Experimental Comparison of Raman Spectroscopy and Microwave Resonant Cavities as ortho-para Hydrogen Composition Sensors

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The extreme conditions required for hydrogen liquefaction pose significant challenges to efficient process design, which are compounded by hydrogen's unique quantum behaviour associated with its nuclear isomer states. Hydrogen molecules exist in two spin-isomers: *ortho* and *para*-hydrogen. At room temperature, hydrogen is thermodynamically stable as a 3:1 mixture of *ortho* to *para*-hydrogen, commonly referred to as "normal" hydrogen. Achieving stable equilibrium in the cryogenic liquid phase mandates the conversion of nearly all *ortho*-hydrogen to create a 99.8% *para*-hydrogen mixture. This isomer conversion is an exothermic process with an enthalpy greater than what is required for hydrogen vaporisation. Thus, if non-equilibrium liquid hydrogen is produced, isomer conversion to its equilibrium state will cause significant boil-off and product loss. Understanding the impact of hydrogen's isomer state on liquid hydrogen production and utilisation requires accurate measurements.

In this work, we compare two measurement systems for hydrogen spin-isomer composition: Raman spectroscopy, a popular direct measurement technique, and microwave resonant cavities, an established technology recently adapted for indirect spin isomer measurement by exploiting differences in their dielectric permittivity. While Raman spectroscopy boasts a well-established reputation, with advantages in rapid data acquisition and a seemingly straightforward analysis procedure, it faces challenges in industrial applications due to its limited operating ranges, high equipment costs, and non-trivial calibration requirements. Microwave resonant cavity sensors are well-suited to an industrial setting due to their in situ capabilities, relatively low construction and operation costs, and extensive operating ranges. However, the difference in dielectric permittivity between normal and equilibrium hydrogen is only significant over a limited temperature range. This work will present data showcasing the capabilities of each sensor type for hydrogen spin-isomer measurements across a range of conditions pertinent to the hydrogen liquefaction industry.