Electron-nuclear spin transitions under molecular mobility conditions

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Electron-nuclear spin transitions of the iminoxyl radical in a plastic crystal are investigated theoretically and experimentally. The intensities of "forbidden" transitions are calculated under conditions of rotational and translational mobility of the molecules. The temperature dependence of the translational mutual diffusion coefficient is derived for cyclohexane molecules and iminoxyl radicals by comparing the calculations and the experimental data. A considerable slowing down of translational diffusion in a plastic crystal near an impurity is observed. Whereas the translational diffusion coefficient in pure cyclohexane is $D_c \approx 10^{-9}$ cm^2/sec, it becomes $D_c \approx 10^{-12}$ cm^2/sec on addition of a small amount of the radical near the radical molecule. Discrete saturation of the radical EPR line under stationary conditions is observed by the double electron-electron resonance technique. A model for the homogenization of the EPR lines is proposed and describes satisfactorily the experimental discrete saturation spectrum. The homogenization rate is determined. A value $\approx 10^{-12}$ cm^2/sec is obtained for the translational diffusion coefficient of the radical in a plastic crystal.

1. INTRODUCTION

"Forbidden" transitions in EPR spectra of paramagnetic impurities in solid matrices were investigated both experimentally[1-4] and theoretically[5]. Of considerable interest is the investigation of forbidden transitions in the case of molecular motion. The study of forbidden transitions in condensed media is not only of interest in itself, but yields considerable information on the molecular mobility. Investigations of this type have already been performed. In particular,[6] qualitative estimates were made of the coefficient of translational diffusion on the study of dynamic polarization of protons in a plastic crystal of cyclohexane with an aminoxyl radical as an impurity. The same system was investigated earlier[7] by the discrete saturation method[2,3] under stationary conditions. It was shown that an investigation of electron-electron double resonance of aminoxyl radicals introduced into a plastic cyclohexane crystal makes it possible to observe discrete saturation of the EPR spectra under conditions of fast rotational diffusion, which averages out the anisotropic hyperfine interaction of the unpaired electron with the N^{14} nucleus and makes it possible to observe separately allowed (three lines of the hyperfine structure of N^{14}) and forbidden transitions.

In this case the forbidden transitions, i.e., the simultaneous flipping of the electron and nuclear spins, and the contour of the inhomogeneously-broadened EPR lines are due to the dipole interaction of the unpaired electron with the cyclohexane protons. It was established that discrete saturation, i.e., cutting out a narrow spin packet within the line contour, is due to saturation of forbidden transitions. The "hole" burned out in the line contour then rapidly spreads over the entire line, i.e., the so-called homogenization takes place. The condition for the appearance of inhomogeneous broadening of an EPR line in the case of simultaneous observation of a hole—a narrow signal and a broad electron-electron double resonance signal, is the relation $T_{1e}V_h \lesssim 1$, where T_{1e} is the spin-lattice relaxation time of the electrons, and V_h is the homogenization rate. It is proposed in the same reference that the homogenization process is due to translational diffusion of the molecules. The very possibility of observing a forbidden transition

under conditions of rotational diffusion of radical molecules is connected with the sufficiently slow translational diffusion of both the radical molecules and the molecules of the plastic crystal. Raising the temperature and increasing the translational diffusion decrease the intensity of the forbidden transition and increase the rate of line homogenization.

The present paper is devoted to a theoretical and experimental study of the influence of translational and rotational diffusion on forbidden transition and the discrete saturation of inhomogeneously broadened EPR lines. We calculate, under diffusion conditions, the probability of forbidden electron-nuclear transitions and analyze the electron-electron double resonance line contour in the case of discrete saturation on the basis of the model of noninteracting spin packets.[6] A comparison of the calculation with experiment makes it possible to estimate the values of the coefficient of mutual translational diffusion of the molecules of the radical and of the plastic crystal, and also of the pure translational mobility of the radical molecules.

2. PROBABILITY OF ELECTRON-NUCLEAR FORBIDDEN TRAKSITION UNDER DIFFUSION CONDITIONS

We assume the concentration of the paramagnetic centers to be low enough to neglect the interaction between them. We consider a system consisting of one electron coupled by a magnetic dipole interaction with N_p surrounding protons of the plastic crystal. We direct the strong external magnetic field H_0 along the z axis. Then the spin Hamiltonian of the system can be written in the form

$$\mathcal{H} = \hbar\gamma_e H_0 \hat{S}_z - \hbar\gamma_n H_0 \sum_{j=1}^{N_p} \hat{J}_j^z + \hat{S}_z \sum_{j=1}^{N_p} A_j \hat{J}_j^z + \hat{S}_z \sum_{j=1}^{N_p} (B_j \hat{J}_j^+ + B_j^* \hat{J}_j^-), \quad (1)$$

where $\hat{S}^z$ and $\hat{J}^z$ are the z-components of the electron-spin operator $\hat{S}$ and the spin $\hat{J}$ of the j-th nucleus, $\hat{J}_j^{\pm} = \hat{J}_j^x \pm i\hat{J}_j^y$. We have neglected the direct interaction of the nuclear spins, since they are much weaker than the interaction of the nuclear and electron spins.

The use of the spin Hamiltonian (1) (exclusion of the

nuclear-spin interaction) corresponds to the model of non-interacting spin packets. In addition, for this model to be valid it is necessary that the time of the nuclear spin-lattice relaxation be much larger than the characteristic times of the EPR line homogenization,[5] as was indeed the case in the described experiments. The independent spin packet model is therefore suitable for our problem.

Owing to the presence of the last term in (1), there appears a nonzero probability of a forbidden transition with simultaneous flipping of the electron and nuclear spins of the type $\Delta(M + m_j) = 0$ or 2, where M and m_j are the magnetic quantum numbers of the electron and of the j-th proton. These transitions occur at frequencies $\omega_e \pm \omega_n$, where ω_e and ω_n are the Larmor frequencies of the electron and the proton. Application of a high-frequency field perpendicular to H_0 and of frequency $\omega_e \pm \omega_n$ to the system excites electron-nuclear transition with simultaneous flipping of the electron and nuclear spins. In the absence of molecular motions, the ratio of the intensities of the forbidden and allowed transitions is $BB*/(\hbar\omega_n)^2$, where

$$B, B^* = -\frac{3}{2}\left(\frac{8\pi}{15}\right)^{1/2} r^{-3} Y_{2,\pm1}(\vartheta, \varphi)\mu_e\mu_n,$$

$Y_{2,\pm1}(\vartheta, \varphi)$ is a spherical function of the polar coordinates ϑ and φ of the vector r that describes the magnetic dipole-dipole interaction of the electron and proton spins, and μ_e and μ_n are the magnetic spin moments of the electron and proton, respectively.[9]

Let us find, under conditions of rotational and translational diffusion, the probability of simultaneous flipping of the electron and proton spins. For electron spins belonging to one packet with center at the frequency ω'_0, the probability of the transition $\Delta(M + m) = 2$ under the influence of an alternating field of frequency ω' is proportional to the quantity

$$w = \frac{1}{2\hbar^2\omega_n{}^2}\int_{-\infty}^{\infty} \exp[-i(\Delta'+\omega_n)\tau-\gamma\tau]\langle\langle B(\tau)B(0)\rangle\rangle d\tau, \qquad (2)$$

where $\Delta' = \omega' - \omega'_0$ is the detuning relative to the center ω'_0 of the packet, and γ is the width of the spin packet, which is described by a Lorentz line. The double angle brackets $\langle\langle...\rangle\rangle$ denote averaging over the random rotations and the translational motion of the molecules. It can be assumed that the rotational and translational motions do not correlate with each other, a feature typical of the plastic crystal.[10]

An analysis of the widths of the hfs components of the spectra of the EPR transitions shows that the correlation time of the radical rotational motions in the region of plasticity of the cyclohexane is $\tau_c \leq 10^{-10}$ to 10^{-11} sec, with $\tau_c \leq 10^{-11}$ sec for the cyclohexane molecules themselves.

At the same time, for the translational motions of the cyclohexane molecules in the temperature interval of interest to us the diffusion coefficient is $D_c = 10^{-9}$ to 10^{-10} sec, which leads to a translational-jump time $\tau_n \approx 10^{-5} - 10^{-6}$ sec, i.e., the ratio of the frequencies of the reorientational and translational jumps is $\approx 10^5$. This enables us to average first over the rotational motions, assuming the centers of gravity of the radical and cyclohexane molecules to be immobile, and then over the translational wandering of the centers of gravity. The width γ of the spin packet is determined by two factors, the proper width of the radical EPR line

without allowance for the interaction with the matrix protons, $\approx T_{1e}^{-1}$ (fast rotations),[12] and the finite lifetime of the electron in a given spin packet. If mutual diffusion of the radical and plastic-crystal molecules takes place, each jump is accompanied by a change of the local proton magnetic field acting on the electron spin. This means that the electron goes over from one spin packet to another.[13] The width of the spin packet is then determined by the expression

$$\gamma = T_{1e}^{-1} + V_h, \qquad (3)$$

where V_h is the homogenization rate and T_{1e}^{-1} is the rate of the electronic spin-lattice relaxation. The packet width γ is determined in part by the change of the mutual placement of the radical molecules and the neighboring molecules of the plastic crystal. A shift of any of these neighboring molecules takes the electron spin out of the packet. On the other hand, the correlator $\langle\langle B(\tau)B(0)\rangle\rangle$ receives a contribution only from that crystal molecule to which the proton in question belongs. Since the number of neighboring molecules is much larger than unity, we can regard the random processes that lead to a change of $B(\tau)$ and determine the homogenization rate to be uncorrelated and consider γ independently of $\langle\langle B(\tau)B*(0)\rangle\rangle$.

Formula (2) yields the probability of the forbidden transition of an electron and one proton, but since we can equally well have the flip of the electron spin and of the spin of another proton from the surrounding of the radical, the total rate of change of the electronic spin-level population as a result of the forbidden transitions is $\dot{W} = Nw$, where N is the number of proton spins that interact effectively with the electron spin and can participate in such a flip. Let N_p be the number of protons belonging to the nearest molecules of the plastic crystal surrounding the radical and producing the inhomogeneous broadening of the EPR line.

For simplicity we assume first that their local fields all have the same absolute value. If we consider a spin packet at the center of an inhomogeneously broadened line (i.e., $\omega'_0 = \omega_0$), then $\bar{N} = N_p/2$, since the number of protons directed parallel and antiparallel to the field H_0 is the same, and only the required half of N_p will take part in the $\Delta(M + m) = 2$ transition. Actually the local fields of the protons are different because of the different placements of the protons around the electron spin. An approximate calculation of the number of protons $\bar{N}$, carried out by us, shows that sufficiently far from the center of the inhomogeneously broadened line we have $\bar{N} = N_p/2$. The chosen model of noninteracting spin packets is evidenced by the small width of the burned-out spin packet observed in experiment (≈ 1 MHz)[7] in comparison with the width of the entire inhomogeneously broadened line (≈ 6 MHz). The Larmor frequency of the electron is determined by the external field H_0 and by the local magnetic field H_{loc} at the spin location. The inhomogeneous broadening of the line of the transition $\Delta M = 1$ is produced, as indicated above, by N_p protons, and the line of the $\Delta(M + m) = 2$ transition is produced by $N_p - 1$ protons. In view of the tremendous value of N_p, the distribution H_{loc} for the allowed and forbidden transition will be practically the same and is described by us by a normalized Gaussian function $H(\omega)$ with a width equal to the width of the allowed $\Delta M = 1$ transition line.

The homogenization rate V_h introduced in (3) will be assumed the same for all spins. The time $1/V_h$ means

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that the Larmor frequency of the electron changes from its initial value to a certain random value within $1/\sqrt{h}$. Since the interaction of the spins with one another is neglected, the process of spectral diffusion occurs in this case because of the translational diffusion of the radical molecules and the plastic-crystal molecules, as a result of which the radical is shifted to a new proton environment.

Averaging over the rotations in (2) leads[14] to the appearance in $\langle\langle\ldots\rangle\rangle$ of factors of the type

$$\frac{1}{4rr_1r_2}\ln\frac{r^2-(r_2-r_1)^2}{r^2-(r_2+r_1)^2}.$$

where r is the modulus of the radius vector joining the centers of gravity of the molecules of the radical and of the matrix, and r_1 and r_2 are the distances of the electron and proton spins from the centers of gravity of the radical molecules and the plastic crystal molecules, respectively. For random motion of the centers of gravity of the impurity and plastic-crystal molecules we assume a continuous diffusion model and take $n(r, r_0, \tau)$ to be the density of the conditional probability that the radius vector r joining the gravity centers of the radical and plastic-crystal molecules has a value r at the instant of time τ if its value of the initial instant of time was r_0. The density $n(r, r_0, \tau)$ satisfies the diffusion equation

$$\partial n/\partial t = D\nabla^2 n, \tag{4}$$

where $D = 1/2(D_c + D_r)$, D_c and D_r are the coefficients of the translational diffusion of the matrix and radical molecules, respectively, for the following initial and boundary conditions:

$$n(r, r_0, 0) = \delta(r - r_0), \quad \nabla_r n(r, r_0, \tau)|_{r=R} = 0. \tag{5}$$

The last condition means that distances between the molecules of the radical and of the plastic crystal are never less than R.

We assume that $R = R_c + R_r$, where R_c and R_r are the Van der Waals radii of the cyclohexane and radical molecules. The normalized solution of Eq. (4) with conditions (5) is

$$n(r, r_0, \tau) = \int_0^\infty A\left(\frac{k}{r}\right)^{1/2}[(zJ_{-3/2}(z) + 3J_{-1/2}(z))J_{3/2}(z)$$
$$+ (zJ_{3/2}(z) - 3J_{1/2}(z))J_{-3/2}(z)]Y_{2,-1}(\vartheta,\varphi)Y^*_{2,-1}(\vartheta_0,\varphi_0)$$
$$\cdot\left(\frac{k}{r_0}\right)^{1/2}[(z_0J_{-3/2}(z_0) + 3J_{-1/2}(z_0))J_{3/2}(z_0) + (z_0J_{3/2}(z_0)$$
$$- 3J_{1/2}(z_0))J_{-3/2}(z_0)]\exp\{-k^2D\tau\}k\,dk, \tag{6}$$
$$A = \left(\frac{\pi z_1}{4Dk}\right)^{1/2}\left(z_1 - 2 - \frac{9}{z_1^2} + \frac{81}{z_1^4}\right)^{-1/2},$$
$$z_1 = kR, \quad z = kr, \quad z_0 = kr_0.$$

The solution (6) of Eq. (4) is more complicated than in the usual treatment of the problem of the influence of the translational diffusion on the magnetic-resonance spectra[9], owing to the introduction of the boundary condition (5). The probability w receives a contribution mainly by the region of the closest approach of the molecules, where $n(r, r_0, \tau)$, owing to the boundary condition (5), differs appreciably from the solution of the free-diffusion equation. Therefore the use of the results of[9] can lead to serious errors. Averaging in succession over the angles and positions of the molecules, we obtain ultimately for $\tilde{w}$:

$$\tilde{w}(\Delta') = \frac{\beta^2 R^3\rho_n}{8\pi Dr_1^2r_2^2\hbar^2\omega_n^2}\int_0^\infty\frac{B_0 + x^2}{A_0^2 + (B_0 + x^2)^2}f(x)\,dx;$$

$$B_0 = \frac{\gamma R^2}{D}, \quad A_0 = \frac{(\Delta' + \omega_n)R^2}{D}, \quad \beta = \frac{3}{2}\left(\frac{8\pi}{15}\right)^{1/2}\mu_e\mu_n,$$

$$f(x) = \frac{x^3}{x^6 - 2x^4 + 9x^2 - 81}\left[\int_1^\infty\{(xJ_{-3/2}(x) + 3J_{-1/2}(x))(xy)^{1/2}J_{3/2}(xy) + (xJ_{3/2}(x)\right.$$
$$\left. - 3J_{1/2}(x))(xy)^{1/2}J_{-3/2}(xy)\}\ln\frac{y^2 - L^2}{y^2 - K^2}dy\right]^2, \tag{7}$$

$$y = \frac{z}{z_1}, \quad x = z_1, \quad L = \frac{(r_2 - r_1)}{R}, \quad K = \frac{(r_2 + r_1)}{R},$$

where ρ_n is the number of cyclohexane protons per cm^3. The observed forbidden-transition line shape $h(\omega)$ is the envelope of many spin packets $\tilde{\omega}(\Delta')$. The total probability of the forbidden transitions at the frequency ω is determined by summation over all the spin packets:

$$W(\omega, \omega_0) = \int_{-\infty}^\infty \tilde{w}(\omega, \omega_0')h(\omega_0', \omega_0)d\omega_0', \tag{8}$$

where $\tilde{w}(\omega, \omega_0')$ is given by formula (7), and $h(\omega_0', \omega_0)$ is the envelope of the spin packets. The EPR signal at the frequency of the forbidden transitions is determined by the population difference

$$\Delta n_f(\omega) = n_0(\gamma_e H_1)^2T_{1e}W(\omega, \omega_0), \tag{9}$$

where n_0 is the equilibrium density of the populations at the levels $(M = -1/2, m = 1/2)$ and $M = 1/2, m = -1/2$. In analogy with (9) the observed value of the signal with $\Delta M = 1$ at the frequency ω_a is given by

$$\Delta n_a(\omega_a) = n_0(\gamma_e H_1)^2T_{1e}W_a(\omega_a, \omega_0), \tag{10}$$

where

$$W_a(\omega_a, \omega_0) = h(\omega_a, \omega_0).$$

For comparison with experiment, it is convenient to use the quantity

$$\alpha = \Delta n_f/\Delta n_a = I_f/I_a,$$

where Δn_f and Δn_a are taken at the centers of the lines of the transitions $\Delta(M + m) = 2$ and $\Delta M = 1$, while I_f and I_a are the amplitudes of the derivatives of the lines of the transitions $\Delta(M + m) = 2$ and $\Delta M = 1$, respectively. We note that expressions (9) and (10) correspond to absence of saturation of the lines. It is impossible to determine (8) analytically, and we therefore calculated α numerically with the BÉSM-6 computer, using the value of T_{1e} from[6]. The remaining parameters were determined from our experiment. The results of the numerical calculation of the dependence of α on the coefficient of the mutual translational diffusion D are shown in Fig. 1. As seen from this figure, the intensity of the forbidden transition begins to change at $D \gtrsim 10^{-12}$ cm^{2}sec^{-1}, i.e., measurements of α can yield information on the molecular mobility only at such values of D.
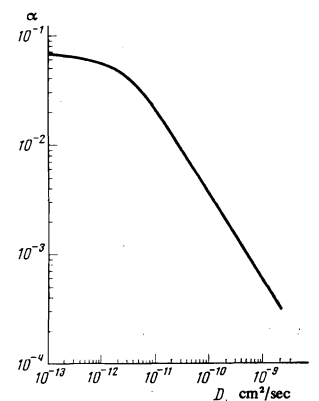

FIG. 1. Theoretical dependence of α on the coefficient D of the mutual translational diffusion of the molecules of the radical and of the cyclohexane. L = 0.1, K = 0.9, R = 7 Å, γ = 0.2 MHz.
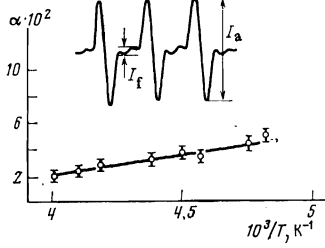
FIG. 2   FIG. 3

FIG. 2. Experiment temperature dependence of $\alpha = I_f/I_a$ of the iminoxyl radical in cyclohexane, $C_r = 6 \times 10^{17}$ spins/cm^3. The upper plot is the spectrum of the iminoxyl radical in plastic cyclohexane at T = 232°K.
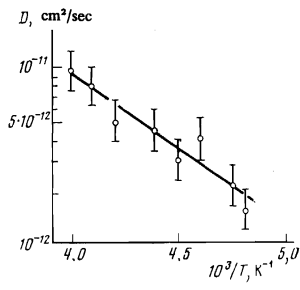
FIG. 3. Temperature dependence of the mutual translational diffusion coefficient of the radical and plastic-crystal molecules.

3. COMPARISON OF THEORY WITH EXPERIMENT

The EPR spectra of the iminoxyl radical in the plastic phase of cyclohexane were obtained with a standard RE-1301 spectrometer ($H_0 \approx 3300$ Oe). For a comparison of the theory with the experiment and to determine D, we measured the α(T) dependence. The samples were prepared by diffusion of the iminoxyl radical in the cyclohexane in a vacuum $\sim 10^{-5}$ mm Hg, so as to narrow down the hfs lines and to make the medium homogeneous. The radical concentration C_r was $\approx 6 \times 10^{17}$ spins/cm^3. The measurements were performed in the absence of saturation of the $\Delta M = 1$ transition line. The temperature was maintained constant within ±1°K. The inhomogeneity of the magnetic field over the sample length was less than 0.08 Oe.

The experimentally obtained plot of α(T) is shown in Fig. 2. Comparison of Figs. 2 and 1 yields the plot of Fig. 3. As seen from Fig. 3, the absolute value of D (10^{-11} to 10^{-12} cm^{2}sec^{-1}) is much smaller than the coefficient of self-diffusion of the cyclohexane molecules in the same temperature interval ($10^{-8}-10^{-9}$ cm^2 sec^{-1}).[15] This conclusion will be corroborated in Sec. 4 and agrees with the assumed abrupt decrease of the self-diffusion of the plastic-crystal molecules around the impurity molecules, and the assumed cluster formation.[6] If it is assumed that the temperature dependence of D is given by the formula $D = D_0 \exp\{-E_a/kT\}$, then, as seen from Fig. 3, the activation energy is $E_a \approx 4$ kcal/mole.

4. HOMOGENIZATION OF EPR LINE UNDER CONDITIONS OF TRANSLATIONAL DIFFUSION

The homogenization of an inhomogeneously broadened EPR line was observed earlier[7] by the electron-electron resonance method. When a forbidden transition at the frequency $\omega_e + \omega_n$ is saturated by a powerful pump field at the frequency ω_e of an allowed transition, one observes under stationary conditions a narrow peak against the background of the broad line due to the homogenization process, i.e., to the spreading of the saturation from the point ω_e over the entire contour of the inhomogeneously broadened line (individual component of the hfs of the N^{14} atom).

Let us consider the homogenization process on the basis of the model of noninteracting spin packets and random spectral diffusion.[13] The difference of the populations of the electronic levels with M = ±1/2 at the

frequency ω in a bandwidth dω is equal to $Nh(\omega)n(\omega)d\omega$, where N is the total number of electron spins, $n(\omega)$ is the difference of the populations under stationary conditions, and $h(\omega)$ was defined above. Let us find the change of the populations at the frequency of the allowed transition, when a high-power high-frequency field acts at the forbidden-transition frequency ω_f. The kinetic equation describing this change of populations takes in the stationary case the form

$$-(\gamma_e H_1)^2 n(\omega)\frac{c\delta}{\delta^2+(\omega-\omega_s+\omega_n)^2} - \frac{n(\omega)-n_0}{T_{1e}}$$
$$-n(\omega)V_h+V_h \int_{-\infty}^{\infty} h(\omega')n(\omega')d\omega'=0. \quad (11)$$

Here the constants c and δ are determined from the plot of $\tilde{w}(\omega, \omega_f)$ against $\omega - \omega_f + \omega_n$ in accord with the numerical data obtained from the computer calculation of $\tilde{w}(\omega, \omega_f)$.

The solution of (11) is

$$n(\omega)=n_0\frac{1/T_{1e}}{1/T_{1e}+V_hS}\left[1-\frac{c(\gamma_e H_1)^2\delta}{c(\gamma_e H_1)^2\delta+(1/T_{1e}+V_h)(\delta^2+(\omega-\omega_s+\omega_n)^2)}\right],$$

$$S=(\gamma_e H_1)^2c\delta \int_{-\infty}^{\infty}\frac{h(\omega')d\omega'}{c(\gamma_e H_1)^2\delta+(1/T_{1e}+V_h)(\delta^2+(\omega'-\omega_s+\omega_n)^2)}.$$

The form of the electron-electron double resonance at the frequency ω, for a pump frequency ω_f, is the first derivative of the absorption signal, which is proportional to $Nh(\omega)[n(\omega, \omega_f) - n_0]$, and is described by a function of the type

$$I=h'(\omega)[n(\omega, \omega_s)-n_0]+h(\omega)n'(\omega, \omega_s). \quad (12)$$

Figure 4 shows the theoretical discrete-saturation spectra obtained from (12) for various homogenization rates, and also the experimental waveform of the signal. It follows from Fig. 4 that the closest to the experimental waveform is spectrum 3 with $V_h = 0.005$ MHz. The time $1/V_h$ in our model corresponds to the time during which the proton surrounding of the electron spin changes noticeably in the case of translational motion of the radical molecule. It is reasonable to assume that such a change of H_{loc} occurs when the radical molecule is displaced one lattice constant of the plastic-cyclohexane d ≈ 6 Å, i.e., $1/V_h = d^2/6D_r$, where D_r is the coefficient of translational diffusion of the radical molecule in the plastic crystal. Using this relation and $V_h \approx 0.005$ sec^{-1}, we obtain $D_r \approx 3 \times 10^{-12}$ cm^{2}sec^{-1}. This is close to the value of the mutual diffusion coefficient D, namely $\approx 5 \times 10^{-12}$ cm^{2}sec^{-1} at this temperature. Thus, the mutual translational diffusion coefficients obtained in vari-
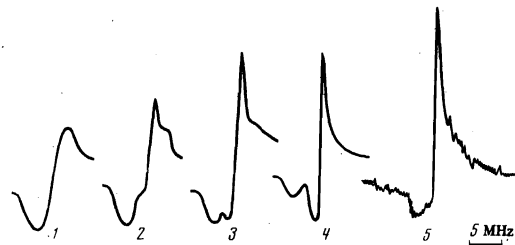

FIG. 4. Spectra of electron-electron double resonance component with $m(N^{14}) = 0$ following saturation of the forbidden transition and passage through the observation frequency. Theoretical: 1) $V_h = 0.05$ MHz, 2) $V_h = 0.01$ MHz, 3) $V_h = 0.005$ MHz, 4) $V_h = 0.002$ MHz; f) Experimental spectrum from [7] at 230°K. All spectra correspond to a pump-field amplitude $\gamma_e H_1 \approx 0.8$ MHz.

ous approaches for the radical molecule are in full agreement with one another, thus confirming the correctness of the results.

The obtained values of D and D_T are smaller by almost three orders of magnitude than the self-diffusion coefficient of the pure plastic crystal.[15] This abrupt decrease of the translational mobility is apparently due to the fact that the vacancies in the plastic-crystal lattice are occupied by the molecules of the impurity (the stable radical), whose Van der Waals diameter (≈ 8 Å) is somewhat larger than the diameter of the cyclohexane molecule (≈ 6 Å). At the same time, further jumps of the molecules become restricted in the crystal lattice, and the translational mobility decreases.

Our study of the molecular motions in the plastic phase of cyclohexane with the aid of the forbidden EPR transitions and discrete saturation under stationary conditions confirms the assumption that self-diffusion of the plastic-crystal molecules is stopped in the presence of the impurity.[6]

We believe that an investigation of forbidden transitions yields direct information on the mobility of molecules in condensed media and can apparently be used as a method for the study of mobility in other substances.

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