

# Quantitative determination of the Q(1) quadrupole hydrogen absorption in the near infrared via off-axis ICOS

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## Abstract

High resolution absorption lineshape measurements of the near-infrared quadrupole absorption (2-0 vibration band, Q(1) line) transition of molecular hydrogen near 1238 nm have been recorded using off-axis integrated cavity output spectroscopy. These measurements were used to determine the integrated absorption strength, pressure shift, and the effects of pressure narrowing (Dicke narrowing) of this transition over a range of pressures (13–900 Torr) of pure hydrogen.

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## 1. Introduction

The strongly forbidden quadrupole spectrum of molecular hydrogen was first recorded by Herzberg [1] in 1950, where he analyzed eight components of the 2-0 and 3-0 bands. Additional bands were recorded by Rank, et al. [2], and later by Fink, et al. [3] in which 15 components of the 1-0, 2-0, and 3-0 bands were measured in a high pressure 44 m White cell with up to 32 passes for a maximum path length of 1408 m. Most recently, Bragg et al. [4] employed Fourier transform spectroscopy in a 434 m White cell to attain highly accurate line positions, absorption strengths, and pressure shifts for several hydrogen transitions in the visible and near-infrared. Although these efforts have resulted in excellent parameterization of the hydrogen rotational constants [5], the reported numbers involved measuring relatively high pressures (0.8–7 atm) of hydrogen and extrapolating the relevant data.

Infrared emission in the near infrared atmospheric window from vibrationally excited states of molecular hydrogen has long been used as a probe of local environments in the Milky Way and other galaxies. The importance of

having accurate molecular transition strengths and related molecular constants for this important interstellar molecule has recently been emphasized by Wolniewicz, et al. [6] who made extensive calculations of the quadrupole transition probabilities for the excited rovibrational states of hydrogen.

Molecular hydrogen is also important in many chemical processes and, until now, there has been no simple method of monitoring its concentration other than indirect methods such as Palladium-diffusion type sensors. These sensors rely upon changes in the physical and electronic properties of Palladium when hydrogen is absorbed into the metal. While these sensors can be very sensitive, they are also typically slow and subject to thermal drift. A sensor technology that directly probes hydrogen in the gas phase would provide real-time monitoring of this gas over the range of concentrations of typical concern for safety and explosion hazard analysis.

In this Letter, we present the first cavity enhanced direct absorption measurements of hydrogen in the near-infrared spectral region by employing off-axis Integrated Cavity Output Spectroscopy (ICOS) to study the H<sub>2</sub> (2-0) band Q(1) line, centered at 8075.31 cm<sup>-1</sup> (1238.34 nm). Measurements were recorded over a range of hydrogen pressures (13–900 Torr) and used to determine the integrated absorption strength and pressure shift for this transition. The Q(1)

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transition also exhibits significant linewidth narrowing with increased pressure. These results are discussed in terms of the competing pressure broadening effects and Dicke narrowing [7].

## 2. Experiment

The off-axis ICOS system has been described previously [8] and only a brief overview will be provided here. In these measurements, a single-mode DFB diode laser providing 12 mW around 1238 nm is directly coupled into a 0.83-m long, high-finesse cavity comprised of two highly reflective 2-in. diameter mirrors (loss = 49.4 ppm) in an off-axis fashion. The latter alignment helps suppress optical interference by making the laser beam propagate several hundred passes within the cavity before overlapping itself. In cavity enhanced absorption measurements, the total effective path length,  $L_{\text{eff}}$ , traveled by the light is given by  $L_{\text{eff}} = L * R / (1 - R)$ , where  $L$  is the cavity length and  $R$  is the mirror reflectivity. Light transmitted through the cavity is focused onto an amplified InGaAs detector (responsivity of 0.9 A/W at 1238 nm).

The effective path length of the cavity used in the present work was measured to be  $L_{\text{eff}} = 16800$  m via off-axis cavity ringdown spectroscopy [9] and exhibited no significant change over the course of the measurements. The laser is current-tuned approximately 30 GHz over the hydrogen absorption feature. The precise spectral position of the laser is determined by monitoring the transmission through a solid etalon (free spectral range = 2.0 GHz) relative to the well known ‘zero pressure’ hydrogen 2-0 band Q(1) line. The exact frequency of the 2-0 band Q(1) line is known with high accuracy ( $\nu_0 = 8075.3114 \text{ cm}^{-1}$ ) and it is taken as the reference frequency at low pressure (13 Torr). Using the etalon trace and this reference frequency, laser current was converted to absolute laser frequency, permitting measurements of the Q(1) pressure shift coefficient, Dicke narrowing parameters, and integrated absorption strengths. These measurements were taken rapidly over a 10-min period covering both an increasing and decreasing sample density. The excellent overlap of this data demonstrates negligible drift in the laser center point frequency over the measurement period.

Pure hydrogen gas (purity >99.99%) was introduced into the off-axis ICOS cell, and the gas pressure and temperature were monitored using a MKS Baratron ( $\pm 1\%$  of reading) and thermocouple ( $\pm 1^\circ \text{C}$ ), respectively.

## 3. Results and discussion

The measured cavity-enhanced spectra of the hydrogen 2-0 band Q(1) absorption feature is shown in Fig. 1, for a range of pressures from 13–900 Torr. The absorption feature is characterized by the Doppler width, measured to be  $0.0707 \pm 0.0002 \text{ cm}^{-1}$  consistent with the expected width of  $0.0706 \text{ cm}^{-1}$  at 298 K. The integrated line strength for this line was determined by Mickelson [4], in an analysis of

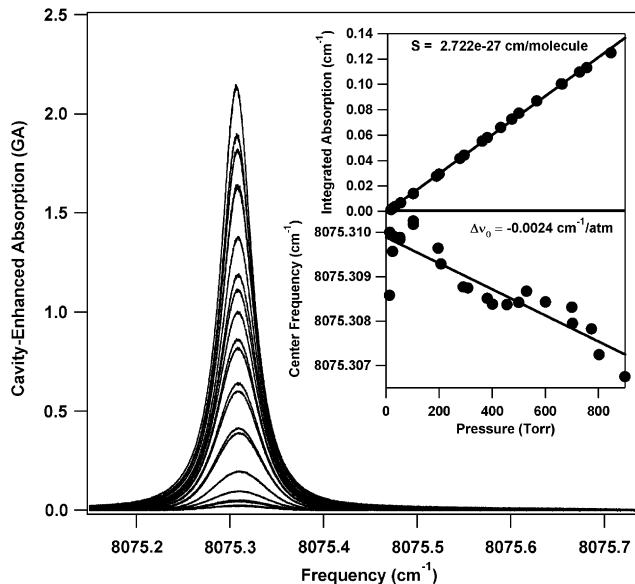


Fig. 1. Measured hydrogen quadrupole Q(1) line of 2-0 band for a series of hydrogen pressures from 13 to 900 Torr. The line center frequency for low pressures is  $8075.3114 \text{ cm}^{-1}$  and is taken from Bragg [4]. The top inset shows the integrated absorption as a function of pressure yielding a line strength of  $S = 2.72 \times 10^{-27} \text{ cm/molecule}$ . The bottom inset shows pressure shift measurements of the Q(1) line center, yielding a pressure-shift coefficient of  $0.0024 \text{ cm}^{-1}/\text{atm}$ .

available data, to be  $A_0 = 6.8 \times 10^{-8} \Delta\nu^{-1} \text{ cm}^{-1} \text{ amagat}^{-1}$ . In order to convert this value into an estimate of the actual absorption expected for a given concentration, sample cell length, and cavity mirror reflectivity (effective gain) we need to estimate the width of the absorption line. For low pressures, the best estimate is the Doppler width,  $0.0706 \text{ cm}^{-1}$ . Using a measurement temperature of 298 K, the calculation of the per-pass fractional absorption is

$$\begin{aligned} I/I_0 &= \exp[-(A_0 \times L \times \rho/T)] \\ &= \exp[-((6.8 \times 10^{-8} \Delta\nu \text{ cm}^{-1} \text{ amagat}^{-1}) \times 83 \text{ cm} \\ &\quad \times (\text{H}_2 \text{ density amagat})/0.0706 \text{ cm}^{-1})], \end{aligned} \quad (1)$$

where we have used the sample cell length of 83 cm for  $L$ . This number represents the single pass fractional attenuation of the laser beam as it traverses the sample cell.

The change in steady-state cavity output due to the presence of an absorbing species is given by

$$\frac{\Delta I}{I} = \frac{GA}{1 + GA}, \quad (2)$$

where the single-pass absorption  $A = 1 - e^{-\alpha(\omega)}$  and  $G \equiv R / (1 - R)$ . For weak absorption ( $GA \ll 1$ ), the cavity provides a linear absorption signal gain, given by  $G$ . Physically,  $G$  equals the number of optical passes occurring within cavity decay time.

Using Eq. (2), and taking the measured cavity mirror loss of 49.4 ppm ( $G = 20240$ ), obtained from cavity ringdown measurements, the cavity-enhanced absorption (GA) measured for each sample pressure (density) is

Table 1  
Measured parameters for the 2-0 Q(1) transition of hydrogen

Author	Zero pressure frequency	Pressure shift	Line strength
Herzberg [1]	8075.398 cm <sup>-1</sup>	–	–
Fink, et al. [3]	8075.3105 cm <sup>-1</sup>	–0.0048 cm <sup>-1</sup> /amagat	0.0078 cm <sup>-1</sup> /km amagat
Bragg [4]	8075.3114 cm <sup>-1</sup>	–0.0048 cm <sup>-1</sup> /amagat	0.0068 cm <sup>-1</sup> /km amagat
This work	–	–0.0026 cm <sup>-1</sup> /amagat	0.0073 cm <sup>-1</sup> /km amagat 2.722 × 10 <sup>-27</sup> cm/molecule

recorded and then plotted as a function of hydrogen pressure to produce the plot seen in Fig. 1. These absorption profiles were then integrated to yield an integrated absorption (cm<sup>-1</sup>) versus pressure (Torr) as shown in the top right inset of Fig. 1. The slope of this plot, the absorption line strength for this transition, yields a value of  $S = 2.722 \times 10^{-27} \pm 0.016 \times 10^{-27}$  cm/molecule = 0.00729 ± 0.00004 cm<sup>-1</sup>/(amagat \* km).

The pressure shift of the Q(1) line was also measured as the hydrogen pressure in the cell was increased and then decreased. The resulting fit is shown in the lower inset in Fig. 1 and provides a measured pressure shift of  $\Delta\nu_0 = -0.0024 \pm 0.0002$  cm<sup>-1</sup>/atm = 0.0026 ± 0.0002 cm<sup>-1</sup>/amagat. The values obtained by previous studies are compared to those listed here in Table 1. The linestrength is in good agreement with the most recent values tabulated by Bragg [4], however there is significant discrepancy in the observed pressure shift of the Q(1) absorption feature. Fink et al. [3] did not directly measure this shift and assumed that it was twice that of the 1-0 Q(1) shift. Bragg et al. [4] measured the 2-0 Q(1) transition of 2.8 and 1.4 atm of hydrogen to determine the line strength and pressure shift. The present work contains a substantially larger set of low pressures and employs a higher spectral resolution (e.g., the diode laser linewidth is less than 10<sup>-4</sup> cm<sup>-1</sup>). Moreover, the 13 Torr spectrum of the 2-0 Q(1) line is used as the wavelength reference in this work, obviating the need for large extrapolations.

#### 4. Dicke narrowing

Hydrogen optical transitions display a marked narrowing of line width with increased pressure; a characteristic termed Dicke narrowing [10]. Dicke narrowing is observed when the absorbing species has a Doppler width that is substantially greater than its pressure broadened line width. In this situation, the effect of increasing pressure (density) acts as a growing ‘cage effect’ and the Doppler width decreases. This is clearly seen in the decrease of the Q(1) line width as the pressure is increased in Fig. 1. We fit the absorption line shape to both Voigt and Galatry (the type of fit that includes Dicke narrowing effects) line shapes [11] producing the fit residuals shown atop Fig. 2. Both the Voigt and Galatry fits give a close approximation to the measured line shape, however the residual plots clearly demonstrate that the Galatry fit more accurately describes the line shape. The Fig. 2 inset shows the absorp-

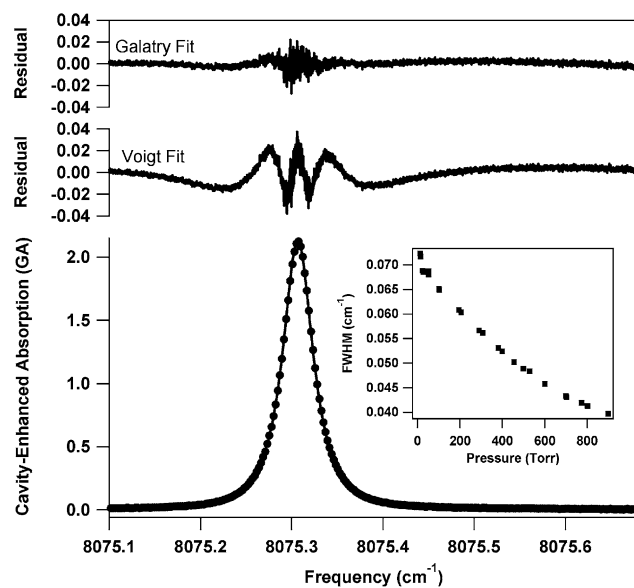


Fig. 2. The hydrogen 2-0 band Q(1) line shape measured at 900 Torr. The absorption line is fit to both a Voigt and Galatry profile, yielding the residual shown atop the figure and demonstrating the advantage of the Galatry fit. The inset shows the line width (FWHM) for the Q(1) line as a function of pressure, clearly demonstrating the dramatic line narrowing.

tion line width as a function of the total hydrogen pressure, with the FWHM line width varying from 0.0707 cm<sup>-1</sup> at 13 Torr to 0.0397 cm<sup>-1</sup> at 900 Torr. The Galatry fit provides a term,  $\beta$ , which is the effective frequency of velocity-changing collisions. For the lineshape measurement at 900 Torr shown in Fig. 2, the fit gives  $\beta = 0.057$  cm<sup>-1</sup> = 0.048 cm<sup>-1</sup>/amagat, consistent with previous results [12].

#### 5. Conclusion

We have reported measurements of the molecular hydrogen (2-0) quadrupole absorption band Q(1) line near 1238 nm using off-axis ICOS and a tunable diode laser. These results are the highest resolution measurements reported for this important transition to date. The high sensitivity and spectral resolution of the present analysis allows for a determination of the pressure shift, line strength, and line width at relatively low pressures (13–900 Torr). Future efforts will involve measurements of other hydrogen quadrupole transitions and extend the measurements to higher pressures to elucidate accurate optical diffusion coefficients and pressure broadening parameters similar to prior work [13].

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