ond-order effect of the magnetic field is the only one operative.

We expect that some of the experimental results on shallow-donor spectroscopy and exciton absorption in a magnetic field may require reanalysis in view of the present findings.

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Submillimeter Microwave Spectrum of $H_2{}^{18}O$†

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The rotational spectrum of $H_2{}^{18}O$ in the ground vibrational state has been investigated by means of high-resolution microwave spectroscopy. We report the measurement of ten new rotational transitions in the 1.0- to 0.4-mm wavelength region. Among these are several low-*J* lines which are of significance in the atmospheric absorption of electromagnetic radiation in the microwave region. The frequencies of newly observed transitions are (in MHz): $5_{1,5} \leftarrow 4_{2,2}$, 322 465.17; $4_{1,4} \leftarrow 3_{2,1}$, 390 607.76; $4_{2,3} \leftarrow 3_{3,0}$, 489 054.26; $6_{2,4} \leftarrow 7_{1,7}$, 517 181.96; $6_{4,3} \leftarrow 5_{5,0}$, 520 137.32; $5_{3,3} \leftarrow 4_{4,0}$, 537 337.57; $1_{1,0} \leftarrow 1_{0,1}$, 547 676.44; $6_{4,2} \leftarrow 5_{5,1}$, 554 859.87; $5_{3,2} \leftarrow 4_{4,1}$, 692 079.14; and $2_{1,1} \leftarrow 2_{0,2}$, 745 320.20. Assignments were based on a weighted analysis of combined microwave and infrared data.

INTRODUCTION

Recently we reported microwave investigations[1,2] of the rotational spectra of $HD^{16}O$ and $H_2{}^{16}O$ in the millimeter and submillimeter wavelength regions. In the present paper we report measurements of ten previously unobserved submillimeter wave transitions of $H_2{}^{18}O$ in the region from 1.0 to 0.4 mm. Only two rotational lines of this isotopic species have been previously observed, neither of which falls in the submillimeter wave region. Among the newly observed transitions are several low-*J* lines which are of significance in the atmospheric absorption of electromagnetic radiation in the microwave region.[3] The measurement of higher-frequency transitions of $H_2{}^{18}O$ has been made possible by a recent extension of the operating range of our tunable microwave spectrometers to a wavelength of 0.368 mm and an accompanying order-of-magnitude improvement in sensitivity in the previously covered submillimeter region.[4]

Lines attributed to the isotopic species $H_2{}^{18}O$ in natural abundance have been identified in the rotation-vibration spectrum of water vapor in a number of past infrared investigations. Rao and his co-workers[5,6] have recorded several rotation-vibration bands of the infrared spectrum of $H_2{}^{18}O$ in isotopically enriched samples. One of the two previously observed microwave lines of $H_2{}^{18}O$, the $6_{1,6} \leftarrow 5_{2,3}$ transition measured by Powell and Johnson,[7] occurs in the centimeter wave region; the other, the $3_{1,3} \leftarrow 2_{2,0}$ transition reported by Steenbeckeliers and Bellet,[8] occurs in the millimeter wave region.

RESULTS

Submillimeter wave energy for this investigation was produced by a klystron-driven crystal harmonic multiplier[9] and detected by an InSb photoconducting detector[10] operated at 1.6 °K. Accurate measurements of the klystron frequency were made with a frequency multiplication chain referenced to WWVB. Typically, a klystron oscillating in the 50-GHz region was used as the fundamental source.

In the present work, an absorption path length of 90 cm was used.

Predictions based on a weighted rotation-distortion analysis, which combined infrared data[5,6] with the two previously measured microwave transitions, were used in the initial search for microwave lines. As additional lines were located and measured, they were included in this analysis to give improved predictions of the higher-J microwave lines. Because the microwave lines of $H_2{}^{18}O$ are widely separated, no confusion was encountered in identifications of the observed transitions. However, some of the observed lines are weak, and the frequencies of some are strongly influenced by large distortion effects. So that there would be no errors due to misassignment of harmonics, each of the new lines was observed from two different combinations of klystron frequency and harmonic number. The frequencies of the newly measured transitions of $H_2{}^{18}O$ and of the two previously measured lines are shown in Table I.

Watson's formulation of the rotation-distortion Hamiltonian[11] was used in the treatment of the data. Procedures of the analysis have been described in previous papers of this series.[1,2,12–14] As for $H_2{}^{16}O$, it was not possible to measure enough microwave transitions to perform a complete rotation-distortion analysis based entirely on microwave data. Consequently, a weighted microwave-infrared distortion analysis which included all 12 of the known microwave lines was made. Because there has been considerably less work on the infrared spectrum of $H_2{}^{18}O$ than on that of $H_2{}^{16}O$, the spectral constants are calculated with somewhat more uncertainty than those which were calculated for $H_2{}^{16}O$. An extension of the infrared work to higher J_{K_{-1},K_1} levels and an accurate measurement of the pure rotational spectrum in the far infrared would be most useful. The rotation-distortion constants which are derived from this analysis are shown in Table II.

TABLE I. Observed microwave rotational transitions of $H_2{}^{18}O$ (MHz).

Transition	Observed frequency	Predicted[a] frequency	Ref.[b]
$6_{1,6} \leftarrow 5_{2,3}$	5 625.147	5 625.48	7
$3_{1,3} \leftarrow 2_{2,0}$	203 407.52	203 406.23	8, c
$5_{1,5} \leftarrow 4_{2,2}$	322 465.17	322 464.52	c
$4_{1,4} \leftarrow 3_{2,1}$	390 607.76	390 608.48	c
$4_{2,3} \leftarrow 3_{3,0}$	489 054.26	489 062.99	c
$6_{2,4} \leftarrow 7_{1,7}$	517 181.96	517 173.97	c
$6_{4,3} \leftarrow 5_{5,0}$	520 137.32	520 138.85	c
$5_{3,3} \leftarrow 4_{4,0}$	537 337.57	537 337.47	c
$1_{1,0} \leftarrow 1_{0,1}$	547 676.44	547 683.68	c
$6_{4,2} \leftarrow 5_{5,1}$	554 859.87	554 858.32	c
$5_{3,2} \leftarrow 4_{4,1}$	692 079.14	692 080.70	c
$2_{1,1} \leftarrow 2_{0,2}$	745 320.20	745 311.71	c

[a] Obtained from a weighted analysis of combined microwave and infrared results (see text) with predicted line removed from the fit.

[b] The observed frequency is taken from the last reference listed.

[c] Present work.

TABLE II. Rotational and distortion constants of $H_2{}^{18}O$ (MHz). Errors quoted are twice the statistical standard deviation.

$$\mathcal{A} = 825\,366.1 \pm 8.7$$
$$\mathcal{B} = 435\,331.6 \pm 8.0$$
$$\mathcal{C} = 276\,950.5 \pm 8.0$$

$$\Delta_J = 37.29 \pm 0.30 \qquad \Delta_{JK} = -170.2 \pm 1.3$$
$$\Delta_K = 959.6 \pm 2.3 \qquad \delta_J = 15.24 \pm 0.12$$
$$\delta_K = 31.5 \pm 1.2$$
$$H_J = (1.41 \pm 0.34) \times 10^{-2} \qquad H_{KJ} = (-4.53 \pm 0.71) \times 10^{-1}$$
$$H_K = 5.09 \pm 0.24 \qquad h_J = (7.9 \pm 1.1) \times 10^{-3}$$
$$h_{JK} = (-1.7 \pm 2.8) \times 10^{-2}$$
$$L_K = (-9.59 \pm 0.83) \times 10^{-2} \qquad l_K = (2.35 \pm 0.24) \times 10^{-2}$$
$$P_K = (1.45 \pm 0.13) \times 10^{-3}$$

While the combination of terms to be retained in the Hamiltonian, weighting, and the selection of infrared data is not unique, the results of this analysis are in good agreement with the results of analyses based on alternative choices of these parameters. The quoted errors were calculated by use of a statistical error analysis which we have previously discussed.[12] As a check on both the method of analysis and the assignment of observed lines, each of the microwave lines, one at a time, was removed from the analysis and its frequency predicted on the basis of the remaining data. The results of this analysis are also shown in Table I. The differences between the observed frequency and predicted frequency are in all cases consistent with calculated uncertainties in the predicted line frequencies.

From the constants of Table II, viz., Δ_J, Δ_{JK}, Δ_K, and δ_J, it is possible to evaluate (see Ref. 13) τ_{aaaa}, τ_{bbbb}, τ_{cccc}, and Watson's τ_1. The first three τ's yield τ_{aabb}, τ_{aacc}, and τ_{bbcc} from the planar relations. These in conjunction with τ_1 yield τ_{abab}. Evaluation of δ_K from these calculated τ's gives 7.0 MHz as compared to the observed value of 31.5 MHz. The poor agreement indicates the errors inherent in the application of the planar relations to molecules of this type.

The $\mathcal{A}$, $\mathcal{B}$, and $\mathcal{C}$ which result directly from this analysis based on Watson's formulation of the distortion Hamiltonian include contributions from the distortion term R_6, and they thereby differ from the A, B, and C of Kivelson and Wilson.[15] The constant R_6 was evaluated from the appropriate τ's, calculated as outlined above. For $H_2{}^{18}O$ this gives

$$A = 825\,422.3, \quad B = 435\,136.6, \quad C = 277\,089.3.$$

TABLE III. Comparison of observed $H_2{}^{18}O$ distortion constants with those calculated from $H_2{}^{16}O$ data.

	Calculated[a] (MHz)	Observed[b] (MHz)
Δ_J	37.57	37.29
Δ_{JK}	-171.1	-170.2
Δ_K	950.6	959.6
δ_J	15.22	15.24

[a]Calculated from $H_2{}^{16}O$ data (Ref. 2) as outlined in text.

[b]Calculated directly from $H_2{}^{18}O$ data (this work).

Similarly, additional distortion terms (τ_{abab}) are absorbed in the definition of A, B, and C of Kivelson and Wilson. The removal of these contributions gives

$$A' = 825\,354.8, \quad B' = 435\,069.1, \quad C' = 277\,190.5.$$

These rotational constants are simply related to the ground-vibrational-state moments of inertia by $I_a = h/8\pi^2 A'$, etc.

It is interesting to compare the results of this analysis of $H_2{}^{18}O$ with the results previously obtained[2] for $H_2{}^{16}O$. For triatomic planar molecules, where the C_{2v} symmetry is unaltered by isotopic substitution, the distortion constants for the isotopic species can be calculated from the distortion constants of the parent species. In particular for $H_2{}^{18}O$,

$$\tau'_{aaaa} = (A'/A)^2\,\tau_{aaaa}\,, \quad \tau'_{bbbb} = (B'/B)^2\,\tau_{bbbb}\,,$$

$$\tau'_{aabb} = (A'B'/AB)\,\tau_{aabb}\,,$$

$$\tau'_{abab} = \left(\frac{A'B'}{AB}\right)\left(\frac{M'm_O}{Mm'_O}\right) \times \left(\frac{1 + (2m_H/m_O)\,\sin^2\theta}{1 + (2m_H/m'_O)\,\sin^2\theta}\right)^2 \tau_{abab}\,,$$

where A, B, and C are the rotational constants; m_H and m_O are the masses of hydrogen and oxygen, respectively; M is the total mass of the molecule; θ is half the HOH angle; and where the primes refer to the isotopic species ($H_2{}^{18}O$). These relations hold strictly for the equilibrium parameters. The distortion constants for $H_2{}^{16}O$ in the above relations were calculated from the observed Δ_J, etc., of Ref. 2 as outlined previously. These τ's were then employed for evaluation of the corresponding τ's for $H_2{}^{18}O$. From these four τ's and the planar relations, the constants Δ_J, Δ_{JK}, Δ_K, δ_J were evaluated for $H_2{}^{18}O$. Table III shows a comparison of the results. Inspection of this table shows that the agreement between the isotopic species is excellent. This is particularly gratifying because the $H_2{}^{16}O$ and $H_2{}^{18}O$ analyses include very different types of infrared data sets as well as different higher-order terms in the Hamiltonian.

Preliminary results of the present investigation have been reported elsewhere.[16]

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