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Performance evaluation of the developed in-situ ortho-to-parahydrogen fraction measurement system for the ESS cryogenic moderator system

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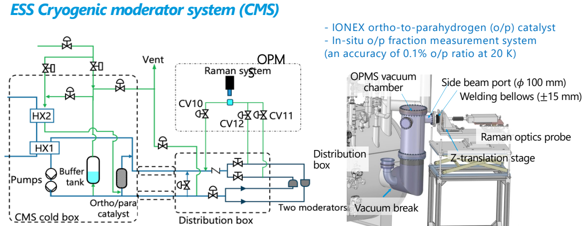
Abstract

At ESS, we developed an in-situ ortho-to-parahydrogen fraction measurement system (OPMS) using a Raman spectroscopy. This system requires an accuracy of 0.1% parahydrogen fraction at around 20 K to observe ortho-to-parahydrogen back-conversion phenomena induced by the neutron irradiation. Initially, we succeeded in detecting the parahydrogen peak at 1245 cm^{-1} (J = 4) in normal hydrogen at 0.3 MPa. This is because the theoretical peak intensity ratio of the third parahydrogen ($J = 4$) to the first orthohydrogen ($J = 1$), $I(4)/I(1)$, is 0.49%, which is equivalent to $I(1)/I(0)$ at 22.7 K. In this study, we measured the Raman spectra of normal hydrogen at ambient temperature and various pressures to clarify the effect of hydrogen density, ρ, on the accuracy of the $I(4)/I(1)$ ratio, instead of $I(1)/I(0)$. Additionally, we measured the Raman spectrum of gaseous hydrogen collected from equilibrium condition at 21 K, at ambient temperature and 0.7 MPa, to evaluate the accuracy of $I(1)/I(0)$ compared with that of $I(4)/I(1)$. The accuracy of $I(4)/I(1)$ decreased following a curve characterized by $\rho^{-0.95}$, and the accuracy of $I(1)/I(0)$ follows a similar trend. For ρ >0.54 kg/m^3, the accuracy decreased below 0.1%. Therefore, it is expected that $I(1)/I(0)$ of liquid hydrogen (ρ =74.7 kg/m^3) would achieve an accuracy of approximately ±0.001%.

Introduction

ESS has developed a butterfly-type hydrogen moderator, optimized for parahydrogen to over 99.5%, to achieve the world's highest luminosity in the neutron beam. The total neutron cross-section of parahydrogen is approximately 2.5 orders of magnitude lower than that of orthohydrogen in the energy region below 14.5 meV. Even a small fraction of orthohydrogen significantly impacts neutron scattering characteristics. High neutron irradiation fields may induce para-to-orthohydrogen production, known as back-conversion, as mentioned by E. B. Iverson and J. M. Carpenter. They successfully measured this back-conversion phenomenon and reported that 1% of parahydrogen was converted over 12 hours under a 1-MW proton beam operation.

ESS Cryogenic moderator system (CMS)

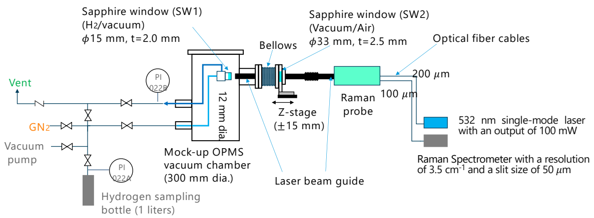


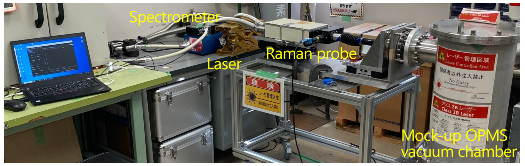
In this study,

(1) we measured Raman spectra of normal hydrogen at ambient temperature and various pressures from 0.1 to 1.1 MPa to evaluate the effect of hydrogen density on the accuracy of the intensity ratio of $I(4)/I(1)$.

(2) we measured the Raman spectrum of gaseous hydrogen collected under equilibrium condition at 21 K using the J-PARC cryogenic hydrogen moderator (CMS) and evaluated the accuracy of $I(1)/I(0)$ compared with that of $I(4)/I(1)$ for the normal hydrogen.

Experimental set up



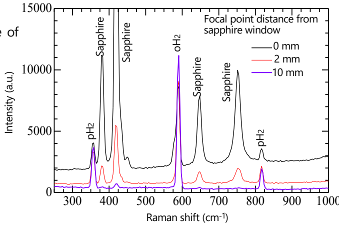


Raman measurement

- Integration time of the Raman measurement was set to 120 s.
  - considering the measurement limitation of the CCD in the spectroscopy (200,000 counts.)
- Each spectrum was averaged over five measured data.
- Back ground noise: Reference spectrum under conditions where the sampling line was evacuated.

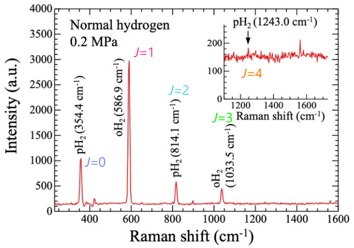
Effect of focal lens location

- Uncoated plano-convex lens with a focal length of 40 mm.
- Focal point position: 10 mm away from the inner surface of the sapphire window,
  - Peak intensities were maximized.
  - Background level was minimized.

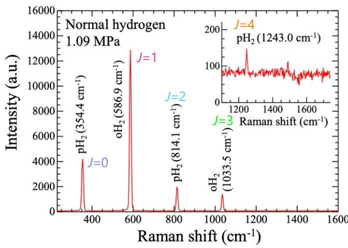


Experimental results – normal hydrogen-

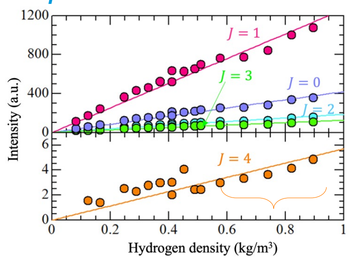
At 0.2 MPa



At 1.1 MPa

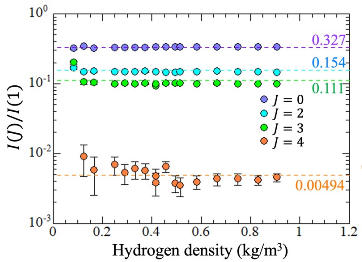


Effect of hydrogen density on peak intensities



- Each peak intensity increased proportionally with hydrogen density.
- However, for J = 4, a deviation from this proportional relationship was observed below 0.58 kg/m^3.

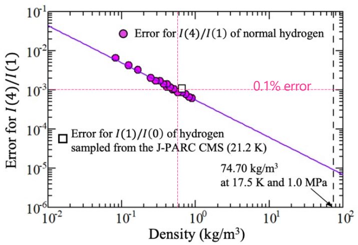
Pressure dependence of I(J)/ I(1)



- $I(J)/I(1)$ for J =0, 2 and 3
  - As hydrogen density increased, the intensity ratios of converged to their theoretical values at densities above 0.25 kg/m^3.
- $I(4)/I(1)$, which corresponded to the ortho-to-parahydrogen ratio for $I(1)/I(0)$ at 22.7 K
  - Intensity converged at pressures above 0.7 MPa.
  - Additionally, the errors decreased with increasing pressure.

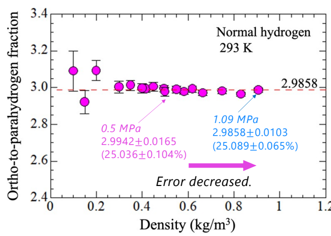
Error estimation

-Effect of the hydrogen density on the error for I(4)/I(1)



- Increasing the hydrogen density by a factor of ten resulted in approximately a tenfold reduction in the error for $I(4)/I(1)$.
  - at ρ = 0.49 kg/m^3 (0.6 MPa at 293 K),
    Error = ±0.105%.
  - at ρ = 0.58 kg/m^3 (0.7 MPa at 293 K),
    Error = ±0.086%.

-Effect of the hydrogen density on the error for ortho-to-parahydrogen fraction of normal hydrogen



Ortho-to-parahydrogen ratio, r

C(=0.98941)

$$r = \frac{I(1)}{I(0)}\frac{r(T)}{5.4}\exp\left(\frac{E(1,0)-E(0,0)}{k_B T}\right)$$

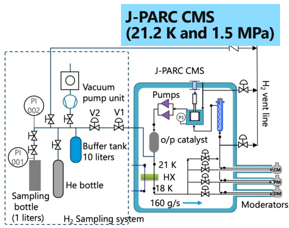
Error, σ_r

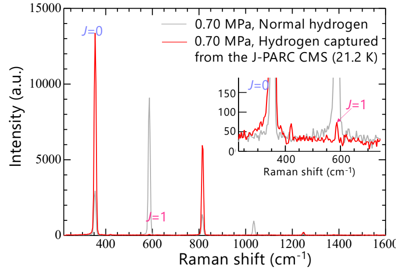
$$\sigma_r = C\sqrt{\left(\frac{\sigma(1)}{I(0)}\right)^2+\left(\frac{I(1)\,\sigma(0)}{I(0)^2}\right)^2}$$

- At ρ = 0.896 kg/m^3, corresponding to 1.09 MPa,
  - Ortho-to-para hydrogen fraction agreed with the theoretical value of 2.9858 at 292 K and its error is ±0.0103.
  - This corresponded to a parahydrogen fraction of 25.089% with an accuracy of ±0.065% (< 0.1% error).

– Hydrogen sampled form J-PARC CMS (under the equilibrium condition at 21.2 K and 1.5 MPa)-

Gaseous hydrogen captured from the J-PARC CMS operating at 21.2 K was collected into the sampling bottle at a pressure of 0.7 MPa.





- Intensities
  - Parahydrogen, $I(0)$: significantly higher compared to that of normal hydrogen.
  - Orthohydrogen, $I(1)$: Considerably small, however it was still discernible above the background level.
- Intensity ratio of $I(1)/I(0)$ = 0.002670±0.001076, which exists on the same curve given by the errors of $I(4)/I(1)$ for normal hydrogen.
  - Ortho-to-parahydrogen ratio =0.002642±0.001065.
  - = Parahydrogen fraction of 99.737±0.106%, which is consistent with the theoretical value at 21.05 K.
- Predicted accuracy under the ESS CMS (17 K and 0.1 MPa):
  Better than ±0.001%, *due to the liquid hydrogen density of 74.70 kg/m^3, which is 129 times greater than the density at 0.7 MPa and 293 K.*

Conclusion

We conducted Raman spectroscopy on normal hydrogen at various pressures to investigate the effect of density, ρ, on the ortho-to-parahydrogen ratio, r, and its associated error, σ_r.

- It became evident that the peak intensities increased proportionally with ρ.
  - Above 0.58 kg/m^3, the intensity ratio of $I(4)/I(1)$ converged to 0.49%, equivalent to the theoretical ratio for $I(1)/I(0)$ at 22.7 K, with the error meeting the 0.1% criterion.
  - With a tenfold increase in ρ, the error of $I(4)/I(1)$ decreased by a factor of 0.1.
- Additionally, we captured gaseous hydrogen under the equilibrium condition at 21.2 K from the J-PARC CMS.
  - The intensity ratio of $I(1)/I(0)$ was measured to be 0.002670 ±0.001076, where r = 0.002642 and σ_r ±0.001065.
  - The error of $I(1)/I(0)$ agreed with a trend given by that of $I(4)/I(1)$ for normal hydrogen.
- It can be predicted that the ortho-to-parahydrogen fraction under the ESS CMS operational conditions can be measured with an accuracy better than ±0.001%, because the density of liquid hydrogen is 129 times higher than the density at 0.7 MPa and 293 K.

Acknowledgement

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