

Raman spectroscopy for parahydrogen quantification

Real-time control and quality assurance across the hydrogen supply chain

This study presents experimental results demonstrating the capability of an Endress+Hauser Raman spectroscopic analyzer system for quantifying parahydrogen conversion during hydrogen liquefaction. Real-time spectral analysis highlights the potential for accurate monitoring in process environments.

Introduction

Hydrogen is increasingly recognized as a cornerstone of the global energy transition, offering a pathway to decarbonize sectors such as fertilizer production, chemical manufacturing, and oil refining.

To meet growing demand, hydrogen is anticipated to be liquefied – similar to natural gas – to facilitate transportation and storage.

Hydrogen exists in two spin isomers: orthohydrogen (ortho- H_2) and parahydrogen (para- H_2), which are in thermodynamic equilibrium, with a temperature-dependent ratio. At

ambient conditions, hydrogen is predominantly ortho (75%), whereas at cryogenic temperatures (at 20 K or $-253\text{ }^\circ\text{C}$), para dominates (>99%).

The ortho-para conversion occurs via spin exchange interactions, typically catalyzed by paramagnetic species or surfaces such as iron oxide or rare earth oxides. This conversion is exothermic, releasing heat that can cause boil-off gas (BOG). If uncontrolled, this phenomenon leads to product losses in liquefied hydrogen (LH_2) logistics. Accurate quantification of hydrogen isomers is therefore critical for optimizing storage, transport, and utilization.



A Raman Rxn5 analyzer (top) and an Rxn-30 probe (bottom)

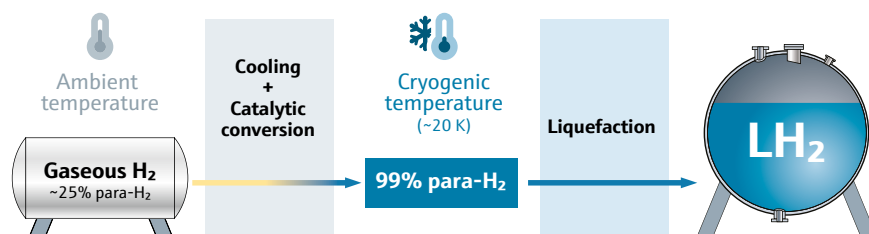


Figure 1. If liquefaction is attempted when para- H_2 content is below 98%, the residual conversion will release heat, causing hydrogen boil-off.

Raman spectroscopy in hydrogen analysis

Raman spectroscopy provides a robust solution for distinguishing ortho- H_2 and para- H_2 through their unique molecular fingerprints.

Key advantages include:

- **Continuous online real-time analysis** in process gas streams.
- **Non-invasive measurement** without sample conditioning.

Importantly, para-to-ortho reversion without a catalyst is extremely slow, allowing gas streams to be analyzed at room temperature conditions while preserving the isomer ratio representative of cryogenic states.

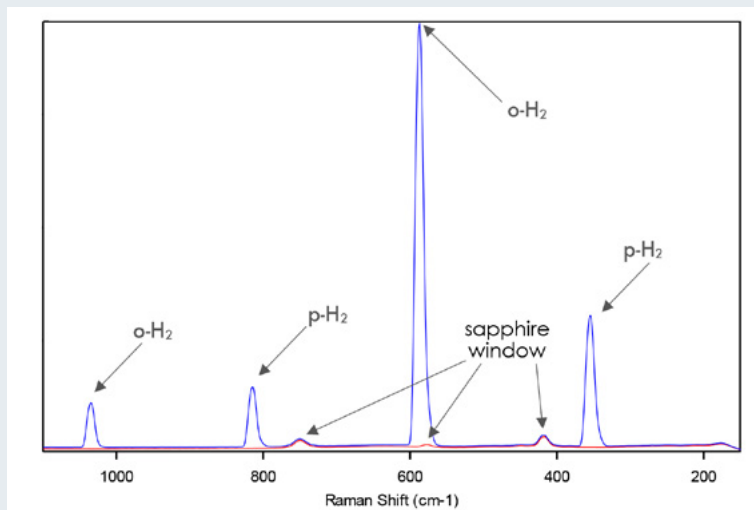


Figure 2. A Raman spectrum of a 25% para- H_2 sample, and a hydrogen-free background spectrum (recorded under a flow of helium), measured with a Raman Rxn5 analyzer and a Raman Rxn-30 probe from Endress+Hauser. The red trace represents the baseline spectrum with no hydrogen present. The blue trace shows the distinct spectral peaks generated by ortho and parahydrogen as the gas flows past the probe.

Experimental method

Parahydrogen quantification was performed using an Endress+Hauser Raman Rxn5 analyzer with an Rxn-30 gas probe. The procedure included:

- **Equilibration:** Various concentrations of para- H_2 were generated by mixing two hydrogen streams. Thermodynamically stable hydrogen at 298 K (25 °C) provides an approximate ratio of 25% para- H_2 / 75% ortho- H_2 . A separate hydrogen stream cooled to 77 K (-196 °C) using a liquid nitrogen bath was exposed to iron oxide catalyst. The catalyst accelerates the hydrogen spin-flip, increasing the concentration of para- H_2 . This setup allows measurement of precise concentrations of each isomer. The concentration was recalculated on a daily basis using exact temperature and atmospheric conditions.
- **Sampling:** The experimental sampling setup controlled the hydrogen introduction into the Raman cell to ensure representative mixing of 25% para- H_2 with 50% ortho- H_2 , producing various ratios of known para- H_2 concentrations between 25 and 50% using calibrated mass flow controllers.
- **Spectral acquisition:** The instrument collected spectra in the range from 1,000 to 200 cm^{-1} to capture rotational transitions unique to each isomer.
- **Data processing:** The concentration of para- H_2 was predicted by a partial least squares (PLS) method. The spectral range from 1,080 to 265 cm^{-1} was generated with GRAMS IQ™ software. 165 spectra were used for calibration and 153 for validation. The PLS model was constructed with 2 PLS factors; the spectra were baseline corrected and mean centered.

Results

The Raman Rxn5 analyzer delivered clear, reproducible separation between ortho and parahydrogen. When the measurement data is processed through a PLS model, the para-H₂ concentrations within +/- 0.25% of the actual concentration can be predicted.

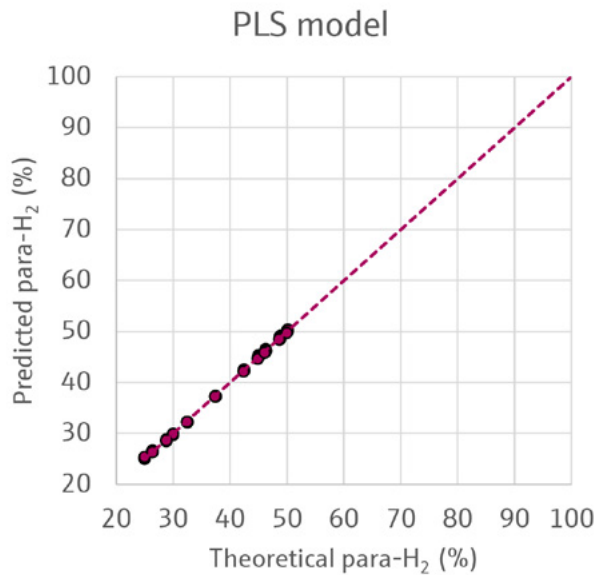


Figure 3. Para-H₂ predicted values vs theoretical values from Raman spectroscopy analysis.

Key findings include:

- Achieved high signal-to-noise ratios and stable peak areas for robust quantification
- Demonstrated excellent repeatability (± 0.25 to 0.5% of reading) across 330 spectra collected over a 2.5-month period
- Confirmed accuracy for process and quality control by matching measured para-H₂ fractions to theoretical equilibrium values
- Measured para-H₂ concentration with an accuracy of $\pm 0.25\%$ within the 25-50% range
- Projected satisfactory accuracy up to 99% H₂ (based on extrapolation of the current spectral dataset from this study)

Discussion

Raman spectroscopy is highly suitable for quantifying ortho and parahydrogen because it provides distinct rotational fingerprints, enabling accurate identification and quantification of each isomer. It is a non-intrusive, real-time technique that ensures safe and efficient monitoring without disturbing the process. Additionally, its high sensitivity and reliability allow clear spectral separation even at low concentrations, supporting precise measurements for process control and quality assurance.

Raman measurements are typically performed at or near room temperature when monitoring ortho–para hydrogen conversion. This approach is chosen because Raman systems operate more reliably under ambient conditions, avoiding the complexity of cryogenic setups. The ortho–para ratio remains preserved since conversion is kinetically very slow without a catalyst, and warming the sample provides a representative measurement of the ratio achieved during liquefaction. Gas-phase analysis at room temperature also simplifies handling and ensures safer, faster analysis.

Traditional methods for determining the ortho–para hydrogen ratio include calorimetric approaches (based on enthalpy changes during conversion) and indirect techniques such as thermal conductivity or speed-of-sound measurements. Any deviation in the pressure or temperature of the gas sample will increase measurement error. These technologies may only measure parahydrogen, so the exact value of the orthohydrogen cannot be distinguished from other sources of error such as catalyst break-down.

Advantages of Raman spectroscopy

By contrast, Raman spectroscopy offers direct identification of spin isomers, enabling fast, accurate, and non-invasive measurements. Unlike other analytical technologies, Raman spectroscopy captures all Raman-active species in a single spectrum. This means that when measuring the para-H₂ signal, any residual ortho-H₂ appears in the same acquisition. This allows immediate identification of remaining ortho-H₂ content and helps operations distinguish true liquefaction-process deviations from potential instrument malfunction—something other techniques cannot reliably indicate. Raman spectroscopy also delivers real-time monitoring without complex calibration, making it particularly well-suited for industrial hydrogen liquefaction and storage processes. This capability is invaluable for hydrogen supply chain operators aiming to manage boil-off gas (BOG), optimize liquefaction, and ensure compliance with parahydrogen specifications.

Conclusion

Reliable parahydrogen measurement is essential for maintaining process efficiency and effective boil-off gas (BOG) management across the hydrogen supply chain. This study demonstrates that the Endress+Hauser Raman technology provides fast, precise, and reproducible quantification of hydrogen isomers. In doing so, it enables real-time monitoring and improved operational decision-making throughout liquefaction, storage and transport, including:

- Quality assurance for shipped or stored hydrogen
- Real-time BOG management through accurate isomer monitoring
- Enhanced process control during liquefaction and storage operations

Together, these capabilities position the Endress+Hauser Raman spectroscopy system as a valuable tool for maintaining product quality, minimizing losses, and supporting the hydrogen sector's growing role in the global energy transition.

References

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