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Observation of the $S_0(3)$ pure rotational quadrupole transition of H_2 with a tunable diode laser

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The $S_0(3)$ pure rotational quadrupole transition of H_2 has been observed using a tunable PbSnSe diode laser and a long-path absorption cell containing H_2 at pressures in the range 0.1–0.9 atm. The observed linewidths (80–170 MHz full width at half maximum) were considerably narrower than the Doppler width (268 MHz for 297 K) owing to the effects of collisional (Dicke) narrowing. The line position was measured to be 1034.6702 ± 0.0007 cm^{-1}, and its intensity was found to agree well with that expected from *ab initio* calculations of the quadrupole moment of H_2.

I. INTRODUCTION

We report here the first observation of the quadrupole pure rotational spectrum of the H_2 molecule. The $S_0(3)$ ($v=0$; $J=5\leftarrow 3$) transition at 9.67 μm has been studied in absorption using a tunable diode laser and a long-path cell. A sub-Doppler linewidth due to Dicke[1] narrowing is observed, and the line intensity is found to be in good agreement with theoretical calculations of the H_2 quadrupole moment.

The rotational spectrum of H_2 has previously been studied by Raman spectroscopy,[2] by collision-induced absorption,[3] and by electric-field-induced absorption.[4] The existence of an electric quadrupole vibrational spectrum was first experimentally established in 1949 by Herzberg,[5] who photographed the 2-0 and 3-0 ($v'\leftarrow v''$) bands in absorption. The 1-0, 2-0, and 3-0 quadrupole bands have since been studied in further detail,[6,7] and the 4-0 band has been detected in planetary spectra.[8] The simplicity of the H_2 molecule enabled detailed calculations of its quadrupole moment to be made in 1938 by James and Coolidge.[9] More recently, the *ab initio* calculations of Kolos and Wolniewicz[10] have been used by Karl and Poll,[11] Birnbaum and Poll,[12] and Dalgarno *et al.*[13] to obtain extensive tables of quadrupole transition moments for H_2 and its isotopes. Measured intensities of lines in the 1-0, 2-0, and 3-0 bands have been found to be in good agreement with these calculations. A tabulation of quadrupole emission probabilities has also been made by Turner *et al.*,[14] who discuss the astrophysical importance of quadrupolar radiative relaxation of H_2.

II. EXPERIMENTAL DETAILS

The experimental apparatus[15] is illustrated schematically in Fig. 1. A PbSnSe diode, supplied by Laser Analytics Inc., is mounted on the tip of a cold head which is cooled by a closed-cycle helium refrigerator. The temperature can be set and controlled accurately in the range 10–70 K. The choice of temperature determines the approximate laser emission wavelength, and fine tuning of this wavelength is obtained by varying the diode drive current. A range of 1020–1100 cm^{-1} is covered by the present diode. The laser output is collected by a 5-cm focal-length lens, chopped at 150 Hz, and focused into a grating spectrometer or a 5-m base-path-length multiple-traversal (White) cell. A HgCdTe detector, a phase-sensitive amplifier, and an X-Y recorder are used to record the laser power as a function of diode current. A portion of the initial laser beam can be split off and directed to a second detector in order to provide ratio detection.

Pb-salt diode lasers do not scan uniformly over large wavelength intervals; competition between longitudinal modes results in a short tuning inter-

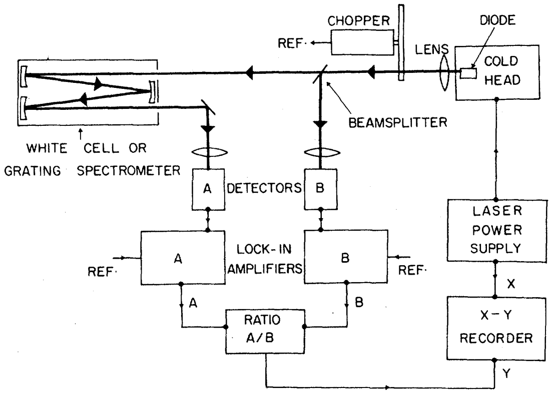

FIG. 1. Schematic diagram of the apparatus. The PbSnSe diode laser was supplied by Laser Analytics Inc., and the base path length of the White cell was 5 m.

val followed by a mode hop. Thus, there is no guarantee that a given diode will tune through a particular wavelength interval. We therefore performed a preliminary experiment to determine if our diode was suitable for detection of the $S_0(3)$ line. The diode beam was passed through the grating spectrometer, and the cold-head temperature and diode current were adjusted to obtain lasing in the 1034.6-cm^{-1} region.[2,4] The diode beam was then switched to pass through the 5-m White cell set for a 300-m path, and a mixture of 10 ppm ozone in air was flowed through the cell at 3 Torr total pressure. By comparing the observed spectrum with the results of Barbe *et al.*,[16] we were able to determine that the exact tuning range of the diode, without mode hopping, was 1034.56–1035.06 cm^{-1}. The laser beam was then passed once more through the spectrometer and it was confirmed that the diode operated in a single mode over this range. Hence, there was no need to use the spectrometer to filter out adjacent modes, and a search was made for the $S_0(3)$ line using only the White cell in the beam path.

A typical result obtained with a pressure of about 500 Torr of H_2 and a path of 300 m is shown in Fig. 2. The lower trace represents a direct scan of laser power versus current employing detector A in Fig. 1. The $S_0(3)$ line of H_2 can clearly be seen, and it gives about 13% peak absorption under these conditions. However, the strongly sloping power output of the diode makes it difficult to obtain accurate intensity and linewidth measurements. The second detector (B in Fig. 1) and a ratio technique were used to eliminate the sloping background. Results are shown in the upper trace in Fig. 2, which was recorded with a 3-s time constant. A slight residual background slope remains due to small imbalances in the ratio system, but the overall signal-to-noise ratio is very good. The noise level is equivalent to about 0.3% in 300 m, or 10^{-5} m^{-1}. We have previously shown that frequency modulation of the laser can increase the sensitivity of the apparatus by a factor of 100,[15] but this technique is not especially well suited to direct measurements of linewidths and intensities.

A problem which arose in the measurement of the width of the $S_0(3)$ line was broadening caused by the finite spectral width of the diode-laser output. Diode lasers can have widths as narrow as 54 kHz when cooled in liquid-He cryostats.[17] However, diodes mounted in closed-cycle refrigerators exhibit wider linewidths owing to the mechanical and thermal shocks they suffer during the refrigeration cycle. Typical linewidths under these conditions are 10–15 MHz for diodes operating at 10 μm. Unfortunately, the diode used here was particularly susceptible to the cycling of the piston in the refrigerator. To obtain an accurate estimate of the effective laser linewidth, several scans of a strong O_3 absorption line[16] at 1034.856 cm^{-1} were made in a low-pressure sample. These, and other linewidth measurements, were calibrated with the aid of a Ge étalon. The measured O_3 linewidth was 80 MHz, whereas the anticipated Doppler width was 55 MHz full width at half maximum (FWHM). Computer fitting of the observed O_3 line shape revealed that the diode-laser output could be well represented by a Lorentzian profile with a width of 43 MHz (FWHM).

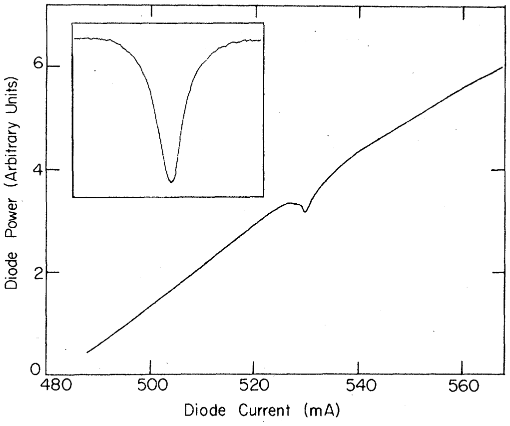

FIG. 2. Direct observation of the $S_0(3)$ quadrupole line of H_2 at 1034.6702 cm^{-1}. The H_2 pressure was 500 Torr, and a path length of 300 m was employed. The lower trace is a direct scan of transmitted laser power as a function of diode laser current. The upper trace (inset) was taken with the two-detector-ratio technique in order to minimize the background slope; the time constant was 3 s.

III. RESULTS

A. Line position

The high resolution of the diode laser enables us to make an accurate measurement of the frequency of the $S_0(3)$ line provided that suitable reference lines can be found. A 7.62-cm-thick solid-Ge étalon was used to determine the displacement of the H_2 line from the chosen reference line. For an initial reference, the $13_{12,1} \leftarrow 13_{12,2}$ line of O_3 at[16] 1034.671 cm^{-1} was chosen and its separation from the H_2 $S_0(3)$ line was measured to be 0.0033 ± 0.0002 cm^{-1}. However, since the O_3 line position was only known[16] to ±0.003 cm^{-1}, we then checked its position against the $R(24)$ laser line of $^{13}C\,^{16}O_2$ at 1034.838 24 cm^{-1}, the position of which is known[18] to within a few MHz. This line was observed in absorption by placing a few Torr of natural CO_2 in the cell. The resulting O_3 line position was

TABLE I. Observed and calculated values for the H_2 $S_0(3)$ transition frequency (in cm^{-1}).

	Observed	Calculated
Present result	1034.6702	···
Buijs and Gush[a]	···	1034.594
Boyd *et al.*[b]	1034.76	1034.739
Foltz *et al.*[c]	···	1034.635
Stoicheff[d]	1034.651	1034.651

[a] Reference 19.
[b] Reference 4.
[c] Reference 20.
[d] Reference 2.

1034.6735 cm^{-1} and the H_2 $S_0(3)$ line position was 1034.6702 ± 0.0007 cm^{-1}. [Most of the error in this measurement arises from an overlap of the $^{13}C\,^{16}O_2$ reference line with the $P(40)$ line of the 9-μm $^{12}C\,^{16}O_2$ hot band. This overlap introduces a slight uncertainty in the exact position of the $^{13}C\,^{16}O_2$ line center.] Any pressure shift of $S_0(3)$ in pure H_2 was found to be less than 10 MHz in the range 100–700 Torr. Our measurement is compared in Table I with previously observed and calculated values; the results of Stoicheff[2] are in closer agreement with the present value than those of more recent workers.[4,19,20] Better measurements of other transitions are clearly required[21] in order to improve upon Stoicheff's ground-state rotational constants for H_2.

B. Line width

Figure 3 shows the measured values of the H_2 $S_0(3)$ linewidth as a function of pressure. The chief sources of error in the widths are slight background slopes and the noise on the traces. The effect of Dicke narrowing[1] on the results is immediately apparent: the measured widths are all considerably narrower than the Doppler width (268 MHz FWHM) even though they include broadening due to the laser linewidth. Similar collisional narrowing effects have previously been noted in the H_2 rotation-vibration bands,[6,7,19] and recently in tunable-diode-laser studies of high-J infrared transitions of H_2O.[23] Detailed studies of Dicke narrowing in H_2 have been made using the Raman effect,[22,24,25] and the variation of linewidth with pressure has been found to fall between limits set by hard- and soft-collision theories. We compare our data in Fig. 3 with the results of a soft-collision model, due to Galatry,[26] which has been most widely used in astrophysical studies[27,28] of H_2 absorption. The solid curve in Fig. 3 is the FWHM predicted by the Galatry theory, and the dashed curve is a convolution of this with the 43-MHz Lorentzian laser-output function determined earlier. There are two adjustable parameters in the theory: for these we used the pressure broadening coefficient measured for $S_0(3)$ in the Raman spectrum by Keijser *et al.*[29] (70 MHz/atm) and the generally accepted value[28,30] ($D \approx 1.30/\rho$ cm^2 amagat/s) for the self-diffusion coefficient of H_2 at 297 K. The agreement between the dashed curve and the experimental points is quite satisfactory and can be improved somewhat by a slight lowering of the assumed value of D. The prediction of too large a width in the low-pressure region (< 0.25 atm) by the soft-collision model is similar to that found in studies[22,24,25] of Raman linewidths. We have not pursued a more detailed comparison of theoretical and experimental linewidths because of uncertainties in the exact form of our diode-laser output line shape.

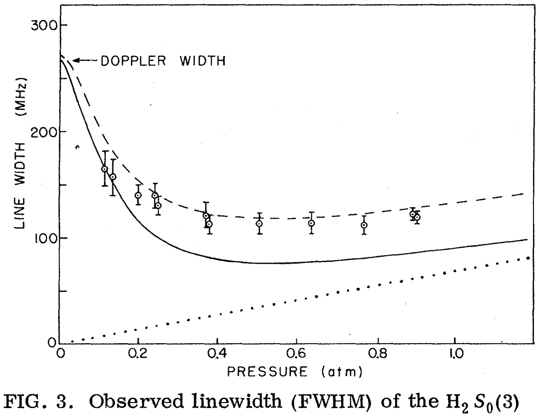

FIG. 3. Observed linewidth (FWHM) of the H_2 $S_0(3)$ transition. The circles represent the experimental data, which includes broadening due to the laser linewidth. The solid curve is a theoretical calculation using the Galatry line shape (see text), and the dashed curve is this calculation broadened by the observed diode-laser line-shape function. The dotted line indicates the contribution due to pressure broadening.

C. Foreign-gas effects

Limited measurements of the effects of foreign gases on the H_2 $S_0(3)$ linewidth and position were made in mixtures of 100 Torr H_2 and 600 Torr of either He, Ar, or N_2. Distinct pressure shifts of +45 MHz in helium, −55 MHz in argon, and −60 MHz in nitrogen were observed. As mentioned above, the shift in pure H_2 at the same pressure was < 10 MHz. The magnitude and direction of the shifts for pure H_2, He-H_2, and Ar-H_2 are similar to those measured for the $S_0(1)$ Raman line by Cooper, May, and Gupta.[22] The experimental linewidths in the mixtures at a total pressure of 700 Torr were about 80, 90, and 120 MHz for He, Ar, and N_2, respectively, which may be compared with the value of about 120 MHz in pure H_2 at the same pressure.

D. Line intensity

Careful intensity measurements were made on traces obtained with 686 Torr of pure H_2 at 24°C and a path length of 260 m. These were computer fitted with the Galatry line shape broadened by the Lorentzian diode-laser line shape. Fortunately, the H_2 transition is well resolved and in a region of reasonably linear absorption (< 20% peak absorption) so that the measured area of the line depends very little on the details of the assumed line-shape functions. The integrated intensity of the $S_0(3)$ transition under these conditions was measured to be $(9.7 \pm 0.4) \times 10^{-4}$ cm^{-1}. The estimated uncertainty includes contributions from fitting the line profile, from the diode-laser tuning rate, and from the determination of the 0 and 100% transmission levels. The integrated intensity calculated for these conditions from the theoretical[8,9] quadrupole matrix element is 9.88×10^{-4} cm^{-1}, in excellent agreement with the measured value. Converting our measured value to an integrated absorption coefficient for $S_0(3)$ at 297 K yields $(4.49 \pm 0.19) \times 10^{-3}$ cm^{-1}/km amagat. In terms of the quadrupole transition matrix element Q, the experimental value is $(0.491 \pm 0.010)ea_0^2$ (where e is the electron charge and a_0 the Bohr radius), that is, 0.660 ± 0.014 D Å or $(2.20 \pm 0.05) \times 10^{-40}$ C m^2 (mks). Since the transition moment is proportional to the square root of the intensity, its fractional uncertainty is reduced by a factor of 2. Theoretical values for Q are $0.4953ea_0^2$ from Birnbaum and Poll[12] and $0.4951ea_0^2$ from Dalgarno *et al.*[13] Karl and Poll[11] have shown that nonadiabatic effects not included in the theory might alter these values by as much as $0.003ea_0^2$.

IV. DISCUSSION AND CONCLUSIONS

The astrophysical significance of the H_2 quadrupole spectrum is well known,[8,14,28] and quadrupole rotation-vibration transitions have been detected in stellar, interstellar, and planetary spectra. Although the pure rotational transitions occur in spectral regions which are less easily accessible, the rapid progress of infrared astronomy should enable them to be studied in the near future. Since $S_0(3)$ lies 0.168 cm^{-1} (5 GHz) below a $^{13}C^{16}O_2$ laser line [$R(24)$ of the 9.8-μm band], the technique of heterodyne astronomical spectroscopy[31] with a CO_2-laser local oscillator may be suitable for its detection, particularly in the spectra of the major planets. Indeed, Goorvitch and Chackerian[28] have recently calculated brightness temperature profiles for the H_2 rotational transitions in Jupiter and Uranus and concluded that they should easily be observable with sensitive instrumentation. These authors did not consider the $S_0(3)$ transition because of the relatively low temperatures of the planetary atmospheres, but we estimate that its strength should in fact be appreciable compared with that of $S_0(2)$ because of the higher nuclear-spin statistical weight of odd-J levels and the ν^3 (ν^5) dependence of the quadrupole absorption (emission) strength.

In conclusion, the frequency, linewidth, and intensity of the $S_0(3)$ quadrupole transition of H_2 have been measured at 297 K in the pressure range 0.1–0.9 atm using a tunable diode laser and a long-path absorption cell. The intensity is found to agree with that derived from *ab initio* calculations of the H_2 quadrupole moment to within the experimental uncertainty (~ 4%).

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