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# Neutron Molecular Spectroscopy: Future Prospects

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*"de l'audace et encore de l'audace et toujours de l'audace!"*

Danton

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# Neutron Molecular Spectroscopy: Future Prospects

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## Abstract

The recent revolution in Neutron Molecular Spectroscopy, caused by extending the spectral range, is briefly reviewed. The need to constantly improve the spectral resolution is underlined and the likely benefits are identified. Recent work on improving the energy resolution on TFXA is presented and three future options for TFXA are outlined. Some preliminary high resolution results, from a mock-up spectrometer, are reported. These clearly show that narrow bands are available in solids and improved resolutions can be achieved to observe them.

" de l'audace et encore de l'audace et toujours de l'audace ! "

## Introduction

The quotation, taken from Danton, shows that there are some approaches that cannot be over-emphasised. In the technique of neutron molecular spectroscopy it is that **resolution should be constantly underlined**. It is surprising then to look back, say twenty years, and see the modest impact of improved resolution. This is explained, in large part, by the limited extent of the improvements in resolution. But another important reason is the very recent and almost silent revolution that has taken place in this field. In 1975 a complete molecular spectrum could only have been obtained using several different spectrometers, each covering different spectral regions with different geometries and different resolution characteristics. This spectrum could not have extended beyond about  $1500\text{ cm}^{-1}$ . The situation was much the same in 1985, except that the spectral range ran out to about  $3000\text{ cm}^{-1}$ . Today this has all changed, a single spectrometer routinely spans from  $20\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$ , and data out to  $8000\text{ cm}^{-1}$  have been analysed. Some appreciation of the dramatic impact that this has had can be obtained by comparing the spectra taken of ammoniated ammonium iodide,  $\text{N}_2\text{H}_7\text{ I}$ , ( See Figure 1 ). Previously the spectroscopist worked by looking within a narrow energy windows. There was no information about events to high energies, and any information at low energies was very difficult to normalise. One particular concern was the understanding of high 'background' levels. Because of the impossibility of observing the extent of strong, but broad, bands the strongest signal in the spectrum could sometimes be ignored. Simultaneous access to both the low energy, intermolecular, vibrations and the high energy, intramolecular, vibrations is essential for correct spectral interpretation.

This access is necessary because phonon-wings must be correctly interpreted ( Phonon-wings are combinations between the intra- and the inter- molecular modes. ) As the momentum transferred in the scattering event increases the importance of phonon-wings also increases. Fortunately modern theory has provided us with a simple, yet quantitative, method of analysing these features. However to perform the analysis of phonon-wings on high energy inelastic bands a picture of the lattice modes, obtained under the same conditions, is needed.

Conventional wisdom directs us to avoid phonon-wings by working at low  $Q$  where their effects are minimised. We can now recognise that this approach is flawed, on several counts; first, the useful information available from phonon-wings is denied; second, working at low  $Q$  is more difficult because of the low scattering crosssections; third, the unwanted phonon-wings have large cross-sections and easily contaminate spectra taken at low  $Q$ , by second-scattering. It is now good practise to accept phonon-wings and incorporate their treatment consistently into the final model.

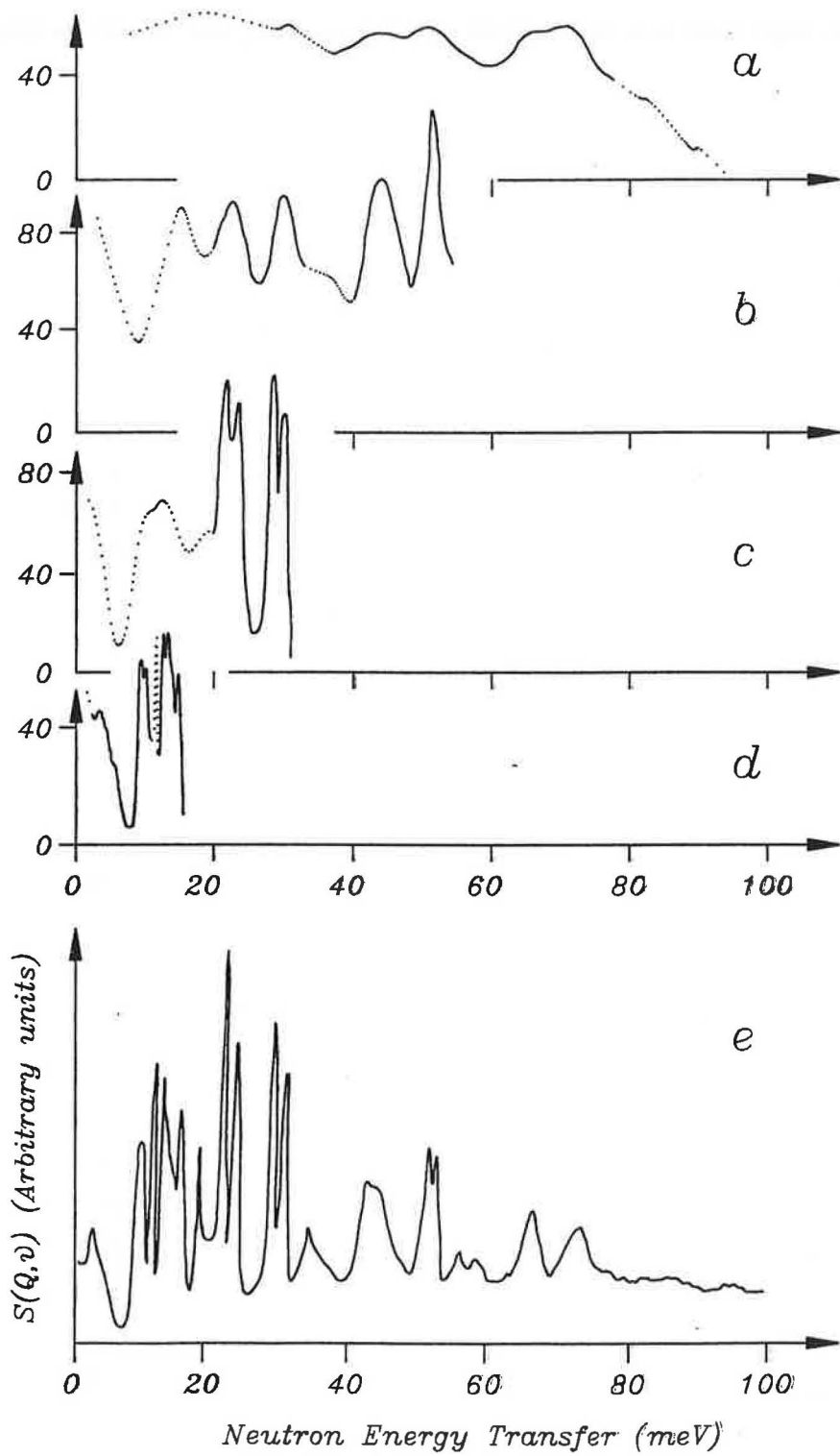


Figure 1. The Neutron Molecular Spectrum of ammoniated ammonium iodide,  $N_2H_7 I$ , obtained on a conventional spectrometer [1], above a,b,c,d. The spectrum of the same compound obtained using TFXA, see below, e.

We believe that further improvement in resolution is both inevitable and desirable, since it is the only sure way to improve spectral quality. The recent increases in instrumental resolution that did occur changed typical values of  $\Delta E_T / E_T$  from *ca.* 5% to 2%, and allow us to identify the benefits of yet further improvement. As energy resolution improves we anticipate that phonon-wings will become separable from their band origins even at very high energy transfers. This allows;

- first,** an identification of the high energy band origins;
- second,** a correct analysis of the phonon-wing data;
- third,** a better correlation between optical and neutron band origin positions.

Further work aimed at improving spectral quality should concentrate on reducing instrumental backgrounds, rather than simply increasing flux. Such work is usually more profitable. Given good backgrounds flux only affects the spectral accumulation rate and, although desirable, is not essential. Below we describe an ISIS spectrometer used for molecular spectroscopy and some recent work to study possible resolution improvements.

### TFXA

The Time-Focused-Xstal-Analyser, TFXA, is a broad-range high-resolution spectrometer suitable for molecular spectroscopy [2]. A pulsed, white, beam of neutrons from the ISIS water moderator illuminates the sample at 12m from the target. Some of those neutrons which have exchanged energy with the sample are scattered towards the secondary spectrometer, as shown in Figure 2.

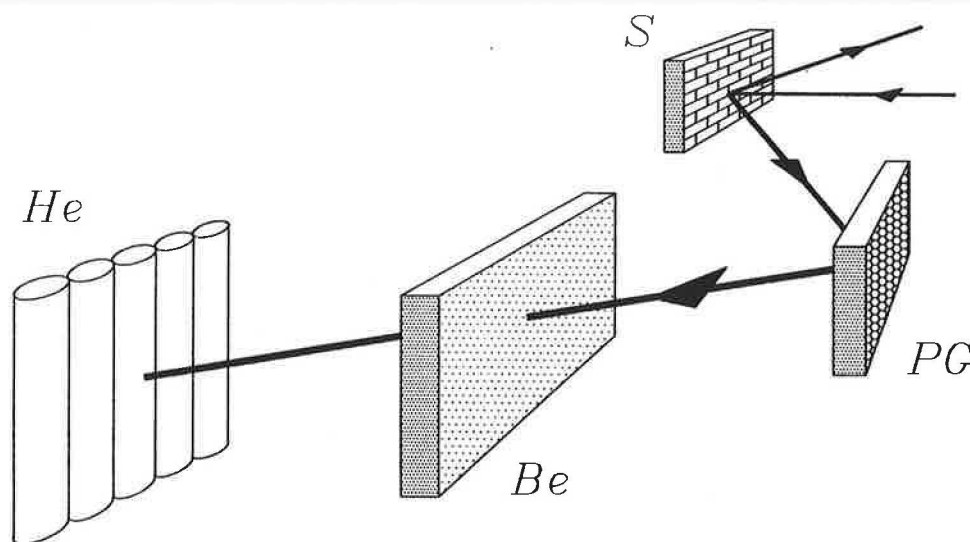


Figure 2. The Neutron Molecular Spectrometer TFXA.

Final neutron energy selection ( $32 \text{ cm}^{-1}$ ) is determined by Bragg reflection at a pyrolytic graphite crystal, higher Bragg orders are suppressed by transmitting the reflected beam through a 150mm cold beryllium filter. Elliptical  $\text{He}^3$  neutron detectors,

with relatively low  $\text{He}^3$  pressures, are used. This low pressure provides a disproportionate discrimination against high energy neutrons, whilst remaining highly ( 80% ) efficient at our final energies. They are aligned with their major axes in the plane of the sample, which is itself perpendicular to the incident neutron wave-vector. Each detector subtends a different Bragg angle at the analyser and has its own particular final energy. Whereas those neutrons detected in the tube closest to the sample are relatively slow and take a short path, those neutrons detected in the tube furthest from the sample are relatively fast, but take a long path. All neutrons exciting the same vibration in the sample appear in the detectors at exactly the same time ( hence time-focusing ). The detected counts in each detector are stored, and analysed, individually. A monitor, slightly up-stream from the sample, is used to normalise the detected counts to the incident flux distribution. Backgrounds on the spectrometer are reduced to a minimum by working in reflection, and allowing the detectors to see only the sample or cadmium. Samples are also backed with cadmium. Although cadmium is ineffective in stopping high energy neutrons it is effectively black to our final energy neutrons.

Once the spectrometer is aligned there are no variables available for the users to change, and this leaves them free to concentrate upon their samples and results. For a neutron spectrometer this is an unusual state of affairs and we have taken advantage of the situation by initiating an automatic analysis program. The control program detects an end-of-run command and launches the analysis program. This procedure has many advantages; first, inexperienced users cannot make mistakes; second, all spectra are in a standard format; third, spectra appear in a form very similar to the much more familiar optical spectra ( and so supports an interdisciplinary approach ). We also encourage users to consult each others spectra, knowing that they were obtained under the same conditions. This avoids the need to repeat 'standard samples' and, at least in principle, allows for the possibility of users 'boot-strapping' from each others work. ( A degree of professionalism is implicit in the ethics of this practice. )

## Resolution Improvements

The FWHH of the resolution function,  $\Delta E_T / E_T$ , of TFXA is given in Figure 3. It will be seen that a crude estimate of the resolution, assessed over the entire range to 500meV, is *ca.* 2%. Although the function appears to become much worse at low values this is more than compensated by the low values of  $E_T$  and the absolute FWHH is small. After the unparalleled success of the Mica analyser crystals on IRIS we originally determined to explore their utility for TFXA. Two features rapidly emerged from this aspect of the study: first, the resolution could indeed be improved using Mica but only in the very low energy transfer region; second, the reflectivity of Mica was remarkably poor compared to graphite. It was the former feature that was of most concern because a Mica analyser spectrometer would have led to a *worsened*  $\Delta E_T / E_T$  above about 30 meV. This was caused by the very low final energy, which amplified the uncertainties in the final flight path. ( Such a resolution function could only be suitable for a specialised spectrometer designed to cover a limited energy transfer range. )

Using the test-beam facility, TEB, ( on the ISIS methane moderator ) we constructed a mock-TFXA arrangement retaining as many of the present spectrometer's items as possible, eg the initial flight path length and the elliptical detectors. By this means the effects of varying the spectrometer lay-out could be quickly determined and we could draw extensively on our TFXA experiences directly. The initial measurements confirmed our previous study of Mica and led instead to a reassessment of pyrolytic graphite. When used with a larger Bragg angle, and so lower final energy, an improvement in instrumental performance was obtained from graphite across the whole spectral range. This is illustrated in Figure 4.

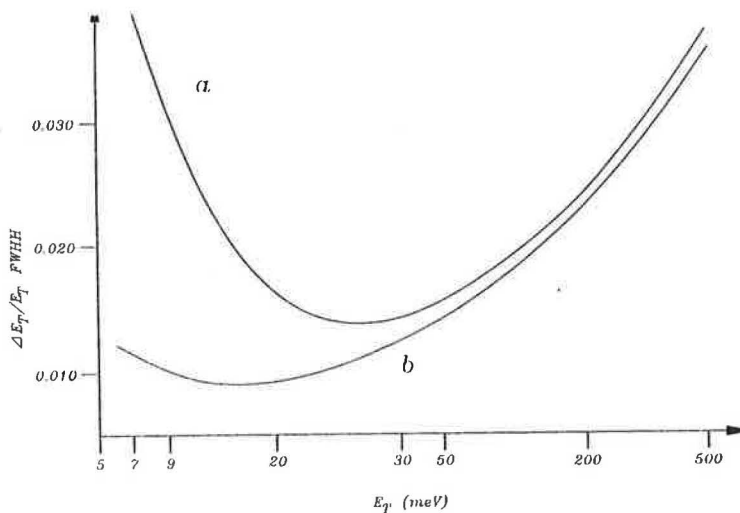


Figure 3. The energy resolution,  $\Delta E_T / E_T$ , of the present TFXA, ( a ) above, and that obtained under test conditions described in the text, ( b ) below.

We identify three options for a future TFXA with improved resolution:

( I )  $\Delta E_T / E_T \approx 1.5 \%$ ; This option involves the replacement of the present detectors with thin, 1mm, scintillators. The thickness of the analyser crystals must be matched to this thickness and so the detected flux could be only half of the present TFXA.

( II )  $\Delta E_T / E_T \approx 1 \%$ ; This option involves the replacement of the present analyser tank to provide larger Bragg angles at the graphite analysers, and would also include thin scintillator detectors. The incident energy resolution will thus be mismatched to that of the secondary spectrometer. Although this arrangement will also increase the final flight path the solid angle at the detector can be maintained, or possibly improved, by increasing the size of the individual elements. The final detected flux will therefore depend on the details of the design but could be close to the present TFXA.

( III )  $\Delta E_T / E_T \approx 0.5 \%$ ; This option involves the replacement of the present spectrometer by an entirely new design with the longer initial flight path of *ca.* 16 m. At this distance an overlap suppression chopper could be required. The secondary spectrometer redesign would match the, now much improved, incident energy resolution. The final choice of Bragg angles and secondary flight path would determine the detected flux, but an increase of about ten-fold over the present TFXA solid angle appears possible.



## Experimental Results

It is appropriate here to give some preliminary results from our mock-up spectrometer. These serve to show that the spectrometer is practicable, and that there are indeed narrower bands to be observed. In Figure 4 the spectra of  $\text{NH}_4\text{Br}$  are given, (a) obtained on TFXA, and (b) the improved resolution version.

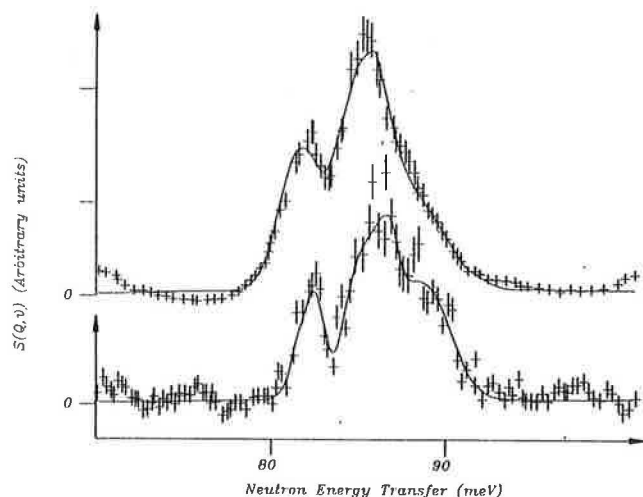


Figure 4. The Neutron Molecular Spectrum of the first librational overtone of ammonium bromide, obtained on TFXA, (a) above; and the same region observed at higher resolution.

This is the spectral region of the first overtone of the  $\text{NH}_4$  libration mode. The splitting is caused by the anharmonicity of the vibrational potential well. The low energy peak at about 81 meV can be described as the creation of a quasi-particle, the bi-phonon. This is separated from the rest of the feature by an amount  $E_B$ , its binding energy. It is narrow because it is a single particle, as opposed to the broad band of dissociated single phonon states about 85 meV. These bi-phonons do not interact strongly with the single phonons of the lattice because  $E_B$  is only 1.7 meV and the observations were made at a temperature of 30K (ca. 2.0 meV). One aspect of this type of quasi-particle that can only be investigated by improved resolution spectrometers are the excited, but still bound, states of tri-phonons.

## Conclusions

The broadest possible spectral range is the most important design aspect of neutron molecular spectrometers. There is however both scope and potential for a continuing effort to improve the resolution of these spectrometers. Such improvements can be paid-off against reduced flux, if the backgrounds are kept low.

## Acknowledgements

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2. J Penfold and J Tomkinson Rutherford Laboratory internal report 1986  
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