

論 文

IR Spectrum and Analysis of ν_2 of $T_2^{18}O$

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Abstract

The rotation-vibration spectrum of ν_2 of $T_2^{18}O$ is reported in the region of 1100 ~ 900 cm^{-1} and analyzed on the basis of a rigid rotor. The band constants (in cm^{-1}) obtained are as follows: $\nu_0=986.35$; $A''=10.935$, $B''=4.857$, and $C''=3.314$ in the ground state and $A'=11.558$, $B'=4.903$ and $C'=3.276$ in the excited state. The r_0 structures derived from the rotational constants of A and B are: $r''=0.9574$ (Å) and $\alpha''=104.80^\circ$ in the ground state and $r'=0.9449$ (Å) and $\alpha'=106.07^\circ$ in the excited state.

Introduction

IR^{1,2)} and microwave^{3,4)} spectra of water including tritium have been studied extensively and rotational constants and molecular structures of the ^{16}O compounds in the ground state have been clarified. On the other hand only a rotation-vibration spectrum¹⁾ has been reported for ν_2 of $T_2^{16}O$.

It is well-known that there are large anharmonicity and a large inertia defect in water molecules. That is, rotational constants in ground and excited states differ quite each other and a rotation-vibration interaction through the Coriolis force is large, as has been reported for $T_2^{16}O$. There results in a difference in a molecular structure between isotope molecules. In the present study we will report the band constants of ν_2 of $T_2^{18}O$ and discuss the molecular structure derived from rotational constants with that of $T_2^{16}O$.

Although a rotational Hamiltonian has been expanded up to the tenth power of angular momenta in the microwave study³⁾ of $T_2^{16}O$, the rotation-vibration spectrum of ν_2 ¹⁾ has been analyzed well for lower energy levels of J'' , $J' \leq 6$ on the basis of the rigid rotor. Thus we analyze the present system under the same condition as the IR study.

Experimental

T₂¹⁸O was obtained from the reaction of 3 Ci of T₂ with excess ¹⁸O₂ on platinum black at room temperature. Because of handling of the small amount of molecule a glass system which was cleaned up carefully to raise the isotopic purity was made as small as possible. The IR spectrum was observed under the condition of the spectral slit width of 0.45~0.55 cm⁻¹ in the region of 1200~800 cm⁻¹ at about 60 °C by use of the JASCO-IRA-3 spectrometer with a data processor.

The observed frequencies were calibrated by 9 bands of a polystyrene film and indene and believed to be accurate within ±0.4 cm⁻¹; they are given in Table 1. The

Table 1. The observed and calculated frequencies (cm⁻¹) and their assignments

Obs.	Calc.	Assign.	
		J' _τ	J'' _τ
1085.5*	1085.40	5 ₃	4 ₁
	1085.19*	5 ₂	4 ₂
1077.3*	1077.03	4 ₄	3 ₂
	1077.00*	4 ₃	3 ₃
1061.0	1060.34	11 ₋₁₀	10 ₋₁₀
	1060.32	11 ₋₁₁	10 ₋₉
1054.7	1054.34	10 ₋₉	9 ₋₉
	1054.25	10 ₋₁₀	9 ₋₈
1050.2*	1050.91	3 ₃	2 ₁
	1050.63*	3 ₂	2 ₂
1047.2	1048.28	9 ₋₈	8 ₋₈
	1048.08	9 ₋₉	8 ₋₇
	1048.06	8 ₋₆	7 ₋₄
1041.9	1042.20	8 ₋₇	7 ₋₇
	1042.05	6 ₂	6 ₀
1037.0	1037.49	4 ₋₁	3 ₋₁
	1037.44	8 ₀	8 ₋₂
1035.1	1035.26	7 ₋₇	6 ₋₅
1030.1*	1030.36*	6 ₋₁	6 ₋₃
	1030.26	6 ₋₅	5 ₋₅
1028.2*	1028.48*	6 ₋₆	5 ₋₄
	1028.43	6 ₋₄	5 ₋₂
	1028.34	5 ₀	5 ₋₂
1024.3	1024.58	5 ₋₄	4 ₋₄
1021.5*	1021.26*	5 ₋₅	4 ₋₃

to be continued

Table 1. (continued)

1017.7	1018.23	7 ₋₁	7 ₋₃
	1018.22	8 ₋₂	8 ₋₄
1013.8*	1013.61	3 ₋₂	2 ₋₂
	1013.48*	4 ₋₄	3 ₋₂
1005.8*	1005.90*	4 ₀	4 ₋₂
996.3*	996.55*	2 ₀	2 ₋₂
977.3*	976.95*	2 ₋₂	2 ₀
970.0	969.99	5 ₋₃	5 ₋₁
963.6	963.80	7 ₋₃	7 ₋₁
	963.73	7 ₋₅	7 ₋₃
959.5*	959.64	3 ₋₂	4 ₋₄
	959.53*	2 ₋₂	3 ₋₂
951.8	959.47	5 ₋₁	5 ₁
	951.65	8 ₋₂	8 ₀
948.4*	951.63	4 ₋₃	5 ₋₅
	948.21*	4 ₋₄	5 ₋₄
944.3*	944.38	2 ₀	3 ₀
	944.37	7 ₋₂	7 ₀
936.8	944.06*	5 ₋₄	6 ₋₆
	936.78	6 ₋₅	7 ₋₇
929.4*	929.91*	2 ₁	3 ₃
	929.63	7 ₋₆	8 ₋₈
922.1	922.63	3 ₁	4 ₁
	922.54	8 ₋₇	9 ₋₉
	922.32	8 ₋₈	9 ₋₈
915.6	915.43	9 ₋₈	10 ₋₁₀
	915.33	9 ₋₉	10 ₋₉
911.4	911.32	3 ₃	4 ₃
	911.29	3 ₂	4 ₄

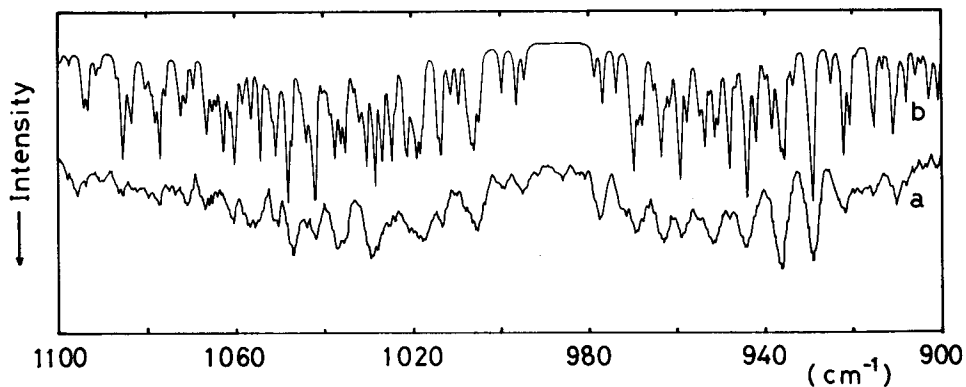


Fig. 1. The observed (a) and calculated (b) spectra in the region of ν_2 of $T_2^{16}O$.

observed spectrum is given in Fig. 1-a.

The rotational energy levels and the line intensities of P, Q and R branches were calculated with reference to literatures^{5,6)} by use of the computer FACOM 230-45S of Toyama University.

Results and Discussion

Since ν_2 is the B-type band, the band origin may be estimated approximately from the observed spectrum. This is also possible from a normal coordinate analysis. We got 986 cm^{-1} by use of the force constants obtained from the A_1 species^{1,7,8)} of $T_2^{16}O$. The rotational constants were estimated initially from the IR study¹⁾ on $T_2^{16}O$. The initial value of the band constants is given in the first column of Table 2, where the band constants of ν_2 of $T_2^{16}O$ are also given in the last column.

A preliminarily calculated spectrum by use of the band constants in Table 2 reproduced considerably the observed one. Then some of the observed bands were assigned definitely.

The band constants were refined by means of the least squares method by use of the discrete and intense bands (noted by * in Table 1) up to J'' , $J' \leq 6$. The band constants obtained are given in the second

Table 2. The band constants (cm^{-1}) of ν_2 of $T_2^{16}O$

ν	$T_2^{16}O$		$T_2^{16}O^b)$
	initial	final	
ν_0	986.0	986.35	995.37
0 A''	10.956	10.935	11.301
B''	4.837	4.857	4.837
C''	3.314	3.314	3.344
$\Delta''^a)$	0.105	0.125	0.105
r'' (Å)	0.9583	0.9574	0.9583
α'' (°)	104.97	104.80	104.97
1 A'	11.618	11.558	11.982
B'	4.868	4.903	4.868
C'	3.288	3.276	3.316
$\Delta'^a)$	0.355	0.413	0.355
r' (Å)	0.9461	0.9449	0.9461
α' (°)	106.41	106.07	106.41

^{a)} $10^{-40}\text{ g}\cdot\text{cm}^2$. ^{b)}From Ref. 1.

column in Table 2. The calculated spectrum by use of the refined band constants and the energy levels of J'' , $J' \leq 15$ is given in Fig. 1-b, where each band width is assumed to be 0.8 cm^{-1} . The calculated frequencies and their assignments (only intense components) are given in Table 1.

It is found from Table 1 that the observed band consists of some strong components and many weak ones (not given). That they split into each component can not be expected from the present resolution.

The centrifugal distortion constants, D_{JK} and D_K , in the ground state³⁾ of $T_2^{16}O$ have been reported to be -0.0007 and 0.0048 cm^{-1} , respectively, in the Watson formulation.⁹⁾ Then we can expect that the energy levels in the higher states of $T_2^{18}O$ differ considerably from those calculated from the rigid rotor approximation. Thus the difference in the resolution between the observed and calculated spectra in Fig. 1 is attributed mainly to the rigid rotor approximation. Since the observed band is not resolved into the components, further refinement by use of the higher order of the Hamiltonian is not important in the present study. It should be noted that the band constants obtained here are as reliable as those in $T_2^{16}O$, because we obtain them under the condition of J'' , $J' \leq 6$.

In Table 2 the inertia defect (Δ) and the r_0 structure (r : atomic distance, α : \angle TOT) derived from A , B are also given. The relation of $^{18}r < ^{16}r$ and $^{18}\alpha < ^{16}\alpha$ in the ground and excited states is explained qualitatively in terms of anharmonicity; the superscript of 18 and 16 denotes the ^{18}O and ^{16}O compounds respectively. This is also true for ν_0 which is higher by 0.35 cm^{-1} than that expected initially.

Since rotational constants obtained are effective ones and affected by a rotation-vibration interaction through the Coriolis force, the r_0 structure means a formal presentation of a molecular structure. Then the relation of $r' < r''$ in both compounds may indicate that the rotation-vibration interaction in the excited state is larger than that in the ground state. On the other hand the relation of $\alpha' < \alpha''$ in both compounds agrees with expectation from anharmonicity. The values of Δ are not examined quantitatively in the present study, because ν_1 and ν_3 have not been confirmed.

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References

- 1) R.A. Carpenter, N.M. Gailar, H.W. Morgan, and P.A. Staats, *J. Mol. Spectrosc.*, **44**, 197 (1972) .
- 2) P.A. Staats, H.W. Morgan, and J.H. Goldstein, *J. Chem. Phys.*, **24**, 916 (1956) .
- 3) F.C. De Lucia, P. Helminger, and W. Gordy, *Phys. Rev.*, **8**, 2785 (1973) .
- 4) P. Helminger, F. C. De Lucia, and W. Gordy, *Phys. Rev.*, **10**, 1072 (1974) .
- 5) C.H. Townes and A.L. Schawlow, "Microwave Spectroscopy," McGraw-Hill, New York (1955) .
- 6) M. Hayashi, "Kozo Kagaku II," Asakura Syoten, Tokyo (1972) .
- 7) W.F. Libby, *J. Chem. Phys.*, **11**, 101 (1943) .
- 8) P. Thirugnanasambandam and S. Mohan, *J. Chem. Phys.*, **61**, 470 (1974) .
- 9) J.K.G. Watson, *J. Chem. Phys.*, **45**, 1360 (1966) ; **46**, 1935 (1967) ; **48**, 4517 (1968) .