

ment lends strong support to our initial assumptions regarding the evaluation of the decoupling factor.

The case when a fourth-moment exchange contribution equals the purely dipolar fourth moment is also plotted in curve (c). Here the line shape is practically Lorentzian near the center of the resonance, but is damped more rapidly for $|x|$ large. A test of this result is not possible at present since experimental exchange-narrowed line-shape data on suitable single crystals is lacking.

In conclusion a decoupling scheme, based on plausible

assumptions is given which describes the many-spin line shape in cubic arrays. Similar assumptions may enable the method to be applied to other line-shape problems, in particular to artificially as well as thermally narrowed lines.

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Triplet-State Electron Spin Resonance of an H-Atom-Methyl-Radical Complex in a Solid Matrix*

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The electron spin resonance of paramagnetic species produced by γ irradiation of solid methane at 4.2°K has been observed. In addition to the expected signals from individual H and CH₃ radicals, weaker signals from exchange-coupled H and CH₃ radicals were observed. The exchange interaction is isotropic, but there is an anisotropic dipole-dipole interaction between the aligned electron spin moments which gives rise to a splitting of 91 G. Analysis of this interaction indicates the separation of the coupled H and CH₃ to be 6.76 Å. The hyperfine splitting by the H is 255 G and that by each proton of the CH₃ group is 11.5 G, or one-half those for the isolated H and CH₃. These features are shown to be in agreement with theoretical predictions. Similar effects were observed for CH₄ irradiated in a krypton matrix at 4.2°K.

EXCHANGE interaction is responsible for diverse phenomena in concentrated magnetic elements in solids. The most prevalent effects on magnetic resonance, those on linewidths and line shapes, have been treated theoretically by Van Vleck¹ and others.^{2,3} Simultaneous flipping of two coupled spins was detected in diethyl copper acetate powder by Lancaster and Gordy,⁴ who suggested that the spins might be coupled through exchange interaction. This species was studied further by Bleaney and Bowers⁵ in single crystals, and the hyperfine structure of the coupled pairs of copper ions was measured and analyzed. Some weak satellite lines observed by Fletcher *et al.*⁶ and by Feher *et al.*⁷ in the resonance of phosphorus-doped silicon semicon-

ductors have been attributed by Slichter⁸ to exchange coupling. The present case, although analogous to that of copper acetate, is novel in that the exchange interaction arises between different magnetic species, in a magnetic-impurity site produced by irradiation. The interaction occurs between the two parts of a dissociated molecule. Although these measurements were not made on single crystals, it has been possible to resolve and analyze the electron-spin-resonance (ESR) spectra in some detail. From the analysis the separation of the two magnetic species in the matrix is found. We have observed these effects in the solid CH₄ matrix and in a krypton matrix at 4.2°K.

Figure 1 shows the first derivative of the ESR absorption curve of γ -irradiated CH₄ observed with high gain at 4.2°K. The spectrometer⁹ and the experimental techniques¹⁰ are described in previous reports from this laboratory. A γ -ray dosage of 6×10^5 R was given the sample from a $\frac{1}{2}$ -kCi cobalt-60 irradiation source. The samples were irradiated in the microwave cavity, which was maintained at 4.2°K throughout the experiment. The observation frequency was 24 kMc/sec. The strong lines which saturate the receiver are due to

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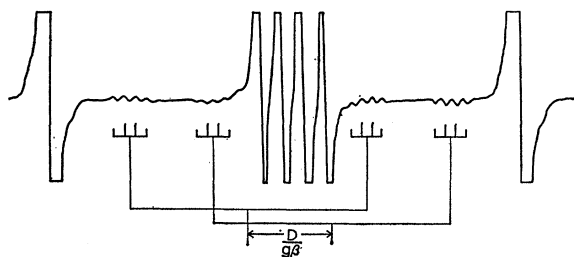


FIG. 1. The electron spin resonance (first derivative curve) of γ -irradiated CH_4 at 4.2°K . The two outside lines separated by 510 G are due to H atoms, and the four central components which saturate the receiver are due to methyl radicals. The four weak sets of quartets corresponding to the theoretical pattern indicated by the bars are due to the exchange-coupled H atoms and CH_3 radicals.

the isolated H atoms and CH_3 radicals in the matrix. The weaker lines which correspond to the theoretical pattern indicated by the bars are due to the coupled H atoms and methyl radicals. The latter spectrum can be completely explained on the assumption that the electronic spins of the H and the CH_3 are coupled through a strong-exchange interaction which aligns the spins in a parallel manner so that the effective spin S equals 1. The system can be treated as a molecule in a triplet state with isotropic exchange interaction $2J\mathbf{s}_1 \cdot \mathbf{s}_2$ which aligns the spins to form a resultant $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2$. The splitting of the resulting triplet-state resonance is caused by an anisotropic dipole-dipole interaction of the spins on the two elements of the system and by the hyperfine structure arising from coupling with the four hydrogen nuclei.

The appropriate spin Hamiltonian for the coupled system is

$$\mathcal{H} = g\beta\mathbf{S} \cdot \mathbf{H} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} + \sum_i A_i \mathbf{S} \cdot \mathbf{I}_i. \quad (1)$$

The g tensor is essentially isotropic and equal to the average $\frac{1}{2}(g_1 + g_2)$ of the separate H atom¹¹ $g_1 = 2.00207$ and the methyl radical¹¹ $g_2 = 2.00242$. Likewise, the nuclear couplings A_i are isotropic and are very closely equivalent to one-half those of the separate H atoms and CH_3 radicals. The spin-spin coupling tensor has the usual form for dipole-dipole coupling, but it can be greatly simplified since the spins are so widely separated that the interacting dipoles can, to a good approximation, be treated as concentrated at the center of the H atom and the center of the CH_3 group. The coupling tensor is then axially symmetric about a line joining the centers of the two interacting units. In the principal axis system, the dipole-dipole terms $\mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}$ can be

expressed as

$$\begin{aligned} \mathcal{H}_d &= D_{11}S_x^2 + D_{\perp}(S_y^2 + S_z^2) \\ &= (D_{11} - D_{\perp})S_x^2 + D_{\perp}S^2 \\ &= D[S_x^2 - \frac{1}{3}S(S+1)], \end{aligned} \quad (2)$$

where $D = D_{11} - D_{\perp}$ and $D_{11} = -2D_{\perp}$.

The peaks we have observed correspond to those for the orientations perpendicular to the symmetry axis, which for geometrical reasons have the greater probability. For observation of the spectra as shown in Fig. 1, the amplitude of the modulation employed in detection of the first-derivative curves is so reduced that a signal is detected only for those coupled units which have their axes approximately perpendicular to the applied magnetic field. When the modulation is increased, distortion is produced by detectable absorption from units with other orientations.

Since both the fine structure and the hyperfine splitting are very small as compared with $g\beta H$, we can find the energy eigenvalues to sufficient accuracy for our purpose with first-order perturbation theory. The constant term $(D/3)S(S+1) = \frac{2}{3}D$ shifts all levels equally and does not affect the resonance frequency. Without loss of generality, we can choose the perpendicular magnetic field along x . Therefore $H_1 = H_x = H$, $H_y = 0$, and $H_z = 0$. The Hamiltonian suitable for our purpose is then

$$\begin{aligned} \mathcal{H}_S &= g\beta H S_x + D(S_x^2 - \frac{2}{3}) \\ &+ \sum_i \{A_i[S_x(I_x)_i + S_y(I_y)_i + S_z(I_z)_i]\}. \end{aligned} \quad (3)$$

With x as the axis of quantization, the diagonal elements of \mathcal{H}_S giving the first-order energies are

$$\begin{aligned} E &= \langle M_S M_I | \mathcal{H}_S | M_S M_I \rangle \\ &= g\beta H M_S + \frac{1}{2}D[S(S+1) - M_S^2] \\ &\quad - \frac{2}{3}D + \sum_i A_i M_S M_{I_i}. \end{aligned} \quad (4)$$

Since $S = 1$ and $M_S = 1, 0, -1$, there are three electronic spin levels:

$$E_1 = g\beta H - \frac{1}{6}D + \sum_i A_i M_{I_i}, \quad (5)$$

$$E_0 = \frac{1}{3}D, \quad (6)$$

$$E_{-1} = -g\beta H - \frac{1}{6}D - \sum_i A_i M_{I_i}. \quad (7)$$

At a constant observation frequency, transitions corresponding to $M_S = -1 \rightarrow 0$ and $0 \rightarrow 1$ occur at magnetic field values

$$H_{-1 \rightarrow 0} = H_0 + \frac{1}{2}(D/g\beta) + (1/g\beta) \sum_i A_i M_{I_i}, \quad (8)$$

$$H_{0 \rightarrow 1} = H_0 - \frac{1}{2}(D/g\beta) + (1/g\beta) \sum_i A_i M_{I_i}. \quad (9)$$

¹¹ C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers, Phys. Rev. **112**, 1169 (1958).

The difference in these values gives the fine structure constant

$$\Delta H = D/g\beta. \quad (10)$$

A fitting of this formula to the experimental curve in Fig. 1 gives the value $D/g\beta = 91$ G.

The nuclear hyperfine splitting is conveniently separated into two parts: that caused by the H atom and that caused by the three equivalent coupling hydrogens of the CH₃ group. Therefore

$$\sum_i A_i M_S M_{I_i} = A_i^H M_S M_I + A_i^{\text{CH}_3} M_S M_T, \quad (11)$$

where $M_S = 1, 0, -1$, $M_I = \frac{1}{2}, -\frac{1}{2}$, and $M_T = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$. The A_i^H and $A_i^{\text{CH}_3}$ terms represent the proton couplings in the triplet state of the exchanged-coupled H··CH₃ system which, as we shall see, are half those for the corresponding coupling constants A^H and A^{CH_3} of the separate H and CH₃ radicals. The M_T values are derived on the assumption that the three methyl protons are equivalent in their couplings.

Although the electronic spin moment in the triplet state is that of the two coupled electrons ($S=1$), only half this moment, on the average, effectively interacts with the H or the CH₃ nuclei. Because of the exclusion principle the two electrons with parallel spins cannot have the same orbital wave function. They can be considered as separately occupying the normalized molecular orbitals:

$$\psi_1 = (1/\sqrt{2})\psi_{1s}(\text{H}) + (1/\sqrt{2})\psi_{2p}(\text{CH}_3), \quad (12)$$

$$\psi_2 = (1/\sqrt{2})\psi_{1s}(\text{H}) - (1/\sqrt{2})\psi_{2p}(\text{CH}_3), \quad (13)$$

formed by combinations of the orbitals of the unpaired electrons of the separated H and CH₃ radicals. Hence there is a resultant spin density of unity for $\psi_{1s}(\text{H})$ and for $\psi_{2p}(\text{CH}_3)$ just as for the separated H and CH₃. Because of their large separation, the interaction of the nuclei of one of the coupled groups with spin density on the other is entirely negligible. Consequently, the nuclear splittings of the $M_S = \pm 1$ energy levels by H and CH₃ should be the same within the accuracy of measurement as those of the $M_S = \pm \frac{1}{2}$ levels of the separated H and CH₃. For this to be true, the coupling constants of Eq. (11) must be half those for the separated H and CH₃, or

$$A_i^H = \frac{1}{2}A^H, \quad A_i^{\text{CH}_3} = \frac{1}{2}A^{\text{CH}_3}. \quad (14)$$

Figure 2 shows a diagram of the resulting energy levels, with the observed transitions indicated by arrows. Because there is no splitting for the $M_S = 0$ levels, it is evident that the resulting hyperfine splitting of the ESR will be only half as much as the corresponding splitting for the uncoupled H and CH₃ even though the splitting of the energy levels for $M_S = \pm 1$ is the same as that for the separated components for which $M_S = \pm \frac{1}{2}$. This is in agreement with the observed curve in Fig. 1, as indicated by the theoretical pattern shown

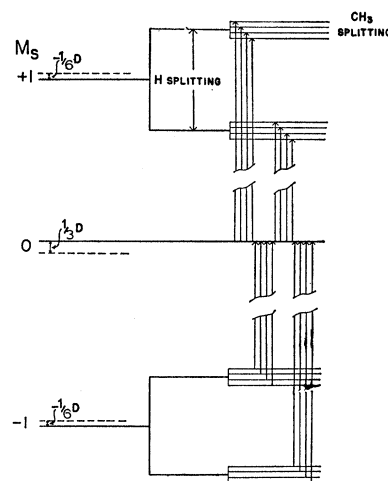


FIG. 2. Energy-level diagram for the exchange-coupled H atoms and CH₃ radicals with the observed transitions indicated by arrows.

below it. The observed splittings yield $A_i^H = 255$ G and $A_i^{\text{CH}_3} = 11.5$ G for the coupled radicals and 510 G and 23 G, respectively, for the separated components.

The fine-structure constant can be used as follows to find the separation R of the interacting H and CH₃ in the matrix. The classical energy of two equivalent magnetic dipole moments μ separated by distance r , when both the moments are aligned in the direction of r , is $2\mu^2/r^3$. In our problem the spin moment of one electron can be considered as on the H and that of the other on the CH₃. The eigenvalue of the electron spin moment along a space-fixed axis is $\langle \frac{1}{2} | g\beta \mathbf{s} | \frac{1}{2} \rangle = \beta$. Alternatively, we may consider the moment of each as half the resultant moment of the two coupled electrons, or $\frac{1}{2} \langle 1 | g\beta \mathbf{S} | 1 \rangle = \beta$. When the moments are aligned along R (or z in our reference system), their interaction energy will be $2\beta^2/R^3$, where R is the effective separation distance. From the Hamiltonian \mathcal{H}_d [Eq. (2)] it is evident that the quantity

$$\langle 1 | D[S_z^2 - \frac{1}{3}S(S+1)] | 1 \rangle = \frac{1}{3}D \quad (15)$$

also represents the dipole-dipole interaction energy when the coupled spins are aligned along the direction z (or R). Hence,

$$\frac{1}{3}D = 2\beta^2/R^3. \quad (16)$$

Since $g=2$,

$$D/g\beta = 3\beta/R^3 = 91 \text{ G},$$

and

$$R = 6.76 \text{ \AA}.$$

Figure 3 shows one possible model of the coupled radicals. In it, the H and the CH₃ are separated by one undamaged methane molecule which has a van der Waals diameter of 4.46 Å. Since the van der Waals radius of H is 1.2 Å, this model with the observed R would indicate that the planar methyl radical has an effective thickness of 1.1 Å. If this model is the correct one, the p orbital of the C probably projects in among three CH bonds of the methane. Although it has the

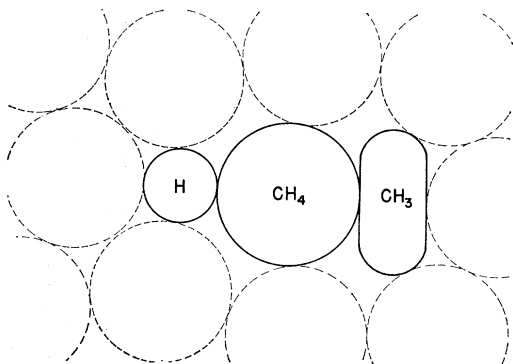


FIG. 3. Cross-section diagram showing possible arrangement of the coupled H atoms and CH_3 radicals in the CH_4 matrix at 4.2°K.

advantage of symmetry, this model would require considerable local alteration in the lattice structure. In the undamaged lattice there are octahedral sites where the H may be trapped, approximately 6.8 Å from possible substitutional sites where the CH_3 could be trapped. Thus one may conclude that the H and CH_3 are simply trapped in these neighboring sites without any further disturbance. However, the maximum dimension of the octahedral sites, about 2.0 Å, is less than the van der Waals diameter of the H, 2.40 Å, and the substitutional sites are somewhat larger than required by the CH_3 . Some local distortion of the lattice certainly occurs, but it is not necessarily of the form or extent indicated in Fig. 3. The octahedral sites are vacant, and a substitutional site is made available when a CH_4 dissociates to produce the H and CH_3 .

It is of interest that the relative intensities of the different sets of quartets of the triplet state resonance are not those to be expected on the basis of Boltzmann equilibrium. Furthermore, their relative intensities appear to be a function of the power level. The satellite quartet corresponding to $M_S=0 \rightarrow 1$, $M_I=\frac{1}{2}$, immediately to the left of the strong primary quartet in the center of the pattern, was weaker under all conditions than the other sets. Likewise, the satellite quartet corresponding to $M_S=0 \rightarrow 1$, $M_I=-\frac{1}{2}$ occurring at the highest field value is somewhat stronger than the others. Probably these differences in intensity are due to variations in the relaxation times of the different transitions, such as are found in other systems.⁹

In a γ -irradiated 2% solution of methane in krypton we were able to observe the components of the $M_S=-1 \rightarrow 0$ transition of coupled H and CH_3 at essentially the same positions as these occur in the methane matrix. Presumably because of the unfavorable relaxation time, the components of the $M_S=0 \rightarrow 1$ transition are too weak for us to obtain a reliable

measurement of D from the separation of the two transitions. However, from the positions of the $M_S=-1 \rightarrow 0$ lines it can be concluded that D , and therefore R , have essentially the same values here as they do for the methane matrix. A superficial interpretation is that the coupled units occur in methane clusters such that the trapping sites are the same as those in pure methane. The difference in the relative intensities of the different components for the two matrices suggests, however, that the medium around the two coupled units is different in the krypton matrix from that in the methane. If one rules out the possibility of clusters and assumes that the coupled H and CH_3 are produced by dissociation of a CH_4 molecule isolated in the krypton matrix, then one must conclude that the H is trapped in distorted substitutional sites in the krypton. In the undistorted lattice the octahedral sites are approximately 6.4 Å from the substituted sites and would thus give a larger value of D than is observed. Furthermore, the radius of the substitutional site, 2.00 Å, is too small to accommodate the CH_4 with its van der Waals radius of 2.2 Å; also the effective radius of the octahedral site, 0.8 Å, is too small to accommodate the H atom, with van der Waals radius of 1.2 Å. Nevertheless, the expansion of the sites required to accommodate the H and CH_3 is about that required to increase the separation distance enough to bring the R into agreement with that calculated from the observed D . It is of interest that no lines identifiable as from triplet states of coupled H and CH_3 could be observed for a similarly irradiated solution of 2% methane in the argon matrix.

In the light of present observations it seems probable that many satellite lines of resonances of atoms or other radicals produced by photolysis or other means of dissociation of molecules trapped in various matrices at low temperature may be explained as arising from triplet states of exchange-coupled pairs of closely spaced radicals produced simultaneously when the molecule is dissociated. Multiple satellite lines of the doublets of H atoms are usually observed^{11,12} when the H atoms are produced by molecular dissociation in a matrix at low temperature. Many of these have been successfully explained¹³ as caused by perturbations of the H atoms by their environment in different trapping sites. However, it now seems possible that some of the unexplained satellites may be due to triplet-state resonances similar to those described here, but with different D values and hyperfine structures.

We wish to thank Michael C. L. Gerry for helpful comments on this problem.

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