Raman and inelastic neutron scattering spectra of (NH$_4$)$_2$SO$_3$, an intermediate for solar hydrogen production

Raúl E. Orozco-Mena, Stewart F. Parker, Eduardo F. Herrera-Peraza, David Chávez-Flores, Hernando Romero-Paredes and Víctor H. Ramos-Sánchez

Published version information


DOI: 10.1016/j.ijhydene.2017.10.094

©2017. This manuscript version is made available under the CC-BY-NC-ND 4.0 Licence.

This version is made available in accordance with publisher policies. Please cite only the published version using the reference above. This is the citation assigned by the publisher at the time of issuing the AAM. Please check the publisher’s website for any updates.
Raman and inelastic neutron scattering spectra of (NH$_4$)$_2$SO$_3$, an intermediate for solar hydrogen production

Raúl E. Orozco-Mena,$^a$ Stewart F. Parker,$^b$ Eduardo F. Herrera-Peraza,$^a$
David Chávez-Flores,$^c$ Hernando Romero-Paredes$^d$ and
Víctor H. Ramos-Sánchez$^{*c}$

$^a$Medio Ambiente y Energía, Centro de Investigación en Materiales Avanzados, S.C.,
Miguel de Cervantes #120, Complejo Industrial Chihuahua, Chihuahua, Chih., México.
C.P. 31136.

$^b$ISIS Pulsed Neutron and Muon Facility, Science and Technology Facilities Council,
Rutherford Appleton Laboratory, Harwell, Didcot, Oxfordshire, OX11 0QX, UK

$^c$Cuerpo Académico de Química Aplicada y Educativa, Facultad de Ciencias Químicas,
Universidad Autónoma de Chihuahua, Nuevo Campus Universitario, Circuito
Universitario, Chihuahua, Chih., México. C.P. 31125.

$^d$Área de Ingeniería en Recursos Energéticos, Universidad Autónoma Metropolitana-
Iztapalapa, Av. San Rafael Atlíxco 186, Col. Vicentina, México, D.F., México. C.P. 09340,

$^*Tel: +52 (614)2366000, mail: vramos@uach.mx

Keywords: Solar Thermochemical Cycle, Photolytic oxidation, Ammonium sulfite, Raman
scattering, Inelastic neutron scattering.
Abstract

The sulfur-ammonia (S-NH$_3$) cycle uses the entire solar radiation spectrum to split water. It uses the UV radiation to promote the photolytic oxidation of ammonium sulfite to produce hydrogen and ammonium sulfate. Here, Raman and inelastic neutron scattering spectra of (NH$_4$)$_2$SO$_3$·H$_2$O at 20 K are discussed, supported by density functional theory (DFT) calculations. The feasibility of photolytic oxidation of this monohydrate to produce hydrogen at room temperature was also demonstrated.
1. Introduction

Hydrogen is an energy vector capable of replacing fossil fuels and providing energy for transportation, industry and households. Such a sustainable model scenario, known as the hydrogen economy, demands finding new methods to produce hydrogen on a large scale, while keeping the use of fossil fuels to a minimum and replacing steam reforming, which is the most widely used process to obtain hydrogen nowadays. Among the viable options are the Thermo Chemical Water Splitting Cycles (TCWSCs). In particular, the sulfur family cycles have been shortlisted as the most promising routes to obtain hydrogen on a large scale. European research projects such as HYTHEC and HYCYCLES have focused on studying the Sulfur-Iodine cycle and the Hybrid Sulfur cycle, respectively [1,2]. An innovative photothermochemical cycle within the same family has been developed: the sulfur-ammonia (S-NH₃) cycle [3,4]. This cycle exploits the entire solar radiation spectrum to split water. It uses the UV radiation to promote the photolytic oxidation of ammonium sulfite to produce hydrogen and ammonium sulfate, an energy carrier and a potential fertilizer respectively, according to Reaction 1.

\[
(NH_4)_2SO_3 + H_2O \xrightarrow{uv} (NH_4)_2SO_4 + H_2 \quad (1)
\]

This step produces high purity hydrogen at room temperature, and it is usually carried out in solution [3-8]. Recent efforts to enhance exploitation of the solar spectrum, within the cycle, relied on the use of photocatalysts, such as CdS and CdSeZnS, which exhibit known toxicity issues [9]. However, even in presence of photocatalysts, quantum efficiency of the photolytic reaction is inherently limited due to water’s UV absorption. Moreover, it is also logical to think that the overall efficiency of the S-NH₃ cycle is adversely affected by excess water in
subsequent operation units that involve water handling. Indeed, the theoretical particle model for the oxygen sub-cycle, lately reported, made evident the implication of managing water in a solar aerosol based reactor [10]. Therefore, an obvious choice would be to explore the reaction in the solid state by directly irradiating ammonium sulfite monohydrate ((NH$_4$)$_2$SO$_3$·H$_2$O).

At this point, it is worthy to mention that sulfur-containing compounds are not only relevant in different areas, such as environmental science [11,12], food science [13], health [14], and material science [15]; but in particular, sulfate solutions ((NH$_4$)$_2$SO$_4$, among these) are also of interest in hydrogen production through electrolytic hydrogen evolution reaction [16,17]. Several studies have been conducted on their molecular structures, using vibrational spectroscopy. Since the Raman cross section of sulfur is particularly favourable, sulfites and sulfates have been investigated in solution, glassy state and solid state, often accompanied by infrared spectroscopy [18-25]. Raman spectroscopy has been also used to study other sulfur family cycle, the S-I cycle, to gain further insights into molecular dynamics of the solutions involved and chemical species occurring within [26-28]. A complementary technique, inelastic neutron scattering (INS) spectroscopy, exhibits a remarkable hydrogen cross section that allows to study either hydrogen bonding, hydrogenated species, adsorbed molecular hydrogen, and even proton conduction [29,30]. It is remarkable the extensive literature available on ammonium vibrational modes, as a counterion in different inorganic salts, obtained by INS [31-38].

Here we aim to demonstrate the feasibility of photolytic oxidation of (NH$_4$)$_2$SO$_3$·H$_2$O in the solid state to produce hydrogen using a UV laser source. We also report a comprehensive study of the vibrational modes of (NH$_4$)$_2$SO$_3$·H$_2$O, especially those associated with the
hydrogen bonding network, and to present the Raman and INS spectra of (NH₄)₂SO₄ and Na₂SO₃, which have not been previously reported. The unique features to choose such techniques were the capability to promote a photochemical process, by irradiating the sample with a 244 nm UV laser within a Raman microscope; and in the case of simultaneous INS and Raman spectroscopy at 785 nm, very low temperature and very low photon energy, which enables the analysis of sulfites without alteration.

2. Materials and Methods

2.1 Reagents

Bulk powders of (NH₄)₂SO₃·H₂O, (NH₄)₂SO₄ and Na₂SO₃ were packed into sample holders, which consist in a two flat-plate aluminium cell sealed with indium wire and a sapphire window at the top, as described elsewhere [39]. All reagents were high purity, 92% or better from Alfa Aesar, and were used without further purification. The aluminium cells were used for the simultaneous recording of the Raman and INS spectra at 20 K.

2.2 Vibrational Spectroscopy

High resolution INS spectra (~1.25% ΔE) were recorded at 20 K with the TOSCA spectrometer at ISIS (Didcot, UK). Simultaneously, Raman spectra were recorded with a customized Renishaw InVia system with 785 nm excitation [39] with improved resolution of ~3 cm⁻¹ and Raman shift threshold of 40 cm⁻¹. Raman spectra were also recorded at room temperature for (NH₄)₂SO₃·H₂O using a Renishaw InVia Raman microscope with 244 nm excitation, this instrument has a resolution of 8 cm⁻¹ and a Raman shift threshold of 400 cm⁻¹.
2.2 Computational Details

Density functional theory (DFT) calculations were carried out with the plane-wave pseudopotential method as implemented in CASTEP [40]. Initial structures of (NH₄)₂SO₃·H₂O, (NH₄)₂SO₄ and Na₂SO₃ were based on the available crystallographic data [41-43]. Note that the lattice parameters were constrained to the experimental values, unless specified otherwise, during the molecular geometry optimisation. The generalized gradient approximation (GGA) Perdew–Burke–Ernzerhof (PBE) functional was used in conjunction with optimized norm-conserving pseudopotentials. The plane wave cutoff was 830 eV in all cases. The k-point sampling was done with Monkhorst-Pack grids of 6×6×4 (36 k-points), 6×4×6 (18 k-points) and 6×6×6 (42 k-points) for (NH₄)₂SO₃·H₂O, (NH₄)₂SO₄ and Na₂SO₃ respectively. In all cases the residual forces were |0.009| eV Å⁻¹. After geometry optimization, the vibrational spectra were calculated at the Γ-point in the harmonic approximation using density-functional perturbation theory [44]. This procedure generates the vibrational eigenvalues and eigenvectors, which allows visualization of the modes within the Jmol 3D software [45] and is also the information needed to calculate the INS spectrum using the program ACLIMAX [46]. We emphasize that none of the calculated frequencies were scaled.

3. Results and Discussion

3.1 Photolytic Oxidation of (NH₄)₂SO₃·H₂O

Figure 1 shows the evolution of the photolytic oxidation carried out within a Raman microscope using a 25 mW 244 nm UV laser focussed onto a crystal of (NH₄)₂SO₃·H₂O. As the reaction occurred, it was evidenced by the appearance of a band at ca. 1086 cm⁻¹ related to the SO₄²⁻ ion (ν₃) and a weakening of the band ca. 1692 cm⁻¹ corresponding to the
scissoring mode of water within the monohydrate; a broad and weak band is observable at ca. 1437 cm\(^{-1}\) presumably due to the symmetric N-H bending mode of the ammonium ion \cite{20,24}. Based on this observation, it is possible to infer the production of hydrogen, which led us to consider the potential application of using moderately concentrated solar radiation to promote this photochemical process. Further knowledge of the lattice dynamics was then required, but avoiding chemical degradation of the monohydrate.

![Raman spectra](image.png)

**Figure 1.** Raman spectra demonstrating the feasibility of photolytic oxidation in the solid state at 25°C using a 25 mW laser at 244 nm.

### 3.2 Vibrational Spectra of (NH\(_4\))\(_2\)SO\(_3\)·H\(_2\)O

The Raman spectrum of (NH\(_4\))\(_2\)SO\(_3\)·H\(_2\)O at 20 K is shown in **Figure 2** together with the Raman spectra of (NH\(_4\))\(_2\)SO\(_4\) and Na\(_2\)SO\(_3\) for comparison. On closer examination of the lower part of **Figure 2**, it is noticeable that the modes were better resolved at low temperature,
since it is possible to observe the individual Raman bands assigned to the S-O stretching and 
O-S-O deformations modes. In the case of $\nu_2$, (see Tables 1-3 for graphical representation of 
normal modes of vibrations) the Raman bands in (NH$_4$)$_2$SO$_3$·H$_2$O and (NH$_4$)$_2$SO$_4$ are almost 
identical in intensity and were identified as two individual peaks ca. 448 and 460 cm$^{-1}$. Note 
that despite contribution of sapphire to the first Raman band this could not solely be 
responsible of such peak, since its ratio of intensity does not correspond to the Raman 
spectrum of sapphire, as shown in the inset of Figure 2. A similar condition was found in the 
wagging mode of water at 647 cm$^{-1}$, which is only present in the monohydrate, where 
intensity in absence of water is exclusively due to sapphire vibrations. Next to this, there is 
the $\nu_4$ deformation band, exhibiting Raman peaks around 610 and 622 cm$^{-1}$. Both the $\nu_2$ and 
$\nu_4$ bands were displaced to higher frequencies in Na$_2$SO$_3$ ca. 498 and 638 cm$^{-1}$, respectively. 
The most intense features in the Raman spectra correspond to the $\nu_1$ mode characterised by 
4 peaks at 973, 957, 923 and 909 cm$^{-1}$ in the monohydrate. Sodium sulfite exhibits a peak 
around 990 cm$^{-1}$ for this mode. Finally, the three peaks at 1043, 1083 and 1130 cm$^{-1}$ were 
assigned to the $\nu_3$ vibrational mode [24, 25]. It is noteworthy that such bands were not visible 
at room temperature for the monohydrate.
Figure 2. Top: Raman spectra of (NH₄)₂SO₃·H₂O, (NH₄)₂SO₄ and Na₂SO₃ at 20K using 785 nm laser excitation. Bottom: Zoom into the lower spectral region. Note: Raman bands contributed by the optical window of the sample holder, made of sapphire, are denoted with a star; i.e. inset shows Raman spectrum of sapphire.

Whereas the Raman spectra are largely dominated by modes involving sulfur, INS intensities are determined by the amplitude of motion of the atoms in the mode and their incoherent scattering cross section. For ¹H, both of these are large and modes involving hydrogen motion will dominate the spectrum. For non-hydrogenous materials, the strongest modes will generally involve the lightest atoms (since they will have the largest amplitude of motion).

To provide a definitive assignment of the vibrational spectra, assignments from the literature were further supported by DFT calculations; the calculated vibrational modes are available in the supplementary material, so readers can easily visualize crystal vibrations using Jmol.
In order to facilitate interpretation of the INS spectra, the theoretical and experimental results are overlaid. Figure 3 shows the experimental INS spectrum obtained at TOSCA and two DFT-calculated spectra. The blue spectral contour was obtained by constraining the calculation to the lattice parameters reported in the literature for \((\text{NH}_4)_2\text{SO}_3\cdot\text{H}_2\text{O}\) and the green spectral contour was calculated by allowing both the lattice parameters and the geometry to freely optimise within CASTEP.

Better agreement was found when the experimental lattice parameters were used to calculate the spectrum. Although there are clear differences between the experimental and theoretical data, it is important to remind the reader that theoretical spectra were not corrected by any scale factor. At the very right of the experimental spectrum shown in Figure 3, is the bending mode of water at \(\text{ca. } 1700\ \text{cm}^{-1}\). The N-H deformation mode in ammonium ions occurs at 1475 cm\(^{-1}\). Around 900 cm\(^{-1}\) there is an out of plane deformation of O···H···O. Then in order to simplify the interpretation five spectral sections are considered. The first covering from 600 to 750 cm\(^{-1}\) involves torsional vibrations of water; the following section in decreasing order goes from 300 to 600 cm\(^{-1}\) and it covers torsional vibrations of ammonium ions at 323, 443 and 508 cm\(^{-1}\). Translational vibrations of ammonium ions and water are localised between 175 and 300 cm\(^{-1}\). Torsional vibrations of sulfites/sulfates are generally seen in the spectral range, 100 – 175 cm\(^{-1}\). Below the aforementioned, the crystal lattice vibrations are found [36,38].
Based on these assignments, \((\text{NH}_4)_2\text{SO}_4\) can also be interpreted. The INS spectra were similarly sectioned, as illustrated in the top part of Figure 4. Here, it was evident that the loss of features associated with water results in more relatively more intense peaks for the torsional vibration of sulfate and the translational vibrations of the ammonium ion, respectively. There is also a noticeably better correlation between experimental and theoretical data. However, the most remarkable correlation between experiment and theory is seen in the INS spectra of \(\text{Na}_2\text{SO}_3\), shown in the bottom part of Figure 4, where, as predicted by the DFT calculations, it is possible to identify the bands conforming the S-O stretching and O-S-O deformations modes, previously observed for \(\text{Na}_2\text{SO}_3\) in Figure 2.

Based on the calculated dispersion curves for \(\text{Na}_2\text{SO}_3\) (see supplementary information),
whereas the torsional vibrations of sulfite exhibited dispersion, the internal modes of vibration of sulfite, in absence of ammonium, were not dispersed.

DFT provides a more accurate description of Na$_2$SO$_3$ as compared to (NH$_4$)$_2$SO$_3$·H$_2$O and (NH$_4$)$_2$SO$_4$ because there is no hydrogen bonding present. The failure of DFT to accurately reproduce the spectra of moderately strongly hydrogen bonded systems has been recognised previously for H$_2$O$_2$ [47]. In this case the O–H bond was too long and the intermolecular hydrogen bond was too short, resulting in overbinding and the vibrational modes being shifted to higher energy, as also observed here for (NH$_4$)$_2$SO$_3$·H$_2$O and (NH$_4$)$_2$SO$_4$. A comparison of a variety of pseudopotentials and exchange-correlation functionals, showed that the error was largely in the latter. A similar cause is likely to be the case here.

Tables 1-3 present the assignments for the salts investigated here.
Figure 4 INS spectra of: Top: (NH₄)₂SO₄: Experimental taken at TOSCA at 20 K (red), Theoretical spectra (blue and green); and Bottom: Na₂SO₃: Experimental taken at TOSCA at 20 K (red), Theoretical spectra (blue).
Table 1. Assignment of vibrational modes based on the Raman and INS spectra of \((\text{NH}_4)_2\text{SO}_3\cdot\text{H}_2\text{O})\.

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Assignment</th>
<th>Graphical Representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>448</td>
<td>(\nu_2) \text{SO}_3</td>
<td><img src="image1" alt="Graphical representation" /></td>
</tr>
<tr>
<td>460</td>
<td>(\nu_2) \text{SO}_3</td>
<td><img src="image2" alt="Graphical representation" /></td>
</tr>
<tr>
<td>647</td>
<td>Wagging \text{H}_2\text{O}</td>
<td><img src="image3" alt="Graphical representation" /></td>
</tr>
<tr>
<td>610</td>
<td>(\nu_4) \text{SO}_3</td>
<td><img src="image4" alt="Graphical representation" /></td>
</tr>
<tr>
<td>622</td>
<td>(\nu_4) \text{SO}_3</td>
<td><img src="image5" alt="Graphical representation" /></td>
</tr>
<tr>
<td>900</td>
<td>Out of plane \text{O}···\text{H}···\text{O} deformation</td>
<td><img src="image6" alt="Graphical representation" /></td>
</tr>
<tr>
<td>973</td>
<td>(\nu_1) \text{SO}_3</td>
<td><img src="image7" alt="Graphical representation" /></td>
</tr>
<tr>
<td>957</td>
<td>(\nu_1) \text{SO}_3</td>
<td><img src="image8" alt="Graphical representation" /></td>
</tr>
<tr>
<td>923</td>
<td>(\nu_1) \text{SO}_3</td>
<td><img src="image9" alt="Graphical representation" /></td>
</tr>
<tr>
<td>909</td>
<td>(\nu_1) \text{SO}_3</td>
<td><img src="image10" alt="Graphical representation" /></td>
</tr>
<tr>
<td>1043</td>
<td>(\nu_3) \text{SO}_3</td>
<td><img src="image11" alt="Graphical representation" /></td>
</tr>
<tr>
<td>1083</td>
<td>(\nu_3) \text{SO}_3</td>
<td><img src="image12" alt="Graphical representation" /></td>
</tr>
<tr>
<td>1130</td>
<td>(\nu_3) \text{SO}_3</td>
<td><img src="image13" alt="Graphical representation" /></td>
</tr>
<tr>
<td>1700</td>
<td>Bending \text{H}_2\text{O}</td>
<td><img src="image14" alt="Graphical representation" /></td>
</tr>
<tr>
<td>1475</td>
<td>N-H deformation</td>
<td><img src="image15" alt="Graphical representation" /></td>
</tr>
<tr>
<td>600 – 750</td>
<td>Torsional vibrations \text{H}_2\text{O}</td>
<td><img src="image16" alt="Graphical representation" /></td>
</tr>
<tr>
<td>300 – 600</td>
<td>Torsional vibrations \text{NH}_4</td>
<td><img src="image17" alt="Graphical representation" /></td>
</tr>
<tr>
<td>175 – 300</td>
<td>Translational vibrations \text{NH}_4/\text{H}_2\text{O}</td>
<td><img src="image18" alt="Graphical representation" /></td>
</tr>
<tr>
<td>100 – 175</td>
<td>Torsional vibrations of \text{SO}_3</td>
<td><img src="image19" alt="Graphical representation" /></td>
</tr>
<tr>
<td>&lt;175</td>
<td>Crystal lattice vibrations</td>
<td><img src="image20" alt="Graphical representation" /></td>
</tr>
</tbody>
</table>
Table 2. Assignment of vibrational modes based on the Raman and INS spectra of (NH₄)₂SO₄.

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Assignment</th>
<th>Graphical Representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>448</td>
<td>ν₂ SO₄</td>
<td></td>
</tr>
<tr>
<td>460</td>
<td>ν₂ SO₄</td>
<td></td>
</tr>
<tr>
<td>610</td>
<td>ν₄ SO₄</td>
<td></td>
</tr>
<tr>
<td>622</td>
<td>ν₄ SO₄</td>
<td></td>
</tr>
<tr>
<td>1475</td>
<td>N-H deformation</td>
<td></td>
</tr>
</tbody>
</table>

300 – 600 Torsional vibrations NH₄
175 - 300 Translational vibrations NH₄
100 - 175 Torsional vibrations of SO₄
<175 Crystal lattice vibrations

Table 3. Assignment of vibrational modes based on the Raman and INS spectra of Na₂SO₃.

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Assignment</th>
<th>Graphical Representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>498</td>
<td>ν₂ SO₃</td>
<td></td>
</tr>
<tr>
<td>638</td>
<td>ν₄ SO₃</td>
<td></td>
</tr>
<tr>
<td>990</td>
<td>ν₁ SO₃</td>
<td></td>
</tr>
<tr>
<td>&lt; 250</td>
<td>Crystal lattice vibrations</td>
<td></td>
</tr>
</tbody>
</table>
4. Conclusions

Photolytic oxidation of ammonium sulfite monohydrate in the solid state using a UV laser and observed with a Raman microscope was achieved at room temperature. However, we note that it is still necessary to demonstrate the feasibility under real conditions of solar irradiation.

Low-temperature Raman and INS spectra of (NH$_4$)$_2$SO$_3$·H$_2$O, (NH$_4$)$_2$SO$_4$ and Na$_2$SO$_3$ were interpreted based on literature assignments or DFT calculations. The models here presented failed to correctly reproduce the hydrogen bonding due to the presence of ammonium and/or water. However, the INS spectra of Na$_2$SO$_3$ exhibited very good agreement between experimental and theoretical data.

5. Acknowledgements

The authors acknowledge the financial support received from the Sector Fund CONACYT-SENER-ENERGY-SUSTAINABILITY 207450 within Strategic Project No. 10, entitled: “Solar Fuels & Industrial Processes”, by which it was possible to carry out experimental work in the UK and complete this manuscript to sustain this line of research. Also, our gratitude to Prof Felix Fernandez-Alonso, Dr Svemir Rudic and all the scientific, technical and administrative staff for the access and support provided during the operation of TOSCA at the ISIS Facility. The STFC Rutherford Appleton Laboratory is thanked for access to neutron beam facilities.
6. References


