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ON THE NATURE OF SPIN-LATTICE INTERACTION

IN MAGNETICALLY DILUTED FREE RADICALS

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1. In magnetically diluted solid free radicals, the influence of pairwise (i.e., magnetic dipole-dipole and exchange) interactions on the relaxation of electron magnetization becomes negligible. This is already evident from the fact that, in the limit of low concentrations of free-radical molecules in a solid (of the order of 10^{-3} mole/l), the relaxation times no longer depend on concentration. It is therefore clear that spin-lattice relaxation in magnetically diluted free radicals is effected by direct interaction of the magnetic molecule with its surroundings.

A specific mechanism of such interaction for radicals in molecular crystals was proposed in the work of I. V. Aleksandrov and G. M. Zhidomirov (1). They consider that the interaction of the spin of the unpaired electron with vibrations of individual atoms of the radical makes a smaller contribution to relaxation than does the interaction of the spin with orientational motions of the radical molecule as a whole. Evidently, orientational vibrations modulate the anisotropic terms in the spin Hamiltonian of the unpaired electron. The resulting time-dependent terms in the spin energy (assuming small angles of deviation of the molecule from the equilibrium position) are treated as a perturbation responsible for relaxation transitions, and the probability of these transitions is estimated. The expressions obtained in (1) for the probabilities of relaxation transitions contain parameters whose experimental determination is extremely difficult, and therefore they are hardly applicable for quantitative calculations. For what follows, however, the essential point is only that the probability W_p of a direct transition with absorption of one orientational phonon is proportional to the absolute temperature

$$W_\mathrm{p} \sim T \tag{1}$$

whereas the probability W_k of a combination transition involving two orientational phonons is proportional to the square of the temperature

$$W_{\mathrm{k}} \sim T^2 \tag{2}$$

provided that $\hbar\Omega \ll kT$ (Ω is the frequency of the rotational vibration of an individual molecule).

We studied electron paramagnetic resonance (EPR) in solid (supercooled) solutions of the free radicals α,α-diphenyl-β-picrylhydrazyl (DPPH) and 2,2,6,6-tetramethylpentamethylene nitroxide (TMPNO). Methanol, ethanol, benzene, toluene, and also mixtures of the indicated alcohols with glycerol and with water were used as solvents. The supercooled glassy state is obtained by freezing alcoholic solutions. In nonpolar solutions, however, it was possible to obtain the supercooled state only in a highly viscous polystyrene medium. The study of EPR spectra in supercooled solutions has the advantage that it makes it comparatively easy to investigate the anisotropic part of the hyperfine structure (h.f.s.) and thereby to reveal the influence of different solvents (2). In addition, the possibility of rapidly preparing frozen solutions be-

becomes especially important in the study of unstable radicals. Although supercooled solutions may differ in structure from the molecular crystals considered in the work of I. V. Aleksandrov and G. M. Zhidomirov (1), nevertheless one may hope that the theory of spin-lattice relaxation developed in (1) is also applicable to frozen solutions of free radicals. In fact, this requires only that the molecules of the free radical take part in motion similar to orientational vibrations. Therefore, studying the temperature dependence of the relaxation times makes it possible to judge the mechanism of spin-lattice interaction of free radicals in a solid.

Measurements of the relaxation times were carried out on a standard RE-1301 radiospectrometer ($\nu = 9320$ MHz) by the continuous-saturation method. The longitudinal relaxation time T_1 was calculated from the well-known Bloch formula

$$Z = (1 + 0.25\gamma^2 H_1^2 T_1 T_2)^{-1}, \tag{3}$$

where Z is the saturation factor, γ is the gyromagnetic ratio, and H_1 is the amplitude of the alternating magnetic field. The transverse relaxation time T_1 was determined from the observed line width. Since the parameters Z and H_2 can be determined experimentally, formula (3) makes it possible to calculate the values of T_1.

Table 1

Values of the spin-lattice relaxation times T_1 (in seconds) in supercooled solutions of DPPH and TMPMOA
($C = 10^{-2}$—10^{-3} **mol/l**)

Fig. 1

Figure 1: Fig. 1

Radical	$T = 77°$K	$T = 170$—$200°$K
DPPH	$> 10^{-3}$	$2.1 \cdot 10^{-4}$
DPPH $+ 0.04 CoCl_2 \cdot 6H_2O$	$2 \cdot 10^{-6}$	–
TMPMOA	$8 \cdot 10^{-6}$	$1.2 \cdot 10^{-6}$

Measurements showed that the spin-lattice relaxation times in supercooled solutions with a radical content of 10^{-2}—10^{-3} mol/l do not depend on the concentration or on the nature of the solvent.

Fig. 1. Saturation of the EPR signal in a methanol solution of DPPH at 77°K (*a*), and the same DPPH spectrum with addition of 0.04 mol/l $CoCl_2 \cdot 6H_2O$ (*b*).

The obtained values of T_1 are presented in Table 1. We note that at 77°K, in solid DPPH solutions the EPR lines are strongly saturated even at the minimum power available on the RE-1301. In this case we were able to estimate only the lower limit of T_1. It was found, however, that the relaxation time T_1 of the radical in the supercooled state can be artificially shortened by adding a certain amount of $CoCl_2 \cdot 6H_2O$ to the initial solution. Thus, in a 0.01 mol/l methanol solution of the radical with an admixture of 0.04 mol/l $CoCl_2 \cdot 6H_2O$, the EPR signal from DPPH molecules was observed at 77°K without any signs of saturation even at higher microwave-field powers (Fig. 1). At the same time, as is known (3), no EPR signal from Co^{2+} ions is observed because of the extremely short relaxation time (10^{-10}—10^{-11} s). In this sense, Co^{2+} ions are especially convenient for increasing the internal magnetic fields in a sample in those cases when the magnetic ions or molecules being studied have very long relaxation times (4).

As can be seen from the data in Table 1, the temperature dependence of T_1 does not contradict (1) and (2). If, furthermore, one takes into account that the smaller TMPMOA molecules exhibit shorter relaxation times T_1, then one may apparently conclude that the mechanism proposed by I. V. Aleksandrov and G. M. Zhidomirov (1) can provide spin-lattice relaxation in solid solutions of free radicals.

In light of the foregoing, the mechanism of spin-lattice relaxation in oils becomes clear. As is known (^{5}), paramagnetic resonance absorption in oils is due to magnetic centers of the radical type and to compounds of tetravalent vanadium. It was shown earlier (^{5}) that the magnetic centers in oils are concentrated in colloidal particles of asphaltenes, and that their concentration is comparatively small (less than 10^{-3} mole/l). Since the colloidal particles are rather large (average molecular weight about 40,000) and are suspended in a very viscous medium, the influence of Brownian motion on relaxation may be neglected. Moreover, one should expect that in such systems spin-lattice relaxation must be provided by the same interactions as in a solid. Therefore, in accordance with (1), long T_1 times may be expected for radical centers in asphaltenes. This is indeed observed in oils not containing vanadium. Thus, in Syryan oil the time $T_1 = 8 \cdot 10^{-6}$ sec at 300° K and $T_1 \gtrsim 10^{-4}$ sec at 77° K. In the presence of magnetic ions (V^{4+} and others), however, the relaxation times for centers of the radical type are considerably shortened. For example, in an oil containing about 0.003% of compounds of tetravalent vanadium, $T_1 = 2 \cdot 10^{-6}$ sec at 77° K. In their shortening effect on relaxation times, V^{4+} compounds are analogous to the above-mentioned action of $CoCl_2 \cdot 6H_2O$ in frozen free radicals. We therefore believe that the main reason for the great diversity of the measured values of T_1 for radical centers in oils (values from 10^{-4} to 10^{-6} sec are cited in the literature ([6])) is the difference in the concentrations of magnetic ions (V^{4+} and others) in the samples studied.

2. As regards spin-lattice interaction in dilute liquid solutions of free radicals, here relaxation of the electronic magnetization may occur: 1) owing to modulation of the anisotropic part of the spin energy of the radical molecule by Brownian motion (the McConnell mechanism) ([7]), and 2) owing to exchange interaction that has time to become established upon collision of radical molecules (the Heitler—Teller mechanism) ([8,9]).

We measured relaxation times in liquid solutions of TMPOA. The measurements were carried out at a frequency $\nu = 460$ MHz by the method described above. Methanol, ethanol and their mixture with water, and benzene, toluene, and chloroform were used as solvents. It had previously been established ([10]) that solvents of the first group form a more or less stable solvation shell around the radical molecule, whereas the second group of solvents does not form a solvation shell.

Measurement of the spin-lattice relaxation times showed that in polar solutions $T_1 = 3.6 \cdot 10^{-7}$ and $7.2 \cdot 10^{-7}$ sec at 300 and 230° K, whereas the corresponding values of T_1 in nonpolar solutions at the same TMPOA concentration (10^{-3} mole/l) are $0.8 \cdot 10^{-7}$ and $1.4 \cdot 10^{-7}$ sec. These data indicate that collisions are less effective in relaxation for solvated radical molecules than for nonsolvated molecules; this is quite natural if one takes into account that the solvation shell prevents overlap of the clouds of unpaired electrons during collisions. We also see that even at concentrations $\sim 10^{-3}$ mole/l, collisions provide more effective relaxation for nonsolvated radical molecules than Brownian rotation of these molecules in a liquid solution. This is also confirmed by the peculiar dependence, noted by us, of the intensity of the EPR signal on the concentration of radical molecules in the range 10^{-3}–10^{-6} mole/l. Namely, the integral signal intensity (beginning from $\sim 5 \cdot 10^{-3}$ mole/l) decreases not in proportion to the concentration, but considerably more strongly. It is evident that at low concentrations collisions occur extremely rarely (the number of pair collisions is proportional to C'). One may therefore suppose that isolated radical molecules, which relax by the McConnell mechanism, have excessively long relaxation times (direct-

A direct calculation of T_1 for DPPH and TMPMOA by McConnell gives $T_1 \gtrsim 10^{-3}$ sec.) and they become saturated even at low microwave-field powers, without participating in the formation of the EPR signal.

Thus, we conclude that in liquid solutions of free radicals the mechanism of spin-lattice relaxation depends substantially on the nature of the solvent.

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CITED LITERATURE

1. I. V. Aleksandrov, G. M. Zhidomirov, ZhETF, **41**, 127 (1961).
2. G. S. Garif' yanov, A. V. Il' yasov, Yu. V. Yablokov, DAN, **149**, No. 4 (1963).
3. N. S. Garif' yanov, DAN, **103**, 41 (1955).
4. N. S. Garif' yanov, V. N. Fedotov, R. Kh. Timerov, Fiz. tverd. tela, **4**, 96 (1962).
5. A. V. Il' yasov, N. S. Garif' yanov, Yu. M. Ryzhmanov, Khimiya i tekhnol. topliv i masel, **1**, 28 (1961); A. V. Il' yasov, ibid., **9**, 63 (1962).
6. T. F. Yen, J. G. Erdman, A. J. Saraceno, Anal. Chem., **34**, 694 (1962).
7. H. M. McConnel, J. Chem. Phys., **25**, 709 (1956).
8. G. E. Pake, T. R. Tuttle, Phys. Rev. Let., **3**, 423 (1959).
9. D. Kivelson, J. Chem. Phys., **33**, 1094 (1960).
10. A. V. Il' yasov, Zhurn. strukturn. khim., **3**, 95 (1962).