Microwave spectrum and molecular constants of $^{16}O^{18}O$†

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Measurements of millimeter-wave fine-structure transitions and the $n(J) = 0(1) \rightarrow 2(1)$ rotational transition of $^{16}O^{18}O$ have been made with high precision. From analysis of the results the following molecular constants of $^{16}O^{18}O$ were obtained: $B_0 = 40\,707.408(10)$ MHz, $B_1 = -0.129$ MHz, $\lambda_0 = 59\,499.097(43)$ MHz, $\lambda_1 = 0.053\,12(80)$ MHz, $\mu_0 = -238.488(7)$ MHz, $\mu_1 = -0.000\,619(116)$ MHz, $B_e = 40\,931.7(6.9)$ MHz, $r_0 = 1.210\,751(16)$ Å, and $r_e = 1.207\,429(103)$ Å. The equilibrium values were obtained with the aid of vibration-rotation interaction constants from optical spectroscopy.

INTRODUCTION

The spectrum of $^{16}O^{18}O$ is interestingly different from that of $^{16}O_2$ or $^{18}O_2$. For the latter two species alternate rotational levels are missing, whereas for $^{16}O^{18}O$ all rotational states occur. Since $^{16}O_2$ and $^{18}O_2$ consist of two identical Bose particles, symmetry considerations dictate that energy levels with even rotational numbers do not occur.[1] In contrast, $^{16}O^{18}O$ consists of two distinguishable particles; the symmetry is broken; and all rotational levels occur. A system of $^{16}O^{18}O$ molecules therefore occupies twice as many states as its homonuclear counterparts and has approximately half as many molecules in any given state. Consequently, the line intensities for $^{16}O^{18}O$ are approximately half as strong as those of the corresponding transitions for $^{16}O_2$ and $^{18}O_2$.

With high precision we have measured nine fine-structure transitions and one rotational transition of $^{16}O^{18}O$ in the ground vibrational state. These measurements have been combined with previous optical measurements[2] to give highly accurate values of the equilibrium constants of the oxygen molecule. The transitions observed are induced by the spin magnetic dipole moment. The strengths of these magnetic dipole transitions are typically the order of ten thousand times weaker than those induced by a 1-D electric dipole moment. Although it is possible that the $^{16}O^{18}O$ molecule possesses an electric dipole moment resulting from its mass asymmetry, this moment is expected to be extremely small. To our knowledge, no electric dipole transitions have been observed in oxygen.

Earlier, less accurate measurements have been reported on a few fine-structure transitions of $^{16}O^{18}O$.[3] After our results were reported in a Ph.D. thesis,[4] we received a report of fine-structure measurements of O_2 by Amono and Hirota[5] which includes some results for $^{16}O^{18}O$. The six $^{16}O^{18}O$ lines which overlap our measurements are in satisfactory agreement with our results.

The experimental procedures and the spectrometer are like those described in the earlier paper on $^{18}O_2$.[6] In preparation of the sample of $^{16}O^{18}O$, equal amounts of $^{16}O_2$ and $^{18}O_2$ were introduced into a 100-ml sample tube; the oxygen molecular bonds were then broken with a Tesla coil discharge. When the oxygen atoms randomly recombined, a 50% sample of $^{16}O^{18}O$ was obtained.

THEORY

The theory of the microwave spectrum of molecular oxygen has evolved from the work of a number of investigators. A summary of the development is given in the previous paper on $^{18}O_2$.[6] The oxygen Hamiltonian,

$$\mathcal{H} = B\vec{N}^2 + \mu\vec{N}\cdot\vec{S} + \tfrac{2}{3}\lambda(3S_z^2 - \vec{S}^2),\tag{1}$$

was used in the analysis of the $^{16}O^{18}O$ results. The first term represents the end-over-end rotational energy of the molecule; the second, the spin-molecular rotation interaction; and the last, the electron spin-spin interaction. Here $\vec{N}$ is the rotational angular momentum; $\vec{S}$ is the spin angular momentum; and S_z is the component of S along the bond axis of the molecule. Corrections for centrifugal distortion effects are included in the parameters of B, μ, and λ by the relations[6,7]

$$B = B_0 + B_1 N(N+1) + \cdots,$$

$$\mu = \mu_0 + \mu_1 N(N+1) + \cdots \text{ for } N = N' \text{ matrix elements},$$

$$\lambda = \lambda_0 + \lambda_1 N(N+1) + \cdots,\tag{2}$$

$$\lambda = \lambda_0 + \lambda_1(J^2 + J + 1) \text{ for } N = J \pm 1 = N' \pm 2.$$

In our previous work[6] the matrix elements of this Hamiltonian were obtained by means of the theory of irreducible tensor operators. Diagonalization of the corresponding energy matrix yields expressions for the energies. The general features of the energy level diagram are depicted in Fig. 1.

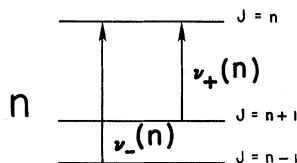The allowed microwave transition frequencies of oxygen may be obtained from the energy expres-
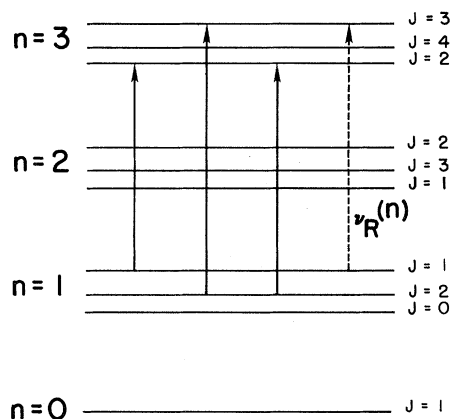
FIG. 1. Energy-level diagram for $^{16}O^{18}O$ indicating the magnetic dipole transitions (solid arrows).

sions given in the previous paper[6] on $^{18}O_2$. The frequencies may be expressed by

$$\nu_R(n) = (2B_0 - 2\mu_1 + \tfrac{4}{3}\lambda_1)(n+1) + 4B_1(n+1)^3,$$

$$\nu_\pm(n) = \lambda_0 + \tfrac{1}{2}\mu_0 - 4\mu_1 + (\lambda_1 + \tfrac{5}{2}\mu_1)(k^2 + k + 2) \qquad (3)$$

$$\pm \left[f(k) - (2k+1)(B_0 + 2B_1[k^2 + k + 1] \right.$$

$$\left. - \mu_1 + \tfrac{2}{3}\lambda_1) \right],$$

where

$$[f(k)]^2 = A^2 + k(k+1)D^2,$$

$$A = (2k+1)\left[(B_0 - \tfrac{1}{2}\mu_0) + (2B_1 - \tfrac{1}{2}\mu_1)(k^2 + k + 1) - \tfrac{3}{2}\mu_1 \right]$$

$$- (2k+1)^{-1}[\lambda_0 + \tfrac{1}{3}\lambda_1(7k^2 + 7k + 4)],$$

$$D = (2k+1)^{-1}[2\lambda_0 + 2\lambda_1(k^2 + k + 1)], \qquad k = n \pm 1.$$

The number n specifies the rotational levels as indicated in Fig. 1.

EXPERIMENTAL RESULTS AND ANALYSIS OF DATA

The observed millimeter and submillimeter transitions for $^{16}O^{18}O$ are listed in the second column of Table I. A chart recorder tracing of the rotational transition $n(J) = 0(1) \to 2(1)$ is shown in

TABLE I. Observed and calculated transition frequencies of $^{16}O^{18}O$.

Transition	Observed frequency (MHz)	Predicted frequency (MHz)	Difference
$\nu_+(3)$	58 656.447(65)	58 656.313(27)	+0.134
$\nu_+(6)$	60 094.935(17)	60 095.012(31)	−0.077
$\nu_+(8)$	60 801.121(58)	60 800.64(64)	+0.157
$\nu_-(4)$	60 861.117(114)	60 861.240(39)	−0.123
$\nu_-(5)$	60 105.612(77)	60 105.615(45)	−0.003
$\nu_-(6)$	59 539.420(56)	59 539.445(42)	−0.025
$\nu_-(7)$	59 074.760(67)	59 074.722(30)	+0.038
$\nu_-(8)$	58 670.780(73)	58 670.743(33)	+0.037
$\nu_-(9)$	58 306.003(55)	58 306.058(95)	−0.055
$0(1) \to 2(1)$	233 946.179(61)	233 946.178(52)	+0.001

Fig. 2. All errors quoted in Table I are one standard deviation.

The experimental data listed in Table I were analyzed by means of a nonlinear weighted least-squares fitting of the data. With the exception of the rotational line, each predicted transition was excluded from the data used in the analysis.

The values of the $^{16}O^{18}O$ parameters obtained in the present work are listed in Table II. For comparison, parameters for $^{16}O_2$ and $^{18}O_2$ are also listed. The $^{18}O_2$ parameters are those reported in our previous paper[6]; the $^{16}O_2$ parameters were obtained from a least-squares fitting of the fine-structure data reported by Welch and Mizushima[8] combined with the remeasured rotational transition at 424 GHz.[6] The B_1 values given for $^{16}O^{18}O$ and ^{18}O were not derived from these measurements but from the B_1 of $^{16}O_2$ by standard isotopic substitution techniques.

The effective internuclear distance r_0 for the ground vibrational state of oxygen was obtained from B_0 with the expression
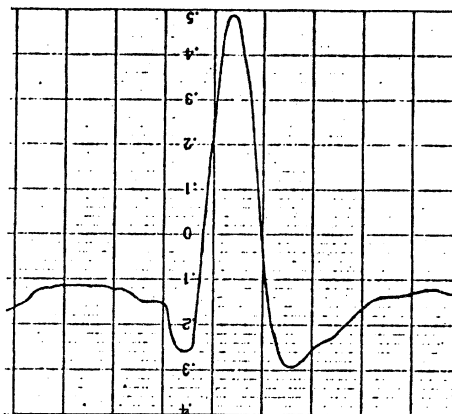

FIG. 2. Second derivative of the absorption contour in the $n(J) = 0(1) \to 2(1)$ rotational transition of $^{16}O^{18}O$ at 233 946.179 MHz.

TABLE II. Molecular parameters of oxygen[a].

	$^{16}O_2$	$^{16}O^{18}O$	$^{18}O_2$
B_0	43 100.460(6)	40 707.408(10)	38 313.730(7)
B_1	−0.145 01(27)	−0.129	−0.115
λ_0	59 501.341(4)	59 499.097(43)	59 496.698(11)
λ_1	0.058 48(2)	0.053 12(80)	0.052 11(42)
μ_0	−252.586(1)	−238.488(7)	−224.439(3)
μ_1	−0.000 247(1)	−0.000 619(116)	−0.000 351(54)
B_e	43 344.7(7.5)	40 931.7(6.9)	38 518.6(6.3)
r_0	1.210 850(16)	1.210 751(16)	1.210 650(16)
r_e	1.207 433(106)	1.207 429(103)	1.207 427(100)

[a]All quantities, except r_0 and r_e, have the units of MHz; r_0 and r_e have the units of angstroms. All errors quoted are one standard deviation.

$$r_0 = (h/8\pi^2 \mu B_0)^{1/2}, \qquad (4)$$

where h is Planck's constant and μ is the reduced mass of the molecule. With $h = 6.62559(16) \times 10^{-27}$ erg sec, ^{16}O mass $= 2.655844(32) \times 10^{-23}$ g, and ^{18}O mass $= 2.988635(36) \times 10^{-23}$ g,

$$(r_0)_{16, 18} = 1.210751(16) \text{ Å}.$$

The equilibrium values for B_e and r_e were derived in the following manner. Corrections for the ground-state vibration effects were calculated with the first-order expression[1]

$$B_e' = B_0 + \tfrac{1}{2}\alpha, \qquad (5)$$

with the α obtained from that for $^{16}O_2$. Albritton et al.[9] obtained a value of $\alpha = 477.6(15.0)$ MHz from an analysis of the complete set of early optical measurements of Babcock and Herzberg.[2]

The value of α for $^{16}O^{18}O$ is obtained from the mass-dependent expression[1]

$$(\alpha)_{16, 18} = (\mu_{16, 16}/\mu_{16, 18})^{3/2} (\alpha)_{16, 16}. \qquad (6)$$

A correction was also made for the rotation of the nonspherically distributed electron cloud with the relation[10]

$$B_e = (1 - g_r)B_e', \qquad (7)$$

where g_r is the molecular rotational g factor. The value of g_r for $^{16}O_2$ was found by Evenson and Mizushima[11] to be $-1.25(8) \times 10^{-4}$. If it is assumed that g_r is the same for all isotopes of oxygen, then we obtain

$$(B_e)_{16, 18} = 40 931.7(6.9) \text{ MHz}$$

and

$$(r_e)_{16, 18} = 1.207 429(103) \text{ Å}.$$

The ratios of r_e values of the three isotopic species

$$(r_e)_{16, 16}/(r_e)_{16, 18} = 1.000 003(122),$$

$$(r_e)_{16, 16}/(r_e)_{18, 18} = 1.000 005(121),$$

$$(r_e)_{16, 18}/(r_e)_{18, 18} = 1.000 002(119),$$

are self-consistent and equal to one, within experimental error.

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