

## ProtonDeuteron Hyperfine Structure in Paramagnetic Resonance: A $\pi\delta$ Interaction

Balu Venkataraman and George K. Fraenkel

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If one neglects contributions from multiply occupied cells,

$$\frac{K_{ab}}{K_a K_b} = \frac{I_{1(a)1(b)}}{I_{1(a)} I_{1(b)}} = \frac{\int \int g_{1(a)1(b)} \exp\{-\beta(\psi_{1(a)} + \psi_{1(b)})\} d\mathbf{x}_{1(a)} d\mathbf{x}_{1(b)}}{\int \int \exp\{-\beta(\psi_{1(a)} + \psi_{1(b)})\} d\mathbf{x}_{1(a)} d\mathbf{x}_{1(b)}} \quad (50)$$

This integral will be evaluated approximately by expanding  $g_{1(a)1(b)}$  in powers of  $\beta(\Phi_{1(a)1(b)} - \Psi_{1(a)1(b)} - \Psi_{1(b)1(a)} + U_{1(a)1(b)})$ , neglecting cubes and higher powers. The linear term vanishes when inserted in (50), because of the definitions in (18) and (24) of  $\Psi_{1(a)1(b)}$  and  $U_{1(a)1(b)}$ . Hence  $K_{ab}/(K_a K_b)$  is approximately the average value of  $\frac{1}{2}\beta^2\{\Phi_{1(a)1(b)}^2 - U_{1(a)1(b)}^2\}$ , the average being calculated with the weight factor  $\exp\{-\beta(\Psi_{1(a)} + \Psi_{1(b)})\}$ , or, again approximately, the average value

TABLE III.

$(v_0/v)^2$	0.7	0.6	0.5	0.4	0.3	0.2	0.1
$\beta(\lambda_a^0 - \lambda_a)$	0.028	0.033	0.029	0.022	0.016	0.013	0.009
$\beta(p^0 - p)v^*$	+0.076	-0.042	-0.067	-0.045	-0.015	-0.003	-0.002

of  $\frac{1}{2}\beta^2\{\Psi_{1(a)1(b)}^2 - U_{1(a)1(b)}^2\}$ , the average being calculated with the weight factor  $\exp(-\beta\Psi_{1(a)})$ . The values of  $\beta(\lambda_a^0 - \lambda_a)$  calculated in this way for  $\beta\Lambda = 10$  are shown in Table III. In the last row are the corrections contributed by clusters of two cells to the values of  $\beta p v^*$  calculated in the previous section. It will be noticed that the quantitative effect of these corrections is to this approximation not great, and to this extent the cell model is vindicated. But the introduction of cell clusters is necessary if one wishes to achieve a self-consistent model for a particular cell size. Actually this self-consistency remains rather theoretical in the above calculation: one still cannot use (39) to calculate the pressure, owing to the fact that multiple occupation of cells has been disregarded. However, one is assured that if more detailed calculations were made, no mathematical contradiction would be found.

## Proton-Deuteron Hyperfine Structure in Paramagnetic Resonance: A $\pi$ - $\sigma$ Interaction\*

BALU VENKATARAMAN AND GEORGE K. FRAENKEL

Department of Chemistry, Columbia University, New York 27, New York

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The mechanism of the hyperfine splitting observed in paramagnetic resonance spectra of certain aromatic free radicals containing protons adjacent to the aromatic ring is examined. It is shown that the magnitude of the interaction between an unpaired electron in a  $\pi$  orbital and a vibrating hydrogen atom is insufficient to account for the observed splitting. Such a vibrational mechanism is considered to be untenable: (i) on the basis of quantitative calculations, (ii) by the failure to observe lines corresponding to the first excited vibrational state, and (iii) by a comparison of the splitting caused by protons and deuterons. It is suggested that the unpaired electron is not in a purely  $\pi$  state and that the splitting may be accounted for by configuration interaction between  $\pi$  and  $\sigma$  states.

RECENT studies of the paramagnetic resonance spectra of solutions of aromatic free radicals have shown the existence of small but complex fine structure.<sup>1-3</sup> It was tentatively concluded that this structure was caused by intramolecular hyperfine interactions between protons and the unpaired electron, and a confirmation of this hypothesis was provided by performing complete analyses of the spectra of methyl-substituted and unsubstituted *p*-benzosemiquinone

ions.<sup>4,5</sup> One interesting feature of the spectra, which is considered in detail in the present article, is the existence of a splitting, of the order of two gauss, attributable to the protons on the aromatic ring.

Clearly, since the unpaired electron in a conjugated system is in a  $\pi$  state, and since the splittings measured in solution are caused by an unpaired-electron density at the proton in question,<sup>6</sup> a proton in the plane of the aromatic ring, which is the nodal plane of a  $\pi$  orbital, should not give rise to any interaction. Weissman and co-workers have suggested that the requisite splitting

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<sup>1</sup> Weissman, Townsend, Paul, and Pake, J. Chem. Phys. **21**, 2227 (1953).

<sup>2</sup> S. I. Weissman, J. Chem. Phys. **22**, 1135 (1954); Lipkin, Paul, Townsend, and Weissman, Science **117**, 534 (1953); Chu, Pake, Paul, Townsend, and Weissman, J. Phys. Chem. **57**, 504 (1953).

<sup>3</sup> H. S. Jarrett and G. J. Sloan, J. Chem. Phys. **22**, 1783 (1954).

<sup>4</sup> B. Venkataraman and G. K. Fraenkel, J. Am. Chem. Soc. **77**, 2707 (1955).

<sup>5</sup> B. Venkataraman and G. K. Fraenkel, J. Chem. Phys. **23**, 588 (1955).

<sup>6</sup> S. I. Weissman, J. Chem. Phys. **22**, 1378 (1954).

could arise from the zero-point vibrations of the protons,<sup>1</sup> and Jarrett and Sloan have proposed an indirect coupling between the electron and proton moments through the chemical bond,<sup>2</sup> of a type similar to the coupling between nuclear moments observed in nuclear magnetic resonance spectra.<sup>7,8</sup> An account is given in the following of three different approaches that have been used to study the nature of this interaction: the magnitude of the splitting has been calculated on simple theoretical grounds; a search has been made for the spectrum that should arise, assuming the existence of a vibrational mechanism, from the first excited vibrational state; and a study has been made of the spectrum of the deuterated *p*-benzosemiquinone ion.

The calculation of the magnitude of the interaction caused by a vibrational mechanism proceeds as follows: The Hamiltonian contains a term that depends on the nuclear spin of the form  $\sum_i a_i \mathbf{S} \cdot \mathbf{I}_i$ , where  $\mathbf{S}$  and  $\mathbf{I}_i$  are electron and nuclear spin angular momenta, respectively, in units of  $\hbar/2\pi$ , and the summation is extended over all nuclei possessing magnetic moments. The expectation value of the parameter  $a_i$  is given by a formula due to Fermi<sup>9</sup>:  $a_i = (8\pi/3)g\beta g_i\beta_N |\psi(i)|^2_{av}$ , where  $g$  is the spectroscopic splitting factor of the electron ( $g = 2.0023$  for a free electron),  $\beta$  is the Bohr magneton,  $g_i$  is the nuclear  $g$  factor of the  $i$ th nucleus, and  $\beta_N$  is the nuclear magneton.  $|\psi(i)|^2_{av}$  is the density of the unpaired electron at the  $i$ th nucleus averaged over the vibrational motions; the average introduced here is an appropriate modification of Fermi's result. The calculation of the hyperfine splitting thus requires an evaluation of  $|\psi(i)|^2_{av}$ .

We first calculate the interaction for one  $\pi$  electron on a carbon atom adjacent to a proton. It is assumed that the carbon orbital is adequately represented by a Slater-type<sup>10</sup>  $2p$  orbital (the Hartree-Fock wave function of Torrance gives similar results<sup>11</sup>) and that the vibration is equivalent to a one-dimensional oscillator performing simple harmonic motion in a direction parallel to the direction of the  $p$ -orbital. The average over the vibrational motion of the density of the  $2p$  orbital at a distance  $x$  from the carbon atom, in a direction perpendicular to the orbital, is given by

$$|\psi_{2p}|^2_{av} = (3.25/a_0)^5 (1/32\pi) \hbar [(n + \frac{1}{2}) / (4\pi^2 \nu m)] e^{-3.25x/a_0},$$

where  $n$  is the vibrational quantum number,  $m$  is the effective reduced mass of the appropriate normal mode with frequency  $\nu$ , and  $a_0$  is the Bohr radius. For simplicity, we assume that  $m$  is the mass of the proton and  $\nu$  is the frequency of the perpendicular C—H bonding

mode in benzene ( $\nu/c = 671 \text{ cm}^{-1}$ ).<sup>12</sup> Although the proper decomposition of the motion into normal modes is not carried out, the result will not be seriously in error. By using this formula for  $|\psi_{2p}|^2_{av}$ , the value of the splitting constant for one  $2p$ -carbon orbital and a proton executing zero-point vibrations at a distance of 1.08 Å (C—H bond distance) is found to be  $a_i = 0.68$  gauss.

To determine the interaction constant for a semiquinone molecule, the coefficient of the  $2p$  wave function for a carbon atom adjacent to a proton in the total orbital of the unpaired electron must be determined. An estimate of the coefficient was made by performing a rudimentary molecular orbital calculation in which all but nearest neighbor exchange integrals and all overlap integrals were neglected,<sup>13</sup> and in which the Coulomb integral for oxygen was assumed to differ from that for carbon by the resonance integral  $\beta$ . ( $H_{OO} - H_{CC} = \beta$  in Coulson's notation.) The unpaired electron occupies the fifth orbital (energy  $E = E_0 + 0.2541\beta$ ) and the wave function is

$$\psi_5 = 0.4700(\phi_O - \phi_{O'}) + 0.3505(\phi_1 - \phi_4) - 0.2795(\phi_2 - \phi_3 - \phi_5 + \phi_6),$$

where  $\phi_1$  to  $\phi_6$  are the six  $2p$ -carbon orbitals numbered according to the usual chemical convention, and  $\phi_O, \phi_{O'}$  are the  $2p$ -oxygen orbitals. The calculated splitting constant for a proton in the *p*-benzosemiquinone ion is therefore  $a_H = (0.68) \times (0.2795)^2 = 0.053$  gauss.

This estimate of 0.053 gauss is about one-fiftieth of the experimental value of 2.4 gauss. In all probability, because of the tendency for the  $\pi$  orbital to follow the vibrational motion and thus remain perpendicular to the C—H bond,<sup>14</sup> this calculated value is an overestimate. Conventional ideas about  $\pi$  orbitals and vibrational motion cannot therefore account for the experimentally observed splitting.

It is conceivable that a vibrational mechanism is possible but that for some unexplained reason the magnitude of the wave function of the unpaired electron at the protons is in error. If this were the case, the spectrum of molecules in the first excited vibrational state should be detectable, and the splitting constant for the excited molecules should differ from the constant for molecules in the ground state. Assuming a frequency of  $671 \text{ cm}^{-1}$ , the population of molecules in the first excited vibrational state at room temperature is about 4% of the population of the ground state. Since by this mechanism the splitting constant is determined by the mean-square vibration amplitude, the constant for the excited state should be three times the constant for the

<sup>7</sup> Gutowsky, McCall, and Slichter, *J. Chem. Phys.* **21**, 279 (1953).

<sup>8</sup> N. F. Ramsey, *Phys. Rev.* **91**, 303 (1953).

<sup>9</sup> E. Fermi, *Z. Physik* **60**, 320 (1930).

<sup>10</sup> J. C. Slater, *Phys. Rev.* **36**, 57 (1930).

<sup>11</sup> C. C. Torrance, *Phys. Rev.* **46**, 388 (1934).

<sup>12</sup> G. Herzberg, *Molecular Spectra and Molecular Structure: II. Infra-Red and Raman Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1954), first edition, p. 363.

E. B. Wilson, *Phys. Rev.* **45**, 706 (1934).

<sup>13</sup> C. A. Coulson, *Valence* (Oxford University Press, New York, 1953), first edition, p. 238.

<sup>14</sup> P. J. Wheatley and J. W. Linnett, *Trans. Faraday Soc.* **45**, 897 (1949); D. F. Eggers, Jr., *J. Chem. Phys.* **23**, 221 (1955).

ground state, and therefore all but the central line of the spectrum of the excited state of the *p*-benzosemiquinone ion should occur outside the spectrum due to the ground-state vibration. A search, which was made under conditions of spectrometer sensitivity such that a 1% rather than a 4% contribution of the excited state should have been detectable, failed to reveal the presence of these lines.

The above argument assumes that the line width in the excited state is the same as in the ground state. The line width is probably determined by the lifetime of a spin state, and if a vibrational mechanism were responsible for the hyperfine interaction, the lifetime of a spin state would be determined by the lifetime of the vibrational state. Since these lifetimes are controlled by collisions, it is unlikely that the lifetime of an excited vibrational state should be markedly different from the lifetime of the ground state and, therefore, the widths of lines from ground and excited states should be of the same order of magnitude. Furthermore, since the lines have a width of only 0.3 gauss or about 1 Mc/sec, a spin state persists for the order of  $10^7$  oscillations of a vibrational state with frequency  $671\text{ cm}^{-1}$ . Since a lifetime of  $10^{-6}$  sec for a vibrational state in solution is excessively long, the narrowness of the observed absorption lines also points to the impossibility of a vibrational mechanism for the hyperfine structure.

A third prediction can be made from the theory of the vibrational mechanism: since the ratio of the splitting constants for protons and deuterons ( $a_H$  and  $a_D$ , respectively) will be

$$(a_H/a_D) = (g_H/g_D)(|\psi(H)|^2_w/|\psi(D)|^2_w),$$

a measurement of the experimental ratio would give the ratio of the average odd-electron density at the protons and the deuterons. If a vibrational mechanism is responsible for the splitting, the mean odd-electron density is determined by the mean-square vibration amplitude which, in turn, is inversely proportional to the square-root of the mass of the vibrator. Neglecting the proper normal modes and reduced mass, this implies that, since  $g_H/g_D = 6.514$ ,<sup>15</sup>  $a_H/a_D \cong \sqrt{2} \cdot 6.5 = 9.2$ . If a vibrational mechanism is not primarily responsible for the splitting, a ratio of  $a_H/a_D = 6.514$  would be expected.

The deuterated *p*-benzosemiquinone ion was prepared from the deuterated hydroquinone by atmospheric oxidation of the hydroquinone in alkaline ethanol solution. The deuterated hydroquinone was obtained by allowing ordinary hydroquinone to exchange with 0.1 M NaOH in  $D_2O$  at  $150^\circ C$  for three days<sup>16</sup>; the exchange was carried out in a sealed tube in the absence of oxygen to avoid oxidation of the hydroquinone. The deuterated hydroquinone was recovered by freezing the tube in dry

<sup>15</sup> N. F. Ramsey, *Nuclear Moments* (John Wiley and Sons, Inc., New York, 1953), p. 78.

<sup>16</sup> I. P. Gragerov and A. I. Brodskii, *Doklady Akad. Nauk S. S. R.* **79**, 277 (1951); I. P. Gragerov and G. P. Miklukhin, *Zhur. Fiz. Khim.* **24**, 582 (1950).

FIG. 1. Paramagnetic resonance spectrum of partially deuterated *p*-benzosemiquinone ion. Upper half: entire spectrum. Lower half: the low field portion of the spectrum including part of the central peak.



ice before opening the tube to the atmosphere, adding sufficient HCl to the opened tube to neutralize the alkali, and then evacuating the tube before the mixture was allowed to thaw. The slightly acidic solution thus obtained was dried under reduced pressure, the residue was extracted with ether four or five times, and the residue obtained by evaporating the ether extracts was recrystallized from 99%  $D_2O$ .<sup>17</sup>

The predicted spectrum of the completely deuterated *p*-benzosemiquinone ion consists of nine equally spaced lines with intensity ratios 1:4:10:16:19:16:10:4:1. The predicted spectrum for the deuterated ion with three deuterons and one proton consists of fourteen lines which, taking the central line of the completely deuterated species as the origin, would be spaced at  $\pm(3a_D + a_H/2)$ ,  $\pm(2a_D + a_H/2)$ ,  $\pm(a_D + a_H/2)$ ,  $\pm a_H/2$ ,  $\pm(a_D - a_H/2)$ ,  $\pm(2a_D - a_H/2)$ ,  $\pm(3a_D - a_H/2)$ , and would have intensity ratios 1:3:6:7:6:3:1:1:3:6:7:6:3:1. If the ratio  $a_H/a_D \sim 6.5$ , all but four lines (the two extreme pairs) of the partially deuterated molecule containing three deuterons and one proton would lie very close to the lines of the completely deuterated species and as such would not be distinguishable if the partially deuterated compound were at very low concentration. The actual spectrum contains thirteen lines, in agreement with a prediction based on a mixture of the fully deuterated and the 3-1 partially deuterated molecules. The eleven strongest lines are shown in Fig. 1; the two outside lines are too weak to be seen on the scale used in the photograph.

The other partially deuterated molecules containing fewer deuterons could not be detected in our sample. The failure to detect these other partially deuterated

<sup>17</sup> Ordinary water probably could have been used for the recrystallization.

molecules is consistent with the relative concentrations predicted by assuming equilibrium between all protons and deuterons in the reaction mixture. If the isotope effect is neglected, the concentrations of the molecules containing 4, 3, 2, 1, and 0 deuterons in the ring would be, respectively, in the ratio  $d^4:4d^3h:6d^2h^2:4dh^3:h^4$ , where  $d$  and  $h$  are the fraction of hydrogen isotopes in the reaction mixture in the form of deuterons and protons, respectively. The value of  $d$  calculated from the stoichiometric proportions used in the reaction mixture is 0.986; while that estimated from the spectrum (assuming the ratio of the 4-deuteron compound to the 3-deuteron compound is given by  $d/4h$ ) is 0.97. This discrepancy is presumably caused by incomplete equilibrium and by the neglect, in the calculations, of the isotope effect. The value of  $d=0.97$  means that the mixture contained at least 80% of the completely deuterated species.

The hyperfine splitting constant for the deuteron in the *p*-benzosemiquinone ion,  $a_D$ , was found to be 0.365 gauss. This value is somewhat uncertain because of overlap between the hyperfine components and contamination of the spectrum by the 3-1 partially deuterated species. To obtain this value the spacings between the different peaks of the spectrum had to be corrected for overlap. The spectrum was assumed to consist of individual lines arising from the fully deuterated and 3-1 partially deuterated molecules and an estimate of the ratio of the concentration of the two types of molecules was made. This estimate was obtained by comparing the observed spectrum, using successive approximations, with a computed derivative spectrum assuming that the lines were of Lorentz-type shape with identical widths.<sup>4</sup> Since the line width of the deuterated compound depended slightly on the concentration of the radical, which in turn decreased with time, only an approximate estimate of the line width could be made. The width between extrema on the derivative of the spectrum was found to be approximately 0.18 gauss, corresponding to a full width at half-intensity for a Lorentz line of 0.32 gauss. The uncertainties in the line width and concentration of the partially deuterated species made the corrections for overlap somewhat uncertain, and we estimate that the splitting constant  $a_D$  may be in error by as much as 2%.

The splitting constant of the protons in the *p*-benzosemiquinone ion was remeasured and found to be  $2.366 \pm 0.006$  gauss. The ratio is therefore  $a_H/a_D = 6.48$  to within about 2%. Since the value of  $g_H/g_D = 6.514$ , these measurements indicate that the unpaired-electron density at either deuterons or protons is the same within experimental error. The value for this ratio of about 9

predicted on the basis of a mechanism involving vibration of the hydrogen atoms is clearly incompatible with the experimental observations, and therefore such a vibrational mechanism can only contribute a minor amount to the splitting.

In the search for a satisfactory explanation of the hyperfine splitting, the suggestion of Jarrett and Sloan<sup>8</sup> that an indirect coupling between the electron and proton moments through the chemical bonds, similar to the coupling between nuclear moments observed in nuclear magnetic resonance spectra,<sup>8</sup> has to be considered. Not only have no quantitative estimates of this mechanism been made but, in addition, it is not clear that such a mechanism is qualitatively correct: no demonstration has been given that a nonvanishing **S**·**I** interaction of this nature could arise from an electron in a  $\pi$  orbital. We are thus at present forced to find another mechanism.

It is suggested that the unpaired electron is partly in a  $\sigma$  state; this hypothesis is a contradiction of the previous assumption that the odd electron is in a purely  $\pi$  state. Just as the hyperfine interaction between the unpaired electron and the methyl-group protons in methyl-substituted semiquinones is believed to be due to hyperconjugation,<sup>5</sup> it is suggested that the interaction between the unpaired electron and the ring-proton is due to configuration interaction between  $\sigma$  and  $\pi$  states. Configuration interaction can give rise to an odd-electron density at the ring protons either by uncoupling one C-H  $\sigma$  bond, promoting one of the  $\sigma$  electrons to an excited  $\sigma$  state, or by unpairing two such bonds simultaneously and promoting one electron from each bond to  $\pi$  states. Altmann has pointed out that the usual Hückel approximation for the treatment of the energy levels of conjugated systems, in which the  $\pi$  electrons and  $\sigma$  electrons are considered independently, is adequate for the ground state, but that the effect of  $\pi$ - $\sigma$  interactions is of great importance in computing excited state energies.<sup>18</sup> Although such a  $\pi$ - $\sigma$  interaction would leave a finite odd-electron density at the ring protons, only quantitative calculations along the lines suggested by Altmann for the ethylene molecule<sup>19</sup> could show whether or not this effect is of sufficient magnitude to account for the interaction constant observed.

#### ACKNOWLEDGMENTS

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<sup>18</sup> S. L. Altmann, Proc. Roy. Soc. (London) **A210**, 327 (1951).

<sup>19</sup> S. L. Altmann, Proc. Roy. Soc. (London) **A210**, 343 (1951).