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ESR ABSORPTION AND RELAXATION MECHANISM
FOR p-BENZOSEMIQUINONE IN THE ZEEMAN REGION

J. V. Acrivos

August 1962
ESR Absorption and Relaxation Mechanism
for p-Benzosemiquinone in the Zeeman Region

J. V. Acrivos

Inorganic Materials Research Division of the Lawrence Radiation Laboratory, University of California Berkeley, California

Abstract

The spin-lattice interaction for a free radical undergoing rapid Brownian motion, in the absence of electronic exchange, has been studied in the Zeeman region. The experimental and theoretical investigation indicates that the following relaxation mechanisms are all present in the case of the p-benzosemiquinone ion in sodium ethylate-ethanol solutions: (a) the intramolecular anisotropic hyperfine interaction, (b) the spin-orbit-phonon, Raman type, interaction; and (c) the modulation of the isotropic hyperfine energy of interaction by the electron distribution in the neighborhood of the free radical.
INTRODUCTION

The ESR absorption of the p-benzosemiquinone ion in sodium ethylate-ethanol has been studied in the field range of ±10 oe, in the temperature interval of 25° to -50°C, and at radio frequency energies less than the corresponding zero field hyperfine splittings, for the purpose of investigating the dominant relaxation mechanisms of this free radical. In this region, all the Zeeman transitions, including the hyperfine transitions, which had not been observed to this date by direct electromagnetic detection, have been completely resolved and identified.

The relaxation mechanisms for the different spin eigenstates of a paramagnetic ion undergoing rapid Brownian motion in solution is determined by the transitions that are induced by any or all of the following possible mechanisms: (a) the time dependent perturbation of inter and intramolecular anisotropic hyperfine interactions$, ^1,2,3,4$, (b) the spin-orbit coupling, $^4,5,6,7$ where the transitions induced by the anisotropy of the electronic g-factor $^4,6$ and the spin-orbit-phonon interactions are special cases, and (c) the electronic $^8$ and chemical $^9$ exchange interactions where the latter introduce a modulation of the isotropic hyperfine coupling constant, $^{10,11}$ by disturbing the electron distribution in the neighborhood of the free radical.

Fraenkel et al.$^4,12$ investigated the relaxation mechanisms for the p-benzosemiquinone in the Paschen-Back region and concluded that case (a) above was the dominant process. However, in the Zeeman region it has been found that all three cases mentioned above significantly affect the lifetime of the Zeeman levels. Moreover, for free radical concentrations of the order of $10^{-3}$M, the same line widths have been observed in high,$^{13,14}$ as well as in low fields, a fact which excludes the possibility of relaxation via the
anisotropy of the g-factor since, for this case, the line widths should be proportional to the square of the resonance frequency.

EXPERIMENTAL RESULTS

The ESR of 0.001 to 0.006M p-benzoquinone in 0.04M NaOC,H in C,H,OH were determined with a Varian 4200 wide line spectrometer, at the constant frequencies: ν = 16.416; 16.217; 13.590 and 9.916 Mc/sec. The laboratory field, H, homogeneous to 0.10 oe within the volume of the sample, was sinusoidally modulated at a frequency ν = 4420 cps, with an amplitude of H = 0.02 oe and the spectra were recorded at the rate of |dH/dt| = 0.01 oe/sec., in the range of ±10 oe. A fresh sample was prepared for each run and the free radical concentration was found to be constant throughout the recording time of a complete spectrum, as evidenced by the reproducibility of the intensity about zero field, shown in Fig. 1. The spectra in Fig. 1 are identified as those of the p-benzoquinone ion, at room temperature. The ESR absorption was studied in the interval t = 25° to -50°C, where the temperature was measured to ±0.5°C by means of a copper-constantan thermocouple. The low temperature Dewar has been described elsewhere. In addition to the proton hyperfine interaction at low temperatures, the ESR absorption indicates the existence of a hyperfine interaction with two sodium ions. This ESR absorption at t = -49.5°C is shown in Fig. 2 for the central proton hyperfine component.

ANALYSIS OF THE ESR SPECTRA

The ESR absorption obeys the selection rules:

$$|ΔF| = 0 \text{ or } 1, \Delta F^z = ±1,$$

where at room temperature,

$$I_0 = S + \sum_{i=1}^{4} I_{i} \quad (S = \frac{3}{2}, I_H = \frac{1}{2}).$$
The steady state spin eigenfunctions of $H^2$ and $F^2$, transform within
the $D_{2h}$ group, according to the symmetry operations of the molecule ion
where the irreducible representation is:

$$\Gamma = 2_A + 1_B + 1_{2u} + 1_{3u} + 2 \sigma_{1g}.$$  \hspace{1cm} (2)

The superscript gives the total nuclear spin angular momentum for the
symmetry species.

The ESR spectra are analyzed according to the spin Hamiltonian:

$$\mathcal{H}^s = \left[ |g_e|^2 - g_p \sum_{i=1}^4 I_i^2 \right] H + A \sum_{i=1}^4 \mathbf{S}_i \cdot \mathbf{S} + J \sum_{i>j} \mathbf{S}_i \cdot \mathbf{S}_j \cdot (n=0; m;p)$$

$g_e = g_e^0$ and $g_p = g_p^0$ are the gyromagnetic ratios for the free electron and
the proton respectively, where $|g|$ and $g_0$ are the Bohr and nuclear magneton.$$
A$ and $J$, $n=0$, $m$, $p$, are the isotropic electron-proton, and proton-proton
spin coupling constants for, respectively, ortho, meta and para protons.$$

The room temperature steady state spin eigenfunctions are given in Table 1
and the Breit-Rabi\textsuperscript{16} energy levels are shown in Fig. 5. The nuclear hyperfine
energy is not included in the Breit-Rabi levels, since, in this case, the
levels of the same symmetry are shifted equally by the nuclear interaction,
and therefore do not contribute to the ESR spectrum. Also, $J_\alpha \approx 10$ cps\textsuperscript{17} whereas
$A \approx 6.6$ Mc/sec\textsuperscript{12,13} at low temperatures the total quantum number is given by
$F^s = F + \sum_{i=1}^2 L_i$ and the steady state spin eigenfunctions are obtained from
the reduced direct product of the eigenfunctions in Table 1 with those of the
two sodium ions. The latter reduce in the $C_2$ symmetry group according to:

$$\Gamma = 3_A + 2_B + 1_A + 0_B$$  \hspace{1cm} (4)

Table 2 gives the spin eigenfunctions for the spin system $2 \text{Na}^{25}$. 
The theoretical ESR absorption spectra, shown in Fig. 1, were calculated according to the functional dependence of the resonance field given in Table 3. At $t = 49.5^\circ C$ the $(Na^{23})_2$ hyperfine splitting of the proton $^{0}A_g$ transitions, shown in Fig. 2, was calculated by making use of the spin eigenfunctions and energies given in Table 2 correct to second order in the sodium coupling constant with respect to the applied field. The measured coupling constants are:

\[ \begin{align*}
A(e - H^2) &= 6.631 \pm 0.003 \text{ Mc/sec}.
A'(e - Na^{23}) &= 0.34 \pm 0.05 \text{ Mc/sec},
\end{align*} \]

The ESR absorption line widths between the points of maximum slope at 16.416 Mc/sec. are

- a) for $T = 298^\circ K$
  \[ \Delta v_{ms} = 258 \pm 5 \text{ kc/sec}, \text{ for } ^0A_g : |1/2, 1/2> \leftrightarrow |1/2, -1/2> \]
  \[ < \Delta v_{ms} > = 297 \pm 40 \text{ kc/sec, all others}. \]
- b) for $T = 223.5^\circ K$
  \[ \Delta v_{ms} = 150 \pm 15 \text{ kc/sec}. \]

for the $(Na^{23})_2$ proton hyperfine components of the $^0A_g$ transitions. The line widths were found to be independent of the initial concentration of the p-benzoquinone for concentrations below 0.005 M.

The hyperfine transitions which are observed when the rf energy is less than the zero field splitting, are of negative polarity with respect to the electronic transitions, since $\Delta W^2$ is of opposite sign, as shown by the Breit-Rabi energy levels in Fig. 3. This effect appears as a change in sign of the slope of the absorption derivative in Fig. 1. Also, in zero field, when $hv = 2.5 |A|$ and $1.5 |A|$, there will be theoretically no ESR absorption due to the fact that two identically probable transitions of opposite polarity are present. This is shown in Fig. 4 and 5.
Table 1. Spin Functions of the p-Benzoquinonemine Ion in the D$_{2h}$ Group

<table>
<thead>
<tr>
<th>Spin Function</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2A_g \rightarrow ^2F^g$</td>
<td></td>
</tr>
<tr>
<td>1. $</td>
<td>5/2, 5/2\rangle = \alpha (a_g)_{5/2}$</td>
</tr>
<tr>
<td>2. $</td>
<td>3/2, 3/2\rangle = \alpha (a_g)_{3/2}$</td>
</tr>
<tr>
<td>3. $</td>
<td>5/2, 3/2\rangle = \beta (a_g)_{5/2}$</td>
</tr>
<tr>
<td>4. $</td>
<td>3/2, 1/2\rangle = \alpha (a_g)_{3/2}$</td>
</tr>
<tr>
<td>5. $</td>
<td>5/2, 1/2\rangle = \beta (a_g)_{5/2}$</td>
</tr>
<tr>
<td>6. $</td>
<td>3/2, -1/2\rangle = \alpha (a_g)_{3/2}$</td>
</tr>
<tr>
<td>7. $</td>
<td>5/2, -1/2\rangle = \beta (a_g)_{5/2}$</td>
</tr>
<tr>
<td>8. $</td>
<td>3/2, -3/2\rangle = \alpha (a_g)_{3/2}$</td>
</tr>
<tr>
<td>9. $</td>
<td>5/2, -3/2\rangle = \beta (a_g)_{5/2}$</td>
</tr>
<tr>
<td>10. $</td>
<td>5/2, -5/2\rangle = \beta (a_g)_{5/2}$</td>
</tr>
</tbody>
</table>

$^0A_g$

<table>
<thead>
<tr>
<th>Spin Function</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>11. $</td>
<td>1/2, 1/2\rangle = \alpha (a_g)_{1/2}$</td>
</tr>
<tr>
<td>12. $</td>
<td>1/2, 1/2\rangle = \alpha (a_g)_{1/2}$</td>
</tr>
<tr>
<td>13. $</td>
<td>1/2, -1/2\rangle = \alpha (a_g)_{1/2}$</td>
</tr>
<tr>
<td>14. $</td>
<td>1/2, -1/2\rangle = \alpha (a_g)_{1/2}$</td>
</tr>
</tbody>
</table>
Table 1 - (continued)

\( \chi_{1g}^1 \quad \chi_{2u}^1 \quad \chi_{3u}^1 

\begin{align*}
&15. \quad (3/2, 3/2) = \alpha (\Gamma)_1 \quad (\Gamma = \chi_{1g}^1 \quad \chi_{2u}^1 \quad \chi_{3u}^1) \quad \frac{1}{2} |r_e^1| - |r_p^1| H + \frac{3}{2} A + K(\Gamma) \\
&16. \quad (1/2, 1/2) = \beta (\chi_{1g}^1) \times \alpha (\Gamma)_0 \quad -\frac{1}{2} |r_p^1| H - \frac{1}{2} A + K(\Gamma) + c^1 \\
&17. \quad (3/2, 1/2) = \beta (\Gamma)_1 \quad -\frac{1}{2} |r_p^1| H - \frac{1}{2} A + K(\Gamma) - c^1 \\
&18. \quad (1/2, -1/2) = \beta (\chi_{1g}^1) \times \alpha (\Gamma)_{-1} \quad \frac{1}{2} |r_p^1| H - \frac{1}{2} A + K(\Gamma) + c^1 \\
&19. \quad (3/2, -1/2) = \beta (\Gamma)_0 \quad \frac{1}{2} |r_p^1| H - \frac{1}{2} A + K(\Gamma) - c^1 \\
&20. \quad (3/2, -3/2) = \beta (\Gamma)_{-1} \quad -(\frac{1}{2} |r_e^1| - |r_p^1| H + \frac{3}{2} A + K(\Gamma)
\end{align*}

The nuclear spin functions are expressed according to the species in the \( D_{2h} \) group from which they are generated, thus:

\( \langle \Gamma \rangle_2 = \frac{1}{g} \sum P \chi^P (\Gamma) \xi_2 |z^2 \rangle \)

where \( P \) represents all the symmetry operations of the group, of dimension \( g = 8 \), and \( \chi^P (\Gamma) \) are the corresponding characters for the species \( \Gamma \). \( \alpha \) and \( \beta \) are the spin eigenfunctions of \( S^2 \), \( S^z \) with \( S = \frac{1}{2} \).

The \( R(\hat{e}) \) are the proper two dimensional rotation operators:

\[
R(\hat{e}) = \begin{pmatrix}
\cos \theta & \sin \theta \\
-\sin \theta & \cos \theta
\end{pmatrix}
\]

where

\[
\begin{align*}
\cos 2 \theta_n &= \frac{A_n}{c_n} \\
\sin 2 \theta_n &= \frac{c_n}{A_n} \\
A_n &= \frac{1}{2} \left( |r_e^1| + |r_p^1| H + \frac{A}{2} \right) \\
c_n &= \frac{1}{2} \left( |r_e^1| \pm |r_p^1| H + \frac{A}{2} \right)^{1/2}
\end{align*}
\]

for \( n = 0 \),

\[
\cos 2 \theta_0 = \frac{1}{2} \left( \frac{2J^1}{J_0} - 1 \right) \\
\sin 2 \theta_0 = \frac{3}{2} \left( \frac{J - J_0}{J_0} \right)
\]

\( J = J_0 + \frac{1}{2} \sum_{m} L_m \cdot \tau_p \)
\[ c \pm 3 = 1 \]
\[ c \pm 1 = \frac{\sqrt{3}}{2} \]
\[ \beta \pm 1 = \frac{1}{\sqrt{2}} \]

...  

\[ B_{1g}, B_{2u}, B_{3u} \] are degenerate, except for the nuclear spin coupling energy, thus:

\[ K (B_{1g}) = \frac{1}{2} J - \frac{1}{2} J \]
\[ K (B_{2u}) = \frac{1}{2} J - \frac{1}{2} J \]
\[ K (B_{3u}) = \frac{1}{2} J - \frac{1}{2} J \]

---
TABLE 3: Spin Eigenfunctions for the System E_2^3 in the C_2 Group

<table>
<thead>
<tr>
<th>Spin Function:</th>
<th>1_A</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>3, 3 \rightarrow a a</td>
</tr>
<tr>
<td>2.</td>
<td>3, 2 \rightarrow 2^{-1/2}(ab + ba)</td>
</tr>
<tr>
<td>3.</td>
<td>3, 1 \rightarrow 5^{-1/2}(3^{1/2}bb + ab' + b'a)</td>
</tr>
<tr>
<td>4.</td>
<td>3, 0 \rightarrow 20^{-1/2}[(aa' + a + 3(bb' + b'b)]</td>
</tr>
<tr>
<td>5.</td>
<td>3, -1 \rightarrow 10^{-1/2}(2b' - 3^{1/2}(a' + ba'))</td>
</tr>
<tr>
<td>6.</td>
<td>3, -2 \rightarrow 2^{-1/2}(a'ba')</td>
</tr>
<tr>
<td>7.</td>
<td>3, -3 \rightarrow a'a'</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Spin Function:</th>
<th>1_B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>2, 2 \rightarrow 2^{-1/2}(ab - ba)</td>
</tr>
<tr>
<td>2.</td>
<td>2, 1 \rightarrow 2^{-1/2}(ab' + b'a)</td>
</tr>
<tr>
<td>3.</td>
<td>2, 0 \rightarrow 2^{-1/2}(aa' + a' + bb' - b'b)</td>
</tr>
<tr>
<td>4.</td>
<td>2, -1 \rightarrow 2^{-1/2}(a'ba')</td>
</tr>
<tr>
<td>5.</td>
<td>2, -2 \rightarrow 2^{-1/2}(a'ba')</td>
</tr>
</tbody>
</table>

---

The spin eigenfunctions are given with respect to the value of the s component of angular momentum. Here a, b, b', a' correspond to \( I_s^a = 3/2, 1/2, -1/2, -3/2 \), respectively.
Table 7: Transition Fields and Energies for the Zeeman Spectrum of the p-Benzoquinone Ion.

<table>
<thead>
<tr>
<th>Allowed Transition</th>
<th>Resonance Field at Constant Frequency</th>
<th>Relative Intensity</th>
<th>Limits of the Transition Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(</td>
<td></td>
<td>\gamma_e</td>
</tr>
<tr>
<td>(2A : F^2 = -\frac{5}{2})</td>
<td>(-2 - \frac{2}{c})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. (\Delta F = 1)</td>
<td>(e \pm 2.5A -</td>
<td>\gamma_e</td>
<td></td>
</tr>
<tr>
<td>2. (\Delta F = 0)</td>
<td>(\sin^2 \theta_{-3})</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(F^2 = -\frac{3}{2} - \frac{1}{2})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. (\Delta F = 1)</td>
<td></td>
<td>(\cos^2 \theta_{-3} \cos^2 \theta_{-1})</td>
<td>(-2.5A)</td>
</tr>
<tr>
<td>4. (\Delta F = -1)</td>
<td>(\pm \frac{A^2 \left[ e^2 A^2 \frac{22}{44} (1 - \frac{A^2}{4c^2}) \right]}{4c^2} )</td>
<td>(\sin^2 \theta_{-3} \sin^2 \theta_{-1})</td>
<td>2.5A</td>
</tr>
<tr>
<td>5. (\Delta F = 0)</td>
<td>(\sin^2 \theta_{-3} \cos^2 \theta_{-1})</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6. (\Delta F = 0)</td>
<td>(\cos^2 \theta_{-3} \sin^2 \theta_{-1})</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
### Table 3: (Continued)

| Allowed Transition | \((|r_e| - r_p)R\) | a Relative Intensity | Zero Field \(\varepsilon - \hbar\nu\) | Limits of the Transition Frequency |
|--------------------|----------------|---------------------|----------------|---------------------------------|
| \(F = \frac{1}{2} \leftrightarrow \frac{3}{2}\) | c | | | |
| 7. \(\Delta F = 1\) | \(\cos^2 \theta_1 \cos^2 \phi_1\) | -2.5A | 1.5 | \(|r_e|H_0\) | 1 |
| 8. \(\Delta F = -1\) | \(\sin^2 \theta_1 \sin^2 \phi_1\) | 2.5A | 1.5 | - | 0 |
| \(+0.9970\) | | | | |
| 9. \(\Delta F = 0\) | \(\sin^2 \theta_1 \cos^2 \phi_1\) | 0 | 0 | .5A | \(d_{02}\) |
| 10. \(\Delta F = 0\) | \(\cos^2 \theta_1 \sin^2 \phi_1\) | 0 | 0 | - .5A | \(d_{02}\) |
| \(F = \frac{1}{2} \leftrightarrow \frac{3}{2}\) | d | | | |
| 11. \(\Delta F = 1\) | \(\cos^2 \theta_1 \cos^2 \phi_3\) | -2.5A | .5 | \(|r_e|H_0 + A\) | 1 |
| 12. \(\Delta F = 1\) | \(\sin^2 \theta_1 \sin^2 \phi_3\) | 2.5A | 3 | - | 0 |
| \(+0.9970\) | | | | |
| 13. \(\Delta F = 0\) | \(\sin^2 \theta_1 \cos^2 \phi_3\) | 0 | 0 | .5A | \(d_{01}\) |
| 14. \(\Delta F = 0\) | \(\cos^2 \theta_1 \sin^2 \phi_3\) | 0 | 0 | - .5A | \(d_{02}\) |
Table 3: (Continued)

<table>
<thead>
<tr>
<th>Allowed Transition</th>
<th>Resonance Field at Constant Frequency</th>
<th>Limits of the Transition Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(</td>
<td>\tau_e</td>
</tr>
<tr>
<td>(F^2 = \frac{3}{2} \leftrightarrow \frac{5}{2})</td>
<td>(\cos^2\theta_3)</td>
<td>0</td>
</tr>
<tr>
<td>15. (\Delta F = 0)</td>
<td>(\cos^2\theta_3)</td>
<td>0</td>
</tr>
<tr>
<td>16. (\Delta F = 1)</td>
<td>(\sin^2\theta_3)</td>
<td>2.5(A)</td>
</tr>
<tr>
<td>(^0A_e; F^2 = \frac{1}{2} \leftrightarrow \frac{3}{2})</td>
<td>(\cos^2\theta_{-1})</td>
<td>-1.5(A)</td>
</tr>
<tr>
<td>17. (\Delta F = 0)</td>
<td>(\cos^2\theta_{-1})</td>
<td>-1.5(A)</td>
</tr>
<tr>
<td>18. (\Delta F = 1)</td>
<td>(\sin^2\theta_{-1})</td>
<td>0</td>
</tr>
<tr>
<td>19. (\Delta F = 0)</td>
<td>(\cos^2\theta_{-1})</td>
<td>0</td>
</tr>
</tbody>
</table>
\begin{table}
\centering
\caption{Continued.)}
\begin{tabular}{cccccc}
\hline
\multicolumn{2}{c}{Resonance Field at Constant Frequency} & \multicolumn{4}{c}{Limits of the Transition Frequency} \\
\hline
Allowed Transition & \((|\tau_e|, |\tau_p|)\) & Relative Intensity & Zero Field & Paschen-Back Region \\
\hline
\( \frac{1}{2} \leftrightarrow \frac{3}{2} \) & & & & & \\
20. \( \Delta \nu = 1 \) & \( \frac{\beta}{2} \cos \theta \cos \theta \cos \theta \) & -1.5 & 1.5 & \( |\tau_e| B_0 \) & 3 \\
21. \( \Delta \nu = -1 \) & \( 3 \sin \theta \cos \theta \cos \theta \) & 1.5 & 1.5 & - & 0 \\
22. \( \Delta \nu = 0 \) & & 0 & 0 & \( -0.5 \) & 3 03 \\
23. \( \Delta \nu = 0 \) & & 0 & 0 & \( 0.5 \) & 3 03 \\
24. \( \Delta \nu = 0 \) & \( 3 \cos \theta \cos \theta \) & 0 & 0 & \( |\tau_e| B_0 + A \) & 3 \\
25. \( \Delta \nu = 1 \) & \( 3 \sin \theta \cos \theta \) & 1.5 & 4.5 & \( -0.5 \) & 3 03 \\
\hline
\end{tabular}
\end{table}
Table 3: (Continued)

(a) The energy is doubly degenerate in $H$, and here the intensity is to be assigned according to the limiting value of $\alpha$ when $H=0$.

(b) The transitions have been assigned assuming $A$ is negative. If $A$ were positive, although the line assignments would be incorrect, the features of the spectrum remain unchanged.

(c) In order to correct for the gyromagnetic ratio of the proton, $\epsilon$ is to be replaced by $\epsilon - g \gamma_H$.

(d) The hyperfine transitions in high fields are of a relative intensity:

\[ o_1 = \frac{17}{4} \left( \frac{\alpha}{\Delta} \right)^2 + 4 \left( \frac{\gamma_e}{\gamma_p} \right)^2 \]

\[ o_2 = \frac{13}{4} \left( \frac{\alpha}{\Delta} \right)^2 + 6 \left( \frac{\gamma_e}{\gamma_p} \right)^2 \]

\[ o_3 = \frac{5}{4} \left( \frac{\alpha}{\Delta} \right)^2 + 6 \left( \frac{\gamma_e}{\gamma_p} \right)^2 \]
**Relaxation Mechanisms**

The fact that the linewidths observed in low as well as in high fields are of the same magnitude excludes the possibility of a relaxation mechanism through the anisotropy of the g-factor which predicts that the linewidths should be proportional to the square of the free electron Larmor precession frequency. Hence, at the dilutions used, the possible relaxation mechanisms should proceed through the inter and intramolecular anisotropic hyperfine interactions, through the spin-orbit interactions and through the time dependent variations of the isotropic hyperfine coupling constant. These processes, thus determine the steady state population subject to the conditions:

\[ H_k = \sum_j W_{kj} H_j - H_k \sum_j W_{kj} = 0 \quad (k=1, 2 \ldots n) \]

or

\[ W \cdot H = 0 \quad (5) \]

where \( W \) is the lattice and radiation field induced transition probability matrix and \( H \) is the population distribution vector, with components \( H_k \) equal to the population of the state \( k \). The room temperature transition probability matrix \( W \) is factored according to the symmetry of the spin states as follows:

\[ W \cdot H = \begin{pmatrix}
W_{2A_g} & 0 & \cdots & 0 \\
W_{1B_{1g}} & W_{1B_{2g}} & \cdots & 0 \\
0 & 0 & \cdots & W_{1B_{3u}}
\end{pmatrix} \cdot \begin{pmatrix}
H_{2A_g} \\
H_{1B_{1g}} \\
\vdots \\
H_{1B_{3u}}
\end{pmatrix} = 0 \quad (6) \]

where the normalization conditions are:

\[ \frac{1}{N} \sum_{k \text{ in } 2A_g} W_k = \frac{5}{16} \]

\[ \frac{1}{N} \sum_{k \text{ in } 0A_g} W_k = \frac{2}{16} \]
The differential equation of the electron

where $A$ and $B$ are the differential equations of the state $i$ for a Boltzmann distribution and in the presence of an external which induce excitations be determined by the

The equation parameter, $\eta$, is

and

where $N$ and $O$ are the respective populations of the state $i$ for a Boltzmann distribution.
Table 4: Saturation of the ESR absorption of the p-Benzosemiquinone Ion at v = 16.416 Mc/sec.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Relative Intensity of the Transition $a_{\text{rel}}$, $1 \rightarrow 2 &gt;$</th>
<th>Theoretical</th>
<th>low power</th>
<th>Experimental power increase by MB</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g :</td>
<td>5/2, 3/2 \rightarrow</td>
<td>5/2 \rightarrow 5/2 &gt;$</td>
<td>2.23</td>
<td>2.1 ± 1</td>
</tr>
<tr>
<td>$B_{1g} \cdot B_{2u} \cdot B_{3u} :</td>
<td>3/2, 1/2 \rightarrow</td>
<td>3/2, 3/2 &gt;$</td>
<td>0.68</td>
<td>0.73 ± 0.05</td>
</tr>
<tr>
<td>$B_{1g} \cdot B_{2u} \cdot B_{3u} :</td>
<td>1/2, -1/2 \rightarrow</td>
<td>5/2, 3/2 &gt;$</td>
<td>0.68</td>
<td>0.66 ± 0.05</td>
</tr>
<tr>
<td>$A_g :</td>
<td>3/2, 1/2 \rightarrow</td>
<td>5/2, 3/2 &gt;$</td>
<td>0.70</td>
<td>0.76 ± 0.05</td>
</tr>
<tr>
<td>$B_{1g} \cdot B_{2u} \cdot B_{3u} :</td>
<td>1/2, 1/2 \rightarrow</td>
<td>3/2, -3/2 &gt;$</td>
<td>0.70</td>
<td>0.76 ± 0.05</td>
</tr>
</tbody>
</table>

(a) The experimental intensities are the averages for the observed spectra about zero field.

(b) At this frequency there is an accidental degeneracy of two transitions.
distribution in the neighborhood of the free radical, neither of which
influences the lifetime of the states of $A_g$ symmetry. These will be influenced
only by perturbations independent of the proton nuclear spin quantum number
such as the spin-orbit-phonon interactions. In this case,

In the general formulation, the lattice induced transition probabilities
are obtained from the Master equation:1,19,20

$$w_{jk}^0 = \sum_{l} \frac{2 \tau_{cl}}{1 + \omega_{jk} \tau_{cl}^2} \quad \langle k | \lambda(t) | j \rangle^2$$  \hspace{1cm} (8)

where $\lambda(t)$ is the time dependent perturbation which causes the lattice to
exchange energy with the spin states, $\tau_{cl}$ is the correlation time of the per-
turbation, and $\hbar \omega_{jk}$ is the energy separation between the states $j$ and $k$. Hence
the processes under investigation contribute to Eq. 8 as follows:

(a) The intramolecular anisotropic hyperfine interaction with respect
to the axis of quantization, in the direction of the applied field, gives rise
to a random time dependent perturbation with a correlation time given by the
Debye1,21 theory so that $\tau_{ca} \approx 1.1 \times 10^{-10} \text{ sec.}$ when the p-benzoquinone
ion is approximated by a sphere of radius $= 5.4 \: \text{Å}$ in alcohol at room
temperature, with a viscosity $\eta = 0.011 \: \text{poise} \: \text{at } T = 50^\circ \text{C}$, $\eta = 0.0687$ and
$\tau_{ca} = 6 \times 10^{-10} \: \text{sec.}$ The contribution to Eq. 8 is:

$$\langle j | \lambda_{1a}(t) | k \rangle^2 = I_1 (I_1 + 1) \sum_{m} A_{21}^m \langle P_j^m \sum_{k} A_{21}^m | P_k^m \rangle^2$$  \hspace{1cm} (9)

where

$$A_{21}^0 = \frac{2}{3} I_1^2 s^2 - \frac{11}{6} \left( I_1^+ s^- + I_1^- s^+ \right)$$

$$A_{21}^1 = \frac{1}{\sqrt{6}} \left( I_1^+ s^+ + I_1^- s^- \right), \quad A_{21}^{-1} = (A_{21}^1)^*$$

$$A_{21}^2 = \frac{1}{\sqrt{6}} I_1^+ s^+, \quad A_{21}^{-2} = (A_{21}^2)^*$$
\(( r, \theta, \phi) \) are the spherical polar coordinates of the vector connecting the two interacting spins with respect to a molecular axis, and \( Y_{2,m} \) are the associated spherical harmonics of order 2. Using Sidman's \(^{23}\) SCF \( \pi \)-MO's together with the integrals in \(^{4,24}\) the contributions to Eq. (8) at \( \omega = 16 \) Mc/sec. are:

\[
W_{jk} \sim 4 \times 10^4 \cdot I_\Gamma (I_\Gamma + 1) \cdot | \langle F_j F_k \rangle | \sum_{m,i} A_{2i}^m | F_k F_k^z |^2
\]  

(10)

where the limits correspond to \( \pm 25^\circ \) and \(-50^\circ \)C, respectively. \( I_\Gamma \) is the total nuclear spin quantum number for the symmetry species \( \Gamma \). The matrix elements of \( | A_{2i}^m \rangle \) for the spin eigenfunctions given in Table 1 are presented in Table 5.
Table 5: Matrix Elements of the Anisotropic Hyperfine Interaction

| $^2A_0$ | \( |S,1/2\rangle \to |S,1/2\rangle \) | \( |S,3/2\rangle \to |S,3/2\rangle \) | \( |S,1/2\rangle \to |S,-1/2\rangle \) | \( |S,3/2\rangle \to |S,-3/2\rangle \) | \( |S,3/2\rangle \to |S,-1/2\rangle \) | \( |S,1/2\rangle \to |S,-1/2\rangle \) | \( |S,3/2\rangle \to |S,-3/2\rangle \) | \( |S,1/2\rangle \to |S,-3/2\rangle \) | \( |S,3/2\rangle \to |S,-1/2\rangle \) |
|-----|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| \( |S,1/2\rangle \to |S,1/2\rangle \) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| \( |S,3/2\rangle \to |S,3/2\rangle \) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| \( |S,1/2\rangle \to |S,-1/2\rangle \) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| \( |S,3/2\rangle \to |S,-3/2\rangle \) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| \( |S,3/2\rangle \to |S,-1/2\rangle \) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| \( |S,1/2\rangle \to |S,-1/2\rangle \) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| \( |S,3/2\rangle \to |S,-3/2\rangle \) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| \( |S,1/2\rangle \to |S,-3/2\rangle \) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
Table 5: (continued)

| $|\alpha, B_{2u}, B_{3u}|$ | $|3/2, 3/2>|$ | $|3/2, 1/2>|$ | $|3/2, -1/2>|$ | $|3/2, -3/2>|$ | $|1/2, 1/2>|$ | $|1/2, -1/2>|$ |
|---|---|---|---|---|---|---|
| $|3/2, 3/2>|$ | $c_2(1)$ | $\cos^2 \theta_1$ | $0$ | $c_1'(1 + \frac{\pi}{2})$ | $\sin^2 \theta_1$ |
| $|3/2, 1/2>|$ | $\frac{1}{\sqrt{2}} (\frac{1}{2\sqrt{3}})$ | $\frac{1}{4} \cos^2 (\frac{\theta_1 + \theta_2}{2})$ | $\sin^2 \theta_1$ | $A_2(1 \hat{1})$ | $\frac{1}{4} \cos^2 (\theta_1 + \theta_2)$ |
| $|3/2, -1/2>|$ | $\frac{1}{2\sqrt{3}}$ | $0$ | $c_1(-1 + \frac{3}{2})$ | $\frac{1}{4} \cos^2 (\theta_1 + \theta_2)$ | $A_2(1 + \frac{\pi}{2})$ |
| $|3/2, -3/2>|$ | $0$ | $\frac{1}{2\sqrt{3}}$ | $0$ | $\frac{1}{4} \cos^2 (\theta_1 + \theta_2)$ | $c_1(-1 + \pi)$ |
| $|1/2, 1/2>|$ | $\frac{1}{\sqrt{2}} (\frac{1}{2\sqrt{3}})$ | $1/\sqrt{2}$ | $0$ | $1/\sqrt{2}$ | $1/\sqrt{2}$ |
| $|1/2, -1/2>|$ | $0$ | $\frac{1}{2\sqrt{3}}$ | $0$ | $\frac{1}{2\sqrt{3}}$ | $0$ |

| $|0_{\alpha}, 1/2, 1/2>|$ | $|1/2, 1/2>|$ | $|1/2, -1/2>|$ | $|1/2, 1/2>|$ | $|1/2, -1/2>|$ |
|---|---|---|---|---|
| $|1/2, 1/2>|$ | $0$ | $\frac{1}{5\cos^2 \theta_0}$ | $0$ | $0$ |
| $|1/2, -1/2>|$ | $0$ | $0$ | $\frac{1}{5\cos^2 \theta_0}$ | $0$ |
| $|1/2, 1/2>|$ | $\frac{1}{5\cos^2 \theta_0}$ | $0$ | $0$ | $0$ |
| $|1/2, -1/2>|$ | $0$ | $\frac{1}{5\cos^2 \theta_0}$ | $0$ | $0$ |
(a) The proton-proton anisotropic hyperfine interaction has been neglected with respect to the electron-proton terms.

(b) According to the spin eigenfunctions given in Table 1,

\[ c_1(i) = \frac{2}{3} \left[ \cos \theta_1 - \frac{1}{2} \sin \theta_1 \right]^2 \]
\[ c_2(i,j) = \frac{1}{6} \left[ \cos \theta_1 \cos \theta_j + \sin \theta_1 \cos \theta_j - \frac{\sqrt{3}}{2} \sin \theta_1 \sin \theta_j \right]^2 \]
\[ a_1(i) = \left[ \sin 2\theta_1 + \frac{\cos 2\theta_1}{2} \right]^2 \]
\[ a_2(i) = \left[ \sin 2\theta_1 + \frac{\cos 2\theta_1}{\sqrt{3}} \right]^2 \]
\[ c_1(r) = \frac{1}{6} \left[ \cos \theta_1 - \frac{\sqrt{3}}{2} \sin \theta_1 \right]^2 \]

(c) The elements given below the diagonal are the limiting values of the transition probability in the Paschen-Back region and in zero field.

(d) For brevity, s and c correspond to the sine and cosine functions.

(e) The transition probabilities are obtained by multiplying each element by: \( \left( \frac{\hbar^2}{\beta} \right) \frac{2s^2}{r_{pp}} \frac{1}{r_{pp}} \), where \( r_{pp} \) is the distance between the interacting protons.

Hence, according to Table 5, the states \( 2A_g \), \( 1B_{2g} \), \( 1B_{2u} \), and \( 1B_{3u} \) may exchange energy with the lattice through intramolecular anisotropic electron-proton and proton-proton spin hyperfine interactions. However, the intramolecular anisotropic hyperfine operator induces transitions in the state \( 3A_g \) only through proton-proton spin interactions, which are less probable than the electron-proton transitions by the factor:

\[ \left( \frac{\gamma_p}{\gamma_e} \right)^2 \]

This effect leads to a maximum broadening of the state \( 3A_g \) of \( 26 \pm 10 \) cps,15 which is negligible.
At the dilutions used, one free radical ion/3. × 10⁵ Å³, the intermolecular electron-electron spin anisotropic interaction are two orders of magnitude smaller than the intramolecular proton-electron spin interactions and therefore may be neglected with respect to the latter. The intermolecular electron-proton interactions with the solvent molecules may also be neglected.

(b) The spin-orbit-phonon interactions provide a relaxation mechanism⁵,⁷,¹⁶ which is independent of the nuclear spin quantum number. Indeed, the departure of the spectroscopic splitting factor, g = 2.0048,¹³,¹⁴ from the free electron value, g₈ = 2.0023,²⁵ indicates that the spin-orbit interaction has prevented a complete quenching of the orbital angular momentum by the crystalline electric field.²⁶ This mechanism, thus, must account for the lifetime of the ⁰A₈ spin states.

The spin-orbit interactions is:²⁷

\[ \chi_{\lambda,b} = \chi_{\lambda^0} = \beta^2 \left[ -i \text{grad} V \cdot \mathbf{p} + 2 \mathbf{\xi} \cdot \text{grad} V \times \mathbf{\xi} \right] \]  

(11)

\( \mathbf{p} \) is the linear momentum of the unpaired electron, of spin \( S = \frac{1}{2} \) which moves in the Coulomb field of all the nuclei in the free radical ion plus all the surrounding molecules and ions. \( V = -\sum_k Z_k/\rho_k \) where \( Z_k \) is the effective change of the kᵗʰ species above, at a \( \rho_k \) distance from the unpaired electron. The first term in \( \chi_{\lambda^0} \) is zero for non s-electrons in spherically symmetric fields, but for aromatic hydrocarbons in solution, where \( V \) is of lower symmetry,²⁸,²⁹,³⁰ it vanishes when the second term is non zero. Hence, in this case, for a field \( V \) of any symmetry:

\[ \chi_{\lambda^0} = \chi_{\lambda^0} = \sum_k \sum_{\xi} \left( \lambda_\xi L_\xi \right)_k \cdot \mathbf{\xi} \]  

(12)
where

\[
\lambda_\rho = -\alpha^2 \frac{1}{\rho} \frac{\partial V}{\partial \rho}, \quad \lambda_\theta = -\alpha^2 \frac{1}{\rho^2} \frac{\partial V}{\partial \theta}, \quad \lambda_\phi = -\beta^2 \frac{1}{\rho^2 \sin \theta} \frac{\partial V}{\partial \phi}
\]

\[
L^2 = -\rho \frac{\partial}{\partial \rho} \rho \frac{\partial}{\partial \rho} + \rho^2 \left( \sin \theta \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \cos \theta \frac{\partial}{\partial \phi} \cos \theta \frac{\partial}{\partial \phi} \right)
\]

\[
L_\rho^+ = e^{i\theta} \left( \frac{\partial}{\partial \rho} - \cot \theta \frac{\partial}{\partial \theta} \right), \quad L_\theta^+ = -e^{i\phi} \left( \rho \frac{\partial}{\partial \rho} + i \frac{\partial}{\partial \phi} \right), \quad L_\phi^+ = e^{i\phi} \left( \sin \theta \frac{\partial}{\partial \theta} - \rho \cos \theta \frac{\partial}{\partial \rho} \right)
\]

\[
L^- = -L_\rho^-, \ etc.
\]

\((\rho, \theta, \phi)_k\) are the spherical polar coordinates of the unpaired electron with respect to the \(k\)th species and a molecular axis of symmetry.

The spin-orbit interaction contributes to the value of the spectroscopic splitting factor as follows: In p-benzoquinone, \(n \leftrightarrow \) a singlet-triplet and singlet-singlet transitions have been observed at 2.5 and 2.7 ev., respectively.\(^{31,32}\)

For the free radical, the wave functions for the ground and excited states are:

\[
|\psi_0, S^z = \frac{1}{2} > \propto \left\{ \sum \prod \right\} (n^2) (n')^2 \]

\[
|\psi_{n^2}, S^z = \frac{1}{2} > \propto \left\{ \sum \prod \right\} (n^2) (n')^2 \sin(n')^2 (n) \]

(13)

where \(\prod\) is the antisymmetrization operator and \(\sum\) and \(\prod\) represent the closed sigma and pi electron configurations. \(n\) and \(n'\) are the non-bonding orbitals localized at each oxygen atom, and \(x\) is the lone pair occupied by the unpaired electron in the ground state. Also, due to the \(b_{2g}\) symmetry of \(x\) in the \(D_{2h}\) group, only \(\psi_{n^2}\) contributes to the spin-orbit interaction. Hence, from the expression for the spectroscopic splitting factor in solution:

\[
< g > = g_s [\sum_{j=x, y, z} \sum_{k, m} \sum_{\xi=(\rho, \theta, \phi)_k} < \lambda_\xi L^z_\xi > \alpha_{ij} (E_j - E_0) ] (14)
\]
where \( \psi \) and \( \phi \) designate the ground and excited states, separated in energy by \( \Delta E \), the contribution from the \( n_x \) interaction is:

\[
\langle \Phi_{n_x} \rangle = N \phi_n \phi_x \lambda^2 \left[ \frac{1}{2} \int \rho \, d\mathbf{r} \right]
\]

where \( \lambda_{co} \) is the spin-orbit interaction term, which may be evaluated according to Eq. (12):

\[
\lambda_{co} = -\frac{1}{2} \left[ \frac{R}{\mathbf{R}} \right] ^2 \int_0^R \left[ \mathbf{R} \right] ^2 \, d\mathbf{r} + \int_0^R \mathbf{R} \, d\mathbf{r} \left[ \frac{1}{2} \right] \rho \, d\mathbf{r}
\]

\( \lambda^2 \) is the spin orbit coupling constant for the oxygen atom, whereas the asymmetric term, due to the neighboring carbon atom at a bond distance \( R = 1.50 \) \( \text{Å} \), is only \(-1 \text{ cm}^{-1} \) for a Slater 2p radial wave function, which justifies the use of the spherically symmetric potential approximation to evaluate the \( g \)-factor. The lattice terms are also negligible. \( \rho_0 \) is the unpaired electron density at the oxygen atom, which can be evaluated from the splitting \( \Delta = \omega^2 \) \( K \) between the singlet-triplet and singlet-singlet transitions for the neutral molecule where \( K \) is the exchange integral between orthogonal oxygen 2p atomic orbitals. For \( K = 0.905 \) \( \text{ev} \), \( \rho_0 = 0.221 \). \( \Delta \) is equal to the average of the above \( n_x \) transitions, corrected for the difference in two center Coulomb integrals for the free radical and neutral molecule. Thus:

\[
\Delta = 2.5 \text{ ev} + \left\langle \frac{1}{r_{12}} \right\rangle, (a_1)^2 (a_2)^2 \right\rangle - \left\langle \frac{1}{r_{12}} \right\rangle, (a_1)^2 (a_2)^2 \right\rangle
\]

\( \Delta \approx 2.9 \text{ ev} \).

The two center integrals were evaluated making use of the \( 2s \times 2p \) MO's obtained by Sidman for p-benzoquinone. This leads to \( \left\langle \frac{1}{r_{12}} \right\rangle \approx 2.00 \text{ ev} \), and if one assumes that the contribution from the ring spin-orbit interactions is the same as for aromatic hydrocarbon negative ions, where \( \left\langle \frac{1}{r_{12}} \right\rangle = 2.00 \text{ ev} \), then the calculated \( g \) value is in agreement with the observed quantity, \( g = 2.0048 \pm 0.0001 \).
The spin-orbit-phonon coupling between the states \( j \) and \( k \) is, thus:

\[
| \langle j \mid \chi_{1, b} \mid k \rangle |^2 = \beta_{d} \cdot | \langle F_{j} \mid F_{k}^{2} \rangle \mid^2
\]  

(18)

where correct to third order approximation:

\[
\beta_{d} = \sum_{i} \left[ \frac{\langle X_{0i} > \chi_{1} < X_{0i} > k}{E_{j} - E_{i}} + \frac{\langle X_{0i} > \chi_{1} < X_{0i} > k}{E_{j} - E_{i}} \right]
\]

\[
+ \sum_{i,i'} \left[ \frac{\langle X_{0i} > \chi_{1} < X_{0i} > k}{(E_{j} - E_{i})(E_{j} - E_{i})} \right] + \text{all possible permutation terms}
\]

The \( | \langle \beta | \rangle |^2 \) matrix elements, presented in Table 6, are independent of the \( \mu \alpha \)
nuclear spin quantum number and were evaluated from the corresponding eigenfunctions in Table 1. The second order terms in \( \beta_{d} \) correspond to Zeeman interactions which are balanced by the emission or absorption of a phonon by the lattice. These processes are, therefore, proportional to the square of the resonance frequency and may be neglected according to the experimental evidence. The third order terms are of importance because they define the Raman mechanism by which a spin transition at a frequency \( \omega_{0} \) is balanced by the emission of a photon and the absorption of another at the respective frequencies \( \omega \) and \( \omega' \), in such a manner that \( \omega - \omega' = \omega_{0} \), where \( \omega \) takes all the possible values \( \omega_{0} \leq \omega \leq \omega_{\text{cut off}} \) so that the transition probability does not depend on the value of the resonance frequency. \( \omega_{\text{cut off}} \) is an upper cut off frequency characteristic of the system. An order of magnitude estimate of the contribution of the Raman processes to Eq. (8) is carried out as follows:

\[
< \chi_{m}^{n} >_{0, n} \langle \beta_{d} \rangle \sum_{i} \frac{\delta V_{i}}{\alpha_{j}} \cdot q_{j} >_{1, i'} + \text{higher order terms, } (i, i' = 0, n, n+1)
\]  

(19)
Table 6: Matrix Elements of the Spin-Orbit Interactions: $| f | > f$

<table>
<thead>
<tr>
<th>$^0!A_g$</th>
<th>$\frac{5}{2}, \frac{5}{2}$ &gt;</th>
<th>$\frac{5}{2}, \frac{3}{2}$ &gt;</th>
<th>$\frac{5}{2}, \frac{1}{2}$ &gt;</th>
<th>$\frac{5}{2}, -\frac{1}{2}$ &gt;</th>
<th>$\frac{5}{2}, -\frac{3}{2}$ &gt;</th>
<th>$\frac{5}{2}, -\frac{5}{2}$ &gt;</th>
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<th>$\frac{3}{2}, \frac{1}{2}$ &gt;</th>
<th>$\frac{3}{2}, -\frac{1}{2}$ &gt;</th>
<th>$\frac{3}{2}, -\frac{3}{2}$ &gt;</th>
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<tbody>
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<td>$\frac{5}{2}, \frac{5}{2}$ &gt;</td>
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<td>$\frac{1}{2}\cos^2 \theta_3$</td>
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<td>0</td>
<td>0</td>
<td>$\frac{1}{2}\sin^2 \theta_3$</td>
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<td>0</td>
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<td>$\frac{1}{2}\cos^2 \theta_3 c^{\theta_3}$</td>
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<td>$\frac{3}{2}, -\frac{1}{2}$ &gt;</td>
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Table 6: (continued)

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where
\[ v_{\text{GO}} = \sum_{l,k} \sum_{j,m} \frac{k_n}{R_{1k}} \left( \frac{r_1}{R_{1k}} \right)^l Y_{l,m}(\theta, \phi) e^{i \gamma} \left( \frac{R_{1k}}{r_1} \right)^m Y_{l,m}^*(\theta, \phi) \]
and the states in Eq. (15) are indicated by the subscript: \( (\beta, \gamma), (R, \beta, \gamma)_{kl} \) and \( (r, \theta, \phi)_i \) are, respectively, the spherical polar coordinates of the axis of symmetry parallel to the CO bond with respect to the applied field, and of the point charge \( E_k \) and the unpaired electron with respect to the \( i^\text{th} \) atom and the axis of symmetry. \( Y_{l,m} \) are the associated spherical harmonics of order \( l \), and \( Q_j \) are the normal coordinates. In particular, the significant contributions to \( < \gamma_{\text{OL}} > \) must arise from the stresses on the CO bond, so that the transition probability between two spin states is:

\[ W_{jk,b} \sim \frac{(172.8)^2}{10^5} \times 5 \times \left( \frac{kT}{m v^2} \right)^2 \times \left( \frac{\rho_0 \lambda_c}{\Delta^2} \right)^2 \times \left( \frac{e^{2}}{D} \right)^2 \times \left( \frac{< r^2 >}{pp} \right)^2 \left( \frac{< r >}{pd} \right)^2 \times \Omega \times |< j | \Omega | k > |^2 \]  

(20)

where an isotropic distribution of the density of modes was assumed, and \( \Delta \approx kT \approx \omega \omega' \approx \omega_0 \). \( v \) is the velocity of sound in the system of mass \( m \), \( < r^2 > \) and \( < r > \) are the radial integrals for an oxygen atom electron of the given symmetries and the non zero contribution is obtained by attributing a \( 3d_{zx} \) character, \( \epsilon = 10^{-3} \) to \( 10^{-4} \), to the nonbonding oxygen orbital which may be introduced by the bending of the CO bonds on collision. Hence, the transition probability for this system is:

\[ W_{jk,b} \sim \left( \frac{9}{258} \right)^2 \times |< j | \Omega | k > |^2 \times 10^6 \text{ sec}^{-1} \]  

(21)

where \( < r^2 > \approx 30 \lambda_c^2 \) and \( < r > \approx 1.75 \lambda_c \) for Slater type orbitals, \( R = 2.46 \ \text{ ao} \), \( m = 16 \), \( v \approx 1.24 \times 10^5 \ \text{ cm/sec} \) for the velocity of sound in ethanol at room temperature, and \( \approx 5 \times 10^{13} \text{ sec}^{-1} \) for the characteristic frequency for the CO symmetric stretching mode.
In the absence of chemical exchange, the validity of this mechanism can be tested for the temperature square law dependence of the line widths, in the region where the other parameters remain constant. These experiments, however, should be carried out in aprotic solvents, where the motional effects, introduced by the isotropic hyperfine interactions with the solvent molecules and ions, does not affect the line widths in the temperature interval studied. Nevertheless, the ESR absorption line widths for the \( ^{7}A_\text{g} \) transitions at \( T = 298 \text{K} \) and its \( (^{3}P^{23})_{2} \) hyperfine components at \( T = 223.5 \text{K} \) do obey the square law dependence, where

\[
\left( \frac{T}{T'} \right)^2 = \frac{\Delta v_{\text{MS}}(T')}{\Delta v_{\text{MS}}(T)} = 1.0 \pm 0.1 \quad (22)
\]

\((c)\) In dilute solutions, where the electronic exchange is negligible, the random time dependent perturbation introduced by the electron density distribution in the neighborhood of the free radical will influence the lifetime of the Zeeman hyperfine levels of the same total symmetry and total component of angular momentum through the isotropic hyperfine interaction.\(^{10,11}\)

The completely orthonormalized unpaired electron wave function \( \phi_e \) is:

\[
\phi_e = \left[ \phi_o - \sum_{k \neq o} \langle \phi_k | \phi_o \rangle \phi_k \right] \left[ 1 - \sum_{k \neq o} | \langle \phi_k | \phi_o \rangle |^2 \right]^{1/2} \quad (23)
\]

where \( \phi_o \) is the SCF wave function for the isolated free radical, and the Schmidt orthogonalization insures that the Pauli Principle is obeyed where the overlap integral \( \langle \phi_o, \phi_k \rangle \) is zero. \( \{ \phi_k \} \) is the orthonormal set which describes the surrounding molecules and ions. The electron density, correct to second order in the overlap integral is thus:

\[
\rho = \left[ \rho_{oo} - \sum_{k \neq o} \rho_{ok} \langle \phi_k | \phi_o \rangle + \sum_{k, k' \neq o} \rho_{kk'} \langle \phi_k | \phi_o \rangle \langle \phi_{k'} | \phi_o \rangle \right] \left[ 1 - \sum_{k \neq o} | \langle \phi_k | \phi_o \rangle |^2 \right]^{-1} \quad (24)
\]
where \( \rho_{nm} = \rho_{ml} = |\langle \phi_n \phi_m \rangle| \). Hence, for a system undergoing rapid Brownian motions, the isotropic hyperfine energy of interaction with a nucleus of spin \( I_p \) is modulated by the time dependence of the electron density distribution as follows:

\[
\mathcal{H}_{\text{hfs}} = \left[ A_0 + A(t) \right] \mathcal{I}_p \cdot \mathcal{E}
\]

(25)

where

\[
A_0 = \delta_n \left[ \rho_{oo} + \sum_{k \neq 0} (\rho_{oo} + \rho_{kk}) |\langle \phi_k, \phi_o \rangle|^2 \right] \text{ at } \mathcal{I}_p
\]

\[
A(t) = \delta_n \sum_{k \neq 0} \rho_{ok} \langle \phi_k, \phi_o \rangle \left[ 1 + \sum_{k \neq 0} |\langle \phi_o, \phi_k \rangle|^2 \right] \text{ at } \mathcal{I}_p
\]

The contribution to Eq. (8) is thus:

\[
W_{J, k, 0} \frac{2 \mathcal{I}_p}{\Delta H} \cdot \mathcal{I}_p^{I_p} (I_p+1) |\langle \mathcal{F}_o \rangle^2| \cdot |\langle \mathcal{F}_o \mathcal{F}_o^\dagger \rangle| \sum_i \mathcal{I}_d_i \cdot \mathcal{E}_i |\mathcal{F}_k \mathcal{F}_k^\dagger| \geq 2 \]

(26)

where

\[
\mathcal{I}_p = \mathcal{I}_p^{\text{axial}}; \Delta H = 0
\]

\[
|\langle \mathcal{F}_o \rangle^2| = \delta_n^2 \left[ \sum_k \rho_{ok} |\langle \phi_k, \phi_o \rangle|^2 \right] \text{ at } \mathcal{I}_p
\]

\[
= A_0 \left[ \delta_n \sum_k |\phi_k|^2 \left( \sum_{\alpha=1}^5 \frac{\hbar \omega_{\alpha}}{\Delta H} + \frac{\hbar \omega_{\alpha}}{\Delta H} \right) \right] \text{ at } \mathcal{I}_p
\]

\[
|\langle J \mathcal{I}_d_i \cdot \mathcal{E}_i |\mathcal{F}_k \rangle| \geq 2 = \left( \frac{(J \mathcal{I}_d_i)(I_p^{2} \mathcal{F}_k^2 + 1)}{\Delta H (1 + \mathcal{F}_k^2) (J \mathcal{I}_d_i)^2 + (I_p^{2} \mathcal{F}_k^2)(J \mathcal{I}_d_i)^2 + (J \mathcal{I}_d_i)^2 (\mathcal{F}_k^2)^2 + 1} \right)^{\frac{1}{2}}
\]

The correlation time is a function of the dissociation of the complex formed by the free radical and the two sodium ions, \( \varphi(\text{Na})_2 \).
where at room temperature the rate constant for the dissociation reaction is greater than the coupling constant, \( A^2 = 3.4 \times 10^5 \text{ sec}^{-1} \). For a solution with \([Q]\) = 0.006 M, the ESR absorption line broadening ensues at \( T = 270^\circ \) to \( 275^\circ \)K, which indicates that at room temperature \( \tau_{co} \approx 1.7 \times 10^{-5} \text{ sec} \), where an Arrhenius Law dependence is assumed for the rate constant. Since the hyperfine splitting in aprotic and ionic solutions are known for this free radical, \( \langle |\mathbf{F}_0|^2 \rangle \) can be evaluated semiempirically, so that from Eq. (25) and (26):

\[
\langle |\mathbf{F}_0|^2 \rangle \approx |A_0 + 3A| \tag{28}
\]

where \( A_0 = -2.419 \) \( \text{G} \) is the proton hyperfine splitting in an aprotic solution and \( 3A = |A| - |A_0| = -0.057 \) \( \text{G} \). Hence,

\[
W_{\parallel} = \frac{1.4 \; c_n^2 \times 10^5 \; I_n(I_n + 1)}{(1 + 2A)^2 + 4 \; c_n^2 (A_B^2)} \text{ sec}^{-1} \tag{29}
\]

is of the same order of magnitude as the transition probability given by the other mechanisms considered above. However, according to Eq. (29), \( W_{\parallel} \) vanishes in zero fields, so that only mechanism (a) and (b) can contribute to the line width of the hyperfine transitions.

**CONCLUSIONS**

The transition probability between the Zeeman levels of the p-benzoquinone ion has been found to be of the same order of magnitude, \( W \approx 10^5 \text{ sec}^{-1} \), for the three mechanisms under study, but only the spin-orbit-phonon interactions contribute to the lifetime of the proton \( ^{2}A_g \) hyperfine states. Hence these
transitions should, and indeed they do saturate faster than the rest. However, the predicted line width variation between the different hyperfine components, except for the $^3\text{P}_0$ transitions was not detected within the experimental uncertainty limits.

ACKNOWLEDGMENTS

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References

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23. J. W. Sidman, J. Chem. Phys. 27, 429 (1957), Table II.
List of Figures

1. ESR absorption derivative of the p-benzoquinoimine ion at (a) 16.217 Mc/sec, (b) 13.590 Mc/sec and 9.916 Mc/sec. The theoretical spectrum is represented below the experimental one.

2. ESR absorption derivative for the $O_{A_{g}}$ proton hyperfine component of the p-benzoquinone ion at $t = -49.5^\circ C$. The spectrum was calculated for $\Delta v = 61Mc/sec$.

3. Breit-Rabi diagram for the p-benzoquinone ion. Note that $\Delta E^2$ is of opposite sign for the hyperfine and electron transitions.

4. Zeeman splitting as a function of applied field.

5. Intensity of the ESR absorption lines, as a function of the applied field. The dashed lines indicate absorption of opposite polarity to the solid ones.
Fig. 3
\[
\frac{\varepsilon}{|A|}
\]

\[
\frac{|\gamma_e - \gamma_p|}{|A|} \frac{H}{|A|}
\]

**Fig. 4**
Fig. 5