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Technical notes

Practical in-situ determination of ortho-para hydrogen ratios via fiber-optic based Raman spectroscopy

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ABSTRACT

An experiment was designed and developed to prototype a fiber-optic-based laser system, which measures the ratio of ortho-hydrogen to para-hydrogen in an operating neutron moderator system at the Los Alamos Neutron Science Center (LANSCE) spallation neutron source. Preliminary measurements resulted in an ortho to para ratio of 3.06:1, which is within acceptable agreement with the previously published ratio. The successful demonstration of Raman Spectroscopy for this measurement is expected to lead to a practical method that can be applied for similar in-situ measurements at operating neutron spallation sources.

1. Introduction

The Los Alamos Neutron Science Center (LANSCE) at the Los Alamos National Laboratory (LANL) uses an 800-meter long linear accelerator (LINAC) that is capable of accelerating both, H^+ and H^- ions [1]. The LINAC delivers 100 MeV H^+ ions (protons) to the Isotope Production Facility and 800 MeV H^- ions to several research facilities, such as Proton Radiography, Ultra-Cold Neutrons (UCN), and Weapons Neutron Research (WNR) facilities as well as to the Lujan Center (LC). Three of these facilities, UCN, WNR, and LC, use spallation neutrons that are generated by the 800-MeV proton impinging on a tungsten target. Research efforts at the LC utilize thermal and cold neutrons, emerging from a Target Moderator Reflector System (TMRS). The TMRS Assembly contains a split tungsten spallation target surrounded by a beryllium reflector and six embedded neutron moderators [2]. Neutron beams are delivered to various scientific instruments via 16 neutron flight paths. Thermal neutrons are generated in four chilled-water moderators and two liquid-hydrogen moderators are used to produce cold neutrons. The present work seeks to understand changes occurring in the ortho–para ratio of the hydrogen used in these moderators. For more details about the TMRS, see Ref. [2].

Hydrogen molecules (H_2) exist in two spin states: ortho-hydrogen and para-hydrogen. In the ortho state, the hydrogen spins are aligned (spin 1), whereas in the para state, the spins are anti-parallel (spin 0). Para form is the lower-energy state, and therefore dominates at equilibrium so that about 99.8% of the hydrogen molecules are in the para form at liquid-hydrogen temperature (20 K). By contrast, at room temperature, hydrogen gas has a para-form concentration of approximately 25%. Upon hydrogen liquefaction, the ortho form converts to para-hydrogen at a natural conversion rate, slowly approaching the 99.8% equilibrium value. This process has been extensively studied and is relatively well understood for unperturbed systems [3]. However, very little is known about these conversion processes in high-radiation environments created in liquid-hydrogen neutron moderators.

Since the energy difference between the ortho and para states is only 14.7 meV, the hydrogen molecule spin is expected to significantly affect the total thermal-neutron-scattering cross-section at neutron energies below 20–30 meV. Therefore, neutronic performance of a liquid-hydrogen moderator depends strongly on the ortho-para hydrogen ratio [2]. In the case of the LANSCE moderators, we are presently unable to measure or monitor the ortho–para ratio in the production system. Hence, very little data exist that can help us to control the liquid-hydrogen moderator performance. This work serves as a proof of concept with the aim eventually to build and test the first ortho/para measurement system at a production liquid-hydrogen cooling loop servicing the LC's TMRS.

The main goal of this work was to develop an approach that would enable in-situ monitoring of the otho/para ratio of the hydrogen in the liquid-hydrogen loop in the TMRS at any time during the accelerator run-cycle without having to compromise or

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disrupt the operation of the TMRS systems. The work included the design and assembly of an experimental setup that would produce accurate baseline data from hydrogen gas at ambient temperature and at known pressure values. At room temperature and atmospheric pressure, the ortho–para ratio has been shown to be 3:1 or 75/25, respectively [4]. Also, it has been shown that as the temperature of the hydrogen changes, the ratio also changes over time [4]. Using Raman Spectroscopy, information about the properties of hydrogen molecules can be collected and by combining a high-powered laser with a spectrometer, the vibrational and rotational states of hydrogen molecules can be probed [5].

2. Experiment details

A schematic of the bench top experimental apparatus is shown in Fig. 1. The major components of the apparatus include a 488-nm argon gas laser (Modu-Laser), a small hydrogen gas chamber with a sapphire glass window, 30 m of optical fibers each with a diameter of 365 μm, a fiber-optic Raman sampling probe (Inphotonics), and a spectrometer (Ocean Optics) with USB readout capability. The hydrogen gas chamber, shown in the figure below, is a small cross with CF flanges where H_2 gas enters the chamber through the left extension and gets purged out the top. The experiment starts with the light traveling from the laser to the probe through the optical fiber. The excitation area occurs a few millimeters from the window inside the chamber. Then the light returns from the probe to the spectrometer which is located at the end of the second optical fiber.

It is important to note that for the initial tests, the gas chamber had to be filled and pressurized with hydrogen up to 1379 kPa. Therefore, the sapphire-glass window, located inside the flange mounted on the gas chamber, had to be able to safely withstand these high pressures. A 1.57-mm (0.062-in.) thick sapphire window was selected and a maximum pressure limit of 4509 kPa was calculated using Eq. (1) [6]:

$$\Delta P_w = \left[\frac{t_w}{0.5A_w}\right]^2 * \frac{S_f}{k_w f_s} \quad (1)$$

here t_w is the window thickness, A_w is the aperture diameter,k_w is the support condition,f_s is the safety factor, and S_f is the fracture strength. A pressure test was performed to demonstrate safe pressurization of the window up to 1379 kPa.

The Raman probe, used in the experimental setup (Fig. 1), is specifically designed to filter out the anticipated strong silicon Raman scattering signal from the optical fibers [7]. Also, an additional filter is included in the probe's optical design so that the primary laser wavelength is highly attenuated while the desired shifted wave lengths from Raman scattering of the sample are passed unattenuated. Furthermore, what makes the probe most suitable for the intended application is that its optical system is built in a very compact container, measuring only 106.7 mm × 38.1 mm × 12.7 mm. This includes optical elements such as mirrors, long-pass filters, band-pass filters, focusing lenses, and collimating lenses. Its working distance, selectable between 5 mm and 10 mm, was set at a standard distance of 7.5 mm. Additional features include the ability withstand moderately high temperatures, and adaptability for operation in high vacuum, a feature which is a requirement for the final application.

Because Raman scattering is known to have a very weak signal, the signal to noise ratio tends to be too low for most instrumentation. To detect these very small peaks and to sufficiently reduce the electronic noise level, it is critical for the spectrometer to have a sufficiently high resolution. Therefore the spectrometer selected for this experiment has a resolution of 0.4 nm. As a consequence, the spectral range of the spectrometer was also significantly reduced from 2000 nm to only 100 nm. The remaining high background noise levels seen during the collection of spectra were further reduced by collecting and subtracting dark spectra.

3. Results and discussion

3.1. Silica Raman

As the light travels through the fiber optic cables, scattering also occurs inside the fiber's core. Since we use glass fibers, the strong scattering signal anticipated and observed is well known and identified as silica Raman, (Fig. 3 of Ref. [8]). Relatively long (30 m) fiber-optic cables were required which presents a major challenge to the measurement of the weak hydrogen signal, given the magnitude of the Raman silica signal even after attenuation by the filter. Fig. 2 shows a measured silica scattering signal represented by the broad peak centered around 400 cm^{-1} with a height just over 15,000 counts. The peaks of interest are comparable to those shown in the reference spectrum at Raman shift 400 cm^{-1}, 600 cm^{-1}, 800 cm^{-1}, and 1050 cm^{-1}. The tall narrow peaks are believed to be associated noise from ion emission lines from the Ar-ion laser. Hydrogen signals expected in the wavenumber range 300–100 cm^{-1} show peaks much smaller by comparison.

To verify that the probe was working, a baseline test was conducted using ethanol instead of hydrogen gas. The resulting spectrum represented published ethanol spectra and confirmed that the laser system provided credible results and sufficient confidence to proceed with the collection of spectra on hydrogen gas (Fig. 3) [9].

Next, the chamber was pressurized with ultra-pure hydrogen to 1379 kPa. During successive shots several spectra were recorded using the Spectrasuite software package. An integration period of 1 min was used for each spectrum. A total of 10 dark spectra and 10 signals were taken. Both spectra sets were averaged before subtracting the dark signal from the hydrogen signal. The resulting hydrogen spectrum is shown in Fig. 4.

Four clearly defined peaks are visible at Raman shift 355 cm^{-1}, 586 cm^{-1}, 812 cm^{-1}, and 1032 cm^{-1}. By comparing the hydrogen

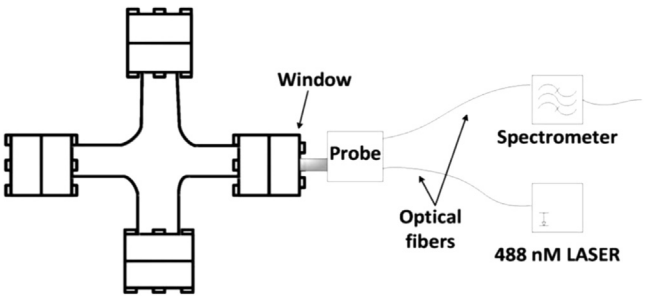

Fig. 1. Schematic of bench top experimental apparatus, showing the main components.

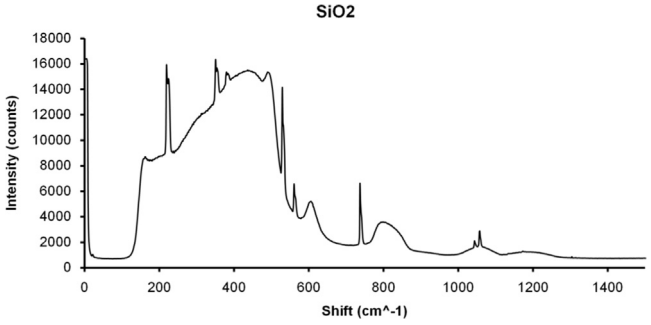

Fig. 2. Silica Raman spectrum signal showing peaks exceeding 15,000 counts.