HIGH-RESOLUTION CARS MEASUREMENT OF RAMAN LINEWIDTHS OF H_2

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High-resolution coherent anti-Stokes Raman spectroscopy (CARS) has been performed in hydrogen gas using a cw system. Accurate measurements of the Raman linewidths of the Q(0) through Q(3) transitions of molecular hydrogen have been made at pressures ranging from 0.75 to 40 atm at room temperature. The pressure-broadening coefficients determined for these lines are important in analytic and diagnostic applications of CARS in high-pressure media.

The use of coherent anti-Stokes Raman spectroscopy (CARS) as a spectroscopic and diagnostic tool has been increasing in recent years [1]. This paper reports on high-resolution CARS measurements of the Raman linewidths of the Q(0) through Q(3) transitions of the hydrogen molecule made at pressures ranging from 0.75 to 40 atm at room temperature. Because of the extreme sensitivity of the CARS signal to the Raman linewidth, accurate measurement of these linewidths in high-pressure and/or high-temperature environments is essential for practical applications of CARS as a diagnostic tool in such environments [2]. The two most recent complete linewidth measurements [3,4] available on hydrogen were obtained more than a decade ago through spontaneous Raman experiments, and gave results which were too significantly different from each other to make either very reliable. Although some more recent high-resolution linewidth data are also available [5,6], they are confined to the strongest Q(1) line and are, thus, of limited value for general diagnostics applications.

A schematic diagram of the experimental system used in the present experiment is shown in fig. 1. An Ar-ion laser operating in single-mode at 488 nm with a power of 800 mW produced the pump beam used in the CARS process. A tunable ring dye laser pumped by another Ar-ion laser produced the Stokes beam. The output power of the dye-laser beam was approximately 200 mW, with a linewidth of 30 MHz at the Stokes frequencies used in this experiment. The two beams were combined collinearly by a dichroic mirror and focused into a high-pressure sample cell containing hydrogen gas at varying pressures. Upon leaving the cell, the beams were recollimated by the second

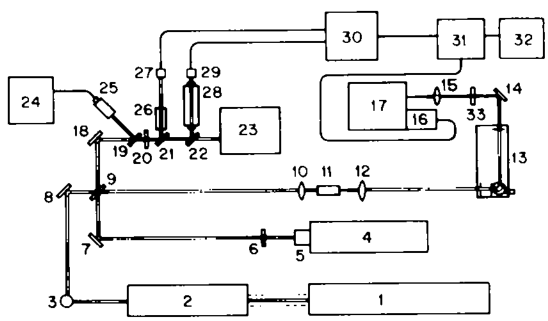

Fig. 1. Schematic diagram of the experimental system. The components are as follows: argon-ion lasers 1, 4; dye laser 2; periscope 3; mirrors 7, 8, 14, 18; dichroic mirror 9; lenses 10, 12, 15; sample cell 11; Pellin-Broca prism dispersing system 13; long-pass filters 6, 20; narrow-band filter 33; half-wave plate 5; photomultiplier 16; monochromator 17; beam splitters 19, 21, 22; scanning interferometer 25; oscilloscope 24; iodine cell 26; PIN diodes 27, 29; Fabry-Perot interferometer 28; wavemeter 23; chart recorder 30; photon counting system 31, 32.

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lens and dispersed by a Pellin-Broca prism. The anti-Stokes component beam generated was spatially filtered with a pin-hole and detected by a photomultiplier through a narrow-band interference filter and a monochromator. The photomultiplier output was processed by a photon-counting system whose analog output was sent to a two-pen chart recorder.

The portions of the pump and Stokes beams separated from the main beam by the dichroic mirror were used for beam diagnostics. A scanning Fabry–Perot interferometer was used for simultaneous monitoring of the frequencies of the pump and Stokes lasers on an oscilloscope and detecting any mode hopping during the laser scan. An iodine absorption spectrum produced with the Stokes beam was used as the frequency standard [7] for calibrating the Stokes beam. A commercial wavemeter, while not sufficiently accurate for absolute frequency calibration, greatly facilitated the laser tuning and frequency calibration process. In addition, a semi-confocal Fabry–Perot interferometer having a free spectral range of 124 MHz was used to generate a frequency marker.

Various combinations of signals from these diagnostic systems and the CARS signal were alternately fed to the two channels of the recorder during the experiment. For example, in order to calibrate the free spectral range of the semi-confocal Fabry–Perot interferometer, the output of the interferometer and the iodine absorption spectrum were recorded simultaneously; for the Raman linewidth measurement, however, the CARS signal and the throughput of the semi-confocal interferometer were recorded simultaneously.

The results of the linewidth measurement of the Raman transitions of the hydrogen molecule are shown in fig. 2. These results are in good general agreement with the linewidth data on Q(1) made by Henesian et al. [5] in a previous cw CARS experiment. Note that the linewidths of the lines diverge substantially from one another as the density increases, although they are within 10% of each other at the lower end of the density scale near 1 amagat. Although the measurement could not be extended much below 1 amagat (1 amagat is equal to the number density of gas at 1 atm at 273 K) for all lines, it is reasonable to expect that the linewidths of the lines will remain almost equal in that density range since the predominant broadening mechanism there

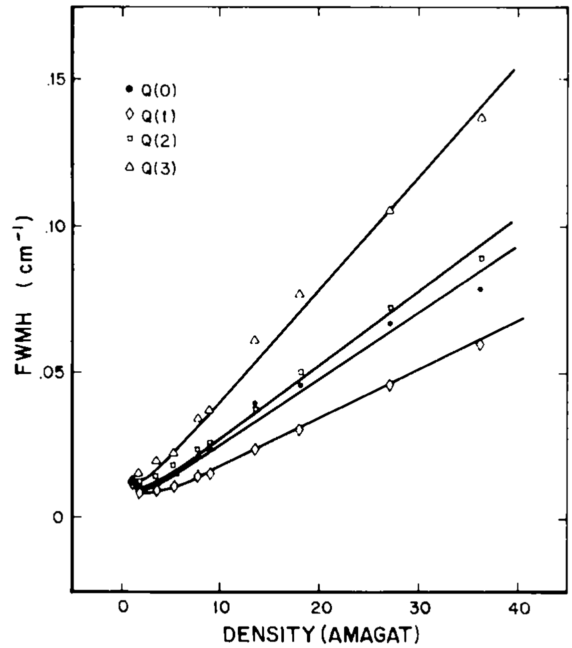

Fig. 2. Raman linewidths of H_2 as function of density at room temperature. Solid lines represent the best fit of the experimental data.

(Dicke-narrowed Doppler broadening) is independent of the quantum number of the rotational levels involved in the transition.

The fact that the linewidths are roughly equal in the density range of 1 amagat or lower is responsible for the success of the theoretical models which are based on equal linewidths for all lines in diagnostic applications of CARS with respect to H_2 in that density range. However, the fact that the linewidths differ substantially at higher densities must be taken into account in the analysis for diagnostics applications in high-density media.

Pressure broadening coefficients were determined for the lines through a least-squares routine using the diffusion model which incorporates the effect of the Dicke narrowing. According to this model, the linewidth is given by [8]

$$\Delta\nu = 4\pi D_0/\lambda^2 c\rho + a\rho \,, \tag{1}$$

where $\Delta\nu$ is the linewidth (FWHM in cm^{-1}), λ is the wavelength of the Raman transition (in cm), ρ is the gas density (in amagats), a is the pressure-broadening coefficients (in cm^{-1}/amagat), and D_0 is the self-

Table 1
Pressure broadening coefficients (a) and self-diffusion coefficients (D_0) of H_2

Transition	Present study			Murray and Javan			Allin et al.	Owyoung	
	a	D_0	δ	a	D_0	δ	a	a	D_0
Q(0)	2.35	1.60	1.1	2.2	1.36	5	2.32		
Q(1)	1.68	1.35	0.2	1.5	1.36	1.5	1.40	1.71	1.39
Q(2)	2.58	1.43	0.8	2.6	1.36	8	2.53	–	
Q(3)	3.90	1.43	1.2	5.5	1.36	10	3.66	–	–

a in [10^{-3} cm^{-1}/amagat]; D_0 in [cm^{-2} amagat/s]. δ: rms error of the fit in [10^{-3} cm^{-1}].

diffusion coefficient at 1 amagat. The results of the simultaneous fit for the broadening coefficients (a) and the diffusion coefficients (D_0) are presented in table 1. Note that the value of the diffusion coefficients vary somewhat from line to line. Attempts to fix the diffusion coefficient at a single value for all lines resulted in an unacceptably large fitting error, although the value of the broadening coefficients was only slightly affected. Also shown in the table are the broadening coefficients obtained in previous spontaneous Raman measurements by Murray and Javan [3] and by Allin et al. [4], along with that for Q(1) obtained by Owyoung in a high-resolution stimulated Raman gain experiment [6]. Comparison of the data in the present experiment with those of Murray and Javan reveals some discrepancy, particularly for the Q(3) line. In fact, it is interesting to note that the results of Allin et al. obtained using a system having a poorer resolution than Murray and Javan's are in better overall agreement with ours. In view of the vast improvement of the fitting error of the present work over that of Murray and Javan, it is clear that the present data represent the best set of broadening coefficients available at this time. The excellent agreement between our results and Owyoung's provides further validation for the set of pressure broadening coefficients obtained in the present experiment.

In summary, a high-resolution CARS measurement of the Raman linewidths of hydrogen gas has been made and the pressure-broadening coefficients have been determined. The present results which indicate that the linewidths of various Raman lines diverge substantially in the high-pressure region from a common value in the low-pressure region are significant, and the data are useful in the development of practical CARS diagnostics.

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