Spin isomers in the ISIS TS1 cryogenic hydrogen moderator

Molly Probert, Goran Škoro, Svenimir Rudić, Giovanni Romanelli, Robert Bewley, Stephen King, David Haynes, John Webster, Felix Fernandez-Alonso and Maciej Krzystyniak
ISIS Neutron and Muon Source, Science and Technology Facilities Council, Rutherford Appleton Laboratory, Didcot OX11 0QX, United Kingdom
E-mail: molly.probert@stfc.ac.uk

Abstract. As part of the ISIS TS1 project, work has been carried out on the cryogenic hydrogen moderator system, the main focus being understanding and improving the ratio of spin isomers in the liquid hydrogen moderator.

1. Introduction
Hydrogen comes in two spin states: ortho (o-H\textsubscript{2}) and para (p-H\textsubscript{2}). Of the two spin states the para state is preferable for the neutronics performance of the moderator [1, 2, 3]. At ambient temperature (so-called normal, n-H\textsubscript{2}) hydrogen the ortho/para ratio is 3 : 1, which should convert to an equilibrium state of nearly 99.8% para at the 24K temperature of the moderator. However, the conversion process is very slow without a catalyst and the effects of radiation on the back conversion are relatively unknown (see [4] and the references therein). Catalysis of the relaxation process is necessary as the process is slow with rate of approximately 2% per hour [5] taking weeks to happen naturally with no external encouragement. Catalysis can take the form of magnetic centres on the containment material such as stainless steel, or other materials that decouple the hydrogen molecule [6], as it will naturally tend to recombine in the lowest energy state for the temperature of the environment.

2. Current ISIS TS1 hydrogen cryogenic system
The hydrogen cryogenic system at ISIS Target Station 1 (TS1) was designed and built in the 1980’s. The moderator itself started out as a supercritical liquid hydrogen moderator with a cadmium decoupler but the moderator was never run super critical and the decoupler was removed in 2006. Some of the key parameters of the system as it operates currently are displayed in Table 1. There are five instruments that view the hydrogen moderator: CRISP, IRIS, LOQ, OSIRIS and SURF [7]. The hydrogen system is purged and filled with low pressure helium after each user cycle, and purged and refilled with a new batch of n-H\textsubscript{2} at the end of the shutdown. This generally happens about a week before the user run starts as the moderators need to be cold during beam physics. This allows a certain amount of time for the hydrogen to convert naturally with some help from the stainless steel pipework it flows through (the cool down and liquefaction takes between 6 and 8 hours). The original design of the hydrogen cryogenic system...
Table 1. Current Hydrogen system parameters

| Parameter                  | Value | Units |
|----------------------------|-------|-------|
| LH2 Volume in Moderator    | 1     | Litre |
| Flow Rate                  | 0.5   | L/s   |
| Mass Flow Rate             | 36.5  | g/s   |
| Beam Heat                  | 200   | W     |
| Delivery Temperature       | 23    | K     |
| Delivery Pressure          | 8     | bar   |
| Catalyst Volume            | 1.2   | cm³   |

had a very small amount of Ferric Oxide (Fe₂O₃) catalyst that was not of sufficient size to convert the volume of hydrogen in the system at any noticeable rate (see Figure 1). There has also been no reactivation or increase in volume of the catalyst during the lifetime of the cryogenic cold box. Now we are at the stage of designing a replacement system to incorporate a properly sized catalyst and hopefully an in-situ measurement device that should fit in with the existing transfer lines and cold box footprint.

3. Spin isomers ratio determination
The ortho/para ratio affects each of the instruments in a different way due to their operational differences. They all also have their own method of normalising out any effects a change in p-H₂ concentration would have on any of their experiments. This has led to the ortho/para ratio being a known problem but never a high priority to control or investigate the nature of how it changes. Due to the ongoing ISIS TS1 Project the need for better understanding of the ratio of spin isomers in the liquid hydrogen moderator has become greater. A detailed study has been performed in an attempt to characterize the ortho/para H₂ fraction using data from the LOQ incident beam monitor collected over the last 10 years [8, 9]. The main idea was that the variations of count rates (and wavelength dependence of these variations) in a single cycle, if combined with Monte Carlo simulation results, could give an indication about the ortho/para conversion. The simulations are important for an interpretation because neutron intensity fluctuations as a function of wavelength depend strongly on the starting/final values of the para-hydrogen fraction (especially at long wavelengths). So, the cycles where the variations are relatively large or where something happened (for example, the hydrogen system was purged and restarted during a cycle) were of special interest (see Figure 2). The analysis of those special events and comparison with Monte Carlo simulations show that the hydrogen behaviour is compatible with the so-called natural conversion scenario and that the maximal value of the H₂ para-fraction during the last 10 years was around 80%. This value is in nice agreement with the value obtained from comparison of the shape of the experimental time-of-flight data from the OSIRIS instrument with corresponding simulation results [10]. In addition to these, the diffraction setup added to the CRISP instrument has been used to measure pulse widths as a function of wavelength over a cycle. The full width at half maximum (FWHM) values of the time pulse lie between the simulated values from 80% and 100% para hydrogen content (Figure 3), suggesting a maximal para-fraction value of 90% [11].
3.1. Grab sample measurements

A system was devised for taking ambient temperature grab samples from the TS1 and TS2 H₂ systems after a cycle. To alleviate the possibility of back conversion due to contact with stainless steel, cylinders with internal PTFE coating and brass fittings were used as they have been proved to be effective elsewhere [12]. Various methods, including Cavity Ringdown Spectroscopy [13], thermal conductivity measurements and neutron transmission measurements have been attempted to obtain the para hydrogen fraction from these samples. A method that is currently being implemented is based on the direct measurement of the neutron transmission through thin hydrogen samples (with different para-hydrogen fractions) using the VESUVIO instrument [14] at ISIS, combined with measurements of thermal conductivity of the same hydrogen samples using a para-hydrogen gauge (and a para-hydrogen generating cell) [15] originally built for use by the TOSCA instrument [16]. The samples from the hydrogen moderators at TS1 and TS2 were taken at the end of user cycle just before shutdown and measured with the thermal conductivity rig, then when the next user cycle started a couple of weeks later the measurements were repeated and compared to a neutron transmission measurement on the VESUVIO instrument. The initial results of these tests have provided a sound proof of concept and further tests are planned for the next few cycles [17].

4. Upgraded hydrogen system

The TS1 Project aims to increase flux, where possible, but not decrease the performance of the instruments viewing the LH₂ moderator. The expected gain in neutronics performance [18] is due to the presence of water premoderator, increased thickness of the moderating material (from current value of 8 cm to 10 cm) and increased para-hydrogen fraction (from current value of about 80 % to 99 %). As can be seen, the functionality of the associated cryogenic system will be broadly similar. The moderator itself will increase in volume hence the flow speed might change if the heat loads are significantly altered but the needs of the system to have an abundance of p-H₂ is still the same. A catalyst (Ionex, Fe₂O₃) of around 5 litres will be added to the system, which is enough to convert the total LH₂ inventory within an hour. Whilst it is simple to make
this larger to convert the whole inventory in a single lap, in practice this is never necessary, as the cool down of a new charge of hydrogen takes upwards of 6 hours, mostly due to the heat load of the stainless steel transfer lines. The back conversion from the radiation in the moderator head is minimal compared to the initial conversion from n-H\textsubscript{2}. Installation of an in-situ measurement device to determine the ortho/para ratio during a cycle is also in the process of being designed. From several options, the easiest to implement is a relative measurement of the temperature change across the catalyst (a robust calibration will be needed) to monitor its "activity". Access to the catalyst will also be designed to allow for reactivation/replenishment (if necessary), as well as, a facility for hydrogen sample extraction so future results can be compared to the current experiments.

5. Conclusions
The work to characterise the ortho/para ratio in the LH\textsubscript{2} moderator on the ISIS TS1 is ongoing. We have worked from various angles to determine the ortho/para ratio of the hydrogen, from numerical simulations via flux measurements to taking hydrogen samples from the moderator and using different techniques to perform measurements of ortho/para hydrogen fractions. As the system currently stands the catalyst is severely undersized for the volume of liquid hydrogen. Therefore, introducing a suitable catalyst to the system as part of the upgrade and techniques for in-situ measurements during future running of the system are proposed.

Acknowledgments
The work presented in this paper is the combination of a great deal of time and effort by a large number of people. We would like to acknowledge the main contributors to the project here (listed in alphabetical order): John Chapman, Rob Dean, Beth Evans, Stephen Harrison, David Jenkins, Mark Kibble, Andy Robinson, Chris Russell from ISIS and Michele Gianella and Grant Ritchie from the Theoretical Physical Chemistry Laboratory at Oxford University.

References
[1] Harada M et al 2005 Nucl. Instr. and Meth. in Phys. Res. A 539 345362.
[2] Mezei F et al 2013 https://arxiv.org/pdf/1311.2474.
[3] Grammer K B et al. 2015 Phys. Rev. B 91 180301.
[4] Iverson E B and Carpenter J M 2003 Proceedings of ICANS-XVI, Dusseldorf, Germany p. 707-717.
[5] Enss C and Hunklinger S 2005 Low-Temperature Physics (Berlin: Springer).
[6] Matthews M, Petipas G and Aceves S 2011 App. Phys. Lett. 99 081906
[7] http://www.isis.stfc.ac.uk/
[8] Škoro G and Probert M 2015 TS1 Hydrogen moderator: ortho/para conversion puzzle ISIS Internal Report.
[9] Škoro G, Probert M et al 2016 Cold moderators at ISIS Talk at 2nd RCM IAEA Coordinated Research Project on Advanced Moderators for Intense Cold Neutron Beams in Materials Research, Vienna, Austria.
[10] Bewley R 2016 TS-1 baseline: experiment vs. simulations Talk at 2nd ISIS TRAMSNEG Meeting.
[11] Bewley R 2016 TS-1 baseline: experiment vs. simulations Talk at 3rd ISIS TRAMSNEG Meeting.
[12] Tom B et al 2009 Rev. Sci. Instr. 80, 016108.
[13] Gianella M 2016 Hydrogen ortho/para ratio The Ritchie group report.
[14] http://www.isis.stfc.ac.uk/instruments/vesuvio/
[15] Evans B, Bones J and Goodway C 2010 Para-Hydrogen Gauge Technical Report ISIS Internal Report.
[16] http://www.isis.stfc.ac.uk/instruments/tosca/
[17] Romanelli G et al. 2017 Direct measurement of proportion of H\textsubscript{2} para/ortho isomers in liquid hydrogen moderators at ISIS This Proceedings.
[18] Škoro G, Lilley S and Bewley R 2017 Neutronics analysis of target, moderators and reflector design for the ISIS TS-1 project Physica B (to be published).