and Raman spectroscopy.

As the cation \([\text{C}_2\text{mim}]^+\) is the same in all the cases, the shifted bands are possibly due to weak intermolecular interactions of various anions or/and cation/anion interactions. The maxima of these bands is shifted towards lower wavenumbers following the order:
This trend suggests a decrease of the interaction energy between cations and anions from [SCN$^-$] to [NTf$_2^-$]. The breadth of the bands made precise assignments difficult, but the \textit{ab initio} calculated frequencies for the clusters ($[\text{C}_2\text{mim}][\text{N(CN)}_2]_m$, for $m = 2, 4, 6, 8$ are shown in Figure 5.4. Although sharp bands were calculated, there are a multitude of predicted vibrational bands in this region, making interpretation difficult [91].

These authors also made a linear correlation between intermolecular vibration frequencies and the specific interaction energies obtained by \textit{ab initio} calculations for these four ionic liquids. The calculated binding energies ($E_{\text{bin}}$) per ion of the hexamers, ($[\text{C}_2\text{mim}][\text{SCN}]_6$, ($[\text{C}_2\text{mim}][\text{N(CN)}_2]_6$, ($[\text{C}_2\text{mim}][\text{EtSO}_4]_6$, and ($[\text{C}_2\text{mim}][\text{NTf}_2]_6$) are -217.34 kJ mol$^{-1}$, -205.40 kJ mol$^{-1}$, -194.05 kJ mol$^{-1}$, and -168.29 kJ mol$^{-1}$, respectively. The binding energies trend agreed with the shift in frequencies, probing the cohesive energy between cation and anion for these imidazolium ionic liquids. However, they did not identify the cation-anion interaction bands definitively. Also, according to the equation of the simple harmonic oscillator, \textbf{Equation (4.1)}, a vibrational frequency is obtained from the square root of the ratio between the force constant, $k$ and the reduced mass, $\mu$. As seen in \textbf{Section 4.1.3}, the frequency shifts in the spectrum can be caused by changing force constants or to different reduced masses or both. Both effects can cancel each other and no frequency shift would be observed. Thus, it is difficult to classify the strength of the interactions in these ionic...
liquids. The shift in frequencies can be explained not only by the increasing force constant due to stronger interactions, also due to a decrease of the reduced masses.

To resolve the situation, the same authors returned to the issue a few years later, this time using ionic liquids with the same cation, \([\text{C}_2\text{mim}]^+\) but with anions with similar molecular masses \([196b], [\text{NO}_3^-], [\text{CH}_3\text{COO}]^-, [\text{SCN}]^-, \text{and } [\text{N(CN)}_2]^-\). Again they use far-infrared spectroscopy between 300 and 20 cm\(^{-1}\). As before, the frequencies at around 120 cm\(^{-1}\) were assigned to stretching modes ‘C-H(2)···A’ of the cation-anion interaction. \([\text{C}_2\text{mim}]^+\text{[CH}_3\text{COO}]^-\) behaved slightly differently, exhibiting the stretching mode at 136 cm\(^{-1}\). As the reduced mass is similar, such a strong frequency increase is possibly due to the increase of the interaction strength between cation-anion. DFT (B3LYP/6-31+G*) calculations supported their findings. The energy per ion pair was 35 kJ mol\(^{-1}\) higher for this imidazolium ethanoate ionic liquid than for the rest. It is well known that among other ionic liquids, imidazolium ethanoate ionic liquids are capable of disrupt cellulose-cellulose interaction due to the basicity of the anion.

The group retained a strong interest in the question: “Is the origin of the frequency shift the charging forces or and/or the reduced masses?” In 2010, they studied \([105a]\) imidazolium ionic liquids with similar reduced masses and the same anion, again by far-infrared spectroscopy. The hydrogen atom in the cation is substituted by a group that is not able to form hydrogen bonding, which caused the disappearance of the frequency bands (see Figure 5.5 and Figure 5.6).

**Figure 5.5** Structures of the cations for the ionic liquids: 1,2,3-trimethylimidazolium bis{(trifluoromethyl)sulfonyl}amide, \([\text{C}_1\text{C}_1^2\text{mim}]^{[\text{NTf}_2]}\) (1); 1,3-dimethylimidazolium bis{(trifluoromethyl)sulfonyl}amide, \([\text{C}_1\text{mim}]^{[\text{NTf}_2]}\) (2); 1,2-dimethylimidazolium bis{(trifluoromethyl)sulfonyl}amide, \([\text{HC}_1^2\text{mim}]^{[\text{NTf}_2]}\) (3); and 1-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide, \([\text{Hmim}]^{[\text{NTf}_2]}\) (4). Possible hydrogen bonds are represented by dotted lines-red for strong, black for weak \([105a]\).
Figure 5.6 FIR spectra of the ionic liquids: [C\textsubscript{1}C\textsubscript{1}(\textsuperscript{2})mim][NTf\textsubscript{2}] (1); [C\textsubscript{1}mim][NTf\textsubscript{2}] (2); [HC\textsubscript{1}(\textsuperscript{2})mim][NTf\textsubscript{2}] (3); and [Hmim][NTf\textsubscript{2}] (4), at 323 K for 2-4 and 383 K for 1. The arrow indicates the maximum intensity peak of the anion-cation interaction [105a].

As can be seen in Figure 5.6, the potential formation of hydrogen bond increases in the sequence:

[C\textsubscript{1}C\textsubscript{1}(\textsuperscript{2})mim][NTf\textsubscript{2}] < [C\textsubscript{1}mim][NTf\textsubscript{2}] < [HC\textsubscript{1}(\textsuperscript{2})mim][NTf\textsubscript{2}] < [Hmim][NTf\textsubscript{2}]

According to these authors, the stretching vibrational bands of hydrogen bonds ‘C-H(2)···A’ and/or ‘N-H···A’, are observed at 62.3 cm\(^{-1}\) for [C\textsubscript{1}C\textsubscript{1}(\textsuperscript{2})mim][NTf\textsubscript{2}], 85.7 cm\(^{-1}\) for [C\textsubscript{1}mim][NTf\textsubscript{2}], 96.7 cm\(^{-1}\) for [HC\textsubscript{1}(\textsuperscript{2})mim][NTf\textsubscript{2}], and 100.7 cm\(^{-1}\) for [Hmim][NTf\textsubscript{2}], respectively. This bands shift to higher frequencies in the order:

[C\textsubscript{1}C\textsubscript{1}(\textsuperscript{2})mim][NTf\textsubscript{2}] < [C\textsubscript{1}mim][NTf\textsubscript{2}] < [HC\textsubscript{1}(\textsuperscript{2})mim][NTf\textsubscript{2}] < [Hmim][NTf\textsubscript{2}]

which indicated an increase of the interaction energies. As the ionic liquids [C\textsubscript{1}mim][NTf\textsubscript{2}], and [HC\textsubscript{1}(\textsuperscript{2})mim][NTf\textsubscript{2}] have the same reduced masses, Ludwig and coworkers [105a] corrected the reduced masses for [C\textsubscript{1}C\textsubscript{1}(\textsuperscript{2})mim][NTf\textsubscript{2}], and [Hmim][NTf\textsubscript{2}] in function of [C\textsubscript{1}mim][NTf\textsubscript{2}], and [HC\textsubscript{1}(\textsuperscript{2})mim][NTf\textsubscript{2}] and extrapolated new vibrational frequencies. The reduced masses are then, 79.529 amu, 72.079 amu, 72.079 amu and 64.054 amu, for [C\textsubscript{1}C\textsubscript{1}(\textsuperscript{2})mim][NTf\textsubscript{2}], [C\textsubscript{1}mim][NTf\textsubscript{2}], [HC\textsubscript{1}(\textsuperscript{2})mim][NTf\textsubscript{2}] and [Hmim][NTf\textsubscript{2}], respectively. It can be seen that the change in the reduced masses varied only slightly the vibrational frequencies (3-6 cm\(^{-1}\)). Thus, the frequency shifts were believed to be a consequence of mainly the force constants, with the different reduced masses having a negligible effect. The findings were supported by \textit{ab initio} DFT calculations. The frequencies between 250 cm\(^{-1}\) and 200 cm\(^{-1}\) were assigned to
intramolecular vibrations of the anion, [NTf$_2$]. They concluded that the cation-anion interaction was enhanced by the formation of a hydrogen bond in the C(2)-H position. The importance of hydrogen bonding from the C(2)-H position and its effect on the properties of ionic liquids was first reported by Abdul-Sada et al. [87,88b], and has been recognised for thirty years.

As seen in Section 1.4, one of the strong points of disagreement is the C(2)-H···anion interaction in imidazolium ionic liquids. The alkyl substitution in a series of 1,3-dialkylimidazolium cations, unusually increase the melting point and viscosity. Several studies have tried to explain this phenomenon: since “entropy theory” by Hunt [95] to “configurational variations” by Noack et al. [197] going though “defect hypothesis” by Fumino [91] and Wulf [105a]. The studies have been focused in different areas of research such as, structural and thermodynamic properties, thermal calorimetry, physicochemical methods, MD simulations and spectroscopic analysis, such as, NMR and FIR.

The FIR spectroscopic study by Fumino et al. [98] of four imidazolium ionic liquids showed possible local and directional interactions via C(2)-H, C(5)-H, or N-H. The common anion is again [NTf$_2$]; the cation (1,2,3,4,5-pentamethylimidazolium, 1,2,3,4-tetramethylimidazolium, 1,3,4,5-tetramethylimidazolium and 1,2,4,5-tetramethylimidazolium) structures are shown in Figure 5.7.

![Figure 5.7](image-url)
Figure 5.8 FIR spectra cation for the ionic liquids 1,2,3,4,5-pentamethylimidazolium (black), 1,2,3,4-tetramethylimidazolium (red), 1,3,4,5-tetramethylimidazolium (blue) and 1,2,4,5-tetramethylimidazolium (purple) [98].

The FIR spectra (150-10 cm$^{-1}$) of these imidazolium salts (see Figure 5.7) are shown in Figure 5.8. Despite the broadness of the bands, and that different contributions from different kind of interactions cannot be separated, the authors arrived at their conclusions without even deconvoluting their peaks. Bands at 60 cm$^{-1}$ are said to describe the cation-anion interaction, according to DFT B3LYP/6-31+G* calculations. As 1,2,3,4,5-pentamethylimidazolium bistriflamide does not have hydrogen available to form hydrogen bonds, the arrow in Figure 5.8 indicates a band due mainly to Coulomb forces and dispersion forces. For the ionic liquid 1,2,3,4-tetramethylimidazolium bistriflamide, however, which does contain a hydrogen bond donor, C(5)-H, the highlighted interaction occurs at almost the same frequency. In the cases of 1,3,4,5-tetramethylimidazolium and 1,2,4,5-tetramethylimidazolium bistriflamide, their spectra showed maxima at 77 and 102 cm$^{-1}$, respectively, which again the authors stated are due to hydrogen bonds [98].

An FIR spectroscopic study of [C$_2$mim][NTf$_2$] and [C$_2$C$_1$mim][NTf$_2$] from the same group is shown in Figure 5.9 [93c].
By switching off the C(2)-H interaction, the only possible formation of hydrogen bonds may occur via C(4)-H and C(5)-H positions of the imidazolium cation. As shown in Figure 5.9, in general, the intensities of \([\text{[C}_2\text{C}_1\text{mim}]\text{[NTf}_2\text{]}\) are lower and the bands are shifted to a lower frequencies, from 83.5 cm\(^{-1}\) to 79 cm\(^{-1}\) [93c]. These bands have been reported by the authors as stretching and bending modes which, in the case of \([\text{[C}_2\text{C}_1\text{mim}]\text{[NTf}_2\text{]}\), are supressed due to increased Coulombic interactions, which the authors stated are stronger than hydrogen bonds. Ab initio calculations were performed at the B3LYP level, using the 6-31+G\(^*\) basis set.

The ability to form hydrogen bonds varies from aprotic to protonic liquids, and hence a different spectroscopic pattern is expected in the low frequency range. The comparison between three aprotic ionic liquids: \([\text{[C}_4\text{mim}]\text{[BF}_4\text{]}\), \([\text{[C}_4\text{mim}]\text{[BF}_4\text{]}\), \([\text{[C}_4\text{mim}]\text{[NO}_3\text{]}\) and one protonic: \([\text{[N}_0\text{O}_3\text{][NO}_3\text{]}\) was carried out by FIR spectroscopy [99]. The spectra for the frequency range 600-30 cm\(^{-1}\) are shown in Figure 5.10. The band assigned to hydrogen bonding interactions (marked by arrows in Figure 5.10) is shifted to higher frequencies for the protonated ionic liquid as compared to the three aprotic ionic liquids. Based on DFT B3LYP calculations provided, they reported that within the envelope of this large band, the frequencies of 224 cm\(^{-1}\) and 159 cm\(^{-1}\) are due to asymmetric and symmetric stretching modes of the hydrogen bonds, respectively. Bands at 78 cm\(^{-1}\) were assigned to the hydrogen bond bending modes.
5.2 Instrumentation and experimental methods

5.2.1 ISIS: a source of neutrons

Neutrons are produced in several research infrastructures around Europe (see Figure 5.11) [198].

There are two kinds of neutron sources: reactor and spallation. Nuclear reactors use the fission process to produce neutrons. Most of the current reactor sources were built in the 60s and 70s, for testing materials destined for nuclear facilities. The biggest
Inelastic Neutron Scattering

reactor source in Europe is the ILL in France. Neutrons can also be produced by the pulsed spallation sources, in which high-energy protons strike a solid target. The main advantages of reactors is that they can produce 6 times more neutron per unit heat than by pulsed spallation. This work was carried out at the ISIS Rutherford Appleton laboratories, which is the world leading spallation neutron source (160kW) [199].

ISIS is made up of many components, but the main part is the accelerator: that consists of an injector and a synchrotron. At the very beginning of the injector, there is an ion source which produces negative hydrogen. These hydrogen anions are separated and accelerated using a linear accelerator. At this point, the ions are travelling at 37% of the speed of light. Acceleration continues in the synchrotron, which is a ring with powerful magnets that focus the beam into a circle. When H⁻ ions enter the synchrotron, a thin aluminium foil detaches the electrons, leaving only a beam of protons. Once enough protons have been collected into the synchrotron, they are accelerated to 84% of the speed of light. The proton bunches then travel on and collide with a tungsten target. Neutrons are produced in the target by spallation. These high energy protons hit the tungsten nuclei of the atoms and produce intense neutron pulses. The neutrons are slowed to useful velocities for condensed matter studies by an array of hydrogenous moderators placed around the target. They then sent to different instruments, where samples are studied (see Figure 5.12) [200].

![Figure 5.12 Scheme of the spallation source at ISIS](image-url)
5.2.2 TOSCA instrument

The instrument used to collect inelastic neutron scattering data was TOSCA (see Figure 5.13), which is a spectrometer specifically for the study of molecular vibrations in the solid state. The neutrons coming from the water moderator, hit the sample, and are scattered in all directions. Some of them will impact on a graphite crystal. According to Bragg’s law, only neutrons with the right wavelength will be scattered, and the rest will pass through the crystal to be absorbed by the shielding. Those neutrons, at multiples of the fundamental wavelength, are scattered by the beryllium filter and the remaining neutrons are then detected by the $^3$He filled detector tubes. Only neutrons with an energy of ca. 1.25 meV (10 cm$^{-1}$) are passed to the detectors.

The difference between the final and the initial energy is the energy transferred to the sample in a vibrational mode that is observed in the INS spectra. Since the final energy, $E_f$, the distance to the analyser system, $l$, and the length of the flight path from the moderator to the sample, $L$, are all known, the time of arrival at the detector is the only variable that defines the initial energy, $E_i$, and thus, the energy transfer at the sample, $E_{\text{trans}}$. This allows conversion of time-of-flight to energy. On TOSCA the design is such that there is only one value of Q for each energy, ($Q^2 \approx E_{\text{Trans}}/16$).

![Figure 5.13](image)

**Figure 5.13** Scheme of (a) the TOSCA instrument and (b) a section through one of the analysers [200].

5.2.3 Sample preparation

All the samples were prepared in aluminium cells due to their liquid nature. The can consists of two outer cases sealed with indium wire and a thickness of 1 mm to assure good resolution (see Figure 5.14). Due to the fact that the ionic liquids under study are highly hygroscopic, the empty cans (already assembled) were loaded into a dinitrogen glovebox. The two outer cases were secured with small screws.
Once the sample was loaded in the can with a syringe, and the injection points closed with two plastic screws, the cell was removed from the glovebox. It was then connected to the centre-stick and the stick inserted into the cryostat, as shown in Figure 5.15. The set-up ensures that the sample is aligned perpendicular to the beam, so that the maximum amount of the sample can surface is exposed to the beam.
5.2.4 INS data: Mantid software and a-CLIMAX

The samples were measured according to the procedure described in the computer script, monitored in a cabin next to the sample area. The script was set to accumulate to a minimum of 300 or 400 μA neutron counting, which meant that data were collected for a minimum of 2 h. TOSCA data analysis was performed by the software Mantid, which allowed visualisation, manipulation and analysis of the experimental data. The software a-CLIMAX [201] was used to generate the calculated INS of the model molecule, using the output of normal modes obtained by Density Functional Theory calculations of vibrational modes (CASTEP, see Sections 4.1.7 and 4.2.4). In other words, a-CLIMAX takes CASTEP outputs to generate a spectrum from a spectrometer. This fact make easier to relate theory and experiment.

5.2.5 INS spectra

INS spectrometers cover the molecular vibrational range of 16-4000 cm⁻¹, see Figure 5.16. Of particular interest here, the lower energy range (below 500 cm⁻¹) is accessible. An INS spectrum shows how the strength of the neutron scattering changes with the energy transfer and momentum transfer, S(Q,ω) [185].

![Inelastic neutron scattering spectrum](image)

**Figure 5.16** Comparison of INS spectroscopy with other optical spectroscopies [185].
The spectrum is typically in neutron energy loss, which occurs when the energy is transferred from the neutron to the atom. The information content of an INS spectrum is best considered in terms of frequency and intensity:

- The frequencies, as in IR and Raman spectroscopies, are function of the structure of the molecule and its intramolecular forces. For INS spectroscopy, these are obtained by the energy loss of the neutron.
- The intensities, which are function of the atomic displacement during the vibration, and the momentum lost by the neutron. The displacement depends on the structure of the molecule and its intramolecular forces. The momentum transferred is recorded by INS spectrometer.

5.3 Results and discussion for pure ionic liquids

5.3.1 Diethylammonium nitrate, \([\text{[N}_2\text{O}_2\text{Z}]\text{[NO}_3\text{]}\]

Diethylammonium nitrate has been use as an archetype for the vibrational analysis of the series of alkylammonium nitrates, as seen in Chapter 4. Theoretical calculations using CASTEP, carried out at the Rutherford Institute, by Dr Sanghamitra Mukhopadhyay software, have been used to support the assignment of the main vibrational modes, such as hydrogen bonds at frequencies below 500 cm\(^{-1}\).

5.3.1.1 Experimental analysis and comparison with IR and Raman

Although INS does not have selection rules, the effect of the Debye-Waller factor is an important feature to take into account, as it influences the observed spectral intensity. As seen in Section 5.1.2 and Equation 5.5, the intensity of a vibrational mode in INS is giving mainly by two terms:

- The pre-exponential: \(Q^2 U_i^2\)
- The Debye-Waller factor: \(\exp(-Q^2 U_{\text{total}}^2)\)

At low momentum values (frequency), the intensity increase is driven by the pre-exponential factor, but at high values of momentum, the intensity is supressed by the Debye-Waller factor (see Figure 5.17).
$Q^2U_i^2$ has significant temperature dependence through the atomic displacement, $U_i$. To increase the observed intensities, the samples are studied at cryogenic temperatures. An example of this fact can be seen in Figure 5.18. At lower frequencies, below 500 cm$^{-1}$, the intensity and sharpness of the bands in INS spectra are well defined, but this definition is lost at higher frequencies.

Figure 5.18 Vibrational spectroscopic analysis of [N$_6$O$_{2.2}$][NO$_3$] using: (a) INS (black), (b) infrared (red) and (c) Raman (blue) spectroscopies.
5.3.1.2 Theoretical calculations and comparison with its deuteriated analogue.

The beauty of the INS technique is the wealth of well-defined bands which are observed in the low frequency region, \(< 500 \text{ cm}^{-1}\). However, this added complexity, in a region which has not been well studied historically, means that assignments here will be rather difficult.

Besides hydrogen bonds, other interionic interactions (e.g. cation-anion) and lattice modes can be found. Theoretical calculations will be needed to support the analysis of the bands in this region. CASTEP uses the crystal structure (.cif file) of solid crystalline \([\text{N}_0\text{O}_2\text{2}]\text{[NO}_3\text{]}\) as input data in order to calculate properties, such as vibrational frequencies. The calculated and the empirical frequencies for \([\text{N}_0\text{O}_2\text{2}]\text{[NO}_3\text{]}\) and \([\text{N}_D\text{O}_2\text{2}]\text{[NO}_3\text{]}\) are compared in Figure 5.19.

The spectra contain an abundance of information. First-principles calculations performed within the framework of DFT reproduced the experimental crystal structures to within 3%. There is a visible agreement between the experimental spectrum and the calculated spectrum for \([\text{N}_0\text{O}_2\text{2}]\text{[NO}_3\text{]}\) (see Figure 5.19 (a) and (b)). A similar good agreement was observed for the deuteriated analogue \([\text{N}_D\text{O}_2\text{2}]\text{[NO}_3\text{]}\) (see Figure 5.19 (c) and (d)). In both cases, small differences between experimental and calculated spectra may be due to the CASTEP calculations having been performed on a single crystal cell with perfect periodicity. Although the nature of a solid (i.e. amorphous, polycrystalline or single crystal) can give rise to different
periodicity, the calculations corroborate that these differences are most likely to be due to hydrogen bonds.

For [N$_{0\,0\,2\,2}$][NO$_3$], the peak around 924 cm$^{-1}$ is due to a combination band of the rocking motions of the CH$_2$ and CH$_3$ groups with the N-H bending modes. The peak at 888 cm$^{-1}$ is due to symmetric C-C and C-N stretching motions in the alkyl chains. The NO$_3$ out of plane bending occurs at 858 cm$^{-1}$. The peak at 800 cm$^{-1}$ is composed of many complex motions, including N-H bending. The NO$_3$ deformation in-plane mode can be found at 717 cm$^{-1}$, in agreement with the IR and Raman spectra (see Section 4.3.1).

The INS spectra of [N$_{D\,D\,2\,2}$][NO$_3$] shows a small peak due to N-D bending at 672 cm$^{-1}$, which is not present in the spectrum of [N$_{0\,0\,2\,2}$][NO$_3$]. This band was predicted by the CASTEP calculation for the deuterated salt, but not for the protonated. In the IR study of [N$_{0\,0\,2\,2}$][NO$_3$] (see Section 4.3.1 and Figure 4.19), the contribution of NH$_n$ and CH$_n$ bending motions was seen at 790 cm$^{-1}$. This band was not visible in the deuteriated analogue. Calculated on the basis of a 1.30 ratio $\tilde{v}_{OH}/\tilde{v}_{OD}$, it was assumed that the band was shifted to about 607 cm$^{-1}$, below the observed IR range. CASTEP calculations confirmed that this band observed in the [N$_{0\,0\,2\,2}$][NO$_3$] spectrum at 800 cm$^{-1}$ is shifted to lower frequencies upon deuteration, and it is observed in the INS spectrum at 672 cm$^{-1}$.

A closer view of the INS experimental measurements for [N$_{0\,0\,2\,2}$][NO$_3$] is shown in Figure 5.20.
Figure 5.20 shows bands at 424 cm\(^{-1}\) and 314 cm\(^{-1}\) which are not present in the deuteriated analogue. This strongly suggested that they are due to vibrations of the N-H···O system.

The INS calculated spectra for \([\text{N}_0\text{O}_2\text{2}][\text{NO}_3]\) also shows these bands, and the view of the CASTEP files (see Appendix E) confirms the vibrations at the frequencies 423 and 417 cm\(^{-1}\) and 339 and 329 cm\(^{-1}\) are due to bending and stretching of the hydrogen bond, respectively.

For \([\text{N}_D\text{D}_2\text{2}][\text{NO}_3]\), these predicted bands are calculated to be shifted approximately 20 cm\(^{-1}\) to lower frequency, at 409-404 cm\(^{-1}\) and 319-303 cm\(^{-1}\), respectively. As seen in Section 5.1, the cross section of the deuterium atom is ten times smaller that of protium. This implies that the bands in the deuteriated salt would be ten times weaker that in protonated salt, and hence easily masked by other bands. Thus, in Figure 5.20, the symmetric of C-C stretching mode and the CNC bending mode at 412 cm\(^{-1}\) and the CH\(_n\) bending mode at 295 cm\(^{-1}\) may be masking the bending and stretching modes of the N-D···O bond, respectively.

An additional interesting difference is observed between the experimental spectra of \([\text{N}_0\text{O}_2\text{2}][\text{NO}_3]\) and \([\text{N}_D\text{D}_2\text{2}][\text{NO}_3]\). The wagging modes of CH\(_n\) and the twisting modes of CNC for the deuteriated compound are shifted to lower frequencies about 14 cm\(^{-1}\), respect the protonated.

Below 200 cm\(^{-1}\), experimental spectra for \([\text{N}_0\text{O}_2\text{2}][\text{NO}_3]\) and \([\text{N}_D\text{D}_2\text{2}][\text{NO}_3]\) are virtually indistinguishable, suggesting strongly, that there are no significant contributions to this spectral region associated with hydrogen bonding. This region is commonly associated with phonons and lattice modes, which are associated with the three dimensional structure of the lattice rather than with individual molecular interaction. Although this region could provide important information about cation-anion interactions, it is strongly populated. Beyond cation-anion interactions, other contributions such as weak intramolecular vibrational modes or unspecified librational motions or lattice modes lead to great difficulty in band assignments. For this reason, frequencies below 200 cm\(^{-1}\) will not be considered in this work.

Comparison of the experimental results and the theoretical predictions is presented in Table 5.3. In some cases, CASTEP vibrational modes are given as a range of frequencies, because the observed motions corresponding to these bands are very similar or visually undistinguished.
Table 5.3 Experimentally observed and calculated CASTEP INS bands for [N$_{0\,0\,2\,2}$][NO$_3$] and [N$_{0\,D\,2\,2}$][NO$_3$].

<table>
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<th>Mode assignment</th>
<th>[N$_{0,0,2,2}$][NO$_3$]</th>
<th>[N$_{0,D,2,2}$][NO$_3$]</th>
</tr>
</thead>
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<tr>
<td>Wavenumber / cm$^{-1}$</td>
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<td>CASTEP</td>
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<tr>
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<td>915</td>
</tr>
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<td>852</td>
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</tr>
<tr>
<td>$\rho$(NH$_n$), $\rho$(CH$_n$)</td>
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<td>790</td>
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<td>-</td>
</tr>
<tr>
<td>$\rho$(NO$_3$)</td>
<td>717</td>
<td>727, 726</td>
</tr>
<tr>
<td>$\rho$(N-H$\cdots$O)</td>
<td>424</td>
<td>423 - 417</td>
</tr>
<tr>
<td>$\rho$(N-D$\cdots$O)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\nu$(C-C)</td>
<td>414</td>
<td>409 - 408</td>
</tr>
<tr>
<td>$\rho$(CNC)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\nu$(N-H$\cdots$O)</td>
<td>314</td>
<td>339 - 329</td>
</tr>
<tr>
<td>$\nu$(N-D$\cdots$O)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\tau$(CH$_n$)</td>
<td>296</td>
<td>302 - 281</td>
</tr>
<tr>
<td>$\omega$(CH$_n$)</td>
<td>254</td>
<td>261 - 257</td>
</tr>
<tr>
<td>$\tau$(CNC)</td>
<td>215</td>
<td>217 - 209</td>
</tr>
</tbody>
</table>

5.3.2 Analysis of monoalkylammonium nitrates

INS spectra of [N$_{0\,0\,0\,2}$][NO$_3$], [N$_{0\,0\,0\,3}$][NO$_3$], [N$_{0\,0\,0\,4}$][NO$_3$] and their deuteriated analogues in the range between 500 and 25 cm$^{-1}$ are shown in Figure 5.21, Figure 5.23, and Figure 5.25, respectively. The assignments will be based on the assignment for [N$_{0\,0\,2\,2}$][NO$_3$], but of course, will be different in the specifics.
5.3.2.1 \([N_{0\,0\,2}]\text{[NO}_3\text{]}\) and \([N_{D\,D\,2}]\text{[NO}_3\text{]}\)

Overall, the spectra of \([N_{0\,0\,2}]\text{[NO}_3\text{]}\) and \([N_{D\,D\,2}]\text{[NO}_3\text{]}\) (see Figure 5.21 and Table 5.4) showed significant differences, but also share some common features.

Figure 5.21 INS spectra for (a) \([N_{D\,D\,2}]\text{[NO}_3\text{]}\) (black) and (b) \([N_{0\,0\,2}]\text{[NO}_3\text{]}\) (red).

Table 5.4 INS bands for \([N_{0\,0\,2}]\text{[NO}_3\text{]}\), \([N_{D\,D\,2}]\text{[NO}_3\text{]}\) and \([N_{0\,0\,2}]\text{[NO}_3\text{]}\).

<table>
<thead>
<tr>
<th>Mode assignment</th>
<th>([N_{0,0,2}]\text{[NO}_3\text{]})</th>
<th>([N_{D,D,2}]\text{[NO}_3\text{]})</th>
<th>([N_{0,0,2}]\text{[NO}_3\text{]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\rho(N-H\cdots O))</td>
<td>424</td>
<td>-</td>
<td>424</td>
</tr>
<tr>
<td>(\rho(N-D\cdots O))</td>
<td>-</td>
<td>404(^a)</td>
<td>-</td>
</tr>
<tr>
<td>(\nu(C-C))</td>
<td>386</td>
<td>386</td>
<td>414</td>
</tr>
<tr>
<td>(\rho(CNC))</td>
<td>-</td>
<td>326(^a)</td>
<td>-</td>
</tr>
<tr>
<td>(\nu(N-H\cdots O))</td>
<td>346</td>
<td>-</td>
<td>314</td>
</tr>
<tr>
<td>(\nu(N-D\cdots O))</td>
<td>-</td>
<td>326(^a)</td>
<td>-</td>
</tr>
<tr>
<td>(\tau(CH_n))</td>
<td>278</td>
<td>278</td>
<td>296</td>
</tr>
<tr>
<td>(\omega(CH_n), \tau(CNC))</td>
<td>261</td>
<td>247</td>
<td>254</td>
</tr>
<tr>
<td>(\nu(C-C))</td>
<td>215(^a)</td>
<td>215(^a)</td>
<td>215</td>
</tr>
</tbody>
</table>

\(^a\)This frequency is approximated as there is not a well-defined band.
The similarities between [\text{NO}_3^2] and [\text{NO}_3^2] are found in the intense band at 386 cm\(^{-1}\), which is due to symmetric stretching modes of the carbon atoms in the alkyl chain, \(\nu_C(\text{C}-\text{C})\), as well as the rocking modes of CNC. This was found at 414 cm\(^{-1}\) for [\text{NO}_3^2] (see Table 5.4). Twisting modes of the CH\(_n\) groups are found at about 278 cm\(^{-1}\) for [\text{NO}_3^2] and [\text{NO}_3^2]. For [\text{NO}_3^2], these modes were found at 296 cm\(^{-1}\). The wagging mode of CH\(_n\) groups and the twisting mode of CNC for [\text{NO}_3^2] are found at 261 cm\(^{-1}\), and for [\text{NO}_3^2] at 247 cm\(^{-1}\), being at 254 cm\(^{-1}\) for [\text{NO}_3^2]. These wagging and twisting modes were shifted by 14 cm\(^{-1}\) for [\text{NO}_3^2] with respect to [\text{NO}_3^2], and a similar effect was found for [\text{NO}_3^2] and [\text{NO}_3^2].

Again, below 200 cm\(^{-1}\), the spectra for [\text{NO}_3^2] and [\text{NO}_3^2] are very similar, with the exception of a broad shoulder between 200 and 170 cm\(^{-1}\). This shoulder may be due, among other interactions, to an asymmetric stretching mode of C-C, and to partial contributions of hydrogen bonds in the lattice region (purple circle in Figure 5.21).

The two bands of the spectrum of [\text{NO}_3^2] at 424 cm\(^{-1}\) and 346 cm\(^{-1}\) in Figure 5.21, highlighted as 1 and 2, which are not visible in the spectrum of [\text{NO}_3^2], are due to the bending and stretching of the N-H···O system, respectively. N-D···O bands for these modes (by the assumption made of \(\tilde{e}_{\text{ab}}/\tilde{e}_{\text{oo}}\) for [\text{NO}_3^2] and [\text{NO}_3^2]) should occur shifted by about 20 cm\(^{-1}\) to lower frequencies for [\text{NO}_3^2]. Thus, these bands should be found at about 404 cm\(^{-1}\) and 326 cm\(^{-1}\), at indicating in Figure 5.21(a). As seen for [\text{NO}_3^2], the bending and stretching bands of the N-D···O are about ten times weaker (see Section 5.3.1), and so difficult to observe as they may be masked by other vibrational modes. The assignments, in Figure 5.21(a), of these bands as shoulders must be considered as extremely tentative.

Ludwig and coworkers [102] also studied [\text{NO}_3^2] by FIR between 600 and 30 cm\(^{-1}\) (see Figure 5.22). In their study, the deconvolution of the spectra allowed the identification of three contributory bands: the first between 199 cm\(^{-1}\) and 224 cm\(^{-1}\), the second between 134 cm\(^{-1}\) and 159 cm\(^{-1}\), and the third around 60-78 cm\(^{-1}\). The calculated frequencies of clusters of [\text{NO}_3^2] suggested that can be attributed to asymmetric stretching, symmetric stretching and bending modes of hydrogen bonds, respectively. This could explain the absence of this broad shoulder upon deuteriation in our study observed at about 180 cm\(^{-1}\). However, calculations of these small clusters are poor approximations to predictions in the region traditionally associated with lattice modes.
Figure 5.22 Measured FIR spectra of $[N_{0002}]NO_3$ deconvoluted to distinct vibrational bands, which can be assigned helped by the calculated frequencies by DFT [102].

5.3.2.2 $[N_{0003}]NO_3$ and $[N_{DDD3}]NO_3$

In the study of propylammonium nitrate and its deuteriated analogue, Figure 5.23 and Table 5.5, a slightly different pattern is observed. Again, below 200 cm$^{-1}$, both spectra are effectively identical. Between 250 cm$^{-1}$ and 226 cm$^{-1}$ the spectrum of $[N_{0003}]NO_3$ shows a broad shoulder less intense for $[N_{DDD3}]NO_3$, which was also observed for $[N_{0002}]NO_3$. The most intense band, at 268 cm$^{-1}$ for $[N_{0003}]NO_3$ and at 264 cm$^{-1}$ for $[N_{DDD3}]NO_3$ corresponds to the wagging modes of the CH$_n$ groups and the twisting modes of CNC. The band at 283 cm$^{-1}$ for $[N_{0003}]NO_3$ can be clearly referred to the twisting mode of CH$_n$ groups, which is shifted by 14 cm$^{-1}$ to lower frequency in the spectrum of $[N_{DDD3}]NO_3$, being masked by the strong wagging vibrational band of the CH$_n$ groups. A similar shift was also observed in the deuteriated spectra for $[N_{0002}]NO_3$ and $[N_{0002}]NO_3$. The band belonging to the symmetric stretching modes of the carbon atoms in the alkyl chain, $\nu_s$(C-C), as well as the bending modes, $\rho$(CNC), are found at 422 cm$^{-1}$. The bands due to the bending and stretching modes of N-H···O occurs at 446 cm$^{-1}$ and 378 cm$^{-1}$, respectively. By the assumption made in Section 5.3.1, these bands are shifted in the deuteriated analogue to 426 cm$^{-1}$ and 358 cm$^{-1}$, respectively. The assignments, in Figure 5.23(a), of these bands as shoulders must be considered as extremely tentative.
Figure 5.23 INS spectra for (a) [N$_{003}$][NO$_3$] (black), and (b) [N$_{003}$][NO$_3$] (orange).

<table>
<thead>
<tr>
<th>Mode assignment</th>
<th>[N$_{003}$][NO$_3$]</th>
<th>[N$_{003}$][NO$_3$]</th>
<th>[N$_{003}$][NO$_3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$(N-H···O)</td>
<td>446</td>
<td>-</td>
<td>424</td>
</tr>
<tr>
<td>$\rho$(N-D···O)</td>
<td>-</td>
<td>426$^a$</td>
<td>-</td>
</tr>
<tr>
<td>$\nu$(C-C)</td>
<td>422</td>
<td>424</td>
<td>414</td>
</tr>
<tr>
<td>$\rho$(CNC)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\nu$(N-H···O)</td>
<td>378</td>
<td>-</td>
<td>314</td>
</tr>
<tr>
<td>$\nu$(N-D···O)</td>
<td>-</td>
<td>358$^a$</td>
<td>-</td>
</tr>
<tr>
<td>$\tau$(CH$_3$)</td>
<td>283</td>
<td>-</td>
<td>296</td>
</tr>
<tr>
<td>$\omega$(CH$_3$)</td>
<td>268</td>
<td>264</td>
<td>254</td>
</tr>
<tr>
<td>$\tau$(CNC)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\nu$(C-C)</td>
<td>230</td>
<td>230</td>
<td>215</td>
</tr>
</tbody>
</table>
Propylammonium nitrate was also studied by Ludwig and coworkers [99] using far infrared spectroscopic and DFT calculations (see Figure 5.24). The intense band around 450 cm\(^{-1}\) was assigned by them as the bending mode \(\rho\) (NCC) of the cation. This band is split into two contributions referring to the bending modes of the trans (465.0 cm\(^{-1}\)) and cis (451.9 cm\(^{-1}\)) isomers, respectively. The most intense vibrational bands at 332.6 cm\(^{-1}\) are referred to as the bending modes (CCC) of the propyl group. The torsional mode of the propyl group can be found at 286.6 cm\(^{-1}\).

The calculated frequencies of the clusters of \([\text{N}_0\text{O}_3]\)[NO\(_3\)] indicated that the bands at about 224 cm\(^{-1}\) and 159 cm\(^{-1}\) could be due to the asymmetric and symmetric stretching modes of the hydrogen bonds. The vibrational bands around 78 cm\(^{-1}\) are possibly the corresponding bending modes of these hydrogen bonds. Again these conclusions are open to other interpretations.

\[
\text{Figure 5.24} \text{ Measured FIR spectra of } [\text{N}_0\text{O}_3][\text{NO}_3]: \text{a) deconvoluted to vibrational bands, which can be assigned with the help of calculations; b) DFT calculated vibrational modes of } ([\text{N}_0\text{O}_3][\text{NO}_3])_m \text{ clusters, with } m = 1, 2, 3, \text{ or } 4 [99].
\]

5.3.2.3 \([\text{N}_0\text{O}_4][\text{NO}_3]\) and \([\text{N}_{\text{D}}\text{D}_4][\text{NO}_3]\)

In Figure 5.25 and Table 5.6 are shown the comparison between \([\text{N}_0\text{O}_0\text{O}_4][\text{NO}_3]\) and \([\text{N}_{\text{D}}\text{D}_0\text{D}_4][\text{NO}_3]\), and again the vibrational bands below 200 cm\(^{-1}\) are very similar. The peak at 230 cm\(^{-1}\) is due to asymmetric C-C stretching. This band was found at 215 cm\(^{-1}\) for \([\text{N}_0\text{O}_2\text{O}_4][\text{NO}_3]\). At about 250 cm\(^{-1}\) there are two small bands (marked with a circle in Figure 5.25). They were also observed for \([\text{N}_0\text{O}_0\text{O}_3][\text{NO}_3]\) and \([\text{N}_0\text{O}_0\text{O}_2][\text{NO}_3]\). The most intense band at 283 cm\(^{-1}\) for \([\text{N}_0\text{O}_0\text{O}_4][\text{NO}_3]\) and \([\text{N}_{\text{D}}\text{D}_0\text{D}_4][\text{NO}_3]\) correspond to the bending modes of the \(\text{CH}_n\) groups, both twisting and wagging, and the CNC
twisting mode. The band at 431 cm\(^{-1}\) for \([\text{N}_{0.0.4}]\text{NO}_3\), which has a shoulder at approximately 420 cm\(^{-1}\), is probably due to symmetric stretching modes of the carbon atoms in the butyl chain, \(\nu_s (\text{C-C})\), as well as the bending modes, \(\rho (\text{CNC})\). Upon deuteriation, these bands resolved into two better defined modes at 409 cm\(^{-1}\), and 395 cm\(^{-1}\).

The N-O···H bending and stretching vibrations are shown at 464 cm\(^{-1}\) and 402 cm\(^{-1}\), respectively for \([\text{N}_{0.0.4}]\text{NO}_3\). These bands, after deuterium substitution, are shifted to lower frequencies by about 20 cm\(^{-1}\), appearing as two small peaks for \([\text{N}_{D.0.4}]\text{NO}_3\). The assignments, in Figure 5.25(a), of these bands as shoulders must be considered as extremely tentative.

![Figure 5.25](image-url) Vibrational INS spectra for (a) \([\text{N}_{D.0.4}]\text{NO}_3\) (black) and (b) \([\text{N}_{0.0.4}]\text{NO}_3\) (green).
Table 5.6 INS bands for \([\text{N}_0\text{O}_0\text{O}_4]\text{[NO}_3\text{]}, \ [\text{N}_0\text{D}_0\text{D}_4]\text{[NO}_3\text{]}, \ [\text{N}_0\text{O}_2\text{2}]\text{[NO}_3\text{].}

<table>
<thead>
<tr>
<th>Mode assignment</th>
<th>([\text{N}_0\text{O}_0\text{O}_4]\text{[NO}_3\text{]})</th>
<th>([\text{N}_0\text{D}_0\text{D}_4]\text{[NO}_3\text{]})</th>
<th>([\text{N}_0\text{O}_2\text{2}]\text{[NO}_3\text{]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\rho(\text{N-H···O}))</td>
<td>464</td>
<td>-</td>
<td>424</td>
</tr>
<tr>
<td>(\rho(\text{N-D···O}))</td>
<td>-</td>
<td>450</td>
<td>-</td>
</tr>
<tr>
<td>(\nu (\text{C-C}))</td>
<td>431</td>
<td>409</td>
<td>414</td>
</tr>
<tr>
<td>(\rho(\text{CNC}))</td>
<td>431</td>
<td>395</td>
<td>-</td>
</tr>
<tr>
<td>(\nu (\text{N-H···O}))</td>
<td>402</td>
<td>-</td>
<td>314</td>
</tr>
<tr>
<td>(\nu (\text{N-D···O}))</td>
<td>-</td>
<td>380</td>
<td>-</td>
</tr>
<tr>
<td>(\tau(\text{CH}_n))</td>
<td>283</td>
<td>283</td>
<td>286, 254</td>
</tr>
<tr>
<td>(\omega (\text{CH}_n))</td>
<td>283</td>
<td>283</td>
<td>286, 254</td>
</tr>
<tr>
<td>(\tau(\text{CNC}))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\nu_{as}(\text{C-C}))</td>
<td>230</td>
<td>225</td>
<td>215</td>
</tr>
</tbody>
</table>

5.3.2.4 Comparison of \([\text{N}_0\text{O}_0\text{O}_1]\text{[NO}_3\text{]}, \ [\text{N}_0\text{O}_0\text{O}_2]\text{[NO}_3\text{], \ [N}_0\text{O}_0\text{O}_3]\text{[NO}_3\text{], and \ [N}_0\text{O}_0\text{O}_4]\text{[NO}_3\text{.}

The comparison of the vibrational spectra for \([\text{N}_0\text{O}_0\text{O}_1]\text{[NO}_3\text{]}, \ [\text{N}_0\text{O}_0\text{O}_2]\text{[NO}_3\text{], \ [N}_0\text{O}_0\text{O}_3]\text{[NO}_3\text{], and \ [N}_0\text{O}_0\text{O}_4]\text{[NO}_3\text{] are shown in Figure 5.26. Some alkylammonium nitrate INS data were taken from Stana's thesis [106] for the comparative study of all the monoalkylammonium nitrates. By increasing the length of the alkyl chain, the vibrational frequencies for \(\nu(\text{O···H})\) are shifted to higher frequencies, which means that stronger hydrogen bonding are formed. As seen in Figure 5.27, the INS spectra for higher \((n > 4)\) alkyl chain length is more complex, and it is more difficult to identify the hydrogen bonds interactions, as expected. As the chain get longer, the hydrogen bond interactions become less significant (i.e. weaker) compared with the sum of the other molecular vibrations. However, the same trend is observed, and it can be assumed that the stretching and the bending frequencies of O-H mode are becoming slightly weaker. Figure 5.26 and Figure 5.27 also shown an increase in the stretching frequency of the alkyl chain, \(\nu_6\) (C-C), as well as the bending modes, \(\rho(\text{CNC})\).
Figure 5.26 INS spectra for (a) \([N_000][NO_3]\) (brown), (b) \([N_002][NO_3]\) (red), (c) \([N_003][NO_3]\) (orange), and (d) \([N_004][NO_3]\) (green).

Figure 5.27 INS spectra of (a) \([N_002][NO_3]\), (b) \([N_004][NO_3]\), (c) \([N_007][NO_3]\), (d) \([N_009][NO_3]\), (e) \([N_010][NO_3]\), (f) \([N_012][NO_3]\), (g) \([N_014][NO_3]\), (h) \([N_016][NO_3]\), and (i) \([N_018][NO_3]\).
5.3.3 Analysis of triethylammonium nitrate

The INS spectra for \([N_{0222}]\text{[NO}_3\text{]}\) can be found in Figure 5.28. As there was no beam time available to collect INS data for \([N_{0222}]\text{[NO}_3\text{]}\), the assignment of the bands (see Table 5.7) must be tentative, but are based on the earlier studies of the mono- and di- alkyl salts reported above. As expected, the triethylammonium salt shows more peaks than either \([N_{0022}]\text{[NO}_3\text{]}\) or \([N_{0002}]\text{[NO}_3\text{]}\). The symmetric stretching modes of the carbon atoms, \(v_s\) (C-C), as well as the bending modes, \(\rho\) (CNC) are found at 416 cm\(^{-1}\). These motions were found at similar frequency for \([N_{0022}]\text{[NO}_3\text{]}\) (414 cm\(^{-1}\)). The bending modes of the CNC are found at 316 cm\(^{-1}\) and 290 cm\(^{-1}\). This band was not visible in the spectra of \([N_{0022}]\text{[NO}_3\text{]}\). The twisting modes of \(CH_n\) groups are at 256 cm\(^{-1}\), about 30 cm\(^{-1}\) shifted to lower frequencies respect to those for \([N_{0022}]\text{[NO}_3\text{]}\). Wagging modes of the \(CH_n\) groups and CNC twisting modes for \([N_{0222}]\text{[NO}_3\text{]}\), are found at about 241 cm\(^{-1}\). The C-C asymmetric stretching mode are found at 225 cm\(^{-1}\). In general all the frequencies for \([N_{0222}]\text{[NO}_3\text{]}\) are shown at higher frequencies than those for \([N_{0022}]\text{[NO}_3\text{]}\), with the exception of the bending modes for \(CH_n\) groups, and CNC twisting modes.

![INS spectrum for \([N_{0222}]\text{[NO}_3\text{]}\)](image-url)
Table 5.7 INS bands for $[\text{N}_0\text{2 2 2}] [\text{NO}_3]$ and $[\text{N}_0\text{0 2 2}] [\text{NO}_3]$.

<table>
<thead>
<tr>
<th>Mode assignment</th>
<th>$[\text{N}_0\text{2 2 2}] [\text{NO}_3]$</th>
<th>$[\text{N}_0\text{0 2 2}] [\text{NO}_3]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu (\text{N-H\cdots O})$</td>
<td>476</td>
<td>424</td>
</tr>
<tr>
<td>$\nu (\text{N-H\cdots O})$</td>
<td>358</td>
<td>314</td>
</tr>
<tr>
<td>$\tau (\text{CNC})$</td>
<td>316, 290</td>
<td>-</td>
</tr>
<tr>
<td>$\omega (\text{CH}_n)$</td>
<td>256</td>
<td>286</td>
</tr>
<tr>
<td>$\tau (\text{CNC})$</td>
<td>241</td>
<td>254</td>
</tr>
<tr>
<td>$\nu_{as} (\text{C-C})$</td>
<td>225</td>
<td>215</td>
</tr>
</tbody>
</table>

5.3.4 Comparison of $[\text{N}_0\text{0 2 2}] [\text{NO}_3]$, $[\text{N}_0\text{2 2 2}] [\text{NO}_3]$, and $[\text{N}_0\text{2 2 2}] [\text{NO}_3]$

The comparison of $[\text{N}_0\text{0 2 2}] [\text{NO}_3]$, $[\text{N}_0\text{2 2 2}] [\text{NO}_3]$, and $[\text{N}_0\text{2 2 2}] [\text{NO}_3]$ is shown in Figure 5.29 and Table 5.8.

Table 5.8 $\text{N-H\cdots O}$ frequencies modes of $[\text{N}_0\text{0 0 2}] [\text{NO}_3]$, $[\text{N}_0\text{0 2 2}] [\text{NO}_3]$, $[\text{N}_0\text{2 2 2}] [\text{NO}_3]$.

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Bending mode</th>
<th>Stretching mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{N}_0\text{0 0 2}] [\text{NO}_3]$</td>
<td>424</td>
<td>346</td>
</tr>
<tr>
<td>$[\text{N}_0\text{0 2 2}] [\text{NO}_3]$</td>
<td>424 (423 – 417)$^a$</td>
<td>314 (339 – 329)$^a$</td>
</tr>
<tr>
<td>$[\text{N}_0\text{2 2 2}] [\text{NO}_3]$</td>
<td>476</td>
<td>358</td>
</tr>
</tbody>
</table>

$^a$ calculated by CASTEP.

By increasing the number of the alkyl chains, the spectra are more complex, as there are more low frequency modes due to C-C, CH$_n$, and C-N-C. Based on the zeroth order model of charge, the triethylammonium cation exhibits the strongest hydrogen bond, and this is what is observed. The simpler model predicts that the
diethylammonium nitrate will show stronger hydrogen bonds than the ethylammonium nitrate, whereas these two salts exhibit similar frequencies. Indeed the frequencies for diethylammonium nitrate are reproduced well by CASTEP calculations.

Figure 5.29 INS spectra of (a) [N_{0 0 0 2}][NO_3] (grey), (b) [N_{0 0 0 3}][NO_3] (red), and (c) [N_{0 2 2 2}][NO_3] (blue). Bending and stretching mode of hydrogen bonds were highlighted with stars.

5.4 Results and discussion of mixtures

For a better understanding of hydrogen bonds in the low frequency range, spectra of binary mixtures have been additionally measured by INS. Mixtures of the deuteriated salts were also studied.

5.4.1 Binary mixtures of monoalkylammonium nitrates

5.4.1.1 Equimolar mixtures of [N_{0 0 0 2}][NO_3] and [N_{0 0 0 3}][NO_3], and of [N_{D D 2}][NO_3] and [N_{D D D 3}][NO_3]

Experimental INS spectra for \{[N_{0 0 0 2}][NO_3] and [N_{0 0 0 3}][NO_3]\} and \{[N_{D D 2}][NO_3] and [N_{D D D 3}][NO_3]\} were compared with its mathematically simulated† analogue (see Figure 5.30 and Figure 5.31, respectively).

† The simulation was formed by adding the two experimental spectra of the pure components together generating a picture of what the mixture would look like if there were no cross-interactions between the cations and the anions.
Figure 5.30 INS spectra of $\{[\text{N}_{0.0.2}]_{0.5}[\text{N}_{0.0.3}]_{0.5}][\text{NO}_3]\$: (a) experimental (grey), and (b) a spectrum simulated by summing equimolar amounts of the experimental spectra of $[\text{N}_{0.0.2}][\text{NO}_3]$ and $[\text{N}_{0.0.3}][\text{NO}_3]$ (purple).

Figure 5.31 INS spectra of $\{[\text{N}_{0.0.2}]_{0.5}[\text{N}_{0.0.3}]_{0.5}][\text{NO}_3]\$: (a) experimental (black), and (b) a spectrum simulated by summing equimolar amounts of the experimental spectra of $[\text{N}_{0.0.2}][\text{NO}_3]$ and $[\text{N}_{0.0.3}][\text{NO}_3]$ (purple).
Experimental INS spectra for \([\{N_{0.0.2}\}_{0.5}[N_{0.0.3}]_{0.5}\][NO_3]\) and its simulated analogue are similar below 300 cm\(^{-1}\) (see Figure 5.30). Above this frequency, there are major differences between the simulated and the experimental spectra. In particular, two peaks observed in \([N_{0.0.2}][NO_3]\) at 386 cm\(^{-1}\) and 346 cm\(^{-1}\), and dominant in the simulations, are completely missing in the actual experimental spectrum. This strongly suggested that the structure of the individual components is destroyed in the mixture, and new speciation dominates. In other words, the mixture \([\{N_{0.0.2}\}_{0.5}[N_{0.0.3}]_{0.5}\][NO_3]\) shows new interactions which were not a result of simply adding the two pure components, and thus new species were generated. The lower resolution in the mixture, corresponding to broader bands, suggest a range of different hydrogen-bonded species. Experimental INS spectra for \([\{N_{D.D.D.2}\}_{0.5}[N_{D.D.D.3}]_{0.5}\][NO_3]\) and its simulated analogue are also very similar (see Figure 5.31). Again, as found in Figure 5.30 for the protonated species, the experimental bands in the mixtures are broad and poorly resolved, suggesting a range of interaction is formed. Thus, the binary mixtures (both protonated and deuterated) do not form as much regular long-range order as the independent pure materials, which is perhaps not surprising.

The INS experimental spectra for pure \([N_{0.0.2}][NO_3]\) and \([N_{0.0.3}][NO_3]\), their equimolar binary mixture, \([\{N_{0.0.2}\}_{0.5}[N_{0.0.3}]_{0.5}\][NO_3]\), and its deuterated analogue, \([\{N_{D.D.D.2}\}_{0.5}[N_{D.D.D.3}]_{0.5}\][NO_3]\) in the range from 500-30 cm\(^{-1}\) are shown in Figure 5.32, Figure 5.33 and Figure 5.34.

![Figure 5.32 Experimental INS spectra of (a) \([N_{0.0.2}][NO_3]\) (red), (b) \([\{N_{0.0.2}\}_{0.5}[N_{0.0.3}]_{0.5}\][NO_3]\) (grey), and (c) \([N_{0.0.3}][NO_3]\) (orange).](image-url)
Figure 5.33 Experimental INS spectra of (a) [ND$_3$D$_2$][NO$_3$] (red), (b) ([ND$_3$D$_2$]$_{0.5}$[ND$_3$D$_3$]$_{0.5}$)[NO$_3$] (black), and (c) [ND$_3$D$_3$][NO$_3$] (orange).

Figure 5.34 Experimental INS spectra of: (a) ([NO$_2$D$_3$]$_{0.5}$[NO$_2$D$_3$]$_{0.5}$)[NO$_3$] (black), and (b) ([NO$_2$D$_3$]$_{0.5}$[NO$_2$D$_3$]$_{0.5}$)[NO$_3$] (grey).
In Figure 5.32, the symmetric stretching modes of the carbon atoms in the alkyl chain, $v_s$(C-C), as well as the rocking modes of CNC for the mixture $\{[N_{0.02}0.5][N_{0.03}0.5]\}[NO_3]$, were found at 410 cm$^{-1}$, in a slightly broad band. A similar mode was found at 386 cm$^{-1}$ for $[N_{0.003}][NO_3]$, and at 424 cm$^{-1}$ for $[N_{0.002}][NO_3]$, giving rise to two sharp peaks. Hence, the mixture gives a band slightly closer to the vibrational frequency for $[N_{0.003}][NO_3]$. Bending modes of the CH$_n$ groups, and the twisting mode of CNC, are found in a very broad band with a maximum at 273 cm$^{-1}$. The set of bands marked with a circle in Figure 5.32, corresponding to interactions such as the asymmetric stretching mode of C-C, to partial contributions of hydrogen bonds in the lattice region, is placed at approximately half way $\{[N_{0.02}0.5][N_{0.03}0.5]\}[NO_3]$, compared to the two pure ionic liquids.

The N-H···O bending mode of $\{[N_{0.02}0.5][N_{0.03}0.5]\}[NO_3]$ is well-defined and was found at 446 cm$^{-1}$ (see Figure 5.32). This mode was found at 424 cm$^{-1}$ for $[N_{0.002}][NO_3]$, and at 446 cm$^{-1}$ for $[N_{0.003}][NO_3]$, the latter at the same position as found in the mixture. The N-H···O stretching mode, again, is not clearly visible, as seen for $[N_{0.003}][NO_3]$. Thus, there is evidence of new interactions upon the formation of the mixture, and it can be seen that these interactions for $\{[N_{0.02}0.5][N_{0.03}0.5]\}[NO_3]$ are stronger influenced by $[N_{0.003}][NO_3]$, than for $[N_{0.002}][NO_3]$.

Now, focussing on the deuteriated mixture, the spectrum of $\{[D_{0.0}D_{0.5}][D_{0.0}D_{0.5}]\}[NO_3]$ is not very well-defined above 300 cm$^{-1}$ (see Figure 5.33). However, there are two small shoulders possibly due to the symmetric stretching modes of the carbon atoms in the alkyl chain, $v_s$ (C-C), as well as the rocking modes of CNC. The bands due to the vibrations of N-D···O are about ten times weaker, and so difficult to observe as they may be masked by other vibrational modes.

A comparison of the experimental spectra for the protonated and deuteriated mixtures, $\{[N_{0.02}0.5][N_{0.03}0.5]\}[NO_3]$ and $\{[D_{0.0}D_{0.5}][D_{0.0}D_{0.5}]\}[NO_3]$, is shown in Figure 5.34. A broad band observed for the former at 273 cm$^{-1}$, that belongs to the bending modes of the CH$_n$ groups and the twisting mode of CNC, was slightly shifted to lower frequencies in the latter (by 14 cm$^{-1}$). This phenomenon was also observed for the deuteriated analogues of all the pure ionic liquids studied (see Section 5.3). Below 200 cm$^{-1}$, spectra for $\{[N_{0.02}0.5][N_{0.03}0.5]\}[NO_3]$ and $\{[D_{0.0}D_{0.5}][D_{0.0}D_{0.5}]\}[NO_3]$ showed a broad band not well-defined.

All the data presented in Figure 5.30, Figure 5.31, Figure 5.32, Figure 5.33 and Figure 5.34 suggested the same interpretation: the mixtures contain much lower long-range order than the pure components. This may be due to new speciation, such as nitrate hydrogen-bonded to two different cations, and also to additional stable
conformers of the propyl chain. Thus, the mixtures contain many more species, and
conformers of those species, leading to broader, less well-defined bands.

5.4.1.2 Equimolar mixtures of $[\text{N}_0\text{O}_0\text{O}_3][\text{NO}_3]$ and $[\text{N}_0\text{O}_0\text{O}_4][\text{NO}_3]$, and of
$[\text{N}_0\text{D}_0\text{D}_3][\text{NO}_3]$ and $[\text{N}_0\text{D}_0\text{D}_4][\text{NO}_3]$

Experimental INS spectra for $\{[\text{N}_0\text{O}_0\text{O}_3]_{0.5}[\text{N}_0\text{O}_0\text{O}_4]_{0.5}\}[[\text{NO}_3]]$ were compared with its
simulated analogue (see Figure 5.35).

![INS spectra](image)

Figure 5.35 INS spectra of $\{[\text{N}_0\text{O}_0\text{O}_3]_{0.5}[\text{N}_0\text{O}_0\text{O}_4]_{0.5}\}[[\text{NO}_3]]$: (a) experimental (grey), and (b) a
spectrum simulated by summing equimolar amounts of the experimental spectra of
$[\text{N}_0\text{O}_0\text{O}_3][\text{NO}_3]$ and $[\text{N}_0\text{O}_0\text{O}_4][\text{NO}_3]$ (purple).

Unlike, the mixture $\{[\text{N}_0\text{O}_0\text{O}_3]_{0.5}[\text{N}_0\text{O}_0\text{O}_4]_{0.5}\}[[\text{NO}_3]]$ (see Section 5.4.1.1), the
experimental INS spectrum for $\{[\text{N}_0\text{O}_0\text{O}_3]_{0.5}[\text{N}_0\text{O}_0\text{O}_4]_{0.5}\}[[\text{NO}_3]]$ and its simulated analogue
are very similar. Thus, this implies that for the mixture of propyl- and butyl- ammonium
salts, the original speciation of the pure materials appears to be retained in the
mixture. However, this may be an oversimplification: there is a much smaller
difference between propyl and butyl (butyl is 33% longer than propyl) than there is
between ethyl and propyl (propyl is 50% longer than ethyl). This can be seen in Figure
5.36: the differences between the pure $[\text{N}_0\text{O}_0\text{O}_3][\text{NO}_3]$ and $[\text{N}_0\text{O}_0\text{O}_4][\text{NO}_3]$ are much
smaller than those found between $[\text{N}_0\text{O}_0\text{O}_3][\text{NO}_3]$ and $[\text{N}_0\text{O}_0\text{O}_3][\text{NO}_3]$ (see Figure 5.32).

In more detail, the vibrational bands for pure $[\text{N}_0\text{O}_0\text{O}_3][\text{NO}_3]$ and $[\text{N}_0\text{O}_0\text{O}_4][\text{NO}_3]$, their
equimolar binary mixture, $\{[\text{N}_0\text{O}_0\text{O}_3]_{0.5}[\text{N}_0\text{O}_0\text{O}_4]_{0.5}\}[[\text{NO}_3]]$, and their deuteriated
analougues are shown in the range from 500-30 cm$^{-1}$ in Figure 5.36, Figure 5.37, and Figure 5.38.

**Figure 5.36** Experimental INS spectra of (a) [N$_{0.03}$][NO$_3$] (orange), (b) ([N$_{0.03}$]$_{0.5}$[N$_{0.04}$]$_{0.5}$)[NO$_3$] (grey), and (c) [N$_{0.04}$][NO$_3$] (green).

**Figure 5.37** Experimental INS spectra of (a) [N$_{0.03}$][NO$_3$] (orange), (b) ([N$_{0.03}$]$_{0.5}$[N$_{0.04}$]$_{0.5}$)[NO$_3$] (black), and (c) [N$_{0.04}$][NO$_3$] (green).
The vibrational frequencies of the mixtures lie between the pure components from which they were made (see Figure 5.36). The symmetric stretching modes of the carbon atoms in the alkyl chain, $\nu_s$ (C-C), and the rocking modes of CNC for the mixture $\{[N_0\,0\,0\,3]_0.5[N_0\,0\,0\,4]_0.5][NO_3]\$, are found at 424 cm$^{-1}$, and 420 cm$^{-1}$ and in a split band. The same mode, was found as a single band at 422 cm$^{-1}$ for $[N_0\,0\,0\,3][NO_3]$ and at 431 cm$^{-1}$ for $[N_0\,0\,0\,4][NO_3]$. Hence, at similar vibrational frequency than those for $[N_0\,0\,0\,3][NO_3]$. Bending modes of the CH$_n$ groups, and the twisting mode of CNC are found in a very broad band with a maximum at 287 cm$^{-1}$. This broad band, although with a similar shape to $[N_0\,0\,0\,3][NO_3]$, contains features of both pure ionic liquids. The set of bands marked with a circle for $\{[N_0\,0\,0\,3]_0.5[N_0\,0\,0\,4]_0.5][NO_3]\$ in Figure 5.36 (corresponding to interactions such as the asymmetric stretching mode of C-C, and to partial contributions of hydrogen bonds in the lattice region) occurs at approximately half way between bands in the two pure ionic liquids. The N-H···O bending mode for $\{[N_0\,0\,0\,3]_0.5[N_0\,0\,0\,4]_0.5][NO_3]\$ appears at 444 cm$^{-1}$ (purple arrow in Figure 5.36) shifted to lower frequencies compared to the same mode for pure compound, $[N_0\,0\,0\,3][NO_3]$ and $[N_0\,0\,0\,4][NO_3]$. Similarly, the N-H···O stretching mode, which is found at 392 cm$^{-1}$ for $\{[N_0\,0\,0\,3]_0.5[N_0\,0\,0\,4]_0.5][NO_3]\$, lies between the pure components.

As for $\{N_{0\,D\,D\,2.5}[N_{0\,D\,D\,3}]_0.5][NO_3]\$ (see Section 5.4.1.1), the spectrum of $\{N_{0\,D\,D\,3}]_0.5[N_{0\,D\,D\,4}]_0.5][NO_3]\$ is not well-defined (see Figure 5.37 and Figure 5.38).
All the data presented in Figure 5.35, Figure 5.36, Figure 5.37 and Figure 5.38 again suggested that the mixtures contain much lower long-range order than the pure components. However, there is a greater similarity between propyl and butyl than between ethyl and propyl, and so the differences are less apparent.

5.4.1.3 Mixtures of $[\text{N}_2\text{O}_2][\text{NO}_3]$ and $[\text{N}_4\text{O}_4][\text{NO}_3]$, and of $[\text{D}_2\text{D}_2][\text{NO}_3]$ and $[\text{D}_4\text{D}_4][\text{NO}_3]$

As the major differences between the studied monoalkylammonium ionic liquids are expected to be found between $[\text{N}_2\text{O}_2][\text{NO}_3]$ and $[\text{N}_4\text{O}_4][\text{NO}_3]$, two binary mixtures composition were studied.

5.4.1.3.1 EQUIMOLAR: $[[\text{N}_2\text{O}_2]_{0.5}[\text{N}_4\text{O}_4]_{0.5}][\text{NO}_3]$ 
Experimental INS spectra for $[[\text{N}_2\text{O}_2]_{0.5}[\text{N}_4\text{O}_4]_{0.5}][\text{NO}_3]$ and $[[\text{D}_2\text{D}_2]_{0.5}[\text{D}_4\text{D}_4]_{0.5}][\text{NO}_3]$ were compared with their simulated analogues (see Figure 5.39 and Figure 5.40, respectively).

*Figure 5.39* INS spectra of $[[\text{N}_2\text{O}_2]_{0.5}[\text{N}_4\text{O}_4]_{0.5}][\text{NO}_3]$: (a) experimental (grey), and (b) a spectrum simulated by summing equimolar amounts of the experimental spectra of $[\text{N}_2\text{O}_2][\text{NO}_3]$ and $[\text{N}_4\text{O}_4][\text{NO}_3]$ (purple).
Figure 5.40 INS spectra of {\([\text{ND}_2\text{D}_2]_{0.5}[\text{ND}_4\text{D}_4]_{0.5}\)}[\text{NO}_3]: (a) experimental (black), and (b) a spectrum simulated by summing equimolar amounts of the experimental spectra of [\text{ND}_2\text{D}_2][\text{NO}_3] and [\text{ND}_4\text{D}_4][\text{NO}_3] (purple).

The spectrum of {\([\text{NO}_0\text{O}_0\text{O}_0\text{2}]_{0.5}[\text{NO}_0\text{O}_0\text{O}_0\text{4}]_{0.5}\)}[\text{NO}_3] and its simulated analogue (see Figure 5.39) shows significant differences, as seen before for {\([\text{NO}_0\text{O}_0\text{O}_0\text{2}]_{0.5}[\text{NO}_0\text{O}_0\text{O}_0\text{3}]_{0.5}\)}[\text{NO}_3] in Section 5.4.1.1. Indeed, the lack of structure in the experimental curve for the mixture compared with the simulated curve is even more exaggerated than for the mixture of {\([\text{NO}_0\text{O}_0\text{O}_0\text{2}]_{0.5}[\text{NO}_0\text{O}_0\text{O}_0\text{3}]_{0.5}\)}[\text{NO}_3]. This implies even greater long-range disorder, and with the formation of a variety of new mixed species, and conformers of these.

A similar effect was observed for {\([\text{ND}_2\text{D}_2\text{D}_2]_{0.5}[\text{ND}_4\text{D}_4\text{D}_4]_{0.5}\)}[\text{NO}_3] and its simulated spectrum, as seen in Figure 5.40. Indeed, the experimental curve shows very little structure, in fact, even less than found for {\([\text{ND}_2\text{D}_2\text{D}_2]_{0.5}[\text{ND}_4\text{D}_4\text{D}_4]_{0.5}\)}[\text{NO}_3] (see Figure 5.31).

The vibrational bands for pure [\text{NO}_0\text{O}_0\text{O}_0\text{2}] [\text{NO}_3] and [\text{NO}_0\text{O}_0\text{O}_0\text{4}] [\text{NO}_3], their equimolar binary mixture, {\([\text{NO}_0\text{O}_0\text{O}_0\text{2}]_{0.5}[\text{NO}_0\text{O}_0\text{O}_0\text{4}]_{0.5}\)}[\text{NO}_3], and their deuteriated analogues in the range from 500-30 cm\(^{-1}\) are shown in Figure 5.41, Figure 5.42 and Figure 5.43. The patterns see in these three figures reflect the pattern seen in Sections 5.4.1.1 and 5.4.1.2, except that for the ethylammonium/butylammonium nitrate mixture, the loss of structure is even more profound. The spectrum of {\([\text{NO}_0\text{O}_0\text{O}_0\text{2}]_{0.5}[\text{NO}_0\text{O}_0\text{O}_0\text{4}]_{0.5}\)}[\text{NO}_3] (see Figure 5.41) do not show a good resolution of peaks. However, a few features can be spotted. There are two sets of bands: at about 450-400 cm\(^{-1}\) and about
300-200 cm$^{-1}$. In the higher frequencies set, there are three distinguished bands. The bending vibrational mode of N-H···O, which lie slightly shifted to lower frequencies respect to the pure, at 422 cm$^{-1}$ and the symmetric stretching modes of the carbon atoms in the alkyl chain, $\nu_s$ (C-C), and the rocking modes of CNC, which are at 402 cm$^{-1}$. The stretching vibrational mode of N-H···O is shown at about 349 cm$^{-1}$. This band is also a bit shifted to lower frequencies respect to the pure.

The broad shoulder about 300-200 cm$^{-1}$ contained bending modes of the CH$_n$ groups, and the twisting mode of CNC. The region marked with a purple circle belong to partial contributions of asymmetric stretching mode of C-C, and hydrogen bonds, was also shifted for [{N$_0$002}$_{0.5}${N$_0$004}$_{0.5}$][NO$_3$], and lie between the [N$_0$002][NO$_3$] and [N$_0$004][NO$_3$].

In the study of [{N$_D$D$D$3}$_{0.5}${N$_D$D$D$4}$_{0.5}$][NO$_3$] (see \textbf{Figure 5.42} and \textbf{Figure 5.43}), the bands for the symmetric stretching modes of the carbon atoms in the alkyl chain, $\nu_s$ (C-C), and the rocking modes of (CNC), are observed at 394 cm$^{-1}$. The band belong to the N-D···O bending mode is not visible, and the N-D···O stretching is shifted to lower frequencies. The bending modes of the CH$_n$ groups, and the twisting mode of CNC was slightly shifted about 10 cm$^{-1}$ to lower frequencies for [{N$_D$D$D$3}$_{0.5}${N$_D$D$D$4}$_{0.5}$][NO$_3$] respect [{N$_0$002}$_{0.5}${N$_0$004}$_{0.5}$][NO$_3$].

\textbf{Figure 5.41} Experimental INS spectra of: (a) [N$_0$002][NO$_3$] (red), (b) [{N$_0$002}$_{0.5}${N$_0$004}$_{0.5}$][NO$_3$] (grey), and (c) [N$_0$004][NO$_3$] (green).
Figure 5.42 Experimental INS spectra of: (a) $[\text{ND}_{3}\text{D}_2][\text{NO}_3]$ (red), (b) $[[\text{ND}_{3}\text{D}_2]_{0.5}[\text{ND}_{4}\text{D}_4]_{0.5}][\text{NO}_3]$ (black), and (c) $[\text{ND}_{4}\text{D}_4][\text{NO}_3]$ (green).

Figure 5.43 Experimental INS spectra of: (a) $[[\text{ND}_{3}\text{D}_2]_{0.5}[\text{ND}_{4}\text{D}_4]_{0.5}][\text{NO}_3]$ (black), and (b) $[[\text{ND}_{3}\text{D}_2]_{0.5}[\text{ND}_{4}\text{D}_4]_{0.5}][\text{NO}_3]$ (grey).
5.4.1.3.2 Mixture: $\{[N_{0\ 0\ 0\ 2}]_{0.75}[N_{0\ 0\ 0\ 4}]_{0.25}]\text{[NO}_3\text{]}$

The vibrational bands for pure $[N_{0\ 0\ 0\ 2}]\text{[NO}_3\text{]}$ and $[N_{0\ 0\ 0\ 4}]\text{[NO}_3\text{]}$, their equimolar binary mixture, $\{[N_{0\ 0\ 0\ 2}]_{0.75}[N_{0\ 0\ 0\ 4}]_{0.25}]\text{[NO}_3\text{]}$, and its deuteriated analogue in the range from 500-30 cm$^{-1}$ are shown in Figure 5.44. It is interesting to note that the same pattern was observed for both binary mixtures, and that 1:1 and a 3:1 mixture of ethylammonium and butylammonium cation appear to produce similar breakdown in the long-range structure of the mixture. The bands belonging to the $\text{N-H} \cdots \text{O}$ systems for $\{[N_{0\ 0\ 0\ 2}]_{0.75}[N_{0\ 0\ 0\ 4}]_{0.25}]\text{[NO}_3\text{]}$ (indicated by arrows) are shifted to lower frequencies with respect to the pure components, and are much broader, weaker, and less well-defined.

![INS spectra](image)

**Figure 5.44** INS spectra of (a) $[N_{0\ 0\ 0\ 2}]\text{[NO}_3\text{]}$ (red), (b) $\{[N_{0\ 0\ 0\ 2}]_{0.75}[N_{0\ 0\ 0\ 4}]_{0.25}]\text{[NO}_3\text{]}$ (dash line), (c) $\{[N_{0\ 0\ 0\ 2}]_{0.75}[N_{0\ 0\ 0\ 4}]_{0.25}]\text{[NO}_3\text{]}$ (black), and (d) $[N_{0\ 0\ 0\ 4}]\text{[NO}_3\text{]}$ (green).

5.4.1.3.3 Comparison of $\{[N_{0\ 0\ 0\ 2}]_{0.5}[N_{0\ 0\ 0\ 4}]_{0.5}]\text{[NO}_3\text{]}$ and $\{[N_{0\ 0\ 0\ 2}]_{0.75}[N_{0\ 0\ 0\ 4}]_{0.25}]\text{[NO}_3\text{]}$ and their deuteriated analogues

The comparison of binary mixtures of $[N_{0\ 0\ 0\ 2}]\text{[NO}_3\text{]}$ and $[N_{0\ 0\ 0\ 4}]\text{[NO}_3\text{]}$, and their deuteriated analogues, are shown in Figure 5.45. As noted earlier, the spectrum of $\{[N_{0\ 0\ 0\ 2}]_{0.5}[N_{0\ 0\ 0\ 4}]_{0.5}]\text{[NO}_3\text{]}$ and $\{[N_{0\ 0\ 0\ 2}]_{0.75}[N_{0\ 0\ 0\ 4}]_{0.25}]\text{[NO}_3\text{]}$, are practically the same, as both compositions exhibit profound disruption to the long-range order. What is
remarkable is the spectral similarities between curves (b), (c), (d), and (e), in Figure 5.45. The loss of the characteristic bands of both pure components, even in a 3:1 mixture, shows a phenomenon which could be compared to glass formation, which is very common in ionic liquid chemistry.

![INS spectra of different mixtures](image)

**Figure 5.45 INS spectra of (a) [N\_0\_0\_2][NO\_3] (red), (b) [[N\_D\_D\_2]_0.75[N\_D\_D\_4]_0.25][NO\_3] (dash purple), (c) [[N\_D\_D\_2]_0.5[N\_D\_D\_4]_0.5][NO\_3] (dash black), (d) [[N\_0\_0\_2]_0.5[N\_0\_0\_4]_0.5][NO\_3] (purple), (e) [[N\_0\_0\_2]_0.75[N\_0\_0\_4]_0.25][NO\_3] (black) and (f) [N\_0\_0\_4][NO\_3] (green).**

### 5.4.2 Binary mixtures of [N\_0\_0\_2][NO\_3] and [N\_0\_0\_2][NO\_3]

The INS spectra of [N\_0\_0\_2][NO\_3] and [N\_0\_0\_2][NO\_3] and their binary mixtures, ([N\_0\_0\_2]_p[N\_0\_0\_2]_1-p)[NO\_3] (p = 0.9, 0.8, 0.7) are shown in Figure 5.46. The INS spectra of [N\_D\_D\_2][NO\_3] and [N\_D\_D\_2][NO\_3], and their binary mixtures ([N\_0\_0\_2]_p[N\_0\_0\_2]_1-p)[NO\_3] (p = 0.9, 0.7) are shown in Figure 5.47. The INS spectra for ([N\_0\_0\_2]_p[N\_0\_0\_2]_1-p)[NO\_3] and ([N\_D\_D\_2]_p[N\_D\_D\_2]_1-p)[NO\_3] for p = 0.9 are shown in Figure 5.48, and for p = 0.7, in Figure 5.49.

The comparison of the experimental of the INS of the binary mixtures of [N\_0\_0\_2][NO\_3] and [N\_0\_0\_2][NO\_3] showed that, even at 10% of diethylammonium nitrate and 90% of ethylammonium nitrate, the structure of the dialkylammonium nitrate is clearly dominating the mixture between 500-300 cm\(^{-1}\) (see Figure 5.46). Moreover, even at the 10 % composition the bands are significantly broader and less well-
defined. These vibrational frequency range is characteristic of hydrogen bonds. As \([\text{N}_0\text{O}_2\text{2}][\text{NO}_3]\) may have stronger hydrogen bonds than \([\text{N}_0\text{0}_0\text{2}][\text{NO}_3]\), results are in agreement. And again a broadening and loss of resolution was observed for the mixtures. Twisting and wagging modes of the \(\text{CH}_n\) groups and the twisting mode of CNC for \([\text{N}_0\text{0}_0\text{2}][\text{NO}_3]\) found at 278 and 261 cm\(^{-1}\), respectively, became a single broad band with maximum at about 271 cm\(^{-1}\) for all the binary mixtures (see Figure 5.46).

![INS spectra](image)

**Figure 5.46** INS spectra of (a) \([\text{N}_0\text{0}_0\text{2}][\text{NO}_3]\) (red), (b) \([\text{N}_0\text{0}_0\text{2}0.09\text{N}_0\text{0}_0\text{2}0.1][\text{NO}_3]\) (orange), (c) \([\text{N}_0\text{0}_0\text{2}0.06\text{N}_0\text{0}_0\text{2}0.2][\text{NO}_3]\) (pink), (d) \([\text{N}_0\text{0}_0\text{2}0.07\text{N}_0\text{0}_0\text{2}0.3][\text{NO}_3]\) (blue), and (e) \([\text{N}_0\text{0}_0\text{2}][\text{NO}_3]\) (brown).

Upon deuteration, twisting and wagging modes of the \(\text{CH}_n\) groups and the twisting mode of CNC were found at 263 cm\(^{-1}\) (see Figure 5.47). The symmetric stretching modes of the carbon atoms in the alkyl chain, \(\nu_s(\text{C-C})\), as well as the rocking modes of CNC found at 414 cm\(^{-1}\) for \([\text{N}_0\text{D}_2\text{2}][\text{NO}_3]\), and 386 cm\(^{-1}\) for \([\text{N}_0\text{D}_2\text{2}][\text{NO}_3]\), seems to split in two bands at for \([\text{N}_0\text{D}_2\text{2}0.9\text{N}_0\text{D}_2\text{2}0.1][\text{NO}_3]\) (see Figure 5.48), and \([\text{N}_0\text{D}_2\text{2}0.7\text{N}_0\text{D}_2\text{2}0.3][\text{NO}_3]\) (see Figure 5.49).
Figure 5.47 INS spectra of (a) $\text{[N}_2\text{D}_2\text{D}_2][\text{NO}_3]$ (red), (b) $\{\text{[N}_0\text{D}_2\text{D}_2]_{0.9}[\text{N}_0\text{D}_2\text{D}_2]_{0.1}\}[\text{NO}_3]$ (orange), (c) $\{\text{[N}_0\text{D}_2\text{D}_2]_{0.7}[\text{N}_0\text{D}_2\text{D}_2]_{0.3}\}[\text{NO}_3]$ (blue), and (d) $\text{[N}_2\text{D}_2\text{D}_2][\text{NO}_3]$ (brown).

Figure 5.48 INS spectra of (a) $\{\text{[N}_0\text{D}_2\text{D}_2]_{0.9}[\text{N}_0\text{D}_2\text{D}_2]_{0.1}\}[\text{NO}_3]$ (dash line), and (b) $\{\text{[N}_0\text{O}_2\text{D}_2]_{0.9}[\text{N}_0\text{O}_2\text{D}_2]_{0.1}\}[\text{NO}_3]$ (solid line).
5.5 Conclusions

5.5.1 Pure ionic liquids

The vibrational state of diethylammonium nitrate below 500 cm\(^{-1}\) was investigated by DFT calculations. Experimental INS studies of this salt and other alkylammonium nitrate ionic liquids: ethylammonium nitrate, triethylammonium nitrate, propylammonium nitrate, and butylammonium nitrate provided a vibrational profile for these salts, with an enhancement of bands associated with hydrogen atoms, the vibrational frequencies of \(\text{N–H} \cdots \text{O}\) hydrogen bonds. As seen in Chapter 4, the strong infrared signals due to the N–H stretching mode of the series of alkylammonium nitrates is a signal of the presence of hydrogen bonds. However, this is not the hydrogen bond itself, but a reflection of its presence. Inelastic neutron scattering was proved to be a useful tool to study hydrogen bonds at low frequency for alkylammonium nitrates.

Binary mixtures of the six ionic liquids were also studied. Deuteriated analogues of all the salts studied were also investigated, again with only the acidic cationic protons exchanged. The vibrations involving deuterium atoms were both lower intensity and lower frequency than those of the protonated analogues. The vibrations of the deuterium, about ten times weaker than those of protium, have a cross section similar to other atoms, and hence could be easily masked by other bands. This could explain the absence of deuteriated bands in some cases.

![INS spectra](image)

**Figure 5.49** INS spectra of (a) \([\text{D}_2\text{D}_2\text{D}_2]_0.7[\text{N}_0\text{D}_2\text{O}_2]_0.3][\text{NO}_3]\) (dash line), and (b) \([\text{N}_0\text{O}_2\text{O}_2]_0.7[\text{N}_0\text{O}_2\text{O}_2]_0.3][\text{NO}_3]\) (solid line).
Although the obtained INS spectra for diethylammonium nitrate contained an abundance of information, especially in the low frequency range (below 500 cm\(^{-1}\)), the interpretation of the resultant spectra was achieved using an advanced theoretical model, and comparison with its deuteriated analogue, allowed identification of the hydrogen bonds as distinct from other bands. However, it should be emphasised, particularly in this low energy region, that there are no pure vibrational modes: the hydrogen bonds contains contributions from the cationic skeleton, and the skeletal modes contain contributions from the hydrogen bonds.

The region below 200 cm\(^{-1}\), characterised by weak intramolecular vibrational modes of the anions or cations or from unspecific librational motions or lattice modes, was not studied in this work. Indeed, experimental spectra for [\(N_{0\ 0\ 0\ 2}\)][NO\(_3\)] and [\(N_{0\ 0\ 0\ 2}\)][NO\(_3\)] below 200 cm\(^{-1}\) are virtually indistinguishable, suggesting strongly that there are no significant contributions to this spectral region associated with hydrogen bonding.

The analysis of the hydrogen bonds frequencies below 500 cm\(^{-1}\) for the series of alkylammonium nitrates are presented in Table 5.9. The effect of the length of the alkyl chain can be seen by comparing [\(N_{0\ 0\ 0\ 1}\)][NO\(_3\)], [\(N_{0\ 0\ 0\ 2}\)][NO\(_3\)], [\(N_{0\ 0\ 0\ 3}\)][NO\(_3\)], and [\(N_{0\ 0\ 0\ 4}\)][NO\(_3\)]. By increasing the length of the alkyl chain, the vibrational frequencies for \(\nu(\text{N-H} \cdots \text{O})\) are shifted to higher frequencies, which means that stronger hydrogen bonding are formed.

**Table 5.9** Hydrogen bonds frequencies modes of [\(N_{0\ 0\ 0\ 2}\)][NO\(_3\)], [\(N_{0\ 0\ 0\ 3}\)][NO\(_3\)], [\(N_{0\ 0\ 0\ 4}\)][NO\(_3\)], [\(N_{0\ 0\ 2\ 2}\)][NO\(_3\)], [\(N_{0\ 2\ 2\ 2}\)][NO\(_3\)] and their deuteriated analogues.

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>(\nu(\text{N-H} \cdots \text{O}))</th>
<th>(\nu(\text{N-H} \cdots \text{O}))</th>
<th>(\nu(\text{N-D} \cdots \text{O}))</th>
<th>(\nu(\text{N-D} \cdots \text{O}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wavenumber / cm(^{-1})</td>
<td>Wavenumber / cm(^{-1})</td>
<td>Wavenumber / cm(^{-1})</td>
<td>Wavenumber / cm(^{-1})</td>
</tr>
<tr>
<td>[(N_{0\ 0\ 0\ 2})][NO(_3)]</td>
<td>424</td>
<td>346</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[(N_{0\ 0\ 0\ 2})][NO(_3)]</td>
<td>-</td>
<td>-</td>
<td>404(^b)</td>
<td>326(^b)</td>
</tr>
<tr>
<td>[(N_{0\ 0\ 0\ 3})][NO(_3)]</td>
<td>446</td>
<td>426</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[(N_{0\ 0\ 0\ 4})][NO(_3)]</td>
<td>-</td>
<td>-</td>
<td>378(^b)</td>
<td>358(^b)</td>
</tr>
<tr>
<td>[(N_{0\ 0\ 2\ 2})][NO(_3)]</td>
<td>464</td>
<td>450</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[(N_{0\ 2\ 2\ 2})][NO(_3)]</td>
<td>-</td>
<td>-</td>
<td>402(^b)</td>
<td>380(^b)</td>
</tr>
<tr>
<td>[(N_{0\ 0\ 2\ 2})][NO(_3)]</td>
<td>424</td>
<td>314</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[(N_{0\ 2\ 2\ 2})][NO(_3)]</td>
<td>-</td>
<td>-</td>
<td>409 – 404(^a)</td>
<td>319 – 303(^a)</td>
</tr>
<tr>
<td>[(N_{0\ 2\ 2\ 2})][NO(_3)]</td>
<td>476</td>
<td>358</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\) calculated by CASTEP; \(^b\) estimation of the position of the deuteriated bands.
Although further studies will be required to reinforce this conclusion, it would appear that the monoprotonated cation form the strongest individual hydrogen bonds, but they are localised, whereas, the triprotonated cation form the weaker hydrogen bonds, but they are involved in an extensive bifurcated network.

5.5.2 Binary mixtures
Experimental INS spectra for \(\{[N_{0002}]_{0.5}[N_{0003}]_{0.5}]NO_3\}, \{[N_{0003}]_{0.5}[N_{0004}]_{0.5}]NO_3\}, \{[N_{0002}]_{0.5}[N_{0004}]_{0.5}]NO_3\}, \{[N_{0002}]_{0.75}[N_{0004}]_{0.25}]NO_3\} and their deuteriated analogues were also studied. In comparison to the pure materials, the bands describable to N-H···O were broader and weaker in the mixtures, and shifted in position. In particular, the observed spectra of the mixtures did not correspond to a simple summation of the pure components. This is because the binary mixtures (both protonated and deuteriated) do not form as much regular long-range order as the independent pure materials. This may be due to new speciation, such as nitrate hydrogen-bonded to two different cations (see Figure 5.50), and also to additional stable conformers. Thus, the mixtures contain many more species, and conformers of those species, leading to broader, less well-defined bands.

![Figure 5.50](image)

**Figure 5.50** Structure of a possible new specie for \(\{[N_{0002}]_{0.5}[N_{0003}]_{0.5}]NO_3\}.

Experimental INS of the binary mixtures of \([N_{0002}]NO_3\) and \([N_{0022}]NO_3\) were also investigated. The comparison showed that, even at 10% of \([N_{0022}]NO_3\) and 90% of \([N_{0002}]NO_3\), the structure of the dialkylammonium nitrate is clearly dominating the mixture. This indicates that \([N_{0022}]NO_3\) may form stronger hydrogen bonds than \([N_{0002}]NO_3\).
6 Quasi-elastic Neutron Scattering
In order to separate out different types of molecular motion, and understand the contribution of individual hydrogen groups on the N and C atoms, the proton transfer in structurally simple alkylammonium nitrate ionic liquid and its partially deuteriated analogue at different temperatures have been studied. *Quasi*-elastic neutron scattering (QENS) may give a better understanding of the dynamics of these compounds, being connected with the other methods studied in previous chapters. This was a preliminary study, with only limited instrument access, but indicates the nature of the phenomenon and the need for further study.

6.1 Introduction

Since ionic liquids consist, in principle, only of ions, the equilibrium between the acidic and the basic forms of the protonic must lie at least 99% towards the ionic species for the mixture to be considered a true ionic liquid, $pK_a \approx 2$ [202], as is the case for the alkylammonium nitrates. Protonic ionic liquids are excellent proton carriers in fuel cell electrolytes [203], providing electrolytes of a type that are simply not available in systems in which water acts as an acid or base in the proton transfer process.

Until 2006, it had not been realised that mixtures of inorganic salts (namely, the ammonium salts) can be used as protonic electrolytes for fuel cells running above 80 °C (hydrazinium salts could be used at much lower temperatures). Applied as fuel cell electrolytes, the ammonium salts gave more stable performance than electrolytes containing organic cations. The conduction mechanism in protonic conductors is a sequence of alternating translational and rotational steps of proton transfer. The proton exchange occurs via a hydrogen bridge between different molecular subunits (see Figure 6.1).

![Figure 6.1](image)

**Figure 6.1** A schematic representation of a unidimensional chain of four water molecules interconnected via hydrogen bonds [204].
Subsequently, the acceptor molecule transfers the proton via different hydrogen bonds through reorientational motion, hence the rotating molecule remains on its site (Grotthuss mechanism) [204]. The repeating occurrence of this process is responsible for proton migration and thus protonic conductivity. This is a simple representation of the mechanism. The details of the reorientational or “localised diffusive” motion happening when a proton can be considered as a part of a particular molecular subunit, and before long-range diffusion sets in, depend on the local structure on the length scale of the nearest and their neighbouring distances. Vice versa, the study of these motions can provide insight on the structure and involved interatomic and intermolecular interactions. This information can be obtained by the means of quasi-elastic neutron scattering measurements.

### 6.1.1 Quasi-elastic neutron scattering. Why?

A complete description of the diffusion process of a molecule requires the study of several properties by different experimental approaches. However, depending on the phenomenon of diffusion of interest, a specific technique must be chosen. QENS focuses on the diffusive motion approaching atomic resolution (10 Å) and covering the picosecond-nanosecond time window. Diffusion coefficients above $10^{-6}$ cm² s⁻¹ and over atomic distances can be measured [205]. For this reason, this technique has been used to probe dynamics in a wide range of fields:

- **Material science:** hydrogen storage [206], surface science [207].
- **Soft matter:** polymer nanocomposites and blends [208], organic photovoltaics [209].
- **Biology:** drug delivery [210], protein binding [211].
- **Chemistry:** ionic liquids [212], porous media [213].

Among other advantages of this technique, it is able to differentiate diffusion from confined dynamics, because it can be used as a systematic tool for comparison and complements other experimental techniques, and because the time and spatial scales are directly comparable to results from Molecular Dynamic simulations [205]. In some cases, QENS is the only way to view motions, e.g. isotopic contrast, experimentally.

As seen in **Chapter 5**, in the interaction of the neutron with the nuclei, there can be an exchange of momentum and of energy. If there is no energy exchange, $\hbar \omega = 0$ and it is called elastic scattering. If there is energy exchange, $\hbar \omega \neq 0$ and the interaction is called inelastic scattering; the process occurs in discrete energy steps, such as vibrational modes. In quasi-elastic scattering interactions, there is a small
energy exchange, \( \hbar \omega \neq 0 \approx \text{neV or } \mu\text{eV} \), due to processes occurring with a distribution of energies, such as rotations and translations (see Figure 6.2 and Figure 6.3).

Figure 6.2 Scheme of the three types of nuclei-neutron interaction [214].

Figure 6.3 Schematic representation of the scattering function, \( S(Q, \omega) \) with the energy transfer, \( \omega \) for different types of motions [214].

QENS refers to those inelastic processes in neutron scattering that are almost elastic. The term is usually considered to mean a broadening of the elastic line in the energy spectrum, rather than the appearance of discrete peaks representing inelastic events. As seen in Chapter 5 and Equation (5.1), the scattering function is composed of a mixture of two components, incoherent and coherent. The incoherent, which contains no information about structure and describes the dynamic of individual particles, and the coherent, which contains information about the structure and describes the collective dynamics of nuclei. QENS contains both coherent and incoherent components. As our interest falls in the study of stochastic motions,
rotational and translational diffusion, the incoherent contribution should be several times higher than the coherent.

6.1.2 The coherent and incoherent scattering strength

The degree in which a sample can be regarded as giving rise to coherent or incoherent scattering depends on the sample structure. Consider for instance, a diatomic solid AE, with the A atoms in a sublattice and the atoms E on another. In this ideal situation, all the scattering will be coherent as the structure has long range order and translational symmetry. In contrast, if the AE sample has its atoms arranged randomly, as occurs in many cases, then the translational order is relatively maintained: long range order persists in the monoatomic order where the pseudo atom is AE [185]. Hence, the coherent features, although present (because the order AE is still present) are weaker. The local areas of the crystal at short range have changed, reducing the coherent component, and producing a level of incoherent background. In other words, solids that are made just for one single nuclear type will give just coherent signals. However, the technique is sensitive to different isotopomers of the system being studied (e.g. chlorine, made of $^{35}\text{Cl}$ and $^{37}\text{Cl}$, will give different behaviour). From the diffraction point of view, inelastic and incoherent contributions are “background” effects. In our case, as our interest is focussed on the scattering mechanism for hydrogen atoms, the incoherent component of our sample should be significantly higher than the coherent contribution, assuming that the coherent component is minimised.

6.1.3 Is the incoherent scattering component of our ionic liquids higher than the coherent component?

Atoms both scatter and absorb neutrons, and so, the total cross section is given by Equation (6.1).

$$\sigma = \sigma_{\text{coherent}} + \sigma_{\text{incoherent}} + \sigma_{\text{absorption}}$$  \hspace{1cm} (6.1)

For practical reasons, as $\sigma_{\text{absorption}}$ is very small and not relevant, this term is not taken into account for calculations when planning the neutron experiment. Table 6.1 summarises the neutron scattering (coherent and incoherent) and neutron scattering absorption cross sections for the atoms hydrogen, deuterium, carbon, nitrogen, and oxygen. It is worth pointing out that the scattering cross sections of the atoms tabulated in Table 6.1 are being obtained from the equations described in Appendix C, and the neutron scattering length [215] are derived from experimentally
measured cross sections. There is no theoretical route to calculate them from other nuclear properties [103c].

**Table 6.1** Incoherent, coherent and absorption cross section for the atoms of H, D, C, N and O. $\sigma_{abs}$ is giving for 2200 m s$^{-1}$ neutrons. 1 barn = $10^{-28}$ m$^2$.

<table>
<thead>
<tr>
<th>Element (Relative atomic mass)</th>
<th>$\sigma_{\text{incoh}}$/ barn</th>
<th>$\sigma_{\text{coh}}$/ barn</th>
<th>$\sigma_{\text{abs}}$/ barn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen (1.0079)</td>
<td>80.3</td>
<td>1.8</td>
<td>0.33</td>
</tr>
<tr>
<td>Deuterium (2.0141)</td>
<td>2.0</td>
<td>5.6</td>
<td>0.00</td>
</tr>
<tr>
<td>Carbon (12.011)</td>
<td>0.001</td>
<td>5.6</td>
<td>0.00</td>
</tr>
<tr>
<td>Nitrogen (14.007)</td>
<td>0.5</td>
<td>11.0</td>
<td>1.90</td>
</tr>
<tr>
<td>Oxygen (15.999)</td>
<td>0.001</td>
<td>4.0</td>
<td>0.00</td>
</tr>
</tbody>
</table>

**Table 6.2** Summary of the neutron scattering cross sections for a series of ionic liquids studied. $\sigma_{abs}$ is giving for 2200 m s$^{-1}$ neutrons. 1 barn = $10^{-28}$ m$^2$.

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>$\sigma_{\text{incoh}}$/ barn</th>
<th>$\sigma_{\text{coh}}$/ barn</th>
<th>$\sigma_{\text{abs}}$/ barn</th>
<th>$\sigma_{\text{incoh}}$/ $\sigma_{\text{total}}$(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[NO$_3$]$^-$</td>
<td>0.503</td>
<td>23.00</td>
<td>1.90</td>
<td>2.14</td>
</tr>
<tr>
<td>[N$_{0.01.1}$][NO$_3$]</td>
<td>481.81</td>
<td>50.40</td>
<td>5.78</td>
<td>90.53</td>
</tr>
<tr>
<td>[N$<em>{0.1}$D$</em>{0.1}$][NO$_3$]</td>
<td>247.90</td>
<td>61.80</td>
<td>4.79</td>
<td>80.05</td>
</tr>
<tr>
<td>[N$_{0.01.1}$][NO$_3$]</td>
<td>645.40</td>
<td>59.60</td>
<td>6.44</td>
<td>91.55</td>
</tr>
<tr>
<td>[N$<em>{0.1}$D$</em>{0.1}$][NO$_3$]</td>
<td>486.81</td>
<td>67.20</td>
<td>5.78</td>
<td>87.87</td>
</tr>
</tbody>
</table>

For totally protonated alkylammonium nitrates, the incoherent contribution makes up more than 90% of the total scattering cross section (see **Table 6.2**). However, that situation is influenced by hydrogen-deuterium exchange. The anions give rise to about half of the coherent scattering contribution, which nevertheless, in comparison with the scattering of the total molecule, remains much less intense than the incoherent one. Hence, it is possible to focus on the single particle dynamics of these ionic liquids, and the analysis of the spectra in this thesis is generally based on the assumption that coherent contribution can be excluded from consideration.
6.1.4 Principle of QENS

As seen in Chapter 5 and Equation (5.1), in a QENS experiment the scattering function, $S(Q, \omega)$ is measured. This corresponds mainly to the incoherent signal. In general terms, the incoherent scattering function can be written for ionic liquids as translation, rotational motion on the whole and of different parts, and vibration behaviour of the ions. Assuming no correlation between these motions (their energy scale differs enormously), the dynamic structure factor can be defined as a convolution of the corresponding dynamic structure factor for different types of motions, see Equation (6.2).

$$S_{\text{incoh}}(Q, \omega) = S_{\text{vib}}(Q, \omega) \otimes S_{\text{trans}}(Q, \omega) \otimes S_{\text{rot}}(Q, \omega)$$  \hspace{1cm} (6.2)

Vibrations are usually outside the energy range of QENS experiments. In *quasi-*elastic experiments, the vibrations are considered to contribute only to the intensity through the Debye-Waller factor. Hence, the incoherent scattering in the *quasi-*elastic region is the convolution of the translational (global) and rotational (localised) dynamic structure factors, multiplied by a Debye-Waller factor, Equation (6.3).

$$S_{\text{incoh}}(Q, \omega) = \exp(-Q^2U_{\text{total}}^2)S_{\text{glob}}(Q, \omega) \otimes S_{\text{loc}}(Q, \omega)$$  \hspace{1cm} (6.3)

As the incoherent scattering allows probing of the self-diffusion, and the measured intensity is proportional to the scattering function $S_{\text{incoh}}(Q, \omega)$, Equation (6.2) can be written as Equation (6.4), assuming in a model-independent approach, for simplicity, that each term is considered as independent motions.

$$I_{\text{self}}(Q, t) = I_{\text{vib}}(Q, t) \times I_{\text{trans}}(Q, t) \times I_{\text{rot}}(Q, t)$$  \hspace{1cm} (6.4)

where $I$, is the intensity of the different motions.

6.1.4.1 Vibrations: Debye-Waller factor

Nuclei, even in a rigid crystal, are not stationary. These motions cause a decrease in the intensity of the diffracted beam, as the waves are no longer well in phase, and this effect is a function of temperature. Assuming that vibrations of atoms in a molecule are harmonic and isotropic, the Debye-Waller factor can be expressed by Equation (6.5)

$$\text{DWF} = \frac{1}{3} \exp \left( Q^2 \langle u^2(T) \rangle \right)$$  \hspace{1cm} (6.5)
where \( \langle u^2 \rangle = U \), the mean-square displacement, MSD and it is measured as a function of temperature in the QENS experiment. The Debye-Waller factor represents the contribution of the internal atom vibrations. MSD curves are dominated by vibrational motions, as well as other contributions.

### 6.1.4.2 Analysis of stochastic motions

Neutrons exchange a small amount of energy with the atoms during a single scattering event due to stochastic motion (diffusion and rotation) of the particles.

#### 6.1.4.2.1 Elastic Window Scan

Measurement of the elastic intensity as a function of the temperature is a common tool used to analyse data from QENS spectrometers. It is resembles a DSC scan and it is used to localise transitions. This is used for integrating the elastic window region of a quasi-elastic spectrum. The first step of the QENS study is usually to perform an elastic window scan [216].

#### 6.1.4.2.2 Simple Translational Diffusion

Concerning the different types of stochastic diffusional motions, which can be studied by QENS, the simplest translational motion, \( S_{\text{trans}}(Q, \omega) \), is the continuous long range isotropic translational diffusion. In this case, particles follow Fick’s law [205]. If the diffusion process is treated by assuming that all the diffusion particles start at the origin at time zero, this leads to Equation (6.6) [217].

\[
S_{\text{trans}}(Q, \omega) = \frac{1}{\pi} \frac{\Gamma}{(\Gamma^2 + \omega^2)}
\]

(6.6)

which is a Lorentzian function, and \( \Gamma \) is the half width at half maximum (HWHM; see Figure 6.4), which in this case is \( DQ^2 \), Equation (6.7).

\[
\Gamma = \text{HWHM} = DQ^2
\]

(6.7)

\( D \) (m\(^2\) s\(^{-1}\)) is the diffusion coefficient. The broadening of the curve varies as \( DQ^2 \) as a function of the momentum transfer, \( Q \), and it leads to the determination of the diffusion constant, \( D \). Thus, incoherent neutron scattering provides a direct determination of the diffusion coefficient, but just for small \( Q \) and small energy transfer, \( \omega \) [205]. At higher momentum transfers, the HWHM deviates from a straight line because the system cannot be considered anymore as continuous, this deviation is characteristic of a jump diffusion [218].
Figure 6.4 Scattering law corresponding to the simple translational diffusion model. The half width at half maximum, HWHM, by Fick's law is represented by an arrow, and corresponds to $\Gamma$ [214].

Not all the motions are as simple as the simple translational diffusion, and in many cases the diffusion shows deviations from Fick's Law. Diffusion can be restricted by strong interactions, bonding restrictions, or diffusion happening in jumps. Nevertheless, there are two features aim of this thesis: the dependence of the shape of the quasi-elastic broadening with the temperature, and of its half-width-half maximum, HWHM, as a function of the energy and the momentum transfer.

6.1.4.2.3 JUMP DIFFUSION

In many cases, the experimental diffusion shows deviations from Fick's Law, and so, it cannot be interpreted as simple translational diffusion. Given consideration of the structure, it is anticipated that jump diffusion may occur, and hence other theoretical models are needed. Here are described the most general models to deal with the incoherent quasi-elastic scattering measured data of the alkylammonium nitrates.

In the case of Brownian motion, the diffusion is assumed to happen in infinitely small, elementary jumps, and result in a linear variation of the broadening as a function of $Q^2$. For small $Q$ values, the exact trend of the translational diffusion is observed and it follows the Fick's law. At large values of $Q$, the translational diffusion model does not apply anymore [205]. Different models have been developed for different jump length distributions, for instance, the model of Chudley and Elliott (with a fixed jump length) [219], the Singwi and Sjölander model [220] or the model of Hall-Ross [221].

In the Chudley and Elliott model, an atom is enclosed in a cage by other atoms and remains vibrating on a given site. From time to time, the atom may move rapidly to a neighbouring cage site. In this case, $\Gamma$ reads as in Equation (6.8) [205].
\[
\Gamma = \frac{1}{\tau} \left[ 1 - \frac{\sin(Ql)}{Q} \right] \quad (6.8)
\]

where \( \tau \) is the residence time, and \( l \), the jump length.

In the Singwi and Sjölander model \([220]\), the authors evaluated the differential cross section when an atom oscillates for a mean time, \( \tau_0 \). Then diffuses for a mean time, \( \tau_0 \), changing the type of motion, continuously. In this model, the scattering function is described by Equation (6.9).

\[
S_{\text{trans}}(Q, \omega) = \frac{1}{\pi} \frac{\Gamma}{(\Gamma^2 + w^2)} \quad (6.9)
\]

where \( \Gamma \) is given by Equation (6.10),

\[
\Gamma = \frac{DQ^2}{l + DQ^2\tau} \quad (6.10)
\]

and the diffusion coefficient is directly obtained from \( D = l^2/6\tau \).

The dependence on momentum transfer of the quasi-elastic energy broadenings was also predicted by the model of Hall-Ross \([221]\), in which one-dimensional continuous diffusion is calculated and compared with the predictions of models for diffusion in unbounded media. This model provide a description of quasi-elastic scattering of neutrons by molecules undergoing localised random motions.

6.1.4.2.4 ROTATIONS

The final localised motions that can be studied by QENS are rotations, the last term in Equation (6.2). The tool to investigate whether a particular motion is a rotational motion is the elastic incoherent structure factor, EISF, which is defined as a fall in the elastic intensity as a function of \( Q \), see Equation (6.11).

\[
\text{EISF} = \frac{S_{\text{elastic}}(Q)}{S_{\text{incoherent}}(Q) + S_{\text{quasi-elastic}}^{\text{incoherent}}(Q)} \quad (6.11)
\]

Mathematically, EISF is the area of the elastic curve divided by the total area. For purely translational diffusion, the EISF is everywhere zero except at \( Q = 0 \). For the rotational diffusion of a particle, the EISF is unity at \( Q = 0 \) and falls to a minimum at a specific \( Q \) values. In other words, the shape of the EISF is indicative of the geometry.
of the diffusional process. For instance, for a jump between two sites gives rise to the shape seen in Figure 6.5.

![Image](image_url)

**Figure 6.5** The EISF as a function of the product of the wave vector, $Q$, and the distance, $d$, for a jump between two sites [214].

In contrast, a jump between three sites, as found for a methyl group rotation, gives rise to the profile shown in Figure 6.6. Thus, when rotations occur in the ionic liquids being studied, different (and more complex) models will have to be applied, such as rotational diffusion, diffusion on a sphere, or rotational diffusion on a circle.

![Image](image_url)

**Figure 6.6** EISF as a function of the product of the wave vector, $Q$ for a model of jump among three sites, $N=2, 3, \text{ and } 4$ [222].

### 6.1.4.3 Overall picture

In general, for an atom which diffuses, the incoherent scattering function $S_{\text{inc}}(Q, \omega)$ in the elastic region is separable into a purely elastic component, and a quasi-elastic component. The first term (EISF) provides information on the geometry of the diffusing entity (rotations) and the second (Lorentzian term) information on the time scale of its
diffusion (translation). The Debye-Waller factor represents the contribution of the internal atom vibrations. Also, taking into account the resolution of the instrument, see Equation (6.12).

\[ S'(Q, \omega) = S(Q, \omega) \otimes R(Q, \omega) \]  

(6.12)

where \( R \) is the resolution function applied for the data analysis, and \( S' \) is the real dynamic structure factor, and is a convolution of the theoretical dynamic structure factor and the resolution function. The instrumental resolution sets the lower limit of the time/energy window, below which processes cannot be observed with this instrument.

Although, both Lorentzian and Gaussian shaped profiles can be used to describe the quasi-elastic energy measurements, here (as for other ionic liquids, analysed elsewhere [223]) only Lorentzian solution have been considered. The quasi-elastic broadening of simple profiles follow the general laws of momentum transfer. The quasi-elastic broadening is defined by the FWHM of quasi-elastic profile.

### 6.1.5 QENS of ionic liquids

Inelastic neutron scattering (INS), as seen in Chapter 5, was demonstrated to be a very useful probe of the vibrations of ionic liquids at 4 K. By applying QENS, the opportunity to study the onset of molecular motions and diffusion presents itself. It permits the evaluation of motions for ionic liquids in the fraction of picoseconds to nanoseconds range.

The first study of QENS on ionic liquids was reported in 2003 by Triolo et al. [224], who studied the dynamics of 1-butyl-3-methylimidazolium hexafluorophosphate, \([\text{C}_4\text{mim}]\text{[PF}_6\text{]}\), as a function of temperature in the range 250-320 K. Their results were supported by molecular dynamic simulations. QENS data showed that the dynamics of this salt consisted in (at least) two different processes: A fast process that was measured, and an evidence of a slower process that was unresolved, as it was below the resolution of the instrument. They surmised that the fast process was the result of highly localised librational motions, associated with the hydrogen atoms of \([\text{C}_4\text{mim}]^+\). For such motion, negligible temperature, \( T \), and momentum transfer, \( Q \), dependence was expected. Subsequently, most of the studies have been focussed on neat ionic liquids [217,223b,225], but a few of them are studies of ionic liquids confined in solid host networks, such as ionogels [226] or carbon [223c].
6.2 Experimental

6.2.1 IRIS instrument

To study dynamical processes in the alkylammonium nitrates, QENS experiments at several temperatures were carried out on IRIS. IRIS is a high-resolution quasi and inelastic neutron scattering spectrometer, and also used for long-wavelength diffraction (see Figure 6.7). It is an inverted or indirect geometry spectrometer, such that neutrons scattered by the sample are energy-analysed by means of Bragg scattering from two crystal-analyser arrays. The two analysers (pyrolytic graphite and muscovite mica) can work simultaneously, allowing high resolution over wide energies and momentum transfer ranges. In common with the TOSCA instruments described in Section 5.2.2, the time-of-flight technique is used for data analysis. Further description of the instrument can be seen in the Appendix C3.

Figure 6.7 Schematic of the IRIS spectrometer, and its principal components [200].

6.2.2 Sample preparation

The cylindrical sample cans used on IRIS are made of aluminium. For alkylammonium nitrate samples, the can used was 55 mm high by 24 mm of diameter (see Figure 6.8). A hollow cylindrical insert is placed inside, resulting in an annular cross section. This sample geometry is a clear advantage compared to the flat can, as there are no edge effects that could influence the measurements. Also, multiple scattering is avoided by this annular shape. As these samples are solids, the easiest way to introduce them into the can is to load them into an aluminium foil sachet first. Due to
the fact that the ionic liquids under study are highly hygroscopic, the preparation of the sachet, and the sample loading, were carried out in a dinitrogen-filled glovebox. An indium-wire seal was also used due to the air-sensitive nature of the samples. The two samples holders were then secured with small screws.

![Figure 6.8 A separated IRIS cell.](image)

The sample should cover as much of the beam area as possible. Since the width of the can is bigger than that of the beam, solid samples should be loaded into a sachet, and this positioned in the centre of the can before assembly. Once the sample was loaded in the can and securely seal, the cell was removed from the glovebox. It was then connected to the centre-stick. A correct alignment between the beam direction and the sample can was assured by manual adjustment. The stick is inserted into the cryostat, as shown in Figure 6.9. The IRIS sample loading-area is shown in Figure 6.10.

![Figure 6.9 IRIS centre-stick (left); and centre-stick inserted in the cryostat (right).](image)
6.2.3 During a QENS experiment
During \textit{quasi}-elastic neutron scattering experiments, the scattered neutrons are analysed by means of Bragg scattering. IRIS offers a selection of a particular analyser reflection, hence, resolution. The analyser used in these experiments was PG002, pyrolytic graphite, which provided an energy resolution of 17 µeV (FWHM). The efficiency of the detectors was calibrated by measuring a vanadium sample. The vanadium spectra were also used as the resolution function for the instrument. For the selected wavelength of incident neutrons, the dynamic range amounted to \([-2.0 \rightarrow 2.0]\) meV. Fifty detectors, covering the \(Q\)-range 0.5-2.0 Å, provided a moderate momentum transfer resolution. In addition to scattering data, the instrument records the neutron diffraction pattern for the sample.

6.2.4 Data reduction
The QENS method allows the derivation of the dynamical structure factor \(S(Q, \omega)\). IRIS provides 2D-data sets, where intensity counts depends on the time, when a neutron is registered at a detector, and the angle of this detector. Data reduction is needed to compute the dynamic structure factor, \(S(Q, \omega)\), which is independent of the instrument parameters, and depends only on the dynamics of the sample measured. The data reduction includes:
Conversion of time-of-flight to energy transfer.

Grouping the spectra and conversion of the detector angles into momentum transfer values, $Q$.

Correcting the sample container scattering, and multiple scattering.

The reduction of the IRIS data was performed using Mantid [227], and then the output was used for the analysis of the spectral shapes and measured peak widths, which then could be compared to possible theoretical models in a subsequent study.

### 6.2.4.1 Energy transfer [216]

The first step of the data reduction is the conversion of the time-of-flight data to energy transfer. The flight path and the scattering angles for IRIS are fixed, as illustrated in Figure 6.11. If the distance from the moderator (M) to the sample (S) is $L_1$, and time-of-flight is $t_1$ and secondary distance from the sample (S) to the detector (D) is $L_2$ and time of flight is $t_2$, then the final energy detected by any detector is given by Equation (6.13).

$$E_f = \frac{1}{2}m_n v^2 = \frac{1}{2}m_n \left( \frac{L_2}{t_2} \right)^2 \quad (6.13)$$

where $v$ is the velocity of the neutron, and $m_n$ is its mass.

![Figure 6.11 Scheme of the operation of IRIS.](image)

This final energy can be also written as a function of angles and d-spacing by Equation (6.14).

$$E_f = \frac{1}{2} \left( \frac{p^2}{m_n} \right) = \left( \frac{1}{2m_n} \right) \left( \frac{h}{\lambda} \right)^2 = \left( \frac{1}{2m_n} \right) \left( \frac{h}{2d \sin(\theta)} \right)^2 \quad (6.14)$$
where $\lambda$ is the wavelength of neutron, $d$ is the $d$-spacing of the crystal analyser, and $\theta$ is the angle of reflection. As $L_2$, $d$, and $\theta$ are known parameters, $t_2$ can be easily calculated by Equation (6.15).

$$t_2 = \frac{2m_nL_2d \sin(\theta)}{h}$$ (6.15)

Thus, the energy transfer, $\Delta E$, gained or lost, can be calculated from Equation (6.16).

$$\Delta E = E_i - E_f = \frac{\hbar}{2m_n} \left[ \left( \frac{L_1}{t-t_2} \right)^2 - \left( \frac{L_2}{t_2} \right)^2 \right]$$ (6.16)

### 6.2.4.2 Momentum transfer, $Q$

The momentum transfer, $Q$, can be also determined by the time-of-flight data and the IRIS instrument parameters, as seen in Figure 6.12.

![Figure 6.12 Scheme of the exchange of momentum in the interaction between the neutron and the nucleus [222].](image)

The conservation of linear momentum is given in Equation (6.17):

$$Q = k_i - k_f$$ (6.17)

where $k_i$ is the wave vector of the incident neutron from the moderator, and $k_f$, is the wave vector of the scattered final neutron arriving at the detectors. Hence, the energy conservation principle is redefined by Equation (6.18).

$$\left( \frac{\hbar^2 k_i^2}{2m_n} \right) - \left( \frac{\hbar^2 k_f^2}{2m_n} \right) = E_i - E_f = \Delta E$$ (6.18)

So, from Figure 6.12 and Equation (6.17), $Q$ can be defined by Equation (6.19).
\[ Q^2 = k_i^2 - 2k_i k_f \cos(\phi) + k_f^2 \]  \hspace{1cm} (6.19)

Measurement can be improved by collating data from groups of detectors. To summarise, a neutron scattering process is associated with a set of values of \( Q \) and energy. The main objective of a quasi-inelastic neutron scattering experiment is to measure scattered intensities as a function of \( Q \) and \( \Delta E \). A scheme of the QENS experiments is shown in Figure 6.13 [209].

![Diagram of QENS setup](image)

**Figure 6.13** QENS setup [209]. The momentum of the incident (\( k_i \)) and scattered (\( k_f \)) neutrons, the corresponding (elastic) change in momentum (\( Q \)), which is related to the scattering angle (2\( \phi \)), and the energy transferred in the quasi-elastic scattering event (\( \Delta E \)) are indicated. Measurement statistics can be improved by averaging data from groups of detectors (\( Q \) groups). A schematic quasielastic scattering spectrum is indicated from one of the detectors, part of this signal is elastic (that is, \( \Delta E = 0 \)) [209].

### 6.3 Results and discussion

This section contains the results of the QENS studies on methylammonium nitrate, and its deuteriated analogue. The data analysis was performed with the help of Dr. Mukhopadhyay.
6.3.1 Methylammonium nitrate, \([\text{N}_0\text{O}_1\text{O}_1\text{][NO}_3]\)

Methylammonium nitrate, \([\text{N}_0\text{O}_1\text{O}_1\text{][NO}_3]\), is a salt formed by the neutralisation of methylamine with nitric acid. This ionic liquid was first used as an explosive during World War II [228], due to its similar hypergolic properties to ammonium nitrate. The goal of this work is the fundamental understanding of the dynamics of alkylammonium nitrates, starting with the most structurally simple example. The structure of this salt is shown in Figure 6.14.

![Figure 6.14 Structure of \([\text{N}_0\text{O}_1\text{O}_1\][\text{NO}_3]\).](image)

6.3.1.1 Synthesis and purification

The synthesis and purification of \([\text{N}_0\text{O}_1\text{O}_1\text{][NO}_3]\) was carried out by Dr. Stana [106]. Nitric acid (65 wt % aqueous solution; 67.28 g; 290 mmol) was added dropwise to a slight excess of methylamine (40 wt % aqueous solution; 25 g; 322 mmol) in a one-neck one-litre round-bottomed flask, cooled to -78 °C with dry ice and propanone. The flask was kept closed after each acid addition, and cooled by adding more dry ice when necessary. The reaction is very exothermic; thus, maintaining the low temperature is very important. After all the acid had been added, the mixture was allowed to warm to room temperature, over approximately two hours, and then stirred at room temperature for one hour. Water was removed by the freeze drying technique (see Appendix B1), at 0.03 mbar pressure. After a twelve hours cycle, the water content was checked by Karl Fischer titration (see Appendix B4). The freeze drying cycle was repeated three times, until no decrease in the water content was observed by Karl Fischer titration. The purity of the salt was confirmed by IR, \(^1\text{H}\) and \(^{13}\text{C}\) NMR. The resulting salt, \([\text{N}_0\text{O}_1\text{O}_1\text{][NO}_3]\) is hygroscopic, and therefore was kept under dinitrogen atmosphere, in the glovebox.
6.3.1.2 Variation of the scattering function with the temperature.

The QENS spectrum of the intensity against $S(Q,\omega)$ for $[N_{0001}]$[NO$_3$] in the range from -240 °C to 115 °C is shown in **Figure 6.15**.

![Figure 6.15](image)

**Figure 6.15** The normalised QENS spectrum of the intensity of the scattered neutron versus $S(Q,\omega)$, from -240 °C to 115 °C, for $[N_{0001}]$[NO$_3$].

From the variation of $S(Q,\omega)$ with temperature for $[N_{0001}]$[NO$_3$], the molecular motions can be seen to be temperature dependent. The energy resolution of the spectrometer is 0.017 meV, which is the minimum measurable by the IRIS instrument. **Figure 6.15** shows that this experiment is in the range that can be reliably measured by this instrument. Analysing the change of the curve with temperature, it can be seen that, at low temperature (-240 °C, and -140 °C), no motions can be detected, and the signal is effectible elastic. With increasing temperature, a broad quasielastic component is observed, due to the sum of the motions of all the atoms, mostly hydrogens, as its incoherent scattered contributions is higher in comparison with other atoms. An expanded view of **Figure 6.15** is shown in **Figure 6.16**.
The differential scanning calorimetry, indicating phase transitions of \([\text{N}_0\text{O}_1]\text{[NO}_3\text{]}\), are shown in Figure 6.17.

Figure 6.17 Differential Scanning Calorimetry results for \([\text{N}_0\text{O}_1]\text{[NO}_3\text{]}\) at a standard heating and cooling rate of 5°C min\(^{-1}\).
As seen in Figure 6.17 on the heating cycle, [N\textsubscript{0.0.1}]NO\textsubscript{3} has a solid-solid phase transition at 77.7 °C before melting at 108.9 °C, with an endothermic effect quite large (10.85 KJ mol\textsuperscript{-1}) compared to its melting transition (4.79 KJ mol\textsuperscript{-1}). [N\textsubscript{0.0.1}]NO\textsubscript{3} showed possible characteristics of a plastic crystal. Plastic crystals were first reported by Timmermans [229]. He observed that one of the key features of compounds that exhibited plastic phases was that the final entropy of melting, \(\Delta S_f\), of these compounds was usually less than 20 J K\textsuperscript{-1} mol\textsuperscript{-1}. This fact is known as Timmermans’ criterion for the existence of a plastic crystal phase. However, it has been seen that some ionic plastic crystalline phases may not follow this rule [230]. In any case, the final entropy of melting, \(\Delta S_f\) for [N\textsubscript{0.0.1}]NO\textsubscript{3} was found 12.6 J K\textsuperscript{-1} mol\textsuperscript{-1}.

A closer view of \(S(Q,\omega)\) in Figure 6.16, shows there are quasi-elastic signals at temperatures below the melting point at 108.9 °C. At temperatures below 20 °C, practically nothing is moving. From 20 °C to 70 °C, (pink and light blue lines, respectively) there is some motions occurring inside the material, as indicated by the change in the shape of the curve between these two temperatures. As seen in the DSC (Figure 6.17), possible due to solid-solid transition mentioned above. There is a changing dynamics before melting at 108.9 °C, showing by the gap in the quasi-elastic signal (between the red line, at 109 °C and the black line at 115 °C. Molecular motion become faster indicated by the progressive broadening of the quasielastic signal with the temperature. There is no motion changing during melting because between 70 °C and 109 °C there is an overlapping in quasielastic signal (light blue, blue, green and red colour lines). At 115 °C the completely melted [N\textsubscript{0.0.1}]NO\textsubscript{3} shows quasielastic broadening.

The instrument collected neutron diffraction pattern for the sample simultaneously with the QENS data. This strongly suggested that, between -240 °C and +100 °C, there were no solid-solid phase transitions, so that any detected motion was no related to positional changes either the cation or the anion.

6.3.1.3 Variation of the scattering function with the temperature at fixed values of \(Q\).

Figure 6.18 and Figure 6.19 show the scattered intensity as a function of the energy transfer, to or from the incident beam. Spectra are shown for different temperatures, at two fixed values of \(Q\): \(Q = 0.48\ \text{Å}^{-1}\) for Figure 6.18, and \(Q = 1.6\ \text{Å}^{-1}\) for Figure 6.19. \(Q\) is determined by the scattering angle, as seen in Section 6.2.4.2. To improve the measured data, the detectors were grouped by 15 (see Figure 6.13), measuring values of \(Q\) from 0.4 to 1.8 \(\text{Å}^{-1}\).
Figure 6.18 Scattering data for [NO₃][NO₃], from -240 °C to 115 °C, at $Q = 0.48 \text{ Å}^{-1}$.

Figure 6.19 Scattering data for [NO₃][NO₃], from -240 °C to 115 °C, at $Q = 1.6 \text{ Å}^{-1}$.
As the temperature increases, the scattering intensity of the elastic line decreases due to the Debye-Waller factor. In other words, a fraction of the elastic scattering intensity is redistributed to the inelastic vibrational modes. Also, a significant reduction of the elastic intensity with the temperature can be due to a freezing or melting transition, which means that the dynamic became faster due to the movement of the species after a certain temperature. It leads to a more quasi-elastic signal, which means that the motions are more localised. This effect is more pronounced at high values of $Q$.

6.3.1.4 Variation of the scattering function with values of $Q$ at fixed temperatures

QENS measurement of intensity against energy transfer (meV), for groups of 15 detectors, corresponding to different momentum transfer, $Q$ for $[N\_0\_0\_0\_1][NO\_3]$ are shown in Figures 6.20-6.24.

![Scattering data for molten $[N\_0\_0\_0\_1][NO\_3]$ at 115 °C.](image-url)
Figure 6.21 Scattering data for solid \([N\textsubscript{0 0 1}][\text{NO}_3]\) at 70 °C.

Figure 6.22 Scattering data for solid \([N\textsubscript{0 0 1}][\text{NO}_3]\) at 20 °C.
If $Q$ is dependent on temperature, this implies that diffusion is occurring, and that the molecule is moving in one direction. In contrast, if $Q$ is independent of the
temperature, then the motions are localised (as opposed to diffusive), and correspond to rotations. For \([\text{N}_0\text{O}_0\text{N}][\text{NO}_3]\), at 115 °C and 70 °C, Figure 6.20, and Figure 6.21, respectively, there is a notable dependence of \(Q\) upon \(T\), defining the motion as diffusive. At +20 °C (Figure 6.22) and -20 °C (Figure 6.23), the dependency of \(Q\) on temperature decreases, which means that the sample exhibits less diffusion than at higher temperatures, as expected. At -140 °C (Figure 6.24), there are no motions, as was seen in Figure 6.15 and Figure 6.16 (where from -240 °C to -140 °C, there was no change in the quasi-elastic broadening curve).

6.3.1.5 Elastic intensity

The elastic incoherent structure factor, EISF, gives information about the motions. As seen in Figure 6.25, at low temperatures, nothing is moving. The system is static. There is only the Debye Waller factor and hence vibrations of the atoms on the lattice sites. As the temperature increases, the intensity of the elastic line will be reduced. If the intensity decreases to zero, it would mean that all motions have been quenched.

![Figure 6.25 Elastic intensities obtained from -240 °C to 120 °C for [N\(_0\)O\(_0\)N][NO\(_3\)]: (a) cooling (black line), and (b) heating (red line).](image)

In the heating from 70 °C to 100 °C, there is a radical change in the slope of the line, indicating that the molecules are moving. This correlates well with the DSC, which shows a pre-melting peak at 77 °C (see Figure 6.17). In the cooling from 70 °C to 20 °C (Figure 6.25), there is another change in the slope corresponding to the plastic phase, also observed by the DSC (see Figure 6.17). So to summarise, in addition to the DWF, with the increasing temperature, the elastic intensity decreases, and quasi-
elastic signal increases, which means the molecules are moving. In the case of methylammonium nitrate, a molecular motion is activated between 20 °C and 100 °C, probably corresponding to a proton transfer from the cation to the anion.

6.3.1.6 Diffusion dynamics

6.3.1.6.1 Analysis of the liquid state
For a temperature above the melting point, 108.9 °C, the dynamics of \([\text{N}_0\text{001}]\text{[NO}_3\text{]}\) became more diverse. As a first step, the \(S(Q, \omega)\) spectra at \(Q = 0.48 \text{ Å}^{-1}\) (Figure 6.26) and \(Q = 0.96 \text{ Å}^{-1}\) (Figure 6.27), were determined and analysed with an appropriate fitting model (see section 6.1.3 and 6.2.4); the residuals are given at the bottom of each figure.

For the data analysis, the experimental data at particular selected \(Q\) values (black line) were fitted by:

- A delta function centred at zero energy transfer, describing the elastic scattering.
- Two Lorentzians that describe very well the measured QENS spectra.
The solid blue line corresponding to $S(Q, \omega)$ is the model consisting of the convolution of the instrument resolution with an elastic peak.

![Graph](image)

**Figure 6.27** Upper panel: QENS spectrum of [N\textsubscript{001}][NO\textsubscript{3}] sample, measured at 115 °C and $Q = 0.96$ Å\(^{-1}\), together with the curve fitting (blue line). The dashed functions (red dashed line), are two Lorentzians and a delta function, of which the model is composed. Lower panel: the residuals between the fitted curve and the measured intensities.

The data sets presented and compared in **Figure 6.26** and **Figure 6.27** demonstrated that the measured quasi-elastic spectra of [N\textsubscript{0001}][NO\textsubscript{3}] can be satisfactorily described as a superposition of two Lorentzian curves and a delta function. The Lorentzian 1 contribution tends to $I = 0$ at small $Q$-values (see **Figure 6.26**), in the same way as for long-range diffusional processes.

Above the melting point, the measured data have the characteristic shape of a liquid spectra. Even though both, methyl group rotations and the localised proton dynamics of -NH\textsubscript{3} persist in the liquid phase, two new mechanism (as indicated by two Lorentzians) dominate the diffusion dynamic above the melting point for [N\textsubscript{0001}][NO\textsubscript{3}].

6.3.1.6.2 FROM 20 °C TO 108.9 °C

From 108.9 °C to 20 °C, the representative quasi-elastic spectra, was also modelled by two Lorentzians, and a delta function. This suggested that, even though, the sample is not molten a molecular motion is activated between 20 °C and 100 °C,
probably corresponding to a proton transfer from the cation to the anion, in agreement with what was found in Section 6.3.1.5)

6.3.1.6.3 ANALYSIS OF THE SOLID PHASE

To study the nature of the low-temperature processes, similar analysis than in Section 6.3.1.6.1 was carried out for \([\text{N}_0\text{O}_0\text{O}_1\text{][NO}_3\text{]}\) at -20 °C. \(S(Q,\omega)\) spectrum at \(Q = 0.48\) Å\(^{-1}\) and \(Q = 0.96\) Å\(^{-1}\) are shown in Figure 6.28 and Figure 6.29.

![Figure 6.28 QENS spectrum of \([\text{N}_0\text{O}_0\text{O}_1\text{][NO}_3\text{]}\) sample, measured at -20 °C and \(Q = 0.48\) Å\(^{-1}\), together with the curve fitting (blue line). The dashed functions (red dashed line), are a Lorentzian and a delta function, of which the fitted curve is composed. Lower panel: the residuals between the fitted data and the measured intensities.]
Figure 6.29 Upper panel: QENS spectrum of $[N_{0001}][NO_3]$ sample, measured at -20 °C and $Q = 0.96 \, \text{Å}^{-1}$, together with the fitted curve (blue line). The dashed functions (red dashed line), are a Lorentzian and a delta function, of which the fitted curve is composed. Lower panel: the residuals between the model and the measured intensities.

Figure 6.28 and Figure 6.29 show that the scattered intensity as a function of energy (transferred to or from the incident neutron beam owing to movement of the hydrogen nuclei within $[N_{0001}][NO_3]$) is well modelled by a fitted curve comprising one Lorentzian and an elastic peak (delta function), convoluted with the instrument resolution function (measured using a vanadium sample, as seen in Section 6.2.. No additional modes of motion were needed to describe the measured data at -20 °C, Also, from -240 to -20 °C, the same fitted curve, with only one type of motion (one Lorentzian) was obtained for the measured data of $[N_{0001}][NO_3]$. Results showed that the intensity of the elastic contribution, given by the delta function, increased at lower temperatures. A possible explanation is that if the protons of the $[N_{0001}][NO_3]$ became immobile on the time scale of the QENS measurement, thus contributing only to the elastic signal, it is expected that the fraction of the elastic scattering fraction will increase [223a].
6.3.1.6.4 **FULL WIDTH HALF MAXIMUM OF THE LORENTZIAN FUNCTION**

Once, the number of the motions has been established by the quasi-elastic broadening spectra for \([\text{N}_0\text{.001}][\text{NO}_3]\) at different temperatures, the next step is to identify the motions associated with each component. This is given by the full width half maximum (FWHM) of each Lorentzian as a function of the momentum transfer square \((Q^2)\) plotted for a range of temperatures (see Figure 6.30, Figure 6.31 and Figure 6.32).

**Figure 6.30** FWHM of the Lorentzian 1 function used to fit the QENS data for \([\text{N}_0\text{.001}][\text{NO}_3]\) as a function of momentum transfer squared from 115 °C to 20 °C.

**Figure 6.31** Parameters of the 115 °C data for \([\text{N}_0\text{.001}][\text{NO}_3]\).
As seen in Section 6.3.1.6.1, and Section 6.3.1.6.2 the QENS data showed that the dynamics of \([\text{N}_0\text{O}_0\text{I}]\text{[NO}_3\text{]}\) consisted of two different processes from 115 °C to 20 °C:

**Lorentzian 1 (Figure 6.30):** At 115 °C, above the melting point (109 °C), the Lorentzian 1 contribution tends to zero at small \(Q\)-values (see Figure 6.31), in the same way as for long-range diffusional processes. At 109 °C, the dynamic of the salt started to change, indicated by a different trend in the plot for this temperature. Below the melting temperature, the shape of the Lorentzian 1 contribution is definitively different and this dynamic is maintained to 20 °C, which is indicated from the shape of the measured data.

**Lorentzian 2 (Figure 6.32):** The width of Lorentzian 2 exhibits a less pronounced temperature dependent character at all temperatures investigated. It also shows non-zero values of FWHM at low \(Q\)-values, which is consistent with localised motions.

As Section 6.3.1.6.3, at temperatures below 20 °C, the data can be successfully fitted using a simple Lorentzian. The full width half maximum (FWHM) of each Lorentzian as a function of the momentum transfer square (\(Q^2\)) for at -20 °C can be seen in Figure 6.33.

**Figure 6.32** FWHM of the Lorentzian 2 function used to fit the QENS data for \([\text{N}_0\text{O}_0\text{I}]\text{[NO}_3\text{]}\) as a function of momentum transfer squared from 115 °C to 20 °C.
From Figure 6.33, at low temperature, the motion is characteristic of localisation as opposed to translation. The QENS study of $[N_{0\,0\,1}][NO_3]$ at -20 °C Figure 6.33 provides a profile revealing that FWHM is effectively invariant with the values of $Q^2$. When this profile is compared with the possible mechanisms of jump diffusion for proton transfer (see Section 6.1.4.2) that are summarised in Figure 6.34, it would appear that the mechanism operating for $[N_{0\,0\,1}][NO_3]$ most closely resembles the Hall-Ross model.

Burankova et al. [231] reported QENS data for triethylammonium triflate. They also found a jump diffusion model, although the shape of their curves differed (see Figure 6.35). This is not surprising since it has been demonstrated in Chapter 5 that trialkylammonium salts form stronger and more localised hydrogen bonds than alkylammonium salts, which form weaker, bifurcated, extended hydrogen-bonded networks. In addition, the triethylammonium salt will have a large contribution from the motions of the hydrogen atoms in the alkyl chains that may influence the total dynamic contribution.
Figure 6.34 Jump diffusion model for quasi-elastic neutron scattering data. TD is translational diffusion, CE is the Chudley and Elliott model, HR is the Hall-Ross model and the SS is the Singwi and Sjölander model [218].

Figure 6.35 Comparison of the fit results for the line width of the slow diffusional process obtained for the completely protonated triethylammonium triflate (dashed lines) and partially deuterated samples (dots) [231].
6.3.2 Deuteriated methylammonium nitrate

With respect to the internal dynamics of \([\text{N}_0\text{O}_0\text{O}_1]^+\), one may expect proton contributions from the methyl group, and contributions from the protons of the -\(\text{NH}_3\). In order to separate out the two contributions, its partially deuteriated salt \([\text{N}_D\text{D}_1\text{D}_1]\text{[NO}_3\text{]}\), was also investigated.

6.3.2.1 Deuteriation of \([\text{N}_0\text{O}_0\text{O}_1]\text{[NO}_3\text{]}\)

Deuteriated methylammonium nitrate was prepared following the same procedure described in Section 4.2.1.

6.3.2.2 Variation of the scattering function with the temperature.

The QENS spectrum of the intensity against \(S(Q,\omega)\) for \([\text{N}_D\text{D}_1\text{D}_1]\text{[NO}_3\text{]}\), in the range from -240 °C to 109 °C is shown in Figure 6.36 and Figure 6.37.

![Figure 6.36](image)

Figure 6.36 The normalised QENS spectrum of the intensity of the scattered neutron versus \(S(Q,\omega)\), from -240 °C to 109 °C, for \([\text{N}_D\text{D}_1\text{D}_1]\text{[NO}_3\text{]}\).
From the variation of $S(Q,\omega)$ with temperature for $[\text{ND}_3\text{ND}_1][\text{NO}_3]$, the molecular motions can be seen to be temperature dependent. Analysing the change of the curve with temperature, it can be seen that, at low temperature (-240 °C, -140 °C and -20 °C), no motions can be detected, and the signal is effectively elastic. With increasing temperature, a broad quasi-elastic component is observed for $[\text{ND}_3\text{ND}_1][\text{NO}_3]$, with the same type of motion from 20 °C to 100 °C. Finally, at 109 °C and 115 °C the signal, which is practically the same at both temperatures, is classically quasi-elastic.

In the case of $[\text{N}_0\text{N}_0\text{N}_1][\text{NO}_3]$ (see Figure 6.15), the signal at the melting temperature (109 °C) lies at the same energy transfer as this at 100 °C. A comparison of the QENS spectrum of the intensity of the scattered neutron versus $S(Q,\omega)$ for $[\text{N}_0\text{N}_0\text{N}_1][\text{NO}_3]$ and $[\text{ND}_3\text{ND}_1][\text{NO}_3]$ between 115 °C and 100 °C can be seen in Figure 6.38 and Figure 6.39. This indicates that, although the melting temperature for both salts given by DSC are the same, there must be slightly different dynamic associated with the melting process.
Figure 6.38 The normalised QENS spectrum of the intensity of the scattered neutron versus $S(Q,\omega)$, at 100 °C, 109 °C, and 115 °C for $[\text{N}_0\text{O}_0\text{O}_1]\text{[NO}_3\text{]}$.

Figure 6.39 The normalised QENS spectrum of the intensity of the scattered neutron versus $S(Q,\omega)$, at 100 °C, 109 °C, and 115 °C for $[\text{N}_0\text{D}_0\text{D}_1]\text{[NO}_3\text{]}$. 
6.3.2.3 Elastic intensity

The elastic intensity gives information about the motions. The elastic intensities obtained from -240 °C to 115 °C for [ND₃][NO₃] are shown in Figure 6.40. Upon heating from -240 °C to 0 °C (black line), the system is static. At 0 °C, there is a radical change in the slope of the line, indicating an onset of motions. From 20 °C to 100 °C, the change in the slope becomes more gradual. From 100 °C to 109 °C, there is again a rapid change in the gradient, indicating the onset of melting. This correlates well with the trend seen in Figure 6.37 and Figure 6.39. A comparison of the elastic intensities from -240 °C to 115 °C for [ND₃][NO₃] and [ND₃][NO₃] is shown in Figure 6.41.

As seen for the protonated salt, see Section 6.3.1.5, low temperatures motion are associated to localised motions. By transforming -NH₃ into -ND₃, the only motions available for study are those due to the methyl group. As in the deuteriated methylammonium nitrate, no motion was observed, from -240 °C to 0 °C, and yet in the protonated analogue, significant motions were observed, it is clear that the rotations of the methyl group is not active in this region, but motions associated with -NH₃ are active. This has been observed in [223a].

![Figure 6.40](image_url) Elastic intensities obtained from -240 °C to 115 °C for [ND₃][NO₃]: (a) cooling (red line), and (b) heating (black line).
Figure 6.41 Elastic intensities obtained from -240 °C to 115 °C for (a) [NdD1][NO₃]: cooling (red line), and heating (green line), and (b) [Nd0.0.1][NO₃]: cooling (blue line), and heating (pink line).

6.4 Conclusions

The dynamics of methylammonium nitrate both in the liquid state and the solid state were studied in this thesis. The measurements were performed using an indirect geometry spectrometer, IRIS, and showed that above the melting point (109 °C), unsurprisingly, the motions are predominantly translational. Between 100 °C and 20 °C, the solid was characterised by the presence of restricted translational motions (jump diffusion) and localised motions, such as methyl group rotation. At lower temperatures, from 20 °C to -140 °C, the motions become purely localised. In this preliminary study, the best interpretation suggests that the presence of a jump model most accurately represents the diffusive motion.

The results of the dynamical study of the totally protonated and N-deuteriated sample were compared for all temperatures. Although a future, more detailed, analysis is required for a deeper understanding, it can be seen that there must be slightly different dynamic associated with the melting process for [NdD1][NO₃] with respect to [Nd0.0.1][NO₃], indicated by the variation of $S(Q,\omega)$ with temperature between 100 °C and 115 °C. The study of [CH₃ND₃]⁺, were compared to [CH₃NH₃]⁺, allow the motions of the ammonium moiety to be distinguished from the motions of the methyl group. N-H seems to dominate the general contribution of localised motions below 0 °C, by a proton jump mechanism where the proton is transferred from the cation to the anion via the hydrogen bond.
7 Neural Network Analysis
In the present chapter, the data reported in Chapter 3 for both pure ionic liquids and their binary mixtures were analysed using an artificial neural network (ANN), in order to probe the effect of composition, temperature, and molecular weight on their viscosity, conductivity, and density.

7.1 Introduction

As seen in previous chapters, the purity of the ionic liquids is essential in order to assure a high quality of data. When impurities such as water or halides are present in ionic liquids, the values of these properties are strongly influenced [60]. Prior to the usage of ionic liquids in industry, the evaluation of their thermophysical properties is necessary to choose the right ionic liquid for the process. In order to check the validity of the obtained physicochemical data, reliable models are required. Additionally, when full sets of properties are available, an evaluation of the purity of ionic liquids could be performed using these mathematical models (the purity of an ionic liquid can be indirectly assessed by comparison of the estimated value obtained by the mathematical model and the experimental one).

Therefore, development of mathematical models that are able to work with ionic liquids is essential in order to use ionic liquids in industrial processes [232]. Artificial neural networks (ANNs) have proven to be a useful mathematical model, as an alternative to other used methods [233]. ANNs are mathematical tools known for establishing non-linear relationships between dependent and independent variables in large databases. ANNs are restricted to the database range, which must contain enough data points with an acceptable experimental and statistical quality, as well as an adequate distribution in the whole chosen range to maximise the statistical performance [234]. ANNs are also strongly affected by their topology and the information which is provided initially. In other words, both the quality and accuracy of the model will highly depend on the independent variables selected and their relation with the estimated dependent ones [235]. Therefore, changing the number of independent variables, or the particular information provided by them, will affect the final efficiency of ANN.

Torrecilla and co-workers presented computational models of gas solubility in ionic liquids [236]. They used both neural network- and multiple regression-based models for forty-eight ionic liquids and twenty-three industrially important gases. Molecular polarisabilities and special Lewis acidity and basicity descriptors were calculated for the ionic liquid cations and anions, as well as for the gaseous solutes, and these were used as input parameters. The quality of fit “observed versus predicted Henry’s law constants” was especially good for the neural network model.
Torrecilla et al. also developed an optimised ANN model for predicting the melting point of a group of ninety-seven imidazolium salts with various anions [237]. Each cation and anion in the model was defined using molecular descriptors. This model had a mean prediction error of 1.30%, a regression coefficient of 0.99 and a mean $P$-value of 0.92. The ANNs prediction performance depended mainly on the anion size. Specifically, the prediction error decreased as the anion size increased.

Rothenberg and coworkers also attempted the prediction of the melting points of ionic liquids [238]. A descriptor modelling approach for two separate sets of ionic liquids was presented with cations and the anions modelled separately, using quantitative structure-property relationships. Both models involved constitutional, topological and geometric descriptors as well as quantum mechanical ones. This approach gave access to $(n \times m)$ ionic liquids using only $(n + m)$ calculations. The protocol was tested and validated with good correlations and predictions for the melting points of two sets, comprised of 22 and 62 imidazolium-based ionic liquids. The degree of sphericity (a measure of asymmetry) happened to be the most important variable for the anion, while for the cation the main descriptors turned to be three radial distribution functions that described three different sections in the cation (see Figure 7.1). These characterised the ionic interactions, the symmetry-breaking region, and the length of the side chains.

![Figure 7.1](image)

**Figure 7.1** An optimised structure of a 1-methyl-3-octadecylimidazolium cation showing the structural regions that are important for determining the melting point [238].

Torrecilla et al. developed and evaluated neural network models for the prediction of the liquid-liquid equilibrium data and aromatic/aliphatic selectivity values [239]. Four ternary systems composed of toluene, heptane, and the ionic liquids 1-ethyl-3-methylimidazolium ethylsulfate, or 1,3-dimethylimidazolium methylsulfate were investigated at 313.2 and 348.2 K at 0.1 MPa pressure.
7.2 Artificial neural network (ANN)

The work described in the rest of this chapter was performed by Prof. José Torrecilla from the Complutense University of Madrid using the data generated in Chapters 3 of this thesis.

Mathematical models are a useful tool to evaluate and create predictive patterns to determine the physicochemical properties of ionic liquids. In order to estimate the density, viscosity, and conductivity properties of the alkylammonium nitrates studied, a calculation process was followed using the temperature, the composition of the mixture, and the molecular weight as independent variables of the model. The mathematical model used is based on a supervised artificial neural network model, which employs non-linear interpolation to perform the calculations, known as a multilayer perceptron (MLP). As they are supervised algorithms, they require target data (labelled data) to be trained properly [240].

Multilayer perceptrons, as their name suggests, are layered algorithms. They possess three kinds of layers, which are the input, hidden, and output ones. The input layer is formed by nodes, which are only in charge of introducing the independent variables of the model. The hidden and output layers are formed by neurons, which are in charge of the calculations of the system. The number of neurons in the output layer are equivalent to the number of dependent variables in the system (in this case, equivalent to the number of properties estimated), whereas the hidden neuron number (HNN; *vide infra*) and hidden layer number must be correctly optimised (due to the size of the databases: the number of hidden layers was set to one in all cases, to avoid over-fitting) [241].

Once the number of units (nodes and neurons) in each layer, or network topology, have been defined, the training process of the multilayer perceptrons may begin. The objective of this process is to optimise the weights that are contained within the model. There will be as many weights as connections between units in neighbouring layers (node-hidden neurons and hidden neurons-output neurons). The correct optimisation of the weights is vital for multilayer perceptrons to operate correctly, and this process is carried out during a series of training cycles, or epochs. These cycles modify the values of the weights with the goal set to lower the error of the estimation for a training dataset (better property estimations in this case). This error may potentially reach zero if no precautions are followed, leading to an over-fit model. For this reason, the total database is initially divided into training and verification datasets (usually 80:20), where the former is used to modify the weights, and the latter to verify that the multilayer perceptrons can perform well with samples that are not involved in this process. When the error for the verification dataset rises
during six straight epochs, the training process is stopped, and the model is optimised [242].

The training function of the multilayer perceptron is in charge of the calculations which modify the weights. The one chosen here was the Bayesian regularisation (trainBR), as it originates models that generalise well (not over-fit) and facilitates locating the optimal topology in small to medium-sized databases [243]. On the other hand, the transfer function is in charge of introducing the non-linearity in the calculations as well as limiting the range of the values of the responses given by each neuron.

The selected option was the sigmoid function, which limits the values between zero and one [244]. A schematic representation of the created multilayer perceptrons is shown in Figure 7.2.

Besides the weights and the mentioned functions, there are other parameters that have to be correctly selected or optimised to reach a fully operational multilayer perceptron. They are the HNN, the training and transfer functions, and a set of network parameters (Marquardt adjustment parameter) such as: learning coefficient (Lc), decrease factor for Lc (Lcd), and increase factor for Lc (Lci):

- Optimising the HNN is crucial, as an excessive number will most likely originate over-fit models, and a low one will not allow the MLP to reach its maximum calculating potential. It was optimised heuristically during this research [245].
- Finally, the Lc parameter is analogous to the learning coefficient in classic back-propagation algorithms [246], and its value is decreased and increased.
by Lcd and Lci, respectively, until the modifications of Lc originate a worse statistical performance [243].

In this work, the training and transfer functions, as well as the values of the network parameters (Lc, Lcd, and Lci), were stabilised in order to be able to estimate the properties of the ionic liquids studied.

### 7.3 Results and discussion

In the present work, the model developed uses composition, temperature, and molecular weight to estimate viscosity, conductivity, and density of pure samples and binary mixtures. The different neural network parameters and functions employed can be seen in Table 7.1.

**Table 7.1** MLP parameters and functions employed, and its statistical performance.

<table>
<thead>
<tr>
<th>MAIN MLP CHARACTERISTICS</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Input nodes</td>
<td>3</td>
</tr>
<tr>
<td>HNN</td>
<td>3</td>
</tr>
<tr>
<td>Output neurons</td>
<td>3</td>
</tr>
<tr>
<td>Transfer function</td>
<td>Sigmoid</td>
</tr>
<tr>
<td>Training function</td>
<td>TrainBR</td>
</tr>
<tr>
<td>Lc</td>
<td>0.001</td>
</tr>
<tr>
<td>Lcd</td>
<td>0.1</td>
</tr>
<tr>
<td>Lci</td>
<td>10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MLP STATISTICAL RESULTS</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>Viscosity</td>
</tr>
<tr>
<td>Mean prediction error / %</td>
<td>0.27</td>
</tr>
<tr>
<td>Correlation coefficient</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Once the parameters of the models were defined, the different multilayer perceptrons were ready to be validated in order to ensure that they are able to generalise well, and are not over-fit towards the training dataset. During this analysis, a k-fold cross validation (k = 6) was performed for each one of the individual multilayer perceptrons. During this validation process, every single sample from a database is employed to test the model and, therefore, its result covers the entire range of the data [241]. The final statistical performances of the models are calculated by averaging the results from each test (six in this case, as k = 6). The final results that were provided by the k-fold cross-validation tests can be found in Table 7.1, as well
as the network parameters and functions employed. The mean prediction error, MPE, which verify the prediction error, together with the adjusted correlation coefficient, were used to analyse the results of the neural network design.

In order to carry out the validation of the optimised model, the estimated statistical results were plotted against the experimental data, in Figure 7.3, Figure 7.4, and Figure 7.5, for density, dynamic viscosity and ionic conductivity, respectively.

![Figure 7.3 Neural network model performances for density.](image)

![Figure 7.4 Neural network model performances for dynamic viscosity.](image)
The statistical results of estimated versus real values are found, $R^2 < 0.98$ and MPE < 4.6%. As expected, different fit qualities were found for each of the three different physical properties. However, according to the statistical results of the validation process, the NN model is accurate enough to estimate reliable values for density, viscosity and conductivity within the set of ionic liquids studied. Thus, it should be possible for many engineering applications to estimate the physical properties of binary mixtures without resorting to extensive experimental measurements.

### 7.4 Conclusions

To sum up, it is possible to accurately estimate density, viscosity and conductivity values for binary mixtures of alkylammonium nitrates using Multilayer perceptron and Artificial Neural Networks. The mean prediction errors obtained were 0.27%, 4.52%, and 4.10%, for density, viscosity and conductivity, respectively. These results, which have been estimating using only temperature, composition and molecular weight, suggested that binary mixtures of similar composition can be also monitored, making this mathematical model a useful tool to evaluate ionic liquids physical properties. The high accuracy of the model was assured by the high purity of the compounds used for the empirical studies.
8 Summary
8.1 Overview

This thesis aims to establish the nature of hydrogen bonding in protonic ionic liquids, and the manner in which the hydrogen bonding determines the physical properties of both pure ionic liquids, and their binary mixtures.

Six protonic alkylammonium nitrates were synthesised. The nitrate anion was chosen because of its highly symmetrical structure, D$_{3h}$, and it well-recognised hydrogen-bond acceptor ability. In addition, the low molecular weight of the nitrate anion and the short chain of the ammonium cation made these systems particularly accessible for ab initio DFT calculations. By varying the sites available for hydrogen-bond donation, it was possible to systematically observe and evaluate the nature of this interaction as a function of both the number of the hydrogen-bond donor sites and the length of the alkyl chain. All these compounds were fully characterised by elemental analysis, Karl Fisher titration, $^1$H and $^{13}$C NMR, DSC, TGA, and some were studied by X-ray crystallography and powder diffraction. The elemental analysis of the ionic liquids showed acceptably low deviation from the theoretical values. The water content was found to be within acceptable bounds for these hygroscopic materials. Storage under a dinitrogen atmosphere was essential to prevent further water uptake. The high purity of the samples was demonstrated in the $^1$H and $^{13}$C NMR spectra. The thermal stability of these ionic liquids, checked by TGA and DSC, was in good agreement with the literature. The crystal data of butylammonium nitrate, [N$_{0004}$][NO$_3$], and diethylammonium nitrate, [N$_{0022}$][NO$_3$] reveal that both materials contain a network of hydrogen bonds, with every hydrogen-bond donor and every hydrogen-bond acceptor contributing to that network.

The thermophysical properties of three monoalkylammonium nitrate ionic liquids [N$_{0002}$][NO$_3$], [N$_{0003}$][NO$_3$] and [N$_{0004}$][NO$_3$], and their binary mixtures were studied. The measured thermophysical data follow the expected trends: the dynamic viscosity values increased with the length of the alkyl chain, and with the number of carbons present in the cation or composite cation.$\dagger$ In contrast, density and ionic conductivity followed the opposite trend. These results confirm that ideal behaviour is a good model description for these binary alkylammonium nitrate mixtures. Binary mixtures, composed of [N$_{0002}$][NO$_3$] and an increasing mole fraction of homologous ionic liquids with decreasing numbers of hydrogen-bond donors in the cation: [N$_{0022}$][NO$_3$], [N$_{0222}$][NO$_3$] and [N$_{2222}$][NO$_3$], were also studied. The results showed that, besides the expected influence of increasing the number of carbon atoms in an

$\dagger$ In order to study possible deviations from ideality, the selected mixtures were compared with systems with equivalent numbers of carbon atoms in the cation, referred to as composite cations.
ionic liquid cation, there are other interactions affecting the thermophysical properties of these binary mixtures. In contrast with the results for monoalkylammonium nitrate mixtures, the excess molar volume of these systems revealed a clear deviation from ideal behaviour as the number of ethyl chains is increased on the ethylammonium cation. This reinforced the complicated behaviour of simple and binary protonic ionic liquids.

Pure alkylammonium nitrates, their binary mixtures, and their deuteriated analogues were also investigated by vibrational spectroscopic methods - infrared and Raman spectroscopies at high frequencies, and inelastic neutron scattering at frequencies below 500 cm\(^{-1}\). Diethylammonium nitrate was analysed from a molecular dynamics perspective, alongside vibrational spectroscopy, to assess the nature of the hydrogen bonds. There was an exceptional agreement between the empirical and the theoretical results. Assignments for diethylammonium nitrate were used as a template for the analysis of the other ionic liquids, and all the assignments were self-consistent.

The Raman spectra showed distinctive signals for the vibrations of the nitrate anion, and strong well-defined signals for the C-H stretching frequencies of the cation. In contrast, infrared spectroscopy clearly identified the N-H and N-D stretching and bending modes for pure ionic liquids and their binary mixtures. Overall, it was concluded that increasing the number of N-H hydrogen atoms also leads to bifurcated intermolecular bonds, which tend to be weaker.

Inelastic neutron scattering revealed that by increasing the length of the alkyl chain, the vibrational frequencies for \(\nu(N-H\cdots O)\) are shifted to higher frequencies, which means that stronger hydrogen bonding are formed. Although further studies will be required to reinforce this conclusion, it would appear that the monoprotonated cation forms strongest individual hydrogen bonds, but they are localised, whereas the tripotatronated cation forms weaker hydrogen bonds, but they are involved in an extensive bifurcated network.

In comparison to the pure materials, the bands describable to N-H\cdots O for the monoalkylammonium binary mixtures were broader, weaker, and shifted in position. The observed spectra of the mixtures did not correspond to a simple summation of the pure components. This may be due to new speciation, such as nitrate hydrogen-bonded to two different cations, and also to the presence of additional stable conformers. Thus, the mixtures contain many more species, and conformers of those species, leading to broader, less well-defined bands. Experimental INS of the binary mixtures of \([N_002][NO_3]\) and \([N_002][NO_3]\) showed that, even at 10\% of \([N_002][NO_3]\) and 90\% of \([N_002][NO_3]\), the structure of the dialkylammonium nitrate
is clearly dominating the mixture. This indicated that $[\text{N}_0\text{O}_2]\text{[NO}_3\text{]}$ may form stronger hydrogen bonds than $[\text{N}_0\text{O}_2]\text{[NO}_3\text{]}$.

In a preliminary study, the dynamics of methylammonium nitrate in both the liquid and solid state were studied in this thesis. The results suggested that a jump model accurately represents the diffusive motion in the solid state. The dynamical studies of the $[\text{CH}_3\text{ND}_3]^+$ and the $[\text{CH}_3\text{NH}_3]^+$ samples were compared over the temperature range -240 °C to +115 °C. Although further analysis is required, it can be seen that there must be slightly different dynamic associated with the melting process for $[\text{ND}_3\text{D}_1]\text{[NO}_3\text{]}$ with respect to $[\text{N}_0\text{D}_1]\text{[NO}_3\text{]}$.

Finally, binary mixtures of alkylammonium nitrates were investigated using multilayer perceptrons and artificial neural networks in a collaboration with Professor José Torrecilla (from the Complutense University of Madrid). It was possible to accurately estimate density, viscosity and conductivity values from molecular weight, composition and temperature. These results highlighted the possibility, for many engineering applications, to estimate the physical properties of binary mixtures without resorting to extensive experimental measurements.

### 8.2 Suggestions for future work

There are several research lines which could be instigated in the future. These include:

- Crystallographic characterisation of more related series of alkylammonium nitrates, which will enable more CASTEP calculations to be performed.
- Further investigations into the properties of more binary systems.
- QENS studies of $[\text{CD}_3\text{NH}_3]\text{[NO}_3\text{]}$ to complete the analysis of the methylammonium nitrate system.
- QENS studies of systems based on dimethylammonium nitrate and trimethylammonium nitrate.
- A neural network analysis of the correlation between structural parameters and the vibrational frequencies of the hydrogen bonds.

All of these studies would build upon the data and findings presented in this thesis, and would add to our understanding of these fascinating systems.
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to be continued


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