THE JOURNAL OF CHEMICAL PHYSICS VOLUME 37, NUMBER 12 DECEMBER 15, 1962

Solvent Effects in Electron Spin Resonance Spectra*

JULIEN GENDELL, JACK H. FREED,† AND GEORGE K. FRAENKEL
Department of Chemistry, Columbia University, New York 27, New York

(Received July 16, 1962)

It has been shown that a simple model can account for the available data on the solvent dependence of the hyperfine splittings in the ESR spectra of organic free radicals. We have assumed that the changes in splittings arise entirely from a redistribution of the pi-electron spin density, and that the spin density is affected only by localized complexes between the solvent and polar substituents or heteroatoms in the radical. This model predicts that the magnitudes of the changes in proton splittings should often be small, although large fractional changes at positions of small spin density can sometimes occur. The large variations found for the nuclei of many electron atoms are shown to arise because their splittings are very critical functions of the spin density.

The effect of the solvent on the proton hyperfine splittings in the semiquinones has been treated by assuming that the solvent alters the electronegativity of the oxygen atoms and by performing molecular-orbital calculations to estimate spin density changes. These calculations reproduce both the directions and magnitudes of the changes in proton splittings with solvent and are in agreement with the very large fractional changes observed at some positions with small splittings.

An analysis of the effects on the ESR spectra of the exchange reactions between the different solvent complexes has shown that the spectra normally observed result from systems undergoing rapid exchange. A simple model for a radical with only one functional group which can interact with the solvent (e.g., the nitrobenzene anion), is shown to account very well for the observed variations in hyperfine splittings as a function of the composition of a binary solvent mixture. The treatment of the exchange reactions by use of the modified Bloch equations is compared with the spectral density method. The contribution to the linewidth from solvent-induced fluctuations in the spin-density distribution is calculated for a simple two-jump case, and other factors affecting the linewidths of radicals subjected to random solvent interactions are discussed.

I. INTRODUCTION

A NUMBER of recent studies of the electron spin resonance spectra of organic free radicals in solution have indicated that the isotropic hyperfine interactions vary with solvent. The nitrogen splitting in the nitrobenzene anion radical, for example, was found[1] to be 10.32 G in acetonitrile solution, while in *N*,*N*-dimethylformamide (DMF) it has the value[2] 9.70 G. Similar results have been observed for substituted nitrobenzene anion radicals.[2,3] Adams has shown that addition of water to an acetonitrile solution of the nitrobenzene anion causes a rapid increase in the nitrogen splitting followed by an asymptotic approach to a limiting value at appreciable water concentrations.[4] Deguchi observed a large solvent variation of the nitrogen splitting in the diphenylnitric oxide radical.[5]

The differences in the proton splittings in the nitrobenzene anion in acetonitrile and DMF solutions is much less than the variation of the nitrogen splitting, the changes being only 1%–2%, and no significant changes in proton splittings with solvent were reported until the work of Stone and Maki.[6] They found a number of instances in which the proton splittings of semiquinone anion radicals in dimethylsulfoxide solution (DMSO) were markedly different from the splittings obtained in ethanol–water solution. The magnitude of the variations depended on the compound, and the particular position of the proton in the compound, in an apparently unsystematic manner. Table I, taken from the work of Stone and Maki, shows the observed variation in proton splittings. Stone and Maki also found that the C^{13} splitting from the carbon atom in the carbonyl position of the *p*-benzosemiquinone anion changed from the value of ±0.4 G[7] in an alkaline alcoholic solution to ±2.13 G in DMSO.

Since a number of authors have used isotropic hyperfine splittings obtained from ESR spectra to estimate pi-electron spin densities,[2,8–16] and thus to make comparisons with valence theory calculations, large solvent effects might invalidate much of the theoretical framework which has been constructed in this field. It is the purpose of the present communication to assess the

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* Supported in part by the U. S. Air Force Office of Scientific Research.

† National Science Foundation Predoctoral Fellow, 1959–1962.

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[2] P. H. Rieger and G. K. Fraenkel (to be published).

[3] J. H. Freed and G. K. Fraenkel, J. Chem. Phys. **37**, 1156 (1962).

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[5] Y. Deguchi (private communication).

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[7] M. R. Das and B. Venkataraman, J. Chem. Phys. **35**, 2262 (1961).

[8] H. M. McConnell, J. Chem. Phys. **24**, 633, 764 (1956); H. M. McConnell and H. H. Dearman, *ibid.* **28**, 51 (1958); H. M. McConnell and D. B. Chesnut, *ibid.* **28**, 107 (1958); and other papers cited therein.

[9] E. de Boer and S. I. Weissman, J. Am. Chem. Soc. **80**, 4549 (1958); A. Carrington, F. Dravnieks, and M. C. R. Symons, J. Chem. Soc. **1959**, 947; A. D. McLachlan, Mol. Phys. **1**, 233 (1958); M. Karplus, J. Chem. Phys. **30**, 15 (1959); J. Schug, T. H. Brown and M. Karplus, *ibid.* **35**, 1873 (1961).

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

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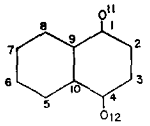
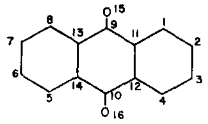
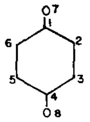
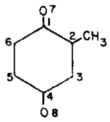
[16] I. Bernal, P. H. Rieger, and G. K. Fraenkel, J. Chem. Phys. **37**, 1489 (1962).

TABLE I. Solvent effects, semiquinones.

		Proton splitting, $\lvert a^{\mathrm{H}} \rvert$ (gauss)		
Semiquinone anion	Position[a]	Ethanol–Water[b]	DMSO[c]	% Difference[d]
1,4-Naphthosemiquinone	2, 3	3.23 ± 0.01	3.31 ± 0.02	$+2.5 \pm 0.9$
	5, 8	0.513 ± 0.005	0.300 ± 0.004	-41.5 ± 2.0
	6, 7	0.655 ± 0.005	0.633 ± 0.007	-3.5 ± 1.8
9,10-Anthrasemiquinone	1, 4, 5, 8	0.550 ± 0.007	0.303 ± 0.006	-44.9 ± 2.0
	2, 3, 6, 7	0.962 ± 0.005	0.986 ± 0.006	$+2.5 \pm 1.0$
p-Benzosemiquinone 	2, 3, 5, 6	2.368 ± 0.001	2.419 ± 0.003	$+2.2 \pm 0.2$
p-Tolusemiquinone	CH_3	2.045 ± 0.001	1.83 ± 0.01	-10.5 ± 0.5
	3	1.764 ± 0.001	1.952 ± 0.003	$+10.7 \pm 0.2$
	5 or 6	2.537 ± 0.002	2.702 ± 0.003	
	6 or 5	2.462 ± 0.002	2.440 ± 0.002	

[a] The identification of the splittings for the 1,4-naphthosemiquinone, the 9,10-anthrasemiquinone, and the smallest splitting for the *p*-tolusemiquinone with proton positions, for ethanol-water and DMSO solutions, was made on the basis of agreement with molecular-orbital calculations (see Sec. IV and footnote 12). Since the difference in the two other ring-proton splittings for *p*-tolusemiquinone in both ethanol-water and DMSO solution is very small, it is not possible to make an unambiguous assignment of these splittings on the basis of the MO calculations. Position 5, however, was assigned the larger splitting in ethanol-water solution by Venkataraman *et al.* (see reference in footnote b of this table), so as to agree with the postulate of additivity of substituent effects and this assignment is consistent with the molecular-orbital calculations of Vincow and Fraenkel.[12]

[b] From data of Vincow and Fraenkel[12] and B. Venkataraman, B. G. Segal, and G. K. Fraenkel, J. Chem. Phys. **30**, 1006 (1959).

[c] From data of Stone and Maki.[6] DMSO=dimethylsulfoxide.

[d] Percentage difference calculated as $100(a_{\mathrm{DMSO}}^{\mathrm{H}}-a_{\mathrm{E-W}}^{\mathrm{H}})/a_{\mathrm{E-W}}^{\mathrm{H}}$. E-W=ethanol-water.

significance of solvent interactions, to determine under what circumstances they are likely to be appreciable, and to ascertain their effect on the theoretical interpretation of the spin-density distributions determined from ESR spectra. In Sec. II we consider in a qualitative fashion how solvent interactions affect the hyperfine splittings and indicate why some splittings are much more strongly influenced than others. In Sec. III the dynamics of the exchange phenomena between different types of solvent-radical complexes are discussed, and it is shown how the splittings vary with the composition of mixed solvents. In Sec. IV a simple model based on conventional molecular-orbital calculations is employed to account for the solvent variation of the pi-electron spin densities in the semiquinones.

In the Appendix the treatment of the exchange reactions by use of the modified Bloch equations is compared with the spectral density method. The contributions to the linewidths from random solvent interactions are also discussed.

II. QUALITATIVE DEPENDENCE OF SPLITTINGS ON SOLVENT

We shall assume that the most important radical–solvent interactions occur at substituents (e.g., a nitro group or a carbonyl oxygen atom), or at heteroatoms (e.g., heterocyclic nitrogen or oxygen atoms). Strong interactions are to be expected between polar groups and polar solvents, between groups and solvents that can form hydrogen bonds, and the like. Ion-pair interactions are also expected to be significant, but bulky counter ions are not likely to cause the very large effects observed between anion radicals with polar substituents and alkali metal cations.[17] We assume that the radical-solvent interactions cause a polarization of the pi-electron charge and spin-density distributions, and therefore that the hyperfine splittings vary with the strength and nature of the radical-solvent complexes. The solvent variation of the splittings from a particular nucleus will thus depend on the location of the nucleus in the radical and on the functional relation between the spin density and the hyperfine splitting.

Many different complexes between the radical and solvent may exist in a particular solvent system, and if the complexes were sufficiently long lived, each could give rise to a different ESR spectrum. We show in Sec. III, however, that only a single spectrum is obtained when the rate of exchange between the various complexes is rapid. The resulting hyperfine splittings are then a suitable average over the splittings of the individual complexes.

The isotropic hyperfine splittings in pi-electron radicals have been shown to be linearly related to the pi-electron spin densities.[14] For protons bonded directly to a carbon atom in the pi system, it is usually assumed, following McConnell,[8] that

$$a_i^{\mathrm{H}}=Q_{\mathrm{CH}}{}^{\mathrm{H}}\rho_i{}^{\pi} \tag{2.1}$$

where a_i^{H} is the proton hyperfine interaction in gauss and $\rho_i{}^{\pi}$ is the pi-electron spin density on the carbon atom i to which the proton is bonded. We shall assume that the quantity $Q_{\mathrm{CH}}{}^{\mathrm{H}}$ is a constant with the value $Q_{\mathrm{CH}}{}^{\mathrm{H}}=-23.7$ G,[13] although it may deviate from constancy under certain circumstances.[13,16] If the primary solvent interactions result from a localized complex with a polar substituent or heteroatom, the changes in proton splittings must arise from the transmission through the pi system of the solvent-modified influence of the substituent. Except for strong specific interactions, such as the conversion of a group like $-\mathrm{O}$ to $-\mathrm{OH}$ or $-\mathrm{NH_2}$ to $-\mathrm{NH_3}$ on increasing the acidity of the solvent, most solvent interactions will not cause a very great alteration of the substituent effects. As a result, only small changes in the magnitude of the proton splittings with solvent are anticipated under usual conditions. Calculations show, however, that some positions of small spin density can show large *fractional* changes in proton hyperfine splitting on altering the solvent (see Sec. IV).

The prediction of isotropic hyperfine splittings from nuclei such as N^{14} or C^{13} is considerably more complicated than for protons. Karplus and Fraenkel[13] proposed that the splitting a^{X} arising from the nucleus of an atom X with three sp^2 hybrid bonds could be written as

$$a^{\mathrm{X}}=\Big(S^{\mathrm{X}}+\sum_{i=1}^{3}Q_{\mathrm{XY}_i}{}^{\mathrm{X}}\Big)\rho_{\mathrm{X}}{}^{\pi}+\sum_{i=1}^{3}Q_{\mathrm{Y}_i\mathrm{X}}{}^{\mathrm{X}}\rho_{\mathrm{Y}_i}{}^{\pi}, \tag{2.3}$$

where $\rho_{\mathrm{X}}{}^{\pi}$ and $\rho_{\mathrm{Y}_i}{}^{\pi}$ are the pi-electron spin densities on atoms X and Y_i, respectively; S^{X} gives the contribution to the splitting from the 1s electrons of atom X; and the Q's give the contribution of the 2s electrons, where, for example, $Q_{\mathrm{Y}_i\mathrm{X}}{}^{\mathrm{X}}$ is the parameter for the nucleus of atom X resulting from the interaction between the bond Y_iX and the pi-electron spin density on atom Y_i. The following values of the parameters for C^{13} splittings were estimated for the $\mathrm{CHC_2}$ fragment (with equivalent sp^2 hybrids)[13]: $S^{\mathrm{C}}=-12.7$ G, $Q_{\mathrm{CH}}{}^{\mathrm{C}}=19.5$ G, $Q_{\mathrm{CC'}}{}^{\mathrm{C}}=14.4$ G, and $Q_{\mathrm{C'C}}{}^{\mathrm{C}}=-13.9$ G.

The appropriate form of Eq. (2.3) for a C^{13} nucleus at the carbonyl position in a semiquinone or a ketyl is

$$a_1{}^{\mathrm{C}}=\big(S^{\mathrm{C}_1}+2Q_{\mathrm{C}_1\mathrm{C}_2}{}^{\mathrm{C}_1}+Q_{\mathrm{C}_1\mathrm{O}}{}^{\mathrm{C}_1}\big)\rho_1{}^{\pi}+Q_{\mathrm{C}_2\mathrm{C}_1}{}^{\mathrm{C}_1}(\rho_2{}^{\pi}+\rho_{2'}{}^{\pi})$$
$$+Q_{\mathrm{OC}_1}{}^{\mathrm{C}_1}\rho_{\mathrm{O}}{}^{\pi}, \tag{2.4}$$

where 1 is the carbonyl carbon atom, 2 and 2′ are the two carbon atoms to which atom 1 is bonded, and O is the oxygen atom. For the nitrogen splitting in a nitro group, Eq. (2.3) becomes

$$a^{\mathrm{N}}=\big(S^{\mathrm{N}}+2Q_{\mathrm{NO}}{}^{\mathrm{N}}+Q_{\mathrm{NC}}{}^{\mathrm{N}}\big)\rho_{\mathrm{N}}{}^{\pi}+2Q_{\mathrm{ON}}{}^{\mathrm{N}}\rho_{\mathrm{O}}{}^{\pi}+Q_{\mathrm{CN}}{}^{\mathrm{N}}\rho_{\mathrm{C}}{}^{\pi}, \tag{2.5}$$

where N and O are the nitrogen and oxygen atoms of the nitro group, and C is the carbon atom to which the nitro group is bonded. Reliable values for the parameters in Eqs. (2.4) and (2.5) are not available, but by analogy with the $\mathrm{CHC_2}$ fragments some of them are expected to be positive and others negative.

The presence of large terms of opposite sign but comparable magnitude in Eqs. (2.4) and (2.5) is of special significance in determining the magnitude of the solvent effects because small variations in spin densities can cause appreciable change in the splittings. There is also a large solvent variation of the N^{14} splitting in an $-\mathrm{NO_2}$ or $>\mathrm{NO}$ group, or of the C^{13} splitting of a $>\mathrm{C{=}O}$, because the oxygen atoms are probably the atoms most directly affected by solvent interactions. A large change in the pi-electron spin density of the oxygen atom, however, can be compensated by large changes in the spin density on the nitrogen or carbon atom bonded to the oxygen, and thus only small changes may occur in spin densities throughout the rest of the molecule.

III. DYNAMICS OF SOLVENT INTERACTIONS

Let us first consider a radical with a single functional group, such as the nitro group in the nitrobenzene anion radical, and assume that the only significant solvent interactions take place in the neighborhood of the functional group. We shall be interested in the ESR spectra of the radical in two different pure solvents, $\mathrm{S_A}$ and $\mathrm{S_B}$, and in mixtures of the two solvents. For simplicity, we shall assume that the radical RX forms relatively stable one-to-one complexes with each of the pure solvents, so that the predominant species in

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[17] R. L. Ward, J. Am. Chem. Soc. **83,** 1296 (1961).

the mixed solvent are RXS_A and RXS_B. These radical species will be assumed to exchange solvent molecules according to the reaction

$$RXS_A+S_B \underset{k_B}{\overset{k_A}{\rightleftarrows}} RXS_B+S_A. \qquad \text{(I)}$$

In general the hyperfine splitting arising from a particular nucleus in complex RXS_A, say a_A, will be different from the splitting a_B from the same nucleus in the complex RXS_B. The spectrum obtained will depend on the rate of the exchange reaction in the same way that it does in the analogous and familiar nuclear magnetic resonance experiment in which a proton exchanges between two sites of different chemical shift.[18–21] Thus for slow exchange, the spectrum will contain both splittings a_A and a_B, and for fast exchange, only a single splitting of an appropriate average value will be observed. We shall assume that the rate of exchange is fast, i.e., that the lifetimes τ of the radical species are short compared to the differences in hyperfine splittings, or $\tau \ll [\gamma \mid a_A-a_B \mid]^{-1}$, where γ is the magnetogyric ratio of the electron and the splittings are measured in gauss. For fast exchange, it is readily shown (see the Appendix) that the observed splitting is given by

$$\bar{a}=p_Aa_A+p_Ba_B, \qquad (3.1)$$

where p_A and p_B are the fractions of the total amount of radical in the forms RXS_A and RXS_B, respectively. Expressions for these quantities are

$$p_A=\tau_A/(\tau_A+\tau_B)=1/(1+K\alpha) \qquad (3.2a)$$

and

$$p_B=\tau_B/(\tau_A+\tau_B)=K\alpha/(1+K\alpha), \qquad (3.2b)$$

where the lifetimes of RXS_A and RXS_B, τ_A and τ_B, respectively, are given by

$$\tau_A=1/k_A[S_B] \qquad (3.3a)$$

and

$$\tau_B=1/k_B[S_A]. \qquad (3.3b)$$

On the right-hand side of Eqs. (3.2), K is the equilibrium constant, $K=k_A/k_B=[RXS_B][S_A]/[RXS_A][S_B]$ and α is the ratio $\alpha=[S_B]/[S_A]$ of solvent concentrations. Equation (3.1) is an adequate description in the limit of small concentrations of one solvent, say S_B, even though τ_A becomes large, because the relative amount of RXS_B then becomes too small to make a measurable contribution to the spectrum. The average observed splitting for fast exchange is thus

$$\bar{a}=(\tfrac{1}{2})(a_A+a_B)+(\tfrac{1}{2})[(K\alpha-1)/(K\alpha+1)]\Delta, \qquad (3.4)$$

where

$$\Delta=(a_B-a_A). \qquad (3.5)$$

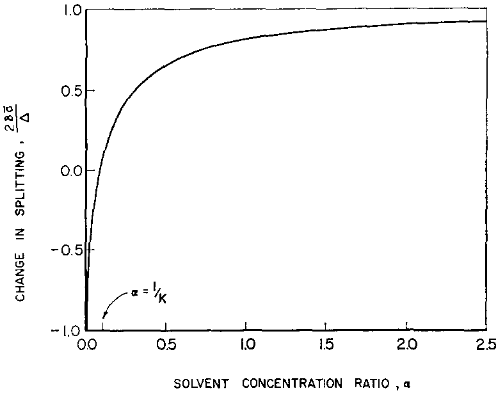

FIG. 1. Plot of Eq. (3.4) for the variation of the average splitting with solvent composition for a radical undergoing exchange reaction (I). Twice the difference of the average splitting from the arithmetic mean, $2\delta\bar{a}=2[\bar{a}-\frac{1}{2}(a_A+a_B)]$, in units of the difference in splitting $\Delta, \Delta=a_B-a_A$, is plotted along the ordinate, and the ratio of the solvent concentrations α is plotted along the abscissa. The graph has been drawn for $K=10$.

Equation (3.4) is plotted in Fig. 1. Twice the difference of the average splitting from the arithmetic mean, $2\delta\bar{a}=2[\bar{a}-(\frac{1}{2})(a_A+a_B)]$, in units of Δ, is plotted along the ordinate, and the ratio of solvent concentrations α is plotted along the abscissa. The graph has been drawn for $K=10$. This value of K was arbitrarily chosen to illustrate the form of Eq. (3.4) for the case in which the complex with solvent S_B is considerably stronger than the complex with solvent S_A. There is a rapid change in the splitting $\bar{a}$ from the value a_A in pure solvent $S_A(\alpha=0)$ as a small amount of solvent S_B is added, and for small values of $K\alpha$,

$$\bar{a} \cong a_A+K\alpha(a_B-a_A). \qquad (3.6)$$

As larger amounts of solvent S_B are added, the splitting approaches the limiting value a_B asymptotically. Figure 1 is of exactly the same form as that observed by Adams[4] for the nitrogen splittings in the nitro-groups of the nitrobenzene, *p*-nitroaniline, and *o*-nitroaniline anion radicals dissolved in acetonitrile–water mixtures. When there is no appreciable complexing with one of the solvents, so that the exchange reaction is

$$RX+S_B \underset{k_B}{\overset{k_A}{\rightleftarrows}} RXS_B, \qquad \text{(II)}$$

Eq. (3.4) is also obtained provided that α is replaced by $[S_B]$ and τ_B is set equal to k_B^{-1}.

If all of the species RX, RXS_A, and RXS_B (or even other species involving more than one solvent molecule, or different complexes with a single solvent) are important, Eq. (3.1) can be generalized. The result for

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[18] J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High-Resolution Nuclear Magnetic Resonance* (McGraw-Hill Book Company, Inc., New York, 1959).

[19] H. S. Gutowsky and A. Saika, J. Chem. Phys. **21**, 1688 (1953); H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *ibid.* **21**, 279 (1953).

[20] H. M. McConnell, J. Chem. Phys. **28**, 430 (1958).

[21] P. W. Anderson, J. Phys. Soc. Japan **9**, 316 (1954).

TABLE II. Solvent effects, *p*-benzosemiquinone.

Solvent composition[a]	Splitting (gauss)[b]		
	$\lvert a_1^C \rvert$	$\lvert a_2^C \rvert$	$\lvert a_2^H \rvert$
DMSO, 100%[c]	2.13 ±0.02	...[d]	2.419±0.003
H_2O–DMSO mixtures			
H_2O, 4%	1.71 ±0.02	...[d]	2.41 ±0.01
H_2O, 23%	1.12 ±0.02	...[d]	2.393±0.005
H_2O, 48%	0.647±0.015	0.497±0.015	2.385±0.005
C_2H_5OH–DMSO mixtures			
C_2H_5OH, 4%	2.00 ±0.02	...[d]	2.41 ±0.01
C_2H_5OH, 34%	1.47 ±0.02	...[d]	2.41 ±0.01
C_2H_5OH, 63%	1.19 ±0.03	0.44 ±0.06	2.40 ±0.01
D_2O–DMSO mixtures			
D_2O, 4%	1.77 ±0.02	...[d]	2.41 ±0.01
D_2O, 29%	1.06 ±0.03	0.45 ±0.06	2.40 ±0.01
C_2H_5OH—H_2O[e]	0.4 ±0.04[f]	0.594[g]	2.368±0.001[h]

[a] DMSO=dimethylsulfoxide. Composition is given in volume percent.

[b] Position numbers correspond to those in Table I.

[c] From Stone and Maki.[6]

[d] See reference 26.

[e] Alkaline solution of hydroquinone. Semiquinone produced by air oxidation.

[f] C^{13} enriched sample. From Das and Venkataraman.[7]

[g] From Strauss and Fraenkel.[28]

[h] From Venkataraman *et al.* (see Table I, footnote b).

the limit of fast exchange is (see the Appendix):

$$\bar{a}=\sum_i p_i a_i. \tag{3.7}$$

When a number of complexes are simultaneously present in significant concentrations, general relations for the variation of the observed splitting with solvent composition can be derived, but they are not particularly helpful when information about the relative magnitudes of the rate and equilibrium constants is unavailable. In favorable circumstances, however, the equilibrium constants can be obtained from the detailed analysis of the experimental variation of the splitting.

Special consideration is required for radicals like the benzosemiquinones or the dinitrobenzene anions that have two functional groups which can form solvent complexes. In a pure solvent, the singly solvated species has a lower symmetry than the unsolvated or doubly solvated radicals, and there are two forms of singly solvated species, say SXRX and XRXS, which are not equivalent. For example, the splitting of a proton at position 2 in the 1,4-dinitrobenzene anion for a complex formed with the nitro group at position 1 will, in general, be different from the value for a complex formed with the group at position 4. Hence, the protons at positions 2 and 3, which are equivalent in the unsolvated 1,4-dinitrobenzene radical, are inequivalent in a singly solvated asymmetric complex, and if the exchange rates are slow, different splittings a_2^H and a_3^H will be observed. It is readily shown, however, that this inequivalence is averaged out if the exchange rates are fast. This result for fast exchange follows directly from Eq. (3.7) and the fact that the concentrations of asymmetric species like SXRX and XRXS are always equal.[22] Similar considerations govern the appearance of the spectra of carbonyl-substituted anion radicals.[2,23,24] The foregoing analysis is readily extended to a mixture of solvents.

The averaging effects of fast exchange also explain why hyperfine splittings are not normally observed from solvent nuclei even though strong solvent–radical complexes may exist. Suppose, for simplicity, that a strong hydrogen bond is formed between the solvent and a functional group of the radical. A complex of this sort might be expected to give a splitting a_s^H from the solvent proton, although in many radicals the splitting would be small. If now the lifetime of the complex τ is short in the sense that $\tau(\gamma a_s^H)\ll 1$, the environment of the unpaired electron changes rapidly from one with solvent protons of spin of $+\frac{1}{2}$ to one with protons of spin $-\frac{1}{2}$, and the splitting averages to zero. In contrast, the observation of alkali-metal hyperfine splittings[17,25] implies a long-lived complex. Specifically, the lifetime of the complex must be greater than or comparable to

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[22] Consider, for example, the 1,4-dinitrobenzene anion in a pure solvent, and let $a_i^H(j)$ be the splitting of the proton at position i when a complex is formed with the nitro group at position j. Then the contribution of the two singly solvated species to the average splitting observed from the proton at position 2 is $(a_2^H)_{Av}=(\frac{1}{2})[a_2^H(1)+a_2^H(4)]$, and since $a_2^H(1)=a_3^H(4)$ and $a_2^H(4)=a_3^H(1)$, this average is equal to the average splitting from the proton at position 3, $(a_3^H)_{Av}=(\frac{1}{2})[a_3^H(1)+a_3^H(4)]$.

[23] A. H. Maki and D. H. Geske, J. Am. Chem. Soc. **83,** 1852 (1961).

[24] A. H. Maki, J. Chem. Phys. **35,** 761 (1961); P. H. Rieger and G. K. Fraenkel, J. Chem. Phys. **37,** 2811 (1962).

[25] F. C. Adam and S. I. Weissman, J. Am. Chem. Soc. **80,** 1518 (1958); N. M. Atherton and S. I. Weissman, *ibid.* **83,** 1330 (1961).

the reciprocal of the splitting (in frequency units), and the splitting must be greater than or comparable to the linewidth, i.e., $\tau \gtrsim [\gamma a_s^H]^{-1}$ and $a_s^H \gtrsim \Delta H$.

The C^{13} splitting from the carbon atom at the carbonyl position in the *p*-benzosemiquinone anion was observed by Stone and Maki[6] to have a considerably larger value in DMSO solution than that found by Das and Venkataraman[7] for alkaline–ethanol solution. If the preceding analysis is correct, the C^{13} splitting should be a monotonic function of the solvent composition in a binary solvent mixture, and although Stone and Maki[6] performed measurements in which water was added to pure DMSO, they did not report any change in the C^{13} splitting. We therefore performed a series of measurements on electrochemically generated *p*-benzosemiquinone radicals in mixtures of DMSO and water. Spectra were also obtained in DMSO–ethanol solutions and DMSO–D_2O solutions. From the results given in Table II, it will be noted that, in accord with our model, the C^{13} splitting from the carbonyl carbon atom, a_1^C, decreases monotonically in the direction of the ethanol–water result as the percentage of DMSO is decreased. Spectra were also obtained in pure water and pure absolute ethanol, but the splitting from the natural abundance of C^{13} nuclei at the carbonyl position was not detectable.[26] Since there are two functional groups in the *p*-benzosemiquinone anion that can complex with the solvent, the analysis given above for a radical with one functional group, as expressed in Eq. (3.4), would not be expected to be applicable. Nevertheless, although the data for the C^{13} splitting in the *p*-benzosemiquinone anion do not properly fit this equation, they are consistent with the appropriate form of Eq. (3.7) for the case of a radical with two functional groups. This result, however, is not an adequate test of Eq. (3.7) since the limiting value of a_1^C for either pure water or pure ethanol is not known and, if it were known, additional observations at many different concentrations would be necessary.

IV. EFFECT OF SOLVENT INTERACTIONS ON THE SPIN DENSITIES OF SEMIQUINONES

Proton Splittings

According to the model proposed in Sec. II, the variation of the proton splittings of the semiquinone anion radicals with solvent is caused by a solvent-induced redistribution of the pi-electron spin density. The changes in spin density are assumed to result directly from the formation of a localized complex between the solvent and the polar substituents in the radical, and solvents such as water or ethanol undoubtedly interact primarily by hydrogen bonding to the oxygen atoms of the semiquinones. Dipolar forces from these highly polar solvent molecules might also be important. The oxygen atoms in a semiquinone anion would therefore be expected to be more electronegative in solvents like water and ethanol than in nonhydrogen bonding and less polar solvents.

These considerations suggest that it might be possible to account for the changes of the splittings of the semiquinones with solvent merely by performing molecular–orbital calculations in which the effective electronegativities of the oxygen atoms are allowed to vary with the solvent. We have therefore performed a series of spin-density calculations for a range of values of the Coulomb integral for the oxygen atom. Since it is assumed that the major part of the solvent effect arises from changes in the electronegativity of the oxygen atoms, only the Coulomb integral was varied in the calculations associated with different solvents, and the resonance integral for the carbon–oxygen bond was left unchanged.

Hückel–LCAO molecular–orbital calculations of the spin densities in the *p*-benzo-, 1,4-naphtho-, and 9,10-anthrasemiquinone anions have been performed by Vincow and Fraenkel[12] and by Brandon and Lücken.[15] In these calculations the Coulomb integral for the oxygen atom and the resonance integral for the carbon–oxygen bond were adjusted by varying the parameters δ_O and γ_{CO} in the relations $\alpha_O = \alpha + \delta_O\beta$ and $\beta_{CO} = \gamma_{CO}\beta$ (where α and β are the Coulomb and resonance integrals, respectively, for benzene; α_O is the Coulomb integral for the oxygen atom; and β_{CO} is the resonance integral for the carbon–oxygen bond) in an attempt to fit the proton splittings observed from these radicals in ethanol–water solutions.

We have re-examined the calculations applicable to ethanol–water solutions on the assumption that Q_{CH}^H should be a constant for all positions in all the radicals in the series and have taken its value to be $Q_{CH}^H = -23.7$ G.[13] We have also applied corrections to the spin densities obtained from the Hückel calculations by using the approximate configuration interaction theory suggested by McLachlan.[10] For the Hückel calculation, the best values of the parameters δ_O and γ_{CH} were found to be $\delta_O = 0.9$ and $\gamma_{CO} = 1.4$, and the best values of the parameters for the McLachlan calculation were found to be $\delta_O = 1.6$ and $\gamma_{CO} = 1.55$. The parameter λ which occurs in the McLachlan procedure was given the value 1.2. The results of these calculations are listed in Table III.

A somewhat better fit to the data for ethanol–water solutions is obtained from the Hückel calculation than from the McLachlan calculation. The difference between the experimental and Hückel spin densities ranges from 1% to 6%, with an average deviation of 3%, while for the McLachlan spin densities the range is 2% to 16% and the average deviation is 7%.

Molecular-orbital calculations were then performed in an attempt to fit the data for proton splittings in dimethylsulfoxide (DMSO) solution by adjusting the value of δ_O. For the Hückel calculation γ_{CO} was fixed

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[26] In many cases a C^{13} splitting was not detected due to the low natural abundance of C^{13} nuclei and because the splitting was not sufficiently large compared to the linewidth (see reference 28).

TABLE III. Calculated and experimental spin densities.

Semiquinone anion	Position[a]	Spin density, ρ_i^π Ethanol–Water Exptl.[c]	Ethanol–Water Hückel	Ethanol–Water McLachlan	DMSO[b] Exptl.[c]	DMSO[b] Hückel	DMSO[b] McLachlan
1,4-Naphthosemiquinone	2, 3	0.1363	0.1317	0.1386	0.1397	0.1373	0.1418
	5, 8	0.02165	0.02208	0.02435	0.01266	0.01229	0.01453
	6, 7	0.02764	0.02942	0.02916	0.02671	0.02780	0.02787
	1, 4		0.09885	0.14286		0.06073	0.1092
	9, 10		0.03662	0.03236		0.04157	0.03920
	11, 12		0.1814	0.1326		0.2203	0.1674
9,10-Anthrasemiquinone	1, 4, 5, 8	0.02321	0.02225	0.01953	0.01278	0.01350	0.01107
	2, 3, 6, 7	0.04059	0.03970	0.03993	0.04160	0.04127	0.04037
	11, 12, 13, 14		0.05605	0.05621		0.06395	0.06403
	15, 16		0.1575	0.1145		0.1945	0.1461
	9, 10		0.1065	0.1541		0.0680	0.1229
p-Benzosemiquinone	2, 3, 5, 6	0.09991	0.09918	0.1032	0.10206	0.1000	0.1035
	7, 8		0.2089	0.1585		0.2453	0.1953
	1, 4		0.09276	0.1349		0.05465	0.09763

[a] See Table I for numbering of positions.

[b] DMSO = dimethylsulfoxide.

[c] Experimental spin density calculated from data in Table I and $\rho_i^\pi = |a^H| / |Q_{CH}^H|$, taking $Q_{CH}^H = -23.7$ G.

at 1.4, the value used for the ethanol–water solutions. The value of δ_O which gave the best fit to the experimental data in DMSO was found to be $\delta_O = 0.4$. A similar adjustment of δ_O was made using the McLachlan procedure with γ_{CO} fixed at 1.55, the value for the ethanol–water solutions, and the best fit was obtained with $\delta_O = 1.26$. The results of the calculations are given in Table III. It will be observed that a larger value of δ_O is required to fit the ethanol–water results than the dimethylsulfoxide data. Since β is negative, this larger value of δ_O corresponds to a more negative value of the Coulomb integral α_O for the ethanol–water solution and is therefore in the anticipated direction. Although the energy difference implied by this change in α_O is large, it is not unreasonable for hydrogen bonding to an oxygen atom with a large negative charge, and of course molecular-orbital parameters do not have a precise physical significance.

TABLE IV. Relative change in spin density.

Semiquinone anion	Position[b]	% Change in spin density[a] Experimental	Hückel	McLachlan
1,4-Naphtho-semiquinone	2, 3	+2.5±0.9	+4.3	+2.3
	5, 8	−41.5±2	−44.3	−40.3
	6, 7	−3.4±1.8	−5.5	−4.4
9,10-Anthra-semiquinone	1, 4, 5, 8	−44.9±2	−39.3	−43.3
	2, 3, 6, 7	+2.5±1	+4.0	+1.1
p-Benzosemi-quinone	2, 3, 5, 6	+2.2±0.2	+0.8	+0.3

[a] % Change calculated as $100(\rho_{DMSO}^\pi - \rho_{E\text{–}W}^\pi)/\rho_{E\text{–}W}^\pi$. ρ_{DMSO}^π = spin density for dimethylsulfoxide solution. $\rho_{E\text{–}W}^\pi$ = spin density for ethanol-water solution.

[b] See Table I for numbering of positions.

Of primary interest here is the change in spin density with solvent, and the percentage changes

$$100(\rho_{DMSO}^\pi - \rho_{E\text{–}W}^\pi)/\rho_{E\text{–}W}^\pi$$

are tabulated in Table IV for both the experimental and calculated spin densities. As in the table, DMSO and E–W are abbreviations for dimethylsulfoxide and ethanol–water solutions, respectively. It will be noted that in every case the calculated change is in the same direction as the experimental change. Indeed, the magnitudes of the calculated percentage changes, particularly for the McLachlan calculation, are in excellent agreement with the experimental results. This agreement is achieved even though the differences in percentage changes within a single compound are very large; thus, for example, they are +2.5, −3.5, and −41.5 percent in the 1,4-naphthosemiquinone ion. The calculated change for the *p*-benzosemiquinone ion is somewhat small, and in fact the calculated spin density at the unsubstituted positions in this radical is quite insensitive to variations of the parameter δ_O.

An attempt was made to extend the Hückel and McLachlan calculations to the *p*-tolusemiquinone ion by using, in addition to the oxygen parameters, the methyl-group parameters suggested by Coulson and Crawford[27] and modified by Bersohn.[11] As previously found by Vincow and Fraenkel,[12] however, the spin densities at some positions are in poor agreement with the experimental data. The calculated change in the spin densities with solvent using the variation of δ_O previously derived from the data on the unsubstituted semiquinones is similarly in poor agreement with the experimental change in splittings.

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[27] C. A. Coulson and V. A. Crawford, J. Chem. Soc. **1953,** 2052.

C^{13} Splittings

The appropriate form of Eq. (2.3) for the C^{13} splitting from the ring carbon atom a_2^C in the *p*-benzosemiquinone anion, using the sigma–pi parameters given in Sec. II, is

$$a_2^C = 21.7\rho_2^\pi - 13.9\rho_1^\pi. \quad (4.1)$$

If calculated spin densities from Table III are substituted into this equation, a_2^C is predicted to be positive, although precise agreement with the experimental value is not obtained.[28] The sign of this splitting may also be estimated from its variation with solvent composition (see Table II). This data shows that the magnitude of a_2^C increases as the percentage of DMSO is decreased. Since ρ_2^π (as measured by the proton splitting a_2^H) is essentially unaffected by the solvent composition and the calculations summarized in Table III give an increase of ρ_1^π with a decreasing percentage of DMSO, these considerations indicate the a_2^C should be negative. This conclusion does not depend on the precise values of any of the sigma–pi parameters. Thus, if we assume that the calculated direction of change of ρ_1^π on decreasing the amount of DMSO in the solvent is correct, agreement with the experimental splitting a_2^C is only obtained if the sigma–pi parameters are altered, and a change of only 20% in these quantities is sufficient to give agreement with experiment. Alternatively, if it is assumed that the sigma–pi parameters are essentially correct, there must be an appreciable error in both the magnitudes of the calculated spin densities and in the predicted variation of ρ_1^π with solvent composition. At present, we have insufficient evidence to decide between these two possibilities, but it is interesting that information about the signs of splittings and the validity of calculations of both the spin-densities and the sigma–pi interaction parameters can be obtained from observations of the changes of splittings with solvent composition.

Since the semiempirical estimation of the parameters Q_{CO}^C and Q_{OC}^C in Eq. (2.4) depends critically on the sigma–pi parameters and the experimental C^{13} splitting constants, the uncertainties in these quantities preclude a better estimate of Q_{CO}^C and Q_{OC}^C than that given by Strauss and Fraenkel.[28]

V. CONCLUSIONS

It has been shown that a simple model can account for the available data on the solvent dependence of the hyperfine splittings in the ESR spectra of organic free radicals. We have assumed as a first approximation that the changes in splittings arise entirely from a redistribution of the pi-electron spin density, and that the spin density is affected only by localized complexes between the solvent and polar substituents or heteroatoms in the radical. It is assumed that the various complexes undergo rapid exchange with each other so that the observed spectrum results from an average over all the different species.

This model predicts, for several reasons, that the magnitudes of changes in proton splittings should often be smaller than those for the nuclei of many electron atoms, although large fractional changes in the proton splittings at positions of small spin density can sometimes occur. The larger variations for nuclei of many electron atoms arise primarily because their splittings are very critical functions of the spin density at both the atoms containing the nucleus and at the contiguous bonded atoms. In addition, the spin densities which affect the C^{13} splitting from a carbonyl group, or the N^{14} splitting from a nitro group, are in the neighborhood of the localized solvent complex and are therefore the most strongly influenced by solvent interactions. Thus splittings from the nuclei in these groups are strongly solvent dependent.

The effect of the solvent on the proton hyperfine splittings in the semiquinones has been treated by assuming that the solvent alters the electronegativity of the oxygen atoms. Hence the variation in the spin-density distribution with change in solvent has been estimated by molecular-orbital calculations in which only the Coulomb integral of the oxygen atoms was altered. These calculations reproduce both the directions and magnitudes of the changes in proton splittings with solvent, and are even in agreement with the very large fractional changes observed at some positions with small splittings. They also show that the spin densities at the oxygen and carbonyl carbon atoms change to a much greater extent than those at other positions in the radical, and therefore the solvent has a large effect on the C^{13} splitting at the carbonyl carbon position. Since the MO calculations employed here are essentially semiempirical, it is not possible to give a precise physical interpretation to the change of the Coulomb-integral parameter with solvent.

An analysis of the effects on the ESR spectra of the exchange reactions between the different solvent complexes has shown that the spectra normally observed result from systems undergoing rapid exchange. A simple model for a radical with only one functional group that can interact with the solvent (e.g., the nitrobenzene anion), accounts very well for the observed variations in hyperfine splittings as a function of the composition of a binary solvent mixture. The general form of the relations necessary to describe more complicated situations have also been outlined.

The estimation of substituent effects from ESR spectra is thus not rendered meaningless by solvent interactions. On the contrary, these results show that ESR spectra are sensitive enough to detect solvent effects that would not show up in many other kinds of investigations.

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[28] H. L. Strauss and G. K. Fraenkel, J. Chem. Phys. **35**, 1738 (1961).

APPENDIX

Chemical exchange effects in nuclear magnetic resonance have usually been treated in terms of a modified form of the Bloch equations,[18–21,29] and under certain circumstances the results can be directly applied to the exchange between solvent complexes of organic free radicals. We shall first discuss the two-site problem for which reaction (I) of Sec. III is an example. Consider a radical in the state A with $i=1, 2, \cdots, n$ sets of equivalent nuclei, and let $a_A{}^i$ be the hyperfine splitting (in gauss) for the ith set. In the high-field approximation, the transition frequencies in the ESR spectrum, $\omega_A/2\pi$, are given by

$$\omega_A(a_A{}^i, M_i) = \gamma H + \sum_{i=1}^{n} \gamma a_A{}^i M_i, \tag{A1}$$

where γ is the magnetogyric ratio of the electron, H is the applied steady magnetic field, and M_i is the z component of the total nuclear spin of the ith set of equivalent nuclei. A separate transition frequency $\omega_A(a_A{}^i, M_i)$ is obtained for each allowed combination of the M_i. A similar set of frequencies $\omega_B(a_B{}^i, M_i)$ exists for a radical in the state B, and in general $a_A{}^i \neq a_B{}^i$. When an exchange reaction is taking place between states A and B, the modified Bloch equations may be applied to each pair of transition frequencies ω_A and ω_B belonging to the same combination of values of the M_i, provided the effects of nuclear spin relaxation which interconnect energy levels belonging to different values of the M_i may be neglected. The relevant equations are given, for example, by Pople, Schneider, and Bernstein[18] for the random exchange of a nucleus of spin $\frac{1}{2}$ between two magnetically inequivalent sites, and in the limit of fast exchange[30,31] they lead directly to Eq. (3.1).

Modified Bloch equations can also be formulated for an exchange taking place between many sites, and in principle a set of coupled equations can be developed to take account of nuclear spin relaxation, but the solutions of the equations would be exceedingly complex. Anderson's[21] treatment is subject to similar difficulties. In the limit of fast exchange,[31] however, there is an alternative approach which does not suffer from these limitations. According to this procedure, the effects of the exchange reactions are considered to be equivalent to a rapid random modulation of the hyperfine splittings, and it is then possible to calculate the positions of the lines in the spectrum, as well as their shapes and widths, in terms of the appropriate spectral densities.[32,33]

The total Hamiltonian $\hbar\mathcal{H}$ for the spin system is divided into two parts: a main part $\hbar\mathcal{H}_0$, which is constant in time and gives rise to a sharp-line spectrum, and a perturbation $\hbar\mathcal{H}_1(t)$, which is considered to be a random function of time with a time-average value of zero. The zero-order Hamiltonian $\hbar\mathcal{H}_0$ is obtained from the total Hamiltonian by averaging the latter over all the random motions, and the form appropriate for the ESR spectra of organic free radicals in solution has been discussed elsewhere.[34,35] For the present application we have to add an additional random perturbation, that of the fluctuations in spin-density distribution caused by rapidly varying solvent interactions. The primary effect of the spin-density changes is the time-dependent modulation of the isotropic hyperfine interaction parameters $a(t)$. The isotropic hyperfine interaction for a particular nucleus appears in the total Hamiltonian $\hbar\mathcal{H}$ as the term

$$\hbar\gamma a(t)\mathbf{I}\cdot\mathbf{S} \tag{A2}$$

and its contribution to the zero-order Hamiltonian $\hbar\mathcal{H}_0$ is the time average over all the rapidly exchanging species designated above by A, B, etc. The term in $\hbar\mathcal{H}_0$ is thus

$$\hbar\gamma\langle a(t)\rangle\mathbf{I}\cdot\mathbf{S}, \tag{A3}$$

where

$$\langle a(t)\rangle = \sum_{j=A,\,B,\,C,\,\ldots} p_j a_j, \tag{A4}$$

and p_j is the fraction of all the radical species present in the state j. Equation (A4) is the desired result, Eq. (3.7). There is no limitation in Eq. (A4) on the number of states A, B, etc., between which exchange reactions can take place. Nor is the result in Eq. (A3) subject to special restrictions on the rate of the nuclear spin relaxation processes. There is, of course, a general restriction on the rate of all the relaxation processes, nuclear spin as well as others, in order that there be a resolvable hyperfine structure in the spectrum. This requirement is that the relaxation times be long compared to the reciprocal of the hyperfine separations (in frequency units), i.e., long compared to[36] $(\gamma a_j)^{-1}$.

The fluctuations in spin-density distribution also affect the magnitude of the randomly varying Hamiltonian $\hbar\mathcal{H}_1(t)$, and thus the modulation of the $a(t)$ makes a direct contribution to the traverse relaxation time T_2. As an illustration of the calculation of T_2, which follows standard methods,[37] we shall outline the procedure for the simple two-jump case. Let the lifetimes of the two states A and B be given by τ_A and τ_B, respectively. The probability that a molecule

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[29] F. Bloch, Phys. Rev. **70**, 460 (1946).

[30] Reference 18, p. 221, Eqs. (10)–(19).

[31] The exchange reactions are fast in the limit that the lifetimes τ of the states A, B, etc., are short compared to the reciprocal of the difference in hyperfine splittings (in frequency units), i.e., $\tau \ll [\gamma \mid a_A{}^i - a_B{}^i \mid]^{-1}$.

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

[33] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, England, 1961).

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

[35] D. Kivelson, J. Chem. Phys. **33**, 1094 (1960).

[36] It will be noted that the modified Bloch equations and the spectral density method give the same spectrum (but not the same linewidths) in the fast exchange limit.

[37] J. H. Freed and G. K. Fraenkel (to be published).

initially in the state A is still in the state A at a later time t is given by

$$P_A(A;t)=p_A+p_B\exp(-t/\tau), \qquad (A5)$$

while the probability that it is in the state B at time t is given by

$$P_B(A;t)=p_B[1-\exp(-t/\tau)], \qquad (A6)$$

where

$$\tau=\tau_A\tau_B/(\tau_A+\tau_B). \qquad (A7)$$

Similar expressions can be written for the probabilities when the molecule is initially in the state B. The coefficient of $\hbar\boldsymbol{I}\cdot\boldsymbol{S}$ in $\hbar\mathcal{H}_1(t)$ is

$$g(t)=\gamma[a(t)-\langle a(t)\rangle], \qquad (A8)$$

and the correlation function of $g(t)$ is

$$\langle g(t)g(t-t')\rangle=\gamma^2(a_A-a_B)^2p_Ap_B\exp(-t'/\tau). \qquad (A9)$$

The contribution of the modulation of the isotropic hyperfine interaction to the inverse of the transverse relaxation time for a radical with a single magnetic nucleus of spin I is then[37]

$$(1/T_2)_{\Delta a,\,\mathrm{exch.}}=\gamma^2(a_A-a_B)^2p_Ap_B\tau\{m^2+\tfrac{1}{2}(1+\omega^2\tau^2)^{-1}\times[I(I+1)-m^2]\}, \qquad (A10)$$

where m is the z component of the nuclear spin angular momentum. The first term in the curly brackets in Eq. (A10) arises from the secular perturbation $g(t)I_zS_z$ and the other term arises from the nonsecular part $(\frac{1}{2})g(t)[I^+S^-+I^-S^+]$. For a group of equivalent nuclei, the secular contribution can be shown to have the same form if m is replaced by M, but the nonsecular contribution will not in general lead to a simple result and may cause deviations from a Lorentzian line shape.[37]

A number of other complicating factors may affect the linewidths of radicals subjected to random solvent interactions. For example, a group of nuclei which have the same splittings in an unsolvated radical will not, in general, have instantaneously equivalent splittings in the solvated species. Although this inequivalence disappears on the average (see Sec. III), the splitting fluctuations affect the linewidth, and there is a complicated dependence of both the secular and nonsecular contributions on the value of M. One aspect of these effects which has recently been observed experimentally[3,38] is an alternation of the linewidths in the spectra of several dinitro derivatives of benzene anion radicals.[39] Lines corresponding to $M_N=\pm1$ (where M_N is the total z component of the nuclear spin angular momentum of the two nitrogen nuclei) are found to be considerably broader than those for $M_N=0, \pm2$.

The perturbations arising from solvent interactions will in general not be the same for different complexes. Thus, they may also affect the linewidth by altering the contribution from the anisotropic intramolecular dipolar, quadrupolar, and g-tensor relaxation mechanisms. For example, a singly solvated form of the p-benzosemiquinone anion has a lower symmetry than an unsolvated anion, and this can result in an enhanced g-tensor anisotropy, which could lead to an increase in the linewidth for the singly solvated form. The correlation functions of the anisotropic perturbations which determine the width depend on the combined tumbling motion of the radical and the rapid exchange between solvent complexes. For a line which results from fast exchange between solvent–radical complexes, the width can be shown to be an appropriate average of the widths that would be obtained in the slow exchange limit for each of the separate species.[37] An example of a type of solvent-dependent linewidth effect has been observed in the p-benzosemiquinone anion spectrum. The width of the hyperfine lines can be expressed[35,40] as a quadratic function of M, the total z component of the nuclear spin angular momentum, and the linear term in the quadratic results from a combination of the g-tensor and anisotropic intramolecular dipolar interactions. We did not detect this linear dependence in the spectrum of the radical generated in pure DMSO solution, but it was present when the radical was generated in mixtures of DMSO and water. It has also been observed in alkaline ethanol–water solutions.[40]

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[38] J. H. Freed, P. H. Rieger, and G. K. Fraenkel, J. Chem. Phys. **37,** 1879 (1962).

[39] In reference (3) the solution of this problem by the spectral density method is outlined. But the procedure for the modified Block equations discussed above can also be applied, and it is found that in the fast exchange limit it yields the same results for the secular contributions to the linewidth.[37]

[40] J. W. H. Schreurs and G. K. Fraenkel, J. Chem. Phys. **34,** 756 (1961).