

The differences between the H and D cell constants agree very well with those originally obtained by Robertson and Ubbelohde,⁴ and so there is little reason to doubt the directions of magnitudes of minimum and maximum expansion they obtained.

The structures were refined by standard least-squares methods, the refinement being carried out on F^2 . All atoms, including H and D, were refined anisotropically. A correction for secondary extinction was included in the refinement. The usual R and weighted R factors (on F^2) after refinement are: H, 4.1%, 6.6%; D, 5.6%, 6.3%.

The bond lengths in the oxalate fragment are invariant to isotopic substitution. For H and D the C-C, C-O₁, and C-O₂ bond lengths are: 1.545(3), 1.543(3); 1.284(2), 1.286(2); 1.208(2), 1.207(2) Å. The effects of deuteration are thus localized in the hydrogen bonds.

Figure 1 displays the bond distances found between oxalate and water.⁵ Clearly the assumption⁴ that only the strong H bond is affected by deuteration is in error. (This assumption leads to the short O-H-O bond being 0.041 Å shorter than the O-D-O bond.) The greatest change on deuteration occurs in the longest bond! Moreover, there is a significant change in the length of that bond which is very nearly along the direction of minimum expansion (actually reported⁴ to be a contraction of -0.0001 per unit length). Thus there is no correlation of bond-length changes with lattice-constant changes in OAD. From these results and the fact that OAD is a three-dimensional network structure of hydrogen bonds one expects the effects of deuteration to be long range. This result may be of importance in biological systems and tends to invalidate conclusions which have been reached on the changes which occur in protein structures on deuteration.⁶

Thus it is only in exceptionally simple systems (e.g., one independent H bond in the crystallographic unit) that one is conceivably justified in deriving bond-length changes from lattice-constant changes. Few of the available data on this effect can be trusted and there is a need for parallel studies of the sort described here to obtain new reliable information. There is clearly also a need for new theoretical calculations to explain isotope effects such as those displayed in Fig. 1, and hence lead to a better understanding of the hydrogen bond.

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⁵ The differences in bond lengths are invariant to the various

models for correction of bond lengths for effects of thermal motion.

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On Heisenberg Spin Exchange in Liquids*

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IT has recently come to our attention that the two theoretical treatments^{1,2} that have been developed for the analysis of the effects of spin-spin or Heisenberg exchange on ESR spectra of free radicals in dilute liquid solutions, must, in fact, be mutually incompatible. Thus, while both theories predict an initial broadening followed by a coalescence of the hyperfine structure into a single exchange-narrowed line, the detailed expressions for the spin exchange are different. The Kivelson treatment¹ of the initial broadening (which bears some similarity to Bloembergen's treatment³ of the somewhat different problem of a spin-exchange interaction between paramagnetic ions and solvent protons) separates the problem into a secular effect (from the $JS_{1z}S_{2z}$ terms) and a nonsecular effect (from the $JS_{1\pm}S_{2\mp}$ terms) and finds for example that, when $a^2\tau_1^2 \ll 1$, where τ_1 is a mean encounter time and a the hyperfine splitting, both effects contribute equally to the incipient broadening of the hyperfine lines. One disadvantage of Kivelson's approach is that it cannot describe the region intermediate between good hyperfine resolution and strong narrowing. Currin's treatment² can cover the complete range, although the formalism is somewhat unfamiliar and the physical nature of some of the mathematical assumptions is not always clear. Currin examines carefully the case when $J, \tau_1^{-1} \gg a$ and obtains results which suggest that the spin-exchange broadening mechanism is purely a nonsecular effect. That is, following Pake and Tuttle,⁴ one may define an effective exchange frequency $f_e = \rho/\tau_2$, where τ_2 is a mean time between collisions and ρ is the probability of exchange per encounter of the radical pairs. But the ρ as obtained by Currin is just that which may be calculated simply from the well-known quantum-mechanical solution to transitions induced under the action of a constant perturbation⁵ taken as $JS_{1\pm}S_{2\mp}$. Thus the spin exchange becomes a lifetime-broadening-only mechanism in contrast to more typical linewidth phenomena which have important secular (or frequency-modulation) effects. This was a conclusion reached earlier by Wittke and Dicke⁶ in their treatment of gas-phase spin exchange of H atoms in low fields.

We wish, in this Communication, to briefly indicate

the probable reason for the breakdown of the more common approach as given by Kivelson, and to present some results of another theoretical approach, which has the advantage of being more familiar, hence perhaps easier to interpret, than that of Currin and to compare them.

One criticism of Kivelson's approach is simply that $J\mathbf{S}_1 \cdot \mathbf{S}_2$ commutes with the spin Hamiltonian (including Zeeman and hyperfine terms) as long as electron spins 1 and 2 are on molecules having the same nuclear spin configurations, and it also commutes with the rf Hamiltonian $\mathcal{H}_{\text{rf}} = -\hbar\gamma_e B_1(S_{1x} + S_{2x}) \cos\omega t$, so that for this case the exchange term (whether modulated or not) cannot have any effects on the ESR spectrum.⁷ Thus a first correction to the Kivelson treatment would be the inclusion of a statistical factor in p which effectively neglects collisions between like spins, and this is obtained naturally in Currin's treatment. (We have, in fact, obtained preliminary experimental verification of such a factor.) However, if $\tau_1^{-1} \gg a$, then, when dimers are formed from spins having *different* nuclear environments, the uncertainty in lifetime broadening of the exchanging pair is much greater than any hyperfine differences, so that such differences are unimportant and one must treat all spins as identical. Thus, we can neglect any broadening effects of $J\mathbf{S}_1 \cdot \mathbf{S}_2$ on the dimer states as a result of its commutation with \mathcal{H}_0 for the short-lived dimer. (It is also important to note that we are assuming $\tau_2 \gg \tau_1$, so that the dimers themselves make a negligible direct contribution to the spectrum.)

When the dimer breaks apart, however, the probability that a spin exchange has occurred (resulting in different eigenstates for the separated radicals) depends on the magnitudes of $J S_{1\pm} S_{2\mp}$ and τ_1 . Thus, all one sees is the effect of transition of the individual radicals to different spin states; clearly a lifetime-broadening type of process.

This all may be analyzed by making use of the Kaplan⁸-Alexander⁹ theory¹⁰ with separate density-matrix equations written for the monomer and dimer species in a manner very similar to that used by Lynden-Bell¹¹ in the analysis of a related problem involving triplet-triplet interactions. The main difference from her treatment is the use of the high-field Hamiltonian \mathcal{H}_0 appropriate to free radicals.^{12,13} Under the assumption that

$$\tau_1^{-1} \gg \tau_2^{-1}, \gamma_e B_1, a, \quad (1)$$

the effects of the dimer states are readily calculated, and then one obtains for the off-diagonal density matrix elements Z_i of the monomer in the notation of Ref. 12:

$$\Delta\omega_i Z_i - i f_e' [(1 - P_i) Z_i - \sum_{j \neq i} P_j Z_j] + d(\sigma_{i+} - \sigma_{i-}) = D_i q \omega_i d, \quad (2)$$

where the subscripts i, j refer to the i th and j th hyperfine lines and P_i gives the normalized statistical weight of the i th line. Also $f_e' = 2f_e$ and

$$p = \frac{1}{2} J^2 \tau_1^2 / (1 + J^2 \tau_1^2). \quad (3)$$

Thus, one obtains a set of coupled equations for the Z_i which will predict all phases of the exchange broadening and coalescence phenomenon. We note that when $J\tau_1 \gg 1$ the probability of exchange per encounter is just $\frac{1}{2}$ as expected intuitively.^{12a} The factor of 2 in f_e' arises because two radicals are dimerized whenever there is an encounter. Equation (3) is essentially the same as that obtained by Currin, but we have not found it necessary to require $J \gg a$ in agreement with our intuitive description. One can also readily obtain the effects of spin exchange on the diagonal elements of σ . (This is not directly available from Currin's type of treatment.) The result is that

$$f_e' \sum_j D_j (\sigma_{i+\sigma_{j-}} - \sigma_{i-\sigma_{j+}}) = 2d \operatorname{Im}(Z_i), \quad (4)$$

or there is an effective transition probability (or rate constant) for the bimolecular processes given by f_e' . This result has been used elsewhere^{12b} in analyzing the saturation effects of Heisenberg exchange. Thus, for the conditions specified by Eq. (1), the linewidth broadenings and exchange-induced transition probabilities are identical. It may be noted that there is a close correspondence between the term which in Lynden-Bell's notation is $\sigma = \sigma' - \rho \times \rho$ and terms which in Currin's treatment represent pair correlations. We note also that *all* components of $J\mathbf{S}_1 \cdot \mathbf{S}_2$ must be retained in order to obtain the result Eq. (2) as is consistent with the intuitive picture.

Further details and considerations of different microscopic processes affecting τ_2 and p for which the above considerations are important will be given elsewhere.

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¹³ Note added in proof: We have learned of a similar calculation by C. S. Johnson, Jr.