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THE PARAMAGNETIC RESONANCE SPECTRUM OF 1/ g OXYGEN MOLECULE

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THE PARAMAGNETIC RESONANCE SPECTRUM  
OF THE  $^1\Delta_g$  OXYGEN MOLECULE

Berkeley, California

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Arnold M. Falick, Bruce H. Mahan, and Rollie J. Myers

FEB 1965

The Paramagnetic Resonance Spectrum of the  $^1\Delta_g$  Oxygen Molecule

by

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Recently there has been considerable interest in the chemistry<sup>1,2</sup> and emission spectra<sup>3,4</sup> of both discharged oxygen and the product of the hydrogen peroxide-hypochlorite reaction. It is known<sup>4,5</sup> that oxygen molecules in the  $^1\Delta_g$  state are present in these systems. We have detected and analysed the paramagnetic resonance spectrum of  $^1\Delta_g$  molecules in discharged oxygen and established a method for determining their absolute concentration.

Industrial grade oxygen at pressures of 0.3-0.5 torr was passed through a glass wool packed trap at  $-183^\circ\text{C}$ , then through a 2450 mc/s 500 watt discharge and down a 10 mm dia. quartz tube located in a Varian V-4531 e.p.r. cavity. At these pressures flow rates were 100-150  $\text{cm}^3/\text{sec}$  and the time elapsed between the discharge and the detection cavity was approximately  $3/4$  sec.

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\* National Science Foundation Predoctoral Fellow 1962-64.

† Alfred P. Sloan Fellow

We have observed the  $\Delta M_J = 1$  transitions for the  $J = 2$  rotational state. These transitions are split into a nearly symmetric quartet by the effect of the off-diagonal Zeeman interaction with the  $J = 3$  state. The energy for the interaction of the magnetic moment associated with  $\Lambda$  and an external magnetic field  $H$  can be expressed as

$$\begin{aligned} \epsilon &= \frac{-g_L \Lambda^2 H}{J(J+1)} M_J + \text{higher order terms} \\ &= -g_J H M_J + \text{higher order terms} \end{aligned}$$

In our case  $J = \Lambda = 2$  and  $g_L \sim -1$  so that  $g_J \sim -2/3$ . The higher order terms can be directly calculated from the known<sup>6</sup> rotational constant of the  ${}^1\Delta_g$  state of  $O_2$ . A comparison of observed and calculated  $g$  values is given in Table I.

It can be seen from Table I that a single adjustable parameter  $g_J = -0.66662$  gives a very good fit to the data. There is a small systematic deviation between the calculated and observed values that could be eliminated by using a  $B_0$  value which is smaller by  $3 \times 10^{-3} \text{ cm}^{-1}$  from the spectroscopic value. It is not clear at this time if this correction is justified.

Our assigned  $g_J$  value must contain some contribution from the rotational magnetic moment, but with only transitions of a single  $J$  value it is not possible to determine  $g_r$ . If the  $g_r$  value for the  ${}^1\Delta_g$  state is identical to that for the ground  ${}^3\Sigma_g^-$  state,<sup>7</sup> then one can obtain a value for  $g_L = -0.99987$ . This value differs from  $-1.0$  by about the same

amount that the Landé  $g$  value for the O-atom  $^3P$  state<sup>8</sup> differs from its simple theoretical value, corrected for the electron spin anomaly. From this fact we can conclude that most of the reduction in the  $g_L$  value is due to a diamagnetic correction and not due to rotationally induced mixing with  $^1\Sigma$  and  $^1\pi$  states.

The size of the  $^1\Delta_g$  signal indicated a concentration of 10% of the  $^3\Sigma_g^-$  ground state of  $O_2$ . Under the same conditions, the concentration of oxygen atoms was approximately 20% of the total. The concentration of molecules in the  $^1\Delta_g$  state was unaffected by removal of the cold trap or addition of water vapor prior to the discharge. When oxygen atoms were completely removed by titration with  $NO_2$  at a point immediately downstream from the discharge, only a slight diminution of the  $^1\Delta_g$  signal occurred, and this change could be attributed to dilution effects. Thus  $^1\Delta_g$  molecules are formed principally in the discharge region, and not by recombination of atoms downstream. Furthermore, oxygen molecules in the  $^1\Delta_g$  state do not react rapidly, if at all with  $NO$  or  $NO_2$ .

In some experiments double titrations were performed. Oxygen atoms were removed with  $NO_2$  immediately after the discharge, and ethylene was added at a point halfway between the discharge and the detection cavity. The signal from  $^1\Delta_g$  oxygen molecules was reduced and could be eliminated by the addition of small amounts of ethylene. When ethylene alone was added, the green  $NO-O$  afterglow from the discharge could be extinguished without diminishing the  $^1\Delta_g$  signal. Thus

oxygen molecules in the  $^1\Delta_g$  state react with ethylene at a rate which is smaller than that of the ethylene-oxygen atom reaction.

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Table I

The Observed Spectrum for  ${}^1\Delta_g \text{O}_2$ 

Transition $M_J$	Field (gauss)	$h\nu/\mu_o H$	
		obs. (a)	cal. (b)
-2 $\rightarrow$ -1	10,090.3	0.65596	0.65598
-1 $\rightarrow$ 0	9,988.7	0.66264	0.66265
0 $\rightarrow$ 1	9,885.6	0.66956	0.66955
1 $\rightarrow$ 2	9,781.4	0.67670	0.67668

(a)  $\mu_o/h = 13.9960 \times 10^5 \text{ G}^{-1} \text{ sec}^{-1}$ .

(b) With  $g_J = -0.66662$  and assuming  $B_o = 1.4178 \text{ cm}^{-1}$  (see ref. 6).

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