Raman Spectroscopy as an ortho-para diagnostic of liquid hydrogen moderators

R. C. Gillis\textsuperscript{1,†}, T. Bailey\textsuperscript{2,3}, F. X. Gallmeier\textsuperscript{1}, M. A. Hartl\textsuperscript{2}, E. B. Iverson\textsuperscript{1}

\textsuperscript{1} Oak Ridge National Laboratory, Oak Ridge, Tennessee, 37831, USA
\textsuperscript{2} European Spallation Source ERIC, Box 176, S-221 00 Lund, Sweden
\textsuperscript{3} North Carolina State University, Raleigh, North Carolina, USA
\textsuperscript{†} Email: gillisrc@ornl.gov

Abstract.

The intense radiation environment of a neutron moderator provides a mechanism for significant up-conversion of parahydrogen to orthohydrogen inside the moderator, as well as intrinsically catalyzing relaxation of orthohydrogen to parahydrogen. It is plausible that the steady-state orthohydrogen fraction of a moderator in a radiation environment such as at the Spallation Neutron Source (SNS) or the European Spallation Source (ESS) is as high as 30\% without supplemental catalysis. Direct measurement of the orthohydrogen fraction in the liquid hydrogen flow itself is essential to predict and monitor moderator performance, especially for thick or flat moderator concepts such as the ones that have been proposed for the ESS and for upgrades to the SNS. Raman spectroscopy provides a well-known method for directly measuring the hydrogen make-up in an unambiguous way. We describe our tests of Raman spectroscopy for application to the measurement of the orthohydrogen fraction of the hydrogen moderators at SNS and at the ESS. As part of this work, we have additionally developed a sample holder that has been used to perform simultaneous Raman and neutron vibrational spectroscopy on the VISION spectrometer at SNS. We discuss our plans to incorporate such a system as a diagnostic for liquid hydrogen moderators at SNS and at the ESS.

1. Relevance of the orthohydrogen fraction to hydrogen moderators

The neutron scattering cross section of orthohydrogen is much greater than that of parahydrogen at neutron energies less than 15 meV (by about a factor of about 50 at 10 meV). [1] As a result of this fact, it is likely that the optimization of essentially any hydrogen moderator design will depend on an optimal orthohydrogen fraction. In the case of the flat or thick moderators that are being proposed for the ESS and for upgrades to the SNS, it is expected that the difference between <1\% and 30\% orthohydrogen content would be a factor of two or three.

This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (http://energy.gov/downloads/doe-public-access-plan).
in the moderator brightness (prediction relating to flat moderator brightness courtesy of ESS Neutronics). If the freedom does not exist at the design stage to specify an orthohydrogen fraction determined by the figures of merit of instruments served by the moderator, then compromises are made in the design that give up significant performance gains. A system for controlling and monitoring the moderator orthohydrogen content should pay for itself many times over in terms of enhanced facility performance.

The rate of self-conversion [2] between ortho- and para-hydrogen is slow, both on the time scale at which hydrogen flows through a moderator loop and on the time scale over which catalyzed conversion [3] can be made to occur. In the absence of other conversion mechanisms, it is therefore possible to control the orthohydrogen fraction by continuously flowing it through a chamber filled with ortho-para conversion catalyst. In this scenario, the entire volume of hydrogen assumes an asymptotic orthohydrogen fraction that corresponds to thermal equilibrium with the catalyst. However, the environment of a moderator introduces uncertainties associated with the fact that the intense radiation field is expected to give rise to radiolysis of the hydrogen. [4] The energy released during recombination of the radiolysis products is such that recombination occurs in a 3:1 orthohydrogen:para-hydrogen ratio, and it has been estimated that the orthohydrogen fraction of a liquid hydrogen moderator at an advanced spallation source may in fact be as high as 30 % in the absence of a catalytic chamber.

2. A system for monitoring the orthohydrogen fraction in the moderator loop

Given the uncertainties associated with the orthohydrogen fraction in the moderator loop of an advanced spallation source, it is important to put in place a system that directly monitors the orthohydrogen fraction. Sampling the hydrogen to transport it to a lab for analysis is not the most favorable option as extreme care is required to account for all sources of catalysis when doing so. Furthermore, a real-time monitoring system would allow us to watch the moderator performance evolve as a function of the orthohydrogen fraction, and therefore to develop insight into the physics of moderators and of radiolysis and catalysis of the hydrogen. Raman spectroscopy is interesting as it allows for the signature of molecular species to be identified, and would therefore allow us to see whether the trihydrogen ion (a hypothesized radiolysis product) is present to a significant extent.

With the objective in mind of building a Raman system to monitor the orthohydrogen fraction of the hydrogen in the moderator loop, we have built a sample holder for performing simultaneous Raman and neutron vibrational spectroscopy on the VISION spectrometer at SNS. This equipment, which was designed and built as a collaborative effort between the ESS and the SNS, holds material samples in the neutron beam within the cryogenic environment of the VISION spectrometer, allowing for samples to be studied at temperatures as low as 5 K. An assembly of optical components for directing and filtering light (shown in Fig. 1) is located inside a vacuum chamber within the cryogenic volume at VISION, in physical proximity to the sample. For the measurements discussed in this paper, the sample container was coupled optically to the optical assembly in the vacuum chamber by a 13 mm diameter fused quartz rod. In the case of our studies with hydrogen, the background from the quartz rod was separable from the signal; as such it allowed us to normalize the hydrogen Raman signal to the transmitted laser power.

Raman data of a sample of liquid hydrogen at 17 K taken on VISION using this sample holder are shown in Fig. 2. The ratio of areas of the two peaks can serve as a measurement of the orthohydrogen fraction. With our setup we were able to measure this ratio to within about 3 % uncertainty. This uncertainty was limited by nonstatistical electronic noise which we expect will be substantially improved when we refurbish the optical spectrometer. We used an approximate method of preparing orthohydrogen mixtures by combining hydrogen from a room-temperature cylinder with hydrogen that had been sitting in contact with Oxisorb ortho-para conversion catalyst at 17 K for an extended period of time. We saw 15 % agreement with the expected
Figure 1: (a) A schematic of the optical assembly, showing the path of the excitation and collected light. (b) A photograph of the optical assembly before it was incorporated into the sample stick. The steel rods emerging at bottom and left were used during alignment and were removed before incorporating the assembly into the sample stick.

Figure 2: A raman spectrum of hydrogen including the background due to scattering in the quartz rod. A relative normalization has been done of the data to the background within the shaded region. The nominal orthohydrogen fraction of this sample as determined by the sample preparation procedure was 72%.

A technical challenge associated with the sample holder on VISION has been the transmission of an optical signal to and from the sample in a cryogenic environment across vacuum-tight boundaries. We do not expect the technical difficulties associated with monitoring the moderator loop to be greater than the ones associated with building the sample holder at VISION. We were able to observe the Raman signal of Fig. 2 with the optics held at 50 K while viewing a liquid sample about 2.5 cm deep, without employing any schemes to amplify the signal. Plans for the hydrogen line involve an installation of optical viewports to allow the Raman probe to view the hydrogen at a stage of the hydrogen loop outside of the moderator.
3. An apparatus for studying radiolysis and catalysis of flowing liquid hydrogen

In addition to monitoring the hydrogen at a stage of the moderator loop that is outside of the moderator, we would like to directly view an irradiated volume of hydrogen to get a better understanding of the nature, relative populations, and lifetimes of the hypothesized radiolysis products. Fig. 3 shows a concept of a benchtop setup that simulates important aspects of the hydrogen loop. It includes a catalysis section, a radiolysis section, and flow of hydrogen through a loop that connects the two sections. This setup bears some similarities to the NPDGamma liquid hydrogen target that is explained in Ref. [6]. Given the low viscosity of liquid hydrogen, [7] and the temperature dependence of the mass density of liquid hydrogen (1.2 % density change per K at 17 K [8]), the hydrogen flow would be generated or assisted by a temperature gradient across the loop. The catalysis section could consist of a chamber or portion of tubing filled with ortho-parahydrogen conversion catalyst, and the radiolysis section could consist of an irradiated chamber or portion of tubing. UV light could serve as a plausible radiation source, and a Raman measurement would allow us to directly view the irradiated hydrogen.

Acknowledgements

This work was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory. It used resources at the Spallation Neutron Source, a US Department of Energy Office of Science User Facility that is operated by Oak Ridge National Laboratory. Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U S Department of Energy.

The authors would like to thank Luke Daemen of VISION for his expertise and assistance in developing the Raman sample stick. The authors would also like to thank Neelam Pradhan, June Safieh and John Wenzel of the SNS Sample Environment Research and Development team for producing design drawings of the vacuum chamber and sample container used on the Raman sample stick.

References

[1] K. B. Grammer et al., Phys. Rev. B, 91, 180301(R) (2015)
[2] Yu. Ya. Milenko, R. M. Sibileva and M. A. Strzhemechny, J. Low Temp. Phys., 107 77–92 (1997)
[3] D. H. Weitzel, W. V. Loebenstein, J. W. Draper and O. E. Park, J. Res. Natl. Bur. Stand., 60, 221–227 (1958)
[4] E. B. Iverson and J. M. Carpenter, Proceedings of the ICANS-XVI, Volume II, pp. 707–717, 2003
[5] I. F. Silvera, Rev. Mod. Phys., 52, 393–452 (1980)
[6] S. Santra et al., Nucl. Instr. Meth. Phys. Res. A, 620, 421–436 (2010)
[7] B. B. Eselson, Yu. P. Blagoi, V. N. Grigorev, V. G. Manzhelli, S. A. Mikhailenko, N. P. Neklyudov, Properties of Liquid and Solid Hydrogen, Israel Program for Scientific Translations, Jerusalem, 1971
[8] J. W. Leachman, R. T. Jacobsen, S. G. Penoncello and E. W. Lemmon, J. Phys. Chem. Ref. Data, 38, 721–748 (2009)