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Laser Magnetic Resonance Measurement of Rotational Transitions in the Metastable $a^1\Delta_g$ State of Oxygen

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Laser magnetic resonance (LMR) for five rotational transitions, $J = 4 \leftarrow 3, 5 \leftarrow 4, 7 \leftarrow 6, 8 \leftarrow 7, 9 \leftarrow 8$, of the oxygen molecule $^{16}O^{16}O$ in its metastable state, $a^1\Delta_g$, $v = 0$, are observed using six fir laser lines. Taking the known values of the g factors, their zero-field frequencies are obtained as 340.0085(6), 424.9810(9), 594.870(1), 679.780(1), and 764.658(1) GHz, respectively. They are fit by $(E/h) = B_0[J(J+1) - 4] + D_0[J(J+1) - 4]^2 + (-1)^J (1/2)qJ\ (J+1)[J(J+1) - 2]$, where $B_0 = 42.50457(10)$ GHz, $D_0 = 153.14(110)$ kHz, and $q = 0.050(90)$ kHz.

INTRODUCTION

The electronic configuration $(1s\sigma_g)^2(1s\sigma_u)^2(2s\sigma_u)^2(2p\sigma_g)^2(2p\sigma_u)^4(2p\pi_g)^2$ in the oxygen molecule gives rise to the three lowest energy electronic states, $X^3\Sigma_g^-$, $a^1\Delta_g$, and $b^1\Sigma_g^+$, all of which are stable against dissociation. The first electronic excited state, $a^1\Delta_g$, is metastable with a radiative lifetime of 45 min (*1*) since the transition to the ground state, $X^3\Sigma_g^-$, is doubly forbidden.

The rotational levels, including the triplet structures, of the ground state, $X^3\Sigma_g^-$, have been thoroughly investigated by both microwave (*2, 3*) and laser magnetic resonance (LMR) (*4*) spectroscopy. The vibronic levels of the $a^1\Delta_g$ state were observed by Herzberg and Herzberg (*5*) in the ir. They obtained $\bar{B}_0 = 1.41783\ \text{cm}^{-1}$ ($\times$42.5055 GHz), and $D_0 = 4.86 \times 10^{-6}\ \text{cm}^{-1}$ (=145.7 kHz) for the rotational constants in the $v = 0$ states.

In obtaining the above values it was assumed that the rotational energies were given by

$$F(J) = \bar{B}_0 J(J+1) - D_0 J^2(J+1)^2. \tag{1}$$

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However, since J, the total angular momentum, has a component $\Lambda = 2$ along the molecular axis, but only the component of J perpendicular to the molecular axis contributes to the rotational energy, it is more appropriate to express the rotational energies as

$$F(J) = B_0[J(J+1) - 4] - D_0[J(J+1) - 4]^2. \tag{2}$$

We see that

$$B_0 = \bar{B}_0 - 8D_0 \tag{3}$$

by comparing (1) with (2). Herzberg and Herzberg's value (*5*) gives $B_0 = 42.5043$ GHz.

The Λ (doubling) perturbation to the rotational energy of the J level of the $a^1\Delta_g$ state should be given by

$$(E_\Lambda/h) = (-1)^J(1/2)qJ(J+1)[J(J+1) - 2], \tag{4}$$

where the coupling coefficient q is defined by Mizushima (*6*). Theoretically, we expect q to be much smaller than D_0. In the case of the $^{16}O^{16}O$, the $a^1\Delta_g$ state is nondegenerate because of the Pauli principle: only c states (Kronig symmetry $(-1)^J$ states) exist for even J and only d states for odd J. Even though no actual doubling is expected, rotational levels of even and odd J should be affected differently by the perturbation, E_Λ. Such effects were not detected in the work of Herzberg and Herzberg (*5*).

The external magnetic field produces additional contributions to each rotational state given by

$$\langle JM|H_z|JM\rangle = \mu_B B\,\frac{4M}{J(J+1)}\,[g - (1/4)(J(J+1) - 4)g_N],$$

$$\langle J-1M|H_z|JM\rangle = \mu_B B\,\frac{2}{J}\,\frac{(J^2-4)(J^2-M^2)}{4J^3-1}\,(g + g_N), \tag{5}$$

where B is the magnetic flux density, μ_B is the Bohr magneton, and g and g_N are the electronic and rotational g factors defined by Mizushima (*6*).

Miller (*7*) observed the EPR spectrum of $a^1\Delta_g$ O_2 in the $J = 2$ and $J = 3$ rotational states ($v = 0$) and found that $g = 0.999866$ and $g_N = -1.234\ 10^{-4}$. This result was confirmed by Arrington *et al.* (*8*).

EXPERIMENTAL DETAILS

Most of the spectra of $a^1\Delta_g$ O_2 were taken with a laser magnetic resonance spectrometer that has been described previously (*9*) (Fig. 1). It consists of an open-structure fir laser cavity pumped transversely by a 30-W, line-tunable cw CO_2 laser. This system has been modified by the addition of a variable coupling mirror, 6 mm in diameter and mounted at 45° on a rod sliding perpendicular to the laser axis. This coupling mirror is inserted a selected distance into the laser mode, and couples a small fraction of the laser power out of a polyethylene side window into the liquid-helium-cooled germanium bolometer.

Metastable O_2 was generated by flowing ultrapure O_2 through a 2450-MHz dis-

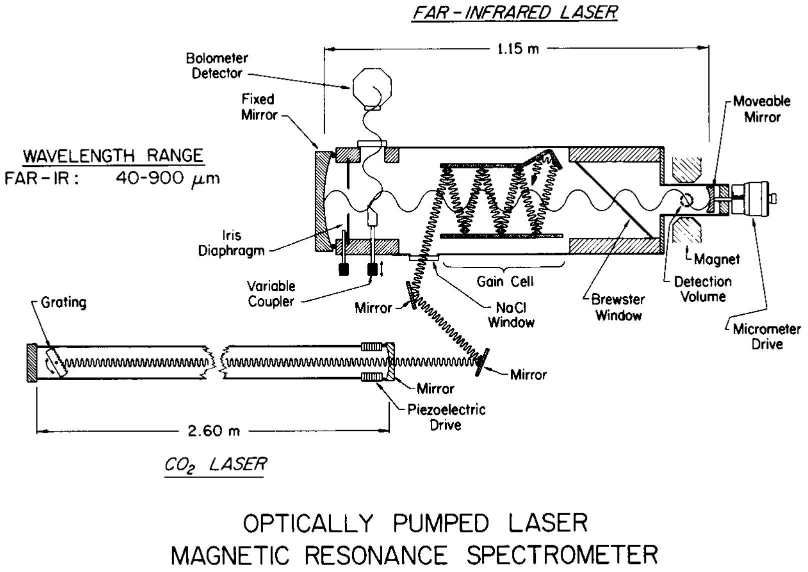

FIG. 1. Diagram of the optically pumped laser magnetic resonance spectrometer.

charge located about 10 cm above the intracavity sample region, which is separated from the laser gain cell by a thin polypropylene membrane set at the Brewster angle. Most of the data were taken at a pressure of 93 Pa (133 Pa = 1 Torr). The density of $a^1\Delta_g$ molecules reaching the detection volume was sufficiently large so that a low operating pressure could be used. For example, the 392-μm CH_3OH LMR spectrum was taken at 8 Pa, so that pressure broadening of this transition ($J = 9 \leftarrow 8$) was reduced below the Doppler limit, and the overlapped sequence of lines was therefore much better resolved.

TABLE I

FIR Laser Lines Used in this Work

Transition	Laser Line	ν_L(GHz)
$J = 4 \leftarrow 3$	888.9 μm ($C_2H_2F_2$)	337.2770*
$J = 4 \leftarrow 3$	889.1 μm ($C_2H_2F_2$)	337.1921*
$J = 5 \leftarrow 4$	699.4 μm (CH_3OH)	428.6285
$J = 7 \leftarrow 6$	503.0 μm (CH_2F_2)	595.9417
$J = 8 \leftarrow 7$	442.2 μm (CH_2CHCl)	678.0061
$J = 9 \leftarrow 8$	392.1 μm (CH_3OH)	764.6426

*Frequencies measured for this experiment (unpublished data, F. R. Petersen and K. M. Evenson). Other data are from Reference 10. Fractional uncertainties in the frequencies (70% confidence limits) are $\pm 5 \times 10^{-7}$, but must be multiplied by $\sqrt{2}$ to account for the resetability of the LMR spectrometer to the center of the gain curve of each FIR line.

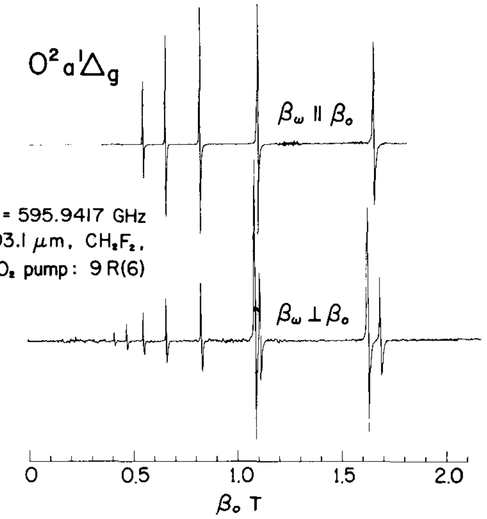

FIG. 2. Laser magnetic resonance spectrum of the $J = 7 \leftarrow 6$ transition of $a^1\Delta_g$ O_2 observed with the 503-μm line of CH_2F_2.

Since O_2 has no permanent electric dipole moment, only magnetic dipole and electric quadrupole rotational transitions are allowed for the $a^1\Delta_g$ state. The magnetic dipole transitions are stronger by several orders of magnitude; all of the observed spectra are of this type. Both $\Delta m = 0$ and $\Delta m = \pm 1$ transitions were observed for each laser line. This was accomplished by rotation of the Brewster angle membrane such that the fir laser $\mathbf{B}_\omega$ field was aligned either parallel or perpendicular to the dc magnetic field $\mathbf{B}$ provided by a 38-cm electromagnet.

A modulation field, varying sinusoidally at 4 kHz, was generated by a set of Helmholz coils wound on the pole faces of the electromagnet. Flux densities as high as 5 mT could be obtained in this manner. Absorption lines magnetically tuned into coincidence with the fir laser frequency were modulated at 4 kHz by this field, and synchronously demodulated with a lock-in amplifier. The resulting lineshape is then approximately the derivative of the absorption.

The magnetic flux densities were measured with an NMR gaussmeter. A correction between the position of the NMR probe and the sample region of the laser cavity was mapped over the entire range of flux densities that were accessible. In this manner, accuracies of 5×10^{-5} T were obtained.

Five different pure rotational transitions were observed with this system. These are listed in Table I. The $J = 7 \leftarrow 6$ transition, observed with the 503.4-μm CH_2F_2 laser line (*11*) is shown in Fig. 2. The upper trace is taken with parallel polarization ($B_\omega \parallel B$), while the lower is taken with perpendicular polarization ($B_\omega \perp B$). The magnetic field was swept from 0 to 2 T; three of the four predicted parallel lines are observed in this range.

The $J = 9 \leftarrow 8$ transition at 392.1 μm (CH_3OH) was also observed in the newly constructed glow discharge LMR spectrometer used previously to detect HBr^+ ions (*12*), 2^3P O atoms (*13*), $a^3\Pi$ CO (*14*), and other transient molecules. In this spec-

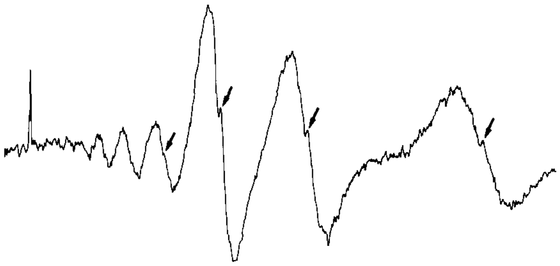

FIG. 3. Laser magnetic resonance spectrum of the $J = 9 \leftarrow 8$ transition of $a\,^1\Delta_g O_2$ observed with the 392.1-μm line of CH_3OH with $B_\omega \perp B_0$. Saturation peaks are marked with arrows.

trometer, the positive column of a dc glow discharge is contained inside the sample region of the laser cavity. The fir gain cell is very similar to that of the previously described system in Fig. 1. The magnetic field is provided by a 33 cm long × 7.6 cm diameter solenoid magnet cooled with liquid nitrogen. Flux densities up to 0.60 T could be obtained with homogeneities of roughly 0.1% over a 15-cm length. The modulation field was provided by a solenoidal coil mounted concentrically with the magnet. Field measurements were made by monitoring the voltage across a precision resistor immersed in constant-temperature oil bath in series with the magnet. The actual field was obtained by measuring the field inside the solenoid with an NMR gaussmeter as a function of magnet current. Field measurements with this system are reliable to $\pm 2 \times 10^{-4}$ T. The rest of the flow discharge spectrometer is similar to the system described earlier. The optimum signal strength was obtained with pressure near 133 Pa and discharge currents near 50 mA in pure O_2. A mixture of He and O_2, which clearly enhanced the 2^3PO atom densities in the discharge (*13*) predictably gave much weaker signals.

Because of the excellent signal-to-noise ratio obtained with the 392.1-μm laser line, we were able to reduce the pressure to as low as 4 Pa. At these low pressures and with the higher power density in this spectrometer, we could clearly observe saturation peaks (inverse Lamb dips) in these magnetic dipole lines. A LMR spectrum of the $J = 9 \leftarrow 8$ transition at 392.1 μm from 0 to 0.1 T, exhibiting the saturated absorption features, is shown in Fig. 3. The peaks appear in the center of the derivative lineshapes with opposite modulation phase from the Doppler line profiles.

ANALYSIS

Each set of data for a given laser line of frequency ν_L was fitted by using the known values of g and g_N, including both first- and second-order Zeeman terms given by (5), and by adjusting the zero-field transition frequency ν_0 for $J \rightarrow J + 1$. Table II,a through f, shows the fits and values of ν_0 obtained in this way for the five transitions we observed.

These zero-field transition frequencies are represented by a sum of the rotational energy E_{rot}, given by (2), and the Λ (doubling) perturbation E_Λ, given by (4). The

TABLE II

LMR Spectra of O_2 ($a^1\Delta_g$, $v = 0$)

a. J = 4←3. ν_L = 337.2770 GHz. ν_0 = 340.0085(6) GHz.

B(Tesla)	0.4939	0.7443
M	3←3	2←2
B theo.	0.4937	0.7441

b. J = 4←3. ν_L = 337.1921 GHz. ν_0 = 340.0085(6) GHz.

B(Tesla)	0.5095	0.7679	1.578	0.3380	0.4347	0.6089	1.0184	1.0270
M	3←3	2←2	1←1	2←3	1←2	0←1	1←0	4←3
B theo.	0.5093	0.7681	1.578	0.3380	0.4347	0.6090	1.0184	1.0256

c. J = 5←4. ν_L = 428.6285 GHz. ν_0 = 424.9810(9) GHz.

B(Tesla)	0.9561	1.2738	1.905	0.6419	0.7715	0.9668	1.2962	1.889	1.961
M	-4←-4	-3←-3	-2←-2	-3←-4	-2←-3	-1←-2	0←-1	-5←-4	1←0
B theo.	0.9556	1.2743	1.910	0.6416	0.7713	0.9670	1.2961	1.885	1.967

d. J = 7←6. ν_L = 595.9417 GHz. ν_0 = 594.870(1) GHz.

B(Tesla)	0.5307	0.6374	0.7978	1.0673	1.613	0.3546	0.3993	0.4567	0.5335	0.6416	0.8049	1.0555	1.0817	1.590	1.652
M	-6←-6	-5←-5	-4←-4	-3←-3	-2←-2	-5←-6	-4←-5	-3←-4	-2←-3	-2←-1	-1←0	-7←-6	1←0	-6←-5	2←1
B theo.	0.5304	0.6372	0.7976	1.0670	1.615	0.3547	0.3994	0.4569	0.5337	0.6419	0.8054	1.0550	1.0811	1.590	1.649

e. J = 8←7. ν_L = 678.0061 GHz. ν_0 = 679.780(1) GHz.

B(Tesla)	1.1674	1.3595	1.626	2.016	0.7767	0.8515	0.9	1.0732	1.2336	1.4501	1.767
M	7←7	6←6	5←5	4←4	8←7	5←6	4←5	3←4	2←3	1←2	0←1
B theo.	1.1671	1.3593	1.6269	2.0235	0.7714	0.8513	0.9484	1.0733	1.2340	1.4509	1.7593

f. J = 9←8. ν_L = 764.6426 GHz. ν_0 = 764.658(1) GHz.

B(Tesla)	0.0123	0.0137	0.0164	0.0194	0.0243	0.0324	0.0479	0.0958	0.0097	0.0109	0.0123	0.0140	0.0161	0.0194	0.0241	0.0320	0.0482	0.0976
*			0.0162		0.0244	0.325			0.0097	0.0108	0.0122	0.0140	0.0162	0.0195	0.0244	0.0325	0.0482	0.0943
M	8←8	7←7	6←6	5←5	4←4	3←3	2←2	1←1	5←6	4←5	3←4	2←3	1←2	0←1	-1←0	-2←-1	-3←-2	-4←-3
B theo.	0.0122	0.0139	0.0162	0.0195	0.0243	0.0323	0.0485	0.0970	0.0097	0.0108	0.0121	0.0139	0.0162	0.0196	0.0242	0.0323	0.0483	0.0960

*Saturation peak measurements

TABLE III

Observed and Calculated Frequencies (GHz) of Rotational Transitions in $^{16}O^{16}O$ ($a^1\Delta_g$, $v = 0$). Molecular Parameters used in the Calculation are $B_0 = 42.50457(10)$ GHz, $D_0 = 153.14(110)$ kHz, $q = 0.050(90)$ kHz

Transition	$3\leftarrow2$	$4\leftarrow3$	$5\leftarrow4$	$6\leftarrow5$	$7\leftarrow6$	$8\leftarrow7$	$9\leftarrow8$
ν(obs.)		340.0085(6)	424.9810(9)		594.870(1)	679.780(1)	764.658(1)
ν(theo.)	255.0182	340.0072	424.9813	509.9373	594.871	679.780	764.657

least-squares fit to the observed five frequencies yielded the following values of the molecular parameters:

$$B_0 = 42.50457(10) \text{ GHz}, \qquad D_0 = 153.14(110) \text{ kHz}, \qquad q = 0.050(90) \text{ kHz}, \quad (6)$$

where the uncertainties are 70% confidence limits. These values are more accurate than the previously proposed values (*5*), $B_0 = 42.5043$ GHz, $D_0 = 145.7$ kHz, and the new term, q, has the correct sign and order of magnitude expected from theory (*6*).

The fit shown in Table III is not quite satisfactory, since the deviation between observed and calculated values is about 1 MHz in two transitions, while the uncertainty in the laser frequencies is about 0.5 MHz. It is desirable to examine low-J transitions more carefully, and we plan to do so soon.

DISCUSSION

In Table III, frequencies for unobserved transitions, $J = 3 \leftarrow 2$ and $6 \leftarrow 5$, are also shown. These results should permit astronomers and atmospheric scientists to search for these transitions in the atmosphere and possibly extraterrestrial sources with higher precision than before.

Since the emission due to the $a^1\Delta_g \rightarrow X^3\Sigma_g^-$ transition at 8000 cm^{-1} is observed in the night airglow (*15*), we expect that some of the rotational lines studied here will be observable in the upper atmosphere; particularly the 255 GHz ($J = 3 \leftarrow 2$) line, which lies between water absorption lines.

The detection of $a^1\Delta_g$ O_2 transitions by LMR will provide a mean to monitor this state in chemical reactions. The role of metastable O_2 in atmospheric chemistry is presently receiving increased attention, and such kinetic studies could well provide important information on atmospheric processes.

Finally, because the $a^1\Delta_g$ state is important in biological, photochemical, and physical chemical systems, and because of interest in using it to pump an energy transfer laser (*16*), it is generally important to thoroughly understand its spectroscopy. With the present study taken in conjunction with the earlier ir and EPR work, we now have a rather complete set of spectroscopic data available for it.

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