Rotational Moment, Rotational $g$ Factor, Electronic Orbital $g$ Factor, and Anisotropy of the Magnetic Susceptibility of $^1\Delta$ O$_2$

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The electron paramagnetic resonance spectrum of the $^1\Delta$ state of O$_2$ has been investigated in both the $J=2$ and $J=3$ rotational levels. The line positions in the $J=2$ state have been determined to a higher accuracy than previously reported and the $J=3$ line positions have been measured for the first time. The combined spectra are analyzed to obtain the rotational constant, rotational $g$ value, electronic orbital $g$ value, and the anisotropy of the magnetic susceptibility of $^1\Delta$ O$_2$. From the anisotropy of the susceptibility the electronic second and quadrupole moments are derived. The experimentally determined parameters are

$$B_0 = 1.41808 \pm 0.00020 \text{ cm}^{-1},$$
$$g_r = -1.234 \pm 0.025 \times 10^{-4},$$
$$g_z = 0.999866 \pm 0.000010,$$
$$x_\Delta = -4.68 \pm 0.94 \times 10^{-20} \text{ erg/molecule},$$

where the symbols are defined in the text. The quoted uncertainties (except for $g_z$) represent two standard errors and correspond to about a 95% confidence limit inclusive of parameter correlation effects.

INTRODUCTION

The singlet delta state of molecular oxygen has received considerable attention recently. It is postulated as an intermediate in a number of organic oxidations. It has also been proposed that it plays an important role in air pollution chemistry. Despite the intense interest in its reactions, very little purely spectroscopic work has been carried out on the state.

Most of our present knowledge about the physical structure of $^1\Delta$ O$_2$ is provided by the classic work of Herzberg and Herzberg on the infrared atmospheric oxygen bands. From their analysis, the rotational and vibrational constants of the $^1\Delta$ state were obtained. More recently, the electron paramagnetic resonance (EPR) spectrum of $^1\Delta$ O$_2$ has been reported. In principle, the EPR and infrared spectra provide partly complementary and partly redundant information about the electronic structure of $^1\Delta$ O$_2$.

However, the previous EPR report indicated a possible discrepancy of about 0.3% in the rotational moment for the $^1\Delta$ state. While such a discrepancy is small, it is beyond the likely errors in either measurement. Moreover, even such a small error in the rotational constant alters the difference in bond lengths between the ground $\Sigma$ and $^1\Delta$ O$_2$ states by about 20%.

The complementary information provided by the EPR spectrum rests in its measurements of the magnetic interaction parameters. Measurements of the rotational $g$ value and the deviation of the electronic orbital angular momentum $g$ value from unity would be very interesting in the $^1\Delta$ state of O$_2$, especially since similar parameters are now accurately known for the ground $^3\Sigma$ state. Unfortunately, previous EPR measurements have been made in only the lowest rotational level, where it is impossible to separate the various magnetic effects.

We have undertaken the measurement of the EPR spectrum of both the $J=2$ and $J=3$ levels of $^1\Delta$ O$_2$. We believe the precision of our measurement is about a factor of 5-10 higher than previous work. From these measurements, we are able to obtain a rotational constant at least as accurate as the infrared value. We are also able to separate the magnetic interactions and obtain accurate measurements of the rotational $g$ value and the deviation of the electronic orbital angular momentum $g$ value from unity. We have also been able to measure the anisotropy of the magnetic susceptibility of $^1\Delta$ O$_2$ and determine the contributions to it from the high-frequency (or paramagnetic) susceptibility and the diamagnetic susceptibility. From this data the electronic second and quadrupole moments for $^1\Delta$ O$_2$ can be determined.

EXPERIMENTAL

The EPR spectrometer used for these experiments was specially designed for gas-phase experiments and has been described previously. For the $^1\Delta$ O$_2$ spectrum, conventional 100 KHz magnetic field modulation was used. In order to minimize errors in magnetic field measurements, the sample volume within the microwave cavity was kept as small as possible. Therefore the experiments have been carried out using a TRF rectangular microwave cavity with the sample gas contained in a 11-mm-o.d. quartz tube.

The $^1\Delta$ state of O$_2$ was excited by a microwave discharge in pure O$_2$. The products of this discharge were then pumped through the spectrometer cavity. The total O$_2$ pressure was maintained at about 0.3 torr. The choice of this pressure represented a compromise between a somewhat better signal-to-noise ratio but wider lines at higher pressures.

The magnetic field position of each line was measured
by a NMR probe located just outside the microwave cavity. The NMR fluxmeter was of the marginal oscillator type with a provision for locking, via a feedback loop, the oscillator frequency to the nuclear resonance frequency. With this arrangement, it was possible to reproducibly measure a given field position to about a milligauss.

The NMR sample was D₂O 0.8M in MnSO₄. A gyromagnetic ratio \(\gamma(D)/2\pi\) of 6.53566 X 10⁹ sec⁻¹ G⁻¹ for the deuteron in pure D₂O may be obtained (assuming the same chemical shielding factor for D₂O and H₂O) by combining the best value of \(\gamma(H)\) for H₂O and the ratio of \(\gamma(H)\) to \(\gamma(D)\) obtained by Wimett. Our D₂O sample was cylindrical while the reported \(\gamma(H)\) is for a spherical sample. Thus, strictly speaking, a shape factor should be included in our calculation since the bulk diamagnetic effects differ in the two cases. However, it may be expected to be no more than \(\sim 1\) ppm, so we neglect it.

There is also a shift for the D resonance in a paramagnetic solution from that in a pure diamagnetic solution due to the Fermi contact interaction. Luz and Shulman have investigated this problem experimentally for protons and Reuben and Fiat have recently related the proton and deuteron effects. Based on these works we can calculate (in the fast exchange limit) the effective \(\gamma(D)\), \(\gamma'(D)\), for deuterons in an 0.8M MnSO₄ solution in D₂O at room temperature. We find \(\gamma'(D)\) to be 10 ppm greater than \(\gamma(D)\) or \(\gamma'(D)/2\pi = 6.53576\) sec⁻¹ G⁻¹. It is this effective gyromagnetic ratio that we have used to determine all the field positions reported in this paper.

Another possible source of systematic error in measuring the field positions of the \(\Delta O₂\) lines was the difference in magnetic field between the NMR probe and the \(\Delta O₂\) sample in the cavity. The error can be made small by very high magnetic field homogeneity over the air gap. For the lower field \(J = 2\) transitions a Varian 15-in. magnet with 4-in. air gap was used. For the higher field \(J = 3\) transitions, the magnet gap had to be changed to 2 ½ in. to obtain sufficient magnetic field intensity, which, of course, decreased the magnetic field homogeneity. To further decrease this error, both before and after the measurements on \(\Delta O₂\), a second NMR probe was inserted into the microwave cavity and located as nearly as possible at the average position of the \(\Delta O₂\) sample. The difference in the magnetic fields were then measured over the entire field range for which \(\Delta O₂\) lines were observed. Plots were made of this field correction vs magnetic field and the outside probe field determination corrected accordingly. The remaining field uncertainty at the sample could be estimated to be about 30 mG, caused primarily by the uncertainty of the average position of the sample within the cavity. (By average position, we mean the average of the geometric position of the sample weighted by the square of the microwave magnetic field times a modulation amplitude function.) The difficulties in determining the exact positions of the EPR transitions plus the uncertainties in the \(\gamma'(D)\) determination lead us to place a limit of 10 ppm on the accuracy of the absolute field positions, although their precision and relative accuracy is somewhat better.

A final and a very important uncertainty in the magnetic field measurement was the random error inherent in determining the center of the \(\Delta O₂\) resonances, both because of intrinsic width and a relatively low signal-to-noise ratio. The pressure-broadened lines had field widths corresponding to a frequency half-width at half-height of approximately 500 kHz. Inspection of the line shape revealed no apparent line-shape asymmetry. With the available signal to noise, it was possible to determine the line center to about 1/50 the width of the \(J = 2\) lines and about 1/25 the width of the \(J = 3\) lines. Hence the line center of the \(J = 2\) lines could be determined to about 10 kHz while the \(J = 3\) line (with twice the field width for the same frequency uncertainty because they have approximately half the effective \(g\) value) centers could be determined to about 20 kHz.

Thus we see that the expected overall precision of \(J = 2\) line positions would be about 20 mG with the \(J = 3\) transition having about twice the field uncertainty. Linearly corrected field measurements to a common frequency showed an average standard deviation of about 30 kHz with the standard deviation for the \(J = 3\) series about double that for the \(J = 2\) series presumably because of the higher signal-to-noise ratio of the latter.

Approximately nine field measurements were carried out on each line. Before and after each field measurement, the microwave frequency was measured with a HP frequency converter and the same frequency counter, a HP 5245 L, used to measure the NMR frequency. The two frequency measurements were averaged. Drift (caused by the fact that the frequency was locked to the sample cavity) was never more than 5 kHz for any data point used and hence the error in the microwave frequency measurement should be negligible compared to the errors in magnetic field measurement.

**THEORY**

The Hamiltonian for \(\Delta O₂\) can be written as a sum of two parts,

\[ \mathcal{H} = \mathcal{H}_R + \mathcal{H}_Z. \]  

\( \mathcal{H}_R \) is the rotational Hamiltonian appropriate to the molecule in zero field. \( \mathcal{H}_Z \) represents the molecule’s interactions with an external magnetic field.

Explicitly,\(^{10}\)

\[ \mathcal{H}_R = B(R)(J - L)^3, \]  

where \( B(R) \) is the rotational constant as a function of internuclear distance and \( J \) and \( L \) are, respectively, the
total and electronic orbital angular momentum. If we may eliminate the vibrational dependence of $B(R)$ in the usual way,  

$$3\kappa = B_0 (J^2 - 2J \cdot L + L^2) + D_J J^2,$$  

where $B_0$ is the rotational constant in the $v=0$ vibrational level, i.e., $B_0 = B_e - \alpha_e (\nu + \frac{1}{2})$ with $\nu = 0$ and $B_e$ the equilibrium rotational constant, and $D_J$ is the centrifugal distortion parameter.

The general Zeeman Hamiltonian for a diatomic molecule has been given by Carrington, Levy, and Miller. We take only that portion which does not vanish in a singlet state:

$$3\kappa = \sum g_i g_H \cdot L_i - g_e g_H \cdot (J - L)$$

$$+ \sum_i \left( \frac{e^2}{8mc^2} \right)(H \times r_i)^2,$$  

where $\beta$ is the Bohr magneton (1.39960 MHz/G), $L_i$ is the electronic orbital angular momentum of the $i$th electron, $g_i$ is the external magnetic field, $g_i \nu$ is the nuclear rotational $g$ factor, $g_i \nu$ is the electronic orbital angular momentum $g$ factor corrected for relativistic and diamagnetic effects, explicitly,

$$g_i \nu = 1 + \delta g_i \nu + \Delta g_i \nu,$$  

where

$$\delta g_i \nu = \left( -\frac{1}{2m_e^2} \right)(p_i)^2,$$  

$$\Delta g_i \nu = - e/2mc \left[ \sum_{j \neq i} \left( \frac{1}{2} \right) \left( \frac{1}{2} \right) \right]$$

$$+ \left[ r_{ij}^{-3} (r_i \times r_{ij}) \cdot (r_j \times p_j) \right].$$

The first term in Eq. (4) is dominant and describes the interaction of the field with the electronic orbital angular momentum. The second term describes the field's interaction with the magnetic moment created by the rotation of the nuclei. The final term describes the diamagnetic interaction of the field with the electrons.

Using the theory of irreducible tensor operators, the diamagnetic interaction $3\kappa$ can be divided into an isotropic portion and an anisotropic interaction,

$$3\kappa = \sum g_i g_H \cdot L_i - g_e g_H \cdot (J - L)$$

$$+ \sum_i \left( \frac{e^2}{8mc^2} \right)(H \times r_i)^2,$$  

where $T$ is an irreducible tensor of second rank. The last term of $3\kappa$ is isotropic; therefore it does not contribute to the electron resonance transition frequencies and hence may be neglected.

As usual in studies of this kind, it is desirable to produce an effective Hamiltonian operator which eliminates the effect of operators connecting different electronic states. The story of this reduction is rather an old one for $\Sigma$ molecules. Ramsey considered these effects for $\Sigma$ and similar analyses for polyatomic molecules have been carried out by Eshbach and Stodberg, and more recently by Flygare and collaborators. The advantages of the irreducible tensor formalism for polyatomic molecules were pointed out by Levy. None of these authors has, however, generalized his results to molecules with unquenched electronic orbital angular momentum. The presence of a permanent component of orbital angular momentum along the internuclear axis introduces subtle changes in the usual formulas and we therefore treat the problem again. We use the irreducible tensor notation of Levy because of the simplicity of the selection rules for the matrix elements of the irreducible tensors. We, however, avoid the complications of the Cartesian tensor notation of other authors as all Cartesian tensors expressed in the cylindrically symmetric molecule-fixed coordinate system can have only two unique components, one parallel and one perpendicular to the internuclear axis. We have recently given a general formalism for obtaining the effective Hamiltonian of an open-shell molecule. Specializing this result to the Hamiltonian of Eqs. (1), (3), and (4), we obtain an effective Hamiltonian $3\kappa$ to second order:

$$3\kappa = B_0 \cdot J^2 + D_J \cdot J^2 - g_e g_H \cdot (J - L)$$

$$+ g_e B_0 \cdot \langle J, \sigma | H, \sigma \rangle \langle J, \sigma | L, \sigma \rangle + \text{c.c.},$$  

where

$$B_0 = B_0 + B_0 \nu,$$  

$$g_e = g_e \nu + g_e \nu \nu,$$  

$$\Delta = - \left( \frac{e^2}{8mc^2} \right) \sum_i T_i^2 (r_i, r_i) + \text{c.c.},$$

where the irreducible tensor components refer to a molecule-fixed coordinate system, and a term in $L^2$ has been omitted because of its assumed constancy.

A number of new constants were introduced by the elimination of the matrix elements between the $\Delta$ and other electronic states. These are defined as follows:

$$B_0 \nu = \sum_{\Psi, \Lambda', \nu'} \left( \frac{1}{2} \right) \left( \frac{1}{2} \right) \left( \frac{1}{2} \right) \left( \frac{1}{2} \right)$$

$$\times \langle \Psi | T_2 \cdot \Lambda', (2BL) | \Psi', \Lambda' \rangle$$

$$\times \langle \Psi', \Lambda' | T_2 \cdot \Lambda', (2BL) | \Psi \rangle,$$  

$$g_e = \sum_{\Psi, \Lambda', \nu'} \left( \frac{1}{2} \right) \left( \frac{1}{2} \right) \left( \frac{1}{2} \right) \left( \frac{1}{2} \right)$$

$$\times \left[ \langle \Psi | T_2 \cdot \Lambda', (2BL) | \Psi', \Lambda' \rangle \langle \Psi', \Lambda' | T_2 \cdot \Lambda', (2BL) | \Psi \rangle \right]$$

$$\times \langle \Psi | T_2 \cdot \Lambda', (2BL) | \Psi \rangle.$$  

The parameter definitions have been taken from Eqs. (35), (48), and (44) of Ref. 17. In Eqs. (14) and (15), the terms in the sum over $f$ in Ref. 17 have been com-
bined to give a single constant. Equation (16) has been written using the fact that \( H^2(1, 1, 0, 0, 2, 0) = T^{0}_0(H, H) \) and the term in \( T^{0}_0(H, H) \) has been dropped as it is a constant for all levels. The last symbol in Eq. (16) is the well-known Clebsch–Gordan coefficient.

The parameters involving excited states have simple physical interpretations. \( B_0 \) corresponds to the rotational moment for the bare nuclei. \( B''_0 \) includes the effect of electronic mass “carried along” by the nuclei during molecular rotation. Likewise, \( g^e \) represents the magnetic moment created by the rotation of the electrons “following” the nuclei. \( \xi'' \) represents the anisotropy of the “high-frequency” paramagnetism.

The other parameters \( \langle \delta g \rangle_{St} \) and \( \langle \delta g \rangle_{o} \) may be defined by\(^{22}\)

\[
\langle \delta g \rangle_{St} = \frac{-1}{2mc^2} \sum_i \left( p_i^2 / L_z \right) \delta \xi_{iz}, \quad (17)
\]

\[
\delta \xi_{ij} = \frac{-e}{2mcL_z} \sum_{j \neq i} \left[ \left( \mathbf{r}_i \times \mathbf{p}_j \right) \cdot \left( \mathbf{r}_i \times \mathbf{p}_j \right) \right] + \left[ \mathbf{r}_i \times \mathbf{p}_j \right], \quad (18)
\]

where for a \( \Delta \) state \( L_z = 2 \).

Our formulas represent the generalization of the well-known formulas for a \( \Sigma \) state, to a state with unquenched electronic orbital angular momentum. There are differences in these formulas from those usually quoted. For instance, the summations extend formally over all singlet \( \pi, \Delta, \) and \( \Phi \) states, rather than over just \( \pi \) states. For \( \Sigma \) states all matrix elements of \( T^0(L) \) diagonal in \( \Delta \) vanish as the eigenvalue of \( T^0_0(L) \) equals zero.\(^{18}\) For a \( \Delta \) state \( T^0_0(L) \) has an eigenvalue of 2; however, it may be shown that the matrix elements of \( T^0_0(L) \) approximately vanish between different \( \Delta \) states.\(^{29}\)

We note, finally, that our definition for \( B_0, B'' \) and \( g^e \) and \( g^n \) reduce for a \( \Sigma \) state to similarly apppellated quantities of other authors.\(^{10}-^{16}\) For a \( \Sigma \) state, \( \xi \) and \( \xi'' \) can be related to previously defined quantities as follows:

\[
\xi'' = \left( \frac{3 \xi_i}{\xi^j} \right) / 6^{1/2}
\]

and

\[
\xi = (\xi_r - \xi_s) / 6^{1/2},
\]

where the \( \xi \)'s are defined by Ramsey.\(^{15}\)

SPECTRAL ANALYSIS

One can see from Eq. (9) that the effective Hamiltonian involves explicitly five molecular parameters. Of these five, there have been reported values for \( B_0 \) and \( D_0 \) only. The electron resonance spectrum is rather insensitive to \( D_0 \) and hence we have assumed the value given by Herzberg and Herzberg.\(^3\) Even if this value for \( D_0 \) were incorrect by 50%, which seems highly unlikely, the quoted values for the other parameters would not be shifted beyond our error limits.

Thus we are left with four unknown parameters in \( 3 \xi \) (as two slightly discordant values for \( B_0 \) have been suggested, we treat it as completely unknown). The observed electron resonance spectrum of \( ^1 \Delta \) \( \mathrm{O}_2 \) consisted of all four possible transitions between adjacent \( M \) states in the \( J = 2 \) state, and four of the six possible transitions in the \( J = 3 \) state. These energy levels as a function of magnetic field are shown in Fig. 1. (The two nonobserved transitions required higher magnetic fields than were obtainable.) Approximately 8–10 magnetic field and microwave frequency measurements were made for each of the observed lines. Table I lists the average field measured for each line corrected to an average microwave frequency, assuming a linear field-frequency relationship.

To obtain the best possible parameter values from the experimental data, a modified version of the nonlinear least squares program of Marquardt\(^{20}\) was employed to determine the parameter values for which the eigenvalues of the Hamiltonian \( [\text{Eq. (9)}] \) (truncated at \( J = 8 \)) best replicated the spectroscopic data. The input data for this program were the 72 pairs of independent field and frequency measurements, rather than the average values given in Table I. By using the original data one obtains a true least squares fit and eliminates any error in assuming a linear field-frequency relationship.

Thus, our quoted constants and error limits are based on the 72 data point fit. However, the constants derived from a least squares fit of the eight data points in Table I were identical to those of the 72 point fit to within at most \( \frac{1}{3} \) the stated error limits. Thus for most purposes the data given in Table I can be considered exact. The average magnitude of the residuals (differences between observed positions and positions predicted from the constants) was about 8 kHz for the \( J = 2 \) series and 24 kHz for the \( J = 3 \) series. We thus see that the overdetermined fit consistently predicts all lines well within their expected experimental error.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Field (G)</th>
<th>Frequency (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1</td>
<td>9 821.816</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>9 927.033</td>
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<tr>
<td>-2</td>
<td>10</td>
<td>10 030.879</td>
</tr>
<tr>
<td>-2</td>
<td>10</td>
<td>10 133.349</td>
</tr>
<tr>
<td>3</td>
<td>-3</td>
<td>19 224.481</td>
</tr>
<tr>
<td>3</td>
<td>-3</td>
<td>19 433.694</td>
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<td>3</td>
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<td>19 698.419</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>20 041.772</td>
</tr>
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</table>
Fig. 1. Lowest rotational energy levels of $^1\Delta \text{O}_2$ as a function of magnetic field (in kilogauss). The eight observed transitions are indicated by solid arrows. The remaining two transitions in the $J=3$ state indicated by broken arrows were not observed because of magnetic field limitations. No attempt has been made to show curvature of the Zeeman levels due to nonlinear Zeeman effects, as on the scale of the figure these effects are barely discernible.

Once the values of the parameters (call them $b_j$) which minimize the sum of the squares of the residuals have been determined, it is important to estimate the confidence regions for these parameters. Such an estimate is nontrivial since the parameters enter both nonlinearly and in a correlated manner into the determination of the line positions. The nonlinearity can be avoided by assuming a linear approximation is valid in the small region of possible error and correlation can be accounted for by including the diagonal coefficient $c_j$ of the inverse matrix of the normal equations of the linearized model.

Under these assumptions one-parameter confidence limits can be computed as

$$b_j - [T_{1-a}(N-k)S_j] \leq B_j \leq b_j + [T_{1-a}(N-k)S_j], \quad (21)$$

where $N$ is the number of data points, $k$ is the number of independent parameters, $T_{1-a}(N-k)$ is the two-tailed point of Student’s $T$ distribution, $S_j$ is the standard error of the parameter including effects of correlation. Explicitly,

$$S_j = \left[ \frac{\hat{\Phi}}{(N-k)} \right]^{1/2} (c_j)^{1/2}, \quad (22)$$

where $\hat{\Phi}$ is the minimized sum of the squares of the residuals. Error limits were calculated using $T_{1-a}(N-k) = 2$ which corresponds to approximately a 95% confidence level. (Alternatively the error limits may be viewed as two standard errors.) Compared to these random error limits, all the determined parameters except $g_e$ were found to be totally insensitive to a possible 10-ppm systematic error in all the absolute field positions (see the experimental section). Thus for all the parameters except $g_e$, the error limits quoted are those determined via Eq. (21). For $g_e$ the error limits determined by Eq. (21) are $\pm 3$ ppm. However, a systematic error in the absolute field determinations of $\pm 10$ ppm would correspond directly to a $\pm 10$-ppm uncertainty in $g_e$. Therefore, for $g_e$, we report a $\pm 10$-ppm error limit.
DISCUSSION

The value of \( B_0' \) which we have determined is slightly larger than either of the previously reported values. However, it is quite close to the value reported by Herzberg and Herzberg.\(^3\) Indeed, though they give no explicit error estimate, it is likely that our value and theirs are equal within the experimental errors of the measurements. We note that from Eq. (10), the measured \( B_0'' \) is a sum of two terms \( B_0 \) and \( B_0'' \). By combining Eqs. (14) and (15) we can approximately determine \( B_0'' \) from \( g_0 \) (see below):

\[
B_0'' \simeq -B_0 g_0 \varepsilon \approx 0.000561 \text{ cm}^{-1},
\]

where one has assumed the integral of the operator \( B \) in Eq. (14) can be replaced by its expectation value in the \( ^1\Delta \) state. This correction to the rotational moment from the effect of electronic mass is more than twice the expected experimental error and hence should definitely be applied to obtain the best internuclear distance from \( B_0 \). We obtain for the internuclear distance \( R_0 \) in the \( v=0 \) vibrational level,

\[
R_0 = 1.21911 \pm 0.00009 \text{ \AA},
\]

where \( R_0 \) has been calculated from \( B_0 \) using the nuclear, rather than the atomic, reduced mass.

Using the value of \( \alpha_n \) from Herzberg and Herzberg, we find the equilibrium internuclear distance, \( R_e \):

\[
R_e = 1.21545 \pm 0.00009 \text{ \AA},
\]

where the error limit makes no provision for uncertainty in \( \alpha \). Making a similar calculation for the ground state of \( \text{O}_2 \) (using the \( B_0 \) of Herzberg and Babcock\(^21\) and the \( B'' \) calculated from the \( g'' \) of Bowers\(^{22} \text{ et al.} \)) one can obtain the equilibrium bond lengthening \( \Delta R_e \) of \( \text{O}_2 \) upon excitation from the ground to the \( ^1\Delta \) state,\(^{23}\)

\[
\Delta R_e (^2\Sigma^-\rightarrow ^1\Delta) = 8.03 \pm 0.09 \times 10^{-4} \text{ \AA}.
\]

Rotational \( g \) Factor

From Eq. (11) the rotational \( g \) factor also is a sum of two parts, one nuclear, the other electronic. It is simple to calculate the nuclear contribution\(^{21}\); hence we obtain the

\[
g^e = g_N = (-1.234 - 2.723) \times 10^{-4}
\]

\[
= -3.957 \pm 0.025 \times 10^{-4}.
\]

It is interesting to compare this to the reported values of \( g^e \) for the ground state of \( \text{O}_2 \):\(^{24} \) -4.1 \pm 0.3 \times 10^{-4} \text{ and } -3.98 \pm 0.12 \times 10^{-4}.\(^{22} \) Within the experimental errors these values are identical.

If we as usual assume that \( B_0' \) may be removed from the electronic integrals, the general expression for \( g^e \) may be written

\[
g^e = -2B \sum_{\nu''\Lambda''} \left[ \langle \eta_0 \lambda_0 | T_{\lambda''-\lambda''} (L) | \eta' \Lambda' \rangle \right]^2 \times \langle \eta'' \Lambda'' | T_{\lambda''-\lambda''} (L) | \eta_0 \lambda_0 \rangle \langle E_{\eta_0 \lambda_0} - E_{\eta'' \Lambda''} \rangle^{-1}.
\]

To the accuracy required, \( B \) is the same for both \( \text{O}_2 \) states; however, for the ground state the summation extends over all \( 1\pi \) states while for the \( ^1\Delta \) state the summation extends over \( 1\pi \) and \( 1\delta \) states.

Van Vleck’s “hypothesis of pure precession”\(^{18} \) has often been invoked for molecular oxygen\(^{24} \) and similar molecules.\(^{20} \) We believe that the near equivalence of the \( g^e \) values for the \( ^1\Delta \) and \( ^2\Sigma \) state of \( \text{O}_2 \) make the invocation of this hypothesis speculative at the least. Consider the values of \( g^e \) under the pure precession hypothesis for the two states,

\[
g^e = B \langle (E_{\lambda''} - E_{\lambda''})^{-1} \rangle_n (L - \lambda_0 + 1) (L + \lambda_0),
\]

where we have omitted the presumably small contribution of \( 1\delta \) states to the value of \( g^e \) in the \( ^1\Delta \) state. \( \langle (E_{\lambda''} - E_{\lambda''})^{-1} \rangle_n \) is the reciprocal sum of the excitation energies to \( 2\pi \) states for the ground state of \( \text{O}_2 \) and \( 1\pi \) states for \( ^1\Delta \) \( \text{O}_2 \). As most excited electronic configurations give rise to both \( 1\pi \) and \( 2\pi \) states of about the same energy, \( \langle (E_{\lambda''} - E_{\lambda''})^{-1} \rangle_n \) would probably be about equal for the two states. We then see that it is impossible to choose any smaller integer value for \( L \) which would make the \( L - \lambda \) dependent term in the braces equal for the \( ^2\Sigma \) and \( ^1\Delta \) states. In fact, the most reasonable value for \( L, L=2 \), causes a 50\% difference in this term.

We believe that the inadequacy of the free precession hypothesis for the \( ^1\Delta \) and \( ^2\Sigma \) states of \( \text{O}_2 \) is not surprising. Van Vleck noted in proposing the hypothesis that it would only be a good approximation when the outer electrons are in very large (approximately centro-symmetric) orbitals. This description probably describes well the valence orbitals in a Rydberg state, but the \( ^2\Sigma \) and \( ^1\Delta \text{O}_2 \) states are in no way Rydbergs.

### Table II. Observed and derived molecular constants of \( ^1\Delta \text{O}_2 \)

| \( B_0' \) | 1.41808 ± 0.00010 \text{ cm}^{-1} |
|\( D_0 \) | 4.86 \times 10^{-6} \text{ cm}^{-1} (Ref. 3) |
|\( \alpha_n \) | 0.0171 \text{ cm}^{-3} (Ref. 3) |
|\( B_0'' \) | 1.42663 ± 0.00020 \text{ cm}^{-1} |
|\( R_0 \) | 1.21911 ± 0.00009 \ang |
|\( R_e \) | 1.21545 ± 0.00009 \ang |
|\( \Delta R_e (^2\Sigma^-\rightarrow ^1\Delta) \) | 8.03 ± 0.09 \times 10^{-4} \ang |
|\( g^e \) | -1.234 ± 0.025 \times 10^{-4} |
|\( g^{2\Sigma} \) | 2.723 \times 10^{-4} (calc) |
|\( g^{1\Delta} \) | -3.957 ± 0.025 \times 10^{-4} |
|\( \eta_0 \lambda_0 \) | 0.9999806 ± 0.000010 |
|\( \langle \eta_0 \lambda_0 \rangle \) | -130 \times 10^{-6} (approx calc) |
|\( \langle \eta_0 \lambda_0 \rangle \) | -4 \times 10^{-6} |
|\( \chi_0 \) | -4.68 ± 0.94 \times 10^{-8} \text{ erg/molecule} |
|\( Q_0 \) | -3.19 ± 0.65 \times 10^{-8} \text{ esu} \cdot \text{cm}^2 |
|\( \Sigma \chi_0 \) | 1.55 ± 0.32 \ang^2 |
|\( \Sigma \chi_0 \) | 8.19 ± 1.62 \ang^2 |
On the other hand, the constancy of $g_e^*$ for the two states makes good sense physically. $g_e^*$ describes the total magnetic moment caused by the electrons "following" the nuclear rotation. The moment would be essentially determined by the geometric distribution of the electron density. As the electrons are in the same orbitals in the two states, to a first approximation, this geometric distribution is unchanged and hence $g_e^*$ is a constant.

Electronic Orbital $g$ Value

From Table II, we see $g_L$ differs from unity by 134 ppm. Using Eq. (12), we obtain

$$
\langle \delta g_L \rangle_\mu = -134 \pm 10 \times 10^{-6}.
$$

(30)

By Eq. (17), $\delta g$ depends only upon the kinetic energy of the $\pi^*$ electrons. The major contribution to this kinetic energy occurs when the electrons are near an O nucleus. Hence, we would expect the $\pi^*$ electron kinetic energy in O$_2$ to be not very different from that of a $p$ electron in the O atom. Using the value of the $p$-electron kinetic energy in the O atom,$^{28}$ we obtain

$$
\langle \delta g_L \rangle_\mu = -130 \times 10^{-6}.
$$

(31)

This leaves for an orbit–orbit correction,

$$
\langle \delta g_L \rangle_\omega \approx -4 \pm 10 \times 10^{-6},
$$

(32)

an essentially unmeasurably small result. There have been no previous measurements or calculations of an orbit–orbit $g$ value correction for a molecule. However, Abragam and Van Vleck$^{28}$ have estimated the orbit–orbital correction to the O–atom $g$ value to be about $-20$ ppm, indicating that either the molecular $\langle \delta g_L \rangle_\mu$ or $\langle \delta g_L \rangle_\omega$ or both have decreased slightly in magnitude from their atomic values.

MAGNETIC SUSCEPTIBILITIES AND ELECTRONIC MOMENTS

From Eq. (13) we see that $\chi$, the parameter describing the quadratic Zeeman interaction, is composed of both paramagnetic and diamagnetic anisotropy contributions. As noted earlier, even for a state with unquenched angular momentum, the paramagnetic susceptibility along the internuclear axis approximately vanishes. Hence from Eqs. (15) and (16), $\chi''$ becomes approximately

$$
\chi'' = -g_\epsilon' B/2B(6^{1/2}),
$$

(33)

where the usual assumption, that $B$ can be removed from the electronic integral, has been invoked.

Combining Eqs. (13) and (33), with the measured values of $\chi$ and $g_e^*$, we obtain the anisotropy of the diamagnetic susceptibility,

$$
\chi_\epsilon = -(e^2/8mc^2) \sum_i (3z_i^2 - r_i^2) = (9.06 \times 10^{-1})h(6^{1/2})
$$

$$
+ g_e^* \beta^2/2B = -4.68 \pm 0.94 \times 10^{-29} \text{ erg/molecule}.
$$

(34)

If we multiply the diamagnetic anisotropy by $4mc^2/\epsilon$, we obtain the electronic quadrupole moment $Q_e$ for the $^1\Delta$ state of O$_2$:

$$
Q_e = \sum_i \frac{1}{\epsilon} (3z_i^2 - r_i^2) = (4mc^2/\epsilon) (-4.68 \pm 0.94 \times 10^{-29})
$$

$$
= -3.19 \pm 0.65 \times 10^{-25} \text{ esu} \cdot \text{cm}^2.
$$

(35)

There has been no previous measurement of $Q_e$ reported for the $^1\Delta$ state of O$_2$, but there has been a number of measurements of the total (nucleus plus electronic) quadrupole moment of O$_2$ in the ground $^2\Sigma$ state.$^{27}$ The determinations from microwave line broadening do not appear particularly reliable, but Buckingham, using the optical birefringence method, has recently reported$^{28}$ a value which would yield $Q_e = -2.82 \times 10^{-25} \text{ esu} \cdot \text{cm}^2$.

If there existed a measurement of the bulk (isotropic) temperature-independent magnetic susceptibility of $^1\Delta$ O$_2$, we could derive the second moments of the electronic distribution. There, of course, has been no such measurement on the $\Delta$ state; in fact, magnetic susceptibility measurements on even the ground state have not been accurate enough to determine the temperature-independent contribution. However, the diamagnetic portion has been calculated from a number of theoretical wavefunctions$^{24,25}$ with good agreement. If we assume that the diamagnetic contribution is the same for both states and take the wavefunction value,$^{29}$ we obtain

$$
\chi_i^d = -(e^2N_0/6mc^2) \sum_i \langle r_i^2 \rangle
$$

$$
= -3.19 \times 10^{-26} \text{ cm}^2/\text{molecule},
$$

(36)

where $N_0$ is Avogado's number. From Eqs. (35) and (36) we obtain

$$
(\sum_i x_i^2) = (\sum_i y_i^2) = 1.55 \pm 0.32 \text{ Å}^2,
$$

$$
(\sum_i z_i^2) = 8.19 \pm 1.62 \text{ Å}^2.
$$

(37)

These may be compared with values calculated for the O$_2$ ground state$^{29}$

$$
(\sum_i x_i^2) = (\sum_i y_i^2) = 1.68 \text{ Å}^2,
$$

$$
(\sum_i z_i^2) = 7.71 \text{ Å}^2.
$$

(38)

We thus see that the experimental second moments of the electron density of the $^1\Delta$ O$_2$ state are not very different from those calculated for ground-state O$_2$.

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On the Elastic Theory of Uniaxial Liquid Crystals

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Simple derivations of the elastic theory of liquid crystals with uniaxial molecular order are given using a molecular Cauchy-like approach and a more general phenomenological approach. In a second-order approximation, both methods lead to the same expression for the elastic energy density, except for the existence of one "Cauchy relation" between the elastic constants in the molecular case. Our phenomenological equation contains nine elastic constants which is two more than in Frank's earlier derivation. Our molecular equation is in agreement with Oseen's original expression. Differences between the molecular and the phenomenological approach and the justification of neglecting terms which do not contribute to the Euler-Lagrange differential equation are discussed. Higher than second-order terms are given for cholesteric liquids. In addition, the consequence of curvature-induced electric polarization for the equilibrium structure of liquid crystals is discussed.

I. INTRODUCTION

The elastic properties of liquid crystals are generally described by an energy density function which depends on the local deformations. For liquid crystals with uniaxial molecular order, an expression for the elastic energy density in terms of elastic constants was first derived by Oseen, who regarded intermolecular forces which he assumed to be additive and of short range. The deformation-dependent part of the energy density is given by Oseen as a linear combination of 10 terms whose coefficients define a total of eight different elastic constants. Five of these terms and three of the elastic constants do not enter the Euler-Lagrange differential equations which determine the possible equilibrium structures of the liquid crystal and they were subsequently omitted by Oseen.\(^\text{1,2}\)

At a later date, Frank derived the theory in a phenomenological approach and thereby reintroduced two of the terms dropped by Oseen. He pointed out how the energy density function simplifies when the liquid crystal lacks polarity or screw sense. Because of too narrow assumptions, Frank missed, however, some of Oseen's original second-order terms.

The elastic properties of liquid crystals are presently discussed in terms of Frank's incomplete version of the theory. It, therefore, seems to be necessary to reconsider the derivations of the theory. In the following, we present simple derivations of the elastic energy density function up to the second order of approximation in a molecular and a phenomenological approach. Higher-order terms which, as will be shown, might be of interest for cholesterics, can easily be obtained. Some aspects concerning terms which do not contribute