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and M. Vicentini-Missoni, J. M. H. Levelt Sengers, and M. S. Green, *J. Res. Natl. Bur. Std. A* **73**, 563 (1969).

⁷⁴ J. S. Rowlinson, *Natl. Bur. Std. (U.S.), Misc. Publ.* **273**, 9 (1966); M. E. Fisher, *ibid.* **273**, 21 (1966).

⁷⁵ P. Heller, *Rept. Progr. Phys.* **30**, 731 (1967).

⁷⁶ E. H. W. Schmidt, in *Natl. Bur. Std. (U.S.), Misc. Publ.* **273**, 13 (1966).

⁷⁷ H. L. Lorentzen, *Acta Chem. Scand.* **7**, 1336 (1953).

⁷⁸ M. Fixman, *J. Chem. Phys.* **33**, 1357, 1363 (1960).

⁷⁹ B. Chu, F. J. Schoenes, and W. P. Kao, *J. Am. Chem. Soc.* **90**, 3042 (1968).

⁸⁰ B. Chu and F. J. Schoenes, *Phys. Rev. Letters* **21**, 6 (1968).

⁸¹ K. Kawasaki private communication; and *Phys. Letters* **30A**, 325 (1969).

⁸² H. L. Swinney and H. Z. Cummins (private communication).

⁸³ L. P. Kadanoff and J. Swift, *Phys. Rev.* **165**, 310 (1968); **166**, 89 (1968).

⁸⁴ J. V. Sengers, *J. Heat Mass Transfer* **8**, 1103 (1965); A. Michels, J. V. Sengers, and P. S. van der Gulik, *Physica* **28**, 1201, 1216 (1962); A. Michels and J. V. Sengers, *Physica* **28**, 1238 (1962).

⁸⁵ See R. D. Mountain, *Rev. Mod. Phys.*, **38**, 205 (1966).

⁸⁶ L. Seigel and L. R. Wilcox, *Bull. Am. Phys. Soc.* **12**, 525 (1967).

⁸⁷ M. Fixman, *J. Chem. Phys.* **47**, 2808 (1967).

⁸⁸ R. D. Mountain and R. Zwanzig, *J. Chem. Phys.* **48**, 1451 (1968).

⁸⁹ J. S. Osmundson and J. A. White, *Bull. Am. Phys. Soc.* **13**, 183 (1968).

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Nonadiabatic Effects in the Internal Rotation of $\cdot\text{CH}_2\text{COO}^-$ in Irradiated Zinc Acetate Dihydrate*

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The EPR spectrum of the $\cdot\text{CH}_2\text{COO}^-$ radical in a single crystal host displays nonadiabatic motional effects. A phenomenological theory is suggested, based on the density matrix of the spin system, and a technique is described for rapid calculation of simulated spectra.

INTRODUCTION

Previous studies of radiation damage of $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ have revealed the presence of two major radical species and one or more unidentified minor species.¹⁻³ One major species is $\text{CH}_3\cdot$, which is produced on irradiation at low temperatures. As the temperature is raised, $\text{CH}_3\cdot$ reacts with the undamaged substrate to form $\cdot\text{CH}_2\text{-CO}_2^-$. The latter radical is rigid at low temperatures, but at higher temperatures rotation about the C-C bond occurs. As a result, the two protons become equivalent and the EPR spectrum collapses from a quartet to a triplet.

The hyperfine constants and the spectroscopic splitting factors have been measured at 133°K. We use the coordinate system and tensors given in Ref. 1.

The rotational motion, which causes the inner pair of lines of a quartet to coalesce, has been analyzed^{1,2} using the modified Bloch equations⁴ to describe transfer of electron magnetization between the two inner lines. The rate equations $\tau^{-1} = 7.25 \times 10^{11} \exp(-5000/RT)$ and $\tau^{-1} = 4.4 \times 10^{12} \exp(-5800/RT)$ are deduced in Refs. 1 and 2, respectively, from this analysis.

It is not hard to show that the modified Bloch equations do not provide an accurate description of the effect of rotation on the spin system of $\cdot\text{CH}_2\text{-CO}_2^-$. One may show from the hyperfine data of Ref. 1 that, for most orientations of the static field, H_0 , the hyper-

fine fields at the two nuclei differ both in magnitude and direction. As a result, the rotation cannot be viewed as merely changing the precessional frequency of the electron. The nuclei must be included in the dynamical equations describing the spin system. One result of a more accurate treatment, not predicted by the modified Bloch equations, is obvious immediately. The splitting of the outer lines must decrease as the rotational rate becomes very large, in order that the hyperfine tensor in this limit approach the average of the two hyperfine tensors. Viewed differently, the two hyperfine fields must be averaged both in magnitude and in direction.

We follow the notation of Ref. 5 to define $h_i(\pm)$ as the vector of effective magnetic field acting upon proton i when the electron spin is (\pm) . At X band the outer line splitting in the slow exchange limit is proportional to

$$|h_1(-)| + |h_2(-)| - |h_1(+)| - |h_2(+)|.$$

At the rapid exchange limit, the outer line splitting is proportional to

$$|h_1(-) + h_2(-)| - |h_1(+) + h_2(+)|.$$

One can expect a more accurate description of the motion to describe the dependence of the position of the outer lines and, perhaps, to modify the dependence

of the splitting of the inner lines on τ . We present a more accurate analysis here and compare it with experiment.

THEORY

Density matrix descriptions of motional effects in magnetic systems have been well developed for many years.⁶ These methods provide an exact, or nearly exact, treatment of a spin system subject to certain driving terms which are supposed to represent the motional effects. Since the driving terms are usually not derived from first principles, the description of the motion is generally phenomenological.

The density matrix methods have not been applied much until lately because of computational difficulties. Recently, however, McGinnis and Gordon have shown how one may calculate the spectra of a wide variety of systems, for which the equations of motion may be cast into a certain form.⁷

Several workers, most recently Binsch,⁸ have shown how to cast magnetic resonance problems into the appropriate form. In general, one utilizes the fact that the set of all second-rank tensors associated with a Hilbert space constitutes a linear vector space called Liouville space. The density matrix is, thus, a vector in Liouville space, as is the Hamiltonian. The idea of using Liouville space seems to have been first proposed by Fano.⁹ The equation of motion of the density matrix in Liouville space proves to be in the appropriate form to apply the method of Ref. 7.

We have an electronic spin interacting with two nuclei. The equation of motion of the spin degrees of freedom is⁶

$$\dot{\rho} = -i[\mathcal{H}, \rho] + \tau^{-1}(\mathbf{R}\rho\mathbf{R} - \rho) + \Omega\rho, \quad (1)$$

TABLE I. Shift in outer line splitting ($A_1 + A_2$) in gauss for various field directions. Both experimental and calculated values are given. Direction cosines to the coordinate system of Ref. 1 are given.

a^*	b	c	Exptl shift	Calc shift
-1	0	0	2.2	1.94
0	0	1	0.2	0.87
0	1	0	2.7	2.09
0.500	0	0.866	4.5	5.15
0.707	0	0.707	4.5	4.70
0.866	0	0.500	2.6	2.93
0.966	0	0.259	1.6	1.80
-0.707	-0.354	0.612	4.6	4.21
-0.707	0.354	0.612	1.9	1.85
-0.500	-0.612	0.612	4.3	4.51
-0.500	0.612	0.612	2.5	2.67
0	-0.707	0.707	3.9	3.26
0	0.707	0.707	5.7	6.55
-0.569	-0.613	0.548	4.0	4.55
-0.569	0.613	0.548	2.5	2.14

where ρ is an 8×8 matrix. We choose the order of the basis functions labeling the rows and columns of ρ , \mathcal{H} , etc., to be $\alpha_1\alpha_2\alpha_{e1}$, $\alpha_1\beta_2\alpha_{e1}$, $\beta_1\alpha_2\alpha_{e1}$, $\beta_1\beta_2\alpha_{e1}$, $\alpha_1\alpha_2\beta_{e1}$, $\alpha_1\beta_2\beta_{e1}$, etc. \mathcal{H} includes both the interaction with the static field and that with the rf field. The second term, which is discussed in Ref. 6, represents the motion. \mathbf{R} is a matrix which describes the effect of the motion on the various basis functions.

In our case \mathbf{R} leaves the electronic degree of freedom alone, but, for instance, replaces $\alpha_1\beta_2$ by $\beta_1\alpha_2$. The lifetime of the system in one of its two sites is given by τ . Our definition differs from that of Ref. 4 by a factor of 2. The third term is meant to be schematic only. Ω is a relaxation operator, the exact nature of which we define later.

We separate the Hamiltonian into the static part, \mathcal{H}_0 , containing the Zeeman and hyperfine parts, and

$$\mathcal{H}_1 = \frac{1}{2}g\beta H_1 \mathbf{S}_+ \exp(-i\omega t)$$

and transform into a coordinate system rotating at frequency ω . We choose the electronic Zeeman term diagonal, equal to $g\beta H_0 m_s = \omega_0 m_s$. Then

$$\dot{\rho} = -i[(\mathcal{H}_0 + (\omega - \omega_0)\mathbf{S}_z), \rho] + \tau^{-1}(\mathbf{R}\rho\mathbf{R} - \rho) + \Omega\rho - \frac{1}{2}ig\beta H_1[\mathbf{S}_+, \rho]. \quad (2)$$

Now, notice that \mathbf{R} is diagonal in electron spin states. If we ignore matrix elements of the hyperfine interaction which are off-diagonal in electron spin variables, \mathcal{H}_0 is also diagonal in electron spin states. We, therefore, try to partition ρ and see if we can solve only a part of the matrix. Write

$$\rho = \begin{pmatrix} \rho_{++} & \rho_{+-} \\ \rho_{-+} & \rho_{--} \end{pmatrix}, \quad (3)$$

where ρ_{++} , ρ_{+-} , etc., are 4×4 . \mathbf{R} takes the form

$$\mathbf{R} = \begin{pmatrix} \mathbf{R}_0 & \mathbf{0} \\ \mathbf{0} & \mathbf{R}_0 \end{pmatrix} \quad (4)$$

and \mathcal{H}_0 the form

$$\mathcal{H}_0 = \begin{pmatrix} \mathcal{H}_H + \mathcal{H}_n + \frac{1}{2}(\omega_0 - \omega)\mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathcal{H}_H + \mathcal{H}_n \\ & & -\frac{1}{2}(\omega_0 - \omega)\mathbf{1} \end{pmatrix}. \quad (5)$$

\mathcal{H}_H is the hyperfine part of the Hamiltonian, and \mathcal{H}_n the nuclear Zeeman term. The spectrum is obtained as

$$I(\omega) = \text{Re}[\text{Tr}(\rho\mathbf{S}_+)] = \text{Re}[\text{Tr}(\rho_{+-})], \quad (6)$$

so we look for an equation of motion for ρ_{+-} . Substitution of Eqs. (3)–(5) into Eq. (2) yields

$$\begin{aligned} \dot{\rho}_{+-} = & -i[\mathcal{H}_H, \rho_{+-}]_+ - i[\mathcal{H}_n, \rho_{+-}] - i(\omega_0 - \omega)\rho_{+-} \\ & + \tau^{-1}(\mathbf{R}_0\rho_{+-} - \mathbf{R}_0 - \rho_{+-}) - T_2^{-1}\rho_{+-} \\ & - \frac{1}{2}ig\beta H_1(\rho_{++} - \rho_{--}). \quad (7) \end{aligned}$$

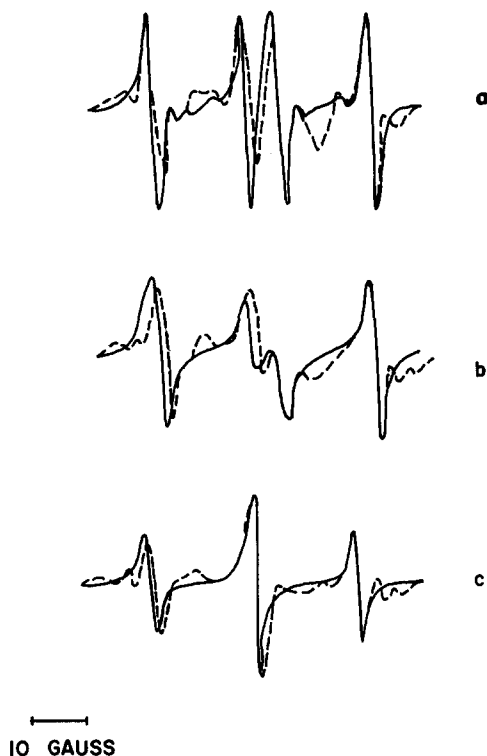


FIG. 1. Simulated (solid line) and experimental (broken line) spectra taken with static field along the direction (0.866, 0, 0.500). Spectrum a: -70°C , $\tau=0.20\times 10^{-6}$ sec; Spectrum b: -31°C , $\tau=0.0334\times 10^{-6}$ sec; Spectrum c: 77°C , $\tau=1.59\times 10^{-9}$ sec. T_2 for all simulated spectra is 0.048×10^{-6} sec, which corresponds to a Lorentzian peak-to-peak linewidth of 1.4 G. The experimental spectra have a peak-to-peak linewidth of about 2.9 G. T_2^{-1} and τ^{-1} are in angular frequency.

The first bracket on the right-hand side is an anti-commutator. The fifth term comes from the relaxation operator and assumes that all of ρ_{+-} decays away uniformly with a transverse relaxation time, T_2 . The last term may be simplified by using the high-temperature approximation (6), which reduces it to

$$-\frac{1}{2}i(g\beta H_1)(g\beta H_0/kT)\mathbf{1}.$$

Equation (7) may be written in Liouville space by writing ρ_{+-} as a vector, columnwise. In other words, one constructs the column vector $\bar{\rho}_v = \{\rho_{11}, \rho_{21}, \rho_{31}, \rho_{41}, \rho_{12}, \rho_{22}, \dots, \rho_{44}\}$. Equation (7) takes the form

$$d\bar{\rho}_v/dt = -i\mathbf{H}\bar{\rho}_v - \mathbf{I}_0\bar{u} - i\mathbf{1}(\omega_0 - \omega)\bar{\rho}_v + \mathbf{R}\bar{\rho}_v. \quad (8)$$

\mathbf{H} contains the first two terms of Eq. (7) and \mathbf{R} the fourth and fifth terms. \mathbf{I}_0 collects the constants in the rf term and \bar{u} is the four-dimensional unit matrix written as a vector.

The slow passage spectrum is obtained by setting $d\bar{\rho}_v/dt = 0$, or

$$[-i(\omega_0 - \omega)\mathbf{1} - i\mathbf{H} + \mathbf{R}]\bar{\rho}_v - i\mathbf{I}_0\bar{u} = 0. \quad (9)$$

The obvious way to solve this inhomogeneous equation is inversion of the operator in the first term. This is

very time consuming, though, because it must be done for many values of ω . The technique of Ref. 7 avoids this problem. Rearrange the equation to

$$(-i\omega_0\mathbf{1} - i\mathbf{H} + \mathbf{R})\bar{\rho}_v + i\omega\mathbf{1}\bar{\rho}_v = i\mathbf{I}_0\bar{u}.$$

The operator in the first term does not depend on ω and may be diagonalized once and for all.

Suppose that

$$\mathbf{T}^{-1}(-i\omega_0\mathbf{1} - i\mathbf{H} + \mathbf{R})\mathbf{T} = \mathbf{\Lambda} \quad (10)$$

and $\mathbf{\Lambda}$ is diagonal. Then

$$\mathbf{\Lambda}(\mathbf{T}^{-1})\bar{\rho}_v + i\omega\mathbf{1}(\mathbf{T}^{-1})\bar{\rho}_v = i\mathbf{I}_0\mathbf{T}^{-1}\bar{u}, \quad (11)$$

$$\bar{\rho}_v(\omega) = i\mathbf{I}_0\mathbf{T}(\mathbf{\Lambda} + i\omega\mathbf{1})^{-1}\mathbf{T}^{-1}\bar{u}. \quad (12)$$

Since \mathbf{T} and $\mathbf{\Lambda}$ are fixed and the matrix to be inverted is diagonal, $\bar{\rho}_v(\omega)$ may be evaluated very rapidly.

RESULTS

We have coded a routine to perform the calculation described by Eq. (12). The heart of such a routine is obviously the diagonalization routine. We have used McGinnis and Gordon's routine called ALLMAT, which they describe in Ref. 7. Coded for execution on a UNIVAC 1107, the calculation of one spectrum of 1000 points takes about 45 sec.

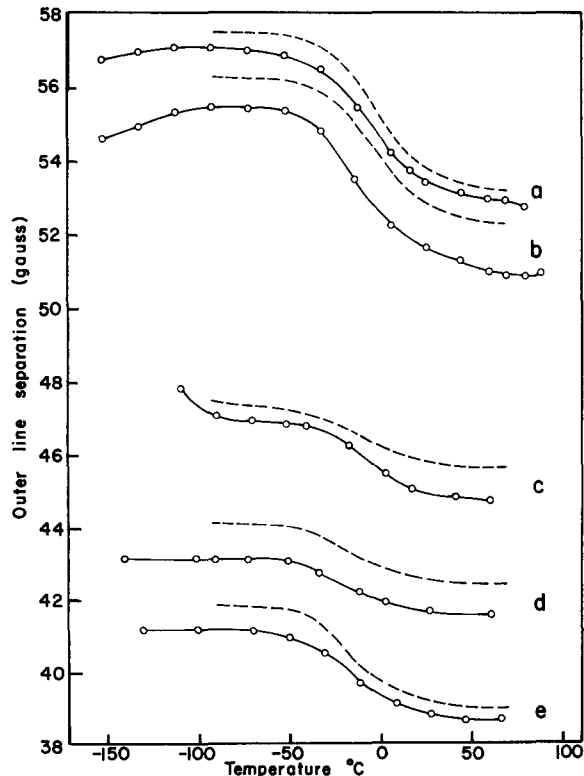


FIG. 2. Calculated (broken line) and experimental (solid line) outer line separations in gauss vs temperature. Static field orientations are: a: $(-0.5, -0.612, 0.612)$; b: $(-0.707, -0.354, 0.612)$; c: $(-1, 0, 0)$; d: $(0.966, 0, 0.259)$; e: $(0.866, 0, 0.500)$.

We give in Table I the shifts of outer line splitting ($A_1 + A_2$) in gauss for various field orientations. The shifts are the differences between the splittings measured at temperatures at which the temperature dependence is nearly level. We discuss below the particular difficulty at low temperature. Figure 1 contains a comparison of calculated line shape with experimental spectra at three temperatures, one to represent each extreme of rotation rate, and one at an intermediate rate. The simulated line shapes are best described as Lorentzian, whereas the experimental spectra are more Gaussian in nature. We have adjusted the linewidth in the simulated spectra to bring the line shapes into rough agreement. The outer line splitting depends upon temperature in a sigmoid fashion. We are able to obtain an Arrhenius rate equation $\tau^{-1} = 5.28 \pm 0.13 \times 10^{11} \exp(-4.63 \pm 0.18 \text{ kcal}/RT)$ based on outer line splitting. The error limits are based on standard deviations obtained by least-squares fitting of fractional shift data from 11 orientations. A temperature was connected with the rotational time that gave the correct fraction of the total shifts of Table I. The rate equation based on line separation data should be more accurate than one based on fitting the shapes of the broadened center lines, since such an analysis depends on the spectral linewidth in the absence of motion, and on a comparison of Lorentzian with Gaussian lines. A comparison of this kind interferes with obtaining a good fit to the line shapes of the center lines in either our treatment or a modified Bloch equation treatment.

We display in Fig. 2 a few determinations of outer line separation vs temperature. As one sees, there is, at some angles, a weak additional dependence of the splitting on temperature at lower temperatures. As a result it is hard to decide just what values of hyperfine components one should use in calculating motional effects. The tensors which we used, as reported in Ref. 1, were based on data taken at -140°C . This

presumably accounts for the fact that our calculated separations tend, at some angles, to be in error by about the same amount at high and low temperatures. Our calculations do not reproduce the changes at low temperature. The changes may be misleading, that is, due to an overlapping line from another radical species, or may be authentic and due to small changes in geometry or crystal structure. We cannot, however, fit them to any particular distortion.

We conclude that the temperature dependence of the EPR spectrum of $\cdot\text{CH}_2\text{COO}^-$ may be described satisfactorily by a simple hopping model, in which the correlation time has an Arrhenius-like temperature dependence, if nonadiabatic effects in the motion of the spin system are included in the treatment.

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¹ W. M. Tolles, L. P. Crawford, and J. L. Valenti, *J. Chem. Phys.* **49**, 4745 (1968).

² H. Ohigashi and Y. Kurito, *Bull. Chem. Soc. Japan* **41**, 275 (1968).

³ M. T. Rogers and L. D. Kispert, *Advan. Chem. Ser.* **82**, 327 (1968).

⁴ H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.* **25**, 1228 (1956).

⁵ H. C. Box, H. G. Freund, and E. E. Budzinski, *J. Am. Chem. Soc.* **88**, 658 (1966).

⁶ C. H. Johnson in *Advan. Magnetic Resonance*, **1**, 33 (1965). A more recent review appears in A. Hudson and G. R. Luckhurst, *Chem. Rev.* **69**, 191 (1969).

⁷ R. G. Gordon and R. P. McGinnis, *J. Chem. Phys.* **49**, 2455 (1968).

⁸ G. Binsch, *Mol. Phys.* **15**, 469 (1958); *J. Am. Chem. Soc.* **91**, 1304 (1969).

⁹ U. Fano, *Rev. Mod. Phys.* **29**, 74 (1957).