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# Recent and future developments on TOSCA at ISIS

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**Abstract**. TOSCA is a high-resolution neutron spectrometer at the ISIS Pulsed Neutron and Muon Source. The instrument is optimised for broadband vibrational spectroscopy in the 0 – 4000 $cm^{-1}$ region and it has been operational since 2000. This paper describes how the instrument has been progressively upgraded in the intervening years to enable new science. Future upgrades are outlined.

## 1. History

An indirect-geometry inelastic neutron scattering (INS) spectrometer optimised for vibrational spectroscopy in the 0 – 4000 $cm^{-1}$ region has been an integral part of the instrument suite at ISIS since the start of neutron beam operations at the facility in 1985 [1]. The first-generation instrument, TFXA, introduced both time and energy focussing to provide unprecedented resolution across the entire energy range [2]. Over the period April 1985 to February 1998, TFXA underwent several minor upgrades that resulted in lower backgrounds and slightly improved resolution.

By 1998, it had become apparent that there was a need for an instrument with greater sensitivity and improved resolution [3], objectives that were subsequently realised in the TOSCA project. The project was jointly funded by CNR (Italy) and HEFCE (UK). The spectrometer was installed in two stages: TOSCA-I had slightly better resolution than TFXA but a larger detector area and hence count-rate [4]. TOSCA-II (hereafter TOSCA) as installed in 2000, is shown in Figure 1, had both improved resolution, by virtue of the primary flight path having been increased from 12 m to 17 m, Figure 2, and sensitivity, by the installation of additional detector banks in forward scattering [2,5].

In its present incarnation, TOSCA is located at the N8 beamline on ISIS Target Station I. It has been operational since 2000. The spectrometer sits at 17 m from a room temperature water moderator

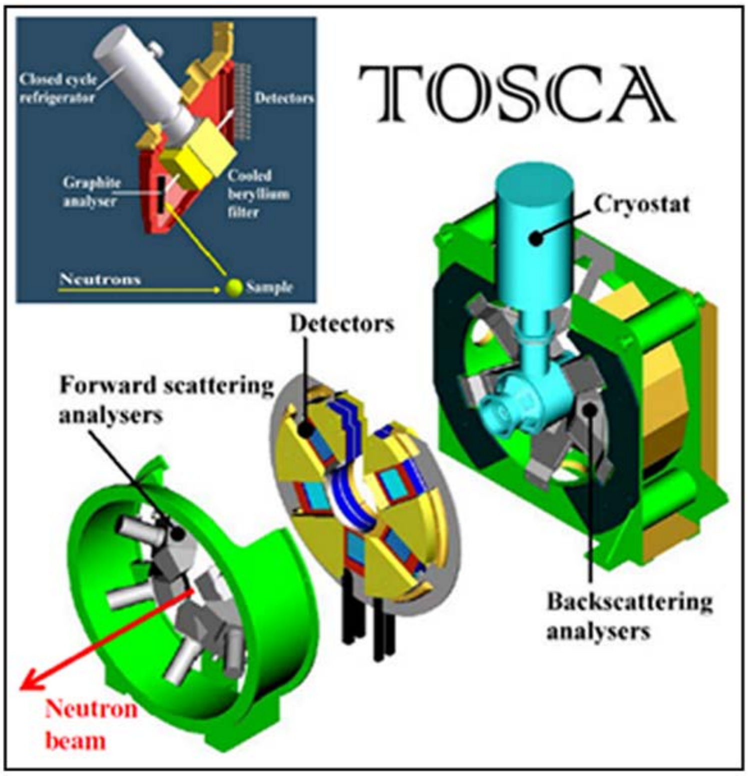

**Figure 1.** Schematic diagram of TOSCA. The inset shows a cross sectional view of a detector module.

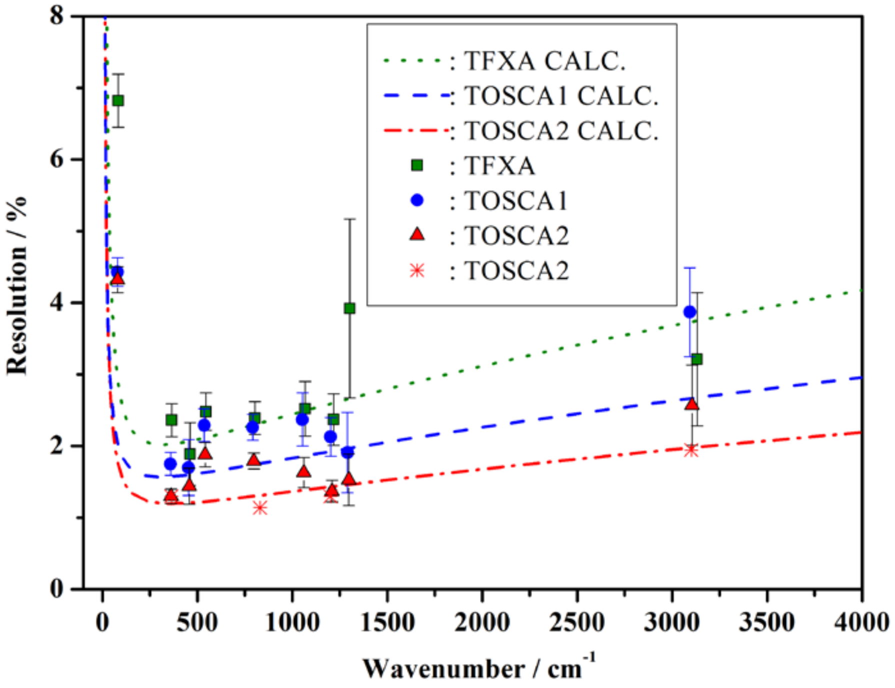

**Figure 2.** Evolution of the spectral resolution on TFXA, TOSCA-I, and TOSCA-II. The lines correspond to analytical estimates.

and it is illuminated by a pulsed polychromatic beam of neutrons. Scattered neutrons are Bragg reflected from a pyrolytic graphite analyser and higher-order reflections beyond (002) are suppressed by a cooled Be filter so as to define a unique final energy of ~32 $cm^{-1}$ (see inset in Figure 1). The detector array is comprised of a total of ten banks each having thirteen 30 × 1 $cm^2$ $^3$He tubes. Five banks are located in forward scattering (scattering angle 45°) and five in backscattering (135°). The use of a low (fixed) final energy translates into a direct relationship between energy transfer ($E_T$, $cm^{-1}$) and momentum transfer ($Q$, $Å^{-1}$) such that $E_T \approx 16Q^2$. A disc chopper to prevent frame overlap is positioned at 8 m from the moderator. TOSCA has been optimised to deliver an outstanding spectral resolution (*ca*. 1.25% $E_T$), arising from the combination of several factors: the narrow bandpass of the PG002/Be analyser, tight moderator pulse widths (~10 μs/Å), a long incident flight path and a time- and energy-focused detector geometry.

The primary aim of this paper is to describe the improvements made to TOSCA since the first neutrons in September 2000, as well as to outline possible developments in the future.

## 2. Upgrades to TOSCA since 2000

### 2.1. Reduction of background

Following its commissioning in 2000, it was found that TOSCA performed as expected in terms of improved resolution and count rate [5]. However, the background was larger than either expected or desired. For organic compounds, the scattering was strong enough that the resulting signal-to-background ratio was high enough that the spectra were acceptable. However, for non-hydrogenous materials, this was not the case and the spectral features were comparable to the background. This

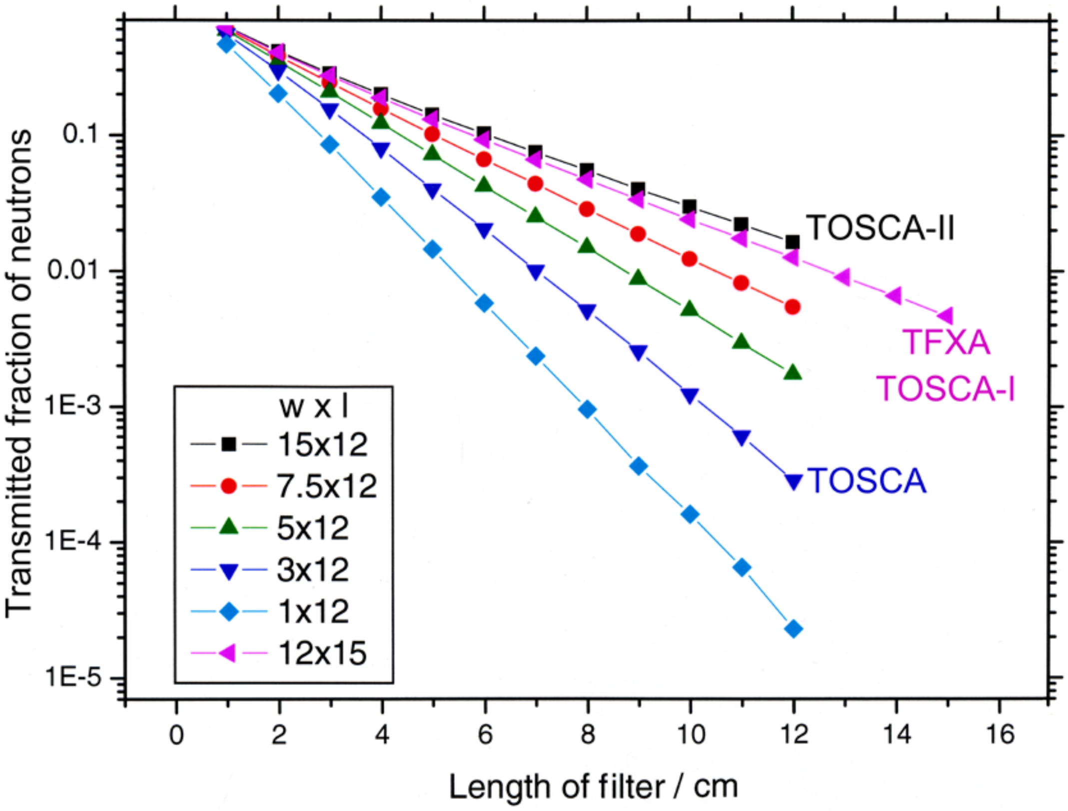

**Figure 3.** Transmission of higher-order neutrons through the beryllium filter as a function of the width (w) and length (l) of the filter, in centimeters. The filter sizes used for TFXA, TOSCA-I and the initial (TOSCA-II) and final implementation (TOSCA) are indicated.

problem was further aggravated by the realisation that the background was sample dependent, thus attempts to run a reference sample and subtract the resulting background were fruitless. The shielding around the sample environment tank, the graphite analysers and the detectors was systematically improved but without any significant reduction in the background.

The problem was finally solved by a series of Monte Carlo simulations of the transmission of the beryllium filter, the results of which are shown in Figure 3. This shows the fraction of higher-order neutrons ($\lambda/2$, $\lambda/3$…, with energies 128, 288… cm$^{-1}$) that pass through the filter as a function of the length and width of the filter. These calculations assume perfectly absorbing sides, a condition that is typically achieved *via* the use of cadmium up to epithermal energies. As such, they represent best-case estimates relative to actual performance in the laboratory, where other secondary sources of background might be possible.

Notwithstanding these limitations, the neutron-transport simulations show that the longer the filter or the narrower the filter, the better the rejection of the higher order neutrons. This explains one of the most puzzling aspects of the problem: why did this not occur with either TFXA or TOSCA-I? There are two factors that are relevant to this discussion: firstly, both used 15 cm long filters, so the rejection was about a factor of four better than the 12 cm long filters used on TOSCA due to space constraints. Secondly, and very fortuitously, the undesired neutrons manifest at about the same time-of-flight as the elastic line when the instrument is at 12 m, thus do not greatly influence the spectrum. With the instrument at 17 m, the 'bad' neutrons still occur at about the same time-of-flight because the incident flight time is not greatly increased for these relatively high-energy neutrons as they must have an energy of at least 128, 288… cm$^{-1}$ *after* scattering, but this time period now corresponds to energy transfers in the 'spectral' range and contaminate the data. This also explains why the background is sample dependent.

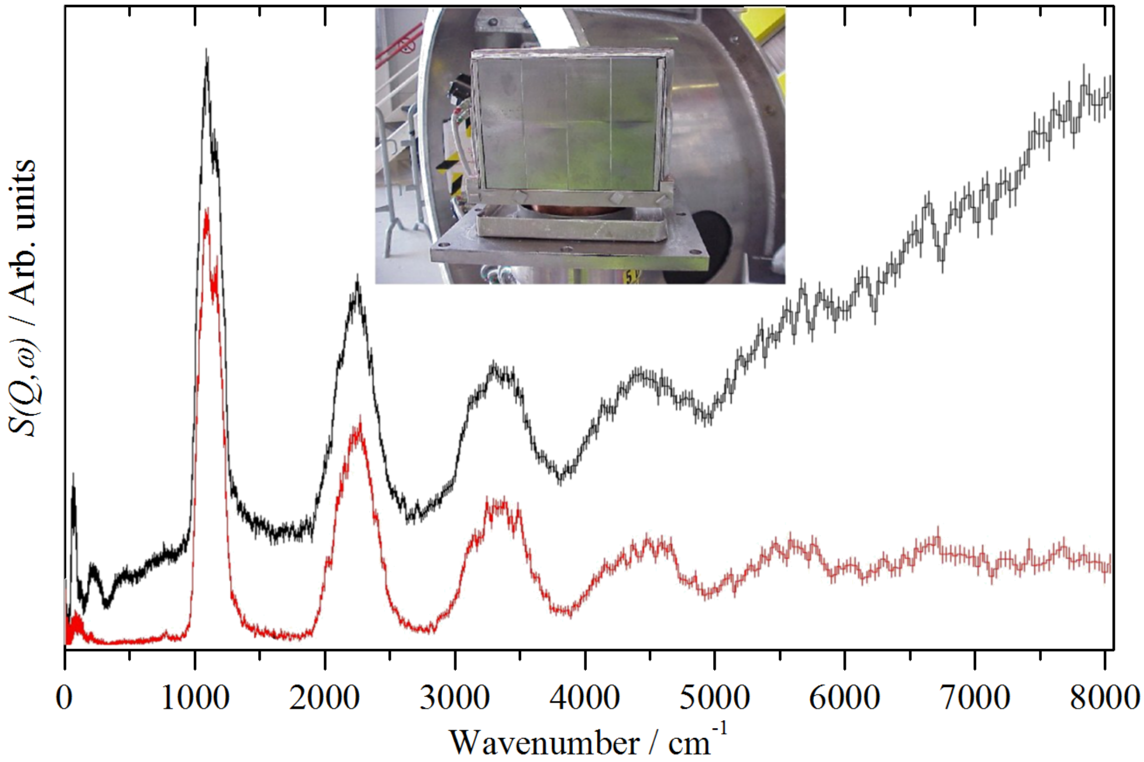

**Figure 4.** Comparison of the INS spectra of $ZrH_2$ before (upper, black) and after (lower, red) the filters were sectioned. The inset shows the beryllium filter after sectioning, the thin vertical lines are the cadmium absorbers.

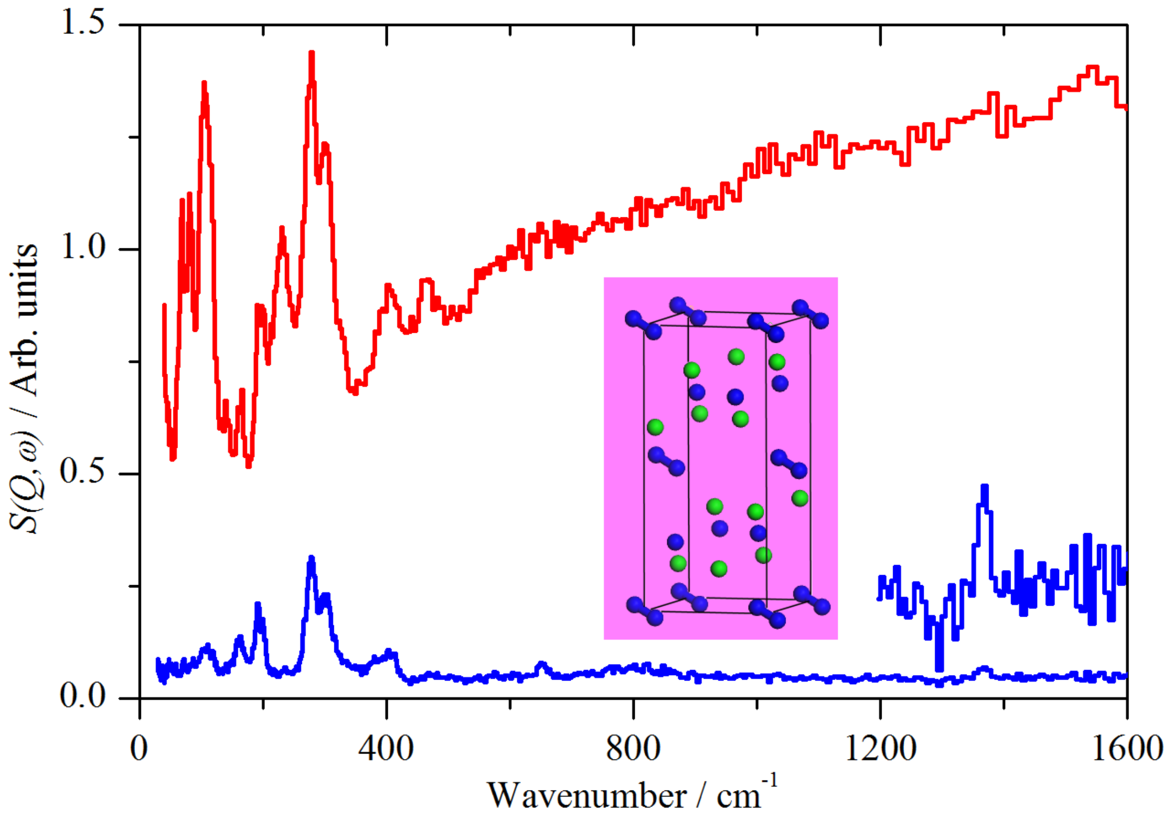

**Figure 5.** Comparison of the INS spectra of SrN [6] recorded before (upper) and after (lower) the filters were sectioned. The region 1200 – 1600 cm$^{-1}$ is shown ×10 ordinate expanded. The crystal structure is shown as an inset (blue = nitrogen, green = strontium).

Previous work [6] has shown that the problem can be effectively addressed by ‘poisoning’ the filters. The effective width of the filter was reduced by slicing the beryllium into 3 cm wide blocks along the direction of flight and inserting 1 mm sheets of cadmium between the beryllium slices. The results are startling, as shown in Figures 4 and 5. These compare INS spectra of the same sample recorded before and after the filters were sectioned. In Figure 4, both spectra were recorded simultaneously and compares two banks of detectors; one where the beryllium was a solid block (upper, black) and the other where the beryllium had been sectioned (lower, red). The reduction in background by almost a factor of 10, with no loss of intensity in the spectral features is obvious. The noise level is lower for the sectioned case (compare the size of the error bars in the black and red traces) because the unwanted background neutrons contribute to the noise level.

For the non-hydrogenous compound SrN [7] (better described as $\{[Sr^{2+}]_4\ [N^{3-}]_2\ [N_2^{2-}]\}$), the decreased background allows observation of the N=N stretch at 1380 cm$^{-1}$. It also shows that most of the features below 200 cm$^{-1}$ are spurious, greatly simplifying the analysis. The lessons learnt over the course of this upgrade of the TOSCA energy analysers have been instrumental in the specification and subsequent design of a new beryllium filter on the OSIRIS spectrometer at ISIS, a project which was recently successfully completed [8].

### *2.2. Extension of the spectral range*

The installation of TOSCA at 17 m greatly improved the spectral resolution but it restricted the energy transfer range to > 25 cm$^{-1}$. This was because the elastic line occurs at ~23000 µs and since ISIS operates at 50 Hz, a neutron pulse occurs every 20000 µs (a frame), thus fast neutrons would overtake

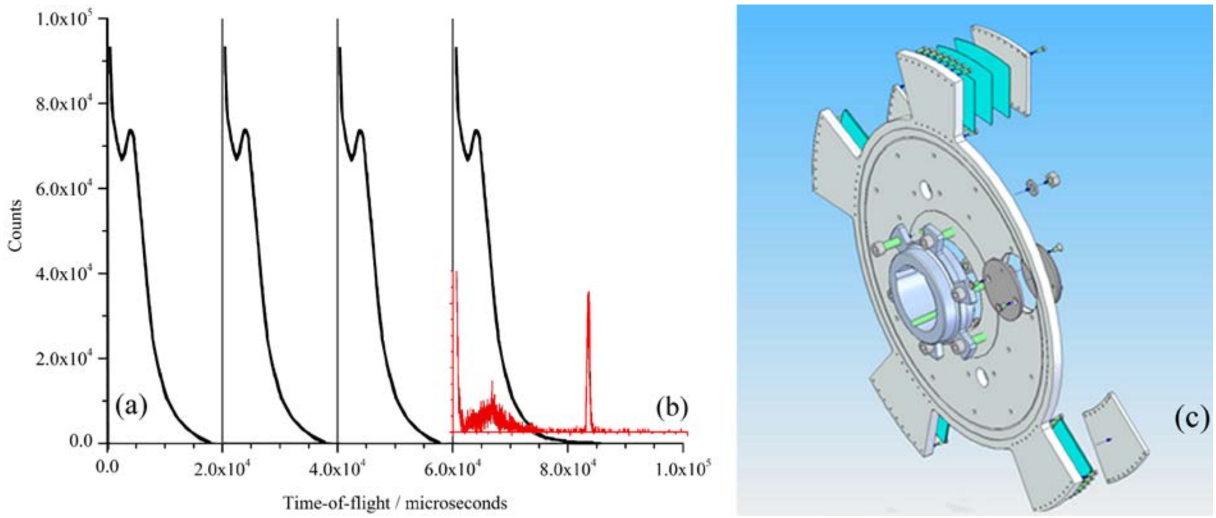

**Figure 6.** (a) Incident monitor spectra (black trace) when TS2 is operating showing the three short 20000 μs frames and the long 40000 μs frame, (b) time-of-flight spectrum (red trace) in an inelastic detector, showing the elastic line at ~23000 μs and (c) schematic of the new disc chopper that enables the long (TS2) frame to be exploited to extend the energy transfer range of TOSCA.

slow neutrons from the preceding pulse. This is catastrophic for time-of-flight analysis since it renders the 'time stamping' that the method depends upon unreliable. In the original form of TOSCA this was prevented by the addition of a 'tail cutter', a sheet of neutron absorbing material on the leading edge of the Nimonic chopper used for suppression of the unmoderated neutrons and γ-rays produced by the proton beam impacting the target. (There was concern that these would cause increased background).

In 2008 ISIS, began operating the second target station (TS2). TS2 takes one pulse in five from the accelerator, resulting in three 20000 μs frames followed by a 40000 μs frame, Figure 6a. Soon thereafter, it was realised that TS2 operation would enable access to energy transfers below 25 $cm^{-1}$, including the elastic line, as shown in Figure 6b. As investigation had shown that the fears concerning background from the prompt pulse were phantasmal, the Nimonic chopper was replaced by a disc chopper, to block the slow neutrons for three pulses and allowed them to pass during the long (TS2) pulse. Note that the spectral range is extended *without* loss of flux. The chopper is shown schematically in Figure 6c.

The result of the innovation is that the energy transfer range now extends to -25 $cm^{-1}$ and includes the elastic line. This development is potentially very useful, as it provides a direct measure of the quantity of orthohydrogen present in a sample when dihydrogen is being studied. The extension to lower energy is illustrated in Figure 7 that compares INS spectra in the low energy region of γ-picoline (4-methylpyridine) recorded on TOSCA and on the high-resolution backscattering spectrometer IRIS. The rotational tunneling transition at 4.2 $cm^{-1}$ is clearly seen in both datasets, the greater resolution of IRIS enables the fine structure of the transition to be observed, (inset at top right of Figure 7).

This development provides overlap between the instruments and potentially allows TOSCA to be used for quasielastic neutron scattering studies of very fast processes, albeit only at two momentum transfer values corresponding to the forward and backscattering detectors. Note that this development is not at the expense of reducing the energy transfer range: the complete spectrum from -25 $cm^{-1}$ to >4000 $cm^{-1}$ is measured.

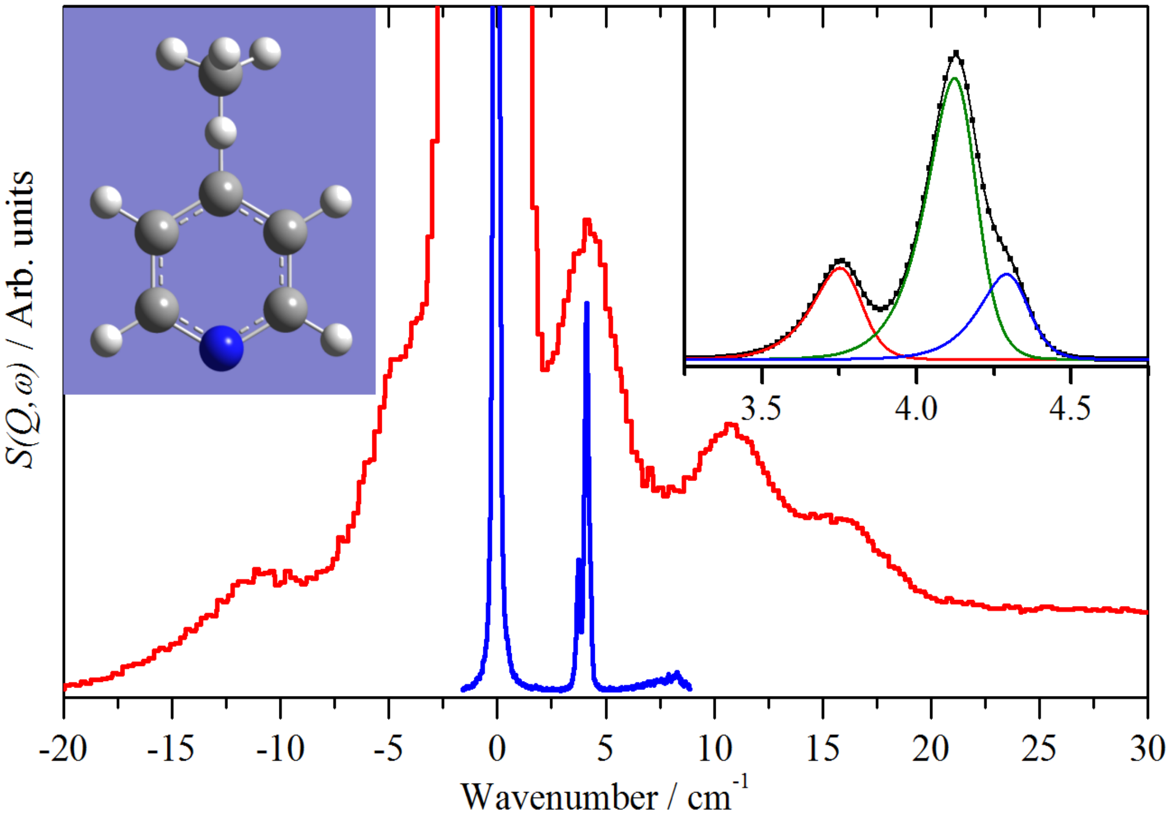

**Figure 7.** Comparison of the INS spectra of γ-picoline (4-methylpyridine, see inset in top left of the figure) recorded on TOSCA (red trace) and on IRIS (blue trace). The rotational tunneling transition at 4.2 cm$^{-1}$ is clearly seen in both datasets, the greater resolution of IRIS at low energy transfers enables the fine structure to be observed, (inset at top right).

## 3. Ongoing and future developments

Neutron guides provide a means to transport neutrons across tens of metres with greatly reduced losses as compared to a simple tube. Mathematically, the process is completely analogous to light transmission along a fibre optic cable except that the transmission occurs for neutrons by total external reflection rather than by total internal reflection as it does for light. When TOSCA was constructed, consideration was given to incorporation of a guide. However, at that time neutron guides typically had $m \approx 1$ (where $m$ is the ratio of the critical angle of the supermirror to that of nickel) and for the relatively hot neutrons required for vibrational spectroscopy, the small gains at low energies did not justify the investment.

In the last decade, both guide technology and the ability to simulate them have advanced significantly. For TOSCA to move forward beyond the current state-of-the-art in key scientific areas such as gas and charge storage, the most urgent need is for greater sensitivity *via* provision of a guide in the primary spectrometer. Simulations of incident flux gains for a series of guide-reflectivity factors are shown in Figure 8. For example, a seamless $m = 5$ guide leads to a *ca.* ×20 increase in flux at the $H_2$ rotational line transition energy (~120 cm$^{-1}$), while a ×3 gain is still attainable at 2000 cm$^{-1}$.

Such an increase in incident flux implies an order-of-magnitude reduction in counting times, a transformational development as it would enable routine studies of industrially relevant systems containing weak neutron scatterers ($CO_2$, $SO_2$, CO, NO) or minute amounts of hydrogen (*e.g.*, proton

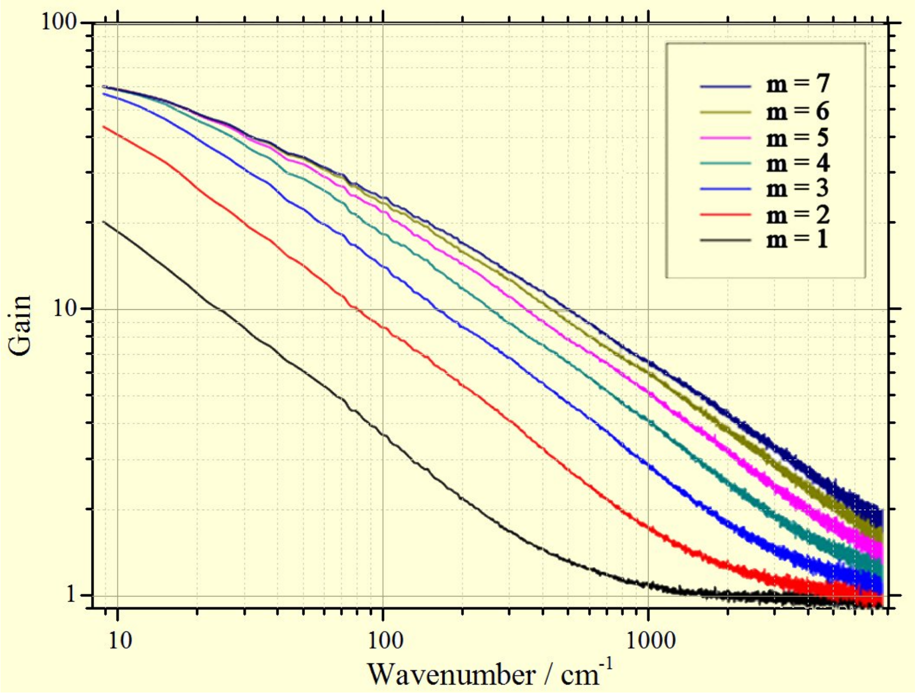

**Figure 8.** Predicted gains in incident flux at the sample position of TOSCA as a function of energy transfer and *m* number.

conductors or supported catalysts). Parametric studies would become routine as well, particularly for hydrogen-containing molecules such as hydrocarbons. This upgrade would also enable access to smaller specimens. At present, 100 mg of a hydrogenous organic sample or several grams of a non-hydrogenous sample remain challenging. A guide should reduce these limits by over an order of magnitude. Likewise, the remit of the (very popular) TOSCA Xpress service could be expanded. These proposals were recently endorsed by an International Review Panel who recommended: '*The panel agreed that the guide upgrade has to be taken up with the highest priority*'.

TOSCA has had modest high-resolution diffraction capabilities since its installation (four $^3$He tubes in backscattering). However, these have not been used extensively because of low count rates and also because coherent scattering is typically swamped by incoherent backgrounds in hydrogenous systems. Given the increasing interest in non-hydrogenous materials, the higher incident flux from a guide would accelerate this on-going trend, also paving the way for much needed simultaneous structural and spectroscopic studies of complex materials under realistic conditions. To this end, additional diffraction modules at 175°, 135° and 45° would significantly (and usefully) extend the *d*-spacing range currently available.

## 4. Conclusions

For the last decade or so, TOSCA has set the standard internationally for broadband, high-resolution vibrational spectroscopy with neutrons. So far, it has out-performed all analogous spectrometers both in terms of spectral resolution and signal-to-background ratio. Across the fingerprint region (800 – 1600 cm$^{-1}$) of the mid-infrared spectral range (400 – 4000 cm$^{-1}$), the resolution of TOSCA has been unmatched by any instrument at ISIS and beyond until relatively recently. Our experience is that in virtually all cases, intrinsic (*e.g.*, heterogeneously broadened) spectral line widths are broader than the instrumental resolution. After a decade of operation, less than half-a-dozen samples have been resolution limited on the instrument.

TOSCA has been such a success that it is the inspiration for VISION [9] at SNS. VISION will have a *ca.* ×100 advantage in detected flux over TOSCA. The similarity of design means that it should also have negligible backgrounds. In addition, the new instrument IN1-Lagrange [10] at ILL delivers a much higher flux than TOSCA (and possibly even more than VISION). However, the resolution remains comparable to TFXA (*i.e.,* similar to that of most currently operating instruments). IN1-Lagrange is probably the spectrometer of choice for very small samples (a few mg or less) and extensive parametric studies, particularly over narrow energy transfer ranges.

The implementation of a guide on TOSCA combined with the planned upgrade in the first target station at ISIS will deliver an instrument that will continue to be at the forefront of vibrational spectroscopy with neutrons in the foreseeable future.

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