Robust measurement of para-ortho H$_2$ ratios to characterise the ISIS hydrogen moderators

Giovanni Romanelli$^{a,b,*}$, Svein Rudić$^a$, Maciej Krzystyniak$^{a,c}$, Felix Fernandez-Alonso$^{a,d}$, Damian Fornalski$^a$, Mark Kibble$^a$, Chris Goodway$^a$, Jon Bones$^a$, Molly Probert$^a$ and Goran Škoro$^a$

$^a$ ISIS Facility, Rutherford Appleton Laboratory, Didcot OX11 OQX, UK
$^b$ Centro NAST, Università degli Studi di Roma Tor Vergata, Via della Ricerca Scientifica 1, 00133 Roma, Italy
$^c$ School of Science and Technology, Nottingham Trent University, Clifton Campus, Nottingham, NG11 8NS, UK
$^d$ Department of Physics and Astronomy, University College London, Gower Street, London, WC1E 6BT, UK
E-mail: giovanni.romanelli@stfc.ac.uk

Abstract. We discuss an experimental approach to determine the concentration of para-H$_2$ in the hydrogen moderators serving the Target Stations 1 and 2 at ISIS. The outcome of the measurements based on this approach is crucial for the Target Station 1 project, where a detailed characterisation of the present performance is needed to test neutronics simulations. The approach described here is based on the measurement of neutron transmission spectra over a wide energy range of samples extracted from the moderators. Pilot experiments were performed on the VESUVIO spectrometer at ISIS and were combined with measurements of thermal conductivity of the same samples using the ISIS para-H$_2$ rig.

1. Introduction
During the preparation for the ISIS Target Station 1 (TS-1) project, special attention has to be paid to the optimisation of the hydrogen (H$_2$) moderator, where the suitability of any potential new design strongly depends on the assumed concentrations of para-H$_2$ (pH$_2$) and ortho-H$_2$ (oH$_2$) nuclear-spin isomers in the moderator. The very same is true for a potential upgrade of the TS-1 H$_2$ moderator where the analysis of the data from the LOQ [1, 2] incident beam monitor over the last 10 years; the diffraction set-up added to CRISP [3, 4] to measure pulse widths over a cycle of experiments; and a comparison between experimental time-of-flight data from OSIRIS [5, 6] with corresponding simulations. On the basis of these results, it is currently assumed that the pH$_2$ concentration, $p_{\alpha}$, should be around 80% in the current TS-1 H$_2$ moderator and that the concentration in TS-2 should be qualitatively higher.

2. Experimental set-up
To determine $p_{\alpha}$ experimentally, Neutron Transmission (NT) measurements were performed on the VESUVIO spectrometer at ISIS [7, 8, 9] using the pH$_2$ Rig (pHR) [10]. The experimental set-up is sketched in Figure 1. Time-of-flight spectra were measured by $^6$Li monitors placed...
between the neutron source and the sample (a) and after the sample (b). Normal H$_2$ (nH$_2$) was commercially available; a high-purity pH$_2$ sample was prepared within the pHR; and the mixtures from TS-1 and TS-2 moderators were collected at the end of the 2016/03 ISIS user-round cycle. The experiment was performed ca. 2 weeks after the collection of the samples and these were stored in PTFE-coated bottles. Gas mixtures were loaded in a flat Al container with sample thickness $d = 0.5$ mm. The temperature of the sample during the experiment was set to 15 K in the liquid phase. The gas-loading procedure was controlled by using 316-type stainless-steel buffers attached to the pHR, and by monitoring the stability of transmission and forward-scattering spectra.

3. Measurements of pH$_2$ concentrations

Neutron cross sections ($\sigma_\alpha$) [11] and heat capacities ($C_\alpha$) [12, 13] largely differ for pH$_2$ and oH$_2$, as shown in Figure 2. At equilibrium conditions and room temperature, nH$_2$ has $p_\alpha = 25\%$, as a consequence of the 3:1 ratio of nuclear-spin states of oH$_2$ (triplet) to pH$_2$ (singlet).

![Figure 1. Schematic design of the VESUVIO instrument at ISIS; the additional set-up for sample loading using 1.0 l buffers; and the gauge for resistance measurements using the pHR.](image)

![Figure 2. Neutron cross sections [11] as functions of the incident-neutron energy $E$ (a) and isochoric heat capacities as function of temperature $T$ [12, 13] (b) of H$_2$ mixtures.](image)

NT spectra $T(E)$, as functions of the incident-neutron energy $E$, are related to the neutron cross section $\sigma_\alpha(E)$ of the sample according to the following expression

$$T_\alpha(E) = \frac{S_\alpha(E) - B(E)}{C(E) - B(E)} = \exp(-n\sigma_\alpha(E)d),$$

where $\sigma(E)$ is affected by the nuclear dynamics and Pauli exclusion principle [14, 15], $S_\alpha(E)$ is the spectrum from the sample $\alpha$ in the container, $C(E)$ is the empty-container spectrum and
$B(E)$ is the empty-instrument background. Spectra were further normalised to incident-monitor counts. One can express the cross section of the sample as the following combination of cross sections of the two nuclear-spin isomers, $\sigma_\alpha(E) = p_\alpha \sigma_p(E) + (1 - p_\alpha) \sigma_o(E)$. It is worth noticing that pH$_2$ and oH$_2$ neutron cross sections, $\sigma_p(E)$ and $\sigma_o(E)$, present the largest differences for incident-neutron energies below 50 meV [11].

Similarly, the calibration gauge in the pHR was used to obtain a relative value of $p_\alpha$ based on the differences in the thermal conductivity of the mixture $\alpha$ with respect to nH$_2$. A similar approach had already been attempted in the past, as for example in Refs. [16, 17] The gas thermal conductivity is inferred from a measurement of the electrical resistance $R$ of a Pt wire at constant current and voltage. When a non-negligible current flows within the wire, its temperature $T$ and its resistance $R$ increase because of the electrical energy released. The external wall of the gauge is maintained at the temperature of liquid $N_2$ and the temperature and resistance of the wire are higher for lower thermal conductivity of the gas mixture. Moreover, for an ideal gas, the thermal conductivity can be considered proportional to the isobaric heat capacity. For the steady system, the heat release in the wire per unit of time is equal to the heat absorbed by the $N_2$ bath. Assuming that the heat capacity can be expressed as $C_\alpha(T) = p_\alpha C_p(T) + (1 - p_\alpha) C_o(T)$, one can determine the value of $p_\alpha$ from the measured resistance $R_\alpha$ of the wire. Alternatively, one can interpolate the measured resistances between two values related to known mixtures, say nH$_2$ and a pure pH$_2$ samples.

![Figure 3. Conversion of pH$_2$ in the PTFE-coated bottles (a) and in the rig buffers (b) compared to the rate $f(t)$.

4. Results and Discussion

Samples from the H$_2$ moderators can be collected at the end of an ISIS cycle only. Therefore, a time of the order of 2 weeks is expected before NT measurements can be performed. To take into consideration this delay, the stability of $p_\alpha$ in the samples over a period of time of 12 weeks has been characterised. Figure 3a shows the change of the resistance measured by the gauge in the pHR as a function of the time the samples spent in PTFE-coated steel bottles. A slow decrease of $p_\alpha$ of the order of 2%/per week was observed, and the conversion process was approximately linear over the 12 weeks of monitoring. The values $R_\alpha$ for nH$_2$ were found approximately constant over the same period. Moreover, the values $R_p$ for pH$_2$ produced with the pHR several times during the 12 weeks were found to be consistent, thus confirming that our pH$_2$ generation process is reproducible. On the other hand, a quick decrease of $p_\alpha$ was measured for pH$_2$ that stayed in the steel buffer for about 30 minutes. The conversion rate is of the form $f(t) = R_p + (R_\alpha - R_p)(1 - \exp(-t/\tau))$ with $\tau \sim$ 9 minutes (see Figure 3b).

NT measurements were performed on the nH$_2$ sample and on the samples from TS-1 and TS-2 moderators partially converted in the buffers. Figure 4 shows the comparison of experimental transmission of the nH$_2$ sample (8 hours of measurement) to MCNP-x simulations [18] of 0.5 mm thick H$_2$ mixtures with $p_\alpha = 25\%$, 70\%, 75\% and 80\%. A good agreement is found between experiment and simulation in the known case of the nH$_2$ sample (green error bars). The case of the partially-converted sample from TS-1 is also shown (black error bars, 2 hours of measurement) as an example of statistical uncertainties for a shorter measurement. By comparison to the simulated predictions with $p_\alpha = 70\%$, 75\% and 80\%, one can assess the
Figure 4. Simulated transmission spectra (markers) for a sample thickness of 0.5 mm. Experimental error bars correspond to nH$_2$ (green) and partially-converted TS-1 (black) samples.

experimental uncertainty on the pH$_2$ percentage within the sample after 2 hours of data acquisition below 10%, that would improve to about 5% after 8 hours of acquisition time.

5. Outlook
In this preliminary study, we have successfully tested an experimental set-up to carry out neutron transmission measurements on VESUVIO to determine the concentration of pH$_2$ in the ISIS H$_2$ moderators. We have characterised the conversion of pH$_2$ in the samples stored in the PTFE-coated bottles and steel buffers. This work paves the way for future transmission experiments.

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