Stark spectroscopy with the CO laser: Lamb dip spectra of $H_2{}^{17}O$ and $H_2{}^{18}O$ in the ν_2 fundamental band[1]

J. W. C. JOHNS AND A. R. W. MCKELLAR

Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ont., Canada K1A 0R6

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Saturated absorption spectra of four different transitions in the ν_2 fundamental bands of $H_2{}^{17}O$ and $H_2{}^{18}O$ have been observed using the technique of intracavity CO laser Stark spectroscopy. The analysis of these spectra yields a direct measurement of the dipole moment change between the ground vibrational state and the $\nu_2 = 1$ state of $H_2{}^{17}O$, as well as the zero-field frequencies for the observed transitions. A collision-induced centre dip ('crossover resonance') which occurs in one spectrum is formed in a four-level system that is probably the most nearly isolated of any yet observed.

Les spectres de quatre transitions de la bande fondamentale ν_2 des molecules $H_2{}^{17}O$ et $H_2{}^{18}O$ ont été observés en absorption saturée à l'aide de la technique laser Stark appliquée dans la cavité d'un laser à CO. L'analyse de ces spectres procure une mesure directe de la différence entre les moments dipolaire des niveaux vibrationnels 000 et 010 de l'état fondamental de la molécule $H_2{}^{17}O$. L'analyse conduit également à la fréquence, en l'absence de champ, des transitions observées.

Un Lamb dip induit par collision, présent dans un des spectres, provient d'un systeme formé de quatre niveaux, qui est probablement le plus isolé des systèmes semblables déjà observés.

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1. Introduction

Laser Stark spectroscopy, in which molecular transitions are tuned into resonance with fixed laser frequencies by means of the Stark effect, has been used to study vibration–rotation bands of a large number of linear (for example, ref. 1), symmetric rotor (for example, ref. 2), and asymmetric rotor (for example, ref. 3) molecules. The molecules in the last category have generally been prolate near symmetric rotors with dipole moments directed along the *a*-axis (μ_a). Molecules with only μ_b do not in general possess large Stark effects because μ_b does not induce a Stark effect between the *K*-type doubling energy levels. Furthermore, in very asymmetric rotors the *K*-doublets tend not to be closely spaced and first-order Stark effects are unlikely. The water molecule falls into these categories, and exhibits only a small Stark effect in spite of its large dipole moment. Only one transition has previously been detected for water by laser Stark spectroscopy: the $6_{24} \leftarrow 6_{15}$ pure rotation transition of D_2O which Duxbury and Jones (4) were able to study thanks to a fortunate coincidence with an HCN laser line at 337 μm.

In this paper, we report the observation of four transitions in the ν_2 (bending) fundamental band of H_2O near 6 μm by means of laser Stark spectroscopy. The spectra, which involve $H_2{}^{17}O$ and $H_2{}^{18}O$, were obtained using the inverse Lamb dip technique with a Stark cell located inside the optical cavity of a CO laser. These isotopically substituted species were utilized partly in order to increase the number of possible close coincidences between H_2O transitions and CO laser lines, but also because absorption by atmospheric water vapour tends to inhibit laser action on lines close to strong $H_2{}^{16}O$ transitions. Although the observations are not extensive enough to allow an analysis of the ν_2 band to be made on their basis alone, they do yield a precise measurement of the ν_2 vibrational dependence of the dipole moment of H_2O. Furthermore, our analysis provides accurate determinations of the zero-field frequencies of the observed transitions.

A number of three- and four-level centre dips (5) ('crossover resonances') were observed in the spectra. The four-level dips, which are due to collisional reorientation transitions with little velocity change, are of special interest because they have previously been observed only in symmetric and near-symmetric rotor molecules.

2. Experimental Details

Our laser Stark apparatus consists of a Stark cell with 20 cm long electrodes mounted inside the 290 cm long optical cavity of a grating-tuned CO laser. The sealed-off CO gain cell has a 190 cm discharge length and may be filled with isotopically substituted $^{13}C^{16}O$ or $^{12}C^{18}O$ as well as normal $^{12}C^{16}O$. More detailed descriptions of the experimental arrangement have been given previously (*1a*, 6).

Electric field measurements made with the Stark cell were calibrated by means of the very accurately

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[1] NRCC No. 16433.

measured (7) ground state dipole moment of H_2CO in combination with our observed laser Stark spectra (3*b*, 8) of H_2CO. Isotopically enriched water (54% $H_2{}^{18}O$, 11%, $H_2{}^{17}O$, 35% $H_2{}^{16}O$) was obtained from Miles Laboratories Inc., and the pressure of the water vapour sample in the Stark cell was about 5 mTorr.

A conventional absorption spectrum of the enriched water sample in the region of the ν_2 fundamental band was also recorded, using the 2 m vacuum infrared grating spectrometer and data reduction techniques described by Johns *et al.* (9). These results, which are not presented in detail here, were used to determine the ground and $(v_1v_2v_3) = (010)$ state rotational constants for $H_2{}^{17}O$ and $H_2{}^{18}O$ which were required for the Stark effect calculations described below.

3. Results

The laser Stark spectrum due to the ν_2 $1_{10} \leftarrow 1_{01}$ transition of $H_2{}^{17}O$ obtained with the 19–18 $(v' \rightarrow v'')$ $P(11)$ line of the $^{12}C^{18}O$ laser at 1613.110 cm^{-1} (10) is shown in Fig. 1. One line was observed with the electric field of the laser radiation parallel to the Stark electric field, and two lines were observed with perpendicular polarization. In addition, there is a weaker centre dip located midway between the two perpendicular lines. The observed lines are saturation resonances (inverse Lamb dips) with total widths of about 1 MHz, and the additional partly resolved structure on each line is hyperfine structure due to the ^{17}O nucleus.

The measured resonant electric fields of the lines are listed in Table 1, along with their assignments. Also given in Table 1 are experimental tuning rates for the transitions. These rates were measured in the following fashion: the laser was locked to a point of minimum output power using a Lansing 80-214 stabilizer unit and the piezoelectric translator on the laser output mirror (the stabilizer is normally used to lock to a power maximum). The laser output spectrum then consisted of two frequencies separated by the axial mode spacing, $c/2l$, where c is the speed of light and l the cavity length. This separation was accurately determined by measuring the radiofrequency beat from an infrared detector with the laser incident upon it. The laser Stark spectrum, consisting of twice the usual number of lines, was recorded at the same time. The known separation of the two axial laser modes, 52 MHz in this case, divided by the separation in electric field of the two lines corresponding to a given transition, then gave the tuning rate of the transition. This rate is, of course, an average over the 52 MHz interval centred on the nominal laser frequency.

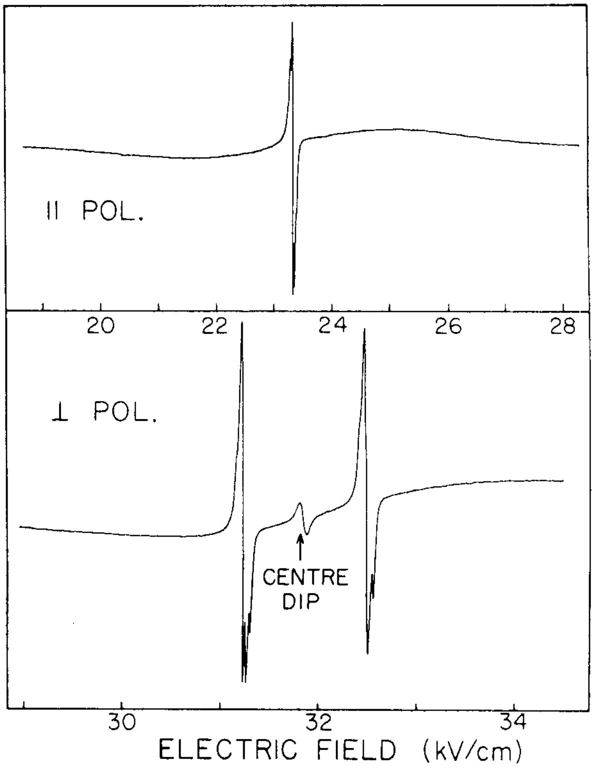

FIG. 1. Laser Stark spectrum of the ν_2 band $1_{10} \leftarrow 1_{01}$ transition of $H_2{}^{17}O$, obtained with the 19–18 $P(11)$ laser line of $^{12}C^{18}O$ at 1616.11 cm^{-1}. The partially resolved structure on each of the three strong lines is ^{17}O hyperfine structure.

The other spectrum observed in $H_2{}^{17}O$ was due to the $4_{22} \leftarrow 4_{13}$ transition and is shown in Fig. 2. It was observed using the 18–17 $P(9)$ laser line of $^{12}C^{18}O$ at 1643.5715 cm^{-1}; measured electric fields and assignments are given in Table 1. Only the perpendicular $(\Delta M = \pm 1)$ spectrum was recorded. The relatively large Stark effect of this transition, and thus its detection by laser Stark spectroscopy, is due to the 'accidental' near coincidence of the 4_{22} and 5_{15} levels in the excited (010) vibrational state. The Stark matrix element connecting these levels is proportional to $(J^2 - M^2)^{1/2}$ with $J = 5$, and thus the fastest moving Stark components are those with low values of M. In this respect, the spectra are very similar to those recorded in CH_2F_2 by Kawaguchi and Tanaka (3*c*) and to some of those recorded in HNO by Johns and McKellar (6). In addition to the eight components of the $4_{22} \leftarrow 4_{13}$ transition listed in Table 1, of which seven are included in the range of Fig. 2, there are a number of centre dips evident in the spectrum. These may be assigned as three-level crossover resonances as indicated in Fig. 2.

Two laser Stark spectra attributable to $H_2{}^{18}O$ were observed, and the results are summarized in

TABLE 1. Observed Stark resonances in the ν_2 fundamental band of $H_2{}^{17}O$

Laser line		Assignment			
Transition	Frequency (cm^{-1})	$J_{K_aK_c}$	M	Resonant field (kV/cm)	Tuning rate[a] (MHz per kV/cm)
$^{12}C^{18}O$ 19–18 $P(11)$	1613.1105	$1_{10} \leftarrow 1_{01}$	$1 \leftarrow 1$	23.345	36.0
			$1 \leftarrow 0$	31.236	27.5
			$0 \leftarrow 1$	32.494	26.4
$^{12}C^{18}O$ 18–17 $P(9)$	1643.5715	$4_{22} \leftarrow 4_{13}$	$0 \leftarrow 1$	20.307	
			$1 \leftarrow 2$	20.546	
			$1 \leftarrow 0$	20.779	
			$2 \leftarrow 3$	21.579	
			$2 \leftarrow 1$	22.111	
			$3 \leftarrow 4$	23.809	
			$3 \leftarrow 2$	24.842	
			$4 \leftarrow 3$	31.069	

[a] The quoted tuning rate applies to the indicated resonant field, and was measured as explained in the text.

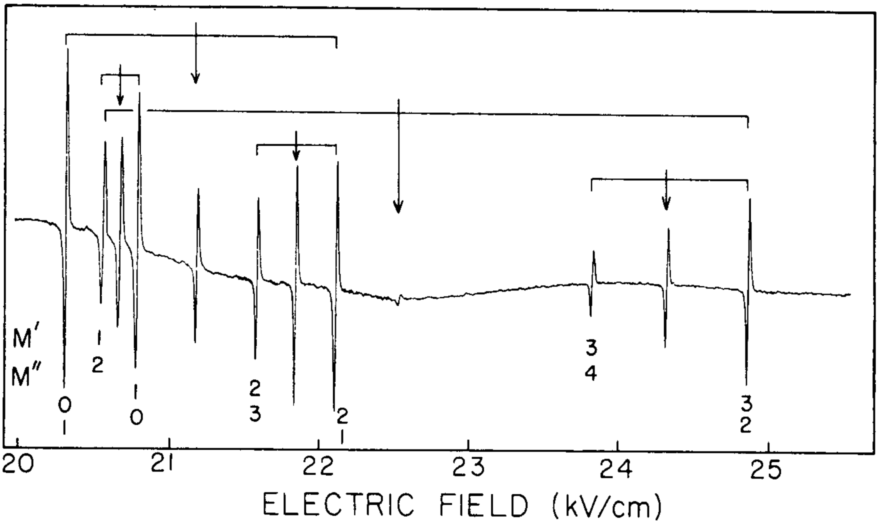

FIG. 2. Laser Stark spectrum of the $4_{22} \leftarrow 4_{13}$ transition of the ν_2 band of $H_2{}^{17}O$, obtained with the 18–17 $P(9)$ line of the $^{12}C^{18}O$ laser at 1643.57 cm^{-1}. The laser radiation was polarized perpendicular to the Stark field, giving rise to $\Delta M = \pm 1$ selection rules. The assignments of the 'real' inverse Lamb dips are indicated (M', M'') below the spectrum, and the centre dips ('crossover resonances') are indicated by the arrows above the spectrum. These are all three-level centre dips.

Table 2. Both spectra occur because of the 4_{22}–5_{15} near resonance in the (010) state, and therefore they closely resemble the $H_2{}^{17}O$ $4_{22} \leftarrow 4_{13}$ transition in Fig. 2. The first spectrum in Table 2, observed with a $^{12}C^{18}O$ laser line at 1640.176 cm^{-1}, is assigned to the transition $5_{15} \leftarrow 4_{13}$. Note that this transition, with $\Delta K_a = 0$, is forbidden at zero field for the *b*-type ν_2 band. However, it becomes allowed when an electric field is applied because of the Stark mixing of the 4_{22} and 5_{15} levels in the upper state. The second spectrum, assigned to the $5_{15} \leftarrow 4_{04}$ transition of $H_2{}^{18}O$ and observed with a $^{12}C^{18}O$ laser line at 1693.733 cm^{-1}, is illustrated in Fig. 3. In addition to the 'real' Lamb dips and the three-level centre dips in Fig. 3, which follow the same patterns as those in Fig. 2, there are additional weak lines in Fig. 3 which can be assigned as four-level collisionally transferred centre dips (5).

All of the observed H_2O laser Stark Lamb dip spectra were considerably more sensitive to power broadening than those of the other molecules we have studied with the CO laser, namely H_2CO (8), NH_3 (2*c*), NO (1*a*), and HNO (6). This is presumably because of a larger vibrational transition moment in H_2O. In order to record spectra with linewidths limited by pressure and transit time

TABLE 2. Observed Stark resonances in the ν_2 fundamental band of $H_2{}^{18}O$

Laser line		Assignment		Resonant field	Tuning rate
Transition	Frequency (cm^{-1})	$J_{K_aK_c}$	M	(kV/cm)	(MHz per kV/cm)
$^{12}C^{18}O$ 18–17 $P(10)$	1640.1760	$5_{15} \leftarrow 4_{13}$	$0 \leftarrow 1$	29.639	
			$1 \leftarrow 2$	29.860	
			$1 \leftarrow 0$	30.371	
			$2 \leftarrow 3$	31.092	
			$2 \leftarrow 1$	31.245	
			$3 \leftarrow 4$	33.819	
			$3 \leftarrow 2$	36.095	
$^{12}C^{18}O$ 15–14 $P(15)$	1693.7326	$5_{15} \leftarrow 4_{04}$	$0 \leftarrow 1$	23.595	
			$0 \leftarrow 0$	23.66	62.7
			$1 \leftarrow 2$	23.849	
			$1 \leftarrow 1$	24.06	61.6
			$1 \leftarrow 0$	24.143	
			$2 \leftarrow 3$	25.041	
			$2 \leftarrow 2$	25.44	59.0
			$2 \leftarrow 1$	25.743	
			$3 \leftarrow 4$	27.631	
			$3 \leftarrow 3$	28.39	54.9
			$3 \leftarrow 2$	29.046	
			$4 \leftarrow 4$	35.14	46.8
			$4 \leftarrow 3$	36.744	

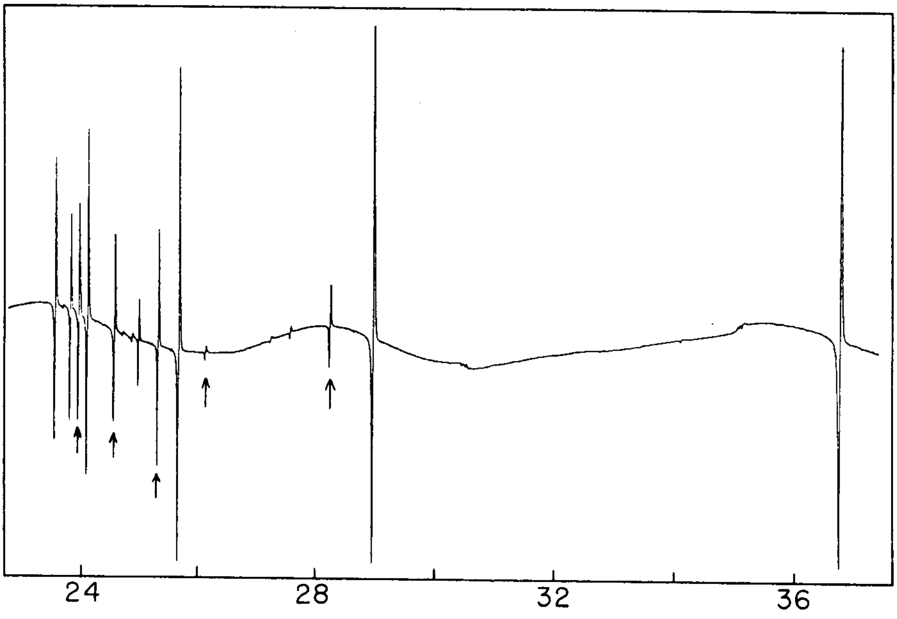

FIG. 3. Laser Stark spectrum of the $5_{15} \leftarrow 4_{04}$ transition of the ν_2 band of $H_2{}^{18}O$, obtained with the 15–14 $P(15)$ line of the $^{12}C^{18}O$ laser at 1693.73 cm^{-1}. The arrows below the spectrum indicate five centre dips which are analogous to the five indicated in Fig. 2. Additional weaker centre dips are also evident here.

broadening (i.e., <1 MHz) it was necessary to operate the laser close to threshold with very low power levels.

4. Analysis

The spectra were analyzed by means of a computer program (3*b*, 6) which incorporates an asymmetric rotor Stark effect subroutine and carries out a nonlinear least-squares fit of the observed transitions. The subroutine sets up and diagonalizes the Hamiltonian matrix for an asymmetric rotor in an electric field as written in a prolate symmetric rotor basis.

TABLE 3. Molecular parameters (in MHz) for the (000) and (010) states of $H_2{}^{17}O$ and $H_2{}^{18}O$ used in the Stark effect calculations

	$H_2{}^{17}O$		$H_2{}^{18}O$	
	(000)	(010)	(000)	(010)
A	830 278	926 698	825 379	921 309
B	435 274	440 193	435 397	440 195
C	277 557	273 055	276 942	272 564
Δ_K	958	1 693	943	1 702
Δ_{JK}	−168	−235	−164	−232
Δ_J	34.8	38.1	37.9	41.6
δ_K	10.1	121	92	198
δ_J	14.2	15.5	15.2	17.3
Φ_K	2.1	12	2.5	10.1
Φ_{KJ}	1.1	−5.6	0.15	−1.4
Φ_{JK}	−0.40	1.02	−0.017	−0.0021
Φ_J	−0.043	(−0.043)	0.018	(0.018)
ϕ_K	−1.04	6.76	1.38	1.81
ϕ_{JK}	−0.46	−0.51	−0.030	−0.029
ϕ_J	−0.0079	(−0.0079)	0.0080	0.0096

NOTE: The parameters in parentheses were fixed at the ground state values indicated. The Hamiltonian used is the "A-reduced" form as defined by Watson (27).

The calculation is thus similar to that used by Brittain *et al.* (11) for D_2O. Rotational constants are, of course, required in this calculation and since these have not been reported previously for the (010) vibrational states of $H_2{}^{17}O$ and $H_2{}^{18}O$, they were obtained from an analysis of the conventional spectrum mentioned in Sect. 2 above. The resulting constants are listed in Table 3, and the analysis was aided by the previous study of the ν_2 band of $H_2{}^{18}O$ by Williamson *et al.* (12). The parameters in Table 3 extend only to sextic centrifugal distortion terms, which would not suffice for a complete study of the ν_2 band. However, these results should be perfectly adequate for the Stark effect calculations involved here. The rotational constants for the ground state in Table 3 agree fairly well with those determined previously from millimetre wave spectra (13), and although some of the distortion constants are rather different, this is no doubt due to our truncation at the sextic level. Ground state energy levels calculated from our constants are in good agreement with those determined elsewhere (12–14). The effects of polarizability on our Stark effect calculations (see Dyke and Muenter (15)) were estimated to be negligible.

There have been numerous investigations of the dipole moment of the water molecule, and the most complete and accurate results are those of Clough *et al.* (16) and Dyke and Muenter (15). From their work, the dipole moment in the ground vibrational state and its rotational dependence are known with an accuracy approaching 0.02%, and the isotopic variation between H_2O and D_2O is known to be remarkably small. We had originally hoped to determine the dipole moment for $H_2{}^{17}O$ and $H_2{}^{18}O$ in the (000) and (010) states from our data. Unfortunately, the observed spectra were rather insensitive to the assumed absolute value of the dipole moment, even when the tuning rate measurements were included in the fit. Any value of the dipole moment in the expected region of 1.85 D (1 D = 3.33564×10^{-30} C m) provided a very good fit to the spectra. However, the $H_2{}^{17}O$ $1_{10} \leftarrow 1_{01}$ spectrum was sensitive to the *difference* in dipole moment between the (000) ground and (010) excited states. The value for this difference, which was obtained from a fit to the data in Table 1, was

$$|\mu(010)| - |\mu(000)| = -0.0310 \pm 0.0042 \text{ D}$$

The recent series of precise intensity measurements in the infrared spectrum of H_2O by Camy-Peyret and Flaud (17–19) make it possible to compare this value with one determined indirectly from dipole moment derivatives. Using the general formula for the vibrational dependence of a molecular quantity (i.e., eq. 20 of Toyama *et al.* (20)) one may obtain the expression

$$\mu(010) - \mu(000) = {}^{22}\mu_x - 3(k_{222}/\omega_2)^2\mu_x - (k_{122}/\omega_1)^1\mu_x + \ldots$$

where k is an anharmonic force constant, ω a harmonic vibrational frequency, and ${}^n\mu_x$ a coefficient of the expansion of the dipole moment in terms of normal coordinates, $\mu_x = {}^0\mu_x + {}^1\mu_x q_1 + {}^2\mu_x q_2 + {}^{22}\mu_x q_2{}^2 + \ldots$ (x denotes the C_2 symmetry axis along which the equilibrium dipole moment lies). Values for k may be obtained from the force constant calculations of Hoy *et al.* (21) (see Table 2 and Appendix 1 of ref. 21), and values for the ${}^n\mu_x$ from the work of

Camy-Peyret and Flaud (17, 18). These lead to the result $\mu(010) - \mu(000) = +0.0347$ D, which, since $\mu(000)$ is known (22) to be negative, yields $|\mu(010)| - |\mu(000)| = -0.0347$ D, in rather good agreement with our directly measured value of -0.0310 D. The calculated value is for $H_2{}^{16}O$, whereas our measured value is for $H_2{}^{17}O$, and furthermore our measurement may be somewhat affected by the purely rotational variation of μ between the 1_{10} and 1_{01} states. However, these effects are probably negligible at the present level of accuracy.

Although the observed spectra are not very sensitive to the absolute value of the dipole moment, they can be used to derive H_2O transition frequencies by assuming a value for $\mu(000)$ and obtaining $\mu(010)$ from the measured dipole moment difference. From the previously observed values of μ for $H_2{}^{16}O$, $HD^{16}O$, and $D_2{}^{16}O$ (11, 16, 17), and allowing for rotational variation, an assumed value of $|\mu(000)| = 1.855 \pm 0.020$ D should be reasonable for $H_2{}^{17}O$. The zero-field transition frequencies, $\nu(H_2O)$, and differences between the laser and H_2O frequencies, $\nu(H_2O) - \nu(\text{laser})$, which result from Stark effect calculations on the data of Tables 1 and 2, are listed in Table 4. The uncertainties quoted for $\nu(H_2O) - \nu(\text{laser})$ reflect the assumed 0.020 D uncertainty in $\mu(000)$, and those quoted for $\nu(H_2O)$ include an additional contribution from the estimated uncertainties in $\nu(\text{laser})$. The values determined for $\nu(H_2O)$ (Table 4) differ by 0.0015 cm^{-1} or less from the three line positions measured in our conventional spectrum (the zero-field forbidden $5_{15} \leftarrow 4_{13}$ transition was, of course, not observed in the conventional spectrum).

The study of the collisional transfer of saturated absorption signals using various infrared–infrared double resonance techniques has shown that collision-induced transitions between certain molecular energy levels can occur with very little velocity change (5, 23–26). Such transitions between the $M = 0$ and 1 components of the 1_{10} and 1_{01} levels are responsible for the centre dip in Fig. 1. Previous studies have involved linear (25), symmetric rotor (5, 23, 24, 26), and near symmetric rotor (5) molecules. The present case of the $H_2{}^{17}O$ $1_{10} \leftarrow 1_{01}$ transition is the most completely isolated four-level system in which this phenomenon has been observed. The interpretation of the observed centre dip is complicated by the fact that our sample contained only 11% $H_2{}^{17}O$. The presence of a buffer gas tends to reduce the strength of a collision-induced centre dip, although in the present case the buffer gas was mostly $H_2{}^{18}O$ which cannot be considered an entirely 'foreign' gas. A further complication was introduced by the laser power effects on the spectrum: the relative strengths of the centre dip and the 'real' Lamb dips were fairly power dependent, with the centre dip growing in relative strength with higher power. Nevertheless, the present observation when analyzed in the way described by Johns *et al.* (5) indicates that of the order of 3 to 15% of the collision-induced transitions experienced by H_2O molecules in the $J = 1$ state are reorientation transitions ($\Delta M = \pm 1$) that change the orientation of the angular momentum without changing its magnitude and that involve only very small changes in translational energy.

TABLE 4. Zero-field transition frequencies in the ν_2 band of H_2O as derived from the results of Tables 1 and 2

Transition	$\nu(H_2O) - \nu(\text{laser})$ (MHz)	$\nu(H_2O)$ (cm^{-1})
$H_2{}^{17}O$ $1_{10} \leftarrow 1_{01}$	$-408(17)$	1613.0969(15)
$H_2{}^{17}O$ $4_{22} \leftarrow 4_{13}$	$-1321(32)$	1643.5274(16)
$H_2{}^{18}O$ $5_{15} \leftarrow 4_{13}$	$-1407(43)$	1640.1291(18)
$H_2{}^{18}O$ $5_{15} \leftarrow 4_{04}$	$-1015(32)$	1693.6987(14)

NOTE: The quantities in parentheses are uncertainties right-adjusted to the last digit of the quoted result. The assumed values for $\nu(\text{laser})$ are those in Tables 1 and 2, and the uncertainties quoted for $\nu(H_2O)$ include contributions due to the estimated uncertainties in the laser frequencies (42, 36, 33, and 27 MHz, respectively) taken from our unpublished results on CO.

5. Conclusions

The observation of four saturated absorption spectra in the ν_2 bands of $H_2{}^{17}O$ and $H_2{}^{18}O$ using the laser Stark technique has yielded a direct measurement of the dipole moment change between the ground (000) and excited (010) vibrational states of H_2O, as well as some accurate transition frequencies. The measured dipole change is in excellent agreement with one calculated from recent infrared intensity measurements.

It would be desirable to observe additional ν_2 band transitions with the CO laser, especially some in $H_2{}^{16}O$. As mentioned above there is an additional experimental difficulty in the latter case due to the presence of absorption due to atmospheric water vapour which tends to prevent oscillation of the CO laser on lines close to strong $H_2{}^{16}O$ transitions. A further prospect is the observation of transitions in the $2\nu_2 \leftarrow \nu_2$, $\nu_1 \leftarrow \nu_2$, and $\nu_3 \leftarrow \nu_2$ hot bands of H_2O which occur in the 4 to 9 μm region. A search for coincidences between these transitions and CO laser lines is encouraged by the recent publication of accurate frequencies for $H_2{}^{16}O$ by Flaud *et al.* (19).

Acknowledgments

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