

## Hydrogen gas sample environment for TOSCA

**Mark G Kibble, Anibal J Ramirez-Cuesta, Chris M Goodway, Beth E Evans and Oleg Kirichek**

ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, OX11 0QX, United Kingdom

E-mail: oleg.kirichek@stfc.ac.uk

**Abstract.** The idea of using hydrogen as a fuel has gained immense popularity over many years. Hydrogen is abundant, can be produced from renewable resources and is not a greenhouse gas. However development of hydrogen based technology is impossible without understanding of physical and chemical processes that involve hydrogen sometime in extreme conditions such as high pressure or low and high temperatures. Neutron spectroscopy allows measurement of a hydrogen atom motion in variety of samples. Here we describe and discuss a sample environment kit developed for hydrogen gas experiment in a broad range of pressure up to 7 kbar and temperatures from 4 K to 473 K. We also describe para-hydrogen rig which produces para-hydrogen gas required for studying the rotational line of molecular hydrogen.

### 1. Introduction

Research on a viable and safe storage medium for hydrogen gas is becoming increasingly important for the development of a clean hydrogen-based economy. Storage of hydrogen gas in solids, able to act as reversible sponges for hydrogen absorption and desorption, is in that sense one of the most promising areas of hydrogen storage medium development [1]. Neutron spectroscopy allows measurement of hydrogen atom motion in solid state samples, which can explain the growing popularity of this technique in hydrogen storage material research.

While neutron diffraction is used to determine and investigate the crystal structure of the material, spectroscopy can measure the atom dynamics and obtain full phonon dispersion curves without the limitations typical in other vibrational spectroscopy techniques (e.g., Raman and IR).

Spectroscopic studies by neutrons are traditionally very well suited to looking into hydrogen physisorption phenomena. Most of the studies that have been done so far using the TOSCA spectrometer [2] refer to low temperature and high pressure experiments. But, thanks to recent instrument upgrades and improvements to the ISIS neutron source, a whole new range of possibilities has opened: even hydrogen chemisorption events can be investigated, requiring much higher temperatures than the conventional use at 77 K. Also hydrogen absorption in nano-porous materials at high pressure could be effectively investigated by TOSCA measurements, but has not been done before mainly due to the lack of sample environment equipment capable of reaching the required temperatures and pressures.

In this paper we describe a sample environment kit developed for hydrogen gas experiments on TOSCA instrument which consists of para-hydrogen gas handling rig, gas handling panels, high pressure intensifiers, sample sticks and sample cells. The kit provides sample environment in a broad range of pressures from vacuum up to 7 kbar and temperatures 4 K – 473 K. The para-hydrogen rig



produces para-hydrogen gas required for studying the rotational line of molecular hydrogen. This sample environment kit allows the investigation of hydrogen properties in confinement from a fundamental as well as from an applied point of view, giving full insight into the dynamics of molecular hydrogen in relation to the host matrix. The kit can be also used on other neutron scattering instruments. Experimental results that demonstrate the use of the para-hydrogen rig in TOSCA experiments are also presented.

## **2. Para-hydrogen gas handling rig**

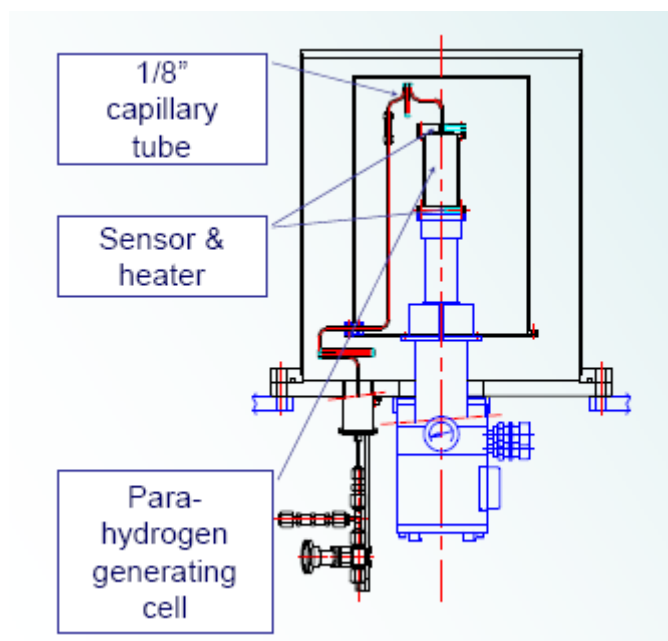
Normal hydrogen gas contains 25% para-hydrogen and 75% ortho-hydrogen. These two forms of hydrogen have different properties and are very useful to researchers studying hydrogen, particularly to those using neutron scattering. Normal hydrogen may be converted to almost 100% para-hydrogen at 20 K [3]. In the case of isolated or non-interacting molecules conversion is usually prevented. However a magnetic field gradient will catalyse this conversion. In the liquid or solid phase the conversion to para-hydrogen occurs very slowly, at a rate of less than 2% conversion per hour, via the interaction of magnetic dipole moments. In the low-density gas phase the conversion rate is extremely slow and high purity para-hydrogen samples can be kept for up to a year with very little reversion. There are techniques that allow the preparation of ortho and para-hydrogen with more than 99% purity.

In the case of liquid hydrogen the natural conversion to a 99% level of para-hydrogen purity is obtained after a few days. If the liquid is put in contact with a paramagnetic catalyst ( $\text{CrO}_3$ ) the conversion can happen within minutes.

Formerly, para-hydrogen was produced at ISIS using a conventional liquid cryogen-based cryostat. The operation of this kind of system required significant resources, created a number of logistical issues including the considerable cost of the required cryogens and posed health and safety problems. The progress in Closed Cycle Refrigerator (CCR) technology now offers a new generation of cryogenic systems with significantly reduced consumption and in some cases the complete elimination of cryogens [4]. There are two fundamentally different CCR based approaches. First, so-called “dry” systems that do not contain liquid cryogens at all, built around a CCR that utilises the cooling power produced by the cold head [5, 6]. The second option is based on the idea of re-condensing the evaporating helium back to a standard cryostat by a CCR [7]. The ISIS sample environment group has decided to design and construct a specific cryogen-free para-hydrogen rig based on the “dry” option.

The cryogenic part of the para-hydrogen rig is shown in figure 1. The assembly consists of a para-hydrogen generating cell, containing a catalyst, mounted on a CCR (Leybold 1040 cold head CR-05 with base temperature of 10K) and wired with temperature sensor and heater. The cell is connected to a gas handling system through 1/8” capillary tube for evacuation and for the control of the hydrogen supply and para-hydrogen extraction.

The base temperature of the para-hydrogen generating cell is 16 K, obtained in 4 hours from room temperature. The vibrations produced by the mechanical cooler sufficiently mix the hydrogen to bring about the maximum possible conversion rate through contact with the catalyst. The conversion process takes less than 12 hours for an efficiency of 98% conversion. Neutron measurements on gas samples have confirmed the maximum conversion to para-hydrogen, but the quality of the para-hydrogen may also be verified in-situ with a custom-built gauge. This gauge uses the difference in thermal conductivities of normal and para-hydrogen to determine the relative percentages of the two forms of hydrogen in a gas sample. Using this gauge the para-hydrogen percentage can be determined with < 2% error.



**Figure 1.** TOSCA para-hydrogen generating rig.

### 3. High pressure hydrogen gas sample environment

The ISIS sample environment group has a broad range of equipment for enabling experiments using high pressure inert gas cells [8, 9]. However the development of components for high pressure hydrogen systems is more difficult because of hydrogen embrittlement: a process whereby certain materials become brittle following exposure to hydrogen. High-strength steels, titanium and aluminium alloys seem particularly vulnerable to this form of corrosion, and fracture can often result from the ingress of atomic hydrogen into a material's crystal structure. During the development of equipment for high pressure hydrogen experiments on the TOSCA spectrometer special attention was paid to the hydrogen compatibility of materials and safety aspects of the equipment design.

The TOSCA high pressure hydrogen kit consists of gas handling panels, high pressure intensifiers, sample sticks and sample cells. The gas handling panels can be used for gas dosing (known volumes), gas mixing, gas flow (including moisture carrying), gas absorption/desorption and condensing, volumetric measurement and catalyst work. All the panels are fitted with pressure relief devices. The standard hydrogen gas handling panel covers a working pressure (WP) range from vacuum to 200 bar. The panel also contains a 124 bar WP 500cc buffer, three gas supply feeds, a pressure transducer and baratron.

### 4. High pressure hydrogen gas intensifier

For high pressure hydrogen gas experiments up to 3.5 kbar a two stage intensifier is used which consists of a first stage diaphragm pump (up to 2500 bar), a second stage hand intensifier (up to 3500 bar), transducer readouts that allow 1bar control increments (via the hand intensifier) and a safety burst disc protection system. The hydrogen two stage intensifier has been used in an experiment to maintain a pressure of 2800 bar for a five day period in an experimental cell at a temperature of 20 K. This experiment was conducted using the Inconel high pressure cell RLI 469, which is one of the two hydrogen high pressure Inconel cells within the ISIS sample environment group.

As a part of the Joint Research Activities FP7 [9] project, ISIS committed to building a 10 kbar hydrogen intensifier. Due to financial restraints, and the difficulty in sourcing a suitable system, it was decided to assemble an intensifier from commercially available components at ISIS. Hydrogen Intensifier with similar technical specifications has been developed at Hahn Meitner Institute (now

Helmholtz-Zentrum Berlin) [10]. This system uses different basic operational principle: the intensifier case is sealed and filled with an inert gas. Sensitive hydrogen gas sensors automatically shut the system down as soon as any presence of hydrogen is detected in the case. As a result the system has got almost zero tolerance to hydrogen gas leaks. The design of ISIS Intensifier allows small leaks which significantly relax demand for the system leak tightness. The system controller constantly monitors the pressure change rate in the high pressure part of the intensifier and if the rate exceeds established limit the system shuts itself down in a safe way. The intensifier frame is a fully welded construction that contains front and rear removable cover panels for accessing the internal components. The frame also includes an electrically isolated and hermetically sealed compartment for electronics. One cover panel houses the extraction port connection for intense ventilation of the system with nitrogen or other inert gas. The intensifier can be transported around the experimental hall using a lifting frame and then wheeled into position by the instrument. The 10 kbar hydrogen intensifier is similar in design to a standard gas intensifier, but with semi-automatic control of the high pressure stage.

The intensifier has a 'Burst disc recovery system' fitted to safely contain  $H_2$  vented in the event of any burst disc rupture in the system including the  $H_2$  centrestick. The 'Burst disc recovery system' comprises of 3 linked 3875cc buffer volumes (1bar Argon filled) connected to the intensifier system burst discs and centrestick burst disc within a closed circuit fitted with monitoring a pressure transducer and pressure relief valve.

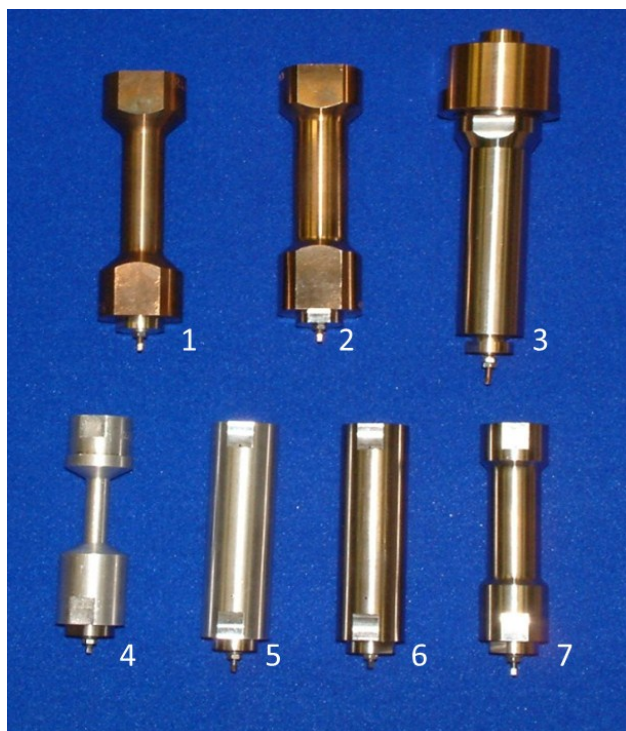
The intensifier has been assembled and tested with helium gas up to 10 kbar and hydrogen gas up to 8.5 kbar. The further testing of the system with hydrogen gas is in progress.

## **5. High pressure centre-sticks**

The ISIS hydrogen gas 10 kbar centre-stick allows a sample cell to be mounted to enable gas loading. The pressure and temperature can be monitored and the system is protected via a pressure relief device. The centre-stick can be used with 100 mm diameter variable temperature inserts and covers a pressure range from vacuum to 10 kbar of working pressure. A 3/16" heated capillary, 10 kbar Stansted transducer, sample cell thermometry and heating connections are also integrated in the design of the centre-stick.

## **6. High pressure sample cells**

Tosca high pressure sample cells are manufactured from neutron friendly materials with high resistance to hydrogen gas exposure to compliment the TOSCA instrument and experimental requirements. The cell wall thickness is a compromise between minimising the cell neutron scattering background and providing enough strength for the safe operation of the cell at its specified pressure and temperature.



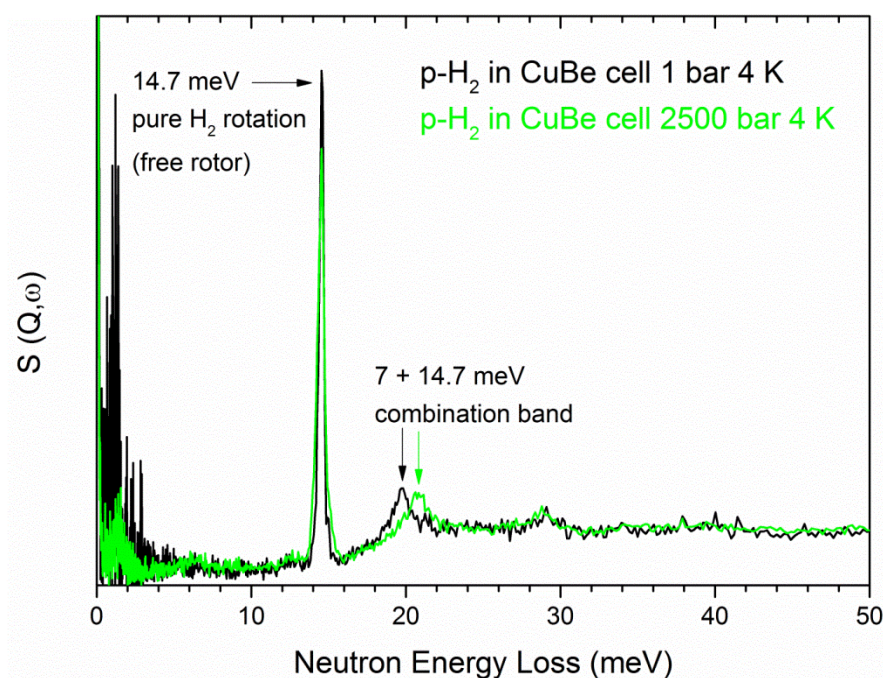
**Figure 2.** High pressure TOSCA sample cells; (1) 6 kbar hydrogen gas BeCu cell with temperature up to 20°C; (2) 7.36 kbar hydrogen gas BeCu cell up to 20°C; (3) 8 kbar hydrogen gas BeCu/TiZr cell (sleeved cell) up to 20°C; (4) 300 bar hydrogen gas Aluminium cell up to 100°C; (5) 4.4 kbar hydrogen gas Aluminium cell up to 20°C; (6) 5.4 kbar inert gas TiZr cell up to 20°C; (7) 6.35 kbar hydrogen gas Inconel cell up to 20°C.

The sample cells presented in figure 2 can be used in a passive or pressure rated regime for powder, liquid or solid samples. There are seven high pressure cells which can be used in TOSCA experiments: (1) 6 kbar hydrogen gas BeCu cell for temperatures up to 20°C, volume 2.23cc; (2) 7.36 kbar hydrogen gas BeCu cell for temperatures up to 20°C, volume 2.25cc; (3) 8 kbar hydrogen gas BeCu/TiZr cell (sleeved cell) for temperatures up to 20°C, volume 2.8cc; (4) 300 bar hydrogen gas Aluminium (7075 T6 Alloy) cell up to 100°C, volume 1.76cc; (5) 4.4 kbar hydrogen gas Aluminium (7075 T6 Alloy) cell up to 20°C, volume 1.77cc; (6) 5.4 kbar inert gas TiZr cell up to 20°C, volume 1.77cc; (7) 6.35 kbar hydrogen gas Inconel cell up to 20°C volume 1.77cc. All materials used for cells are known for high resistance to hydrogen gas exposure [11]. However the embrittlement is resulting from different chemical reactions in copper contained alloys [12] and steel [13] which can explain why BeCu is more popular as a material for hydrogen gas pressure cells. All the cells are tested and registered according to the ISIS high pressure vessel code of practice and have a limitation on the number of experiments they can be used in. For example the design service life of cell (1) is 400 cycles with periodical inspection at (1/2 design life) 200 cycles.

## 7. Neutron spectroscopy experimental results

An example of the use of high pressure cells to study the rotational dynamics of solid para-hydrogen is shown in figure 3.





**Figure 3.** Inelastic neutron scattering spectra of solid para-hydrogen ( $p\text{-H}_2$ ) recorded at a temperature of 4 K for two different pressures: 1 bar (black trace) and 2500 bars (green trace). Namely in both cases the solid  $p\text{-H}_2$  was kept under pressure of normal  $\text{H}_2$ .

Para-hydrogen was produced with the para-hydrogen rig described above. The cell is a BeCu high pressure cell shown in figure 2. The cell is cooled below 20 K and para-hydrogen is dosed into the cell. The cell is then pressurised to 5 bar with para-hydrogen and the temperature dropped to 4 K. Once the cell is cold, the centre-stick is detached from the para-hydrogen rig and connected to the high pressure rig so that the high pressure normal hydrogen can be added to the system. The signal observed is mostly para-hydrogen with the little contamination that arises from the introduction of normal hydrogen at high pressure. In order to minimise multiple scattering during the experiment the cell is filled with a solid cylinder made from aluminium, leaving an annular space of 0.1 mm. The inelastic neutron scattering spectra of solid para-hydrogen ( $p\text{-H}_2$ ) shown in figure 3 was recorded at a temperature of 4 K for two different pressures: 1 bar (black trace) and 2500 bars (green trace). As the normal hydrogen pressure increases the solid para-hydrogen stiffens and consequently the combination band which corresponds to the simultaneous excitation of rotational (14.7 meV) and lattice vibrational modes (7 meV) [14] is somewhat shifted toward higher wavenumbers.

## 8. Conclusions

Here we presented recently developed sample environment kit for hydrogen gas experiment in a broad range of pressure up to 7 kbar and temperatures from 4 K to 473 K. We also describe para-hydrogen rig which produces para-hydrogen gas required for studying the rotational line of molecular hydrogen. This sample environment kit allows the investigation of hydrogen properties in confinement such as hydrogen absorption in nano-porous materials or hydrogen chemisorption.

## Acknowledgements

We are grateful to Prof Felix Fernandez-Alonso, and Drs Stewart F. Parker and Svemir Rudic for valuable discussions, help with data analysis and comments about the manuscript. This research project has been supported by funding under the STFC Facility Research and Development Scheme and by the European Commission under the 7<sup>th</sup> Framework Program JRA (Joint Research Activity)

through the ‘Research Infrastructures’ action of the ‘Capacities’ Programme, Contract No: CP-CSA\_INFRA-2008-1.1.1 Number 226507-NMI3.

## References

- [1] Grochala W and Edwards P P 2004 Thermal decomposition of the non-interstitial hydrides for the storage and production of hydrogen *Chem. Rev.* **104** 1283-1315
- [2] Colognesi D, Celli M, Cilloco E, Newport R J, Parker S F, Rossi-Albertini V, Sacchetti F, Tomkinson J and Zoppi M 2002 TOSCA neutron spectrometer: the final configuration *Appl. Phys. A* **74** S64
- [3] Silvera I F 1980 The solid molecular hydrogens in the condensed phase: fundamentals and statistical properties *Reviews of Modern Physics* **52**, 393-452
- [4] Kirichek O 2012 Impact of the cryogen free revolution on neutron scattering laboratories *Modern Physics Letters B* **26** 1230006
- [5] Oliver E C, Evans B E, Chowdhury M A H, Major R A, Kirichek O and Bowden Z A 2008 Novel testing chamber for neutron scattering measurements of internal stresses in engineering materials at cryogenic temperatures *Meas. Sci. Technol.* **19** 034019
- [6] Evans B E, Down R B E, Keeping J, Kirichek O and Bowden Z A 2008 Cryogen-free low temperature sample environment for neutron scattering based on pulsed tube refrigeration *Meas. Sci. Technol.* **19** 034018
- [7] Kirichek O, Carr P, Johnson C and Atrey M 2005 Nuclear magnetic resonance magnet actively cooled by pulse tube refrigerator *Rev. Sci. Instrum.* **76** 055104
- [8] Done R, Kirichek O, Evans B E and Bowden Z A 2010 NMI6, FP7, JRA: Report on current inert gas pressure cell technology *arXiv* 1007.3135
- [9] Kirichek O, Done R, Goodway C M, Kibble M G, Evans B E and Bowden Z A 2012 Development of high pressure gas cells at ISIS *Journal of Physics: Conference Series* **340**, 012008
- [10] Michael Meißner and Dirk Wallacher private communication
- [11] Louthan M R, Caskey G R, Donovan J A and Rawl D E 1972 Hydrogen embrittlement of metals *Materials Science and Engineering* **10**, 357
- [12] Fast V D 1965 Interaction of mettals and gases *Academic Press*, New York, 54
- [13] Weiner L C 1961 *Corrosion* **17**, 109
- [14] Fernandez-Alonso F, Bermejo F J and Saboungi M L 2011 Molecular Hydrogen in Carbon Nanostructures *Handbook of Nanophysics: Functional Nanomaterials*, ed K D Sattler (Boca Raton, FL, US: CRC Press) chapter **40** 40