

STUDY OF ELECTRON SPIN RESONANCE SPECTRUM OF RECRYSTALLIZED FREE RADICAL SAMPLE AT LOW FIELD

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The width and shape of ESR line of 1,1-diphenyl-2-picryl hydrazyl (DPPH) and its recrystallized sample from methylene chloride have been determined at different temperatures. The ESR line of this recrystallized sample has been found narrower than that of the free radical itself. The Kubo and Tomita theory of ESR line width has been utilized to evaluate the various line width parameters at room temperature. The temperature variation of line width has been utilized to calculate the effective exchange frequency at different temperatures. The variation of line width with temperature has been found in accordance with an empirical formula.

1. Introduction

It is known from earlier ESR study [1-6] that samples of DPPH free radical recrystallized from various solvents show both broader and narrower ESR lines of Lorentzian shape. The changes thus produced in line width have been utilized to explain the possible interactions present in the system. In view of this interest, in the present paper, the ESR spectra of DPPH and its recrystallized sample from methylene chloride have been studied at 19.3 MHz and at different temperatures. We have used the Kubo and Tomita theory of ESR line widths to interpret the experimental data as well as to evaluate the effective exchange frequency at different temperatures. It has also been found that the motional effects also take part in controlling the temperature dependence of the ESR line widths. An empirical formula for line width variation has also been used.

2. Experimental technique and method of measurements

The free radical 1,1-diphenyl-2-picryl hydrazyl (DPPH) obtained from Fluka, Switzerland has been recrystallized with an analar grade solvent namely methylene chloride by slow evaporation technique. The recrystallized sample was placed in a vacuum desiccator

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under continuous pumping for twenty four hours just to remove the loosely attached solvent molecules and the sample was found to be more in weight than that of the free radical used. Microchemical analysis of this sample has also been performed together with density and melting point measurements.

An rf ESR spectrometer working at 19.3 MHz consisting of a Clapp-type oscillator and a pair of Helmholtz coils has been used here, the details of which has been described elsewhere [7, 8]. The sample was kept for a long time in thermostat and the temperature of the bath was measured with the help of properly calibrated copper constantan thermocouple. The ESR spectra have been photographed from an oscillograph display. The measurements of the line shape and line width have been made after enlarging the photographs.

3. Results and discussion

The data of microchemical analysis, density, melting point, colour and ESR line width at different temperature are given in Table I.

TABLE I

Sample	Colour	Density ρ [g/cm ³]	Melting point [°C]	Ratio of free radical to solvent by weight	Full width at half-power points ($\Delta H_{1/2}$) [Oe]			
					300K	273K	201K	90K
DPPH powder	Deep violet	1.29	137	...	1.82	2.10	2.33	2.66
Powdered recrystallized sample of DPPH from methylene chloride	Dark brown	1.54	85	1:1	1.65	1.77	1.86	2.14

Line shape: The normalized line shape graphs of DPPH and its recrystallized sample have been plotted at 300, 273, 201 and 90 K with the help of the line shape expressions given below.

For Lorentzian shape $I(H)/I_{\max} = \{1 + 4[(H_0 - H)/\Delta H_{1/2}]^2\}^{-1}$.

For Gaussian shape $I(H)/I_{\max} = \exp\{-4 \ln 2[(H_0 - H)/\Delta H_{1/2}]^2\}$.

All the lines have been found to be of Lorentzian shape. One representative plot at 90 K is shown in Fig. 1. The presence of Lorentzian shape similar to that of the parent free radical DPPH shows that the factors responsible for the shape of ESR lines have not changed even after recrystallization and cooling. Many workers [3, 4, 8] have shown that DPPH and its recrystallized samples have Lorentzian ESR line shape over a wide frequency and temperature range.

Line width: The line width of the recrystallized sample has been found narrower than that of DPPH. Similar type of the effect has already been observed by Singer [4].

The width of ESR line mainly depends on dipole-dipole interaction, spin-lattice and exchange interactions. The latter plays a greater role in modifying the width of the line. The change in line width of the recrystallized sample shows that interactions responsible for the line width of the parent free radical have been modified after its recrystallization from methylene chloride. The theory of ESR line width has been developed by Van Vleck [9], Anderson and Weiss [10] and Kubo and Tomita [11]. Since the line width

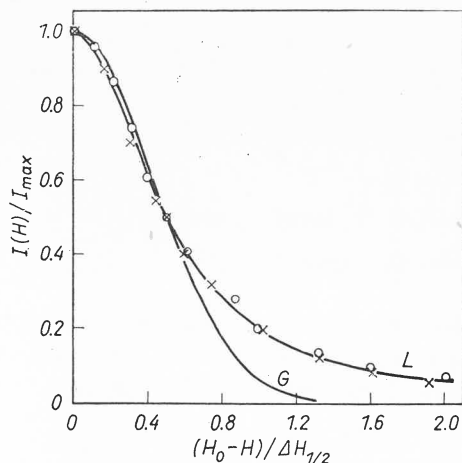


Fig. 1. Plot of calculated values of $I(H)/I_{\max}$ versus $(H_0 - H)/\Delta H_{1/2}$ along with the observed values in the case of DPPH and its recrystallized samples. — — — theoretical Lorentzian and Gaussian line shapes
 ○ ○ ○ — observed points for pure DPPH powder, × × × — observed points for the complex of DPPH recrystallized from methylene chloride

calculated on the basis of Kubo and Tomita theory for DPPH agreed very well with the experimental value, the same theory has been used for evaluating ESR parameters for the recrystallized sample. The expressions given by Chirkov and Kokin [12] obtained from the Kubo and Tomita theory, are given below. The half-width between half-power points:

$$\Delta\omega = 4.18 \omega_{10}^2/\omega_{20} \text{ rad/s}$$

where, the dipolar width $\omega_{10}^2 = 3.97 g^4 \beta^4 \hbar^{-2} d^{-6} \text{ rad}^2 \text{ s}^{-2}$. The exchange frequency $\omega_{20} = 3.65 |J|/\hbar \text{ rad s}^{-1}$ and exchange integral $J = k\theta/12J$. g is the spectroscopic splitting factor, β is the Bohr magneton, k is the Boltzmann constant and θ is the asymptotic Curie temperature. Since the crystal structure of the sample is not known, it can be assumed in a very rough approximation that it has a simple cubic lattice structure. Then

$$\sum_k r_{jk}^{-6} = 8.4 d^{-6}$$

where d is the lattice constant for the crystal and

$$r_{jk}^{-3} = Nm\rho/M$$

where N , m , ρ and M are Avogadro's number, mass of the free radical in one gram of the complex, density of the complex and molecular weight of DPPH respectively. Assuming

a simple cubic lattice and the existence of one unpaired electron in each free radical molecule, the average spin distance of DPPH comes out to be 7.98 Å. The value of asymptotic Curie temperature of DPPH is taken as -10 K [7, 12]. The calculated value of ω_{10}^2 and

TABLE II

Calculated values of ω_{10}^2 , ω_{20} , $|J|$ and θ at room temperature

Sample	$\Delta\omega$ [rad s ⁻¹]	g^1	ω_{10}^2 [rad ² s ⁻²]	ω_{20} [rad s ⁻¹]	$ J $ [J]	θ [K]
DPPH powder	1.60×10^7	2.0036	11.20×10^{17}	29.22×10^{10}	84.40×10^{-25}	7.34
Powdered recrystallized sample of DPPH from methylene chloride	1.45×10^7	2.0035	4.01×10^{17}	11.58×10^{10}	33.45×10^{-25}	2.91

¹ Measured at X-band. Separate communication.

the measured values of $\Delta\omega$ have been used to calculate the exchange frequency ω_{20} and finally this has been used to evaluate $|J|$ and θ at room temperature. All the results of DPPH and its recrystallized sample are given in Table II.

4. Temperature variation of line width

The variation of line width with temperature has been shown in Fig. 2. The nature of the variation of line width can be represented by the empirical formula [8]

$$\Delta H_{1/2} = A + (B/T) + (C/T^{1/2})$$

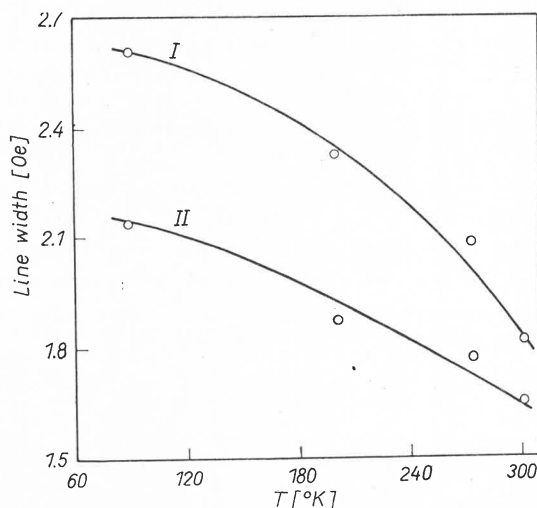


Fig. 2. Variation of line width ($\Delta H_{1/2}$) with temperature of DPPH (I) and its complex recrystallized from methylene chloride (II)

The observed values of line width fit a curve of the form given above for DPPH as well as its recrystallized sample with different values of A , B , and C given in Table III. The empirical formula $\Delta H_{1/2} = 47 + 35700/T$ has been suggested by Bruin and Bruin [7] for the variation of line width of DPPH powder from 200 K to 300 K. It has been suggested by the authors that the first part of the variation which is independent of temperature may be due to the exchange interaction and the second part which is inversely proportional

TABLE III
Values of A , B and C in the same arbitrary units determined by the least-squares method

Sample	A	B	C
DPPH powder	-2.60	-584.27	+111.47
DPPH recrystallized from methylene chloride	+0.21	-151.40	+ 34.30

TABLE IV
Variation of exchange frequency ω_{20} (in 10^{10} rad s^{-1}) and exchange integral J (in $10^{-25}J$) with temperature

Sample	300 K		273 K		201 K		90 K	
	ω_{20}	J	ω_{20}	J	ω_{20}	J	ω_{20}	J
DPPH powder	29.22	84.40	25.33	73.17	22.82	65.91	20.03	57.84
Powdered recrystallized sample of DPPH from methylene chloride	11.58	33.45	10.77	31.12	10.25	29.61	8.94	25.81

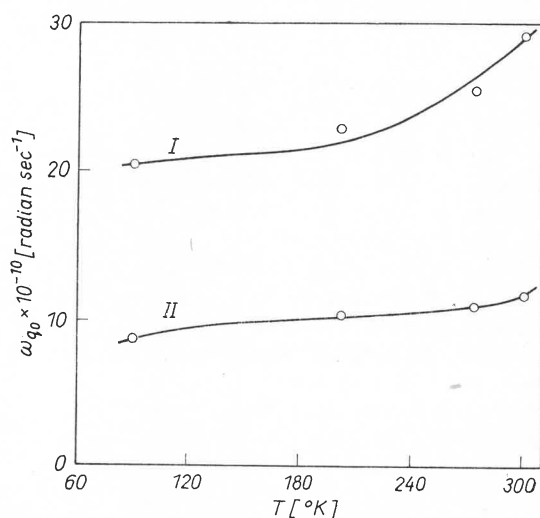


Fig. 3. Variation of exchange frequency with temperature of DPPH (I) and its complex recrystallized from methylene chloride (II)

of the temperature may probably be due to the influence of the molecular motion on the narrowing process.

The dipolar part of the line width is independent of temperature because $\hbar\omega_{nm} \ll kT$, and hence the variation in line width with temperature may only be due to the variations in effective exchange frequency. At lower temperature, the probability of overlapping the wavefunctions of the electrons decreases and thus a net decrease in exchange frequency may be observed. In order to give a quantitative account, the exchange frequency of DPPH and its recrystallized sample at different temperatures have been calculated by using the observed values $\Delta\omega$ and the calculated values of ω_{10}^2 . The values of exchange frequency and exchange integral at different temperatures are given in Table IV. As expected the exchange frequency has decreased with decreasing temperature and this simply shows that molecular motions freeze out more at lower temperature and the motional narrowing does not show much variations at that temperature. The nature of variation of exchange frequency with temperature is shown in Fig. 3.

5. Conclusions

On the basis of these results it can be concluded that when the free radicals are recrystallized from different solvents, molecular addition complexes are formed resulting in some reduction of exchange interaction which modifies the line width. In general, in such cases the line width is found to be inversely proportional to the temperature whereas the exchange frequency is directly proportional to temperature. The changes produced in the dipolar width and exchange frequency have not been found to be effective in changing the shape of the lines.

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