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Uncertainty analysis of Raman spectra for measuring ortho-parahydrogen compositions

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Abstract. Determining ortho-parahydrogen compositions at cryogenic temperatures is an important quality control for liquid hydrogen custody exchange. High orthohydrogen compositions lead to an exothermic reaction resulting in increased boil off and increased venting losses of liquid hydrogen product by either the supplier or consumer. Traditional methods for measuring ortho-parahydrogen compositions such as hot-wire anemometry, nuclear magnetic resonance, and infrared spectroscopy are typically inconvenient at best. As the number of cryogenic hydrogen systems continue to increase, there is an increased need for flexible, standardized techniques for post processing composition measurements. A Raman spectrometer implemented in the Cryo-Catalysis Hydrogen Experimental Facility (CHEF) has demonstrated incredible flexibility for composition measurements of cryogenic hydrogen flows through a wide range of temperatures and pressures with the Raman probe in-situ at cryogenic temperatures. This article analyzes the uncertainty of Raman spectroscopy data of cryogenic hydrogen equilibrated at temperatures in IONEX catalyst. Spectra from hydrogen catalyzed to the equilibrium ortho-parahydrogen composition are processed and compared to expected statistical distributions for method verification.

1. Introduction

Hydrogen exists in two quantum forms, orthohydrogen, and parahydrogen. These two forms are a result of the molecular spin of the hydrogen. The lower energy state of hydrogen, parahydrogen, is more conducive to long-term storage of liquid hydrogen (LH2). Normal hydrogen, consisting of 75% orthohydrogen and 25% parahydrogen, when cooled to normal boiling temperature, undergoes the conversion from normal to parahydrogen (0.02% ortho, 99.8% para) [2,18,19]. This conversion process requires extra cooling as the reaction is exothermic [18]. The natural conversion is quite slow, requiring the use of catalyst materials for an increase in reaction rate. If the conversion is not completed at the liquefier, 18% of the liquified normal hydrogen can boil off on the first day [19]. As of now, there is no low-cost device capable of being implemented in liquid hydrogen systems which can conveniently measure the ortho-parahydrogen composition at arbitrary conditions.

Currently, when a shipment of LH2 is delivered, only indirect methods exist for the recipient to verify that the LH2 has been fully converted to parahydrogen. The hydrogen must be extracted and taken to a lab to analyze the composition and the transit time for this analysis to occur is sufficient to cause considerable change to the composition. This lack of verification leads to a need to standardize the LH2 that is being delivered, which requires a simple device that can be produced in mass for characterization of the LH2 composition.

Ortho-parahydrogen composition can be measured relative to changes in thermophysical properties or absolutely via quantum effects. Relative approaches have been employed in industry for several decades but are range limited. Absolute methods have been historically limited due to cost.

In-situ use of hot-wire anemometry has proven to be complicated when implemented in cryogenic systems. Larger flowrates of hydrogen can cause the fine filament to break if maintained in the flow, rendering the device useless [23]. The maximum sensitivity range of this approach is near 140 K due to the thermal conductivity differences between ortho- and parahydrogen [15]. A currently produced device requires temperatures of 333K for parahydrogen measurements and yields uncertainties of ±2.4% parahydrogen [29]. At least three different experimental factors must be controlled to minimize error: pressure, temperature over the wire, and flowrate of the gas [23]. The resulting measurement should be compared to pure parahydrogen and normal hydrogen for interpolation. Although sound-speed meters have been recently developed, these systems have the similar range limitations as thermal-conductivity based systems requiring temperatures above 253K [29].

Nuclear Magnetic Resonance (NMR) uses external magnetic fields to read small induced magnetic fields in orthohydrogen. Possessing no magnetic dipole moment means that parahydrogen is NMR silent [23], allowing this method to be used to characterize the composition of orthohydrogen in a sample. One source in literature found that using NMR the measurement of parahydrogen had an uncertainty of ±6% [30]. This method is typically cost-prohibitive [4,24].

Raman spectroscopy is also used to view the populations of molecules in each rotational energy level. This method employs the use of a laser to excite the molecules and a spectrometer to view the resulting photons scattered by the molecules. The focus of this paper is to develop a method to conveniently analyze the spectra from Raman spectroscopy to obtain the ortho-parahydrogen composition of a hydrogen sample and compare these results to the predicted value based on statistical thermodynamics. Recently, a study demonstrated the performance of this device with the Raman probe from room temperature to 77 K [24]. However, no study has been conducted that verifies the in-situ performance of a cryogenic Raman probe over a large temperature range. This paper will explore the uncertainty of Raman spectroscopy data for determining ortho-parahydrogen compositions. The ortho-parahydrogen equilibrium curve based on statistical thermodynamics for hydrogen with temperatures 20K - 300K is experimentally recreated using Raman spectroscopy including corresponding uncertainty for averaged equilibrium orthohydrogen measurements.

2. Theory

2.1. Statistical Thermodynamics

For orthohydrogen there are three spin-isomers all with antisymmetric nuclei spin functions while parahydrogen has one spin-isomer of symmetric nuclei spin function. Based on the symmetry of the spin the rotational energy modes populated by parahydrogen can only be J = 0,2,4… (even, symmetric) with orthohydrogen populating the J = 1,3,5… (odd, antisymmetric) rotational energy modes [17]. The equilibrium composition of the two quantum hydrogen forms is dependent on temperature [1,2]. The partition function is used to partition the molecules of hydrogen into the different energy modes. Using this function, the equilibrium composition for hydrogen can be found at different temperatures. At 20 K, the equilibrium composition is 99.8% parahydrogen. Figure 1 below depicts the equilibrium composition of orthohydrogen as a function of temperature.

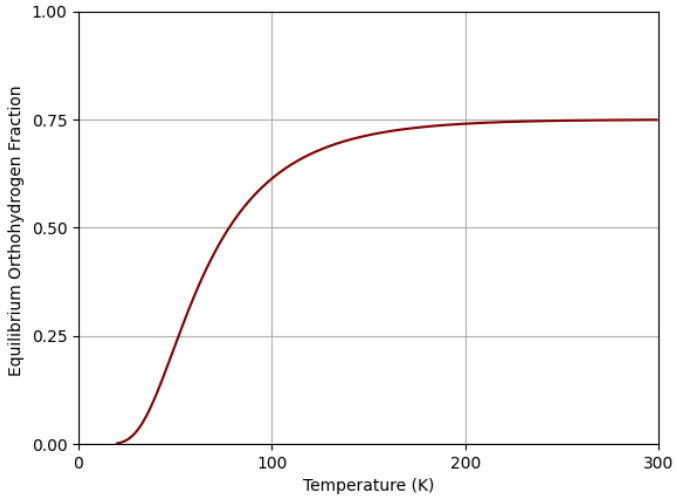

Figure 1: Equilibrium composition of orthohydrogen as a function of temperature.

With the exothermic reaction of ortho- to parahydrogen taking place in liquified normal hydrogen, enough energy can be produced to vaporize 64% of the liquid [3]. Alternatively, the conversion of para- to orthohydrogen is an endothermic reaction absorbing 703 kJ/kg. Thus, if parahydrogen at 20 K were converted fully to normal hydrogen 525 kJ/kg (75% of 703 kJ/kg) of energy would be absorbed by this reaction [23]. The conversion process if left unaided is very slow, producing small amounts of heating or cooling power [18]. Catalyst material is used to accelerate the rate of conversion [20].

2.2. Raman Spectroscopy

When hydrogen is excited by a laser to a higher energy level, the spectrometer analyzes the light scattered by the molecules. The photons are scattered with less energy than the excitation leading to longer wavelengths than that of the laser [7]. These longer wavelengths are characteristic of the Stokes lines typically seen in the Raman effect. The number of molecules populating each energy state is proportional to the scattered Raman light [16]. This allows direct comparison of the relative populations of ortho- and para- for calculating composition.

To observe the energy states of hydrogen, Raman Spectroscopy implements a 532-nanometer laser for exciting the hydrogen molecules. The choice of excitation laser is important for the quality of Raman Spectra. The Raman spectral intensity is inversely related to the fourth power of the laser wavelength [21]. If a lower wavelength is chosen, then higher intensities can be seen in the Raman spectra. Ultraviolet laser use results in higher sensitivity and is unaffected by fluorescence but can lead to specimen degradation [21,22]. A popular choice for laser utilizes a 532 nm wavelength. This laser wavelength provides good sensitivity and scattering efficiency while being commercially available [21].

From the spectrum, the J = 0,1,2,3…intensity peaks can yield the relative population of hydrogen molecules in that mode. With these peaks the ortho-parahydrogen composition can be derived based on the integrated scattering intensities of the J0 and J1 peaks [6,16,24]. Equation 1 below shows the function relating the integrated scattering intensities with the relative composition of the peak.

$$I_J = \frac{(J+1)(J+2)}{(2J+1)(2J+3)} x_J p_J \gamma_J^2 \omega_s^3; \quad J = 0,1,2,\ldots \tag{1}$$

where I_J is the integrated scattering intensity at the J^{th} level, x_J is the gas fraction at the J^{th} level, γ_J is the anisotropy of the polarizability tensor, p_J is the Boltzmann population for the J^{th} level at 295K, and ω_s is

the angular frequency of the scattered light [6,16,24]. p_J must be calculated with Boltzmann's distribution law [9,10] in Equation 2:

$$N_J = N g_J \exp\left(-\frac{J(J+1) * \theta_R}{T}\right); \quad J = 0,1,2,\ldots \tag{2}$$

where N_J is the occupation number, N is the total number of modes and g_J is the rotational state degeneracy $(2J+1)$ [9]. This equation must be used to find the percentage of N_J in terms of the total occupations of the odd or even rotational states, i.e. $p_0 = \frac{N_0}{\sum N_{0,2,4\ldots}}$ for parahydrogen. The value for the rotational temperature of hydrogen, θ_R, can be found with Equation 3 [10,11,24]:

$$\theta_R = \frac{B}{k_B} = \frac{h^2}{8\pi^2 I k_B} \tag{3}$$

Where B is the rotational constant, k_B is Boltzmann's Constant, h is Planck's Constant, and I is the moment of inertia of the molecule. Revealing that θ_R is 87.570 K [12]. The anisotropy of the polarizability tensor γ_J is defined by Equation 4 [13]:

$$\gamma(\omega) = \alpha_{\parallel}(\omega) - \alpha_{\perp}(\omega) \tag{4}$$

Where $\alpha_{\parallel}(\omega)$ and $\alpha_{\perp}(\omega)$ come from Hunt et. al. [14]. Making $\gamma_0 = 2.0238$ and $\gamma_1 = 2.0316$. For the individual peaks J0 and J1, Equation 1 can be rearranged to find x_0 and x_1 or a ratio of the two r which gives the ratio of the gas fractions, hence the para-orthohydrogen ratio [24]:

$$r = \frac{3 * I_0 * p_1 * \gamma_1^2}{5 * I_1 * p_0 * \gamma_0^2} = \frac{x_0}{x_1} \tag{5}$$

The ratio r can be used to calculate the parahydrogen composition in the sample with Equation 6:

$$x_{pH_2} = \frac{r}{1+r} \tag{6}$$

Relating the gas fractions of orthohydrogen and parahydrogen to obtain the total parahydrogen composition. The orthohydrogen composition can be found by subtracting the parahydrogen composition from one.

2.3. Numerical code

Python was utilized to develop a method for quickly and conveniently processing the spectra output from CHEF. The code first obtained the data from the spectrometer Pro-Tools software in the form of a CSV file. This file contains all spectra on the interface at the time of saving. The code then separated the wavelengths (x-axis of the spectrum) from the intensities (y-axis of spectrum) and stored them in new matrices. These new matrices are used for calculations in the main functions of the Python code to allow for easy iteration through the CSV.

Then the code performed the Raman Shift to the wavelengths which allows spectra obtained with different incident energies to be compared on the same scale [5]. The equation to calculate the Raman Shift for the Stokes lines with a laser of given wavelength λ_E in angstrom is shown in Equation 7 [6].

$$\Delta v\ (cm^{-1}) = \frac{10^8}{\lambda_E} - \frac{10^8}{\lambda_R} \tag{7}$$

Where λ_R is the wavelength of the emitted light from the specimen in angstrom. Equation 8 shows the same equation but with the wavelengths of both laser and emitted light in the units of nanometers.

$$\Delta v\ (cm^{-1}) = \frac{10^7}{\lambda_E} - \frac{10^7}{\lambda_R} \tag{8}$$

With the Raman shift performed on all wavelengths, the values for the hydrogen peaks are separated into different arrays for integration. Figure 2 below shows a sample of data at 295 K with the peaks to be integrated shown in different colors.

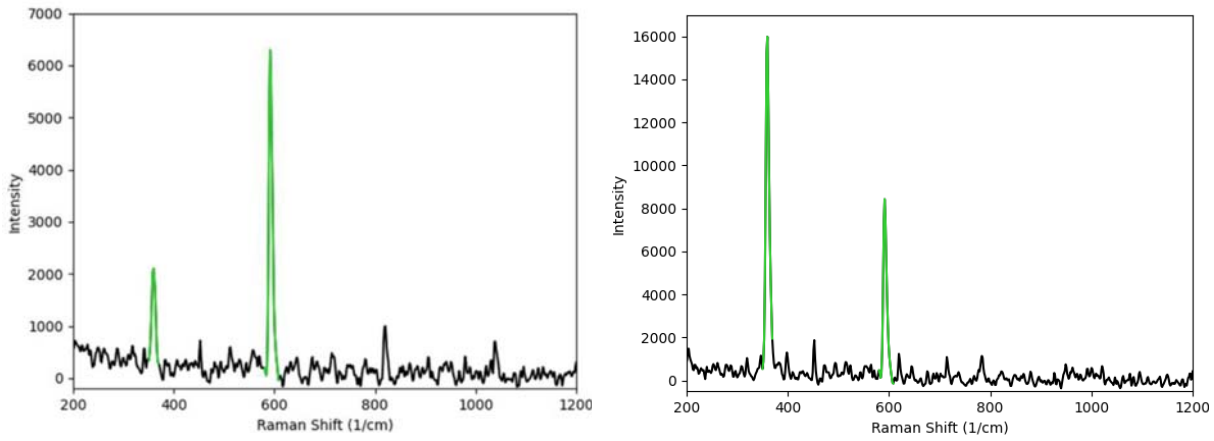

Figure 2: Raman spectrum for a room temperature 295K (left) and 77K (right) sample of hydrogen showing peaks of integration.

The integrated scattering intensities are calculated using trapezoidal discrete integration of the J0 and J1 peaks from the data like those shown above in figure 2. The code then uses Equations 1-7 to output the ortho-parahydrogen composition.

3. Experimental Verification

The Cryo-Catalysis Hydrogen Experimental Facility (CHEF) was designed to test ortho-parahydrogen conversion. It was designed to characterize the performance of reactor materials compared with catalytic models. CHEF utilizes a Sumitomo RDK-500E Gifford-McMahon cryocooler with the capacity to liquify and store 6.7 L of LH2 in the tanks, with activated IONEX bags suspended in the tanks for ortho- to parahydrogen conversion. For a full description of the cryostat see the dissertation by Carl Bunge [23]. The hydrogen flows into the inlet Raman cell where it can be characterized before reaction. The hydrogen then flows through the packed bed reactor and to an outlet Raman cell where the sample is recharacterized for the ortho-parahydrogen composition.

For characterization of catalyst materials, a reactor with an internal volume of 1.138 cm^3 is used in a packed bed configuration. A cold bar and heater are used to maintain steady state for the hydrogen in the reactor. The ortho-parahydrogen composition is measured before and after the hydrogen has passed through the reactor. The Raman system utilizes the following instruments:

- StellarNet Raman-HR-TEC-532 spectrometer
- Laser Quantum Gem 532 – CW 532nm up to 460mW TEM00, horizontal polarization
- Custom manufactured 90° Raman Cell

Spectroscopy Pro-Tools by StellarNet is utilized for the acquisition of spectra [27]. For insitu measurement of hydrogen a dark spectrum must be captured before laser activation. Hydrogen in the tanks is vaporized using heaters creating a flow of gaseous hydrogen which is used to obtain a dark spectrum sample as done with previous experiments [23]. A spectrum is captured for one minute with exposure of 59 seconds and is used to shift the background signals out of the laser induced spectra. With hydrogen flowing, the heaters are adjusted to reach the desired steady state temperature of the hydrogen gas. At this point the laser is activated to excite hydrogen in both inlet and outlet Raman cells. Steady state operation is maintained to capture multiple spectra.

Tests are conducted using CHEF to obtain near equilibrium hydrogen flown through the reactor at approximate temperatures of 20 K, 47 K, 60 K, 77 K, and 85 K to show the viability of Raman spectroscopy for calculation of orthohydrogen compositions in-situ. Based on the desired outlet compositions of the reactor, approximate flowrates were calculated for the experimental system to achieve complete conversion to equilibrium. All uncertainty was propagated through the data.

4. Results

Using CHEF, equilibrium samples of hydrogen were collected at the temperatures above. These samples were analyzed using the method above and the Python code written for this purpose. ASTM E2586 was used for uncertainty analysis of data. This standard utilizes statistical methods to estimate the uncertainty in the data measurements. The random uncertainty of the Raman spectroscopy results can be found with Equation 9 [28]:

$$u_{Random} = t_{1-\frac{\alpha}{2},df}\frac{s}{\sqrt{n}} \tag{9}$$

where t is t-score from a t-distribution found at α the probability that a value will fall between that range for some number of degrees of freedom, df. S represents the sample standard deviation and n the total sample size. For this study six samples were analyzed with 95% probability. The random uncertainty can be added to the bias through root sum square through the Combined Standard Uncertainty [31].

$$u_{Total} = \sqrt{u_{Systemic}^2 + u_{Random}^2} \tag{10}$$

For this analysis, the systemic uncertainty is 1.4% [23]. Combined with the random uncertainty found from the use of ASTM 2586-18 the total uncertainty is found.

Using CHEF's Raman system, the Python code developed for analysis and ASTM E2586-19 the experimental results can be tabulated in Table 1. Based on the results, it can be noted that the 20 K reading from Raman Spectroscopy varies from the theoretical equilibrium when analyzing the data, the spectra show no distinguishable J1 peak. Currently, the code analyzes 20 K the same as other spectra, but with the lack of a J1 peak, a false value for the integrated area is being calculated. The code will be optimized to account for the lack of J1 peak at 20 K. It can also be seen for 47.62 K and 60.09 K that the Raman spectroscopy calculated value for orthohydrogen is outside the uncertainty. One potential cause for this deviation could be that the flowrate used during the experiment didn't allow for full conversion to equilibrium, thus creating the difference between the measured value and theoretical equilibrium that is outside the uncertainty. Accuracy was evaluated for these measurements through comparison with statistical thermodynamic equilibrium values. A lesser flowrate will be explored for these temperatures.

Table 1: Experimental results for Raman Spectroscopy system of equilibrium hydrogen catalyzed with IONEX at six different temperatures.

Temperature (K)	Theoretical Orthohydrogen Equilibrium	Measured Orthohydrogen %	Total Measurement Uncertainty
20	0.17%	1.4%	±1.41%
47.62	20.01%	17.15%	±2.14%
60.09	34.46%	31.48%	±1.63%
77.06	49.42%	50.07%	±1.56%
84.49	54.15%	54.33%	±1.55%
290	74.91%	72.38%	±3.01%

Based on the measured values above, Figure 3 was created to show the Raman Spectroscopy data plotted with the theoretical equilibrium curve. More data points will be further explored to verify the results of this experiment.

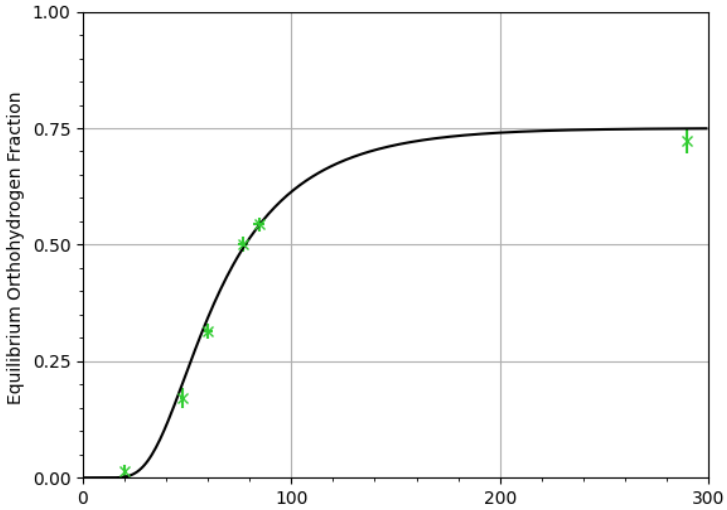

Figure 3: Experimental data results placed over statistical thermodynamics orthohydrogen equilibrium plot.

5. Conclusions

This research has shown that with the use of Raman Spectroscopy the ortho-parahydrogen compositions at arbitrary state conditions can be obtained. With six spectra the uncertainty within the measurements is less than ±3% across a broad temperature range. Increasing the number of spectra results in a smaller uncertainty in the measurements. Future research will consider optimizing the Raman probe and spectrometer for this specific purpose. Such a device will ensure liquid hydrogen delivered from liquefiers has been converted to 99.8% parahydrogen compositions, improving the standardization of liquid hydrogen as a fuel and reducing heat released into storage systems.

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