

High-Resolution CARS Measurement of Raman Linewidths of Deuterium

This note reports a measurement of Raman linewidths of deuterium in a high-resolution coherent anti-Stokes Raman spectroscopy (CARS) experiment. Although the Raman linewidths for certain individual lines of deuterium have been previously measured (1-3), there has not been any high-resolution linewidth measurement covering all the Q -branch transitions normally observed at room temperature. The present measurement has been performed to meet the need for accurate linewidth data which are necessary for correct interpretation of experimental results in diagnostic applications of CARS and other nonlinear Raman techniques (4). The present measurement covered densities ranging from 0.3 to 18 amagat (1 amagat is equal to the number density of gas at 1 atm at 273 K) for $Q(0)$ through $Q(4)$ transitions of the fundamental vibrational Raman band, some of the lines having been measured for the first time. A similar measurement for hydrogen has already been reported (5).

The experimental system used in the present experiment has been described previously (5). Briefly, the optical system is based on a single-mode Ar-ion (Spectra Physics 165) and a ring-dye laser (Coherent 699-21) which provide the pump beam at 514.5 nm and the Stokes beam at 608 nm, respectively. The laser beams were collinearly combined on a dichroic mirror and focused into a sample cell containing deuterium gas. The beams exiting from the sample cell were recollimated, dispersed through a Pellin-Broca prism, filtered with an interference filter, and detected by photomultiplier through a monochromator. The photomultiplier output was processed in a photon-counting system and sent to a recorder. In addition, various beam diagnostic systems are also employed: a scanning Fabry-Perot interferometer for the laser mode stability, a wavemeter and an iodine absorption cell for wavelength calibration of the Stokes beam, and a semiconfocal Fabry-Perot etalon for generation of a frequency marker during the spectral scans. The resolution of the system is limited by the effective linewidth of the single-mode Ar-ion laser which is estimated to be 0.0003 cm^{-1} .

The results of the linewidth measurement for the Raman transitions of the deuterium molecule are presented in Fig. 1. The data points represent an average of three separate measurements. The error bars representing the variation of the linewidth of each individual measurement about the average value are smaller than the symbols used to represent the data points, so they are not shown in the figure. As was the case for hydrogen (5), deuterium linewidths also diverge substantially from one another after undergoing the Dicke narrowing (6) as the density is increased. Pressure-broadening (or more accurately, density-broadening) coefficients and self-diffusion coefficients were determined from the experimental data by means of a general linear least-squares routine on the basis of the diffusion model, according to which the linewidth is given by (6)

$$\Delta\nu = \frac{4\pi\nu^2}{c} \cdot \frac{D_0}{\rho} + a\rho, \quad (1)$$

where $\Delta\nu$ is the linewidth (FWHM in cm^{-1}), ν is the frequency of the vibrational Raman transition (in cm^{-1}), ρ is the gas density (in amagat), c is the speed of light (in cm/sec), a is the pressure broadening coefficient (in $\text{cm}^{-1}/\text{amagat}$), and D_0 is the self-diffusion coefficient at 1 amagat. Note that the inverse proportionality of the diffusion coefficient on gas density has been explicitly recognized in the expression. The results of the fit for the pressure-broadening coefficient, a , and the diffusion coefficient, D_0 , are shown in Table I. Also shown are the values of the coefficients previously obtained by Murray and Javan through spontaneous Raman measurements and by Robertson and Hunt (7) through E -field induced infrared absorption measurements.

It may be noted that the infrared absorption measurements were performed in high-density regions (10-30 amagat), so the diffusion coefficients were not determined and also the fitting error was not reported. In any case, it may be observed that the agreement between the present results and the infrared data is excellent, being within 3% of each other for the $Q(0)$ - $Q(3)$ lines and slightly larger for the $Q(4)$ line. It is quite possible that the smaller density range the present measurements were limited to for $Q(4)$ (<10 amagat)

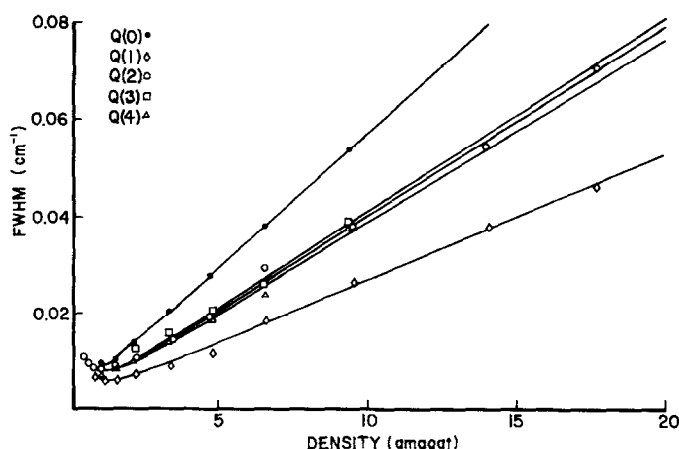


FIG. 1. Raman linewidths of deuterium as a function of density at room temperature. Solid lines represent the best fit of the experimental data.

due to a poor S/N ratio makes that portion of the present data somewhat less reliable. In comparing the present results with those of Murray and Javan, one might be surprised to see that the present pressure-broadening coefficients deviate almost 100% from those of Murray and Javan, when their quoted uncertainty is of the order of only 10–20%. However, the instrument linewidth of the spontaneous Raman spectroscopy system they used for deuterium was 0.053 cm^{-1} which is considerably larger than the Raman linewidths being measured (see Fig. 1), and thus their results were susceptible to a large systematic error. In contrast, it may be recalled that the resolution of the present system is only 0.0003 cm^{-1} . Also, an earlier CARS measurement of the $Q(2)$ linewidth by Henesian *et al.* presented in a graphical form (2) closely agrees with the present results. In light of the fact that the fitting errors for the present measurement are more than five times smaller than those associated with Murray and Javan's measurements, it is evident that the present measurement represents a significant improvement over the previously available data. It might be noted that the J dependence of the self-diffusion coefficients as seen in the table has also been observed in the case of foreign-gas broadening of absorption lines of HF and HCl molecules (8), not to mention the case of H_2 reported previously.

TABLE I
Pressure-Broadening, a , and Diffusion Coefficients, D_0 , of D_2

Transition	This Study			Murray & Javan			Robertson & Hunt
	a	D_0	δ	a	D_0	δ	
Q(0)	5.79 ± 0.08	1.084 ± 0.13	0.6	—	—	—	5.77 ± 0.2
Q(1)	2.63 ± 0.04	0.873 ± 0.09	1.2	1.4 ± 0.15	0.952	7	2.59 ± 0.10
Q(2)	3.91 ± 0.04	0.901 ± 0.06	1.1	2.2 ± 0.2	0.952	7	4.00 ± 0.10
Q(3)	4.11 ± 0.08	1.083 ± 0.13	1.1	2.6 ± 0.5	0.952	8	4.22 ± 0.10
Q(4)	3.87 ± 0.08	0.913 ± 0.20	0.8	—	—	—	4.14 ± 0.15

a in $[10^{-3} \text{ cm}^{-1}/\text{amagat}]$; D_0 in $[\text{cm}^2\text{-amagat/sec}]$;

δ : rms error of the fit in $[10^{-3} \text{ cm}^{-1}]$.

In conclusion, a high-resolution CARS measurement of the Raman linewidths of deuterium gas has been made for the first five vibration-rotation lines, and an accurate determination of the pressure-broadening and self-diffusion coefficients has been made. The present data should be useful not only in studies of molecular kinetics, but also in diagnostics of deuterium using nonlinear Raman techniques such as coherent anti-Stokes Raman spectroscopy and stimulated Raman gain spectroscopy.

Note added in proof. We have learned, since the completion of this work, that recently G. Rosasco of the National Bureau of Standards and his co-workers have also made a similar linewidth measurement using a high-resolution stimulated Raman gain spectroscopy system. Their results appear to be in agreement with ours within approximately 6%. We are grateful to Dr. Rosasco for releasing their data to us prior to publication.

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Received October 17, 1986*

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