ELECTRON PARAMAGNETIC RESONANCE IN CONCENTRATED SOLUTIONS OF α,α-DIPHENYL-β-PICRYLHYDRAZYL

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Abstract

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ELECTRON PARAMAGNETIC RESONANCE IN CONCENTRATED SOLUTIONS OF α,α-DIPHENYL-β-PICRYLHYDRAZYL

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Since in concentrated solutions of α,α-diphenyl-β-picrylhydrazyl (DPPH) there are appreciable exchange interactions, in order to determine the role of exchange in relaxation it is of interest to investigate the dependence of the relaxation times T_1 and T_2 on concentration. At a frequency $\nu = 460$ Mc/s, by the method of continuous saturation, we measured the values of T_1 and T_2 for DPPH solutions with concentration (C) from 0.17 to 0.025 mole/l over the temperature interval 240–320°K. Benzene, toluene, and chloroform were used as solvents. The solutions were placed in the measuring coil of the generator in sealed ampoules, from which the air had previously been pumped out. In the DPPH solutions investigated, the exchange interaction removes the hyperfine structure (h.f.s.), and therefore a single line of paramagnetic absorption is observed. In the most concentrated solution ($C = 0.17$ mole/l) the single absorption line has a width between inflection points $\delta H = 4.3$ oersted. The ratio $\langle \Delta H^4 \rangle^{1/4} / \langle \Delta H^2 \rangle^{1/2} = 1.38$ indicates a Lorentzian form of the absorption curve. In a solution with DPPH concentration $C = 0.025$ mole/l, the exchange interaction is weakened to such an extent that signs of h.f.s. appear; as a result the line broadens at the base.

The time T_2 was calculated from the relation

$$T_2 = \frac{1}{\pi \sqrt{3}\, \delta\nu}, \tag{1}$$

where $\delta\nu$ is the line width expressed in frequency units.

The relaxation time T_1 was determined from the saturation formula

$$Z = \left(1 + 0.25 \gamma^2 H_\nu^2 T_1 T_2\right)^{-1}, \tag{2}$$

where Z is the saturation factor, γ is the gyromagnetic ratio, and H_ν is the amplitude of the high-frequency magnetic field. The magnitude of H_ν was measured with the aid of polycrystalline DPPH obtained from a chloroform solution.

From the results of previous investigations (1) it may be assumed that the molecules of crystalline DPPH obtained from chloroform, in the solutions we studied, are found only in the environment of molecules of the solvent used. In all non-degassed DPPH solutions the oxygen of the air shortens both T_1 and T_2, with T_1 proving to be much shorter than in the case of solid deoxygenated DPPH. The influence of oxygen on T_1 and T_2 was also noted for crystalline DPPH (1).

As is evident from the data in Table 1, the nature of the solvent does not affect the relaxation times of DPPH. The small differences in the values of T_1 and T_2 for the corresponding DPPH concentrations in benzene, toluene, and chloroform solutions lie within the limits of experimental error. In the most concentrated solution ($C = 0.17$ mole/l) the relaxation times T_1 and T_2 are of the same order of magnitude, which indicates a strong exchange interaction. With decreasing concentration, T_1 becomes longer than T_2. The increase in the ratio T_1/T_2, as well as the appearance of a temperature dependence of relaxation times indicates a gradual weakening of the exchange interactions. As is seen from Fig. 1, the values of T_1 for the solution with DPPH concentration $C = 0.17$ mol/l change only insignificantly in the temperature range 240—320° K. Upon dilution of the solutions, the temperature dependence of the relaxation times increases, and in the solution with $C = 0.05$ mol/l it becomes already rather strong.

Table 1

Values of the relaxation times T_1 and T_2 in DPPH solutions at $T = 300°$ K

Solvent	DPPH, mol/l	$T_1 \cdot 10^7$, sec	$T_2 \cdot 10^8$, sec	T_1/T_2	Solvent	DPPH, mol/l	$T_1 \cdot 10^7$, sec	$T_2 \cdot 10^8$, sec	T_1/T_2
Benzene	0.1	2.6	0.8	32.5	Toluene	0.07	3.8	0.63	60
Benzene	0.07	3.8	0.63	60.4	Toluene	0.05	4.6	0.57	81
Benzene	0.05	4.4	0.59	74.6	Chloroform	0.17	0.7	1.47	4.8
Benzene	0.025				Chloroform	0.1	2.1	0.85	24.7
Toluene	0.17	0.8	1.5	5.3	Chloroform	0.07	3.8	0.65	58.5
Toluene	0.1	2.6	0.74	35.1	Chloroform	0.05	4.2	0.57	73.7

The results obtained, as in the case of solid DPPH solutions (2), can be interpreted with the aid of the Blombergen-Wang heat-reservoir model (3). In the most concentrated solution, where the exchange interaction is large, the energy absorbed by the Zeeman system is transferred to the exchange system with relaxation time $T_1 \approx T_2$. The time T_1 plays the role of the spin-lattice time, while T_2 is the spin-spin relaxation time for ordinary paramagnets. The temperature independence of the relaxation times shows that they are not connected with the Brownian motion of the paramagnetic molecules. With dilution the exchange

Fig. 1. Dependence of relaxation time T_1 (sec) on concentration. 1 $-T = 320°$ K, 2 $-T = 300°$, 3 $-T = 273°$, 4 $-T = 240°$

Figure 1: Fig. 1. Dependence of relaxation time T_1 (sec) on concentration. 1 $-T = 320°$ K, 2 $-T = 300°$, 3 $-T = 273°$, 4 $-T = 240°$

decreases, and the role of relaxation occurring due to the Brownian motion of the radical molecules increases.

Fig. 1. Dependence of relaxation time T_1 (sec) on concentration. 1 $-T = 320°$ K, 2 $-T = 300°$, 3 $-T = 273°$, 4 $-T = 240°$

Under very strong exchange, when exchange narrowing predominates over narrowing due to motion ($\omega_e^2 \tau_c^2 \gg 1$), according to Kivelson's theory (^{4}), one should expect a difference in the width of the lines measured at the Zeeman frequency $\omega_0 < \omega_e$ and $\omega_0 \geqslant \omega_e$, where ω_e is the exchange frequency. Our measurements of the EPR line width of a DPPH solution at $C = 0.17$ mol/l at the frequency 9320 MHz gave the value $\delta H = 4.3$ Oe, not differing from δH, measured at $\nu = 460$ MHz. It follows from this that in this solution the exchange frequency is $\omega_e \gg 10^{10}$ sec^{-1}.

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