

PURE ROTATIONAL SPECTRUM OF HYDROGEN DEUTERIDE BY FAR-INFRARED FOURIER TRANSFORM SPECTROSCOPY

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ABSTRACT

The far-infrared spectrum of HD from 170 to 350 cm^{-1} is measured with a frequency accuracy of few parts in 10^7 by means of Fourier transform spectroscopy. A general fit including other existing data provides values for B_0 , D_0 , and H_0 ground-state rotational constants with almost two orders of magnitude improved accuracy.

Subject headings: deuterium — infrared: spectra — laboratory spectra

1. INTRODUCTION

Hydrogen deuteride is of special astrophysical interest. In fact, determination of deuterium abundance in the solar system can provide important cosmological information. Moreover, the comparison between deuterium-hydrogen ratios in the four giant planets provides clues to the formation of Uranus and Neptune.

The possibility of detecting the presence of HD and measuring its abundance directly from rotational transitions generating spectra in the far-infrared, either in the atmosphere of the outer planets (Bézard, Gautier, & Marten 1986) or in dense interstellar objects (Bussoletti & Staniska 1974) has been pointed out.

However, the dipole moment of the hydrogen isotope HD is very small, since it is entirely due to nonadiabatic effects, coupling the electronic and nuclear motion. Wick (1935) predicted its existence, and more recently many *ab initio* computations (Wolniewicz 1976; Ford & Browne 1977; Thorson, Choi, & Knudson 1985) have agreed to give a value of the permanent dipole of about 8.4×10^{-4} D. Still some controversy, however, exists about the dependence of the dipole on the rotational state.

The smallness of the permanent dipole moment is the indirect cause of unique and interesting effects in the spectrum of HD gas. The most striking among these is the anomalous behavior of the intensity of the lines, as a function of density, observed first in the vibration rotation spectrum by McKellar (1973) and studied recently as a function of temperature, in the pure rotational spectrum (Drakopoulos & Tabisz 1987; Ulivi, Lu, & Tabisz 1989). This effect has been interpreted in terms of the interference between the permanent dipole and the dipole moment induced during collisions between molecules. This interference is present in the allowed spectrum of any molecular gas, but it is important only when the permanent dipole is small.

A thorough understanding of the HD dipole spectrum and of all mechanisms responsible for it is needed in order to synthesize spectra at pressures and temperatures not attainable in the laboratory, but certainly present in the solar system.

Recently, a Fourier transform investigation of the funda-

mental vibrational 0–1 band (Rich, Johns, & McKellar 1982) led to the determination of the rotational constants B_0 , D_0 , and H_0 which are reported in Table 1. As for the pure rotational spectrum, measurements of the $R(3)$, $R(5)$, and $R(6)$ lines of the pure rotational spectrum were performed by Essenwanger & Gush (1984), but the improved D_0 and H_0 constants that they derive hardly agree with previous ones (McKellar, Goetz, & Ramsay 1976).

More recently (Evenson et al. 1988) measured with high accuracy the frequency of the lowest rotational transition of HD. They used a tunable spectrometer where coherent FIR radiation is generated by difference frequency of CO_2 lasers in a metal-insulator-metal diode (Evenson, Jennings, & Petersen 1984). It would be desirable, then, to perform measurements of other transitions of the pure rotational spectrum with similar high precision. Unfortunately, only one more HD rotational transition could be accessible, namely the $R(1)$ line, which, however, lies on the boundary of applicability of this technique.

Recently (De Natale et al. 1991; Zink et al. 1990) it has been shown that, using a high-resolution far-infrared Fourier transform spectrometer, the frequencies of transition lines can be measured with an accuracy of the order of 1 MHz, once accurate frequency calibration is assured by means of reference molecular transitions.

In the present work we apply this method to the precise investigation of the HD molecule in the spectral range 70–400 cm^{-1} , directly measuring $R(1)$ to $R(3)$ pure rotational transitions. The analysis of this spectrum, together with the results of Essenwanger & Gush (1984) at higher J -values and with the very precise measurement of the lowest $R(0)$ transition due to Evenson et al. (1988), has permitted us to obtain new values of the HD rotational constants, with almost two orders of magnitude improved accuracy. Accurate frequency determination of unobserved HD lines can speed the search for this species in astrophysical spectra.

2. EXPERIMENTAL APPARATUS AND RESULTS

The FT spectrometer was operated with an optical path difference of 180 cm, and a corresponding unapodized

TABLE 1
ROTATIONAL CONSTANTS OF HD AND THE CORRELATION MATRIX

A. ROTATIONAL CONSTANTS OF HD			
Sources	B_0 (cm^{-1})	D_0 (cm^{-1})	H_0 (10^{-4} cm^{-1})
1.....	44.665379 (31)	0.0257402 (73)	0.19039 (10)
2.....	44.6656 (17)	0.02583 (29)	0.30 (19)
3.....	44.6614 (21)	0.02558 (6)	0.174 (5)
4.....	44.6665 (15)	0.02586 (12)	0.217 (25)
B. CORRELATION MATRIX			
B_0	1	...	...
D_0	0.60	1	...
H_0	0.54	0.96	1

SOURCES.—(1) This work; (2) Rich et al. 1982; (3) Essenwanger & Gush 1984; (4) McKellar et al. 1976.

resolution (full width at half-maximum) of 0.005 cm^{-1} . A silicon bolometer, operated at a temperature of 1.6 K, was used as a detector.

The sample cell was a 20 cm long Pyrex tube, fitted with wedged high-density polyethylene windows. It was filled with $232 (\pm 5)$ mbar of 97% pure HD, purchased from Cambridge Isotope Laboratories. Data were collected in two runs, obtaining identical spectra, for a total measurement time of about 6 hr.

The three $R(1)$, $R(2)$, and $R(3)$ rotational lines have been observed, with a signal-to-noise ratio of the order of 10. In Figure 1 the $R(2)$ rotational line is shown, together with a more intense water line. The integrated intensity of each transition has been derived, calculating the area under a fitted line shape which takes into account the instrumental resolution. The dipole moment thus derived [8.0 ± 0.7 , 8.5 ± 0.3 , $8.8 \pm 0.5 \times 10^{-4} \text{ D}$, respectively, for $R(1)$, $R(2)$, and $R(3)$] is in agreement with theoretical values and with more accurate room temperature measurements (Drakopoulos & Tabisz 1987).

Frequency calibration was obtained comparing observed frequencies of water vapor lines, present in the spectrum, with precisely known values (Johns 1985). For any of the three spectral ranges of interest, an independent linear fit of the frequencies of about 10 water lines has been performed as a function of the measured values. The rms deviation of the measured frequencies from the straight line amounts to 2.7, 4.5, and

2.1 MHz, respectively, for $R(1)$, $R(2)$, and $R(3)$. Since the lines used for calibration are known with a higher precision, these values are assumed to be the uncertainties on the wavenumber scale, after calibration, and have been quadratically added to the uncertainty in the position of each line resulting from the fit.

The resulting line positions were $177.84172(16)$, $265.24116(17)$, and $350.85295(12) \text{ cm}^{-1}$, respectively, for $R(1)$, $R(2)$, and $R(3)$, where the number in parentheses represents the error on the last digits. This does not include potential systematic error on the water-line frequencies used as standard, possibly arising from the linear extrapolation, performed by Johns (1985), to calibrate the frequency scale above 200 cm^{-1} .

3. DATA ANALYSIS

If we fit the rotational constants B_0 , D_0 , and H_0 for the fundamental state of the HD molecule, only to these three transition frequencies, the calculated value of the $R(0)$ frequency is $2674984 (4) \text{ MHz}$, in agreement with the 30 times more accurate value ($2674986.66 \pm 0.15 \text{ MHz}$) measured by Evenson et al. (1988). A good agreement, well inside the combined experimental error, is obtained also with respect to the frequencies measured by Essenwanger & Gush (1984), with the exception of the $R(5)$ transition, which, even considering the quoted uncertainty, falls quite far from the value extrapolated from our measurement.

With the aim of determining new values for the rotational constants, we have chosen to perform a best fit based on our measurement, on the $R(0)$ transition measured by Evenson et al. (1988) and on the $R(3)$ and $R(6)$ measured by Essenwanger & Gush (1984), excluding therefore their determination of the $R(5)$ transition frequency. The line shape of this latter is defective according to the authors themselves (it appears abnormally wide), and we imagine that some difficulty may have arisen also in the measurement of the frequency of this line. The inclusion in the fit of the frequency of the $R(6)$ transition, however, highly increases the accuracy of the H_0 determination.

The rotational constants B_0 , D_0 , and H_0 obtained from this fit are listed in Table 1 and compared with other values in the literature. The accuracy is increased by almost two orders of magnitude, and the agreement with previous results is very good, with the exclusion of the values obtained by Essenwanger & Gush (1984), for the reason already discussed. Table

TABLE 2
EXPERIMENTAL AND CALCULATED VALUES OF PURE ROTATIONAL
TRANSITION FREQUENCIES OF HD MOLECULE

J	Experimental Value (cm^{-1})	Calculated Value (cm^{-1})
0.....	89.227950 (5) ^a	89.227950 (5)
1.....	177.84172 (16)	177.841790 (17)
2.....	265.24116 (17)	265.241119 (55)
3.....	350.85295 (12)	350.85295 (11)
3.....	350.852 (2) ^b	350.85295 (11)
4.....	...	434.14542 (17)
5.....	514.656 (1) ^{b,c}	514.64150 (19)
6.....	591.9327 (3) ^b	591.93270 (30)
7.....	...	655.69279 (78)
8.....	...	735.6915 (18)
9.....	...	801.8081 (36)
10.....	...	864.0455 (65)

^a Evenson et al. 1988.

^b Essenwanger & Gush 1984.

^c This value has not been considered for the fit (see text).

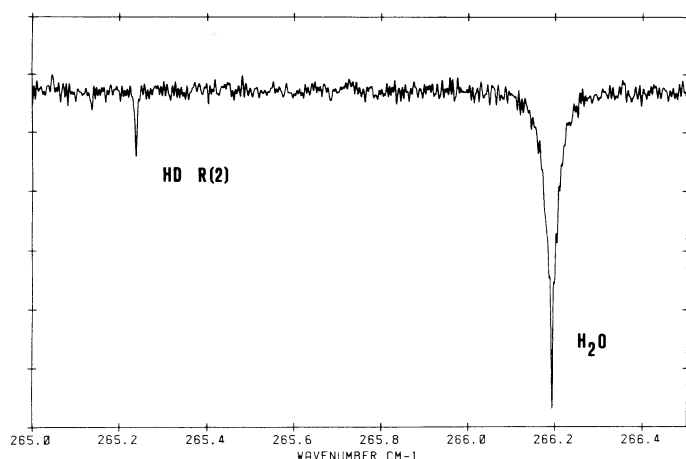


FIG. 1.—Absorption spectrum in the region of the $R(2)$ rotational line. The more intense feature is a water vapor absorption line.

1 also contains the values of the correlation matrix of this newly determined constants.

In Table 2 we report the experimental frequencies used in the fit and those calculated using these new values of the molecular constants. The error given (in parentheses) is one standard deviation and takes into account the correlation between the parameters.

4. CONCLUSIONS

We have measured the pure rotational spectrum of HD in the range $70\text{--}400\text{ cm}^{-1}$, detecting the transitions $R(1)$ to $R(3)$.

The frequency scale was calibrated with reference to water vapor transition lines, allowing an overall precision of frequency determination of about 3 MHz (10^{-4} cm^{-1}). A best-fit procedure of the measured frequencies, including previous experimental values, has permitted us to obtain new values for the HD rotational constants, with an improved accuracy of almost two orders of magnitude.

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