

Pulsed ESR and Molecular Motions

Yu. D. Tsvetkov and S. A. Dzuba

Institute of Chemical Kinetics and Combustion, Novosibirsk, USSR

Received May 29, 1990

Abstract. The possibilities of applying three different pulsed ESR techniques have been considered: 1. Phase relaxation measurements by electron spin echo (ESE) affords the estimation of the correlation time of the motion in the region up to 10^{-5} s. The results of theoretical and experimental analysis of the effect of methyl group rotation in nitroxide radicals have been proposed. 2. The method of pulsed saturation involving detection of ESE signal allows the range of the measured times to be extended up to the values of about 10^{-2} s. The rotation of CH_2 group in the $\dot{\text{C}}\text{H}_2\text{CO}_2^-$ radical and that of the CH_3 group in the $\dot{\text{C}}\text{H}_3\text{CHCO}_2^-$ radical have been investigated. 3. The method of pulsed saturation combined with pulsed scanning of H_0 allows the analysis of the rotationally induced redistribution of the pulsed saturation throughout the ESR spectra of the radicals. This version of pulsed ESR has been used to study the mobility of nitroxide spin labels.

1. Introduction

With regard to the application in chemistry and biology ESR spectroscopy should provide the possibilities for investigating molecular motions in a wide range of characteristic times τ_c . The continuous wave (CW) ESR methods in the region of fast motion (short τ_c times) are limited by a characteristic frequency of 10^{10} Hz (X-band) and of about 10^{11} Hz (mm-range). In the region of slow motion the lower time boundary of the motion up to 10^{-7} s is limited by inhomogeneous line broadening by the magnetic nuclei of the matrix under study. The pulsed methods based on ESE expand substantially this boundary. In this respect this paper is concerned with three types of experiments devoted to the study of slow motions: investigation of phase relaxation by an ESE technique (Sect.2), experiments on pulsed saturation-recovery of ESE signals (Sect.3), experiments on the spectroscopy of saturation-recovery (Sect.4) which is also based on the detection of ESE signals.

Note that the CW methods for studying the saturation-recovery processes also enable the investigation of slow motions. They need, however, information on the relaxation times T_1 and T_2 and the strength of the microwave field H_1 . Besides, they fail to discriminate between different mechanisms of motion.

2. Phase Relaxation in ESE and Intramolecular Motions (Spectral Diffusion due to Exchange)

Spectral diffusion, i.e. the fluctuation of local magnetic fields at the site of an unpaired electron, is one of the fundamental processes leading to the decay of the ESE signal amplitude $V(\tau)$ with increasing time interval τ between 90° and 180° pulses. These local fields are produced by unpaired electrons of other radicals and by nuclear spins of surrounding nuclei. The fluctuation of their dipole fields are caused by spin-lattice relaxation, flip-flop processes for the nuclei and translational, rotational or oscillatory motions of the nuclei surrounding the electron. Thus the ESE signal decay due to spectral diffusion contains information either on the motion of magnetic particles or of its fragments. The contribution of spectral diffusion to the kinetics of the two-pulse ESE signal decay obeys the relation:

$$V = V_0 \langle \exp(i \int_0^t s(t') dt') \rangle_t, \quad (1)$$

where $s(t) = -1$ in the range $(0, \tau)$, $s(t) = +1$ in the range $(\tau, 2\tau)$. Averaging over t means the average over all the possible realizations of processes with the resonance frequency shift $\Delta\omega(t)$ due to one of the magnetic dipole interactions modulated by time dependent processes. The approach based on relation (1) for various random time processes affords the calculation of the contribution of the spectral diffusion to the two-pulse ESE decay kinetics [1].

One of them, important for studying motions by phase relaxation, is the exchange process [1, 2]. The spin resonance frequency is assumed to realize two values ω_1 and ω_2 , between which transitions are possible at an average rate $1/\tau_c$. This model is in fair agreement with motions, when values of the local electromagnetic field varying due to exchange by value $\Delta H = \gamma^{-1}(\omega_1 - \omega_2) = 2\gamma^{-1}\Delta\omega$, correspond to energies of various nuclear spin configurations. For this problem ESE decay kinetics has first been determined by Zhidomirov and Salikhov [2] and it is described by:

$$V(2\tau) = V_0 \exp[-2\tau/\tau_c] [R^2 \text{ch}^2(R\tau) + R\tau_c^{-1} \text{sh}(2R\tau) + \tau_c^{-2} \text{sh}^2(R\tau) + \Delta\omega^2 \text{sh}^2(R\tau)], \quad (2)$$

where $R^2 = \tau_c^2 - \Delta\omega^2$. Function (2) is a rather complex nonexponential form. Time T_f , calculated as e-fold decrease of $V(\tau)/V_0$ is considered as a characteristic time of the process. Calculating the dependence of T_f on the parameter $\Delta\omega$ shows that two regions may be distinguished according to exchange rate $1/\tau_c$. In the region of fast exchange $1/\tau_c \gg \Delta\omega$ which corresponds to the spectral narrowing:

$$V(2\tau) \approx \exp[-\Delta\omega^2\tau_c\tau], \quad (3)$$

i.e. the phase relaxation time is of the form:

$$T_f = 2/\Delta\omega^2\tau_c. \quad (4)$$

With slow exchange, i.e. when $\tau_c^{-1} \ll \Delta\omega$, the $V(2\tau)$ kinetics is more simple and

$$V(2\tau) \approx \exp[-2\tau/\tau_c], \quad (5)$$

with

$$T_f = \tau_c. \quad (6)$$

In the general case a similar behavior connecting the phase relaxation time and the spectral diffusion rate holds for other mechanisms of spectral diffusion: normal and Gauss-Markovian processes [1]. In all cases the intermediate region is close to the correlation time $\tau_c \sim \langle \Delta\omega^2 \rangle^{-1/2}$, where $\langle \Delta\omega^2 \rangle^{1/2}$ is the frequency mean-square deviation from ω_0 in one of the model processes for random frequency changes.

The theory of the ESE signal decay due to spin exchange between two positions has successfully been used in [3] for studying the CH_2 group rotation in the CH_2CO_2 radical (irradiated Zn acetate). Note, however, that it is more convenient to analyze experimentally the temperature dependence of $V(\tau_0)$ than to determine the effective T_f whose value may be influenced by other mechanisms of phase relaxation.

If the exchange process is activated

$$\tau_c = \tau_{c0} \exp[E_A/kT]. \quad (7)$$

The variation of the three parameters $\Delta\omega$, τ_{c0} and E_A allows this dependence to be readily calculated and the values of τ_{c0} and E_A to be determined by

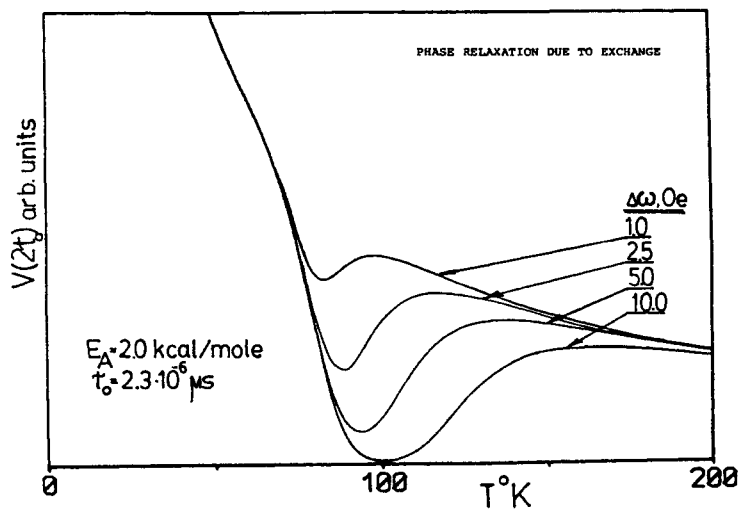


Fig. 1. The computed temperature dependence of ESE signal amplitude $V(2\tau_0)$ for the spectral diffusion due to exchange. Calculations were performed at various $\Delta\omega$.

comparison with the experiment. These calculations based on Eqs. (2) and (7) are shown in Fig. 1. A Curie type temperature dependence of the ESE intensity is included in the calculations.

The exchange between only two positions is a model and of fairly rare practical realization. More often the phase relaxation is due to rotation or exchange between several positions of various groups near the radical centre, e.g. CH_3 or C_2H_5 .

We have investigated the influence of the rotating methyl groups surrounding the N—O radical centre of the nitroxide radical. Rotation causes the exchange between the corresponding hyperfine structure (HFS) components of the spectrum (Fig. 2). The isotropic hyperfine interaction (HFI) constant a_0 is for this case about 0.10 Gs. In the disordered samples (nitroxide solutions) the hyperfine structure due to the interaction with the methyl groups is unresolved.

The two-pulse ESE signal decay kinetics has been calculated as described in [2]. If the radical contains N methyl groups, and the mean value of the frequency deviation in the spectrum during the exchange is $\Delta\omega$, it is derived in a good approximation for fast exchange by:

$$V(2\tau) \approx V_0 \exp[-4N\tau_c\tau(2/3\Delta\omega)^2] \quad (8)$$

and for slow exchange by:

$$V(2\tau) \approx V_0 \left[1 - \frac{8\tau}{9\tau_c} \left(1 - \frac{\sin 2\Delta\omega\tau}{2\Delta\omega\tau} \right) \right]^N, \quad (9)$$

where

$$\Delta\omega = [(a_1 - a_0)^2 + (a_2 - a_0)^2 + (a_3 - a_0)^2]^{1/2} / 3, \quad (10)$$

a_1, a_2, a_3 are the anisotropic HFI constants for CH_3 protons.

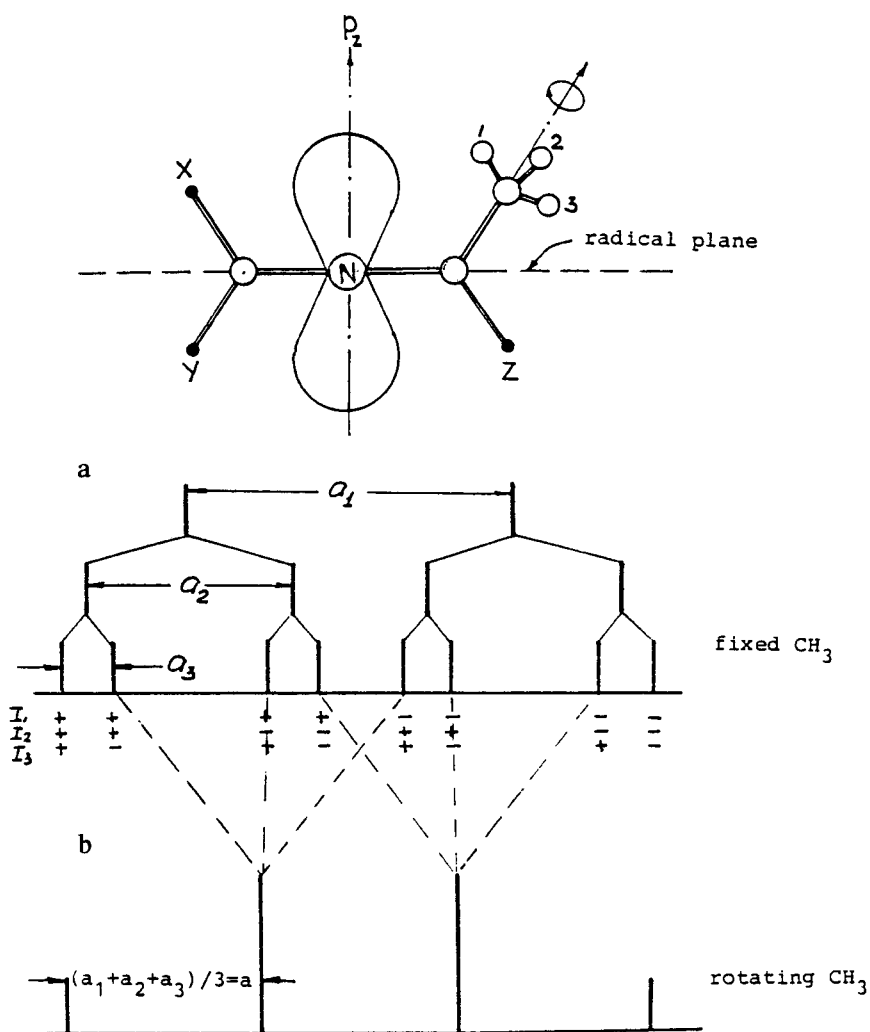


Fig. 2. Model of methyl group rotation in nitroxide radicals. a The ESR spectrum in the absence of exchange (rotation). b Fast rotation.

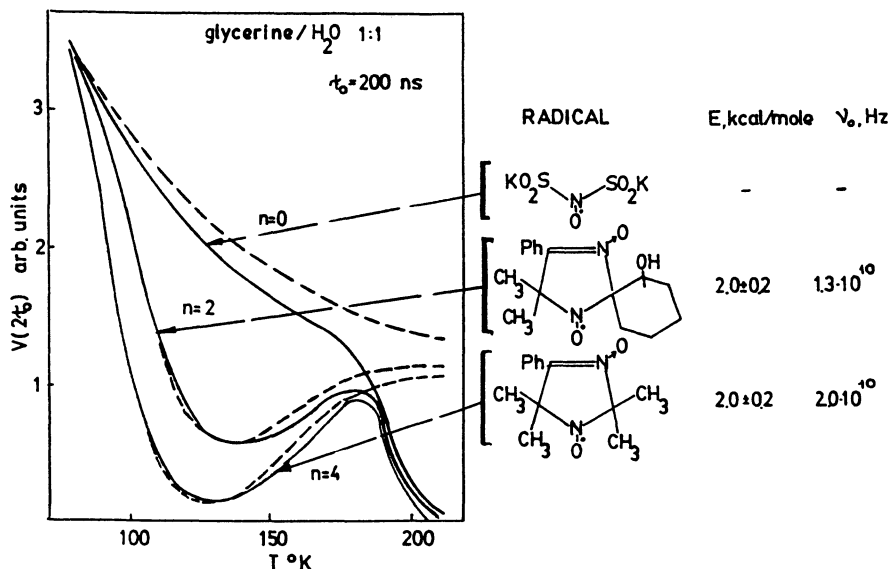


Fig. 3. Experimental data on the temperature dependence of ESE signal amplitude $V(2\tau_0)$ for various nitroxides. E and ν_0 data obtained from these experiments are given.

The radicals the structure of which is shown in Fig. 3 were studied by dissolving in a (1:1) glycerine-water mixture. The radical concentration in all the samples was 5×10^{-3} mol/l. The temperature dependence of the ESE signal intensity $V(\tau)$ was measured at fixed $\tau_0 = 100$ ns between the first and second pulse. The results are shown in Fig. 3. The spectra were excited at the point of the maximum intensity, i.e. on the intermediate line of the ESR triplet of the nitroxide radical. The duration of the pulses was 40 and 20 ns, the repetition frequency being 200 or 500 Hz. In all the experiments the ESE signal intensity was independent of the repetition frequency.

The results presented in Fig. 3 suggest the following:

1. If the nitroxide radical contains no CH_3 groups screening the $>\text{N}-\text{O}$ fragment (Fremi salt) the temperature dependence of the ESE signal intensity in the range of 77–190 K decreases monotonously. The intensity decrease in this range roughly follows the Curie law for the magnetic susceptibility $\chi_0 \sim 1/T$. A drastic decrease in the ESE amplitude at $T \approx 190$ K may be related to the onset of the radical rotation as a whole.
2. At $T > 120$ K the rate of the ESE signal decay with temperature for nitroxide containing CH_3 groups is 2–3 times as large as that assumed from the Curie law. ESE decay rate increases with increasing number of CH_3 groups in the radical structure. The curves pass through a minimum.

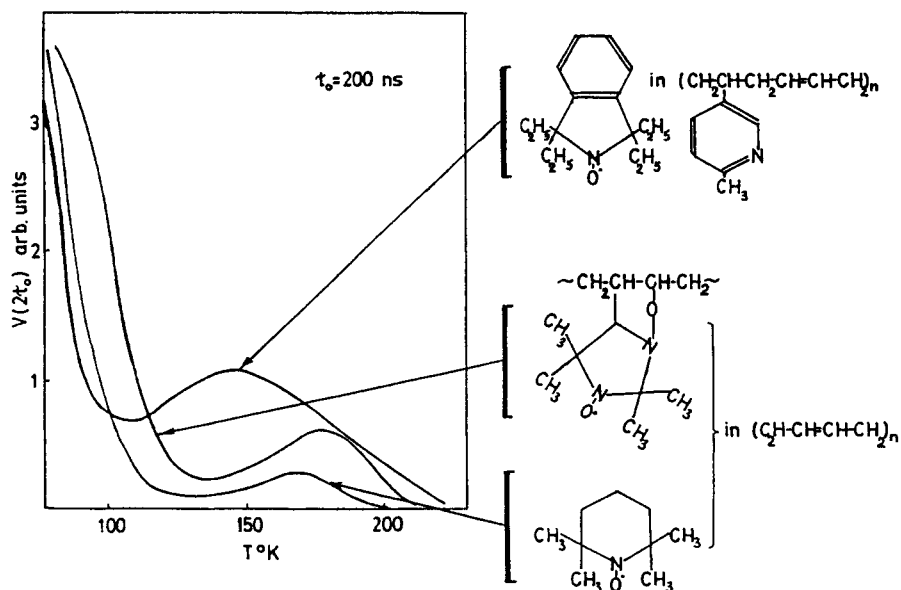


Fig. 4. Experimental data on the temperature dependence of ESE signal amplitude $V(2\tau_0)$ for a series of labels and probes in polymers.

increase at $T \sim 180$ K and then decrease sharply again. Thus their behavior correlates with a spectral diffusion model due to exchange (see Fig. 1) where exchange is caused by the rotation of the methyl groups. Fig. 3 presents not only the experimental but also the calculated curves in accordance with the above theory of the spectral diffusion due to the CH_3 group rotation. The frequency $\nu_0 = \tau_{c0}^{-1}$ of the exchange ($\nu_0 = 10^{10}$ Hz) and the activation energy $E_A \approx 2.0$ kcal/mol have been determined by comparing the experimental and theoretical curves.

3. This method based on the determination of a small-scale spectral diffusion from relaxation data practically inaccessible by CW ESR techniques may also be employed to other systems. Some results for nitroxides diluted in polymers or introduced as labels are given in Fig. 4. Note that Stillman, Schwartz and Freed [4] have also discovered an unusual (extremum at $T = 150$ K) temperature dependence of the phase relaxation time when studying the TEMPON nitroxide in a water-glycerine mixture. Brown [5] has obtained a similar extremum at 140 K when studying TANOL solutions in methyltetrahydrofuran but failed to find it for the Fremi salt. We think that all these effects should be described by the influence of spectral diffusion due to the CH_3 group rotation on phase relaxation in such systems. It might be possible that the rotation of various groups of solvent molecules leads to the same effects.

3. Pulsed Saturation-Recovery Method

The pulsed saturation-recovery method has shown [6] to be useful for studying the intra molecular motions in radicals. The method is easily applied to paramagnetic particles whose ESR spectrum contains the lines of two types: (i) those exchanging on rotation of the radical or atomic group in the radicals and (ii) those insensitive to the rotation induced exchange.

The radicals stabilized in monocrystals due to their fixed orientation are convenient systems for these experiments. The pulse sequence shown in Fig. 5 has been used. One of the exchanging components of the ESR spectrum is saturated by a short (40 ns) 90° or 180° pulse. The reduction of longitudinal magnetization M_z is studied using a two pulse sequence forming the ESE signal that is proportional to the magnetization M_z . At a fairly large time after the saturation pulse the magnetizations of both components are equalized due to the exchange and corresponding saturation transfer between the exchanging lines.

The kinetic equations describing the magnetization exchange in the general case for n equivalent components of the ESR spectrum are of the form:

$$dM_i(t) / dt = [M_0 - M_i(t)] / T_1 - M_i(t) / \tau + (n\tau)^{-1} \sum_{j=1}^n M_j(t), \quad (11)$$

where M_0 is the equilibrium magnetization and τ the exchange time. At the initial moment when the saturating pulse affects the i -component

$$M_i(0) = M_0 \cos \theta, \quad M_{j \neq i}(0) = M_0, \quad (12)$$

where θ is the turning angle $\theta = \gamma H_1 \tau_p$.

These equations may readily be solved for different n , e.g. at $n=2$ the kinetics of the magnetization exchange is of the following form:

$$\ln[1 - M(+)/M_0] = -\ln(1 - \cos \theta) + t/T_1 + \ln[1 + \exp(-t/\tau)]^{-1}. \quad (13)$$

Thus if there is no exchange ($\tau \rightarrow \infty$), relation (13) yields the time T_1 from the slope of a linear function. The exchange distorts the linearity and allows the determination of τ by comparing the theoretical relation (13) and the experimental curves.

The $\dot{\text{C}}\text{H}_2\text{CO}_2$ radicals in irradiated single crystal of zinc acetate have been studied [7]. Their ESR spectrum is given in Fig. 6a. On rotation of the CH_2 groups the inner lines of the quartet exchange, but the external ones are not involved. The experimental results at 155 K are given in Fig. 6b where the

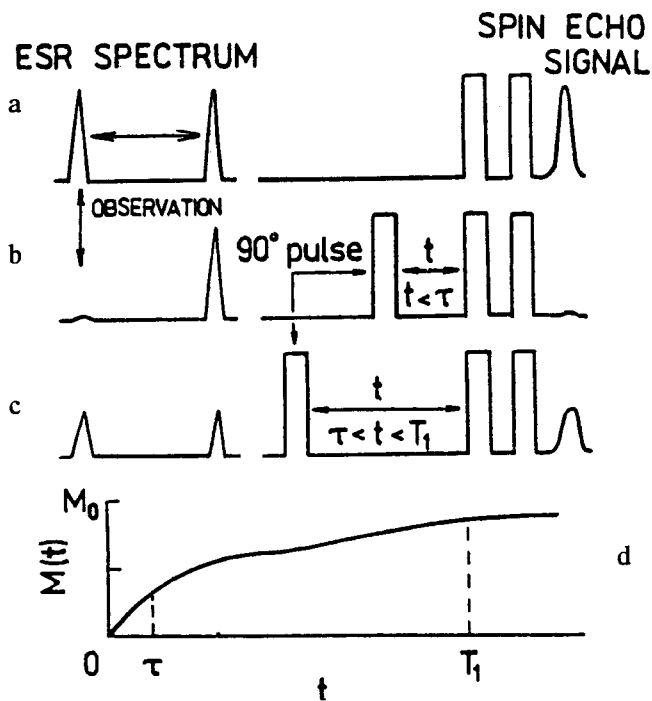


Fig. 5. a, b, c Pulse sequence for the method of saturation recovery. d The kinetic curves for magnetization.

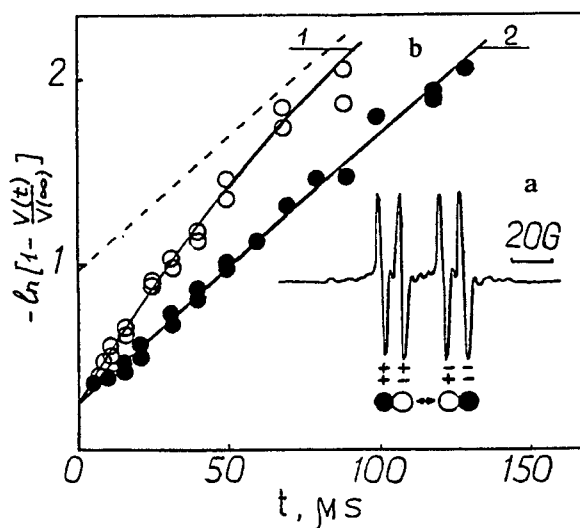


Fig. 6. a ESR spectrum and b the kinetic curves of magnetization recovery for exchanging (1) and non exchanging (2) lines.

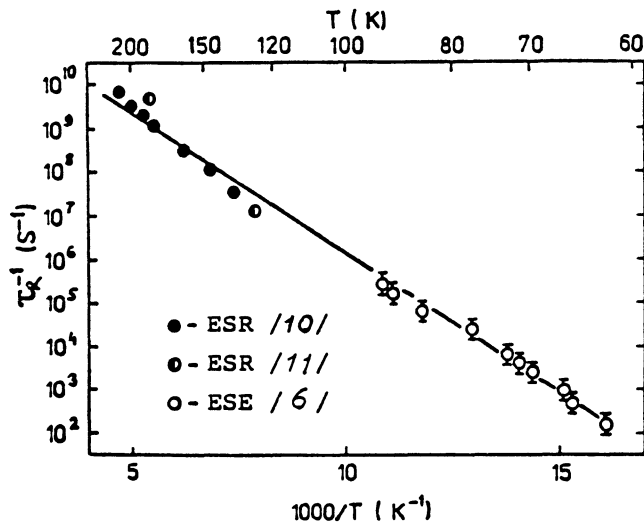


Fig. 7. The temperature dependence of the rotation rate of methyl group in radical $\text{CH}_3\dot{\text{C}}\text{HCO}_2^-$ in irradiated DL- α -alanine.

curve for the non exchanging lines provides $T_1=71 \mu\text{s}$. For the exchanging ones the rotation time $\tau=46 \mu\text{s}$ is obtained by a fit according to Eq.(13). These measurements were performed for zinc acetate within the temperature range 130–170 K. The τ values were determined to be in the range 10^{-3} – 10^{-5} s. Note that earlier the CW ESR techniques [8,9] gave the results in the range 10^{-6} – 10^{-10} s.

Similar measurements were obtained for the classical system of $\text{CH}_3\dot{\text{C}}\text{HCO}_2$ radicals stabilized in the irradiated single crystal DL- α -alanine [6]. This is a case of exchange between three equivalent HFS lines due to the rotation of the methyl group in the radical. The ESR spectrum for this case is more complex but the exchanging and non exchanging lines are readily distinguished. Shown in Fig. 7 are the temperature dependencies in form of Arrhenius plots obtained from the rotation times in the region 90–160 K and those obtained earlier by the CW ESR technique [10,11].

The measurements of the saturation transfer rate need a substantial shift towards the region of slow motions. This is caused by the fact that the spin-lattice relaxation whose rate is usually much lower than the other contributions to the linewidth is in this case the limiting process. The Arrhenius parameters for the CH_3 group rotation in the $\text{CH}_3\dot{\text{C}}\text{HCO}_2$ radical in these experiments have been defined more precisely to be $\nu_0=(3.6\pm 1)\times 10^{12} \text{ s}^{-1}$ and $E=3.0\pm 0.1 \text{ kcal/mol}$.

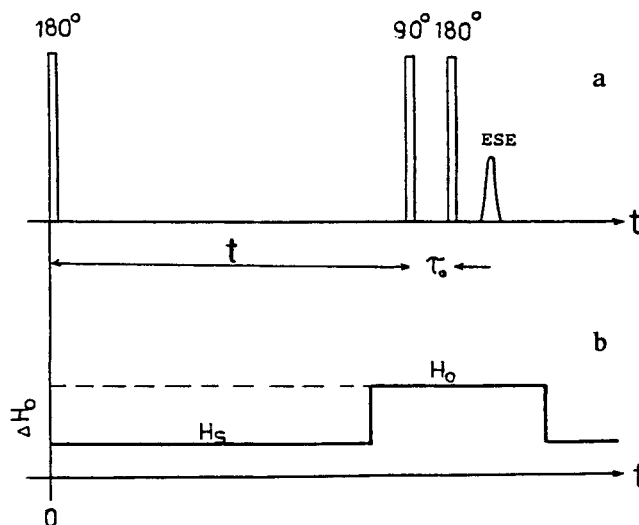


Fig. 8. Microwave pulse sequence and the magnetic field jump in the spectroscopy of pulsed saturation-recovery.

4. Pulsed Saturation-Recovery Spectroscopy

This method uses an ESE spectrometer equipped with the facilities for an additional magnetic field jump. A diagram for the pulse sequence is given in Fig. 8. In any part of anisotropically broadened ESR spectrum the population hole is burnt by a microwave pulse during which a partial or full saturation of the longitudinal magnetization M_z or even its inversion occurs. Then the redistribution of magnetization into other parts of the ESR spectrum is observed. In order to do this a two pulse sequence forming the echo signal whose amplitude is proportional to M_z is used. The magnetic field H_0 is changed by a jump to $H_0 + \Delta H_0$ during the echo signal formation period to provide the measurement of M_z in various parts of the ESR spectrum.

This technique is similar to pulsed ELDOR and may be employed to study the saturation transfer not only in single crystals but also in disordered systems possessing complicated unresolved ESR spectra.

Experiments of two types are presently under way. In the first one the magnitude of the magnetic field jump is fixed and a sweep of time t is realized between the exciting pulse and that forming the ESE signal. This is a well-known method of pulse saturation-recovery. In the second one the time t is fixed and the amplitude of the field jump ΔH_0 is swept. The rate of the field sweep (of the order of 1 min for the total spectrum) is much less

than the repetition frequency of a series of pulses (usually about 10^3 Hz). These experiments allow one to obtain a snapshot of the hole burned in the ESR spectrum.

The characteristic values of the parameters shown in Fig. 8 are the following. The minimum value of time t is determined by the initial front of the magnetic field jump ΔH_0 and is about 2–3 μs . The jump amplitude varies from 0 to 50–60 Gs, its direction may change with respect to H_0 . The experimental details are presented in [12–14]. Note that the magnetic field jump has first been used in the pulse ESR spectrometer by Rengan *et al.* [15] to measure T_1 of a radical undergoing spectral diffusion.

Typical experimental results on hole-burning in the ESR spectrum are given in Fig. 9 for the ^{15}N -nitroxide radical dissolved in a supercooled dibutyl phthalate (glass transition temperature $T_g=166$ K).

At the temperature near T_g the ESR spectrum shape of nitroxides is determined mainly by the anisotropy of g - and HFI-tensors. These may be considered in good approximation as axially symmetric ones with coinciding symmetry axes.

The field positions of the ESR spectral lines corresponding to the different orientations of an axial symmetry axis relative to the direction of an external magnetic field H_0 are given in the bottom of Fig. 9. A noticeable magnetization transfer throughout the spectrum is observed. Since the main contribution to the spectral width is made by the anisotropy of the magnetic tensors this transfer may be attributed to the rotation of the radical. The initial hole form obtained at 77 K is shown by dots in Figs. 9c and 9d. The spectral shape at $t=3$ μs indicates that already at this time magnetization is substantially redistributed. Further increase to $t=23$ μs increases this redistribution (Figs. 9a and 9b). The magnetization transfer between the lines of the different HFS components corresponding to the same orientations is the most noticeable one.

Fig. 10 presents the kinetics of the magnetization evolution at different points of the ESR spectrum when the hole is burnt at the position shown in Fig. 9b. With increasing time all the curves in Fig. 10 converge to one asymptotic straight line. This means that the spectral diffusion caused a full spectral redistribution of the magnetization. Later on only the recovery of magnetization M_z is observed due to spin-lattice relaxation. The tangent of this asymptotic straight line is equal to T_1^{-1} which enables the determination of T_1 .

The convergence rate for the curves in Fig. 10 may be identified to time τ_R^{-1} . When it is of the order of T_1 or exceeds it τ_R may be derived from the data similar to those given in Fig. 10. For nitroxide radicals in glasses τ_R values are measured up to 10^{-3} s [12].

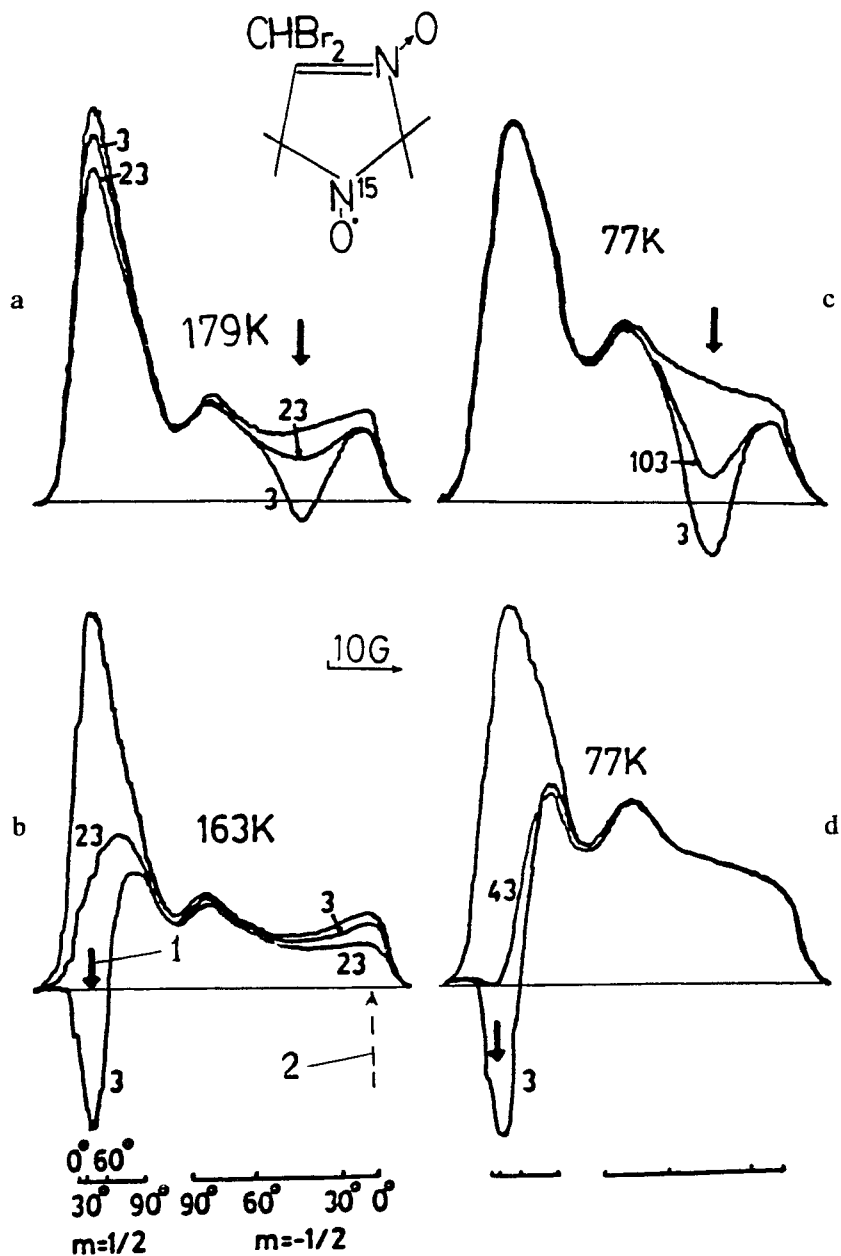


Fig. 9. The time evolution at various temperatures of pulse saturated ESR spectra for different position of the pulse in the spectrum (arrows). The numbers at the curves denote the time in microseconds after the pulse. Shown is a scale of the position of different orientations of axial symmetry axis of g-factor tensor relative to the vector of the external magnetic field H_0 .

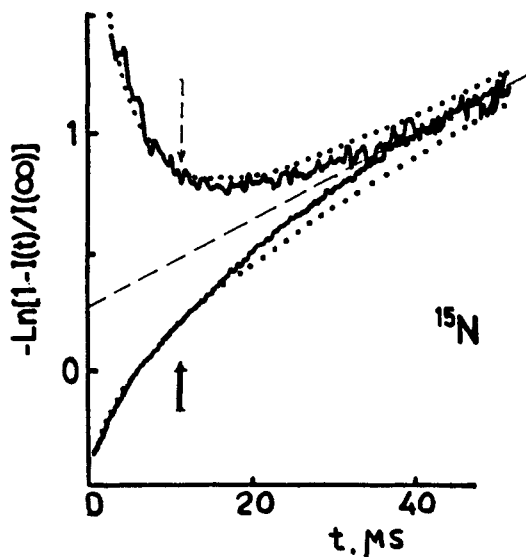


Fig. 10. Kinetics curves of saturation transfer. Conditions of excitation correspond to Fig.9b. The lower curve — recovery at the excitation site (arrow 1); the upper one — at the site, denoted by arrow 2 in Fig. 9.

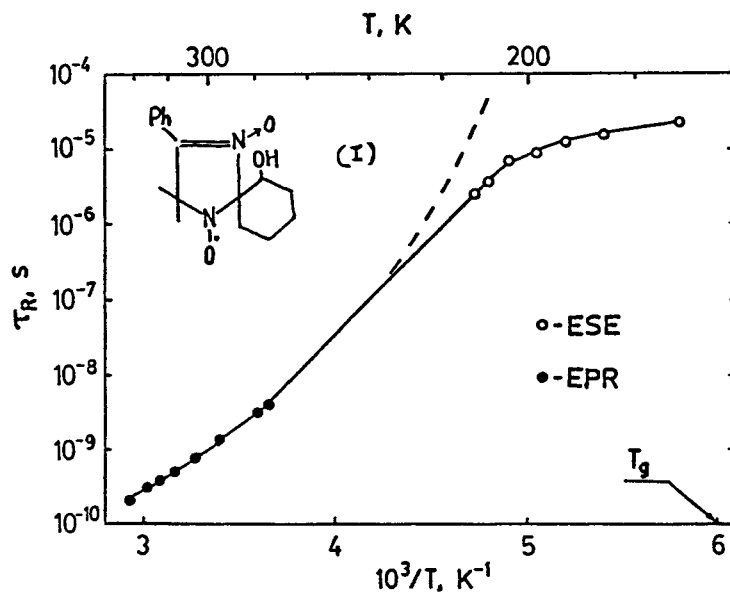


Fig. 11. Temperature dependence of the rotation time τ_R for nitroxide radical (1) in dibutyl phthalate (ESR and ESE data).

The temperature dependence of τ_R was investigated within a wide temperature range, the results for one of the nitroxides is shown in Fig. 11. Included are the results obtained by CW ESR technique. The dashed line shows an assumed temperature dependence that holds when the Stokes-Einstein law is valid (in this law the rotation time is proportional to the viscosity/temperature ratio). A substantial deviation from the Stokes-Einstein law was observed at low temperatures (large viscosities). In other words, an abnormally high molecular mobility was detected. Similar results were obtained by studying other supercooled liquids containing the diluted nitroxide radicals. The abnormal temperature dependence is believed to be caused by the peculiarities in the glass structure (for details see review [16]).

The theoretical calculations of the magnetization transfer in the ESR spectrum of the nitroxide radicals for the jump-rotational model and continuous diffusion model of rotation were performed by Maryasov and Salikhov [13]. These authors have taken into account the rotationally-induced fluctuations in quantization axis for nitrogen nuclear spin. A detailed comparison between theory and experiment was performed in [16,17]. None of the models discussed is shown to agree with experiment. These models fail to account for the main feature of the magnetization transfer in the ESR spectrum: that is highly efficient transfer between the lines of different components corresponding to the same orientations. An agreement between theory and experiment may be achieved [16,17] by eliminating one of the main assumptions of the models proposed, i.e. the molecule may acquire any orientation in the unit cell with equal probability which is not valid for the crystals and, probably, for viscous liquids and glasses.

Liquids and glasses are known to preserve a short-range order for molecular lattice structure. Hence, the development of simple concepts on the mechanism of molecular reorientations may result in a model where the rotations occur within a set of several fixed orientations. Their existence is justified by the fact that most molecules in glass experience a completely rigid (for a microsecond time range) lattice.

The simplest model of fixed molecular reorientations is the model of transitions between only two orientations. In the general case the probability of staying in one of them may be different. This model allows an accurate numerical solution for the magnetization transfer kinetics in the ESR spectra. Comparison between experiment and calculation proved [17] that using this model all the peculiarities of the experimental results for spin probes in viscous liquids and glasses may be explained.

5. Conclusion

The pulsed techniques based on ESR have considerably widened the possibilities of the ESR spectroscopy allowing the studies of slow molecular mo-

tions. The correlation times τ_c of the motions determined in the X-band CW ESR are in the region $10^{-7} - 10^{-10}$ s and are extended in the region of fast motion in the mm-band ESR up to 10^{-11} s. A much wider region $10^{-7} - 10^{-3}$ s is accessible for the pulsed methods based on ESR. The main advantage is the high simplicity of interpretation, the independent determination of T_1 and T_2 . It is also noteworthy that in the regions of fast $\tau_c < 10^{-9}$ s and slow $\tau_c > 10^{-7}$ s motion one may use the methods of two-dimensional ESE spectroscopy developed by Freed *et al.* [18–20].

References

- [1] Salikhov, K.M., Semenov, A.G., Tsvetkov, Yu.D.: Electron Spin Echo and Its Application, Novosibirsk: Nauka 1976.
- [2] Zhidomirov, G.M., Salikhov, K.M.: J. Exper. Theor. Phys. (Rus) **56**, 1933 (1969)
- [3] Kispert, L.D., Bowman, M.K., Norris, J.R., Brown, M.S.: J. Chem. Phys. **76**(1), 26 (1982)
- [4] Stillman, A.E., Schwartz, L.J., Freed, J.H.: J. Chem. Phys. **73**(7), 1 (1980)
- [5] Brown, I.M., in: Time Domain Electron Spin Resonance, (Kevan, L., Schwartz, R.N., eds.), N-J: Wiley 1979.
- [6] Dzuba, S.A., Salikhov, K.M., Tsvetkov, Yu.D.: Chem. Phys. Lett. **79**, 568 (1981)
- [7] Shushakov, O.A., Dzuba, S.A., Tsvetkov, Yu.D.: Chem. Phys. (Rus) **1**, 428 (1982)
- [8] Ohigashi, H., Kurita, J.: Bull. Chem. Soc. Japan **41**, 275 (1968)
- [9] Tolles, W.M., Crawford, L.P., Valenti, J.L.: J. Chem. Phys. **49**, 4748 (1968)
- [10] Miyagawa, I., Iton, K.: J. Chem. Phys. **36**, 2157 (1962)
- [11] Horsfield, A., Morton, J.R., Whiffen, D.H.: Mol. Phys. **5**, 115 (1962)
- [12] Dzuba, S.A., Tsvetkov, Yu.D.: Chem. Phys. (Rus) **1**, 1197 (1982)
- [13] Maryasov, A.G., Dzuba, S.A., Salikhov, K.M., Tsvetkov, Yu.D.: J. Magn. Res. **58**, 95 (1984)
- [14] Shushakov, O.A., Dzuba, S.A., Tsvetkov, Yu.D.: Chem. Phys. (Rus) **3**, 1705 (1984)
- [15] Rengan, S.K., Bhagat, V.R., Sastry, V.S.S., Venkataraman, B.: J. Magn. Res. **33**, 227 (1979)
- [16] Dzuba, S.A., Tsvetkov, Yu.D.: J. Struct. Chem. (Rus) **28**, 15 (1987)
- [17] Dzuba, S.A., Tsvetkov, Yu.D.: Chem. Phys. **120**, 291 (1988)
- [18] Millhauser, G.L., Freed, J.H.: J. Chem. Phys. **81**, 37 (1984)
- [19] Kar, L., Millhauser, G.L., Freed, J.H.: J. Chem. Phys. **88**, 3951 (1984)
- [20] Schwartz, L.J., Millhauser, G.L., Freed, J.H.: Chem. Phys. Lett. **127**, 60 (1986)

Author's address: Dr. S.A.Dzuba, Institute of Chemical Kinetics and Combustion of the Academy of Sciences of the USSR, Novosibirsk 630090, USSR.