A new non-linear high sensitivity spectroscopy in the slow molecular motion regime

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A new non-linear high sensitivity spectroscopy in the slow molecular motion regime

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The application of doubly modulated E.S.R. (DOMESR) to viscous samples is discussed. An experimental study on a model system is reported which points out, in contrast to E.S.R. spectroscopy the very high sensitivity of DOMESR to slow molecular motions. It is shown that a satisfactory phenomenological interpretation may be given in terms of a dressed atom formalism.

1. Introduction

Polymeric liquid crystals represent a wide class of new materials which are attracting scientists' attention for both fundamental aspects and technological applications [1, 2]. Both ordinary polymers and low molar mass liquid crystals are known to exhibit peculiar properties. The first attempts to hybridize them by synthesizing polymers including mesogenic rigid cores were disappointing: the materials were of negligible solubility and with a high thermal stability which precludes fusion. Over the years, however, the constraints which identify the window leading to tractable materials have been clearly defined. Currently, investigations are extensively carried out on (i) semi-flexible linear polymers, (ii) comb-like side chain polymers and (iii) polypeptide solutions. Linear polymers are constituted of mesogenic molecules linked end to end to form a strand via suitable chemical groups named spacers. In side chain polymers the monomeric liquid crystal groups appear as pendant side chains attached by flexible spacers to the main chain, that is, the backbone. The length of the spacer and the flexibility of the monomers are only some of the structural characteristics to be optimized when designing a polymeric liquid crystal.

For two decades electron spin resonance (E.S.R.) spectroscopy has been widely used to characterize both textures and dynamics of low molar mass mesophases. Since the mesophases are constituted of diamagnetic molecules, we usually resort either to labelled macromolecules by attaching paramagnetic groups to the chain [3, 4] or to molecular spin probes, i.e. radicals to be solved in the host matrix [5–7]. The E.S.R. lineshape of spin-labelled molecules is directly affected by the reorientation of the nitroxide group which in turn results from the reorientation of the polymer molecule as a whole, from the reorientation of the main chain segment which it is bound to, and finally from the nitroxide reorientation about the bonds through which it is attached. Indeed when discussing the use of spin probe methodology in the realm of polymeric liquid crystals, the effectiveness of extracting information concerning the *solvent* via the *solute* E.S.R. lineshape is the key point to be addressed in that, as a rule,

the E.S.R. lineshape will reflect the motion and the spatial/angular distribution across the sample of the probes. As a consequence, great care must be exercised when referring the data to the *solvent molecules*. Of course, differences become more and more negligible as the spin probe more and more closely resembles the solvent molecule.

Spatial arrangements of low molar mass liquid crystals are numerous: nematic, cholesteric and several exotic smectic phases have been identified and are presently under investigation. In such phases modelling the probe distribution across the sample is a reasonably simple task. This distribution must be known when simulating the overall E.S.R. lineshape coming from the probes dispersed in the bulk. As far as we are concerned with polymeric mesophases we must recall that macromolecules have a more or less marked flexibility and that a pronounced difference exists between the molecular dimensions of polymers and radicals. This implies that in linear-polymer melts, radicals with low molecular anisotropy will hardly be oriented by the host matrix, so giving rise to an E.S.R. absorption lineshape as expected for usual isotropic liquids. If close packing conditions occur, radicals with high molecular anisotropy (e.g. the cholestane radical) experience the local dynamics of the segments of the neighbouring macromolecules and good alignment of the probe molecule is observed [5]. However, even if the chain-like macromolecules are sufficiently ordered, a lower order for the probes must be expected.

In contrast, due to their inherent structure, comb-like polymers are likely to trap radicals in interstitial positions between the side chains. In consequence the E.S.R. lineshape will reflect the order and the dynamics of the radical, as induced by the teeth of the comb [6].

So far we have discussed the *intramolecular* distribution of the nitroxide group. Nevertheless the distribution of radicals across the sample must also be analysed at an intermediate length scale (extending for several typical macromolecular lengths) in order to account for the spatial organization of macromolecules. Concerning that intriguing topic, we limit ourselves to pointing out that a simple theoretical analysis of that distribution is complicated by the existence of numerous spatial configurations allowed by the finite stiffness of polymers.

In conclusion the spin probe/spin label technique, when applied to polymeric liquid crystals, will be meaningful only if the following two conditions are met: (i) the interstitial positions of the radicals are such as to correlate them with the dynamics of the macromolecules, (ii) the overall angular/positional distribution of the radicals across the sample is known.

In this paper we take for granted the above two conditions and discuss a new kind of non-linear electron spin resonance spectroscopy, namely the doubly modulated E.S.R. (DOMESR) [8–12], which exhibits a marked sensitivity to slow molecular dynamics of the radical ($\tau_c \approx 10^{-7}$–10^{-3} s). Basically DOMESR spectroscopy differs from the usual E.S.R. spectroscopy in that a second modulating field is added to the customary one which is parallel to the static magnetic field. Spectra are recorded when sweeping the frequency of one modulating field, any other adjustable parameter being fixed (see figure 1). It will be shown that DOMESR is completely unaffected by the complications of inhomogeneous broadening.

The motivations for this work are twofold: E.S.R. studies concerning polymeric liquid crystals [5–7] report that typical correlation times fall in the range 10^{-8}–10^{-6} s or longer, where admittedly E.S.R. shows quite a limited ability to discriminate between different regimes of motion [13–15]. The second motivation stems from
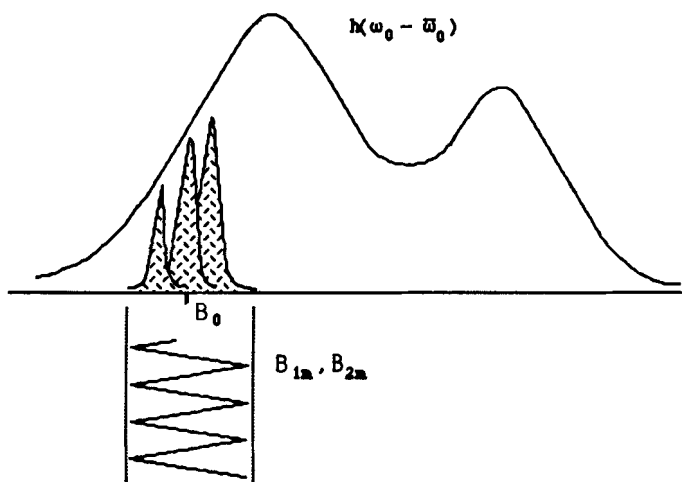
Figure 1. In a DOMESR experiment the two modulating fields B_{1m}, B_{2m} sweep back and forth around the value of the static magnetic field B_0. The overall DOMESR signal comes from the contributions of the different spin packets (dashed peaks) drawn into resonance by the modulating fields. $h(\omega - \bar{\omega}_0)$ is the Larmor-frequency distribution due to inhomogeneous broadening, ω is the microwave frequency and $\bar{\omega}_0 = \gamma B_0$.

the remark that spectroscopies currently being employed when investigating slow motions suffer some rather severe flaws [16]. For example, saturation transfer E.S.R. (ST-ESR), developed by Hyde and Dalton [17], even though it is very sensitive to slow dynamics, depends strongly upon inhomogeneous broadening. This unpleasant feature blurs interesting spectral details and necessitates major assumptions on Larmor frequency distribution when simulating the lineshape. Moreover a standard reflection-type spectrometer is not able to detect the dispersion signals induced by saturation transfer mechanisms. More recently Freed and co-workers overcame the problems originating in the inhomogeneous broadening of the spectral lines by resorting to the electron-spin-echo phenomenon [18]. That methodology provides very detailed information about molecular dynamics but requires quite a complex experimental set-up. Furthermore spectral simulations require careful numerical analysis. In contrast we point out that (i) in the slow motion region of tumbling radicals DOMESR spectroscopy is largely unaffected by inhomogeneous broadening and (ii) a spectrometer for DOMESR experiments is simply derived from a standard E.S.R. spectrometer by adding a subsidiary field modulating unit.

In the following, we briefly describe the technique and the related interpretation. In addition we present some measurements which clearly demonstrate the noticeable dependence of the DOMESR lineshape upon the radical dynamics.

2. Theory

In this section for the sake of completeness we give a brief account of the theoretical treatment of the DOMESR phenomenon exploiting the dressed atom formalism [10]. The complete description of the framework will be published elsewhere [19]. We model the experimental situation as the net result of the contemporary influence exerted on the sample by three fields: the microwave field transverse with respect to the static magnetic field, and the two longitudinal modulating fields. The

theoretical treatment is specialized for both the homogeneous and inhomogeneous broadening.

2.1. *The homogeneous case*

Let us consider a spin system with $S = 1/2$ acted on by a static magnetic field B_0 and irradiated by a transverse r.f. field at angular frequency ω with amplitude B_{mw} and by two modulating fields parallel to B_0 with frequencies ω_{1m}, ω_{2m} and amplitudes B_{1m}, B_{2m}. We write the total hamiltonians as

$$\mathscr{H} = \mathscr{H}_z + \mathscr{H}_m + \mathscr{H}_{mw} + \mathscr{H}_i = \mathscr{H} + \mathscr{H}_i. \tag{1}$$

Here $\mathscr{H}_z = \omega_0 S_z$ is the Zeeman hamiltonian with $\omega_0 = \gamma B_0$ and γ is the magnetogyric factor;

$$\mathscr{H}_m = \omega_{1m} b^+ b + \omega_{2m} c^+ c + \lambda_{1m}(b + b^+)S_z + \lambda_{2m}(c + c^+)S_z$$

is the hamiltonian of the modulation fields and their interaction with the spin system; $\mathscr{H}_{mw} = \omega a^+ a$ is the hamiltonian of the r.f. field and

$$\mathscr{H}_i = \lambda_{mw}(a^+ S_- + a S_+)$$

is its interaction with the spin system. a, a^+; b, b^+; c, c^+ are the annihilation and creation operators for the microwave σ-photons and the modulating fields π-photons respectively while $S_\pm = S_x \pm i S_y$. λ_{mw}, λ_{1m}, λ_{2m} are found to be proportional to B_{mw}, B_{1m}, B_{2m} respectively, if radiation states are described in terms of coherent states [20]. For simplicity we limit ourselves to non-saturating conditions. In consequence the term $\mathscr{H}_i$ is written by resorting to the rotating wave approximation [20]. This position allows the diagonalization of $\mathscr{H}$ on the infinite basis of the direct product of the eigenfunctions of $\mathscr{H}_{mw}$ and $\mathscr{H}_z + \mathscr{H}_m$,

$$\left. \begin{aligned} |\alpha\rangle &= |l + 1, -, m_-^{(1)}, n_-^{(2)}\rangle, \\ |\beta\rangle &= |l, +, p_+^{(1)}, q_+^{(2)}\rangle. \end{aligned} \right\} \tag{2}$$

Here $|\pm\rangle$ are the spin eigenstates and $|l\rangle$ is the r.f. eigenstate in the occupation number representation. The eigenstates of $\mathscr{H}_z + \mathscr{H}_m$ are written as $|\pm\rangle|r_\pm^{(i)}\rangle$. The kets

$$|r_\pm^{(i)}\rangle = \exp[\pm(-\lambda_{im})/2\omega_{im}(b + b^+)]|r^{(i)}\rangle, \quad (i = 1, 2) \tag{3}$$

satisfy the basic commutation rules

$$\begin{aligned} \langle j_\pm^{(i)}|k_\pm^{(i)}\rangle &= \delta_{jk}, \\ \langle j_+^{(i)}|k_-^{(i)}\rangle &= J_{(j-k)}^{(i)}[\gamma B_{im}/\omega_{im}], \\ \langle j_-^{(i)}|k_+^{(i)}\rangle &= J_{(k-j)}^{(i)}[\gamma B_{im}/\omega_{im}], \end{aligned}$$

where $J_k(x)$ is a Bessel function of order k. We name the quantity $\gamma B_{im}/\omega_{1m}$ the ith modulation index. In the following the superscripts of states (3) will be understood.

The infinite eigenvalues in the state basis (3) are obtained by

$$\left. \begin{aligned} \mathscr{H}|\alpha\rangle &= E_\alpha|\alpha\rangle, \\ &= [(l + 1)\omega - \omega_0/2 + m\omega_{1m} + n\omega_{2m}]|\alpha\rangle, \\ &= [(l + 1/2)\omega + \Delta\omega/2 + m\omega_{1m} + n\omega_{2m}]|\alpha\rangle, \\ \mathscr{H}|\beta\rangle &= E_\beta|\beta\rangle, \\ &= [l\omega + \omega_0/2 + p\omega_{1m} + q\omega_{2m}]|\beta\rangle, \\ &= [(l + 1/2)\omega - \Delta\omega/2 + p\omega_{1m} + q\omega_{2m}]|\beta\rangle, \end{aligned} \right\} \tag{4}$$

where $\Delta\omega = (\omega - \omega_0)$ is the detuning. It should be noticed that at this stage the real physical system has been replaced by an effective one with energy levels written in equation (4), picturing the atom as dressed by all the impinging fields and interacting with the microwave field only via $\mathcal{H}_i$.

The response of the physical system to multiple irradiation can be calculated by using statistical quantum mechanics and solving the master equation for the statistical operator ϱ. We define $\varrho = \varrho_0 + D$, where ϱ_0 is the thermodynamic equilibrium contribution and the relaxation processes affect ϱ via D. The solution of the master equation gives the stationary values of D [21]. In order to outline the contributions at different orders in $\mathcal{H}_i$, an iterative procedure is exploited, by using the master equation as a recursive rule which provides the different terms of an expansion of D in increasing powers of $\mathcal{H}_i$,

$$\frac{i}{\tau} D(r + 1) = [\mathcal{H}, D(r)] - \frac{\beta[\mathcal{H}_{mw}, \mathcal{H}]}{2}. \tag{5}$$

The starting condition assumes $D(0) = 0$. $1/\tau$ is the relaxation superoperator, $\beta = 1/kT$ where k is the Boltzmann constant and T is the absolute temperature of the bath. The resulting expansion for D reads as,

$$D(2i) = D^2 + D^4 + \cdots + D^{2i}, \tag{6a}$$

$$D(2i + 1) = D^1 + D^3 + \cdots + D^{2i + 1}. \tag{6b}$$

It is found that $D^i \propto \lambda_{mw}^i \propto B_{mw}^i$, $D(2i)$ connect states with the same spin value and $D(2i + 1)$ connect states with opposite spin value. As a consequence the operator D/τ may be specialized phenomenologically either in $D(2i)/T_1$ or in $D(2i + 1)/T_2$ where, as usual, T_1 and T_2 are the longitudinal and transverse relaxation times of the spin system, respectively. Note that expansions (6) when applied to calculate the expectation value of the magnetization give for the longitudinal (6a) or transverse (6b) components an ascending series of even or odd powers of B_{mw}, respectively. This procedure is consistent with the series expansion of magnetization, as given by solving the Bloch equations.

According to the experimental geometry, the observable of interest is the transverse magnetization component. Hence the absorbed microwave power P can be developed in a series of odd powers of B_{mw} via a suitable trace operation, involving $D(2i + 1)$ as a weighting factor only,

$$P = P^{(1)} + P^{(3)} + \cdots + P^{(2i+1)} + \ldots, \tag{7a}$$

$$P^{(2i+1)} = i\,\mathrm{Tr}\,\{\varrho_{mw}\varrho_{1m}\varrho_{2m}D^{2i+1}[\mathcal{H}_{mw}, \mathcal{H}]\}. \tag{7b}$$

ϱ_{mw}, ϱ_{1m}, ϱ_{2m} are the density matrices of the microwave and the modulating fields respectively, which assume the fields to be in quasi-classical, phase defined, coherent states nearly approaching the classical fields $B_{mw} \cos\omega t$, $B_{1m} \cos\omega_{1m}t$, $B_{2m}\cos\omega_{2m}t$, respectively [20]. It has been remarked elsewhere that $P^{(1)}$, which is quadratic in B_{mw}, does not account for the very features of the DOMESR spectroscopy [9–11].

For our purposes the first term of interest is $P^{(3)}$, which in turn is related to D^3 according to equations (7) (we compute the signal first harmonic at ω_{1m} which is experimentally phase detected):

$$P^{(3)} = 4\beta\omega^2\gamma^4 B_{mw}^4[F\cos\omega_{1m}t + Q\sin\omega_{1m}t]. \tag{8}$$

The in-phase F and quadrature Q components may be written as

$$F = 4 \sum_{r,t>0} \Phi(r, t) \frac{1}{1 + [T_1^{-1}(r\omega_{1m} - t\omega_{2m})]^2}, \tag{9a}$$

$$Q = 4 \sum_{r,t>0} \Theta(r, t) \frac{T_1^{-1}(r\omega_{1m} - t\omega_{2m})}{1 + [T_1^{-1}(r\omega_{1m} - t\omega_{2m})]^2}. \tag{9b}$$

The explicit expressions of $\Phi(r, t)$ and $\Theta(r, t)$ are involved functions of T_2, $\Delta\omega$ and products of Bessel functions and are reported elsewhere [19]. Then, according to the calculations, when sweeping ω_{2m}, the in-phase (quadrature) signal $P^{(3)}$ exhibits an absorption (dispersion) lineshape any time the resonance condition

$$r\omega_{1m} + t\omega_{2m} = 0 \tag{10}$$

is fulfilled. As a consequence our frame predicts that the lineshape of a definite in-phase DOMESR dip is not a pure lorentzian but indeed a sum of lorentzian curves with half width at half eight of each component given by T_1^{-1}/t.

2.2. The inhomogeneous case

By using the spin probe/spin label methodology, the inhomogeneous broadening of the E.S.R. lineshape, which stems from unresolved superhyperfine structure, faces experimentalists. It is worth noting that, provided T_1 exceeds T_2, $P^{(3)}$ is *not* affected by this broadening mechanism, since its resonances are not driven by the Larmor frequency value (see equations (8) and (9)) and $\Phi(r, t)$, $\Theta(r, t)$ flatten as functions of ω_{2m}. In contrast, the first order contribution $P^{(1)}$ to the absorbed power allows resonances when [9–11]

$$\Delta\omega - m\omega_{1m} - n\omega_{2m} = 0. \tag{11}$$

The presence of the detuning $\Delta\omega = \omega - \omega_0$ results in a broadening when a spread in the Larmor frequency ω_0 occurs.

However, even if not enlarged the intensity of a DOMESR transition is modified by inhomogeneous broadening. Theoretically this modification may be accounted for by performing a convolution with a suitable weighting function on contributions coming from different spin packets. In the following we focus on the in-phase signal F; analogous considerations hold true for the quadrature signal Q.

When the convolution is performed, the resulting signal F_c may be written as

$$F_c = \int_{-\infty}^{\infty} d\omega_0 h(\omega_0 - \bar{\omega}_0) F(\omega - \omega_0). \tag{12}$$

All the information about the spread of the Larmor frequency enter into $h(\omega - \bar{\omega}_0)$, $\bar{\omega}_0 = \gamma B_0$, where B_0 is the static magnetic field. We must bear in mind that $\omega_0 = \gamma B_i$, where B_i is the *local* magnetic field. The explicit form to be assigned to $h(\omega - \bar{\omega}_0)$ is often either unknown or involved and these occurrences entail crude assumptions about $h(\omega - \bar{\omega}_0)$. However we may circumvent that flaw by taking advantage of the very different magnitudes in the spin packet linewidth T_2^{-1} and the typical extent Γ of $h(\omega - \bar{\omega}_0)$. In fact, since $\Gamma \gg T_2^{-1}$, we may expand $h(\omega - \bar{\omega}_0)$ around $\omega - \bar{\omega}_0$ without introducing any appreciable error in the integral. Since $F(\omega - \omega_0)$ is an odd function, if we insert equation (9a) into equation (12) we find

$$F_c = \frac{\partial h}{\partial(\omega - \bar{\omega}_0)} \sum_{r,t>0} \left\{ \int_{-\infty}^{\infty} 4\Phi(r, t)(\omega - \omega_0) \, d\omega_0 \right\} \frac{T_1^{-1}}{1/T_1^2 + (r\omega_{1m} + t\omega_{2m})^2}. \tag{13}$$

Equation (13) provides an expression for F_c which removes the need for detailed knowledge of h. Since the static magnetic field in a DOMESR experiment is kept fixed, the derivative appearing in equation (13) is a constant. The term enclosed within curly brackets drives the signal when the modulation indexes $\gamma B_{1m}/\omega_{1m}$, $\gamma B_{2m}/\omega_{2m}$ are varied and in the limit of T_1 longer than T_2 is essentially independent of both ω_{1m} and ω_{2m} [19].

By glancing at equations (12) and (13) we note that the resonating factor has been factorized out of the convolution. In other words, while sweeping ω_{2m}, it acts upon the average just like a quantum filter locked at $r\omega_{1m}/t$ for the inhomogeneous spread. The bandwidth of such a filter is T_1^{-1}, so that DOMESR directly elicits dynamical information by measuring longitudinal relaxation processes affecting the single spin packet. However we are aware that the oversimplified treatment of the spin relaxation in our frame does not allow a safe identification of the parameter T_1 with the longitudinal relaxation time itself of the single spin packet.

3.   Experimental results

The experiments were carried out by means of a standard reflection-type spectrometer; the static magnetic field has a relative stability of 3×10^{-6} per hour and a homogeneity on the sample of 3×10^{-5} G/cm as monitored by an N.M.R. gaussmeter, Bruker ER035M. The resonant cavity employed was a multipurpose rectangular Varian cavity resonating in the TE_{102} mode. Besides the usual equipment for the modulation of the static magnetic field operating 100 kHz, a second power modulation unit was added with a frequency range of 5×10^4–5×10^5 Hz. The unit is made up of a function generator Schlumberger 4432, a 50 W power amplifier Krohn-Hite DCA-50R and a matching transformer. This unit feeds an additional pair of coils, designed with a suitable choice for the quality factor Q so as to balance the two opposite requirements of a flat frequency response during the sweep and a high extracurrent value. It must be pointed out that the addition of this unit is the only modification to the E.S.R. spectrometer required in order to perform DOMESR experiments. In the configuration adopted the standard Varian coils supply a modulating field with a maximum amplitude of about 30 G, while the field amplitude does not exceed about 5 G in the additional pair of coils. Signals are phase-detected by a lock-in amplifier EG&G 5206, tuned at a frequency $\nu_{1m} = \omega_{1m}/2\pi = 100$ kHz simultaneously providing both in-phase and quadrature detection, thus enabling the modulus of the signal to be determined directly. This particular choice was selected in order to avoid both experimental and theoretical difficulties related to the phase changes of the signal. The time spent varying the ν_{2m} frequency was much longer than the integration time of the lock-in amplifier, which was typically 1 s. In this way it was possible to eliminate, or at least to control, the instrumental signal which results in the lock-in response at frequency $n\nu_{1m}$ whenever $|n\nu_{1m} - \nu_{2m}|$ fell in the amplifier bandwidth. This instrumental effect is distinctly recognizable under proper conditions and is superimposed on the DOMESR transitions placed at $\omega_{2m}/\omega_{1m} = p$ where p is an integer.

Measurements were carried out on a model system; the TEMPO radical dissolved in glycerol (5×10^{-3} M) [18]. DOMESR signals were found to be characterized by a good signal-to-noise ratio; however, to increase the accuracy it proved useful to accumulate each recording five times. In figure 2 we show a plot of the inverse of the half linewidth at half height T_1^* of the DOMESR dip placed at $\omega_{2m}/\omega_{1m} = 2$ at different temperatures. The observed trend well illustrates the sensitivity of DOMESR
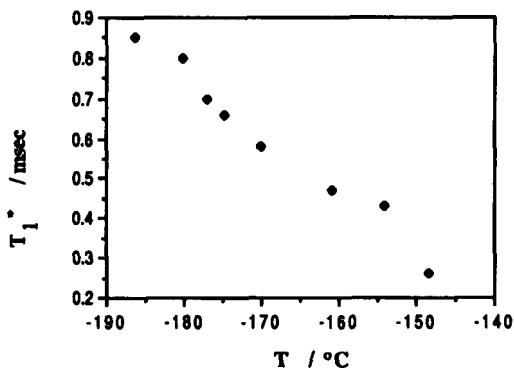
Figure 2.   Plot of the inverse of the half width at half height T_1^* of the DOMESR dip placed at $\omega_{2m}/\omega_{1m} = 2$ versus temperature. The sample is a model system: TEMPO dissolved in glycerol (5×10^{-3} M). It must be stressed that in this range of temperatures the E.S.R. lineshape is completely frozen. $B_{1m} = B_{2m} = 0.3$ mT. No appreciable effect on the linewidth related to the amplitude of the modulating fields was detected. The amplitude of the microwave field is suffiently low as not to saturate the E.S.R. lineshape.

to slow motions and supports the thesis that longitudinal relaxation processes are affected by molecular motion occurring on a long time scale in a more marked way than transverse relaxation processes, as already noted by other authors [18]; we are able to detect variations as large as four times in a limited temperature range. It is worth noting that in the same temperature range the usual E.S.R. lineshape does not show any appreciable modification.

The relation existing between the DOMESR linewidth and the microscopic parameters characterizing the molecular dynamics is still an open question. At present, to our knowledge, no theory concerning this specific topic has been published. The framework which we have developed accomplishes for the first time a fairly adequate explanation of the independence of the DOMESR dips from inhomogeneous broadening and elucidates the role played by the available parameters, namely the static magnetic field and both the amplitude and the frequency of the three employed fields. In the adopted scheme we are satisfied with a phenomenological description of relaxation. However, work is in progress to give a more satisfactory microscopic formulation of relaxation mechanisms involved by DOMESR spectroscopy.

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