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ELECTRON PARAMAGNETIC RESONANCE ABSORPTION IN OXYGEN WITH THE HCN LASER

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Paramagnetic resonance absorption between the $N=3, J=4, M=-4$ and $N=5, J=5, M=-4$ levels of ground state O_2 was observed at the HCN laser frequency of $890\,759 \pm 3$ MHz in a magnetic field of $16\,418 \pm 1$ G. This is the first observation of absorption in a gaseous sample in which laser electron-paramagnetic-resonance techniques were used.

In an extension of previous work,¹⁻⁴ a calculation of the effect of magnetic fields on molecular oxygen has shown that the difference between the $N=3, J=4, M=-4$ and $N=5, J=5, M=-4$ levels of ground-state molecular oxygen equals the HCN laser frequency of 890 GHz in a magnetic field of about 16.4 kG as is shown in Fig. 1. This note reports the first paramagnetic resonance absorption between these levels and the first laser electron paramagnetic resonance (LEPR) absorption⁵ in a gaseous sample. The observations were made utilizing a specially constructed LEPR spectrometer.

An HCN laser 7.5 cm in diameter and 2 m long was tuned to the 337- μ line. The center frequency of this line was measured to be $890\,759.4 \pm 0.1$ MHz⁶ in agreement with Hocker et al.⁷ Significant improvement in the short term (0.1-sec) stability of the laser was obtained by using a current-regulated power supply and 120-mA neon-sign hot hollow cathodes operating at 600 mA. Laser-frequency drift during the 5- or 10-min scan was less than 3 MHz at maximum power output.

The laser beam was focused into a Fabry-Perot interferometer consisting of a 10-cm long cylinder 1.7 cm in diameter with one flat mirror and a 15-cm focal length mirror. Each mirror had a 0.75-mm hole in order to operate the Fa-

bry-Perot interferometer as a transmission cavity whose Q was approximately 5×10^4 . The interferometer was centered in the 2-in. gap of a 15-in. magnet with 5-in., tapered, Rose-shimmed pole faces. Radiation transmitted through the cell was directed by a $\frac{1}{4}$ -in. copper pipe to a Golay cell placed outside the magnetic field 75 cm from the center of the magnet. The output of the Golay cell was connected to a 13.5-Hz phase detector referenced to the modulation of the magnetic field.

Figure 2 shows the derivative of the absorption observed at a pressure of 7.5 Torr with approximately a 10-G modulation field. The maximum absorption in Fig. 2 corresponded to about one part in 10^4 of the radiation transmitted through the Fabry-Perot cavity; this high sensitivity was largely due to the extreme stability of the laser discharge. Linewidths from 3 to 25 G were observed at pressures between 2 and 19 Torr, yielding values of the linewidth parameter of about 1.8 MHz/Torr in agreement with Zimmerman and Mizushima.² An asymmetrical line shape was observed even though linewidths were increased by an order of magnitude by pressure broadening and the modulation reduced to about one-fourth the linewidth.

Since the ground state of the oxygen molecule is $^3\Sigma_g^-$, the rotational quantum number N of the

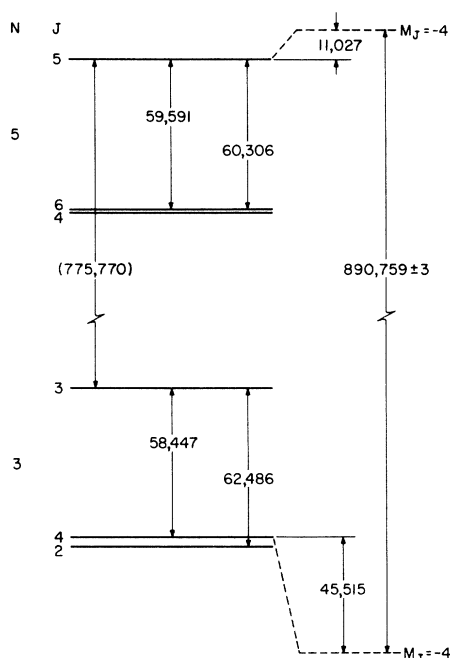


FIG. 1. $N=3$ and $N=5$ levels of the ground state (${}^3\Sigma_g^-$) of the oxygen molecule; dashed line indicates the energy levels of the $M=-4$ states at a magnetic field of 16 418 G between which the observed LEPR transitions take place. The g values for these states from the top to bottom are 0.066 74, 0.3229, -0.3951 , 0.1669, 0.4952, and -0.6667 . Energies are in MHz.

oxygen molecule ($\text{O}^{16}\text{O}^{16}$) can take odd integers only and the spin quantum number $S=1$. The effective Hamiltonian for the rotational levels of

$$\langle NSJM_J | \mathcal{H}' | NSJM_J \rangle = 1.0012 \hbar \mu_B M_J B \left[1 + \frac{2-N(N+1)}{J(J+1)} \right]$$

and

$$\langle NSJM_J | \mathcal{H}' | NS(J+1)M_J \rangle = -1.0012 \hbar \mu_B B \left[\frac{\{(J+1)^2 - M^2\}(J+N)(J+N+3)(J-N+2)(N-J+1)}{(J+1)^2(2J+1)(2J+3)} \right]^{1/2}. \quad (3)$$

The actual wave function of each rotational state of the oxygen molecule is not exactly $|NSJM_J\rangle$ but, due to the λ terms in Eq. (1), is given by

$$\begin{aligned} a_J |J-1SJM_J\rangle + b_J |J+1SJM_J\rangle & \text{ when } N \cong J-1, \\ b_J |J-1SJM_J\rangle - a_J |J+1SJM_J\rangle & \text{ when } N \cong J+1, \end{aligned} \quad (4)$$

and

$$|JSJM_J\rangle \text{ when } N=J.$$

Using the known coupling constants,^{2,4} the calculated mixing coefficients a_J and b_J are shown in Table I.

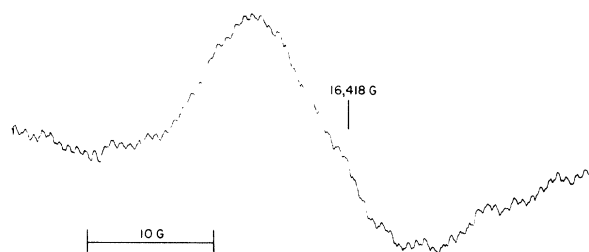


FIG. 2. LEPR trace of the transition between the $N=5, J=5, M=-4$ and $N=3, J=4, M=-4$ levels at a pressure of 7.5 Torr with a modulation of about 10 G and with a 3-sec time constant. A decreasing base line is visible on the trace.

ground-state molecular oxygen is

$$\begin{aligned} \mathcal{H} = & B_0 N^2 + B_1 N^4 + B_2 N^6 + \frac{2}{3}(\lambda_0 + \lambda_1 N^2)(3S_z^2 - S^2) \\ & + (\mu_0 + \mu_1 N^2) \mathbf{N} \cdot \mathbf{S}. \end{aligned} \quad (1)$$

The coupling constants B_0 , B_1 , B_2 , λ_0 , λ_1 , μ_0 , and μ_1 have been determined²⁻⁴ from microwave absorption lines in the 60-GHz region. Hill and Gordy¹ and Zimmerer and Mizushima² observed the Zeeman effect; the electron paramagnetic resonance has been measured by Beringer and Castle,⁸ and by Tinkham and Strandberg^{9,10} in the X-band and S-band regions. An external magnetic field B causes a perturbation given by

$$\mathcal{H}' = 2.0023 \mu_B \mathbf{S} \cdot \mathbf{B}, \quad (2)$$

where μ_B is the Bohr magneton.

If the $|NSJM_J\rangle$ representation is taken with $S=1$ and $J=N, N+1$, or $N-1$, then

Table I. a_J and b_J for zero field.

J	2	4	6	8
a_J	0.990	0.997	0.999	0.999
b_J	0.139	0.077	0.053	0.041

The Zeeman shift of each level is given by $E = 1.399\,57gM_JB$ (MHz, when B is in gauss) where

$$\begin{aligned}
 g &= 2.0023 \left(\frac{a_{N+1}^2}{N+1} - \frac{b_{N+1}^2}{N+2} \right) \text{ when } N \cong J+1, \\
 &= 2.0023 \left(-\frac{a_{N-1}^2}{N} + \frac{b_{N-1}^2}{N-1} \right) \text{ when } N \cong J-1, \\
 &= \frac{2.0023}{N(N+1)} \text{ when } N=J.
 \end{aligned} \quad (5)$$

Numerical values of the g factors are listed below Fig. 1 for the relevant levels. Transition frequencies within each triplet shown in Fig. 1 were measured directly,⁴ while the frequency between $N=3$ and $N=5$ levels is derived from the present measurement. Energy levels of interest at 16 418 G were calculated using the nondiagonal matrix elements given by West⁴ with the mixing coefficients a_J and b_J calculated at zero field (Table I).

The upper state ($N=5$) of the observed transition is such that, if adiabatically followed to zero field, it reduces to the $J=5$ level. In an external magnetic field the wave function of this state is a mixture of $J=6, 5,$ and $4,$ and at 16.4 kG is predominantly $J=4.$

A zero-field energy difference of $775\,770 \pm 10$ MHz between the $N=3, J=3$ and $N=5, J=5$ energy levels was determined by subtracting the calculated 16 418-G energy shifts of the $N=5, J=5$ and $N=3, J=3$ levels (11 027 and 45 515 MHz) and the measured energy difference between $N=3, J=3$ and $N=3, J=4$ (58 447 MHz) from the laser frequency (890 759 MHz). This frequency is theoretically given by

$$\begin{aligned}
 \nu &= f(N=5) - f(N=3), \\
 \text{where} \\
 f(N) &= B_0 N(N+1) + B_1 N^2(N+1)^2 \\
 &\quad + B_2 N^3(N+1)^3.
 \end{aligned} \quad (6)$$

Using values of the parameters $B_0 = 43\,100.3$ MHz, $B_1 = -0.092$ MHz, and $B_2 = (5 \pm 2)$ Hz, obtained from microwave spectroscopy,⁴ $\nu = 775\,730 \pm 50$ MHz, where the uncertainty of ± 50 MHz is due to the uncertainty in $B_2.$ The more precise value from this experiment, $775\,770 \pm 10$ MHz, results from an accurate knowledge of the laser frequency, the previously measured transition between the ($N=3, J=4$) and ($N=3, J=3$) levels, and an accurate calculation of the Zeeman shifts. This satisfactory agreement with the above computed value verifies our identification of the transition.

For the observed transition, $\Delta M=0;$ such transitions have not been observed in X-band EPR absorption because of the small transition moment. Further calculations indicate other possible transitions in this region. Work is now in progress to observe these with an improved version of the present LEPR spectrometer.

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