Electron Paramagnetic Resonance Spectrum of O$_2$(\(\Delta_g\))—Its \(^{17}\)O Hyperfine Coupling and Electronic and Rotational \(g\) Values

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The \(^{17}\)O hyperfine coupling was measured for O$_2$(\(\Delta_g\)) in its \(J=2\) angular momentum state. The coupling constant \(2g_{17O}/\mu_B(S_{17O}/r^3)\) was measured to be \(-424 \pm 1\) MHz. From this value we can follow Harvey's convention and determine \((1/r^3)=39.8 \times 10^{-26}\) cm$^3$. The previous work by Miller et al. on O$_2$(\(2\Sigma_g^+\)) can be used to determine \((1/r^3)=43.6 \times 10^{-26}\) cm$^3$. Even though these two values refer to different electronic states, they are in the same ratio that Harvey found for O(\(3\Pi\)), but they are both appreciably larger than the values he found for O(\(3\Pi\)). The \(g\) values were determined for both the \(J=2\) and \(J=3\) angular momentum states. From these values we obtain \(g_L=0.99986\) and \(g_L=-1.7 \times 10^{-4}\). The \(g\) value is very close to the recent determination of Miller, but the \(g_L\) value does not agree with Miller's work.

Previous work$^1$ has shown that the metastable \(^1\Delta_g\) excited electronic state of O$_2$ can be detected by electron paramagnetic resonance (EPR) spectroscopy in the gas phase. It can be generated by an electrical discharge through O$_2$ and by a variety of chemical techniques. It appears to have considerable importance in oxidation reactions including those involved in the production of photochemical smog. We have continued our EPR work on this species to include the \(^{17}\)O hyperfine interaction and a determination of the electronic and rotational \(g\) values.

Our results for the hyperfine interaction of O$_2$(\(\Delta_g\)) will be compared with the previous work on the atomic and molecular ground states of oxygen, O$_2$(\(2\Sigma_g^+\)) and O(\(3\Pi\)). The \(^{17}\)O hyperfine coupling constant is a measure of \((1/r^3)\) for the unpaired electrons. Accurate theoretical estimates of \((1/r^3)\) are still not available for either electronic state of O$_2$.

The electronic and rotational \(g\) values depend upon a variety of characteristics of the electronic wavefunction. Since they involve absolute field measurements, the experimental determinations of these quantities are difficult. After our work was in manuscript stage we received a copy of a O$_2$(\(\Delta_g\)) \(g\)-value measurement by Miller.$^2$ Comparison will be made with Miller's results which appear to be of high accuracy.

**EXPERIMENTAL**

The \(^1\Delta_g\) state of O$_2$ was generated in a flowing gas stream by an electrical discharge. For the \(^{17}\)O work we used a 2450-MHz 100-W unit and cavity,$^2$ while for the \(g\)-value work we used a 13-MHz radio frequency electrodeless discharge. In the \(^{17}\)O work the gas was recycled by means of a mercury diffusion pump of conventional design. We started with enriched oxygen$^3$ consisting of 50% oxygen-18, 30% oxygen-16, and 20% oxygen-17. At the end of each run the enriched O$_2$ was condensed into an activated charcoal trap at 77$^\circ$K. The enriched O$_2$ could be returned to the flow system by warming the trap to room temperature.

Typical pressures in the \(^{17}\)O work were 0.8 torr. At this pressure it was possible to get the maximum \(^1\Delta_g\) signal and still keep the mercury recycling pump in operation. A single charge of enriched O$_2$ was good for about 20 h of discharge and recycling time. The O$_2$ slowly reacted with the hot mercury in the pump and the percentage of oxygen-16 slowly increased in the recycled gas. For the \(g\)-value work we simply used dry tank O$_2$ in a fast flow system at a pressure of about 0.6 torr.

The \(^{17}\)O measurements were made with a standard 100-kHz field modulated X-band EPR spectrometer. The sample was pumped through a quartz lined Varian V4333 cylindrical cavity. Field measurements were made with a commercial NMR gaussmeter. The cavity frequency in the \(TE_{111}\) mode was 9.082 GHz.

The \(g\)-value measurements were made with a specially constructed S-band spectrometer. A rectangular resonant cavity was made from a section of S-band waveguide in which the center part of the broad wall was replaced with 5X$10^{-4}$ in. silver foil. The gas flowed through a quartz pill box, with side arms, which almost filled the center of the \(TE_{101}\) cavity. The two modulation coils were mounted on the outside of 1/4-in. thick plastic sheets which supported the silver foil walls. The final cavity frequency was about 3.13 GHz, and its \(Q\) was close to 10 000.

The microwave source was a HP 8616A signal generator which was locked to the cavity frequency by means of photon coupling$^4$ and frequency modulation with phase detection at 10 kHz. The cavity was critically coupled to the line and the microwave bridge was constructed using a 4-port S-band waveguide circulator. The magnet had 12-in. diam pole caps and a 2$\frac{1}{2}$ in. gap. The modulation coils were quite close to the pole caps which gave severe eddy current loss at 100 kHz. For this reason, the modulation coils were driven in a nonresonant circuit by a 600 $\Omega$ output impedance power amplifier.

The magnetic field was measured with a proton NMR which was locked to the magnetic field. The circuits for this device were similar to those of Maki and Volpicelli.$^6$ Our primary standard was a proton probe doped to the 0.1-0.2 $M$ level with Cu(NO$_3$)$_2$. With this
level of Cu\textsuperscript{2+} the proton resonance is shifted from its pure water value by less than 0.1 ppm. We used the 1963 N.B.S. value of 4257.59 Hz G\textsuperscript{-1} to convert the proton resonant frequencies to magnetic field values.

In order to correct for the positional field shift between the sample and the primary standard probe we used a commercial Harvey Wells NMR instrument and its associated probe. This probe was placed in the same position in the magnet that the sample occupied and the difference between the two NMR systems was recorded over the full range of magnetic fields employed. We did find that the Harvey Wells probe and our primary standard NMR did not give the same frequency in the same magnetic field. The Harvey Wells probe was found to be shifted to higher frequencies by +10 ppm. It is probable that the encapsulated Harvey Wells probe is doped with Mn\textsuperscript{2+}, Fe\textsuperscript{2+}, or some other ion which gives a large contact shift.\textsuperscript{7} The +10 ppm is a rather large shift and it may be due, in part, to the encapsulation.

Since we wanted to know the centers of the EPR lines for the g-value work as accurately as possible, we averaged the data from several spectra and fit them by a least-squares procedure to a Lorentz line shape. We utilized the magnetic tape data acquisition system and least-squares programs previously described.\textsuperscript{8} Since both the NMR and EPR signals can have a time shift, an average of the line centers for both up-field and down-field sweeps was used. A difference of 0.5 G was typical between the up- and down-field sweeps.

**THE EPR SPECTRUM**

The basic features of the EPR spectrum for O\textsubscript{2}(1\textsuperscript{Δ_g}) can be described in terms of an electronic angular momentum (\(\Lambda = 2\)) which is quantized along the internuclear axis (Hund’s case a). Together with the rotational angular momentum, they form the total angular momentum \(J\) which is quantized along the magnetic field axis (\(M_J\)). The electronic magnetic moment along the internuclear axis has the value of \(2g_L\mu_B\) where \(g_L\) should be close to unity.

The first-order Zeeman energy of this system is

\[ \epsilon(\text{first-order}) = g_J\mu_B H M_J, \]  

where

\[ g_J = 4g_L/(J(J+1)). \]  

Using the selection rule for magnetic dipole radiation of \(\Delta M_J = \pm 1\), one predicts four absorption signals all at \(g_J \approx \frac{3}{2}\) for the lowest total-angular-momentum state with \(J = 2\). The observed \(J = 2\) spectrum\textsuperscript{1} in fact consists of these four absorptions, but they are split apart by a higher-order Zeeman effect. This splitting can be readily explained by a mixing of the \(J\) levels which depends upon the ratio of \(\mu_B H\) to the rotational constant \(B\).

For the \(^{18}\text{O}\) nucleus with \(I = \frac{5}{2}\), we must consider the new states characterized by the values of \(M_J\). Since the \(1\text{Δ}_g\) state has a first-order Zeeman effect, it also has a large component of magnetic field, produced by the orbital moment, which is at the nuclei and parallel to \(H\). This field is much larger than \(H\) itself and it is the dominant interaction for the \(^{18}\text{O}\) nuclei. There is also a small nuclear quadrupole interaction and small second-order terms involving the \(J\) mixing. The \(J = 2\) energy level pattern for a molecule with one \(^{18}\text{O}\) nucleus is shown in Fig. 1.

The exact calculation of these energy levels is simplified by the fact that Eq. (1) is the major term in the Zeeman energy. One can either use the older formalism of Condon and Shortley\textsuperscript{8} as explained by Van Vleck and Frosch and Foley\textsuperscript{9} or the newer and more complete, formulation of Carrington, Levy, and Miller (CLM).\textsuperscript{10} A complete analysis of the \(^{18}\text{O}\) hyperfine interaction is possible from the spectrum of a single \(J\) state, and the work reported here was done on the \(J = 2\) state at X band (9 GHz).

A complete analysis of the \(g\)-value problem is only possible if work is done on two \(J\) states, because one...
must separate the rotational-electronic contributions to the magnetic moment from the purely electronic ones. We chose to operate at S band (3 GHz) so that both the J=2 and J=3 spectra would be within the range of our magnet.

**17O RESULTS**

In our enriched O₂ one can see EPR lines due to ¹⁷O₂, ¹⁸O₂, ¹⁷O¹⁸O, ¹⁸O¹⁷O, and ¹⁷O¹⁷O. The spectral region also includes some strong absorptions due to O₂ in its ground ³Σ⁺ state. One could expect to observe 48 lines from the two ¹⁷O species with the selection rule ΔM_J=0. We could only resolve 28 of these. The signal-to-noise ratio was only about 3:1 for the ¹⁷O lines and, in addition, overlapping of some of the many possible lines from the several species present made complete resolution impossible. The line positions were measured to ±0.5 G for both the M_J=−1 to 0 and the M_J=0 to +1 transitions, and ±1 G for the other sets of transitions.

For a Δ electronic state there is only one important term in the magnetic hyperfine part of the electronic Hamiltonian. Following CLM it can be written for one interacting nucleus α as

\[ \mathcal{H}_{\alpha} = \sum_i a_i \hat{l}_i \cdot \hat{I}_\alpha, \]

where for a single electronic state \( \eta \)

\[ \langle \eta | a_i \hat{l}_i | \eta \rangle = \langle \eta | 2 \mu_B \lambda \mu_B^\alpha | -\hat{I}_\alpha | \eta \rangle. \]

In their evaluation of the electronic-rotational matrix, elements given by Eq. (3), CLM use a JIFM₁ representation. In ordinary magnetic fields Eq. (1) is almost exact with the result that the orbital angular momentum is very nearly quantized along the axis of the field. As a result a JIFM₁ representation is more appropriate for the evaluation of the matrix elements that result from Eq. (3). For J=2 the result is that

\[ e_{\alpha}/(\text{first-order}) = (\langle \alpha | M_J M_I - g_\mu_B H M_I | \eta \rangle, \]

where the constant \( \langle \alpha \rangle \) is defined by

\[ \langle \alpha \rangle = \sum_i \langle \eta | a_i \hat{l}_i | \eta \rangle, \]

where \( z \) is the internuclear axis. Higher-order terms arise from the fact that \( J \) and \( M_I \) do not have exact quantum numbers. These terms can produce shifts of the order of 10 G in the absorption lines while Eq. (5) predicts most of the hyperfine splittings of several hundred gauss as shown in Table I. The final calculations were done by diagonalizing a 72×72 matrix with \( \langle \alpha \rangle \) as an adjustable parameter. No least-squares fitting was attempted. The agreement between the calculated and observed field positions shown in Table I was obtained with \( \langle \alpha \rangle/h = -424 \text{ MHz} \).

The quantity of interest to be obtained from the ¹⁷O results is \( 1/\tau^2 \) for the orbitally unpaired electrons which form the \( ^1 \Delta \) term. Since the experimental parameter \( \langle \alpha \rangle \) contains the orbital angular momentum opera-

### Table I. Observed and calculated hyperfine structure for J = 2.

<table>
<thead>
<tr>
<th>Isotopes</th>
<th>( M_J )</th>
<th>( h\nu/\mu_B)</th>
<th>obs^a</th>
<th>calc^b</th>
</tr>
</thead>
<tbody>
<tr>
<td>16-17</td>
<td>5/2</td>
<td>0.65174</td>
<td>0.65177</td>
<td></td>
</tr>
<tr>
<td>16-17</td>
<td>1/2</td>
<td>0.68272</td>
<td>0.68265</td>
<td></td>
</tr>
<tr>
<td>17-18</td>
<td>1/2</td>
<td>0.67288</td>
<td>0.67276</td>
<td></td>
</tr>
<tr>
<td>17-18</td>
<td>-1/2</td>
<td>0.68377</td>
<td>0.68325</td>
<td></td>
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<tr>
<td>16-17</td>
<td>5/2</td>
<td>0.64472</td>
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<td></td>
</tr>
<tr>
<td>16-17</td>
<td>1/2</td>
<td>0.65606</td>
<td>0.65606</td>
<td></td>
</tr>
<tr>
<td>16-17</td>
<td>-1/2</td>
<td>0.67547</td>
<td>0.67546</td>
<td></td>
</tr>
<tr>
<td>16-17</td>
<td>-3/2</td>
<td>0.68597</td>
<td>0.68603</td>
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<tr>
<td>16-17</td>
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<td></td>
</tr>
<tr>
<td>16-17</td>
<td>1/2</td>
<td>0.65814</td>
<td>0.65819</td>
<td></td>
</tr>
<tr>
<td>16-17</td>
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<td>0.66849</td>
<td>0.66854</td>
<td></td>
</tr>
<tr>
<td>16-17</td>
<td>-3/2</td>
<td>0.67900</td>
<td>0.67904</td>
<td></td>
</tr>
<tr>
<td>17-18</td>
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<td>0.65788</td>
<td>0.65792</td>
<td></td>
</tr>
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<td>17-18</td>
<td>-1/2</td>
<td>0.66819</td>
<td>0.66826</td>
<td></td>
</tr>
<tr>
<td>17-18</td>
<td>-3/2</td>
<td>0.67871</td>
<td>0.67875</td>
<td></td>
</tr>
<tr>
<td>17-18</td>
<td>-5/2</td>
<td>0.68939</td>
<td>0.68940</td>
<td></td>
</tr>
<tr>
<td>16-17</td>
<td>5/2</td>
<td>0.63140</td>
<td>0.63135</td>
<td></td>
</tr>
<tr>
<td>16-17</td>
<td>3/2</td>
<td>0.64130</td>
<td>0.64138</td>
<td></td>
</tr>
<tr>
<td>16-17</td>
<td>1/2</td>
<td>0.63140</td>
<td>0.63155</td>
<td></td>
</tr>
<tr>
<td>16-17</td>
<td>-1/2</td>
<td>0.66172</td>
<td>0.66186</td>
<td></td>
</tr>
<tr>
<td>16-17</td>
<td>-3/2</td>
<td>0.67227</td>
<td>0.67231</td>
<td></td>
</tr>
<tr>
<td>16-17</td>
<td>-5/2</td>
<td>0.68284</td>
<td>0.68290</td>
<td></td>
</tr>
<tr>
<td>17-18</td>
<td>5/2</td>
<td>0.63079</td>
<td>0.63074</td>
<td></td>
</tr>
<tr>
<td>17-18</td>
<td>3/2</td>
<td>0.64068</td>
<td>0.64075</td>
<td></td>
</tr>
<tr>
<td>17-18</td>
<td>-1/2</td>
<td>0.66106</td>
<td>0.66118</td>
<td></td>
</tr>
<tr>
<td>17-18</td>
<td>-3/2</td>
<td>0.67130</td>
<td>0.67161</td>
<td></td>
</tr>
<tr>
<td>17-18</td>
<td>-5/2</td>
<td>0.68218</td>
<td>0.68218</td>
<td></td>
</tr>
</tbody>
</table>

^a With \( \tau/(\text{obs}) \) from 9.0832 to 9.0818 GHz.

^b With \( \alpha/h = -424 \text{ MHz} \).

The 16-17 and 17-18 were not resolved so assumed \( H'(16-17) = H \text{ (obs)} + 1 \text{ G} \).

The same result can be obtained from the final equations of CLM, but not without some difficulty. They assume that the radial and orbital parts of Eq. (6) can always be separated and they express their final...
matrix elements in this form. If one follows their technique, then the first term in Eq. (5) would be written as \((2\alpha/3) M_f M_{M_f}\). Their constant \(\alpha\) is now some kind of weighted average which results when the radial and orbital parts of \(\langle a\rangle\) are separated. For a two-electron problem \(a = \langle a\rangle/2\), but it is still not rigorous to make this separation. The recent paper\(^{10}\) on the interaction in \(SO(\Sigma)\) uses a hyperfine formalism which is similar to ours.

The separation of orbital and radial factors in \(\langle a\rangle\) has been carefully investigated for O atom by Schaeffer \(et\ al.\)\(^{11}\). They added a "polarization wavefunction" to the usual restricted Hartree–Fock treatment in order to include the effects of core polarization. The core polarization was found to be important for both the spin and orbital terms in the hyperfine interaction of the \(3P\) ground state of O atom. The result of their calculations for the orbital term in the hyperfine interaction for O atom is shown in Table II. When they included the effects of core polarization they obtained excellent agreement with the experimental value for \(\langle a\rangle\) obtained for \(O(1^P)\) by Harvey.\(^{12}\) \(1^P\) value for \(\langle 1/r^2\rangle\) was almost 10\% larger than that predicted from the experimental value of \(\langle a\rangle\) and that this was accounted for by the nonseparability of the orbital and radial factors in \(\langle a\rangle\).

Harvey also found that different values for \(\langle 1/r^2\rangle\) were obtained if he used the spin and orbital hyperfine interactions. From the orbital hyperfine interaction he determined what he called \(\langle 1/r^2\rangle\) and from the spin he obtained what he called \(\langle 1/r^2\rangle\). He found that \(\langle 1/r^2\rangle\) was about 11\% larger than \(\langle 1/r^2\rangle\). The calculations of Schaeffer \(et\ al.\) account for this difference by core polarization. The value for \(\langle 1/r^2\rangle\) that we obtained in Eq. (7) should be more properly termed \(\langle 1/r^2\rangle\), and it should be at least 10\% larger than the H–F value for \(\langle 1/r^2\rangle\) in \(O(\Delta_p)\). Table II also shows a \(\langle 1/r^2\rangle\) value obtained for \(O(\Sigma_p^-)\) by Miller \(et\ al.\).\(^{13}\) In Harvey's notation this is a \(\langle 1/r^2\rangle\) value since it is deduced from an electron-spin hyperfine interaction. Since the \(O(\Sigma_p^-)\) value for \(\langle 1/r^2\rangle\) is about 10\% larger than our \(\langle 1/r^2\rangle\) value for \(O(\Delta_p)\), we can conclude that they follow the same pattern that Harvey found for O atoms. Under these circumstances we are forced to conclude that the \(^{17}\)O hyperfine interaction for \(O(\Sigma)\) and \(\Delta\) is consistent within the uncertainties of the method, with the same value of \(\langle 1/r^2\rangle\). It should be possible in the near future to do accurate H–F calculations for \(O(\Sigma)\) and \(\Delta\), and we expect that the values for \(\langle 1/r^2\rangle\) for both the \(\Sigma\) and \(\Delta\) states should be very close in value.

### Table II. Theoretical and experimental oxygen hyperfine parameters.

<table>
<thead>
<tr>
<th>System</th>
<th>Source</th>
<th>(\langle 1/r^2\rangle) in (10^{-24}) cm(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(O(\Sigma))</td>
<td>Theory(^a)</td>
<td>31.3</td>
</tr>
<tr>
<td></td>
<td>Exp1(^b)</td>
<td>31.0</td>
</tr>
<tr>
<td>(O(\Delta))</td>
<td>Exp1(^d)</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>Our work</td>
<td>39.6</td>
</tr>
</tbody>
</table>

\(^a\) Reference 13.
\(^b\) Reference 14.
\(^c\) More properly designated \(\langle 1/r^2\rangle\), see Ref. 14.
\(^d\) Reference 15.
\(^e\) More properly designated \(\langle 1/r^2\rangle\), see Ref. 14.

### Table III. Corrected values for \(J = 2\) at X band.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Field (G)</th>
<th>(hv/\mu_B H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-2\rightarrow 1)</td>
<td>10 090.3</td>
<td>0.65597</td>
</tr>
<tr>
<td>(-1\rightarrow 0)</td>
<td>9 988.8</td>
<td>0.66264</td>
</tr>
<tr>
<td>(0\rightarrow 1)</td>
<td>9 885.9</td>
<td>0.66954</td>
</tr>
<tr>
<td>(1\rightarrow 2)</td>
<td>0 781.9</td>
<td>0.67667</td>
</tr>
</tbody>
</table>

\(^{13}\) Reference 16.
\(^{14}\) With the spectroscopic rotational constants of Ref. 16 and \(2J = 0.66661\).

### Table IV. Experimental S-band results and resultant \(g_J\) values.

<table>
<thead>
<tr>
<th>Transition</th>
<th>(J = 2^a)</th>
<th>(J = 3^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-2\rightarrow 0)</td>
<td>3377.29 0.666633</td>
<td>... ...</td>
</tr>
<tr>
<td>(-1\rightarrow 0)</td>
<td>3365.46 0.666631</td>
<td>6693.36 0.333399</td>
</tr>
<tr>
<td>(0\rightarrow 1)</td>
<td>3353.66 0.666632</td>
<td>6734.34 0.333401</td>
</tr>
<tr>
<td>(1\rightarrow 2)</td>
<td>3341.80 0.666634</td>
<td>... ...</td>
</tr>
</tbody>
</table>

\(^a\) \(p = 3.144236 \times 10^{10}\) Hz.
\(^b\) \(p = 3.144213 \times 10^{10}\) Hz.

It is possible from Table II to see that the \(\langle 1/r^2\rangle\) values for \(O(\Sigma)\) are quite obviously larger than they are in O atom. The readily available explanation for this is that the bonding in \(O(\Sigma)\) produces a contraction of the \(2p\) orbitals so that \(\langle 1/r^2\rangle\) is increased. Confirmation of this will also have to await accurate H–F calculations for \(O(\Sigma)\).

### THE \(g\)-VALUE RESULTS

At least two parameters are required to fit the set of transitions for each \(J\) value. In the absence of higher-order terms in \(H\), the center of each pattern depends only upon \(g_J\). The higher-order terms give a shift of the center and a splitting into \(2J\) transitions. These higher-order terms depend upon the rotational constants characteristic of each \(J\) value. Since a complete assignment of the rotational levels of \(O(\Delta_p)\) has been made,\(^{16}\) we found that it was quite satisfactory to assume the rotational constants and to only fit a \(g_J\) value for each set of transitions.
Our older work\(^1\) on \(J = 2\) at \(X\) band indicated that the spectroscopic rotational constant\(^6\) Bo = 1.4178 cm\(^{-1}\) did not fully account for the splittings. We have subsequently found that this small discrepancy was due to an improper calibration of the magnetic field at the sample. The difference between the field at the sample and at the NMR probe is field dependent. When this is properly corrected for, we obtain the \(J = 2\) results shown in Table III. The field positions shown in this table were also calculated using the 1963 N.B.S. value for the NMR frequency conversion.

We have supplemented these old \(X\)-band (9 GHz) results with new data taken at \(S\) band (3 GHz). We also fit the centers of each EPR line with our least-squares fitting technique.\(^8\) The spectrum shown in Fig. 2 was fitted assuming four Lorentz lines of arbitrary width, intensity and position. One can see that the fit was good and the intensities were close to the 2:3:3:2 pattern expected for \(J = 2\). The centers of these lines could be fitted to a precision of about 0.01 G.

Table IV shows the \(S\)-band result for \(J = 2\) and \(J = 3\) and the values of \(g_J\) necessary to fit the data. Only two of the six possible \(J = 3\) lines were accurately measured. These two have the best signal-to-noise ratio. One can see that the \(g_J\) values from the \(S\)-band data are consistent to within the uncertainties in the magnetic field. Since the \(J = 2\) values obtained at \(S\) band are apparently more accurate than those at \(X\) band given in Table III, we take a weighted average of 0.666630 for \(g_J\) for \(J = 2\). The \(J = 3\) average is obviously 0.333400.

The contribution of the rotational \(g\) value (\(g_r\)) to the \(g_J\) values can be easily calculated, and for the two \(J\) values the results are

\[
0.666630 = \frac{3}{2}g_L - \frac{1}{2}g_r, \quad (8)
\]

\[
0.333400 = \frac{1}{2}g_L - \frac{3}{2}g_r. \quad (9)
\]

If these two equations are solved we obtain

\[
g_L = 0.99986 \quad (10)
\]

and

\[
g_r = -1.70 \times 10^{-4} \quad (11)
\]

or

\[
\mu g_L / \mu_N = -0.313. \quad (12)
\]

In Eq. (11) we express the rotational \(g\) value in units of the Bohr magneton, while in Eq. (12) it is expressed in the more natural unit of the nuclear magneton.

Our value of \(g_L\) agrees very well with Miller's\(^4\) value of 0.999866±0.000010. As Miller points out the small decrease below unity is due to the relativistic contribu-
tions. The work on atoms has been summarized by Hughes. These contributions can be considered as the result of a power series in the fine structure constant $\alpha$. They come from the terms in the series of the order $\alpha^2 \mu_B I$. As a result, we expect that $g_{L}$ should differ from unity by something like $\alpha^2$ and so our experimental difference of $-1.40 \times 10^{-4}$ is of the expected order of magnitude.

For $O$ atom the most important relativistic contribution to the orbital $g$ value comes from the “relativistic increase of mass.” This has a very simple form. It is first, necessarily diamagnetic in that it decreases the value of $g_0$. In order to calculate this term one only needs to know the average kinetic energy of the orbitally unpaired electrons. For $O$ atoms, this quantity has been evaluated and one can show that this term alone should change $g_0$ by $-1.3 \times 10^{-4}$. This is very close to the total change in $g_0$ and the other terms must either not be important, or more likely, they partly cancel.

Our value for $g_0$ differs from Miller’s value of $-1.234 \pm 0.025 \times 10^{-4}$. We are clearly outside of Miller’s estimate of his experimental error. It is quite remarkable that we can agree so well for $g_L$ and still not agree for $g_0$. One can see from Eqs. (8) and (9) that the value of $g_L$ is primarily dependent upon the value of $g_0$ for $J = 2$ and $g_0$ comes mainly from a comparison of the $g_0$ values for both $J = 2$ and $J = 3$. In fact, $g_0$ depends upon how close the $g_{T}$ value is for $J = 3$ to one-half of the value for $J = 2$.

In Eq. (9) if we assume that our value of $g_{T}$ is correct but that Miller’s value for $g_{L}$ correct, then $g_{T}$ for $J = 3$ would have to be decreased by $0.31 \times 10^{-4}$. This is a $10^{-6}$% error in $g_{T}$ or a 0.6 G error in our magnetic field measurement. Since Miller’s measurements were made at $X$ band it would require an even larger error in his field measurement. There errors are about the size of the shift between the NMR probe and the sample, but this shift was corrected for in both sets of experiments. One can conclude that one possible source for the difference between the two $g_{L}$ values would be an error in the field measurements for the $J = 3$ lines.

The ratio of the two values of $g_0$ is close to $4:3$. Our value of $g_0$ is $\mu_0 = g_0 \mu_0 N$, where $N$ is the rotational angular momentum. The same definition was used for $O_2(2\Sigma_g^{-})$ by Bowers, Kamper, and Lustig who obtained $g_0 = -1.2 \times 10^{-4}$. This is identical to Miller’s value for $g_0$ in $O_2(1\Delta_g)$. Miller points out that his value for $g_0$ gives equal electronic contributions to $g_0$ for both the $1\Delta_g$ and $3\Sigma_g^{-}$ electronic states. This is a remarkable result since the perturbation formulas for the electronic part of $g_0$ depend upon different excited electronic states for the $1\Delta_g$ and $3\Sigma_g^{-}$ states. It is to be expected that both values for $\mu_0 g_{T}/\mu_0$ should lie between zero and $-1$, but one would not expect them to be as close as Miller’s result indicates.

At some future date it should be possible for us to make $S$-band measurements on the $J = 4$ lines and thus have an over-determined set of equations to solve for $g_L$ and $g_0$. The possibility of a numerical error in our calculations was eliminated when Miller checked our data with his least-squares programs. He obtained very nearly the same values as we quote for $g_0$ and $g_L$ using his programs on our data. Under these circumstances it is particularly clear that further work should be done in order to determine the exact source of our discrepancy.

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