Paramagnetic Resonance of Molecular Oxygen in Condensed Phases

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Abstract: The electron paramagnetic resonance (epr) absorption of molecular oxygen is observed in a few matrices at temperatures below 10°K. The signal was ascribed to the molecule carrying out some torsional oscillation near the equilibrium position with the molecular axis perpendicular to the external field direction. The height of the potential barrier, 152 and 135 cm^{-1}, was obtained for a nitrogen and a carbon monoxide matrix, respectively. The observed ^{17}O nuclear hyperfine splitting indicates that there is virtually no perturbation on the valence-shell electrons of oxygen in a nitrogen matrix as compared with the gaseous oxygen molecule. Possible reasons for a severe line broadening, which would lead to the absence of the epr signal under most experimental conditions, were presented in terms of the potential field due to the molecular environment.

Paramagnetic resonance absorption of molecular oxygen in the electronic ground state, $^3\Sigma_g^-$, has been studied in detail in the gas phase,[1] and the results of the analysis are well documented. The fine structure constant (one-half of the zero-field splitting), which represents the deviation from the pure Hund's coupling scheme (b), was determined from the field-free microwave spectra.[2] The parameters of ^{17}O nuclear hyperfine Hamiltonian were obtained[3] for the $^{17}O-^{16}O$ molecule, and the analysis gave unequivocal evidence for the electronic configuration with the unpaired electrons in the pπ orbitals.[4] Similar studies have recently been reported for the electronically excited $^1\Delta$ state also in the gas phase.[5,6]

In contrast, no such observations have been, to the author's knowledge, described for molecular oxygen in the condensed phase, except that under a wide variety of conditions oxygen causes a very wide base-line deviation in the epr spectra, and that the liquid oxygen gives a broad resonance at 77°K covering roughly 10,000 G.[7] In principle, such an observation is considered feasible just as in any other triplet molecules.[8] There is in the literature a reference to an unsuccessful search for the epr signal of molecular oyxgen trapped in the β-quinol clathrate compound at 4.2°K;[9] no signal was detected below 14,000 G at X-band microwave frequency. The absence of the signal was attributed by the authors to a short spin-lattice relaxation time.

We have recently succeeded in detecting a variety of epr signals of molecular oxygen in several matrices below 10°K. We find that the observed line width is remarkably sensitive to the type of matrix. In some cases the molecule is in a state of torsional oscillation, and we have determined the potential barrier height experimentally. In a nitrogen matrix, at low oxygen concentrations, ^{17}O hyperfine structure is also observed. Comparison with the gas-phase result indicates that there is little perturbation on the valence shell electrons of the oxygen molecule in this rigid matrix. A possible reason for the absence of an epr signal under most experimental conditions is discussed.

Experimental Section

Materials. Two kinds of oxygen gas, research grade (99.99% minimum) and extra dry grade (99.6% minimum), from Matheson Gas Products were used with identical results. $^{18}O_2$ gas (99.9% enriched, 97.2% pure) was obtained from Oak Ridge National Lab. ^{17}O enriched oxygen (34.8% ^{16}O, 36% ^{17}O, and 29.2% ^{18}O) from YEDA was kindly provided to us by Dr. Hans Cahnmann. The gases used as matrices included nitrogen (99.995%), argon (99.998%), carbon monoxide (99.5%), and xenon (99.995% minimum) from Matheson Gas Products. All gases were used without further purification. The molecular sieves (Applied Sciences Laboratories) and the silica gel (Fisher Scientific Co.) were used after exhaustive degassing by heat evacuation. Each gas mixture was prepared on a vacuum line by standard techniques. For very dilute mixtures of isotopic oxygen, a gas-tight syringe was used in a drybox exhaustively purged with dry nitrogen gas. Contamination by atmospheric oxygen in this procedure was found negligible.

Epr observations were made by using a conventional X-band spectrometer with 100-KHz field modulation. A pair of additional pole caps was attached to a Varian 9-in. magnet to raise the operating magnetic field up to 14,000 G. The magnet was regulated and swept by a Fieldial Mark I. The magnetic field above 10,000 G was calibrated by the ^7Li nuclear resonance signal. Low temperatures (4.7–15°K) were obtained by evaporating liquid He through a single-jacketed variable-temperature dewar placed in the resonant cavity. The temperature was monitored by a calibrated germanium resistor (Cryo Cal CR-1000) immediately underneath the narrow quartz tip of the sample container (50 cc) which was inserted into the dewar.

Results

Most observations were made near 11,500 G in the temperature range of 4.7–10°K in the presence of a matrix. The overall signal intensity is strictly proportional to the amount of oxygen in the sample container under equivalent experimental conditions, and the signal can be completely and reversibly removed by evacuation. Thus molecular oxygen evidently is the source of the resonance absorption. By far the best defined, narrow signal ($\sim$25 G peak-to-peak) was observed in nitrogen matrix at low oxygen concentration ($\leq$30 ppm) (Figure 1a). The characteristically unsymmetric line shape, which is always broader on the low-field side, resembles the so-called perpendicular peak in a randomly oriented system. As the oxygen

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(1) M. Tinkham and M. W. P. Strandberg, *Phys. Rev.*, **97**, 951 (1955).
(2) M. Tinkham and M. W. P. Strandberg, *ibid.*, **97**, 937 (1955).
(3) S. L. Miller and C. H. Townes, *ibid.*, **90**, 537 (1953).
(4) S. L. Miller, C. H. Townes, and M. Kotani, *ibid.*, **90**, 542 (1953).
(5) A. M. Falik, B. H. Mahan, and R. J. Myers, *J. Chem. Phys.*, **42**, 1837 (1965).
(6) C. A. Arrington, Jr., A. M. Falik, and R. J. Myers, *ibid.*, **55**, 909 (1971).
(7) H. Hasegawa, unpublished.
(8) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964), and the references therein.
(9) A. H. Cooke, H. Meyer, W. P. Wolf, D. F. Evans, and R. E. Richards, *Proc. Roy. Soc., Ser. A*, **225**, 112 (1954).

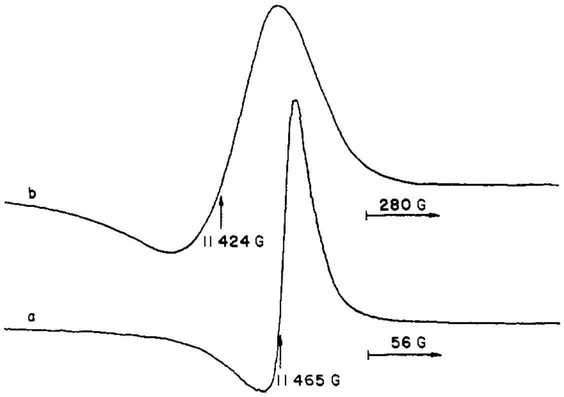

Figure 1. The epr spectra of molecular oxygen in two different matrices observed at 6.8°K. Microwave frequency = 8928.0 MHz. (a) O_2 30 ppm in nitrogen, (b) O_2 0.3% in carbon monoxide.

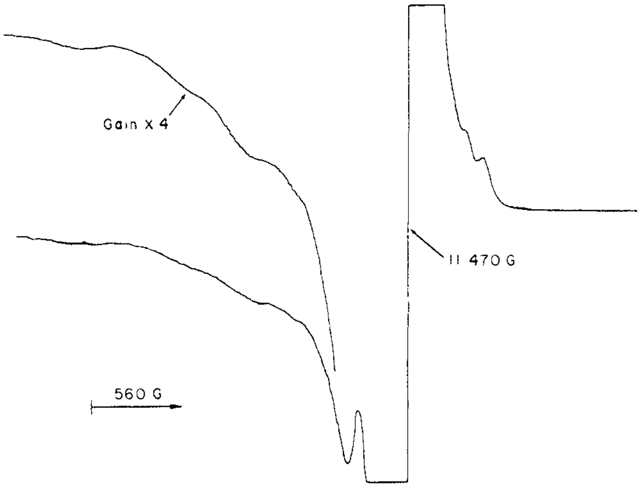

Figure 2. The epr spectra of molecular oxygen showing the typical side bands observed at 0.85% O_2 in nitrogen: temperature = 7.0°K, microwave frequency = 8929 MHz.

concentration is increased, the signal begins to show some broadening at ~100 ppm, and a small side band can be detected at high spectrometer sensitivity on both sides of the main signal. At roughly 1% dilution this side band is readily detectable (Figure 2), and consists of at least two peaks on each side of the main absorption with some additional broad signals on the lower field side, extending over ~2000 G. Further increase in oxygen concentration results in a merging of these additional peaks to form the broad tails of the main signal. The exact origin of these signals is not immediately clear, except that their concentration dependence appears to suggest some type of molecular association. The attempt to reproduce the peak positions on the basis of pairwise dipolar interaction has been unsuccessful. In any event the line width in a nitrogen matrix is strongly concentration dependent and appears to be determined by magnetic dipolar interaction between the oxygen molecules.

In a carbon monoxide matrix, the narrowest line obtained is ~400 G wide peak-to-peak (Figure 1b), no concentration effect being observed below ~0.4%.

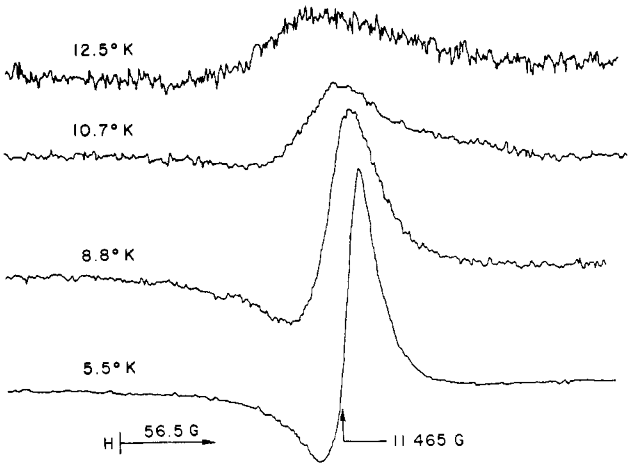

Figure 3. The effect of temperature on the epr absorption of molecular oxygen in nitrogen matrix. The signal position and the line width remain the same below 5.5°K. Above ~13°K the signal is not observable due to the broadening. The spectrometer gain was increased by the ratio 1:2:2:4 as the temperature was raised.

In contrast to these two matrices, an extremely broad band covering almost 10,000 G was observed in argon, regardless of oxygen concentrations. No signal was detected in hydrogen, xenon, and carbon dioxide. These qualitative observations strongly indicate that the structure of the surrounding matrix is a major factor in determining the line width, probably through perturbation of the hindered rotation (or torsional oscillation) of an oxygen molecule in the matrix. There appears to be no obvious correlation between the line width and the melting or boiling point of the matrix relative to that of oxygen. We have also tested the effect of molecular sieves, which would provide empty space for oxygen molecule(s) to be trapped in somewhat analogous manner to the clathrate compound mentioned before. In the presence of molecular sieves, which was exhaustively degassed beforehand, oxygen gave no signal in this high field region regardless of the amount of oxygen used. The same result was obtained with silica gel.[10] A weak broad resonance (~1000 G wide) sometimes observed is considered to be the result of incomplete elimination of nitrogen. In the absence of a matrix no signal was obtained at low oxygen pressure (≤200 mm), probably due to the formation of diamagnetic aggregates and/or strong dipolar broadening.

The line width and the signal position vary depending upon the temperature. In a nitrogen matrix, in which the most accurate observation was possible, both the line width and the position remain the same below ~7°K, while above this temperature the signal begins to broaden and simultaneously shifts toward lower field (Figure 3). Above ~13°K the signal is broadened almost beyond detection. No attempt was made to obtain quantitative measurements of the integrated intensity as a function of the temperature. However,

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(10) In these systems and in some gas matrices a much less intense signal with the half-width of ~90 G was observed near 1600 G. This may correspond to the $\Delta M_s = 2$ transition, which is formally forbidden, but becomes allowed in the presence of rhombic distortion and when the molecule is slightly off the parallel orientation. In silica gel nearly 90% of the signal intensity disappears when the system is heat evacuated. However, the possibility of the signal being due to some heavy metal ion could not be completely ruled out.

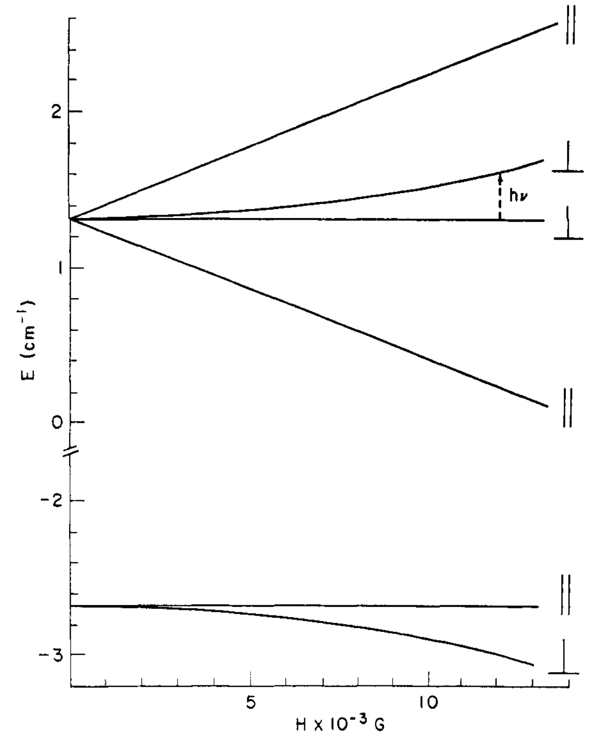

Figure 4. The energy levels of the spin system with $S = 1$ calculated from the axial spin-Hamiltonian with $D = 3.96$ cm^{-1}, the molecular axis being parallel and perpendicular to the external field. The arrow indicates the size of the microwave quantum used.

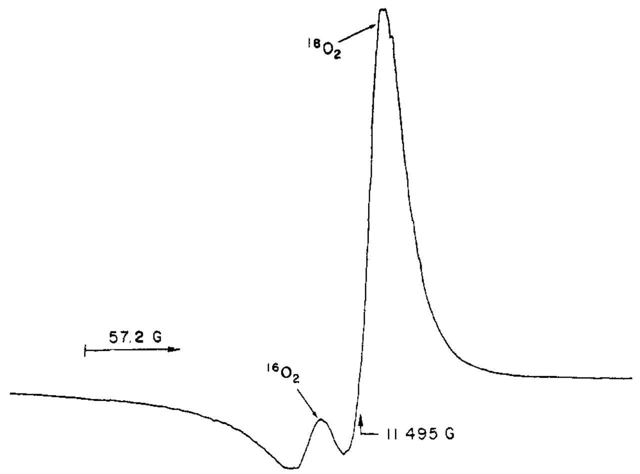

Figure 5. The epr spectrum of $^{18}O_2$ (~50 ppm) with a trace amount of $^{16}O_2$, in nitrogen matrix: temperature = 7°K, microwave frequency = 8926 MHz.

since the resonance absorption corresponds to the transition between the two higher spin states, located approximately 4.2 cm^{-1} above the ground state (see below), it is expected that the total absorption intensity will show a maximum near 4°K and drop sharply at lower temperatures.

Torsional Oscillation and Isotope Effect. In the absence of a rhombic distortion of the valence shell, the spin state of an oxygen molecule is described by the spin-Hamiltonian[8]

$$\mathcal{H} = D[S_\lambda{}^2 - S(S+1)/3] + \mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S}$$

with the total spin $S = 1$, and the λ axis is along the molecular axis. Using the bases, $|m_s\rangle$, the energy levels and the eigenfunctions can be calculated for general orientations of the molecule relative to the external magnetic field direction. The diagram for the parallel and the perpendicular orientation is shown in Figure 4. The transition between the two higher perpendicular spin states, obviously, is the only one which would give rise to a resonance absorption anywhere near 11,500 G at the X-band microwave frequency. However, with the numerical values of the spin-Hamiltonian parameters obtained by the gas-phase spectroscopy,[2] $g = 2.00$ and $D = 3.96$ cm^{-1}, the predicted resonance field is 12,083 G, roughly 600 G higher than the observed. As will be shown later the comparison of ^{17}O hyperfine splitting observed in a nitrogen matrix with that of gaseous oxygen exhibits little perturbation on the valence electrons due to the nitrogen matrix. This difference between the predicted and the observed resonance field was observed quite reproducibly, and can be best explained by assuming that the molecular oxygen is showing some torsional oscillation in the matrix around the equilibrium position,[11,12] which in this case is perpendicular to the magnetic field. Approximating the potential by $V = V_0(1 - \cos 2\theta)$, where θ is the angle between the molecular axis and the equilibrium direction, the effective zero-field parameter, D', is given by $D' = D[1 + 3(\langle\cos 2\theta\rangle_{av} - 1)/4]$ (see Discussion). Since the resonance field, H, and D' are related, for the perpendicular orientation, by $hc\bar{\nu} = -D'/2 + (D'^2 4g^2\beta^2H^2)^{1/2}/2$, where $hc\bar{\nu}$ is a microwave quantum, there will be a downfield shift of the resonance corresponding to the mean angular deviation of the molecular axis from the equilibrium position. Assuming that the two-dimensional harmonic oscillator model is valid at the low temperatures of our observations, then $\langle 1 - \cos 2\theta\rangle_{av} = (\hbar^2/IV_0)^{1/2}$,[11] where I is the moment of inertia for an oxygen molecule. We can calculate the barrier height V_0 from the observed resonance position. In a nitrogen matrix $H = 11{,}465$ G, $\bar{\nu} = 0.2976$ cm^{-1}, and $I = 1.9348 \times 10^{-39}$ g cm^2,[13] we obtain $V_0 = 152$ cm^{-1} and the first vibrational excited state as 42 cm^{-1} above the ground state, or 60°K as compared with ~6°K where the observations were made. Thus the oscillation is the zero-point motion, and, therefore, the harmonic oscillator model is most likely a good approximation. Similar calculations for carbon monoxide matrix gave $V_0 = 135$ cm^{-1} with the first excited state at 39 cm^{-1}. It is remarkable that oxygen exhibits an almost 20 times broader absorption signal in a carbon monoxide matrix than in the nitrogen, in spite of the relatively small difference in the potential barrier.

The above assignment of the resonance signal to the perpendicular transition, and the oscillation hypothesis for the downfield shift can be tested simply by an analogous experiment using $^{18}O_2$. It is predicted, that due to the larger moment of inertia (2.1767×10^{-39} g cm^2),[14] the $^{18}O_2$ resonance will be located at a magnetic field 36 G higher than the corresponding $^{16}O_2$ signal

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(11) H. Meyer, M. C. M. O'Brien, and J. H. Van Vleck, *Proc. Roy. Soc., Ser. A*, **243**, 414 (1958).

(12) E. Wasserman, V. J. Kuck, R. S. Hutton, and W. A. Yager, *J. Amer. Chem. Soc.*, **92**, 7491 (1970).

(13) Calculated from the rotational constant, B_e, given by G. Herzberg, in "Spectra of Diatomic Molecules," Van Nostrand, New York, N. Y., 1950, Table 39.

(14) Calculated by assuming the same interatomic distance as in $^{16}O_2$.

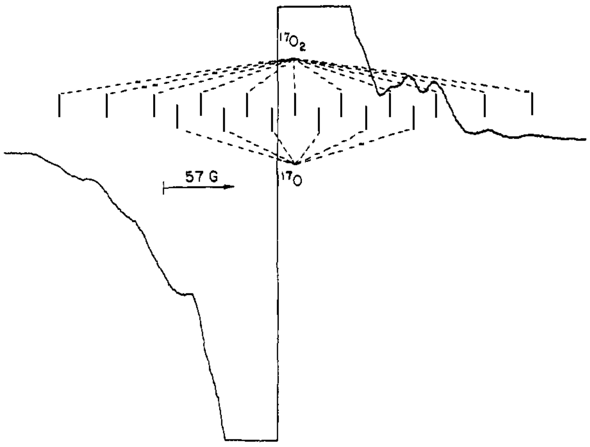

Figure 6. The epr absorption of ^{17}O enriched oxygen diluted in nitrogen matrix (~1%) observed at 6°K. The predicted hyperfine structures are shown for ^{17}O–^{16,18}O and $^{17}O_2$, respectively.

under the same conditions. As shown in Figure 5, the two peaks are indeed separated by 37 ± 1 G in excellent agreement with prediction. This result provides a sound basis for the above interpretation of the spectral data.

^{17}O Nuclear Hyperfine Structure. The epr spectrum of ^{17}O-enriched oxygen in nitrogen matrix is shown in Figure 6. In spite of somewhat poor resolution, especially on the lower field side of the main peak, the equally spaced additional peaks are readily observed. These are considered to be a part of the ^{17}O–^{16,18}O and ^{17}O–^{17}O hyperfine structure due to the nuclear spin $^5/_2$. The difficulty in resolution is probably due to the fact that the specimen used contains the combinations of ^{16}O, ^{17}O, and ^{18}O isotope to comparable degrees (see Experimental Section) and that each species gives rise to a slightly shifted resonance, resulting in a diffuse spectrum. The relative intensity of the hyperfine components seems to be distorted by the same reason.

Miller, Townes, and Kotani[4] fitted the results of their microwave absorption study of gaseous ^{16}O–^{17}O to an axial Hamiltonian, $\mathcal{H}_{\rm hf} = b\mathbf{I}\cdot\mathbf{S} + cI_zS_z$, with $b = -102$ MHz and $c = 140$ MHz. The parameters are defined by $b = 2g_I\beta\beta_n[8\pi\psi^2(0)/3 - \langle(3\cos^2\chi - 1)/2\mathbf{r}^3\rangle_{\rm av}]$ and $c = 6g_I\beta\beta_n\langle(3\cos^2\chi - 1)/2\mathbf{r}^3\rangle_{\rm av}$, where χ is the angle made by the O–O axis and the vector $\mathbf{r}$ pointing from the ^{17}O nucleus to the electron.

In order to compare the present result with the above Hamiltonian, the latter was averaged over the spin functions pertinent for the two states involved in the transition. With $\psi = \xi|1\rangle + \eta|0\rangle + \zeta|-1\rangle$, the result is $\mathcal{H}_{\rm I} \equiv \langle\psi|\mathcal{H}_{\rm hf}|\psi\rangle = (\xi^2 - \zeta^2)(b + c)I_z + b\eta(\xi + \zeta)(I_+ + I_-)/2$. Ignoring the zero-point motion for a moment, the coefficients are calculated to be, for the microwave quantum 0.2973 cm^{-1}, $\xi = -\zeta = 1/\sqrt{2}$, $\eta = 0$ for the lower spin state, and $\xi = \zeta = 0.6837$, $\eta = 0.2549$ for the upper state. Note that the lower state is nonmagnetic and the hyperfine interaction comes only from the upper state through the second term of $\mathcal{H}_{\rm I}$. A splitting of 50.3 MHz is obtained by solving the 6 × 6 matrix with $|m_I\rangle$ as the basis. Thus it is predicted that there are six equally spaced peaks for ^{17}O–^{16,18}O and eleven for $^{17}O_2$ with the separation of 37 G, which is in good agreement with the observed within the accuracy of measurement (±1 G). The fact that the hyperfine parameters obtained in the gas phase can be transferred to the present case probably mean that the valence-shell electrons are not much perturbed in the nitrogen matrix, since the hyperfine interaction is considered to be sensitive to the change of unpaired electron distribution. The small torsional oscillation which we have ignored in this treatment would have no effect, in the first order, on the hyperfine splitting, since the mean square angular deviation from the equilibrium (perpendicular) position can be taken into account by replacing the parameter b in the above equation by αb, where α is a constant factor common to all the matrix elements.

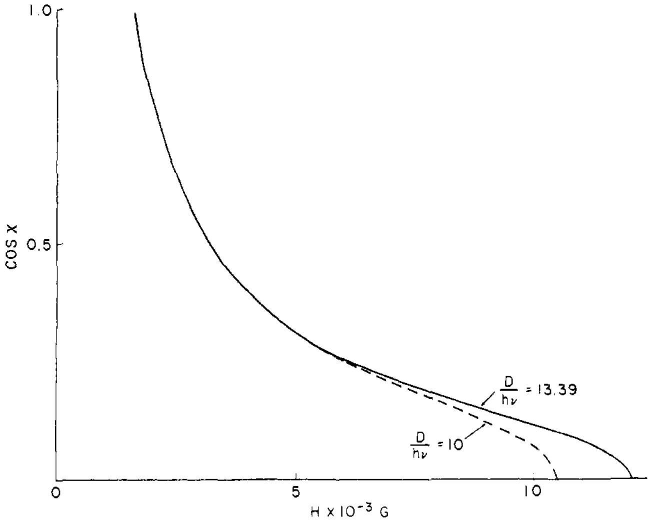

Figure 7. Plot of the epr signal position as the function of the molecular orientation of oxygen ($D/h\nu = 13.39$) and of a hypothetical case ($D/h\nu = 10$). χ is the angle made by the molecular axis and the external field direction. The signal position is especially sensitive near the perpendicular orientation to the change of D.

Discussion

We have seen that molecular oxygen does not exhibit an easily detectable epr signal in many of the rigid matrices tried in the present work. The reason for this difficulty may be traced to the unusually large zero-field splitting of the oxygen molecule, $D \sim 4$ cm^{-1}. One result of such large zero-field splitting is that there would be considerable anisotropy in the resonance signal. As illustrated in Figure 7, the resonance field of oxygen (the curve with $D/h\nu = 13.39$) will cover more than 10,000 G as the molecule is tilted from the perpendicular to the parallel position. Near the perpendicular orientations the resonance position is particularly sensitive to the change of orientation as well as the zero-field parameter. In a nitrogen matrix, the average angular deviation from the perpendicular position is calculated from the observed effective zero-field splitting to be 15°. Thus the resonance would traverse, in this case, roughly 6000 G, which is equivalent to a change in the resonance frequency of ~10 GHz (0.33 cm^{-1}). At first sight this much of the fluctuation appears to be effectively averaged out by the zero-point motion, which has the frequency of the order of 600 GHz (20 cm^{-1}), resulting in a narrow signal such as the one actually observed in a nitrogen matrix. In other matrices this condition may not hold, and the line would be correspondingly broadened, perhaps beyond detection. The oxygen contained in a β-quinol clathrate in which no epr signal was detected[9] may indeed obtain considerable part of the broadening from the low potential barrier of the torsional oscillation (V_0 = 22.3 cm^{-1}) as estimated from the susceptibility measurement.[11]

That this is not the only criterion, however, for the line broadening can be demonstrated by comparing the zero-point frequency and the observed line width for the signals in the nitrogen and carbon monoxide matrix and for the temperature broadened signal in the nitrogen at 12.5°K (Figure 3). The zero-point energies for these, calculated by assuming that the signal position is determined entirely by the torsional oscillation, are roughly the same, 21, 19.5, and 19 cm^{-1}, respectively, while the line width of each is 20, 400, and 85 G. The above treatment was based upon the spin-Hamiltonian written in the laboratory framework

$$\begin{aligned}\mathcal{H} = {}^3/_2D(\cos^2\theta - {}^1/_3)[S_z^{\,2} - {}^1/_3S(S+1)] + \\ {}^1/_2D\sin\theta\cos\theta[(S_+\exp(-i\phi) + S_-\exp(i\phi))S_z + \\ S_z(S_+\exp(-i\phi) + S_-(\exp(i\phi))] + \\ {}^1/_4D\sin^2\theta[S_+^{\,2}\exp(-2i\phi) + S_-^{\,2}\exp(2i\phi)] + g_0H_0S_x\end{aligned}$$

where the magnetic field is along the x fixed in space, and the polar (θ) and the azimuthal (ϕ) angle of the molecular axis are, in general, fluctuating with time. In the present situation, in which the oxygen molecule is in a torsional oscillation around the perpendicular position, the second and the third terms will be averaged out, provided the time change of ϕ is sufficiently rapid and random. The symmetrical precession of the molecule around an equilibrium orientation is a typical such case. Incomplete averaging of these terms would result in a considerable broadening as well as the shift of the resonance field. An order of magnitude estimation by the perturbation method shows that the third term could introduce a maximum fluctuation in the resonance frequency of 7 GHz, at θ = 15°, indicating that the change of ϕ with time is a key factor in determining the broadening and the signal position.

These two terms would effect the broadening, not only through the $1/T_2$ mechanism, but by the spin-lattice relaxation as well. Both of these effects are proportional to D^2, and, therefore, can be at least an order of magnitude greater than in ordinary organic triplet molecules with $D < 1$ cm^{-1}. Thus we can see that the condition for observing a narrow epr signal of molecular oxygen in a matrix would be quite limited; the more rigid lattice and the lower temperature would be needed for the high potential barrier for the rapid torsional oscillation (change of θ), but the lattice must also provide a highly symmetrical potential around the molecular axis so that the precessional motion around this axis would not be perturbed or frozen at the low temperatures required.

Summary

We have demonstrated that the epr signal of molecular oxygen in a matrix is greatly influenced by the immediate molecular environment. The observed line width was found to depend very sensitively upon the shape of the potential well in which an oxygen molecule carries out torsional oscillation and/or precessional motion.

Similar studies using a better defined matrix or a crystal lattice to provide a potential field would yield detailed information concerning the interaction of an oxygen molecule with the environment.

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