ESR Line Width and Exchange Narrowing in Powder Samples

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Electron Spin Resonance Spectra of 1-1 Diphenyl-2-Picryl Hydrazyl (DPPH) recrystallized from some aliphatic and aromatic solvents have been studied at room temperature in the X-band region. Measurements of lineshape, linewidth and *g* value were carried out, all the samples being subjected to microchemical analyses with determination of density and melting point. A theoretical study of ESR linewidths has been carried out by means of the Kubo-Tomita theory of ESR linewidth. A quantitative estimation of dipolar width, exchange frequency, exchange integral and asymptotic Curie temperature for each sample was made. A reduction of exchange narrowing has been suggested to be the main cause of broadening.

Earlier ESR studies[1-7] showed that broader ESR lines with a notable change in shape and *g* value are obtained when free radicals are recrystallized from different solvents. In order to make a detailed theoretical study of various interactions, we used powder samples of 1-1 Diphenyl-2-Picryl-Hydrazyl recrystallized from various organic solvents. The changes obtained in ESR parameters have been quantitatively interpreted with the help of the Kubo-Tomita theory of ESR linewidth. The decrease in exchange coupling has been suggested as the main cause of broadening in the lines. The resulting broadening of the lines has been interpreted in terms of the nature and structure of the solvent used for recrystallization.

Experimental Technique and Method of Measurement

A Bruker X-Band BER 402 Reflection type ESR Spectrometer was used. An Alpha NMR Gaussmeter was used for field measurement, and a Hewlett-Packard frequency counter (hp-525-A) and converter (hp-524-B) for frequency measurement.

The powder free radical DPPH (Purum grade, M/s Fluka, Switzerland) was used. This was prepared from the corresponding hydrazine by oxidation in chloroform solution with lead dioxide. The recrystallized samples were prepared by using analytical grade solvents by slow evaporation technique. The density and melting point of each sample was measured. The linewidth, lineshape and *g*-values were determined by the usual method.[3]

Microchemical analysis of the samples was carried out by direct titration of their solutions in pyridine against chlorauric acid (solution of gold chloride in water) using gallocyanine (in glacial acetic acid) solution as an indicator. The colour changes sharply from bluish green to brownish pink at end point. It was observed that the reaction between chlorauric acid and DPPH takes place in the ratio of 1 : 1, confirmed by potentiometric titration.

Results and Discussion

The results of microchemical analysis, density, melting point and ESR parameters such as linewidth and *g* value are given in Table 1.

Line Shape. The shape of ESR lines depends on crystal structure, magnetic dilution and on exchange coupling. The Lorentzian lineshape of the recrystallized samples suggests that the samples are a case of large exchange effect.[9,10] Samples obtained by recrystallization from other solvents have also been reported to show Lorentzian shape of the ESR lines over a wide range of magnetic dilution, frequency and temperature.[11-14]

Line Width. The data in Table 1 indicate that the linewidth of recrystallized powder samples have increased as compared to that of the parent free radical DPPH. This simply suggests that the factors responsible for narrowing the ESR lines have sufficiently reduced after recrystallization of the free radical. It is known that the linewidth from the single crystal of DPPH are highly anisotropic[15,16] changing by as much as a factor of 2. In the polycrystalline sample, a linewidth is averaged out over all orientations of the crystallites with the result that a broader line should be observed. The linewidth of 1.9 Gauss (K-band) for a single crystal of DPPH changes to 3.7 Gauss in powder.[3]

In free radicals, apart from the anisotropy effect, the main causes of linewidth are dipole-dipole and exchange interactions, the latter playing the main role in narrowing the lines. Hence, it can be assumed that the broadening of the lines of the recrystallized sample excluding the anisotropy effect may be due to the change in exchange coupling. A quantitative estimation of the parameters, dipolar broadening and exchange frequency have been made.

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Table 1.

S. No.	Sample	Density gm/ml	Microchemical analysis ratio of DPPH to solvent by wt.	Mp °C	ΔH_{pp} Oersteds	g values	Mean spin distance dÅ
1.	DPPH Powder	1.29	—	137	1.689	2.0036	7.89
	Its sample recrystallized form						
2.	Benzylamine	1.24	1:19.8	70	6.962	2.0036	22.23
3.	Isobutylamine	1.44	1: 6.0	81	6.069	2.0028	14.69
4.	Dibenzylamine	1.33	1:10.0	90	8.071	2.0034	17.56
5.	Benzaldehyde	1.25	1: 5.9	116	5.526	2.0031	15.35
6.	Benzyl chloride	1.36	1: 5.5	110	7.152	2.0036	14.62
7.	2,4-Dinitrofluorobenzene	1.55	1: 4.5	175	7.176	2.0034	13.23
8.	Dimethyl formamide	1.35	1: 3.2	110	6.857	2.0033	12.69
9.	Chlorobenzene	1.53	1: 1.2	116	7.967	2.0033	9.80
10.	Carbon tetrachloride	1.29	1: 1.2	110	2.027	2.0035	10.38
11.	Benzyl alcohol	1.42	1: 1.1	175	7.596	2.0033	9.89
12.	Chloroform	1.47	1: 1.0	105	1.952	2.0036	9.62
13.	Methylene chloride	1.54	1: 1.0	85	2.019	2.0035	9.47
14.	Benzene	1.03	1: 0.7	120	1.864	2.0036	10.26
15.	n-Propyl cyanide	—	1: 0.25	—	5.168	2.0035	—
16.	Di-n-amylamine	1.05	—	145	5.296	2.0037	—
17.	Diallyl amine	1.51	—	230	8.119	2.0037	—

The theory of linewidth has been developed on the basis of these interactions by van Vleck,[9] Anderson and Weiss[10] and Kubo and Tomita.[17] The expressions given by Chirkov and Kokin[18] from the Kubo-Tomita theory have been used for computation:

The half width between half power points

$$\Delta\omega = 4.18\omega_{10}^2/\omega_{20} \text{ radian s}^{-1} \quad (1)$$

ω_{10}^2, the dipolar width $= 3.79\ g^4\beta^4\hbar^{-2}d^{-6}$ radian^2 s^{-2} (2)

ω_{20}, the exchange frequency $= 3.65|J|/\hbar$ radian s^{-1} (3)

and the exchange integral $J = k\theta/12$

where k is the Boltzmann constant, θ is the asymptotic Curie temperature and all other symbols have their usual meanings. Since the crystal structure and hence d^{-6} is not known for all the samples, we assumed as a very rough approximation that the system has a simple cubic structure. Thus

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

where d is the lattice constant for the crystal, and

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

where N is Avogadro's number, ρ is density and M the molecular weight. This gives an average distance of 7.98 Å between the spins in DPPH powder which is comparable with the value obtained from crystal structure data. Data of microchemical analysis and density (Table 1) have been used to evaluate the value of mean spin distance.

The values of dipolar width ω_{10}^2, exchange frequency ω_{20} and half width between half powder points for DPPH have been computed by taking Curie temperature[1,18] $\theta = -10$ K:

$$\omega_{10}^2 = 15.76\times10^{17} \text{ radian}^2 \text{ s}^{-2}$$
$$\omega_{20} = 3.89\times10^{11} \text{ radian s}^{-1}$$
$$\Delta\omega = 16.54\times10^6 \text{ radian s}^{-1}$$

The full width $\Delta H_{1/2} = 2\Delta\omega/r = 1.88$ Oersteds

The dipolar broadening ω_{10}^2 was computed by means of (2). The values of ω_{20} was obtained by means of (1) by utilizing the computed values of ω_{10}^2 and measured values of $\Delta\omega$. With these values, exchange integral J and asymptotic Curie temperature θ were calculated for all samples including DPPH. The results are given in Table 2. The lower values of ω_{20} of DPPH powder indicate that the linewidth has been averaged out due

Table 2. Variation of half width between half power points $\Delta\omega$, dipolar frequency ω_{10}^2 exchange frequency ω_{20}, exchange integral J and Curie temperature θ at room temperature

Sample	$\Delta\omega$ $\times10^{-7}$ a) s^{-1}	ω_{10}^2 $\times10^{-17}$ s^{-2}	ω_{20} $\times10^{-9}$ s^{-1}	$J\times10^{25}$ Joules	$\lvert\theta\rvert$ K
DPPH powder	2.57	11.2	181.9	52.6	4.6
Its samples recrystallized form					
Benzylamine	10.60	<0.1	0.1	<0.1	<0.1
Isobutylamine	9.24	0.3	1.3	0.4	<0.1
Dibenzylamine	12.29	<0.1	0.3	<0.1	<0.1
Benzaldehyde	8.41	0.2	1.1	0.3	<0.1
Benzyl chloride	10.88	0.3	1.1	0.3	<0.1
2,4-Dinitrofluoro benzene	10.93	0.5	2.1	0.6	<0.1
Dimethyl formamide	10.44	0.7	2.8	0.8	<0.1
Chlorobenzene	12.13	3.3	11.3	3.3	0.3
Carbon tetrachloride	3.10	2.3	31.4	9.1	0.8
Benzyl alcohol	11.56	3.0	10.8	3.0	0.3
Chloroform	3.00	3.7	51.6	15.0	1.3
Methylene chloride	3.07	4.0	61.7	18.0	1.6
Benzene	2.84	2.5	36.6	10.6	0.9

a) $\Delta\omega = \gamma\sqrt{3}\ \Delta H_{pp}/2$ (For Lorentzian line shape) and $\gamma = 1.758\times10^7$.

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to the polycrystalline nature of the free radical. The computed values of dipolar width decrease in all the recrystallized samples. The simultaneous decrease in exchange narrowing ω_{20} is sufficiently large. This is also the case in exchange integral J. Thus it can be said that the exchange is more effective in controlling the linewidth. The difference in decrease of exchange coupling for the same magnetic dilution of two different samples is probably controlled by the nature of solvent. The dilution may be due to the permanent inclusion of solvent molecules in the free radical unit cell[19] or a solvent molecule may have associated with the free radical molecule and a molecular addition complex may have formed.[4-6] It can be concluded from the data of microchemical analysis that a greater affinity of complex formation or association was found for the compounds having benzene ring attached with the amino group and chlorine (solvents 2—4). The samples recrystallized from these solvents show a maximum decrease in the exchange coupling. The amino group was found to be more effective in lowering the value of exchange coupling even without benzene ring *viz.* isobutylamine. These form the first category of solvents used here. The second category of solvents include benzyl alcohol and chlorobenzene. The results of their microanalysis do not indicate much dilution but the change in linewidth is comparable with the samples of the first category of solvents. The unexpected broadening present in their ESR lines may be due to the presence of lone pair of electrons on their oxygen and chlorine atoms. The other solvents (Table 1) form the third catagory where the changes in linewidth and exchange coupling parameters are not abnormal and are in agreement with the data on microchemical analysis.

g *Value.* A different value of g has been obtained for different samples. In general, the g value of a substance depends upon many factors such as nuclear and molecular magnetic fields, crystal orientation and applied magnetic field. Crystal orientation has been found to be very effective in DPPH, with the result that a quite measurable anisotropy in the g value of a single crystal of DPPH[3,20] is observed. In polycrystalline sample one gets g factor averaged out over all possible orientations of the polycrystallites present. Hence the changes in g value contain an unknown contribution of g anisotropy and no definite conclusion can be drawn from the change in g value. The change in structure of the free radical responsible for the change in g values does occur[19] after recrystallization of free radical.

Conclusion. The broadening in ESR lines and resulting decrease in exchange coupling depends upon the nature and affinity of the solvents to form complex with the free radical molecule. The changes thus produced in exchange coupling and structure of the free radical due to addition complex formation have not been effective in changing the shape of ESR lines.

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