

A study of the electric quadrupole fundamental band of D_2 using an infrared difference frequency laser system¹

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Frequency tunable infrared radiation from a difference frequency laser system has been used with a long path cell to study the electric quadrupole vibration-rotation spectrum of the deuterium molecule in the 2.8–3.9 μm region. A ratio method as well as frequency modulation were used to detect the weak absorption. Sub-Doppler linewidths due to collisional narrowing were observed with a D_2 pressure of 1 atm. The wavelengths of 11 transitions were measured relative to infrared reference lines, and improved molecular constants for the $v = 0$ and 1 states of D_2 were determined.

On a utilisé le rayonnement infrarouge à fréquence ajustable fourni par un système laser à fréquence différentielle, ainsi qu'une cellule à long parcours, pour étudier le spectre quadrupolaire électrique de rotation-vibration de la molécule de deutérium, dans la région 2.8–3.9 μm . Pour mesurer la faible absorption, on a utilisé une méthode de rapport ainsi que la modulation de fréquence. Avec une pression de 1 atm de D_2 , on a observé des raies rétrécies par collisions à une largeur inférieure à la largeur Doppler. On a déterminé, pour 11 transitions, les longueurs d'onde relatives à des raies de référence infrarouges, et on a obtenu des valeurs améliorées des constantes moléculaires pour les états $v = 0$ et 1 de D_2 .

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Introduction

In this paper, we report a study of the electric quadrupole vibration-rotation spectrum of the D_2 molecule. Eleven transitions in the O , Q , and S branches of the fundamental ($v = 1 \leftarrow 0$) band have been observed using an infrared difference frequency laser system and a multiple-traversal absorption cell. Wavelength measurements of these transitions, with an accuracy of $\sim 0.005 \text{ cm}^{-1}$, were used to determine improved molecular constants for the $v = 0$ and 1 vibrational states of deuterium. Our measured frequencies are generally rather higher (by from ~ 0.03 to $\sim 0.07 \text{ cm}^{-1}$) than those from earlier studies of the Raman (1–3) and electric-field-induced (4) spectra of D_2 .

The significance of a quadrupole vibration-rotation spectrum of H_2 was pointed out in 1938 by Herzberg (5) and in the same year its strength was calculated by James and Coolidge (6). Such a spectrum was first observed in 1949 by Herzberg (7), who photographed the 2–0 and 3–0 bands in absorption using equivalent paths of up to 55 km atm of H_2 . The 1–0, 2–0, and 3–0 quadrupole bands of H_2 have since been studied in further detail (8–10), most notably by Fink *et al.* (8), and recently the $S(3)$ line of the pure rotational spectrum has been observed (11). These studies have found that the intensities of the transitions are in good agreement with those obtained

from *ab initio* calculations (12–16) of the H_2 quadrupole moment. For many years, the very weak H_2 4–0 band was observed only in planetary spectra (17), but very recently Mickelson *et al.* (18) have succeeded in studying it in the laboratory and furthermore the 5–0 band has been observed in the spectrum of Uranus (19). With regard to isotopically substituted hydrogen, the only previous works are a study of the $S(0)$ quadrupole transition in the HD fundamental band (20) and the detection of the same transition in D_2 during a study of D_2 – rare gas van der Waals complexes (21). Quadrupole vibration-rotation spectra of other molecules have not been observed.

Previous wavelength measurements in the fundamental band of D_2 have been made by means of Raman scattering (1–3) and electric-field-induced infrared absorption (4). The transitions $Q(J)$ with $J = 0$ to 4 were studied using conventional Raman techniques by Stoicheff (1) and Looi *et al.* (2), and recently the $Q(2)$ wavelength has been measured using coherent anti-Stokes Raman spectroscopy (CARS) and high resolution interferometry by Hennesian *et al.* (3). Thirteen transitions in the O , Q , and S branches were measured in the field-induced spectrum by Brannon *et al.* (4). The pressure shifts exhibited in the D_2 fundamental band have also been studied (2–4, 22).

Experimental Details

A multiple-traversal cell with a base pathlength of

¹NRCC No. 16930.

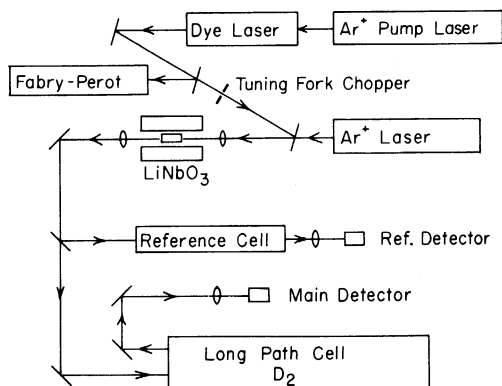


FIG. 1. Schematic diagram of the difference frequency laser system and absorption cells. The LiNbO_3 crystal is contained in a temperature-controlled oven at 250–450°C.

2 m was used to obtain absorption paths in the range 64 to 80 m through D_2 at a pressure of 1 atm and a temperature of 295 K. The infrared difference frequency laser system used in this work, which is based closely on the design of Pine (23, 24), has been described by Bernard and Oka (25). The apparatus is illustrated schematically in Fig. 1. Visible radiation of frequency ν_2 from a cw tunable dye laser is mixed in a LiNbO_3 crystal with blue (4880 Å) or green (5145 Å) radiation ν_1 from a fixed-frequency single-mode Ar^+ laser. The difference frequency, $\nu_3 = \nu_1 - \nu_2$, which results from the nonlinear response of the crystal, is tunable in the infrared wavelength region from ~ 2.2 – $4.2 \mu\text{m}$. Phase matching of the three wavelengths is achieved by placing the LiNbO_3 crystal in a temperature-controlled oven. Typical power levels of the three radiations are: ν_1 , $\sim 300 \text{ mW}$; ν_2 , $\sim 40 \text{ mW}$; ν_3 , $\sim 2 \mu\text{W}$. The linewidth of the tunable infrared radiation is essentially limited by that of the dye laser, and is of the order of 10 MHz.

Spectra were obtained using two different techniques: ratio recording and frequency modulation. In the ratio technique, the infrared radiation was 100% amplitude modulated at 1 kHz by placing a small tuning fork chopper in the path of radiation ν_2 . The infrared beam was split into two portions by a beam-splitter, with one portion passing through the long path D_2 cell to an InSb infrared detector, and the other portion passing through a short cell containing a reference gas to a second detector. After phase sensitive amplification of the signal from each detector, the ratio of the signals was displayed as a function of dye laser scan on an X–Y recorder. Frequency markers at 300 MHz intervals derived from a Fabry–Perot interferometer monitoring the dye laser tuning were also displayed on the recorder.

In the frequency modulation technique, the output

mirror of the Ar^+ laser was mounted on a piezoelectric translator in order to provide frequency modulation of ν_1 and thus of ν_3 . A sinusoidal voltage of $\sim 200 \text{ V}$ (peak to peak) from an audio amplifier and signal generator was used to drive the translator. The modulation was at $\sim 2 \text{ kHz}$ with an rms amplitude of $\sim 100 \text{ MHz}$. The signal from either the D_2 or reference channel was displayed on the X–Y recorder. Normally this technique yielded the first derivative of the transmitted infrared power, but, by setting the phase sensitive amplifier to twice the modulation frequency, the second derivative could also be obtained. In contrast to the ratio technique, in which the amplitude noise of the infrared source was largely eliminated, in the case of the frequency modulation method the active reduction of dye laser amplitude noise by feedback (to the Ar^+ pump laser) proved useful. When this was done, the sensitivity for the detection of weak absorption increased by a factor of 3 to 10 relative to the ratio method.

Results

The wavelength measurements reported here were made by determining the separations between the D_2 lines and known lines of various molecules placed in the reference absorption cell. These separations were measured using the 300 MHz interval markers generated by the Fabry–Perot interferometer which monitored the dye laser output. The D_2 measurements thus depended on the availability of a large number of very accurately measured infrared standards. Fortunately, many such standards have recently become available in the middle infrared, due especially to the work of Guelachvili and collaborators employing high resolution Fourier transform spectroscopy. The results of our measurements are shown in Table 1 together with the reference molecules used and the sources of the reference measurements. Nine of the eleven standards came directly from Guelachvili's measurements (26–30), and the other two (31, 32) had been calibrated relative to them. The absolute accuracy of the standards employed should be about $\pm 0.003 \text{ cm}^{-1}$. Our separation measurements have a somewhat smaller uncertainty, and the estimated total uncertainty of the D_2 measurements is about 0.004 – 0.005 cm^{-1} .

Examples of the observed spectra are shown in Figs. 2–5. The strongest of the observed lines, $S(2)$, is illustrated in Fig. 2 along with the nearby H_2^{18}O reference line (32). This trace was recorded using the ratio technique; absorption in the D_2 cell is down and absorption in the reference cell up on the trace. Higher frequencies lie to the left in this and the other spectra presented. A similar trace of the D_2 $S(0)$ tran-

TABLE I. Measurements of D₂ quadrupole transitions relative to nearby reference transitions (cm⁻¹)

D ₂ transition	$\nu(D_2)$	$\nu(D_2) - \nu(\text{ref})$	Reference molecule	Reference
<i>O</i> (2)	2814.5459(40) ^a	-0.0553	H ₂ CO	31
<i>O</i> (3)	2693.9723(40)	+0.2850	¹⁴ N ¹⁵ N ¹⁶ O	26
<i>O</i> (4)	2572.6428(50)	-0.1833	N ₂ O	27
<i>Q</i> (1)	2991.5043(40)	-0.0448	CH ₂ D ₂	28
<i>Q</i> (2)	2987.2955(40)	+0.0778, +0.0228	CH ₂ D ₂	28
<i>Q</i> (3)	2980.9882(40)	-0.1556	H ₂ O	29
<i>Q</i> (4)	2972.6128(50)	-0.2113	CH ₂ D ₂	28
<i>S</i> (0)	3166.3596(40)	-0.0934, -0.1115	CH ₃ Br	30
<i>S</i> (1)	3278.5222(40)	-0.0985	H ₂ O	29
<i>S</i> (2)	3387.2606(50)	-0.1134	H ₂ ¹⁸ O	31
<i>S</i> (3)	3492.0913(40)	+0.1959	H ₂ O	29

^aUncertainties in parentheses are in units of 0.0001 cm⁻¹.

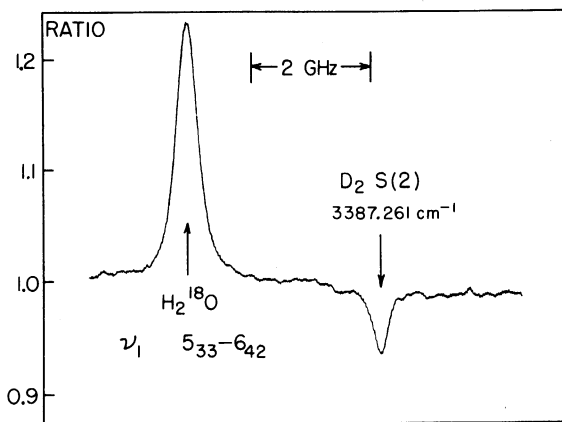


FIG. 2. Spectrum of the D₂ *S*(2) quadrupole transition and H₂¹⁸O reference line. Frequency increases to the left in this and the other spectra. The ratio system results in absorption in the D₂ cell being down, and in the reference cell being up, on the trace. The pressure times path length was ~80 m atm and the time constant for detection was 0.1 s.

sition and CH₃Br reference lines (30) is shown in Fig. 3. Figure 4 illustrates the much weaker *O*(3) transition (~1% peak absorption) as recorded using the frequency modulation technique. A comparison of the first harmonic (as used for Fig. 4) and second harmonic (2*f*) detection schemes used with frequency modulation is shown in Fig. 5, which illustrates the *O*(2) transition.

The *S*(4) transition should be somewhat stronger than some of the lines which were observed, but it was obscured by strong pressure-broadened absorption lines of an impurity molecule in the D₂ cell. The obscuration was almost certainly due to the ν_3 band of HDO, and attempts to minimize it by cooling the D₂ source cylinder to 77 K when filling the cell were only partially successful. Thus *S*(4) was not measured.

The observed widths of the D₂ quadrupole lines were considerably less than the Doppler width. For

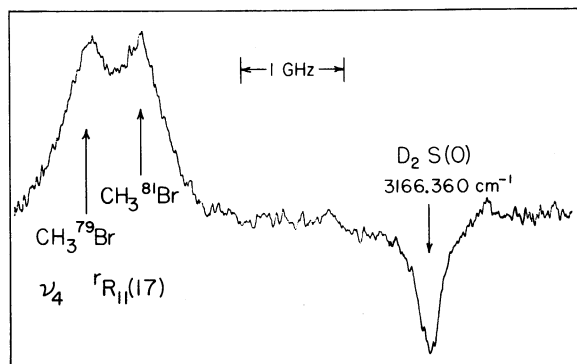


FIG. 3. Spectrum of the D₂ *S*(0) quadrupole transition and CH₃Br reference lines, recorded using the ratio technique as in Fig. 2.

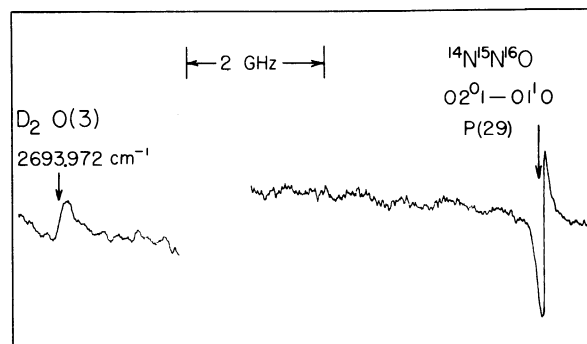


FIG. 4. Spectrum of the D₂ *O*(3) transition and N₂O reference line, recorded using laser frequency modulation with 1*f* phase sensitive detection. The break in the trace results from the change from the main detector signal to the reference detector signal on the X-Y recorder. The time constant of detection was 0.1 s.

example, the *S*(0) line in Fig. 3 had a full width at half maximum of about 350 MHz whereas the anticipated Doppler width is 583 MHz. The difference is caused by collisional narrowing (33), which has

TABLE 2. Comparison of the present results with previous measurements of the D₂ fundamental band (cm⁻¹)

D ₂ transition	Present results		Stoicheff ^b Observed	Brannon <i>et al.</i> ^c Observed	Looi <i>et al.</i> ^d Observed	Henesian <i>et al.</i> ^e Observed
	Observed ^a	Calculated				
2814O(2)	2814.5459(40)	2814.5471		2814.530(40)		
2693O(3)	2693.9723(40)	2693.9718		2694.050(40)		
2572O(4)	2572.6428(50)	2572.6431				
2991Q(1)	2991.5043(40)	2991.5047	2991.446(20)	2991.486(20)	2991.465(20)	
Q(2)	2987.2955(40)	2987.2928	2987.230(20)	2987.268(20)	2987.246(20)	2987.2371(10)
Q(3)	2980.9882(40)	2980.9896	2980.877(50)	2980.967(20)	2980.955(20)	
Q(4)	2972.6128(50)	2972.6115	2972.557(50)	2972.597(30)	2972.568(20)	
S(0)	3166.3596(40)	3166.3593		3166.300(20)		
S(1)	3278.5222(40)	3278.5225		3278.434(20)		
S(2)	3387.2606(50)	3387.2612		3387.220(20)		
S(3)	3492.0913(40)	3492.0911		3492.064(30)		

^aThe uncertainties in parentheses are expressed in units of the last digit of the measurement.

^bReference 1. Raman spectroscopy.

^cReference 4. Electric field induced spectroscopy.

^dReference 2. Raman spectroscopy.

^eReference 3. Coherent anti-Stokes Raman spectroscopy.

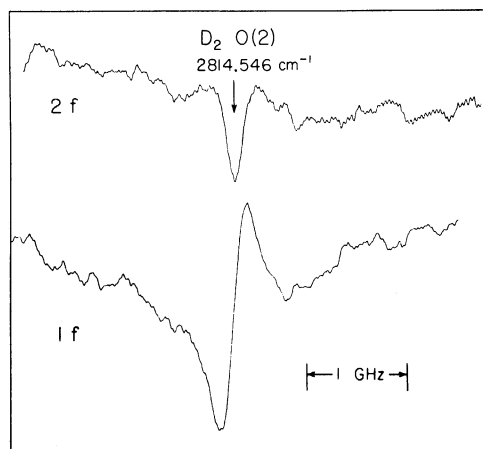


FIG. 5. Spectrum of the O(2) quadrupole transition of D₂, recorded using the frequency modulation technique with 2f (upper trace) and 1f (lower trace) phase sensitive detection. The time constant for detection was 0.4 s. The interference fringes to the right of upper trace are due to the multiple reflection cell.

previously been noted in the H₂ quadrupole transitions (8–11) and extensively studied in the Raman spectra of H₂ and D₂ (22, 34). No attempt was made in the present work to study the pressure dependence of the linewidths.

Analysis

The present measurements are compared in Table 2 with the previous high resolution measurements of the D₂ fundamental band (1–4). The Q-branch measurements of Stoicheff (1) and of Looi *et al.* (2) using conventional Raman spectroscopy are, respectively, about 0.06 and 0.04 cm⁻¹ lower than our

measurements on average. These differences are somewhat outside the combined uncertainty estimates. On the other hand, the measurements by Brannon *et al.* (4) of the field induced spectrum generally agree with our values within uncertainties, though they too are slightly lower (~ 0.02 cm⁻¹) on average. The recent measurement of the frequency of Q(2) by Henesian *et al.* (3) using the CARS method is in serious disagreement with our value; the difference is about 12 times the combined estimated uncertainties. Although the CARS wavelength measurement (3) was made by a very elegant and direct interferometric technique, we believe that our measurement is less subject to large systematic errors and that our uncertainty estimates (Table 2) are realistic. Pine² has also measured this transition using his difference frequency laser system and pressurized (2.1 atm) D₂. His value of 2987.292 ± 0.003 cm⁻¹ agrees well with ours when the pressure shift (see below) is taken into account. It should be noted that our data, and those of ref. 1, refer to a D₂ pressure of 1 atm whereas the other measurements in Table 2 are extrapolated values for zero pressure. The pressure shifts measured for the various lines of the fundamental band, which are approximately equal to one another, have values around -0.0015 cm⁻¹/atm at 295 K (2–4, 22). Thus our measured line positions would be raised by about 0.0015 cm⁻¹ if corrected for the pressure shift. However, this amount is less than our experimental uncertainty and much less than the differences among the various studies in Table 2, and we have thus chosen to ignore it in this work.

The present results were analyzed in a least-squares fit to obtain rotational and centrifugal dis-

²A. S. Pine. Private communication.

TABLE 3. Molecular constants of D₂ (cm⁻¹)

	Present work ^a	Stoicheff ^b	Brannon <i>et al.</i> ^c
B_0	29.9132(8)	29.9105(50)	29.9063(5)
D_0	0.01151(8)	0.01134(30)	0.01140(5)
H_0	6.9(23) × 10 ⁻⁶	3.6(50) × 10 ⁻⁶	7.3(9) × 10 ⁻⁶
B_1	28.8583(9)	28.8482	28.8488(5)
D_1	0.01126(7)	0.01075	0.01096(5)
H_1	6.4(15) × 10 ⁻⁶	(3.6 × 10 ⁻⁶) ^d	3.6(8) × 10 ⁻⁶
ν_0	2993.614(4)	2993.561(20)	2993.606(20)

NOTE: The uncertainties in parentheses are expressed in units of the last digit of the quoted value. Those for the present work are 3 σ from the least-squares fit, and the others are as quoted by the respective authors.

^aFrom a weighted least-squares fit to the present data (Table 1) and the pure rotational data of Stoicheff (1).

^bReference 1.

^cReference 4.

^d H_1 was fixed equal to H_0 .

tortion constants for the $v = 0$ and 1 states of D₂ and the fundamental band origin. Included in the fit were Stoicheff's (1) values for five transitions, $S(0)$ to $S(4)$, of the D₂ pure rotational Raman spectrum. The data in the fit were weighted according to the inverse squares of their estimated uncertainties (0.02 cm⁻¹ for the pure rotational data of ref. 1 and 0.004 or 0.005 cm⁻¹ for the data of Table 1). The results of the fit are given in Table 3, which also lists D₂ constants previously determined in refs. 1 and 4. We believe that the present values are the best currently available for the $v = 0$ and 1 states of D₂. As mentioned above, the true zero-pressure extrapolated value of the band origin is expected to be about 0.0015 cm⁻¹ higher than our 1 atm value, namely 2993.615 cm⁻¹.

Discussion

One aim of the present work was to evaluate the capabilities of our difference frequency laser system for the detection of weak infrared absorption lines. Under the conditions used in the experiment, the strongest D₂ line, $S(2)$, had a predicted peak absorption of about 6% and the weakest, $Q(4)$ and $O(4)$, had absorptions of about 0.7%. From the signal to noise ratios observed for the weakest lines, we estimate the sensitivity of our apparatus to be $\sim 10^{-3}$. For an absorption path of 100 m, this corresponds to a minimum detectable absorption coefficient of $\sim 10^{-7}$ cm⁻¹. It is planned to utilize the high sensitivity and resolution of the system in the future to search for hitherto unobserved spectra of ions and free radicals in the 2.2 to 4.2 μ m region.

Reid *et al.* (35) have recently demonstrated very high sensitivity ($\sim 10^{-5}$) obtained using a tunable diode laser and a long path cell in the 9 μ m region. In their experiment, a gain in sensitivity of ~ 100 was experienced in going from ratio detection to frequency modulation. The sensitivity of our system is considerably less than that of ref. 35, and the im-

provement due to frequency modulation detection is not as great. These facts are probably a reflection of the different noise characteristics of the two laser systems and the different size of multiple reflection cells used. Although the sensitivity of our spectrometer using the difference frequency system is much less than that reported by Reid *et al.* (35) using diode lasers, our system of course has the advantage of a much wider and more continuous tuning range than any single diode laser.

As already noted by Reid *et al.* (35), we have experienced that the most serious sources of noise when frequency modulation is used are various interference fringes caused by optical components. Such fringes cause not only the regular wavy patterns which overlap with spectral lines but also cause random noise when combined with the frequency instability of lasers. After eliminating a few such interferences, two persistent ones remained: one due to the multiple reflection cell and the other due to the LiNbO₃ crystal. The occurrence of these two sets of fringes depended critically on various adjustments and on the frequency of the infrared radiation but we have not been able to control them easily. The interference due to the LiNbO₃ crystal is particularly serious when frequency modulation is used because the spacing of the fringes (~ 1200 MHz) is comparable to spectral linewidths. We have found that a slight variation of the temperature and thus the phase matching condition for the LiNbO₃ crystal changes the intensity of the interference. The traces shown in Figs. 4 and 5 were recorded when such interference was minimized.

Accurate *ab initio* calculations of molecular energy levels for hydrogen have become available in recent years, and a careful comparison of theory and experiment for D₂ has been made by Bredohl and Herzberg (36). They took data from their own analysis of the ultraviolet emission spectrum for levels of the

ground electronic state with $v = 2$ to 21, and data from refs. 1 and 4 for $v = 0$ and 1. These were compared with the theoretical results of Kolos and Wolniewicz (37). Similar comparisons were made as part of a study of HD by Dabrowski and Herzberg (38) using newer calculations by Kolos and Wolniewicz (39). It is interesting to note that the comparison of experiment with theory for D_2 is noticeably improved if the present results (Table 3) are substituted for those of refs. 1 and 4. Our values of B_0 and B_1 are closer to the *ab initio* calculations and are more consistent with the experimental B_v values for higher v (cf. Table 3 and Fig. 10 of ref. 36). Furthermore, our values for D_0 and D_1 lie very close to the smooth curve drawn through the experimental D_v values for higher v in Fig. 4 of ref. 36, and energy levels derived from our constants lie very close to those calculated for D_2 by Bunker *et al.* (40, 41).

In conclusion, the electric quadrupole spectrum of D_2 has been studied using an infrared difference frequency laser system and a long path absorption cell. Eleven transitions of the fundamental band in the 2.8–3.9 μm region were observed, and improved molecular constants for the ground and $v = 1$ vibrational states of D_2 were obtained.

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