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Isotropic Hyperfine Energy of Interaction of Free Radicals in Solution

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The completely orthonormalized unpaired electron wave function for a free radical which interacts weakly with the electron distribution in its neighborhood, is:[1]

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

ϕ_o is the SCF wave function for the isolated free radical, and the Schmidt[2] orthogonalization insures that the Pauli Principle is obeyed where the overlap integral $\langle \phi_o, \phi_k \rangle$ is non zero. $\{\phi_k\}$ is the orthonormal set which describes the surrounding molecules and ions.

The electron density, correct to second order in the overlap integral is, thus,

$$\rho = \left[\rho_{oo} - \sum_{k\neq o} \rho_{ok} \langle \phi_k, \phi_o \rangle + \sum_{k,k'\neq o} \rho_{kk'} \langle \phi_k, \phi_o \rangle \langle \phi_o, \phi_{k'} \rangle \right] \left[1 - \sum_{k\neq o} |\langle \phi_k, \phi_o \rangle|^2 \right]^{-1} . \qquad (2)$$

$\rho_{\ell m} = \rho_{m\ell}$, ($\ell$, m = o, k) are the elements of the one electron density matrix.[3] For a system undergoing rapid Brownian motions, the isotropic hyperfine energy of interaction with a nucleus of spin I_n is, therefore, modulated by the time dependence of the electron density distribution, as follows:

$$\mathcal{H}_{hfs} = \left[A_o + A(t)\right] \underset{\sim}{I} \cdot \underset{\sim}{S} \qquad (3)$$

where

$$A_o \cong \delta_n \left[\rho_{oo} + \sum_{k\neq o} (\rho_{oo} + \rho_{kk}) \, |\langle \phi_k, \phi_o \rangle|^2 \right]$$

$$A(t) = -\delta_n \sum_{k\neq o} \rho_{ok} \langle \phi_k, \phi_o \rangle \left[1 + \sum_{k\neq o} |\langle \phi_o, \phi_k \rangle|^2 \right], \quad \left(\delta_n = \frac{8\pi}{3} g_e \, g_n \, |\beta_e| \beta_o \right)$$

Two major conclusions are to be derived from Eq. (3). The first is the functional dependence of the observed hyperfine splitting constant on the electron density in the neighborhood of the free radical. Hence, since clearly $\rho_{kk} > 0$ in the absence of strong exchange interactions between ϕ_k and ϕ_o, which interactions invalidate Eq. (1), important information on the sign of ρ_{oo} can be obtained from $|A_{oo}|$ and $|A_o|$, the absolute value of the coupling constant measured, for, respectively, a free radical in an almost isolated condition and in the prescence of the strong fields of the surrounding molecules and ions. That is, ρ_{oo} is of the same sign as $\delta A = |A_o| - |A_{oo}|$, except in the case when $\rho_{oo} < 0$, and the nuclear spin is intramolecularly shielded in such a manner that $\rho_{kk} < |\rho_{oo}|$. This theory can be successfully applied to the measurements of the coupling constants for several semiquinones in aprotic and ionic solutions[4,5,6]. These yield $\delta A > 0$ for the methyl protons of the tolusemiquinone, whereas for the ring protons $\delta A < 0$ at two positions and positive at another, which probably corresponds to an intramolecularly shielded position with $\rho_{kk} < |\rho_{oo}|$. Similarly, for the p-benzosemiquinone $\delta A < 0$ for the ring protons and a position identified to be the C^{13}_1. All these results are in agreement with the theory of contact hyperfine interactions in aromatic free radicals[7,8], except for the C^{13}_1, where the reported solvent effects are too large for Eq. (1) to be satisfied.

The second result derived from Eq.(3) is the effect of the secular, time dependent perturbation on the lifetime of the Zeeman hyperfine levels of equal symmetry and total component of angular momentum $F^z = J^z + \sum_n I^z_n$. Hence, in the system $J = 1/2$, $I = \sum_n I_n$, where n spans a set of equivalent nuclei, the transition probability between the above states induced by the time dependent term is given by the Master Eq.,[9,10] as follows:

$$W(\,|F,F^z\rangle \leftrightarrow |F\mp 1,F^z\rangle\,) = \frac{2\tau_c}{1+\omega^2\tau_c^2}\cdot\frac{I(I+1)\cdot(I\mp I^z)(I\pm I^z+1)}{4\left[\left(1+F^z\frac{A_o}{H_o}\right)^2+(I\mp I^z)(I\pm I^z+1)\left(\frac{A_o}{H_o}\right)^2\right]}\langle|A(t)|^2\rangle \qquad (4)$$

$F=I\pm 1/2$, $\tau_c = 10^{-9}$ to 10^{-11} sec.[9,11] is the correlation time during which an electron distribution persists, $\hbar\omega$ is the energy separation between the interacting levels, and H_o is the resonance field. Setting $\rho_{ok}^2 \simeq \rho_{oo}\cdot\rho_{kk}$ for $\rho_{kk} \gg |\rho_{oo}|$, $\langle|A(t)|^2\rangle = |A_{oo}\cdot\delta A|$. Hence, for ring protons with typical values $I = 1/2$, $|A_{oo}| = 2$ oe., and $|\delta A| = .2$ oe.,[4] $W(F,F^z) \simeq 10^3$ and 10^5 sec.$^{-1}$ when $\omega = 9 \times 10^3$ Mc/sec. and 16 Mc./sec., respectively, and it increases very fast with the number of equivalent protons.

For p-benzosemiquinone in sodium ethylate-ethanol solution essentially the same line width, $\Delta\omega_{1/2} = 10^6$ sec.$^{-1}$, has been observed for the ESR absorption in high as well as in low fields. In addition, at t = -50°C, the 16 Mc./sec ESR absorption shows a hyperfine interaction with two sodium ions of .12 oe.,[12] which proves that the fast chemical exchange with the sodium ions at room temperature is responsible for the observed $\delta A = -.051$ oe. with respect to the aprotic solution, where $A_{oo} = -2.419$ oe.[4] Hence, in the Paschen-Back region $W \gtrsim 4.6 \times 10^{14}\,\tau_c\,(1+\omega^2\tau_c^2)^{-1}\,f(F,F^z)$ sec.$^{-1}$, where $f=(0,1,3/2,3/2,1)$ and $(0,1/6,1/6)$ for $(F = 5/2, I^z = 2,1,0,-1,-2)$ and $(F=3/2, I^z=1,0,-1)$, respectively, which is of an identical order of magnitude as the anisotropic hyperfine interaction mechanism proposed earlier to explain the line width of the hyperfine components for this free radical.[13,14]

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