



Measuring hydrogen spin isomers using in-line solid state raman spectroscopy

Authors

Thomas I. Dearing¹, Arman Siahvashi² and John Richmond¹, ¹Thermo Fisher Scientific, 2157 N Northlake Way Suite 240, Seattle, WA 98103, ²Hydrogen Technology and Energy Center, Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA.

Abstract

Hydrogen is an important energy source and its use is expanding rapidly, but for transportation and use, it must be in liquid form. At 298 K, molecular hydrogen consists of 75% orthohydrogen and 25% parahydrogen. For energy efficiency and to prevent boil-off, hydrogen must be converted from the ortho form to the para form. This conversion is normally performed at a temperature of 20 K, the boiling point of hydrogen, using an iron oxide catalyst. At the normal boiling point, hydrogen exists in the para-state, which is thermodynamically preferable. To monitor this low-temperature conversion process, Raman spectroscopy is the ideal analytical technique. Due to its speed of measurement and the stability of the device, and the fact that data analysis can be simplified to peak integration routines for accurate compositional monitoring, Raman spectroscopy is gaining more traction in the analysis of industrial processes like the production of liquid hydrogen.

Introduction

Hydrogen is increasingly viewed as a key player in creating a decarbonized energy future, with trustworthy transportation and storage of liquid hydrogen being pivotal for its widespread use. Ensuring safety and efficiency in its liquefaction and storage is essential for its viability. Crucially, selecting the best liquefaction methods and transport/storage technologies involves analyzing multiple factors, including energy use, material choices, and the management of liquid hydrogen's unique properties, such as its temperature-influenced ortho-para hydrogen conversion and its potential to create boil-off gas¹.

Hydrogen exists as two isomers, ortho and para, based on proton nuclear spin. A temperature-dependent equilibrium dictates their ratio, with a 75% ortho isomer make-up at room temperature shifting to nearly 100% para at liquid hydrogen temperatures (20 K). This transition releases significant energy, impacting liquefaction and storage processes. Due to quantum effects, the ortho-to-parahydrogen transition needs an external catalyst, or it is slow, taking days or weeks if cooled without one. This conversion is exothermic, releasing

more heat (525 kJ/kg) than hydrogen's vaporization enthalpy at its boiling point (448 kJ/kg), which affects storage strategies^{1,2}.

Efficient ortho-to-parahydrogen conversion is crucial for hydrogen liquefaction and storage on an industrial scale. Rapid liquefaction without allowing time for this conversion can lead to excessive boil-off gas and potential over-pressurization of storage tanks, posing safety risks. Additionally, the slow conversion process is a significant barrier to long-term storage, as the heat generated can evaporate over 70% of the stored liquid hydrogen¹.

On the other hand, the reverse reaction, where parahydrogen converts back to orthohydrogen, is an endothermic process that can further cool liquid hydrogen, reducing boil-off. This conversion plays a crucial role in maintaining the cryogenic temperature of stored hydrogen, enhancing its stability and efficiency during storage².

Catalyst materials are incorporated into the design of industrial hydrogen liquefaction systems to expedite the conversion process, achieving it within minutes. However, there is an urgent requirement for detailed data on the reaction rates specific to these catalysts to enhance the accuracy of kinetic models used in reactor design and to identify the most effective reactor configurations³.

In the past decade, Raman spectroscopy has experienced significant advancements and become a powerful analytical technique in various industrial applications. Improvements in lasers, solid-state hardware, and fiber optics have played a crucial role in enabling these developments. Raman spectroscopy, particularly in Process Analytical Technology (PAT) applications, has seen a substantial increase in use: Its ease of interface, non-destructive sampling, and rapid cycle times have facilitated successful integration into diverse sectors such as biopharma, oil and gas, petrochemical, and fermentation applications. The combination of Raman spectroscopy with chemometric methods has expanded its adoption in industrial applications, contributing to its versatility and effectiveness in various fields. As an added benefit, the incorporation of Raman spectroscopy into workflows for in-line measurements requires minimal adjustments.

This study demonstrates the use of a process Raman analyzer performing in-line compositional analysis to calculate the ortho/para ratio and the rate of conversion between the hydrogen isomers under different experimental conditions.

Common Ortho-Para measurement techniques

Raman spectroscopy, NMR spectroscopy, and thermal conductivity measurements are key techniques for detection of ortho and para hydrogen. Raman spectroscopy stands out for this purpose due to its ability to provide relative measurements of the

isomer ratios without the need for calibration, along with its online measurement capabilities². However, questions about its long-term performance in cryogenic conditions and sensitivity at different pressures remain. NMR spectroscopy detects orthohydrogen directly (parahydrogen is NMR invisible) but requires calibration and can face challenges with signal-to-noise ratios at lower temperatures, although advanced techniques can enhance parahydrogen signals⁴. Thermal conductivity measurements exploit the significant thermal conductivity differences between the isomers but are limited by pressure and temperature conditions and are unsuitable for liquid hydrogen⁵.

The fast analysis times and ease of sample interface (using a high pressure at low temperature flow cell) make Raman spectroscopy ideal for tracking the conversion of ortho to parahydrogen. The Raman spectrum of hydrogen contains specific peaks that pertain to the ortho and para isomers of the diatom. Because Raman peaks scale linearly with concentration, the peak areas of the specific ortho and para peaks can be tracked and used to calculate the compositional ratio. A simple background correction and baseline correction further increase the accuracy of the determined peak areas and subsequent compositional ratios.

Experimental

All spectra were collected on a Thermo Scientific™ MarqMetrix™ All-In-One Process Raman Analyzer. The acquisition parameters were set such that a new dark-subtracted spectrum was collected every 10 seconds. The spectra were collected using a Thermo Scientific™ MarqMetrix™ FlowCell Sampling Optic (Figure 1) rated to 2,500 psi and a temperature range from cryogenic temperatures to 350 K.

Once collected the data were processed using Solo 9.2.1 (Eigenvector Research, Inc., Manson, WA). Background removal was performed using a spectrum of helium, followed by trend analysis that accounts for baseline variation. Finally, normalization was performed to account for variation in pressure and flow. The resulting model files were transferred to the Raman instrument and were deployed using Solo_Predictor 4.3 (Eigenvector Research, Inc., Manson, WA) to make real-time determinations of the ortho and para content of the liquid hydrogen (Figure 2).



Figure 1. Integrated high pressure low temperature flow cell.

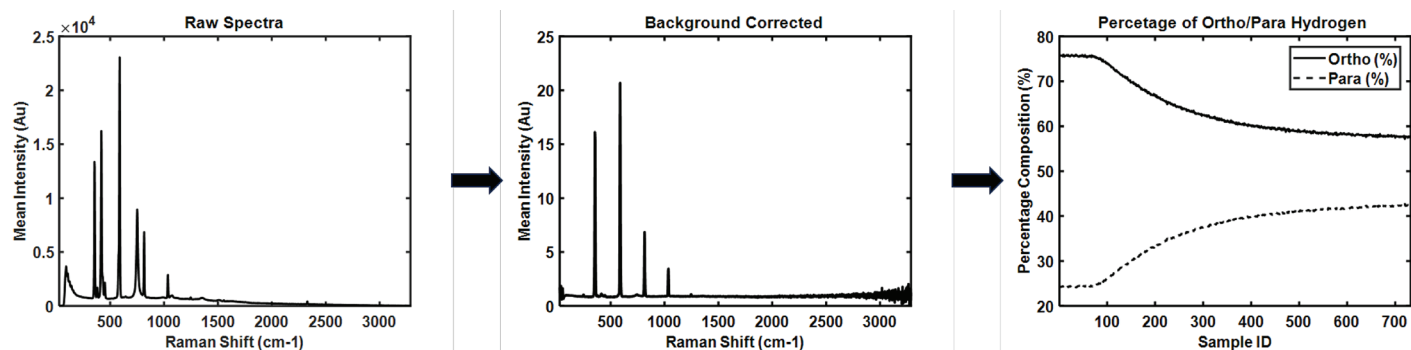


Figure 2. Progression of data analysis.

In this study, hydrogen gas was first cooled in a heat exchanger immersed in liquid nitrogen, then passed through a packed-bed reactor containing a commercially available iron-based catalyst. This process facilitated the conversion of orthohydrogen to parahydrogen, altering its equilibrium from 75% ortho at room temperature to 50%, effectively balancing the ortho-para ratio. Temperature, pressure, and flow rate were monitored and regulated. Downstream of the reactor, a Raman probe was deployed to measure the ortho- and parahydrogen concentrations in real time, providing immediate insights into the efficiency of the conversion process.

Results and discussion

Raman spectroscopy was successfully deployed to measure catalytic conversion of orthohydrogen to parahydrogen. This successful outcome was due in part to the flow cell sampling optic used to make the measurements. The employed flow cell was notably compact and integrated, designed for in-line utilization, and connected via compression fittings. This configuration facilitated a straightforward "plug-and-play" installation and ensured a leak-free operation, eliminating the need for the user to adjust or address potential complications related to the laser's focal points or other adjustments.

The experiments conducted in this study were carried out with the flow cell at ambient temperature. Nonetheless, the flow cell is capable of being submerged in liquid nitrogen (77 K) or operated in conjunction with a cryocooler to achieve temperatures as low as 20 K, assuming the probe stem is sufficiently long and thermally regulated to prevent damage to the electronic components.

The spectra collected using the flow cell showed clear transitions of ortho- to parahydrogen. The signal-to-noise ratio was excellent, allowing clear resolution and discrimination of the relevant liquid hydrogen peaks (Figure 3). The corresponding rotational states (J) and zero vibrational transition states (S) for a measured hydrogen spectrum are shown in Figure 3. The quantified Raman shifts, corresponding to the parahydrogen peaks, are recorded at 354 and 814 cm^{-1} , whereas the orthohydrogen peaks are observed at 587 and 1034 cm^{-1} , respectively. These findings are consistent with the hydrogen Raman spectra delineated in the literature², affirming the reliability and accuracy of the measured shifts within the context of established spectroscopic data.

The instrument sensitivity allowed for a high degree of resolution of subsequent samples and precise tracking of the catalytic conversions. Using these signals, several experiments were undertaken to monitor various factors including conversion efficiency and kinetic rates. The chemometric methods applied required no additional calibration other than the understanding that at room temperature the ratio of ortho to parahydrogen is around 3:1.

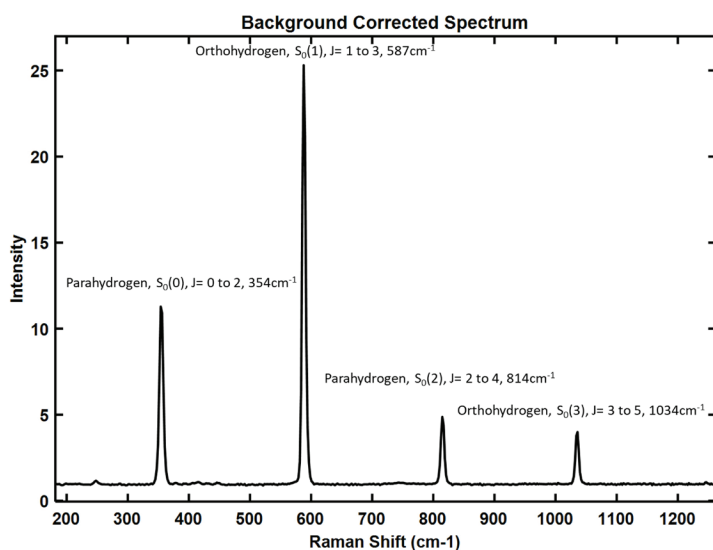


Figure 3. Spectrum of normal hydrogen taken at room temperature and 1000psi pressure after background removal.

Conclusion

This study shows that Raman spectroscopy is an ideal spectroscopic technique for monitoring the ortho-to parahydrogen conversion at cryogenic temperatures. Information on conversion rates, catalyst efficiency and performance are possible due to fast data acquisition rates, excellent signal-to-noise performance, and resolution. By removing background interferants, particularly the 578 cm^{-1} peak, very small changes in peak height and area can be monitored with confidence, resulting in extremely accurate conversion rates.

The cryogenic flow cell enables measurement in liquid hydrogen at 20 K, further enhancing accuracy, precision, and speed of analysis due to the higher density of the liquid phase compared

to the gas phase. It is envisaged that analysis times will reduce from 10 seconds to 200 milliseconds, enabling catalysis research using extremely fast-acting materials. This will enable extremely large volumes of hydrogen to undergo 100% conversion to the parahydrogen form in a short space of time, ensuring efficient storage and transportation of the liquid form with minimal losses due to boil-off.

Furthermore, the success of this application provides a pathway into other arenas that require the accurate determination of hydrogen and its isotopes, such as reducing carbon emissions by blending significant levels of hydrogen into natural gas fuel for power generation or monitoring hydrogen/deuterium feed to a future fusion reactor for power generation.

References

1. Al Ghafri, S.Z. et al., Hydrogen liquefaction: a review of the fundamental physics, engineering practice and future opportunities. *Energy Environ. Sci.*, 2022, 15, 2690-2731.
2. Bunge, C., A High-Fidelity, Continuous Ortho-Parahydrogen Measurement and Conversion System. PhD Thesis (2021), Washington State University.
3. Ilisca, E. and F. Ghiglieno, Nuclear conversion theory: molecular hydrogen in non-magnetic insulators. *Royal Society Open Science*, 2016. 3(9): p. 160042.
4. Krasae-in, S. et al., Development of large-scale hydrogen liquefaction processes from 1898 to 2009. *International Journal of Hydrogen Energy*, 2010. 35(10): p. 4524-4533.
5. Zhou, D. et al., Determination of the Ortho-Para Ratio in Gaseous Hydrogen Mixtures. *Journal of Low Temperature Physics*, 2004. 134(1): p. 401-406.