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ELECTRON SPIN PACKETS IN INHOMOGENEOUSLY BROADENED ESR LINE

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The recently introduced method of detection of electron spin packet lines using double modulation technique has been examined in more detail in order to gain knowledge of its characteristics prior to applications. The theoretical explanation is given for the origin of the double modulation ESR spectrum and previous theoretical treatments are complemented and corrected. The experiments were carried out on irradiated single crystals of tryptamine hydrochloride, malonic acid and succinic acid. The spin packet line intensity exhibitis pronounced saturation behaviour beyond a certain power level. Below the saturation power level the linewidth is constant and increases rapidly at higher microwave power. Temperature studies have revealed that the parameters characterizing the spin packet lines are highly temperature dependent. Hence double modulation technique opens new perspectives in the studies of the molecular and crystal dynamics.

1. *Introduction*

Electron spin resonance (ESR) lines in solids are in general inhomogeneously broadened due to a distribution of local magnetic fields. Portis[1] has conceived inhomogeneously broadened line as an envelope of homogeneous lines called spin packets with a distribution of resonant frequencies. In dilute spin systems, spin packets correspond to the individual spins, while in systems where spins are arranged in clusters with intracluster spin-spin interaction greater than the resonant frequency separations, one may consider that all the spins in a given cluster form a single spin packet[2, 3].

Two interesting problems concerning spin packets within an inhomogeneously broadened line have been given considerable attention. The first was related to the response of the spin system in the case of magnetic field modulation. Weger[4,5] has analyzed numerous modulation conditions among which the most important ones slow passage, adiabatic rapid passage and fast passage. The signal of the inhomogeneous line appears as a convolution of the responses of the individual spin packets. The second point of interest was the width of the individual spin packets. It was measured using the techniques of pulsed ESR by which one could burn a hole in the inhomogeneously broadened line[6–8]. The measured spin packet width was typically two orders of magnitude smaller than the width of the inhomogeneous ESR line. It should be noted, however, that it is practically impossible to burn a hole truly as narrow as the individual spin packets.

Recently, Rakvin et al.[9] have introduced double modulation technique which has enabled measurement of the width of spin packets in inhomogeneously broadened ESR line. In irradiated quartz they found that the spin packet width was only 6.4 kHz, i. e. three orders of magnitude smaller than the width of 5.9 HMz found for the inhomogeneously broadened ESR line. The width of spin packets is a measure of the relaxation time of the off-diagonal density matrix element connecting the two levels involved in the electron spin transition. The possibility of measuring this parameter opens new perspectives in the study of spin interactions in various systems and, in particular, may lead to important applications in the case of the systems which undergo a phase transition at a given temperature. For these reasons it is purposeful to examine the method of double modulation in more detail, which has been the aim of the present work. In particular, we have investigated the effects of saturating microwave field on the spin packet intensity and width in several samples at various modulation frequencies and temperatures.

In subsequent sections we describe first the theoretical and experimental aspects of the double modulation technique and the preparation of the samples chosen for the present study. In the last section we present the experimental results with their interpretation and a discussion.

2. *Methods and samples*

Magnetic field modulation is generally used in ESR in order to improve signal to noise ratio. The theoretical description of the phase detection in a lock-in amplifier of a homogeneous line has been developed starting from the Bloch equations[10], or by using first order time dependent perturbation theory[11]. Physical visualization can best be gained by noting that magnetic field modulation is equivalent to a frequency modulation of the microwave field[10,12]. In the latter case, the microwave field can be considered as a superposition of sideband fields whose amplitudes and relative phases are given by the Bessel functions, while their frequency separations are equal to the modulation frequency[13]. Resonance occurs when one of the sideband fields is within the spectral linewidth. Then, the first harmonic response is due to the perturbation caused by the first neighbour sideband fields on the spin system. The second neighbour fields give rise to the second harmonic of the signal, etc.[12]. Harmonic signal from the inhomogeneously broadened

$$F_{in}^{p} = \sum_{n,n'=-\infty}^{\infty} \mathcal{J}_n(\beta)\,\mathcal{J}_{n+p}(\beta)\,[\mathcal{J}_{n'}(\beta')]^2\,\varrho\,(\delta - n\,\omega_m - n'\,\omega_m'), \tag{1}$$

where $\mathcal{J}$'s are the Bessel functions, $\beta = \gamma\, H_m/\omega_m$ and $\beta' = \gamma\, H_m'/\omega_m'$ are the modulation indices, and ϱ is the usual line shape function for individual spin packets

$$\varrho\,(x) = \frac{T_2}{\pi\,(1 + T_2^2\,x^2)}, \tag{2}$$

where $1/T_2$ is the linewidth parameter. The separation of the microwave frequency ω from the resonance frequency ω_0 of a given spin packet within the inhomogeneously broadened ESR line is denoted by $\delta = \omega - \omega_0$. Eq. (1) predicts resonant response when

$$\delta - n\,\omega_m - n'\,\omega_m' = 0, \tag{3}$$

which means that all the spin packets within the inhomogeneously broadened ESR line whose resonant frequencies are given by

$$\omega_0 = \omega - n\,\omega_m - n'\,\omega_m' \tag{4}$$

should give rise to the harmonic signal. The integers n and n' may go to infinity but appreciable contributions to the signal level are obtained only for values which result in significantly nonvanishing Bessel functions in Eq. (1). In other words, only the spin packets which lie within the modulation width, and satisfy condition (4), contribute significantly to the signal. To each of these spin packets, there corresponds a single term in the sum in Eq. (1). When, by sweeping the second modulation frequency ω_m', one obtains that

$$n\,\omega_m = n'\,\omega_m' \tag{5}$$

for some integers n and n', the spin packets which satisfy the resonant condition (4), do it also for a series of integers altered according to the condition

$$\omega_0 = \omega - n(1-k)\,\omega_m - n'(1+k)\,\omega'_m \tag{6}$$

where k is also an integer (positive or negative). This implies that a given spin packet can contribute more than one resonant term in Eq. (1), and, consequently, the lock-in amplifier will detect a change in the signal level. In particular, for $n' = 1$ double modulation spectrum will consist of peaks at multiples of ω_m.

The above interpretation of double modulation resonances is at variance with the one given previously by Rakvin et al.[9]. Namely, the observed double modulation spectrum was attributed to the response of a single spin packet at $\omega_0 = \omega$. It was considered that inclusion of the other spin packets would result in a broad signal rather than a spectrum with sharp component lines such as that observed, and a quest for a fundamentally different theoretical approach was raised. The present interpretation states clearly that a number of spin packets contribute to the harmonic signal at arbitrary values of ω_m. However, when condition (5) is observed, certain spin packets alter their contributions. In spite of the fact that a multitude of spin packets may be involved, the width of the double modulation resonance should be $1/T_2$, i. e. one observes narrow spin packet lines.

Again, as in the case of the single modulation, physical visualization can best be gained when one notes that double magnetic field modulation is equivalent to double frequency modulation of the microwave field. The latter can be considered as a superposition of sideband fields obtained through a double decomposition so that their amplitudes and relative phases are given by the products of the corresponding Bessel functions. In general, each sideband field is on resonance with one of the spin packets in the inhomogeneously broadened ESR line. However, when the second modulation frequency ω'_m is swept so that condition (5) is reached, certain sideband fields merge in pairs and thus interact with one and the same spin packet. In this simple picture one can easily understand that the width of the double modulation resonance corresponds, indeed, to the width of the spin packets.

In the present work we have used Varian E-109 ESR Spectrometer as the basic instrument. Frequency swept audio signal for the second modulation was provided by PRD 7808 frequency synthesizer and amplified by ENI 3100L 100W broadband power amplifier. The signal from the console of the ESR spectrometer was accumulated in the Hewlett-Packard 5480B Signal Analyzer System and then recorded.

Since the aim of the present work was to gain knowledge about various aspects of the double modulation technique itself, we have chosen to work with a few irradiated organic single crystals which have been extensively studied previously using the standard ESR techniques, e. g. succinic acid[15], malonic acid[15,16], and tryptamine hydrochloride[17].

3. *Results and discussion*

The first question we have raised about the lines detected in double modulation ESR was their dependence on the microwave power. Fig. 1 shows double modula-

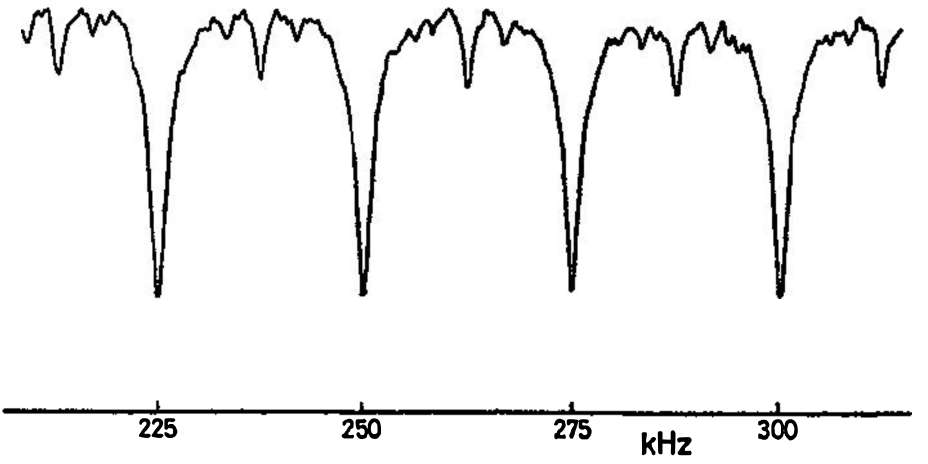

Fig. 1. Double modulation ESR spectrum of free radicals in a single crystals of malonic acid at room temperature. The crystal was irradiated by gamma rays to a dose of 5 Mrad. The fixed modulation frequency was 25 kHz.

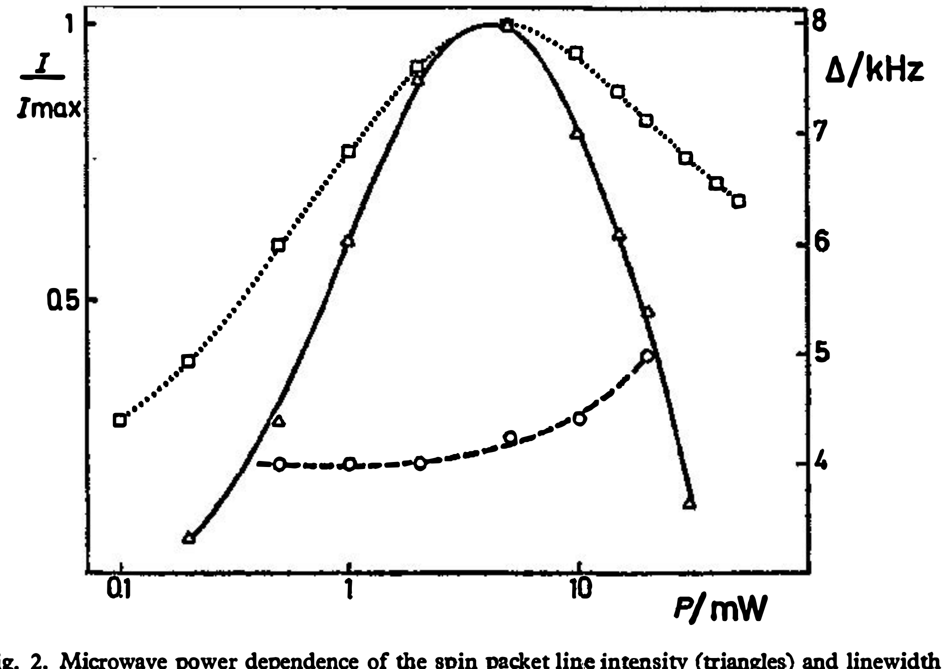

Fig. 2. Microwave power dependence of the spin packet line intensity (triangles) and linewidth (circles) in a single crystal of succinic acid. The line intensity is normalized to its maximum value and scaled on the left vertical axis. The linewidth is scaled on the right vertical axis. Normalized saturation curve for the entire inhomogeneously broadened ESR line (squares) is given for comparison. The crystal was irradiated to a dose of 2 Mrad, and the fixed modulation frequency was 25 kHz.

tion spectrum of malonic acid at room temperature and low microwave power. As the microwave power is increased, the intensity of the lines in the double modulation spectrum increases until a saturation point is reached and then decreases rather rapidly. Fig. 2 shows typical saturation curves for the spin packet lines and for the entire inhomogeneously broadened ESR line. While both lines get saturated at the same microwave power, the former clearly exhibits much sharper saturation phenomenon. Microwave power dependence of the spin packet width is also shown in Fig. 2. Below the saturation point the width is constant and starts to increase rapidly beyond it. Hence, if one wishes to gain knowledge on the transverse relaxation time T_2 due to the spin interactions in the sample, the width of the spin packets should be measured using nonsaturating microwave power.

The next question of interest about the spin packet lines is their temperature dependent behaviour. Generally, as the temperature is reduced from 300 K to 77 K the saturation curve shifts to lower power levels and the linewidths are decreased. Table 1 collects the maxima of the saturation curves and the unsaturated spin packet linewidths for tryptamine hydrochloride, malonic acid and succinic acid at 77 K and 300 K. All the samples were irradiated to the same dose of 5 Mrad. The measurements were made using 50 kHz for fixed modulation frequency. The data in Table 1 show that the saturation point and linewidth are highly temperature dependent. It should be noted also that these parameters vary appreciably from one sample to the other with all the experimental conditions unchanged. This is an additional evidence that the observed resonance are not instrumental artifacts, but depend on the specific spin interactions in the sample.

TABLE 1.

	temperature/K	saturation power/mW	linewidth/kHz
tryptamine hydrochloride	77	0.5	0.9
	300	7	1.7
malonic acid	77	0.7	1
	300	4	3
succinic acid	77	1.2	2.3
	300	13	8.9

All the samples were gamma irradiated to a dose of 5 Mrad.
Saturation power and spin packet linewidths at 77 K and 300 K.

One may notice that the values for succinic acid at 300 K in Table 1 are different from those which can be infered from Fig. 2. Since the only relevant variation is in the radiation dose given to samples, one may conclude that the observed differences are due to a change in the spin interactions as the concentration of the spins increases. Hence, double modulation technique can effectively be used for the studies of the dependence of the spin interactions in the sample on the applied radiation dose. Detailed study of this phenomenon has not been attempted in this work.

The results presented in Table 1 can be related to the pulsed ESR measurements of T_1 in malonic acid by Dalton et al.[18]. It is well known that the linewidth of a homogeneous line is given by[19]

$$\Delta = \frac{1}{\pi}\left(\frac{1}{T_2'} + \frac{1}{2T_1}\right), \tag{7}$$

where $1/T_2'$ represents broadening due to the spin-spin interactions, while the second term in Eq. (7) represents broadening due to spin-lattice interactions which limit the lifetime of the spin states. Since only the latter is temperature dependent, one may write

$$\Delta(300) - \Delta(77) = \frac{1}{2\pi}\left[\frac{1}{T_1(300)} - \frac{1}{T_1(77)}\right]. \tag{8}$$

From Table 1 one finds that the difference in the spin packet linewidths for malonic acid is 2 kHz, while from the temperature dependent curve of T_1[18] one finds the value of 1.4 kHz. The two values are in a very good agreement. The small discrepancies are probably due to different irradiations of the samples. Besides, pulsed ESR technique can never in practice achieve the selectivity of burning a hole truly as narrow as a single spin packet line.

Temperature dependence of the intensities and linewidths of the double modulation spectrum can provide a test of the validity of Eq. (1) and the internal consistency of the method. According to Eq. (1) the signal intensity is proportional to the transverse relaxation time T_2, while the linewidth is inversely proportional to T_2. Since V_2 is the only temperature dependent parameter, the ratio of the signal intensities at two different temperatures should be equal to the inverse ratio of the corresponding linewidths. Care should be taken with the signal intensities since the saturation curve shifts with the temperature. However, in the limit of small microvawe power the saturation curve becomes a straight line whose slope is proportional to T_2. As the temperature of the sample is varied, the slope changes according to the temperature dependence of T_2. Table 2 shows that the agreement of the ratios of T_2 at 77 K and 300 K, found from the slope and linewidth measurements independently, is remarkably good for all the samples. This result confirms the internal consistency of the whole concept of double modulation technique.

TABLE 2.

	$\frac{S(77)}{S(300)}$	$\frac{\Delta(300)}{\Delta(77)}$
tryptamine hydrochloride	2.2	1.9
malonic acid	2.8	3.0
succinic acid	3.7	3.8

The ratios of T_2 at 77 K and 300 K obtained from the signal intensity curve slopes and from the linewidths.

The same measurements as described above were carried out at several other modulation frequencies in the range from 10 kHz to 100 kHz. The same phenomenology was observed at all modulation frequencies. The only important rule to be pointed out was that higher modulation frequency shifted the saturation point to higher power levels.

Transverse relaxation time of spin system is an important indicator of the dynamics of molecular or crystalline systems. Hence, double modulation ESR can be a useful tool in the temperature studies of the dynamics of spin labels[20,21] and other systems.

Lastly, we should mention that the concept of double modulation can be extended to other spectroscopies, too. Thus, we have succeded recently to detect nuclear spin packets in an inhomogeneously broadened ENDOR line using rf frequency double modulation[22].

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ELEKTRONSKO-SPINSKI PAKETI U NEHOMOGENO PROŠIRENOJ ESR LINIJI

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Metoda dvostruke modulacije u ESR spektroskopiji nedavno je upotrijebljena za detekciju spinskih paketa. Na dobro poznatim sistemima, ozračenim organskim kristalima triptamina-hidroklorida, malonske i sukcinske kiseline istražene su mogućnosti primjene ove metode. Osim toga, teorijsko objašnjenje nastanka spektra dvostruke modulacije detaljnije je razrađeno. Opaženo je da se intenzitet linije spinskog paketa zasićuje nakon određene vrijednosti mikrovalne snage. Ispod te vrijednosti širina linije spinskog paketa je konstantna, dok se kod većih mikrovalnih snaga linija proširuje. Temperaturna ispitivanja pokazuju da parametri koji karakteriziraju linije spinskih paketa znatno ovise o temperaturi. Zbog toga tehnika dvostruke modulacije otvara nove perspektive u istraživanju molekularne i kristalne dinamike.