and $C_{31}=C_1+C_2+C_3$ is a constant of integration which has to be determined. With the aid of Eq. (A5), one rewrites Eq. (A4) as

$$G_{31}(\alpha)=\tfrac{1}{4}\ln\frac{(\alpha+1)^4[(\alpha+1)^2+4k^2]^2}{\alpha^2(\alpha^2+4k^2)(\alpha+2)^2[(\alpha+2)^2+4k^2]}+C_{31}. \tag{A6}$$

To determine C_{31} one may assume that $\alpha=\infty$. In this case Eq. (A1) shows that G_{31} is zero. The logarithmic term in Eq. (A6) is also zero as can be seen by rewriting both numerator and denominator as a power series in α. Denoting only the leading terms, one obtains

$$0=\tfrac{1}{4}\ln\left\{\frac{\alpha^8+\cdots}{\alpha^8+\cdots}\right\}+C_{31}. \tag{A7}$$

Using l'Hospital's rule[16] repeatedly, one finds that the bracket has the value of unity and therefore the logarithmic term is zero. For this reason Eq. (A7) can only be satisfied if $C_{31}=0$.

The evaluation of the integrals G_{32}, G_{33}, and G_1, displayed in Eqs. (17), (18), and (19), is done in a quite similar manner.

[16] P. Franklin, *Methods of Advanced Calculus* (McGraw-Hill Book Company, Inc., New York, 1944), p. 15 ff.

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Double Quantum Transition in Electron Spin Resonance of Gamma-Irradiated Acetyl-*d*,*l*-Alanine*

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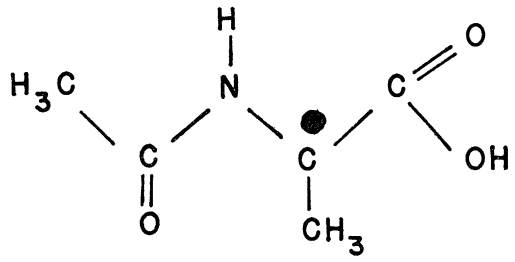
Double quantum transitions were observed at high rf fields in hyperfine spectra of electron spin resonance of the free radical produced by the gamma irradiation of acetyl-*d*,*l*-alanine. The presence of interaction between the free radicals give rise to the double quantum transitions. A theoretical explanation is given.

DOUBLE quantum transitions have been observed in the electron spin resonance of Mn^{++} and Ni^{++} ions as impurities in a single crystal of MgO.[1] The absorption lines were interpreted as arising from the simultaneous absorption of two photons, the absorption being excited from the $S_z=M$ to the $S_z=M+2$ state. Three consecutive energy levels participate in this transition.

In the present article the absorption due to a different kind of double quantum transition is reported in the electron spin resonance of a gamma-irradiated single crystal of acetyl-*d*,*l*-alanine. Here, the four energy levels of two free radicals are taking part in the transition.

The analysis of the electron spin resonance spectra of the free radical produced by gamma irradiation from acetyl-*d*,*l*-analine[2] shows that the free radical has the following form:



The interaction between the unpaired electron and the CH_3 protons is responsible for the hyperfine structure of these spectra.

Figure 1 shows the hyperfine spectra measured at 9 kMc/sec and 23 kMc/sec with varying microwave power. The spectrum measured at 9 kMc/sec using 6 mw of power consists of a quartet, the intensity ratio being 1:3:3:1. As greater microwave power was applied, three weak lines were observed at the midpoints of the main lines. The intensities of these lines increase when the amplitude of the microwave H_1 is raised. The weak lines were observed to have the same separation at 23 kMc/sec as at 9 kMc/sec.

The appearance of forbidden transitions, the simul-

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[1] P. P. Sorokin, I. L. Gelles, and W. V. Smith, Phys. Rev. **112**, 1513 (1958). J. W. Orton, P. Auzins, and J. E. Wertz, Phys. Rev. Letters 4, 128 (1960).
[2] M. Katayama and W. Gordy, Bull. Am. Phys. Soc. 6, 258 (1961).

taneous flipping of both electron and nuclear spins, is highly improbable in this case, since the coupling constant of the quartet is almost isotropic.[3] In addition, absorption lines caused by the forbidden transitions would require that the separations of the weak satellite lines measured at 23 kMc/sec should be different from the spectrum at 9 kMc/sec.

Cole and Heller[4] have observed hyperfine splittings in (HOOC)Ċ^{13}H(COOH) and found them to be dependent upon the orientation of the crystal with respect to the static magnetic field over the range from 8 gauss to 75 gauss. Therefore it is also very unlikely that the weak lines would be due to the presence of C^{13} in natural abundance (1.1%) since the observed lines had separations independent of crystal orientations.

Figure 2(A) shows the saturation of the first-order transition, Fig. 2(B) showing the relation between the intensities of the weak lines and applied microwave power. The intensities of the first-order transition lines

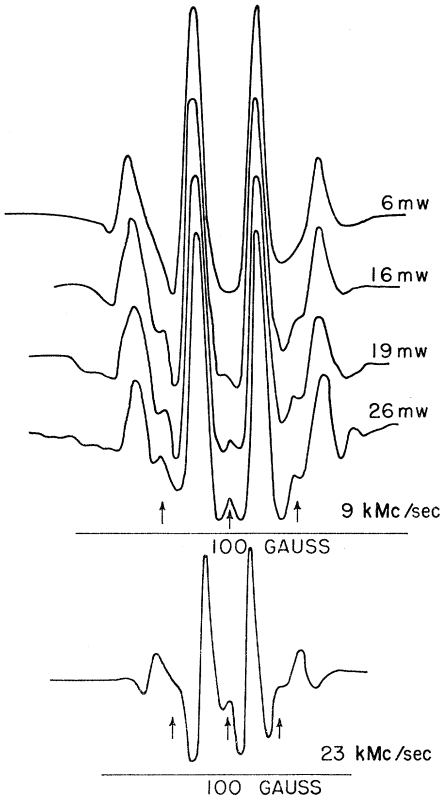

FIG. 1. Appearance of double quantum transitions in the electron spin resonance spectrum of gamma-irradiated single crystal of acetyl-*d*,*l*-alanine. The magnetic field is along the *c* axis. [The definition of crystal axes is the same as P. Groth, Chemishe Krystallographie, Vol. III (1910), Englemann, Leipzig]. The curves represent second derivatives of the actual absorption curves. All the measurements are made at room temperature.

[3] I. Miyagawa and W. Gordy, J. Chem. Phys. **32**, 255 (1960).
[4] T. Cole and C. Heller, J. Chem. Phys. **34**, 1085 (1961).

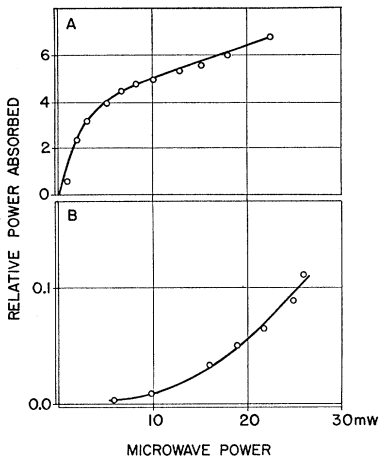

FIG. 2. A. Saturation curve of the first-order transition. B. Power dependence of the intensity of the weak lines.

are proportional to the microwave power when the field H_1 is small enough to avoid saturation. However, the intensities of the weak lines increase more rapidly, going approximately as the square of the power. The ratio of the intensities of the weak lines to the first order lines is roughly 1/100 for the measurements using 20-mw power at 9 kMc/sec, after correcting for the effect of saturation in the first-order transition.

These experimental results indicate that the weak lines are due to the simultaneous absorption of two photon. Our free radical has the electron spin $s=1/2$, coupling with three equivalent protons, nuclear spin $I=3/2$. It is expected that five double quantum transition lines would be observed, two of them coinciding with the central main lines.

For the sake of simplicity, the four energy levels of one of the free radicals are designated as a, b, a', and b' in the following analysis: for example, $(-1/2, +1/2)$, $(-1/2, -1/2)$, $(+1/2, +1/2)$, and $(+1/2, -1/2)$. Here, $(-1/2, -1/2)$ means $S_z=-1/2$ and $I_z=-1/2$. Consider that the two free radicals are initially in the states a and b, respectively. This system of free radicals absorbs a photon k, being excited to the (a',b) or (a,b') states. By a successive absorption of another photon, the free radicals would be excited to the final state (a',b'). Energy would be conserved in the initial and final states as the energy of the photon k is assumed to be

$$k=(E_{a'b'}-E_{ab})/2. \tag{1}$$

Here, $E_{a'b'}$ and E_{ab} are the energies of the states (a',b') and (a,b), respectively.

The transition probability is expressed as follows:

$$\omega=\frac{2\pi}{\hbar}|K|^2\rho=\frac{2\pi}{\hbar}\left|\frac{\langle a,b,2k|H'|a',b,k\rangle\langle a',b,k|H'|a',b',0\rangle}{E_{a'b}-E_{ab}-k}\right.$$
$$\left.+\frac{\langle a,b,2k|H'|a,b',k\rangle\langle a,b',k|H'|a',b',0\rangle}{E_{ab'}-E_{ab}-k}\right|^2\rho. \tag{2}$$

Here $\langle a',b,k|$ represents the wave function of the intermediate state. If the matrix elements $\langle a,b,2k|H'|b',b,k\rangle$ or $\langle a,b,2k|H'|a,a',k\rangle$ have nonvanishing values, the intermediate states $\langle b,b'k|$ and $\langle a,a',k|$ should be taken into account. ρ is the number of final states per unit volume and per energy interval. In our case ρ is obviously proportional to the number of photons, being expressed as

$$\rho \propto \rho_k = k^2 d\Omega/(2\pi\hbar c)^3, \tag{3}$$

where $d\Omega$ is the element of solid angle. H' is the interaction Hamiltonian between the free radicals and the microwave radiation.

The Hamiltonian of the free radicals, which contains the interaction term $A\mathbf{S}_1\cdot\mathbf{S}_2$, is expressed as follows:

$$\mathcal{H}=g\beta H(S_{1z}+S_{2z})+a(\mathbf{S}_1\cdot\mathbf{I}_1+\mathbf{S}_2\cdot\mathbf{I}_2)+A\mathbf{S}_1\cdot\mathbf{S}_2 - g_1\beta_1 H(I_{1z}+I_{2z}). \tag{4}$$

The energy values $E_{a'b}$, $E_{ab'}$, E_{ab}, and $E_{a'b'}$ are evaluated, assuming that second and third terms in the above expression are small. Thus, the ratio of the matrix elements of the second order transition to the matrix elements of the first-order transition would be calculated as follows:

$$K_2/K_1 = A\gamma\hbar H_1/(a^2-A^2). \tag{5}$$

Here, H_1 is the amplitude of the applied electromagnetic radiation; γ is the gyromagnetic ratio.

If the concentration of unpaired electrons is of the order of 10^{17}/cc, some of the values of A are much larger than the hyperfine coupling constant a, and the satellite lines[5] would be observed at the same positions as in our observation. However, this transition is the first order process. On the other hand, the transition probability of the double quantum process would be very large, as the values of A and a are very close. In general, A would be distributed from zero to some large value. Therefore, the transition probability for the double quantum process can be expressed as follows:

$$\omega=\frac{2\pi}{\hbar}\int_0^\infty |K|^2\rho g(A)dA, \tag{6}$$

where $g(A)$ is the distribution function of A. If $g(A)$ has a considerable value, as $A=a\pm 10$ gauss, Eq. (6) would give a reasonable value for the probability of the double quantum process. It is desirable to observe the relation between the concentration of the free radicals and the probability of the double quantum process over a wide range of concentration. However, it is difficult to make our radical of certain ranges of concentrations. Thus, the measurements on suitable samples for this purpose are now undertaken.

As the Q of the cavity used for the data taken at 23 kMc/sec is 4 times larger than that of the cavity used for the 9-kMc/sec observations, the intensity ratio of the second-order lines to the first-order lines is approximately 4 times larger for the 23-kMc/sec data than for those taken at 9 kMc/sec at the same level of incident microwave power.

Therefore it is reasonable to conclude that the weak lines arise from the double quantum process.

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[5] R. C. Fletcher, W. A. Yager, G. L. Pearson, and A. N. Holden, Phys. Rev. **94**, 1392 (1954); C. P. Slichter, *ibid.* **99**, 479 (1955).