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vibrationally excited molecules are formed in (4) they do not contribute significantly to further ozone decomposition, at least when the O atoms in (4) are $O(^3P)$. It is possible that vibrationally excited O_2 is produced in (4), but excess O_3 may quench it efficiently²³ without O_3 decomposition.

$O_2(a^1\Delta_g)$ is a possible product of (4), but we are aware of no evidence that it is produced with a rate comparable to the total reaction rate of (4). If it is, then the present measurement of k_1 is again too low, and measurements of the quenching of emission from $O_2(a^1\Delta_g)$ by O_3 will yield a slower rate for (1) when atomic oxygen is present along with $O_2(a^1\Delta_g)$ than

²³ R. V. Fitzsimmons and D. J. Bair, J. Chem. Phys. **40**, 451 (1964).

when it is absent. Such measurements of the emission quenching would be very helpful in clarifying this point. An attempt was made in the present experiment to remove the atomic oxygen produced in the discharge with a heated HgO coating,¹⁵ but the results were complicated by the appearance of an ion current apparently due to photoionization of mercury.

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We wish to thank Dr. F. Kaufman for stimulating discussions and for advising us of some of his experiences in working safely with ozone. Dr. Fred A. Morse, Dr. M. Ogawa, and Dr. A. B. Prag provided helpful discussions. Mr. L. Chikami provided valuable technical assistance.

Resonance Absorption of *p*-Benzosemiquinone in the Zeeman Region

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(Received 21 April 1967)

The resonance absorption of *p*-benzosemiquinone in sodium ethylate-ethanol solution has been determined from $t = -50^\circ\text{C}$ to room temperature in the Zeeman region at frequencies of the order of the zero field splitting produced by the isotropic hyperfine coupling. At $t = -50^\circ\text{C}$, the resonance absorption indicated free-radical interactions with two sodium nuclei. The isotropic coupling constants measured for the free electron spin- ^1H and ^{23}Na interactions were, respectively, $|A| = 6.63 \pm 0.01$ MHz and $|A'| = 0.34 \pm 0.05$ MHz. Due to the finite widths, resonance absorptions were observed near $H_z = 0$ for rf frequencies of $\nu/|A| = 2.48 \pm 0.01$ and 1.49 ± 0.01 . The observed linewidth inverse temperature dependence for $-20^\circ \leq t \leq 0^\circ\text{C}$ was explained on the basis of the over-all chemical exchange process

whence the first-order rate of disappearance chemical exchange time $\tau_{e,k} = |A'|^{-1} \times \exp[E_a(T^{-1} - T_0^{-1})/R]$ was obtained. The over-all energy of activation was determined to be $E_a = 10 \pm 1$ kcal mole⁻¹ and $T_0 = 253^\circ \pm 5^\circ\text{K}$. Also, since the solvent-free-radical interactions occur at the end oxygen atoms, an estimate was made of the role played by the spin-orbit-lattice interactions introduced in the *p*-benzosemiquinone ion by the asymmetric vibration of the CO bonds. In the Zeeman region, the transition probability per unit time between a participating pair of levels induced by Van Vleck second-order Raman processes was estimated to be of the same order of magnitude, $W \sim 10^4$ sec⁻¹, as other processes considered previously for *p*-benzosemiquinone in solution. This is however two orders of magnitude less than the experimental values.

I. INTRODUCTION

The characteristic ESR spectra of free radicals are usually investigated in the Paschen-Back high-field region for reasons of sensitivity. However, important information may be obtained from studies in the low-field Zeeman region. Here, conversely to what happens in the Paschen-Back region, the spin states of different F (where F is the total spin quantum number) are nondegenerate and all the transitions $\Delta F = 0, \pm 1$; $\Delta F_s = \pm 1$ are allowed. Already, Lloyd and Pake¹ have studied the relaxation mechanisms for the peroxylamine disulfonate ion in solution in the Zeeman regions.

¹ J. P. Lloyd and G. E. Pake, Phys. Rev. **94**, 579 (1954).

The *p*-benzosemiquinone *p*-BSQ⁻ ESR absorption in the Zeeman region has been studied here with the purpose to determine solvent effects and ion cluster formation with Na^+ ions in dry ethanol. This free-radical ion has been extensively investigated in the Paschen-Back region. Stone and Maki² found that complexes of the type $S(p\text{-BSQ}^-)S'$ (where $S, S' =$ water and dimethyl sulfoxide solvent molecules) exist in solution. Khakhar, Prabharanda, and Das³ found that the *p*-BSQ⁻ spectrum in alkali-metal solutions in 1,2-dimethoxyethane and tetrahydrofuran

² E. Stone and G. Maki, J. Chem. Phys. **36**, 1944 (1962); J. Am. Chem. Soc. **87**, 454 (1965).

³ M. P. Khakhar, B. S. Prabharanda, and M. R. Das, J. Chem. Phys. **45**, 2327 (1966).

FIG. 1. Breit-Rabi diagram for the free *p*-benzosemiquinone ion.

gave two different proton coupling constants at $t = -60^\circ\text{C}$. This, together with an observed alternating line broadening suggested the formation of solvent separated ion pairs between *p*-BSQ⁻ and K⁺(S). Schreus and Fraenkel^{4a} found that the dominating relaxation mechanisms for *p*-BSQ⁻ in alkaline aqueous ethanol arise from the random time-dependent perturbation of the anisotropic intra- and intermolecular proton hyperfine interactions and the anisotropy of the *g* tensor. They determined the correlation time for these spin-lattice energy exchange processes to be $\tau_c \approx 7 \times 10^{-11}$ sec. The theory for the free-radical ESR absorption line shapes and relaxation mechanisms in the Paschen-Back region has been developed by Fraenkel and associates,⁴⁻⁸ Stephen,⁹ Kivelson,¹⁰ McLachlan,¹¹ and Freed.¹² Recently, Kivelson^{10b} has developed the theory for spin-orbit-lattice interaction contributions to the spin relaxation times in liquids. The field-in-

dependent terms should be operative in the Zeeman region.

Ion-pairing effects of two different types have been studied recently for aromatic negative ions. These effects were originally proposed by Sadek and Fuoss.¹³ They pointed out that an ion, coordinated with solvent molecules, will approach the counter ion until the relatively rigid solvation shells come into contact. The barrier to further approach required the squeezing out of solvent molecules leading eventually to contact ion pairs. Thus, the association process would involve two steps, the association of ions retaining their solvation shells and the contact ion pairs. This has been confirmed by the work of Eigen, and associates.¹⁴ Also, Atherton and Weissman¹⁵ have measured a temperature dependence of ion pairing effects in the Paschen-Back region ESR absorption of the naphthalene negative ion in sodium-metal-tetrahydrofuran solution. Recently, Slates and Szwarc,^{16a} and Chang, Slates, and Szwarc^{16b} have made conductivity measurements of aromatic radical ions in sodium-metal-tetrahydrofuran solution and dimethoxyethane solutions. From these measurements, the dissociation constants for the contact and solvent-separated ion pairs were obtained.

Now in the Zeeman region, with the achieved

⁴ (a) J. W. H. Schreus and G. K. Fraenkel, *J. Chem. Phys.* **34**, 756 (1961); (b) J. W. H. Schreus, G. E. Blomgren, and G. K. Fraenkel, *ibid.* **32**, 1861 (1960).

⁵ M. Stephen and G. K. Fraenkel, *J. Chem. Phys.* **32**, 1435 (1960).

⁶ B. G. Segal, M. Kaplan, and G. K. Fraenkel, *J. Chem. Phys.* **43**, 4191 (1965).

⁷ J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* **39**, 326 (1963); **41**, 3623 (1964); J. Gendell, J. H. Freed, and G. K. Fraenkel, *ibid.* **41**, 949 (1964).

⁸ G. K. Fraenkel, *J. Chem. Phys.* **42**, 4275 (1965); *J. Phys. Chem.* **71**, 139 (1967).

⁹ M. J. Stephen, *J. Chem. Phys.* **34**, 484 (1961).

¹⁰ (a) D. Kivelson, *J. Chem. Phys.* **27**, 1087 (1957); **33**, 1094 (1960); and **41**, 1904 (1964); (b) **45**, 1324 (1966), and references contained therein.

¹¹ A. McLachlan, *Proc. Roy. Soc. (London)* **A280**, 271 (1964).

¹² J. H. Freed, *J. Chem. Phys.* **43**, 1427, 2312 (1965); **45**, 1251 (1966); *J. Phys. Chem.* **71**, 38 (1967).

¹³ H. Sadek and R. M. Fuoss, *J. Am. Chem. Soc.* **76**, 5905 (1954).

¹⁴ For a recent review see M. Eigen, W. Kruse, G. Maass, and L. DeMayer, *Progr. Chem. Kinetics* **2**, 285 (1964).

¹⁵ N. M. Atherton and S. I. Weissman, *J. Am. Chem. Soc.* **83**, 1330 (1961).

¹⁶ (a) R. V. Slates and M. Szwarc, *J. Phys. Chem.* **69**, 4124 (1965); (b) P. Chang, R. V. Slates, and M. Szwarc, *ibid.* **70**, 3180 (1966).

TABLE I. Steady-state spin eigenfunctions and isotropic energies for the free *p*-BSQ⁻.

Spin eigenfunctions $ \alpha_0\rangle = F, F_z\rangle = \sum_{ij} R_{ij} S_i\rangle K_n, K_{nz}\rangle$ ^{a, b}	Spin energies ^b , $\epsilon\alpha_0$ for $A < 0$ ^d	Proton spin symmetry species
1. $ \frac{1}{2}, \pm\frac{1}{2}\rangle = \pm\frac{1}{2}\rangle 2, \pm 2\rangle$	$\pm(\omega_e/2 + 2\omega_p) + A + J/2$	
2. $\left(\frac{1}{2}, \pm\frac{1}{2}\rangle\right) = R_{\pm 3} \left(\pm\frac{1}{2}\rangle 2, \pm 1\rangle\right)$	$\pm 3\omega_p/2 - A/4 + J/2 + D_{\pm 3}$	
3. $\left(\frac{1}{2}, \pm\frac{1}{2}\rangle\right) = R_{\pm 3} \left(\mp\frac{1}{2}\rangle 2, \pm 2\rangle\right)$	$\pm 3\omega_p/2 - A/4 + J/2 - D_{\pm 3}$	⁵ <i>A_g</i>
4. $\left(\frac{1}{2}, \pm\frac{1}{2}\rangle\right) = R_{\pm 1} \left(\pm\frac{1}{2}\rangle 2, 0\rangle\right)$	$\pm\omega_p/2 - A/4 + J/2 + D_{\pm 1}$	
5. $\left(\frac{1}{2}, \pm\frac{1}{2}\rangle\right) = R_{\pm 1} \left(\mp\frac{1}{2}\rangle 2, \pm 1\rangle\right)$	$\pm\omega_p/2 - A/4 + J/2 - D_{\pm 1}$	
6. $\left(\frac{1}{2}, \pm\frac{1}{2}\rangle_1\right) = \left(\pm\frac{1}{2}\rangle 0, 0\rangle_1\right)$	$\pm\omega_e/2 - J/2$	
7. $\left(\frac{1}{2}, \pm\frac{1}{2}\rangle_2\right) = \left(\pm\frac{1}{2}\rangle 0, 0\rangle_2\right)$	$\pm\omega_e/2 - J/2$	2 ¹ <i>A_g</i>
8. $ \frac{1}{2}, \pm\frac{1}{2}\rangle = \pm\frac{1}{2}\rangle 1, \pm 1\rangle$	$\pm(\omega_e/2 + \omega_p) + A/2 + K$ ^e	
9. $\left(\frac{1}{2}, \pm\frac{1}{2}\rangle\right) = R_{\pm 1'} \left(\pm\frac{1}{2}\rangle 1, 0\rangle\right)$	$\pm\omega_p/2 - A/4 + K + D_{\pm 1'}$	³ <i>B_{1g}</i> , ³ <i>B_{2u}</i> , ³ <i>B_{3u}</i>
10. $\left(\frac{1}{2}, \pm\frac{1}{2}\rangle\right) = R_{\pm 1'} \left(\mp\frac{1}{2}\rangle 1, \pm 1\rangle\right)$	$\pm\omega_p/2 - A/4 + K - D_{\pm 1'}$	

^a The nuclear spin eigenfunctions $|K_n, K_{nz}\rangle$ were generated directly from the D_{2h} group character table as follows:

$$|K_n, K_{nz}\rangle = \frac{1}{P} \sum_P \chi^\Gamma(P) \Pi |I_{Pz}\rangle,$$

where P are all the symmetry operations and $\chi(P)$ is the corresponding character for the species Γ . See Ref. 17, Appendix X.

^b The R_x are the proper two-dimensional rotation operators:

$$R_x = \begin{pmatrix} \cos\theta_x & \sin\theta_x \\ -\sin\theta_x & \cos\theta_x \end{pmatrix}.$$

resolution and the relatively low Larmor frequency (with respect to the above relaxation cutoff frequencies τ_c^{-1}), one expects to get new information on the solvent effects and ion cluster formation for the following reasons: (1) contrary to what happens in the Paschen-Back region, the resonance transitions for the states with total proton spin angular momentum $\mathbf{K}_n = 0$ are completely resolved from those for the states $\mathbf{K}_n \neq 0$ and $K_{nz} = 0$, and (2) the intramolecular proton anisotropic hyperfine interactions are not operative for the $\mathbf{K}_n = 0$ states. Therefore, the ESR transitions for the latter are amenable to the study of the various ion pairing effects that should be present in solution.

II. BREIT-RABI DIAGRAM FOR THE FREE *p*-BENZOSEMIQUINONE

The nuclear spin states for the most abundant isotope of the free *p*-benzosemiquinone $C_6H_4O_2^-$ decompose within the symmetry operations of the D_{2h} group¹⁷ with the structure

$$\Gamma(4 \cdot {}^1H) = {}^5A_g + {}^3B_{1g} + {}^3B_{2u} + {}^3B_{3u} + 2 \cdot {}^1A_g, \quad (1)$$

where the left-hand superscripts indicate the nuclear

where $\cos 2\theta_x = C_x/D_x$; $\sin 2\theta_x = A C_x/D_x$, $c_{\pm 3} = 1$, $c_{\pm 1} = (\frac{1}{2})^{1/2}$, $c_{\pm 1'} = \pm(\frac{1}{2})^{1/2}$, and $C_{\pm x} = \pm\frac{1}{2}(\omega_e - \omega_p + A F_x)$. See Ref. 17, Appendix XIV.

^c $J = J_o + J_m + J_p$ is the sum of the interproton isotropic hyperfine coupling constants for the *ortho*, *meta*, and *para* protons J_o , J_m , and J_p , respectively.

^d The convention $|A| = -A$ used in Ref. 4(a) is used here.

^e The states of B_{1g} , B_{2u} , and B_{3u} symmetry would be degenerate except for the nuclear spin coupling energy: $K(B_{1g}) = J_p - J/2$; $K(B_{2u}) = J_m - J/2$ and $K(B_{3u}) = J_o - J/2$. However, the transitions are truly degenerate.

spin multiplicity $(2K_n + 1)$. The resolution achieved in the Zeeman region is shown by the Breit-Rabi¹⁸ type diagram given in Fig. 1.

The room-temperature spin eigenfunctions and energies for the isotropic spin Hamiltonian (see the Appendix),

$$\begin{aligned} \hbar \langle \mathcal{H}_0 \rangle_{Av} = & \hbar(\omega_e S_z + \omega_n K_{nz}) + \sum_n \langle A_n \rangle_{Av} \mathbf{S} \cdot \mathbf{I}_n \\ & + \sum_{n > n'} \langle J_{nn'} \rangle_{Av} \mathbf{I}_n \cdot \mathbf{I}_{n'}, \quad (2) \end{aligned}$$

are given in Table I. Here standard notation has been used as follows: $\omega_I = -\gamma_I H_z$; γ_I is the magnetogyric ratio of the species I (unpaired electron and 1H); H_z is the static laboratory field; $\hbar \langle A_n \rangle_{Av} = \text{Tr} \mathbf{T}_n$ and $\hbar \langle J_{nn'} \rangle_{Av} = \text{Tr} \mathbf{T}_{nn'}$. $\mathbf{T}_n$ and $\mathbf{T}_{nn'}$ are the electron-nuclear and nuclear-nuclear spin hyperfine coupling tensors.

III. EXPERIMENTAL

The magnetic resonance spectra of 0.001 to 0.006*M* *p*-benzoquinone and 0.04*M* NaOC_2H_5 in dry $\text{C}_2\text{H}_5\text{OH}$ were determined with a Varian 4200 wide-line spectrometer using a 12-in. high-resolution magnet at the constant frequencies: $\nu_0 = 16.416$, 16.217, 13.590, and 9.916 MHz. The laboratory field H_z homogeneous

¹⁷ E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill Book Co., New York, 1955), see Appendix X.

¹⁸ G. Breit and I. I. Rabi, Phys. Rev. **38**, 2082 (1931).

FIG. 2. Magnetic resonance absorption derivative of *p*-benzosemiquinone ion in sodium ethylate-ethanol solution at room temperature and (a) $\nu = 16.217$ MHz, (b) $\nu = 13.590$ MHz and (c) $\nu = 9.916$ MHz. The calculated relative intensities and resonance fields are shown.

to ~ 0.03 G within the volume of the sample, was sinusoidally modulated at $\nu_M = 412$ Hz, with an amplitude $H_M \approx 0.02$ G. The spectra were recorded at the rate of $|dH_z/dt| = 0.01$ G/sec, in the range of ± 10 G. The frequencies, stable to within 0.1 kHz were measured with a Hewlett-Packard 524 counter. 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. The room-temperature spectra are shown in Fig. 2.

Figure 3 shows the transition energy diagram. The resonance fields and relative intensities are given in Table II. Here, the observed transitions are produced by the two components of the rf field:

$$\mathbf{H}_{rf} = 2H_1 \cos\omega_0 t \mathbf{i} = \mathbf{H}_r(\omega_0) + \mathbf{H}_r(-\omega_0), \quad (3)$$

where

$$\mathbf{H}_r(\omega_0) = H_1 \cos\omega_0 t \mathbf{i} + H_1 \sin\omega_0 t \mathbf{j},$$

$H_1 \approx 0.01$ G. The transitions produced by $\mathbf{H}_r(\omega_0)$ are

FIG. 3. Transition energy diagram for the free *p*-benzosemiquinone ion in the Zeeman region.

FIG. 4. Inverse temperature dependence of the $1A_g$ absorption derivative linewidth and, η/T for 0.006M *p*-benzosemiquinone in 0.04 sodium ethylate in ethanol solution. The viscosity η is that of pure ethanol. See Ref. 34, p. 2168.

TABLE II. Steady-state magnetic resonance fields and relative intensities I for the free p -BSQ $^-$.

Transition $ F, F_z \pm 1\rangle \leftrightarrow F', F_z\rangle$		Resonance field given $\omega = \omega_0$ $H_z(-\gamma_e + \gamma_p)$	Limiting values ^{a, b}			
			$H_z = 0$		$(H_z/A)^2 \gg 1$	
			ω	$(I \text{ sign } \omega/\omega^2)$	ω	$(I \text{ sign } \omega)/\omega^2$
$ \frac{5}{2}, -\frac{5}{2}\rangle$	$ \frac{3}{2}, \frac{3}{2}\rangle$	$\frac{(\omega - \omega_p) + 2.5A^c}{1 + 0.5A/(\omega - \omega_p)}$	$-2.5A$	0.8	$\omega_e - 2A$	1
$ \frac{5}{2}, -\frac{5}{2}\rangle$	$ \frac{5}{2}, -\frac{3}{2}\rangle$		0	0	$\omega_p - 0.5A$	0 ¹
$ \frac{5}{2}, -\frac{3}{2}\rangle$	$ \frac{3}{2}, -\frac{1}{2}\rangle$		$-2.5A$	0.48	$\omega_e - A$	1
$ \frac{5}{2}, -\frac{1}{2}\rangle$	$ \frac{3}{2}, -\frac{3}{2}\rangle$	$\frac{A + [A \{[(\omega - \omega_p)/A]^2 + [1.25A/(\omega - \omega_p)]^2 - 5.5\}]^{1/2}}{1 - [0.5A/(\omega - \omega_p)]^2}$	$2.5A$	-0.08	$\omega_e - 2\omega_p - A$	0 ²
$ \frac{5}{2}, -\frac{3}{2}\rangle$	$ \frac{5}{2}, -\frac{1}{2}\rangle$		0	0	$\omega_p - 0.5A$	0 ¹
$ \frac{3}{2}, -\frac{3}{2}\rangle$	$ \frac{3}{2}, -\frac{1}{2}\rangle$		0	0	$\omega_p + 0.5A$	0 ¹
$ \frac{5}{2}, -\frac{1}{2}\rangle$	$ \frac{3}{2}, \frac{1}{2}\rangle$		$-2.5A$	0.24	ω_e	1
$ \frac{5}{2}, \frac{1}{2}\rangle$	$ \frac{3}{2}, -\frac{1}{2}\rangle$	$A \left\{ \frac{[(\omega - \omega_p)/A]^2 - 6.25}{1 - [0.5A/(\omega - \omega_p)]^2} \right\}^{1/2}$	$2.5A$	-0.24	$\omega_e - 2\omega_p$	0 ²
$ \frac{5}{2}, -\frac{1}{2}\rangle$	$ \frac{5}{2}, \frac{1}{2}\rangle$		0	0	$\omega_p - 0.5A$	0 ¹
$ \frac{3}{2}, -\frac{1}{2}\rangle$	$ \frac{3}{2}, \frac{1}{2}\rangle$		0	0	$\omega_p + 0.5A$	0 ¹
$ \frac{5}{2}, \frac{1}{2}\rangle$	$ \frac{3}{2}, \frac{3}{2}\rangle$		$-2.5A$	0.08	$\omega_e + A$	1
$ \frac{5}{2}, \frac{3}{2}\rangle$	$ \frac{3}{2}, \frac{1}{2}\rangle$	$\frac{-A \pm \{[(\omega - \omega_p)/A]^2 + [1.25A/(\omega - \omega_p)]^2 - 5.5\}^{1/2}}{1 - [0.5A/(\omega - \omega_p)]^2}$	$2.5A$	-0.48	$\omega_e - 2\omega_p + A$	0 ²
$ \frac{5}{2}, \frac{1}{2}\rangle$	$ \frac{5}{2}, \frac{3}{2}\rangle$		0	0	$\omega_p - 0.5A$	0 ¹
$ \frac{3}{2}, \frac{1}{2}\rangle$	$ \frac{3}{2}, \frac{3}{2}\rangle$		0	0	$\omega_p + 0.5A$	0 ¹
$ \frac{5}{2}, \frac{3}{2}\rangle$	$ \frac{5}{2}, \frac{5}{2}\rangle$	$\frac{(\omega - \omega_p) - 2.5A^c}{1 - 0.5A/(\omega - \omega_p)}$	0	0	$\omega_e + 2A$	1
$ \frac{5}{2}, \frac{5}{2}\rangle$	$ \frac{3}{2}, \frac{3}{2}\rangle$		$2.5A$	-0.8	$-\omega_p + 0.5A$	0 ¹
$ \frac{1}{2}, \frac{1}{2}\rangle$	$ \frac{1}{2}, -\frac{1}{2}\rangle$	$\omega(\gamma_e - \gamma_p)/\gamma_e$	0	0	ω_e	2
$ \frac{3}{2}, -\frac{3}{2}\rangle$	$ \frac{1}{2}, -\frac{1}{2}\rangle$	$\frac{(\omega - \omega_p) + 1.5A}{1 + 0.5A/(\omega - \omega_p)}$	$-1.5A$	2	$\omega_e - A$	3
$ \frac{3}{2}, -\frac{3}{2}\rangle$	$ \frac{3}{2}, -\frac{1}{2}\rangle$		0	0	$\omega_p - 0.5A$	0 ¹
$ \frac{3}{2}, -\frac{1}{2}\rangle$	$ \frac{1}{2}, \frac{1}{2}\rangle$		$-1.5A$	2/3	ω_e	3
$ \frac{3}{2}, \frac{1}{2}\rangle$	$ \frac{1}{2}, -\frac{1}{2}\rangle$	$A \left\{ \frac{[(\omega - \omega_p)/A]^2 - 2.25}{1 - 0.5A/(\omega - \omega_p)]^2} \right\}^{1/2}$	$1.5A$	-2/3	$\omega_e - 2\omega_p$	0 ²
$ \frac{3}{2}, -\frac{1}{2}\rangle$	$ \frac{3}{2}, \frac{1}{2}\rangle$		0	0	$\omega_p - 0.5A$	0 ¹
$ \frac{1}{2}, -\frac{1}{2}\rangle$	$ \frac{1}{2}, \frac{1}{2}\rangle$		0	0	$\omega_p + 0.5A$	0 ¹
$ \frac{3}{2}, \frac{1}{2}\rangle$	$ \frac{3}{2}, \frac{3}{2}\rangle$	$\frac{(\omega - \omega_p) - 1.5A^c}{1 - 0.5A/(\omega - \omega_p)}$	0	0	$\omega_e + A$	3
$ \frac{3}{2}, \frac{3}{2}\rangle$	$ \frac{1}{2}, \frac{1}{2}\rangle$		1.5	-2	$\omega_p + 0.5A$	0 ¹

^a The relative intensity is given with a relative sign of the rotating component which causes the absorption. Note that for $\omega = \pm 2.5A$ and $\pm 1.5A$, the power absorption at $H_z = 0$ should be identically zero because of the opposite phase of the transitions. See Ref. 29, p. 57.

^b The high-field transition intensities 0¹ and 0² are, respectively, of the order $(A/\omega_e)^2$ and $(\omega_p/\omega_e)^2$ and, $(A/\omega_e)^4$ relative to the allowed electron transitions.

^c ω is of opposite sign for the first transition relative to the others in the group.

^d The positive sign applies except for $[(\omega - \omega_p)/A]^2 \leq 2.75 \pm 6^{1/2}$.

FIG. 5. Absorption derivative of *p*-benzosemiquinone ion in sodium ethylate-ethanol solution at $t = -50^\circ\text{C}$ about $\omega_0 = \omega_0' = 2.476 |A|$. The theoretical spectrum is given below the experimental one. It consists of two superimposed Lorentz absorption derivatives of equal intensity. One has $\Delta\nu_{ms} = 1.1$ MHz. The other was calculated from Table IV with $\Delta\nu_{ms} = 0.25$ MHz and is centered at $\omega_0 = \omega_0'$, 0.27 MHz downfield from the first one.

distinguished from those produced by $\mathbf{H}_r(-\omega_0)$ by the opposite sign of the phase. Bloch-Siegert effects^{19,20} were negligible. This was evidenced by the linear dependence of the resonance field vs ν_0 for the proton 1A_g states from 16 to 9 MHz and for the solid free radical α, γ -bis(disphenylene)- β -phenylallyl.²¹

The linewidth variation for the 1A_g proton states vs $1/T$ is shown in Fig. 4. A seven-line hyperfine pattern begins to appear for $t < -20^\circ\text{C}$ for all the proton states. Temperatures were determined to $\pm 1^\circ\text{C}$ with a Cu-constantan thermocouple. The low-temperature Dewar has been described elsewhere.²² The ESR absorption for the 1A_g proton states at $t = -50^\circ\text{C}$ is shown in Fig. 5. The hyperfine structure was observed for all the transitions at this temperature. The relative intensities

of the *p*-BSQ⁻ room-temperature spectra at two different rf power levels are given in Table III.

IV. DISCUSSION OF RESULTS

The hyperfine structure of the low-temperature resonance spectra arises from the interaction of the *p*-BSQ⁻ with two equivalent ^{23}Na . Here the spin functions for the two sodium nuclei decompose within the operations of the D_{2h} group with the structure

$$\Gamma(2-^{23}\text{Na}) = {}^7A_g + {}^5B_{2u} + {}^3A_g + {}^1B_{2u}. \quad (4)$$

This leads to a reducible representation of all the nuclear spin states for the complex $(\text{Na}^+)_2(p\text{-BSQ}^-)$ with the structure

$$\Gamma(4-^1\text{H})\Gamma(2-^{23}\text{Na}) = ({}^5A_g + {}^3B_{1g} + {}^3B_{2u} + {}^3B_{3u} + 2{}^1A_g) \times ({}^7A_g + {}^5B_{2u} + {}^3A_g + {}^1B_{2u}), \quad (5)$$

¹⁹ F. Bloch and A. Siegert, Phys. Rev. **57**, 522 (1940).

²⁰ G. Whitfield and A. G. Redfield, Phys. Rev. **106**, 918 (1957).

²¹ J. E. Wertz, C. F. Koelsch, and J. L. Vivó, J. Chem. Phys. **23**, 2194 (1955).

²² J. V. Acrivos and K. S. Pitzer, J. Phys. Chem. **66**, 1693 (1962).

²³ J. E. Wertz and J. L. Vivó, J. Chem. Phys. **23**, 2441 (1955); M. Adams, M. S. Blois, and R. H. Sands, *ibid.* **29**, 774 (1959).

TABLE III. Room-temperature saturation of the *p*-BSQ⁻ resonance absorption.

Transition $ F, F_z\rangle \leftrightarrow F', F_z \pm 1\rangle$	Resonance fields $(\omega_s - \omega_p)/ A $ for $\omega/ A = 2.476$		Relative intensity ^{a-c} $I(\frac{1}{2}, \frac{1}{2}\rangle \leftrightarrow \frac{1}{2}, -\frac{1}{2}\rangle)$ $I(F, F_z\rangle \leftrightarrow F', F_z \pm 1\rangle)$		
	Calc ^d	Exptl	Calc	$P_0 \propto (300 \mu A)^2$	$P_1 \propto (500 \mu A)^2$
$ \frac{3}{2}, -\frac{3}{2}\rangle \quad \frac{1}{2}, -\frac{1}{2}\rangle$	1.223	1.20 ± 0.01	0.78	0.73 ± 0.05	0.62 ± 0.05
$ \frac{3}{2}, \frac{3}{2}\rangle \quad \frac{3}{2}, \frac{1}{2}\rangle$	3.308	3.30 ± 0.01	0.70	0.70 ± 0.05	0.55 ± 0.05
$ \frac{5}{2}, \frac{3}{2}\rangle \quad \frac{5}{2}, \frac{1}{2}\rangle$	4.139	4.12 ± 0.01	2.18	2.1 ± 0.1	1.8 ± 0.1

^a The rf power level is given in terms of the transmitter coil current in microamperes.

^b The ESR absorption relative intensities given were obtained from the amplitudes measured directly from the area under the derivative curves (determined by weight) and the $\Delta\nu_{ms}$. The results are averages from measurements on both sides of $H_z = 0$.

^c Only the lines without accidental degeneracy were compared.

^d Corrections for instantaneous C_{2v} symmetry according to Eq. (10) would be $-0.2 \langle \delta^2 \rangle_{AV}/A^2$ for the transition $|5/2, 3/2\rangle \leftrightarrow |5/2, 5/2\rangle$; $+1.66 \langle \delta^2 \rangle_{AV}/A^2$ for the 3A_1 and $-0.15 \langle \delta^2 \rangle_{AV}/A^2$ for the $^3B_2 | 3/2, 3/2\rangle \leftrightarrow |3/2, 1/2\rangle$ transitions, respectively, and $6.6 \langle \delta^2 \rangle_{AV}/A^2$ would be the splitting between the two $^1A_1 | \frac{3}{2}, \frac{3}{2}\rangle \leftrightarrow |\frac{3}{2}, -\frac{3}{2}\rangle$ transitions. The observed deviations cannot therefore be explained by an instantaneous C_{2v} symmetry.

 TABLE IV. Experimental parameters for the *p*-BSQ⁻ magnetic resonance absorption spectra in the Zeeman region compared to other literature values from measurements in the Paschen-Back region.

A. Coupling constants					
Coupling	Zeeman region ^a		Paschen-Back region		Solvent ^b
	Room temperature	$t = -11^\circ C$	Room temperature	$t = -60^\circ C$	
$\langle A \rangle_{AV}(e^{-1}H)$	6.63 ± 0.01 ^h MHz (2.369 G)	Same as room temp. ^e	2.368 ± 0.001 G ^d 2.405 ± 0.005 G ^e 2.357 ± 0.005 G ^f 2.417 ± 0.003 G ^f 2.42 ± 0.01 G ^f	{ 2.165 ± 0.015 G } ^e { 2.658 ± 0.016 G }	0.04M NaOC ₂ H ₅ in dry C ₂ H ₅ OH 0.1M NaOH in 20/80 water/ethanol DME or THF + K metal Water DMSO ACN
$\langle A' \rangle_{AV}(e^{-23}Na)$		$t = -50^\circ C$ 0.34 ± 0.05 MHz (0.12 G)			0.04M NaOC ₂ H ₅ in C ₂ H ₅ OH
B. Linewidths between the points of maximum slope					
Nuclear spin symmetry species	Zeeman region		Paschen-Back region data extrapolated to the Zeeman region		Solvent
	Room temperature	$-50^\circ C$	Room temperature		
1A_g	0.26 MHz (0.092 G)	0.25 MHz ^h and 1.1 MHz	$K_{ns} = 0, 0.189 \text{ MHz}^\pm$		0.04M NaOC ₂ H ₅ in dry C ₂ H ₅ OH
$^3B_{1g}, ^3B_{2g}, ^3B_{3g}$	0.32 MHz (0.12 G)	Envelope: 1.3 MHz	$\pm 1, 0.204 \text{ MHz}^i$		0.1M NaOH in 20/80 water/ethanol
5A_g	0.26 MHz (0.092 G)	(0.49 G)	$\pm 2, 0.219 \text{ MHz}^i$		

^a The values reported in this work are in megahertz. Conversion to Gauss units was made using the Paschen-Back region $|\gamma_s| = 2.7988 \text{ MHz G}^{-1}$ for *p*-BSQ⁻ in dry ethanol (see Ref. 22).

^b The solvents are abbreviated as follows: 1,2-dimethoxyethane DME, tetrahydrofuran THF, dimethyl sulfoxide DMSO, and acetonitrile ACN.

^c At $t = -50^\circ C$ and 16.366 MHz, the proton hyperfine coupling is the same as at room temperature to within ±0.06 MHz.

^d Work reported in Ref. 24.

^e Work reported in Ref. 3. Here two coupling constants were observed at $-60^\circ C$.

^f Work reported in Ref. 2.

^g Work reported in Ref. 4(a). Here the value measured for $K_{ns} = m_J = 0$ was $T_2^{-1} = 1.027 \pm 0.019 \text{ (}\mu\text{sec}^{-1}\text{)}$. Thus for a Lorentz line shape $\Delta\nu_{ms} = (\pi\sqrt{3}T_2)^{-1} = 0.189 \text{ MHz}$.

^h The experimental absorption derivative could be fitted by the sum of two absorptions. One broad absorption with $\Delta\nu_{ms} = 1.1 \text{ MHz}$ and another with hyperfine components at the resonance fields calculated in Table IV, and $\Delta\nu_{ms} \leq 0.25 \text{ MHz}$. See Fig. 5.

ⁱ Work reported in Ref. 4(a). The average of the linewidths reported for $K_{ns} = m_J = \pm 1$ and ± 2 has been taken to eliminate the field-dependent, *g*-factor anisotropy term.

TABLE V. Significant contributions to the spin-lattice interactions of p -BSQ⁻ in the Zeeman region for total quinone concentrations of $\sim 10^{-3}M$.

Rotation tensor rank	p -BSQ ⁻ electron and nuclear spin terms $\mathcal{H}_i' = \sum_{n,l,m} F_n^{(l,m)} \mathcal{A}_n^{(l,m)}$		p -BSQ ⁻ electron spin terms only $\mathcal{H}_i'' = \sum_{k,l,m} F_k^{(l,m)} \mathcal{A}_k^{(l,m)}$	
	$F_n^{(l,m)}$	$\mathcal{A}_n^{(l,m)}$	$F_k^{(l,m)}$	$\mathcal{A}_k^{(l,m)}$
$=0, m=0$	$\delta_p = \langle A_p - \langle A_p \rangle_{AV} \rangle^a$ ($n=p$ =intramolecular protons)	$I_p \cdot S$	$A_k I_{zk}$ $A_k I_{\mp k}$ (k =solvent spins) $-2J_{j,k}$	S_z^b $S_{\pm}$ $S_j \cdot S_k^c$
$l=1$ $m=0$			$F^{(1)} D_{s',s}^{(1)}$	S_z
$m=\pm 1$			$F^{(1)} D_{s',\pm}^{(1)}$	$S_{\pm}/\sqrt{2}$
$l=2$	d			
$m=0$	$(1-3\cos^2\theta_p)/r_p^3$	$\gamma_e \gamma_p [I_{sp} S_z - \frac{1}{2}(I_{+p} S_{-} + I_{-p} S_{+})]$	Same as for $n=k$	
$m=\pm 1$	$[s \cdot \theta_p \cdot c \cdot \theta_p \exp(\mp i\phi_p)]/r_p^3$	$-1.5\gamma_e \gamma_p (I_{\pm p} S_z + I_{sp} S_{\pm})$		
$m=\pm 2$	$[\sin^2\theta_p \exp(\mp 2i\phi_p)]/r_p^3$	$-0.75\gamma_e \gamma_p I_{\pm p} S_{\pm}$	g-factor anisotropy terms are negligible in the Zeeman region	

^a A_p is the proton hyperfine coupling constant.

^b A_k is the electron hyperfine coupling constant with solvent spins, $\langle A_k \rangle_{AV} = 0$. Also, since I_k does not appear in $\langle \mathcal{H}_i \rangle_{AV}$ it may be considered as part of the lattice. (See Ref. 29, p. 310).

^c $J_{j,k}$ is the electronic exchange integral.^{38c} However, this effect was eliminated by dilution.

^d (r_p , θ_p , ϕ_p) are the free-electron spherical polar coordinates with center at the proton in the laboratory coordinate system. s. and c. have been used to abbreviate sine and cosine functions.

^e The $D_{s',m}^{(1)}$ are the elements of $D^{(1)}$, the rotation matrix for first order spherical harmonics. (See the Appendix and Ref. 48.) $F^{(1)}$ in this approximation is given by Eqs. (19) and (20).

whence the resonance fields for the 1A_g proton states shown in Fig. 5 were derived. The experimental parameters are given in Table IV, together with literature values from measurements in the Paschen-Back region.

The proton-electron spin hyperfine coupling constant measured in the Zeeman region is in agreement, within the experimental error, with the value measured in the Paschen-Back region in a similar solvent.²²⁻²⁴ However, although two different proton hyperfine coupling constants were observed at $t = -60^\circ C$ in potassium-tetrahydrofuran solution,³ in dry ethanol at $t = -50^\circ C$ the proton hyperfine coupling constants are the same for all four protons and equal to the room-temperature value. This suggests, therefore, that the Na⁺ ions in the low-temperature ion cluster affect the pi-electron spin density at the ring positions 2, 3, 5, and 6 of the p -BSQ⁻ in the same manner as they do at room temperature. This is in agreement with the work of Stone-Maki.² They found that the formation of solvent coordinated p -BSQ⁻ ions did not affect appreciably the proton hyperfine coupling constant, whereas the 1- p -benzosemiquinone ¹³C-electron spin coupling constant was strongly affected by the co-

ordinated solvent molecules. This they interpreted to be due to the fact that solvation occurred at the two oxygen atoms. It is not surprising, therefore, that two sodium ions associate with the p -BSQ⁻. The Na⁺ ions would indeed be attracted to the regions of highest negative charge density of the p -BSQ⁻, the two oxygen atoms.^{25b}

V. RELAXATION IN THE ZEEMAN REGION

The system under study is described by the Hamiltonian^{4-12,26-29}

$$\hbar \mathcal{H} = \hbar \{ \langle \mathcal{H}_0 \rangle_{AV} + \mathcal{H}_L + \mathcal{H}_I \}. \quad (6)$$

The steady-state spin eigenvalues and functions of $\hbar \langle \mathcal{H}_0 \rangle_{AV}$ for the D_{2h} symmetry p -BSQ⁻ are given in Table I. The unperturbed lattice term $\hbar \mathcal{H}_L$ consists of the translational, rotational, and vibrational contributions to the energy and $\hbar \mathcal{H}_I$ couples the spin system

²⁵ (a) J. W. Sidman, J. Am. Chem. Soc. **78**, 2363 (1956); (b) J. Chem. Phys. **27**, 429 (1957).

²⁶ N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

²⁷ R. K. Wangsness and F. Bloch, Phys. Rev. **89**, 728 (1935); F. Bloch, *ibid.* **102**, 104 (1956).

²⁸ A. G. Redfield, IBM J. Res. Develop. **1**, 19 (1957); and Advan. Magnetic Resonance **1**, 1 (1965).

²⁹ A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961).

²⁴ G. Vincow and G. K. Fraenkel, J. Chem. Phys. **34**, 1333 (1961).

TABLE VI. Matrix elements for the mixing of the symmetry species of the D_{2h} group by $\mathcal{H}_S' = \hbar \sum_p \delta_p \mathbf{I}_p \cdot \mathbf{S}^{a, b}$

D_{2h} Group Symmetry Species	$5A_g$	$3B_{1g}$	$3B_{2u}$	$3B_{3u}$	$1A_g$
$ b\rangle$	$ 5/2, \pm 3/2\rangle$	$ 3/2, \pm 3/2\rangle$	$ 3/2, \pm 3/2\rangle$	$ 3/2, \pm 3/2\rangle$	
$5A_g: 5/2, \pm 3/2\rangle$	$\pm \frac{\Delta(w_e - w_p)}{2 D_{+3}}$	$a_{3,8} \Delta_1$ $a_{2,8} \Delta_1$	$a_{3,8} \Delta_2$ $a_{2,8} \Delta_2$	$a_{3,8} \Delta_3$ $a_{2,8} \Delta_3$	
$3B_{1g}: 3/2, \pm 3/2\rangle$	0	0	$-\Delta_3/8$	$-\Delta_2/8$	
$3B_{2u}: 3/2, \pm 3/2\rangle$	$a_{3,8} \Delta_2$ $a_{2,8} \Delta_2$	0		$-\Delta_1/8$	
$3B_{3u}: 3/2, \pm 3/2\rangle$	0	0	$-\Delta_2/8$	0	
$ b\rangle$	$ 5/2, \pm 1/2\rangle$	$ 3/2, \pm 1/2\rangle$	$ 3/2, \pm 1/2\rangle$	$ 1/2, \pm 1/2\rangle$	$ 3/2, \pm 1/2\rangle$
$5A_g: 5/2, \pm 1/2\rangle$	$\pm \frac{\sqrt{6} \Delta(w_e - w_p)}{4 D_{+1}}$	$a_{5,10} \Delta_1$ $a_{4,10} \Delta_1$	$a_{5,9} \Delta_1$ $a_{4,9} \Delta_1$	$a_{5,10} \Delta_2$ $a_{4,10} \Delta_2$	$a_{5,9} \Delta_2$ $a_{4,9} \Delta_2$
$3B_{1g}: 3/2, \pm 1/2\rangle$	0	0	$\pm \frac{\Delta(w_e - w_p)}{\sqrt{8} D_{+1}}$	$a_{10,10} \Delta_3$ $a_{9,10} \Delta_3$	$a_{10,9} \Delta_3$ $a_{9,9} \Delta_3$
$3B_{2u}: 3/2, \pm 1/2\rangle$	$a_{5,10} \Delta_2$ $a_{4,10} \Delta_2$	0	0	$\pm \frac{\Delta(w_e - w_p)}{\sqrt{8} D_{+1}}$	$a_{10,10} \Delta_2$ $a_{9,10} \Delta_2$
$3B_{3u}: 3/2, \pm 1/2\rangle$	0	0	$a_{10,10} \Delta_2$ $a_{9,10} \Delta_2$	0	$\pm \frac{\Delta(w_e - w_p)}{\sqrt{8} D_{+1}}$
$1A_g: 1/2, \pm 1/2\rangle_1$	0	0	0	$a_{10,6} \Delta_2$ $a_{9,6} \Delta_2$	0
$1A_g: 1/2, \pm 1/2\rangle_2$	0	0	0	0	0

^a Here, for the spin eigenfunctions given in Table I,

$$\Delta = 2\mu_p \delta_p / 4; \quad \Delta_1 = \{(\delta_6 - \delta_2) - (\delta_1 - \delta_5)\}; \quad \Delta_2 = \{(\delta_6 + \delta_2) - (\delta_1 + \delta_5)\}$$

and

$$\Delta_3 = \{(\delta_6 - \delta_2) + (\delta_1 - \delta_5)\},$$

where the protons have been labeled by the same number as the ring carbon they are bonded to in *p*-BSQ⁻. Also,

$$\begin{aligned} a_{1,8}(\theta_{\pm 1}) &= (\cos \theta_{\pm 1} + (\sin \theta_{\pm 1})/2)/4; & a_{2,8} &= a_{3,8}(\theta_{\pm 1} + 3\pi/2); \\ a_{5,10}(\theta_1, \theta_1') &= (\cos \theta_{\pm 1})/2 + (\sin \theta_{\pm 1})/6^{1/2} (\cos \theta_{\pm 1}' \pm \sqrt{2} \sin \theta_{\pm 1}')/4; \\ a_{9,9} &= a_{5,10}(\theta_{\pm 1}, \theta_{\pm 1}') + 3\pi/2; & a_{4,10} &= a_{5,10}(\theta_{\pm 1} + 3\pi/2, \theta_{\pm 1}'); \\ a_{4,9} &= a_{5,10}(\theta_{\pm 1} + 3\pi/2, \theta_{\pm 1}') + 3\pi/2; \\ a_{10,9} &= (\sqrt{2} \cos \theta_{\pm 1}' \pm \sin \theta_{\pm 1}')/2(6)^{1/2}; & a_{9,6} &= a_{10,6}(\theta_{\pm 1}' + 3\pi/2); \\ a_{10,10} &= (\cos^2 \theta_{\pm 1}' \pm \sqrt{2} \sin 2\theta_{\pm 1}')/8; \end{aligned}$$

$$\begin{aligned} a_{2,10} &= a_{10,9} = (\mp 8^{1/2} \cos 2\theta_{\pm 1}' + \sin 2\theta_{\pm 1}')/16, \text{ and} \\ a_{9,9} &= a_{10,10}(\theta_{\pm 1}' + 3\pi/2). \end{aligned}$$

^b The values given below the diagonal are the matrix elements for the special case of instantaneous C_{2v} symmetry for *p*-BSQ⁻ where $\delta_1(t) = \delta_6(t) \cong -\delta_2(t) = -\delta_5(t) = \delta(t)$. In this case $\Delta(t) = \Delta_1(t) = \Delta_2(t) = 0$ and $\Delta_3(t) = 4\delta(t)$.

^c The diagonal elements are $a_{i,i} \Delta$ where $a_{1,1} = 1$;

$$\begin{aligned} a_{2,2} &= (3 \cos 2\theta_{\pm 1} + 4 \sin 2\theta_{\pm 1} - 1)/4; \\ a_{1,1} &= -(3 \cos 2\theta_{\pm 1} + 4 \sin 2\theta_{\pm 1} + 1)/4; \\ a_{4,4} &= [(24)^{1/2} \sin 2\theta_{\pm 1} + \cos 2\theta_{\pm 1} - 1]/4; \\ a_{5,5} &= -[(24)^{1/2} \sin 2\theta_{\pm 1} + \cos 2\theta_{\pm 1} + 1]/4; \\ a_{6,6} &= a_{7,7} = 0; & a_{8,8} &= \frac{1}{2}; \\ a_{9,9} &= (\cos 2\theta_{\pm 1}' \pm 8^{1/2} \sin 2\theta_{\pm 1}' - 1)/4 \text{ and} \\ a_{10,10} &= -(\cos 2\theta_{\pm 1}' \pm 8^{1/2} \sin 2\theta_{\pm 1}' + 1)/4. \end{aligned}$$

with the lattice. The significant contributions to $\mathcal{H}_S'$ in the Zeeman region have been itemized in Table V. These have been separated into two kinds. The first kind introduces relaxation terms for the electron and nuclear spins making up *p*-BSQ⁻. The second kind affects only the electron spin.

The observable is $F_{sn} = S_z + I_{sn}$ and the expectation value $\langle F_{sn} \rangle$ satisfies a rate-of-decay expression:

$$-d\langle F_{sn} \rangle/dt = a_{sn} - a_{0n} \frac{d}{dt} (\langle F_{sn} \rangle - \langle F_{sn} \rangle_0) / T_1, \quad (7)$$

where a_{0n} is the equilibrium value for a_{sn} which, in principle, can be derived paralleling the general

FIG. 6. Room-temperature absorption derivative about $H_z=0$ for $\omega_0=2.476 | A |$.

Bloch²⁷-Redfield²⁸-Abragam²⁹ theory of relaxation. Similarly,

$$-d\langle F_{zn} \rangle^*/dt = b_{zn}^* - b_{n0}^* (\langle F_{zn} \rangle^* - \langle F_{zn} \rangle_0) / T_2, \quad (8)$$

where $F_{zn}^* = \exp(-i\langle \mathcal{H}_0 \rangle_{Nt}) F_{zn} \exp(i\langle \mathcal{H}_0 \rangle_{Nt})$ and an important point of difference with the equations for the Paschen-Back region is that the equilibrium value $b_{n0} \neq 0$ as $H_z \rightarrow 0$.^{20,29} Also, a single longitudinal and a single transverse relaxation time, T_1 and T_2 in Eqs. (7) and (8), apply only to the 1A_g proton states where $\mathbf{F}=\mathbf{S}$. For $\mathbf{K}_n \neq 0$ the density matrix formalism must be developed. This has already been done for the Paschen-Back region ESR absorption.¹² However, since in the Zeeman region the ESR absorption of the 1A_g proton states is well resolved from the rest, the experimental results may be analyzed for these states making use of the equations developed for a total spin $F=\frac{1}{2}$.²⁹ Thus, for the sake of simplicity, the discussion of results will be concerned primarily with the ESR absorption of the $\mathbf{K}_n=0$ proton states. The contributions from the different terms in Table V are as follows.

The terms that transform as a zero-rank tensor of the first kind cause a mixing between the different proton symmetry species in the D_{2h} group. The experimental evidence from work in the Paschen-Back region in other solvents indicates that C_{2v} would be the lowest possible instantaneous symmetry for the ion undergoing interactions with the solvent. Also, the experiments³ indicate that the spin density at the ring positions 2 and 6 increases or decreases at the expense of the spin density at the ring positions 3 and 5 such

that the instantaneous deviations from $\langle A \rangle_N$ for the protons bonded to the corresponding carbon ring atoms are $\delta_6(t) = \delta_2(t) \cong -\delta_3(t) = -\delta_5(t) = \delta(t)$. The four-proton-spin irreducible representation in the C_{2v} group has the structure

$$\Gamma = {}^5A_1 + {}^3A_1 + 2 {}^1A_1 + 2 {}^3B_2, \quad (9)$$

where the species A_g and B_{2u} of the D_{2h} group have gone into A_1 of the C_{2v} group and similarly B_{1g} and B_{3u} have gone into B_2 .¹⁷ As a result, the steady-state energies, correct to second order in the Zeeman region, are now given by the α_0 of Table I plus the correction values:

$$\begin{aligned} \epsilon_1 &= 0, \\ \epsilon_2 &= 8a_{2,2}^2 \langle \delta^2 \rangle_N / (D_{\pm 3} \sin^2 \theta_{\pm 3}), \\ \epsilon_3 &= -8a_{3,3}^2 \langle \delta^2 \rangle_N / (D_{\pm 3} \cos^2 \theta_{\pm 3}), \\ \epsilon_4 &= (\epsilon_4' + \epsilon_4''), \\ \epsilon_5 &= (\epsilon_5' + \epsilon_5''), \\ \epsilon_6 &= (\epsilon_6' + \epsilon_6'') = \{ \mp 4(\omega_e - \omega_p) / 3 + 2A \} \langle \delta^2 \rangle_N / A^2, \\ \epsilon_7 &= 0, \\ \epsilon_8(B_2) &= 0, \\ \epsilon_9(B_2) &= -\epsilon_{10}(B_2) = 8a_{9,10}^2 \langle \delta^2 \rangle_N / D_{\pm 1}, \\ \epsilon_8(A_1) &= -(\epsilon_2 + \epsilon_3), \\ \epsilon_9(A_1) &= -(\epsilon_4' + \epsilon_5' + \epsilon_6'), \\ \epsilon_{10}(A_1) &= -(\epsilon_4'' + \epsilon_5'' + \epsilon_6''), \end{aligned} \quad (10)$$

TABLE VII. Matrix elements of the intramolecular anisotropic hyperfine interaction in *p*-BSQ^{•-}, s-d

I. ⁶A_g proton states

$ s\rangle \backslash d\rangle$	$ 5/2, 5/2\rangle$	$ 5/2, 3/2\rangle$	$ 5/2, 1/2\rangle$	$ 5/2, -1/2\rangle$	$ 5/2, -3/2\rangle$	$ 5/2, -5/2\rangle$	$ 3/2, 3/2\rangle$	$ 3/2, 1/2\rangle$	$ 3/2, -1/2\rangle$	$ 3/2, -3/2\rangle$
$ 5/2, 5/2\rangle$		$B_1(\theta_3)$	$\frac{2}{3} \cos^2 \theta_1$	0	0	0	$B_1(\theta_3, \frac{\pi}{2})$	$\frac{2}{3} \sin^2 \theta_1$	0	0
$ 5/2, 3/2\rangle$	$\frac{2}{3}$ as $H_z \rightarrow \infty$ as $H_z \rightarrow 0$, 1.6/3		$B_2(\theta_3, \theta_1)$	$s^2 \theta_3 s^2 \theta_{-1}$	0	0	$B_3(\theta_3)$	$B_2(\theta_3, \theta_1 + \frac{\pi}{2})$	$s^2 \theta_3 c^2 \theta_{-1}$	0
$ 5/2, 1/2\rangle$	$\frac{2}{3}$	$\frac{1}{6}$		$\frac{1}{4} s^2 (\theta_1 - \theta_{-1})$	$s^2 \theta_1 s^2 \theta_{-3}$	0	$B_2(\theta_3, \frac{\pi}{2}, \theta_1)$	$B_4(\theta_1)$	$\frac{1}{4} c^2 (\theta_1 - \theta_{-1})$	$s^2 \theta_1 c^2 \theta_{-3}$
		.8/3	.64/3							
		0	.25							
$ 5/2, -1/2\rangle$	0				$B_2(\theta_{-3}, \theta_{-1})$	$\frac{2}{3} \cos^2 \theta_{-1}$	$c^2 \theta_3 s^2 \theta_{-1}$	$\frac{1}{4} c^2 (\theta_1 - \theta_{-1})$	$B_4(\theta_{-1})$	$B_2(\theta_{-3}, \frac{\pi}{2}, \theta_1)$
			.48	0						
			0	.25						
$ 5/2, -3/2\rangle$	0	0				$B_1(\theta_{-3})$	0	$c^2 \theta_1 s^2 \theta_{-3}$	$B_2(\theta_{-3}, \theta_1 + \frac{\pi}{2})$	$B_3(\theta_{-3})$
			.48	.64/3						
			0	1/6						
$ 5/2, -5/2\rangle$	0	0	0		.8/3	1.6/3			$\frac{2}{3} \sin^2 \theta_{-1}$	$B_1(\theta_{-3}, \frac{\pi}{2})$
	1/6	1/9	1/6	1						
$ 3/2, 3/2\rangle$					0	0		$B_2(\theta_3, \frac{\pi}{2}, \theta_1 + \frac{\pi}{2})$	$c^2 \theta_3 c^2 \theta_{-1}$	0
		.3	.36	.27	.12					
$ 3/2, 1/2\rangle$	0	0	1/6	0	1			.25	$\frac{1}{4} s^2 (\theta_1 - \theta_{-1})$	$c^2 \theta_1 c^2 \theta_{-3}$
		.4	.02	.06	1/6	.25	1/6	.32	2/3	0
		0	0	0	1/6	.25	1/6	.32	2/3	0
$ 3/2, -1/2\rangle$	0							.08	.25	
			.32	.25	.06	.02	.4	.08	0	
			0	0	1/9	2/3		0	1/6	
$ 3/2, -3/2\rangle$	0	0					0			
			.12	.27	.36	.3		.08	.08	

TABLE VII (Continued)

II. ${}^3B_{1g}$, ${}^3B_{2g}$, ${}^3B_{3g}$ proton states

$ b\rangle \backslash a\rangle$	$ 3/2, 3/2\rangle$	$ 3/2, 1/2\rangle$	$ 3/2, -1/2\rangle$	$ 3/2, -3/2\rangle$	$ 1/2, 1/2\rangle$	$ 1/2, -1/2\rangle$
$ 3/2, 3/2\rangle$		$B_5(\theta_1)$	$1/3 s^2 \theta_{-1}$	0	$B_5(\theta_1 + \frac{\pi}{2})$	$1/3 c^2 \theta_{-1}$
$ 3/2, 1/2\rangle$	1/6		$\frac{1}{12} s^2(\theta_1 + \theta_{-1})$	$\frac{1}{3} \sin^2 \theta_1$	$B_4(\theta_1)$	$\frac{1}{12} c^2(\theta_1 + \theta_{-1})$
$ 3/2, -1/2\rangle$	1/3	2/9	1/12		$B_5(-\theta_{-1})$	$\frac{1}{12} c^2(\theta_1 + \theta_{-1})$
$ 3/2, -3/2\rangle$	0	2/9	0	1/12		$B_4(-\theta_{-1})$
$ 1/2, 1/2\rangle$	1/12	1/18	0	2/9	1/3	$\frac{1}{12} s^2(\theta_1 + \theta_{-1})$
$ 1/2, -1/2\rangle$	0	1/36	1/18	1/12	1/9	
	0	0	1/18	1/6	1/12	
	1/9	1/12	1/36	1/36	0	

III. 1A_g proton states

$ b\rangle \backslash a\rangle$	$ 1/2, 1/2\rangle_1$	$ 1/2, -1/2\rangle_1$	$ 1/2, 1/2\rangle_2$	$ 1/2, -1/2\rangle_2$
$ 1/2, 1/2\rangle_1$		.5	0	0
$ 1/2, -1/2\rangle_1$	.5		0	0
$ 1/2, 1/2\rangle_2$	0	0		.5
$ 1/2, -1/2\rangle_2$	0	0	.5	

FIG. 7. Schematic diagram for Van Vleck second-order Raman transitions induced in *p*-BSQ⁻ by spin-orbit-lattice interactions. The virtual transitions are indicated by (+*j*) and (-*i*) for the absorption and emission of phonons, respectively, and by (ΔF_z) for a transition between the levels of $\hbar \langle \mathcal{H}_0 \rangle_{Av}$.

when $\langle \delta \rangle_{Av} = 0$. Here

$$\epsilon_4' = 16a_{4,9}^2 \langle \delta^2 \rangle_{Av} / (D_{\pm 1} - D_{\pm 1'});$$

$$\epsilon_4'' = 16a_{4,10}^2 \langle \delta^2 \rangle_{Av} / (D_{\pm 1} + D_{\pm 1'});$$

$$\epsilon_5' = -16a_{5,9}^2 \langle \delta^2 \rangle_{Av} / (D_{\pm 1} + D_{\pm 1'});$$

$$\epsilon_5'' = -16a_{5,10}^2 \langle \delta^2 \rangle_{Av} / (D_{\pm 1} - D_{\pm 1'});$$

$$\epsilon_6' = -8a_{6,9}^2 \langle \delta^2 \rangle_{Av} / (D_{\pm 1'} \sin^2 \theta_{\pm 1'}),$$

and

$$\epsilon_6'' = 8a_{6,10}^2 \langle \delta^2 \rangle_{Av} / (D_{\pm 1'} \cos^2 \theta_{\pm 1'}).$$

The $a_{\alpha,\alpha'}$ are given in Table VI. These dynamic effects are different in the Paschen-Back region because there the states with equal S_z and K_{ns} are degenerate. Therefore, terms between the latter do not contribute

to the second-order energies, and the only dynamic second-order contributions are of the order $\langle \delta^2 \rangle_{Av} / H_s$, where $H_s \approx 3 \times 10^3$ G.⁸ The room-temperature correction values obtained from Eq. (10) are compared with the experimental results in Table III. Unfortunately, the correction terms are less than the experimental uncertainty. An upper limit for $\langle \delta^2 \rangle_{Av}$ was obtained from Eq. (10) and the following data. At room temperature a single line was observed for the 1A_g proton states at $\omega_e / |A| = 2.45 \pm 0.01$ when $\omega_0 / |A| = 2.45$. However, if $\langle \delta^2 \rangle_{Av} \neq 0$, the absorption should have appeared midway between $\omega_e / |A| = \omega_0 / |A|$ and $(\omega_0 / |A|)(1 + 8 \langle \delta^2 \rangle_{Av} / 3A^2)$. Thus, from the uncertainty in the measurement, $\langle \delta^2 \rangle_{Av} \leq 0.003A^2$. This is in agreement with Khakhar and associates.³ They found $(\langle \delta \rangle_{Av})^2 \sim 0.01A^2$ for *p*-BSQ⁻ in K-THF at $t = -60^\circ\text{C}$.

Footnotes for Table VII, p. 5399-5400

^a The matrix elements tabulated are

$$b_{ab}' = | \langle a | \sum_n \mathcal{Q}_n^{(2)} | b \rangle |^2 / (2.25 \gamma_e^2 \gamma_p^2),$$

$$| \langle a | \sum_n \mathcal{Q}_n^{(4)} | b \rangle |^2 / (13.5 \gamma_e^2 \gamma_p^2),$$

and

$$| \langle a | \sum_n \mathcal{Q}_n^{(2)} | b \rangle |^2 / (3.375 \gamma_e^2 \gamma_p^2),$$

in order to show continuity with the results of Stephen and Fraenkel⁵ in the Paschen-Back region. That is, the transition probability per unit time between the spin states *a* and *b*, induced by the intramolecular anisotropic hyperfine interaction [see Eq. (3.1) of Ref. 5] is $W_{ab}' = K_n(K_n + 1)b_{ab}K$, where $K = 3.8 \times 10^{14} \gamma_e(1 + \omega_e^2 \tau_e^2)^{-1}$. Also the anisotropic hyperfine interaction introduces mixing of states of different symmetry species through terms in Δ_s of Table VI.

^b For the spin eigenfunctions in Table I

$$B_1(\theta_i) = \frac{2}{3} [\cos \theta_i - \frac{1}{2} \sin \theta_i]^2,$$

$$B_2(\theta_i, \theta_j) = \frac{1}{6} [\cos \theta_i \cos \theta_j + \sin \theta_i \cos \theta_j - (\frac{2}{3})^{1/2} \sin \theta_i \sin \theta_j]^2,$$

$$B_3(\theta_i) = [\frac{1}{2} (\sin 2\theta_i) + \frac{1}{3} (\cos 2\theta_i)]^2,$$

$$B_4(\theta_i) = [\frac{1}{6} (\sin 2\theta_i) + 6^{-1/2} (\cos 2\theta_i)]^2,$$

$$B_4(\theta_i') = [\frac{1}{6} (\sin 2\theta_i') + \frac{1}{6} (\sqrt{2} \cos 2\theta_i')]^2,$$

$$B_5(\theta_i) = \frac{1}{6} [\cos \theta_i - (\frac{1}{2})^{1/2} \sin \theta_i]^2.$$

^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* are used to denote the sine and cosine functions.

^e The matrix elements connect only states of the same symmetry species.

TABLE VIII. Matrix elements $3 \langle | \mathcal{A}^{(1,m)} | \rangle^2 \langle | D_{s,m}^{(1)} |^2 \rangle$.I. 5A_1 proton states

$ a\rangle \backslash b\rangle$	$ 5/2, 5/2\rangle$	$ 5/2, 3/2\rangle$	$ 5/2, 1/2\rangle$	$ 5/2, -1/2\rangle$	$ 5/2, -3/2\rangle$	$ 5/2, -5/2\rangle$	$ 3/2, 3/2\rangle$	$ 3/2, 1/2\rangle$	$ 3/2, -1/2\rangle$	$ 3/2, -3/2\rangle$
$ 5/2, 5/2\rangle$		$\frac{1}{2} \cos^2 \theta_3$	0	0	0	0	$\frac{1}{2} \sin^2 \theta_3$	0	0	0
$ 5/2, 3/2\rangle$	.5 as $H \rightarrow \infty$ as $H \rightarrow 0$, .10		$\frac{1}{2} s^2 \theta_3 c^2 \theta_1$	0	0	0	$\frac{1}{4} \sin^2 2\theta_3$	$\frac{1}{2} s^2 \theta_3 s^2 \theta_1$	0	0
$ 5/2, 1/2\rangle$	0	0		$\frac{1}{2} s^2 \theta_1 s^2 \theta_{-1}$	0	0	$\frac{1}{2} c^2 \theta_1 c^2 \theta_3$	$\frac{1}{4} \sin^2 2\theta_1$	$\frac{1}{2} s^2 \theta_1 c^2 \theta_{-1}$	0
$ 5/2, -1/2\rangle$	0	0	.16		$\frac{1}{2} c^2 \theta_{-1} s^2 \theta_{-3}$	0	0	$\frac{1}{2} s^2 \theta_{-1} c^2 \theta_1$	$\frac{1}{4} \sin^2 2\theta_{-1}$	$\frac{1}{2} c^2 \theta_{-1} c^2 \theta_{-3}$
$ 5/2, -3/2\rangle$	0	0	0	.08		$\frac{1}{2} \cos^2 \theta_{-3}$	0	0	$\frac{1}{2} s^2 \theta_{-3} s^2 \theta_{-1}$	$\frac{1}{4} \sin^2 2\theta_{-3}$
$ 5/2, -5/2\rangle$	0	0	0	0	.16		0	0	0	$\frac{1}{2} \sin^2 \theta_{-3}$
$ 3/2, 3/2\rangle$	0	0	.5	0	0	.10		$\frac{1}{2} c^2 \theta_3 s^2 \theta_1$	0	0
$ 3/2, 1/2\rangle$	0	.40	.16	.04	.5	0	0		$\frac{1}{2} c^2 \theta_{-1} c^2 \theta_1$	0
$ 3/2, -1/2\rangle$	0	0	.24	.24	.12	.5	0	.06		
$ 3/2, -3/2\rangle$	0	0	0	.12	.24	.24	.5	0	.08	
	0	0	0	0	0	.04	.16	.40	.06	

TABLE VIII (Continued)

II. ${}^3B_{1g}$, ${}^3B_{2u}$ and ${}^3B_{3u}$ proton states^a

$ a\rangle$ $ b\rangle$	$ 3/2, 3/2\rangle$	$ 3/2, 1/2\rangle$	$ 3/2, -1/2\rangle$	$ 3/2, -3/2\rangle$	$ 1/2, 1/2\rangle$	$ 1/2, -1/2\rangle$
$ 3/2, 3/2\rangle$		$\frac{1}{2} \cos^2 \theta_1$	0	0	$\frac{1}{2} \sin^2 \theta_1$	0
$ 3/2, 1/2\rangle$	.5		$\frac{1}{2} s^2 \theta_1 c^2 \theta_{-1}$	0	$\frac{1}{4} \sin^2 2\theta_1$	$\frac{1}{2} s^2 \theta_1 c^2 \theta_{-1}$
		1/6				
		0				
$ 3/2, -1/2\rangle$	0			$\frac{1}{2} \cos^2 \theta_{-1}$	$\frac{1}{2} s^2 \theta_{-1} c^2 \theta_1$	$\frac{1}{4} \sin^2 2\theta_{-1}$
			2/9			
			0			
$ 3/2, -3/2\rangle$	0	0			0	$\frac{1}{2} \sin^2 \theta_{-1}$
				1/6		
	0	0	.5			
$ 1/2, 1/2\rangle$		1/3	2/9	1/9		$\frac{1}{2} s^2 \theta_{-1} s^2 \theta_1$
		0	0	.5	0	
$ 1/2, -1/2\rangle$	0					
			1/9	2/9	1/3	2/9

III. All 1A_g matrix elements are zero for D_{2h} symmetry species

The low-temperature septet, shown for the $\mathbf{K}_n=0$ proton states in Fig. 5 could arise from two possible species. One is a three-ion cluster of D_{2h} symmetry, $(\text{Na}^+) \cdot p\text{-BSQ}^- \cdot (\text{Na}^+)$, and the other is an ion pair $(\text{Na}^+) \cdot p\text{-BSQ}^-$ of C_{2v} symmetry with $\langle \delta \rangle_{\text{AV}} \neq 0$. In the first case $I_k=3$ while in the second $I_k=\frac{3}{2}$ but the 1A_1 absorptions are separated by $8(\langle \delta \rangle_{\text{AV}})^2 \omega_0 / 3A^2 = 3A'$, or $(\langle \delta \rangle_{\text{AV}}/A)^2 = 0.022$. However, if $\langle \delta \rangle_{\text{AV}} \neq 0$, the triplet proton states, the two 3B_2 and the 3A_1 , should also be split as follows. The transition frequencies for the 3B_2 proton states are

$$|\frac{3}{2}, -\frac{3}{2}\rangle \leftrightarrow |\frac{1}{2}, -\frac{1}{2}\rangle:$$

$$\omega \cong \omega_0 + a_- \langle \delta^2 \rangle_{\text{AV}} \pm b_- \langle \delta \rangle_{\text{AV}},$$

$$|\frac{3}{2}, -\frac{1}{2}\rangle \leftrightarrow |\frac{1}{2}, \frac{1}{2}\rangle:$$

$$\omega \cong \omega_0 + (a_- + a_+) \langle \delta^2 \rangle_{\text{AV}} \pm \frac{1}{2} [\sin^2 \theta_{1'} - \cos^2 \theta_{-1'} + \sqrt{2} (\sin 2\theta_{1'} + \sin 2\theta_{-1'})] \langle \delta \rangle_{\text{AV}},$$

and

$$|\frac{3}{2}, \frac{1}{2}\rangle \leftrightarrow |\frac{3}{2}, \frac{3}{2}\rangle:$$

$$\omega \cong \omega_0 + a_+ \langle \delta^2 \rangle_{\text{AV}} \pm b_+ \langle \delta \rangle_{\text{AV}},$$

where ω_0 is the resonance frequency for D_{2h} symmetry $p\text{-BSQ}^-$,

$$a_{\pm} = [\frac{1}{2} \mp \frac{1}{8}(8)^{1/2} (\sin 4\theta_{\pm 1'}) - \frac{1}{8}(7 \sin^2 2\theta_{\pm 1'})] (2D_{\pm 1'})^{-1}$$

and

$$b_{\pm} = 1 - \frac{1}{2} [\frac{1}{2} (1 \mp \cos 2\theta_{\pm 1'}) - \sqrt{2} \sin 2\theta_{\pm 1'}].$$

The correction terms for the 3A_1 resonance transitions are of the order of $\langle \delta^2 \rangle_{\text{AV}}/D_{\pm 1'}$. Thus from the expressions for the resonance fields given in Table II, the expected over-all field separations for the above transitions when $\langle \delta \rangle_{\text{AV}} \neq 0$ and $\omega_0/|A| = 2.476$ would be 3.12 $\langle \delta \rangle_{\text{AV}}$, 1.64 $\langle \delta \rangle_{\text{AV}}$, and 1.35 $\langle \delta \rangle_{\text{AV}}$ or 3.14, 1.61, and 1.48 MHz, respectively. However, the observed envelope linewidths at $t = -35^\circ\text{C}$ and $\omega_0/|A| = 2.476$ were the same for the singlet and triplet proton transitions and equal to 1.3 ± 0.1 MHz. Also, a spectrum for an ion pair could not be fitted to the data. But, in Fig. 5 the experimental absorption could be fitted by the superposition of two absorptions of approximately the same intensity, one broad with $\Delta\nu_{ms} = 1.1$ MHz and the other a spectrum calculated from the allowed transitions computed according to Eq. (4) with $\Delta\nu_{ms} = 0.25$ MHz centered at $\omega_e = \omega_0$. Therefore contrary to Khakhar's³ and Lucken's³⁰ observation of $\text{M}^+ \cdot p\text{-BSQ}^-$ ion pairs in other solvents, in dry ethanol in the region $-20^\circ \geq t \geq -50^\circ\text{C}$ the experimental evidence indicates that three ion clusters are formed.

The linewidths at room temperature are greater than the extrapolated values from Paschen-Back region

work,^{4a} see Table IV. The only single-line absorption, the $|\frac{5}{2}, \frac{5}{2}\rangle \leftrightarrow |\frac{5}{2}, \frac{3}{2}\rangle$ transition, was 15% broader. However, the much greater linewidths observed for the triply degenerate proton triplet states and the doubly degenerate proton singlet states suggest an instantaneous C_{2v} symmetry with $\langle \delta^2 \rangle_{\text{AV}} \neq 0$. The linewidth temperature dependence of the $\mathbf{K}_n=0$ proton states may be explained from the general theory.³¹ This predicts that for a single pair of levels separated in energy by $\hbar(a-b) = \hbar\omega_0$,

$$T_2^{-1} = T_2'^{-1} + \frac{1}{2}(t_a^{-1} + t_b^{-1}), \quad (11)$$

where $1/T_2'$ is the linewidth under strong narrowing given by the adiabatic theory, and t_a and t_b are the lifetimes of the spin states $|a\rangle$ and $|b\rangle$:

$$t_a^{-1} = \sum_{c \neq a} W_{ac}$$

and

$$t_b^{-1} = \sum_{c \neq b} W_{bc},$$

where

$$W_{ab} = 2\pi |\langle i | \mathcal{H}_1 | f \rangle|^2 \rho(E_i - E_f)$$

is the general transition probability per unit time between the steady-state spin levels.²⁹ $|i\rangle$ and $|f\rangle$ are the initial and final states of the whole system and $\rho(E_i - E_f) = \rho_{if} \cong \delta(E_i - E_f)$ is the spectral density of final states. E_i and E_f are the total initial and final state energies.

Now, if for $0^\circ \geq t \geq -20^\circ\text{C}$, the lifetime of the spin states is limited by the chemical exchange process

with an over-all first-order rate of disappearance

$$- [dp\text{-BSQ}^-] / dt = [p\text{-BSQ}^-] / \tau_{e,k}, \quad (13)$$

then the chemical exchange time is

$$\tau_{e,k} = \tau_{0,k} \exp(E_a/RT). \quad (14)$$

E_a is an over-all energy of activation.³² The significant contributions to the 1A_0 -proton-state linewidth in the above temperature range are then

$$\Delta\nu_{ms} = ((T_2^{-1})_{\text{DD}} + (T_2^{-1})_{\text{CE}} + (T_2^{-1})_{\text{HE}} + \frac{1}{3}(A'^2 \tau_{e,k}) I_k \times (I_k + 1) \{1 + [1 + (w_s - w_k)^2 \tau_{e,k}^2]^{-1}\} + \dots) / \sqrt{3}\pi, \quad (15)$$

where $(T_2^{-1})_{\text{DD}}$ is the dipolar term, and $(T_2^{-1})_{\text{CE}}$ and

³¹ See Ref. 29, p. 444.

³² S. Glasstone, K. J. Laidler, and A. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Co., New York, 1941), p. 195.

³⁰ E. A. C. Lucken, J. Chem. Soc. 1964, 4234.

$(T_2^{-1})_{\text{HE}}$ are the contributions from the chemical exchange between the diamagnetic $\text{C}_6\text{H}_4\text{O}_2$ and $\text{C}_6\text{H}_4\text{O}_2^-$ and the Heisenberg exchange, respectively. For total concentrations of quinone of $10^{-3}M$, $(T_2^{-1})_{\text{CE}}$ is negligible.¹² The last term or the scalar relaxation of the first kind³⁸ is valid only for $\tau_{e,k} \ll T_1$ and $\tau_{e,k} |A'| \ll 1$. The experimental data in Fig. 4 were fitted with $E_a = 10 \pm 1$ kcal mole⁻¹ such that for $T > T_0$, $\tau_{e,k} |A'| = \exp[E_a(T^{-1} - T_0^{-1})/R]$, where $T_0 = 253^\circ \pm 5^\circ\text{K}$, assuming negligible $(T_2^{-1})_{\text{DD}}$ and $(T_2^{-1})_{\text{HE}}$. For these latter processes the theory^{5,8,10,29} predicts a correlation time, and a linewidth which varies linearly with η/T , where η is the solution viscosity. The lack of correlation between the plots of η/T^{34} and $\Delta\nu_{ms}$ in Fig. 4 is then sufficient justification for neglecting the latter effects when $0^\circ \geq t \geq -20^\circ\text{C}$.

For the states with $K_n \neq 0$, the intramolecular anisotropic hyperfine interaction will contribute to the relaxation times. However, the magnitude will be different in the Zeeman region than in the Paschen-Back region. The induced transition probability per unit time between two spin states $|a\rangle$ and $|b\rangle$ of $\langle \hbar \mathcal{H}_0 \rangle_{Av}$ is, in the Paschen-Back region,

$$W_{ab} = K_n (K_n + 1) b_{ab} K, \quad (16)$$

where $K = 3.8 \times 10^{14} \tau_c / (1 + \omega_0^2 \tau_c^2) \text{ sec}^{-1.5}$ K is less in the Zeeman region. The matrix elements b_{ab} are given in Table VII. The limiting values for b_{ab} as $H_z \rightarrow 0$ and ∞ are also given. The importance of the intramolecular dipolar relaxation in the Zeeman region, due to the nonzero terms in Table VII was made evident by measuring the relative intensities for the singlet proton states at two different power levels with respect to the other transitions. These are given in Table III. However, interpretation of the results is not

simple because at room temperature the correlation time for dipolar interactions is $\tau_c \sim 7 \times 10^{-11} \text{ sec}$,^{4a} whereas $\tau_{e,k} \sim 2.2 \times 10^{-8} \text{ sec}$ for the chemical process in Eq. (12), if one may assume that A' has not changed appreciably with temperature. Also, if the $\text{Na}^+ \cdot p\text{-BSQ}^-$ is an intermediate in Eq. (12) with a chemical exchange time shorter than $\tau_{e,k}$ but longer than τ_c , the intramolecular dipolar interactions take place for C_{2v} symmetry species. This means that when the instantaneous anisotropic hyperfine terms in Δ_3 (see Table VI) are introduced all protons become nonequivalent.

For $H_z = 0$ and $\omega_0/|A| = 2.5$ and 1.5 the theory predicts that two equally intense lines of opposite phase should cancel out completely. See Table II. However, this was not feasible experimentally. Figures 2 and 6 show the near $H_z = 0$ transitions. A probable explanation for this is that the anisotropic hyperfine interaction term has lifted the degeneracy between the states of equal F . That is, when $H_z = 0$ the corresponding secular equation must be solved for every value of F taking into account the dipolar terms explicitly. The time averages of the eigenvalues of $\hbar \mathcal{H}_0$ should then contain nonzero dipolar terms. Thus, although cancellation will occur for a given pair of transitions at $H_z = 0$, they do not all occur at exactly the same frequency. This means then, that a study of near-zero-field transitions versus the frequency should give the magnitude of the intramolecular dipolar interaction terms.

Contributions to the near zero-field linewidths may also arise from spin-orbit-lattice interactions which are field independent.^{10b} Thus, since the eigenvalues of $\hbar \mathcal{H}_0$ can be made as accurate as need be in the Zeeman and spin-orbit terms,³⁵ the ground-state free-radical wavefunction at time $t=0$, in the Zeeman region is

$$| (0, a)_1 \rangle = | 0, a \rangle + \frac{\sum_i \langle 0, a | \beta L \cdot H_z + \mathcal{H}_{\text{SO}} + \sum_p (A_p - A) I \cdot S | i, b \rangle}{(-\Delta_i + a - b)} | i, b \rangle, \quad (17)$$

where $| 0 \rangle$ and $| i \rangle$ are electronic wavefunctions, Δ_i is the excitation energy from the ground state to the virtual state $| i \rangle$, and $\hbar \mathcal{H}_{\text{SO}}$ is the spin-orbit term. In the Zeeman region the shift from the free electron absorption due to the g factor²³ $\Delta H_z = (g - g_s) H_z / g_s = 0.0013 H_z < 0.01 \text{ G}$ is negligible relative to the linewidths observed. Thus, the second-order contributions to $\langle \hbar \mathcal{H}_0 \rangle_{Av}$ due to the spin-orbit terms are negligible here. However, through fluctuations in the free-electron orbit-lattice interaction, spin-orbit-lattice terms can give rise to field-independent relaxation mechanisms.^{1,10b,35-38} Already, Kivelson^{10b} has determined the transition probabilities due to these processes for free radicals in solution. He estimated the field-independent contribution for $(\text{SO}_3)_2\text{NO}^-$ to be $W =$

³³ See Ref. 29, p. 309.

³⁴ *Handbook of Chemistry and Physics*, C. D. Hoggman, Ed. (Chemical Rubber Publ. Co., Cleveland, Ohio, 1958).

³⁵ (a) R. Orbach, Proc. Roy. Soc. (London) **A264**, 458, 485 (1961); (b) *Spin Lattice Relaxation in Ionic Solids*, A. A. Manenkov and R. Orbach, Eds. (Harper and Row Publishers, Inc., New York, 1966).

³⁶ I. Waller, Z. Physik **79**, 370 (1932).

³⁷ R. L. Kronig, Physica **6**, 33 (1936).

³⁸ (a) J. H. VanVleck, Phys. Rev. **57**, 426 (1939); (b) J. Chem. Phys. **7**, 72 (1939); and (c) *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932).

$2 \times 10^4 \text{ sec}^{-1}$. This should be approximately the same for $p\text{-BSQ}^-$. Thus

$$\hbar \mathcal{H}_1^{(1)} = \hbar \left(\mathcal{H}_{\text{OL}} + \sum_j \frac{\mathcal{H}_{\text{OL}} |j\rangle \langle j| \mathcal{H}_{\text{OL}}}{-\Delta_j} + \dots \right), \quad (18)$$

where

$$V = \hbar \mathcal{H}_{\text{OL}} = -e^2 \left(\frac{Z_{\text{O}}}{r_{\text{O}}} + \frac{Z_{\text{C}}}{(r_{\text{O}}^2 + R_{\text{CO}}^2 + -2r_{\text{O}}R_{\text{CO}} \cos \theta_{\text{O}})^{1/2}} + \frac{Z_{\text{S}}}{(r_{\text{O}}^2 + R_{\text{OS}}^2 + 2r_{\text{O}}R_{\text{OS}} \cos \theta_{\text{O}})^{1/2}} + \dots \right),$$

eZ_k are the effective atomic charges, $(r_{\text{O}}, \theta_{\text{O}}, \phi_{\text{O}})$ are the free-electron spherical polar coordinates relative to the oxygen atom O with $Z' \equiv \text{OO}'$ axis of $p\text{-BSQ}^-$,

S represents the solvent molecules and the important contributions are those from the neighborhood of the oxygen atoms.

The first order terms in Eq. (18) are field dependent.^{10b} Therefore, they should be negligible in the Zeeman region. The second-order terms are so called Raman processes^{35,38a} because a transition between a pair of steady-state spin levels $|a\rangle$ and $|b\rangle$ of $\hbar \langle \mathcal{H}_0 \rangle_{\text{av}}$ is accomplished by the absorption of a phonon of energy $\hbar\omega_j$ and the emission of another of energy $\hbar\omega_i$ such that $\hbar(\omega_j - \omega_i) = \hbar\omega_0$ is the energy separation between the participating pair of levels. A schematic diagram is shown in Fig. 7. In the Zeeman region

$$\hbar \mathcal{H}_1^{(1)} = \hbar \sum_m F^{(1)} D_{z',m}^{(1)} \mathcal{A}^{(1,m)}, \quad (19)$$

where

$$\begin{aligned} \langle i | \mathcal{H}_1^{(1)} | f \rangle &= \langle (0, a)_1; n_i, n_j | \mathcal{H}_1^{(1)} | (0, b)_1; n_i - 1, n_j + 1 \rangle \\ &= \sum_{ij} \frac{\langle 0, a; n_i, n_j | \mathcal{H}_{\text{SO}} | i, b; n_i, n_j \rangle \langle i, b; n_i, n_j | \mathcal{H}_{\text{OL}} | j, b; n_i - 1, n_j \rangle \langle j, b; n_i - 1, n_j | \mathcal{H}_{\text{OL}} | 0, b; n_i - 1, n_j + 1 \rangle}{(-\Delta_i + a - b)(-\Delta_j + a - b + \omega_i)} + \text{h.c.} \end{aligned}$$

h.c. stands for Hermitean conjugate and n_i and n_j are the number of phonons in modes i and j . The highest contributions are expected to arise here from the virtual excitations of the free-radical ground state $|0\rangle = \mathcal{Q} \{ \Sigma \Pi n_{\text{O}}^2 n_{\text{O}}'^2 \pi_s \}$ to the $n \rightarrow \pi_s$ excited states $|n_{\pm}\rangle = \mathcal{Q} \{ \Sigma \pi n_{\text{O}} n_{\text{O}}' [(n_{\text{O}}^- \pm n_{\text{O}}'^-)/\sqrt{2}] \pi_s^{\pm} \}$ (where $\mathcal{Q}$ is the antisymmetrization operator, Σ and Π represent the closed sigma- and pi-electron sets, n_{O} and n_{O}' are the n -type orbitals at the oxygen atoms, π_s is the free-electron orbital in the ground state, and the superscript minus on the orbitals indicate negative electron spin). Now, $|n_+\rangle$ and $|n_-\rangle$ are of opposite symmetry with respect to reflection on a bisecting plane normal to the ring and the OO' axis. Therefore, when V is expanded in terms of the normal coordinates of vibration Q_i , $V = \hbar \sum_{i,k} v_{ki} Q_i^k$, the molecular vibrations will contribute nonzero terms to $\hbar \mathcal{H}_{\text{OL}}$. Thus, $\hbar \langle n_+ | v_1 | n_- \rangle \cong e^2 Z_{\text{C}} \sqrt{2} / R_0^2$ for the CO asymmetric stretch where R_0 is the equilibrium CO bond distance in the excited state.³⁹ $\hbar \langle 0 | \mathcal{H}_{\text{SO}} | n_- \rangle \cong (2\rho_{\text{O}} \pi)^{1/2} \lambda_0 \sum_m D_{z',m}^{(1)} \mathcal{A}^{(1,m)}$ is derived in the Appendix.^{25,40-45} Here $\rho_{\text{O}} \pi \cong 0.17$,^{25b} is the free-electron density at the O atom and $\lambda_0 \cong \lambda_{\text{O}}^0 = 152 \text{ cm}^{-1}$ for the free oxygen atom has already been used successfully to evaluate the g factor.^{40b} The $D_{z',m}^{(1)}$ are the rotation matrix elements for spherical harmonics of order 1.⁴⁶ Also, for an order-of-magnitude estimate we note that the $n \rightarrow \pi_s$, $^1A_g \rightarrow ^1B_{1g}$ and 1A_u , and $^1A_g \rightarrow ^3B_{1g}$ and 3A_u transitions for p -benzoquinone were found to be degenerate and equal 2.7 and 2.3 eV,²⁶ respectively, since the energy terms

³⁹ U. Öpik and M. H. L. Pryce, Proc. Roy. Soc. (London) **A238**, 425 (1957).

⁴⁰ (a) H. M. McConnell, J. Chem. Phys. **34**, 13 (1961); (b) H. M. McConnell and R. E. Robertson, J. Phys. Chem. **61**, 1018 (1957).

⁴¹ L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Co., New York, 1955), p. 332.

⁴² M. Mizushima and S. Koide, J. Chem. Phys. **20**, 765 (1952).

⁴³ E. Clementi and M. Kasha, J. Mol. Spectry. **2**, 297 (1958).

⁴⁴ D. S. McClure, J. Chem. Phys. **20**, 682 (1952).

⁴⁵ H. M. McConnell, J. Chem. Phys. **20**, 700 (1952).

⁴⁶ M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957), p. 65.

between the localized n_0 and n_0' orbitals are negligible, for $R_{00'} = 5.5 \text{ \AA}$ in solid *p*-benzoquinone.⁴⁷ Thus, if one may assume that $|n_+\rangle$ and $|n_-\rangle$ for the negative ion are also degenerate and $\Delta_i \cong \Delta_j \cong \Delta_0 \sim 2.7 \text{ eV}$, then

$$\langle i | \mathcal{H}_1^{(1)} | f \rangle = (4\omega/\Delta_0^3)$$

$$\times \langle 0, a; n_i, n_j | \mathcal{H}_{SO} | n_-, b; n_i, n_j \rangle \langle n_-, b; n_i, n_j | \mathcal{H}_{OL} | n_+, b; n_i-1, n_j \rangle \langle n_+, b; n_i-1, n_j | \mathcal{H}_{OL} | 0, b; n_i-1, n_j+1 \rangle, \quad (20)$$

where a Van Vleck cancellation³⁸ has taken place between the h.c. terms because

$$\hbar(a-b) = \hbar\omega_0 \ll \hbar\omega_i \cong \hbar\omega_j = \hbar\omega \ll \hbar\Delta_i \sim \hbar\Delta_j = \hbar\Delta_0 \sim 2.7 \text{ eV}.$$

The induced transition probability per unit time is then

$$W_{ab} = 2\pi \left| \langle i | \mathcal{H}_1^{(1)} | f \rangle \right|^2 \rho_{if} = \sum_m \left| \langle a | \mathcal{A}^{(1,m)} | b \rangle \right|^2 \left| \langle D_{z',m}^{(1)} \rangle \right|^2 I_1, \quad (21)$$

where the matrix elements $\left| \langle \mathcal{A}^{(1,m)} \rangle \right|^2 \left| \langle D_{z',m}^{(1)} \rangle \right|^2$ are given in Table VIII. For a solid^{38a}

$$I_1 = \int_0^\Omega \left| F^{(1)} \right|^2 \rho(w_i) \rho(w_j) dw = \frac{144V^2}{\pi^2 v^6} \times \int_0^\Omega w^6 \left| \frac{\langle 0 | \lambda_0 L_z | n_- \rangle \langle n_- | v_1 | n_+ \rangle \langle n_+ | v_1 | 0 \rangle \langle n_i | Q | n_i-1 \rangle \langle n_j | Q | n_j+1 \rangle}{\Delta_0^3} \right|^2 dw,$$

where V is the volume of a solid containing N atoms, v is the phonon velocity in the solid, and $\Omega/2\pi v = (3N/4\pi V)^{1/3}$ for a monatomic lattice in the Debye theory of elasticity,

$$\langle 0 | \lambda_0 L_z | n_- \rangle / \Delta_0 \sim 4 \times 10^{-3}; \langle n_+ | v_1 | n_- \rangle / \Delta_0 \sim 7 \text{ bohr}^{-1}$$

and

$$\langle n_+ | v_1 | 0 \rangle / \Delta_0 \cong 4(\rho_0 \tau)^{1/2} e^2 Z C \epsilon \langle 2p_{y',0} | r_0 \cos \theta_0 | 3d_{y',z',0} \rangle / R_0^3 \Delta_0 \sim 0.01 \text{ bohr}^{-1}$$

using the best single-exponent Slater orbitals.⁴⁸ $\epsilon \sim 0.01$ is the $3d$ character of the oxygen pi orbital introduced by the CO in the in-plane and out-of-plane bending modes.⁴⁹ Q is expanded in terms of the lattice normal coordinates q_i , $Q = \sum_i a_i q_i$ where a_i are amplitude factors,^{38a} $\left| \langle n_i | Q | n_i-1 \rangle \langle n_j | Q | n_j+1 \rangle \right|^2 = \hbar^2 \left| \langle a^2 \rangle w n(n+1) / (2V d v^2) \right|^2$, where $n = 1/[\exp(\hbar\omega/kT) - 1]$ at thermal equilibrium and d is the density within V . Thus for a solid with the same d and v of alcohol,³⁴

$$I_1 = \frac{\hbar^2 (kT/\hbar)^9}{d^2 \pi^2 v^{10}} \left| \frac{\langle 0 | \lambda_0 L_z | n_- \rangle}{\Delta_0} \frac{\langle n_- | v_1 | n_+ \rangle}{\Delta_0} \frac{\langle n_+ | v_1 | 0 \rangle}{\Delta_0} \langle a^2 \rangle \right|^2 (9i) \sim 4 \times 10^7 (9i \left| \langle a^2 \rangle \right|^2) \text{ sec}^{-1}$$

at $T = 298^\circ \text{K}$, where

$$i = \int_0^{\hbar\Omega/kT} x^8 \csc^2 \frac{1}{2} x dx$$

and $\langle a^2 \rangle$ is given in atomic units. $9i = 4 \times 9!$ for $\hbar\Omega/kT \gg 1$ and $4e/(e-1)^2$ for $\hbar\Omega/kT = 1$.^{35,38a} However, for a polyatomic system, one cannot define a Debye temperature and Ω has to be estimated. Also $\langle a^2 \rangle$ must be estimated. For a liquid the Kivelson^{10b} approach gives

$$I_1 = 32 \left| \frac{\langle 0 | \lambda_0 L_z | n_- \rangle}{\Delta_0} \frac{\langle n_- | v_1 | n_+ \rangle}{\Delta_0} \frac{\langle n_+ | v_1 | 0 \rangle}{\Delta_0} \langle a^2 \rangle \right|^2 \frac{\tau_{c,vib}^{-1}}{1 + \omega_0^2 \tau_{c,vib}^2} \sim 3 \times 10^7 \left| \langle a^2 \rangle \right|^2 \text{ sec}^{-1}, \quad \text{for } \tau_{c,vib} 10^{-12} \text{ sec}.$$

⁴⁷ H. J. M. Bowen, J. Donohue, D. G. Jenkin, O. Kennard, P. J. Wheatley, and D. H. Wiffen, *Interatomic Distances* (The Chemical Society, London, 1958); M194.

⁴⁸ E. Clementi and D. L. Raimondi, *J. Chem. Phys.* **38**, 2686 (1963).

⁴⁹ E. D. Becker, E. Charney, and T. Anno, *J. Chem. Phys.* **42**, 942 (1965).

For $\langle a^2 \rangle \sim 10^{-1}$ bohr² we obtain $W_{ab} \sim 10^4$ sec⁻¹, the same as Kivelson did for $(\text{SO}_3)_2\text{NO}^-$. However, this is a rough order-of-magnitude estimate. The greatest uncertainties are in the values assigned to Δ_i , and Δ_j , which most probably depend on the nature of the solvent,⁴⁵ to Ω and to $|\langle a^2 \rangle|^2$.⁵⁰ Also other vibrations may give rise to higher contributions. These include the solvent effects and the ring deformations.^{10b, 40a, 51} However, the validity of the results could be checked experimentally if, as McConnell⁴⁵ has shown for *p*-benzoquinone, the value of Δ_0 undergoes a blue shift as the solvent polarity is increased from a paraffin to alcohol to water. This means one should see the resonance linewidth narrowing as the solvent is changed from THF to absolute ethanol to water if there are no other effects present. The formation of ion clusters should also affect Δ_0 . Another experimental verification for the existence of these processes could be via studies of the ²³Na and solvent ¹H resonance absorption enhancement by dynamic polarization as carried out by Landesman⁵² for solvent protons in solutions of the peroxyamine disulfonate ion in the Zeeman region.

In summary, the above estimates show that at room temperature, in the Zeeman region the processes in Table V contribute almost equally to the linewidth as given in Eq. (11). The measurements carried out here, however, indicate that the chemical reactions in the neighborhood of the ion do affect the different relaxation processes. This indicates then, that the solvent as well as the counter ion must be taken into consideration in the interpretation of resonance absorption saturation and linewidth studies of free radicals in solution.

VI. CONCLUSIONS

The experimental results have shown that for *p*-BSQ⁻ in absolute ethanol chemical reactions give important contributions to the free-radical relaxation process. The formation of three ion clusters was verified. However, whether these clusters are in contact or are solvent separated was not established. The fact is that the ²³Na hyperfine coupling observed at $t = -50^\circ\text{C}$ is low compared to that for the other three ion clusters of similar nature such as $(\text{Me}_3\text{C})_2\text{CO}^-(\text{Na}^+)_2$ which shows a ²³Na coupling of 1.7 G in THF at -70°C .⁵³ However, this may not be a fair comparison because the coupling will depend on the spin density at the oxygen atom and the temperature as well.

An experimental fact which lends more weight to the formation of contact ion clusters is the correlation of E_a with the well known large entropy of solvation by alcohol for a gas ion.⁵⁴ Thus, due to the size, the degree of solvation of *p*-BSQ⁻ and its three-ion cluster should be much less than for the Na⁺ ion. From Eq. (12) it then follows that

$$\Delta S^\ddagger \cong 2\{S[\text{Na}^+(\text{g})] - S[\text{Na}^+(\text{S})_n]\} = 36 \text{ eu} \quad (22)$$

when the gas ion entropy is given by the Sackur equation and the Na⁺(S)_n entropy in ethanol is assumed to be equal to the entropy measured in methanol by Latimer and Slansky.^{54a} Hence, $\Delta G^\ddagger = 0$, $\Delta H^\ddagger = T\Delta S^\ddagger = 9.5 \text{ kcal mole}^{-1}$, occurs at $T = 264^\circ$ within the temperature interval where the line-broadening processes of activation enthalpy $\Delta H^\ddagger = E_a - RT \sim 9.5 \text{ kcal mole}^{-1}$ occur.

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APPENDIX: HAMILTONIAN FOR *p*-BSQ⁻ IN SOLUTION

The intent of the Appendix is to simplify the interpretation of the experimental observations in the Zeeman region and to describe spin-orbit interactions which may explain the *p*-BSQ⁻ resonance absorption linewidths near zero fields.

The resonance measurements carried out in this work seek information contained in the spin density matrix. In liquids, the total Hamiltonian for the system is written²⁹

$$\hbar\mathcal{H} = \hbar(\langle\mathcal{H}_0\rangle_{\text{av}} + \mathcal{H}_L + \mathcal{H}_I), \quad (A1)$$

where $\hbar\langle\mathcal{H}_0\rangle_{\text{av}}$ and $\hbar\mathcal{H}_L$ are the steady-state spin and lattice Hamiltonians with eigenvalues α and f , respectively. The notation $\langle \rangle_{\text{av}}$ indicates time averages. Here

$$\hbar\mathcal{H}_0 = \hbar\left\{\sum_I Z_I + \mathcal{H}_{\text{IS}} + \mathcal{H}_{\text{SO}}\right\}. \quad (A2)$$

The Zeeman energy is given by the static terms $\hbar Z_S = \beta\mathbf{H}_z \cdot (\mathbf{L} + 2\mathbf{S})$ and $\hbar Z_{I_n} \cong \hbar\langle Z_{I_n} \rangle_{\text{av}} = \hbar\omega_{I_n} I_{zn}$ and

⁵⁰ The correct approach would be to evaluate $\langle a^2 \rangle$ in the manner given by Eq. (12) of Ref. 38(b).

⁵¹ H. M. McConnell and A. D. McLachlan, J. Chem. Phys. **34**, 1 (1961).

⁵² A. Landesman, J. Phys. Rad. **20**, 64, 937 (1959).

⁵³ (a) M. C. R. Symons, J. Phys. Chem. **71**, 172 (1967); (b) G. R. Luckhurst, Mol. Phys. **9**, 179 (1965).

⁵⁴ (a) W. M. Latimer and C. M. Slansky, J. Am. Chem. Soc. **62**, 2019 (1940); (b) W. M. Latimer and W. L. Jolly, *ibid.* **75**, 4147 (1953).

the rf terms:

$$\hbar\mathcal{H}_{1,z}(t) = \hbar \sum_I \omega_{1,I} [I_- \exp(i\omega_0 t) + \text{c.c.}];$$

β is the Bohr magneton. $I = S$, I_n ($n = {}^1\text{H}$, ${}^{23}\text{Na}$), $\mathbf{H}_z = H_z \mathbf{k}$ is the laboratory field, $\mathbf{H}_1 = 2H_1 \cos\omega_0 t \mathbf{i}$ is the rf field, $\omega_I = -\gamma_I H_z$ and $\omega_{1,I} = -\gamma_I H_1$. The spin-spin interaction terms are

$$\hbar\mathcal{H}_{\text{IS}} = \hbar \sum_{n=1}^{\text{H, Na}} \{ \mathbf{S} \cdot \mathbf{T}_n \cdot \mathbf{I}_n + \sum_{n>n'} \mathbf{I}_n \cdot \mathbf{T}_{nn'} \cdot \mathbf{I}_{n'} \}.$$

Here the nuclear spin-spin interaction terms in $\mathbf{T}_{nn'}$ are negligible relative to the electron-nuclear spin terms in $\mathbf{T}_n$ and are not usually retained. The spin-orbit terms $\hbar\mathcal{H}_{\text{SO}}$ are zero in the unperturbed ground state but they do contribute to the energy through

higher-order perturbation terms.^{1,25,41-45} In atomic units

$$\hbar\mathcal{H}_{\text{SO}} = (\beta/e)^2 [(-i \text{grad} V) \cdot \mathbf{p} + 2\mathbf{S} \cdot (\text{grad} V) \times \mathbf{p}],$$

where $V = \hbar\mathcal{H}_{\text{OL}} = -e^2 \sum_k Z_k/r_k$ is the free-electron orbit-lattice interaction term, $\mathbf{p}$ is the linear momentum of the unpaired electron, which moves in the Coulomb field of all the nuclei in the free radical ion plus all the surrounding molecules and ions and eZ_k is the effective charge of the k th species at a distance r_k from the unpaired electron. The first term in $\hbar\mathcal{H}_{\text{SO}}$ is zero for non *s*-electrons in spherically symmetric fields, but for aromatic hydrocarbons, where V is of lower symmetry, it vanishes when the second term is nonzero. For a molecular free radical, then, the complete spin-orbit term is

$$\begin{aligned} \hbar\mathcal{H}_{\text{SO}} = \sum_k & (\lambda_k S'_+ L'_k + \lambda_{\theta_k} \cot\theta_k S'_+ L'_{zk} + i\lambda_{\phi_k} \sin\theta_k (S'_+ L'_{+k} - S'_+ L'_{-k})/2 \\ & + \exp(-i\phi_k) [\lambda_{\theta_k} S'_+ L'_{zk} + i\lambda_{\phi_k} \cos\theta_k (S'_+ L'_{+k} - S'_+ L'_{-k})]/2 \\ & + \exp(i\phi_k) [\lambda_{\theta_k} S'_- L'_{zk} - i\lambda_{\phi_k} \cos\theta_k (S'_- L'_{-k} - S'_- L'_{+k})]/2 \\ & + [\exp(-i\phi_k) (\lambda_{\theta_k} - i \cos\theta_k \lambda_{\phi_k}) S'_+ - \exp(i\phi_k) (\lambda_{\theta_k} + i \cos\theta_k \lambda_{\phi_k}) S'_-]/2 \\ & + i\lambda_{\phi_k} \sin\theta_k S'_z \} r_k (\partial/\partial r_k), \quad (\text{A3}) \end{aligned}$$

where $\lambda_k = 2(\beta/e)^2 r_k^{-1} (\partial V/\partial r_k)$; $\lambda_{\theta_k} = [2(\beta/e)^2 r_k^{-2}] (\partial V/\partial \theta_k)$; $\lambda_{\phi_k} = [2(\beta/e)^2 (r_k^2 \sin\theta_k)^{-1}] (\partial V/\partial \phi_k)$; $L'_{\pm k} = \hbar \exp(\pm i\phi_k) [\pm \partial/\partial \theta_k + i \cot\theta_k \partial/\partial \phi_k]$ and (r_k, θ_k, ϕ_k) are the spherical polar coordinates of the free electron relative to the center k , in the molecular coordinate system. Here z' is parallel to the *p*-BSQ⁻ CO bonds and if (α, β, γ) are the Euler angles of the molecular axes relative to the unprimed laboratory coordinate system $(-S'_+/ \sqrt{2}, S'_z, S'_-/ \sqrt{2}) = (-S_+/ \sqrt{2}, S_z, S_-/ \sqrt{2}) \mathbf{D}^{(1)}(\alpha, \beta, \gamma)$ where $\mathbf{D}^{(1)}$ is the rotation matrix for first-order spherical harmonics.⁴⁶ For free ions in a spherically symmetric field only the first term in Eq. (A3) is nonzero. Here, the first term also gives the highest contribution to the *p*-BSQ⁻ ion through the effects caused by the oxygen atoms in the molecule.^{40b} However, in aromatic hydrocarbons the terms of lower-field symmetry may be important. The steady-state energies correct to second order are then

$$\hbar \{ \langle 0 | \mathcal{H}_0 | 0 \rangle \}_{\text{av}} - \sum_{i \neq 0} \langle | \langle 0 | \mathcal{H}_0 | i \rangle |^2 / \Delta_i \rangle_{\text{av}} \} = \hbar \langle \mathcal{H}_0 \rangle_{\text{av}} + \Delta H_z^2, \quad (\text{A4})$$

where $\hbar\Delta_i$ is the excitation energy from the ground state $|0\rangle$ to the virtual state $|i\rangle$. The terms in H_z^2 are usually dropped because they represent an additive constant, important only in diamagnetic susceptibility measurements.⁵⁵

In addition to $\hbar\mathcal{H}_{1,z}(t)$ the contributions to the spin-lattice term are expressed following the general

theory by²⁹

$$\hbar\mathcal{H}_1 = \hbar \sum_q \mathcal{A}^{(q)} F^{(q)} = \hbar \sum_{l,m} \mathcal{H}_1^{(l,m)}, \quad (\text{A5})$$

where $\mathcal{A}^{(q)}$ and $F^{(q)}$ are, respectively, spin-only and lattice-only operators. Also, for the sake of simplicity the different term contributions, given in Table V, have been separated according to their transformation properties under rotation and whether or not $\mathcal{A}^{(q)}$ is a more-than-one-spin operator.

⁵⁵ B. Bleaney and K. W. H. Stevens, Rept. Progr. Phys. 16, 108 (1953).