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Invited Article

The role of non-linear electron spin resonance spectroscopies

Perspectives in microscopic studies of liquid-crystalline polymers

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The advantages and the limits of electron spin resonance applied to the study of microscopic interactions in liquid crystalline polymers are discussed. Difficulties of current E.S.R. techniques in studying the very slow molecular dynamics suggest the search for novel techniques. Two non-linear C.W. E.S.R. techniques are described; multiple irradiation schemes are studied in a unified theoretical treatment. These methods give direct measurements of the longitudinal relaxation dynamics and are completely independent of the inhomogeneous broadening of the spectral lines. Their capabilities for investigating ultra-slow relaxation rates are evidenced.

1. Introduction

In the last decade an increasing effort has succeeded in synthesizing and characterizing a new class of polymeric materials containing mesogenic groups. The presence of these mesogens leads the host polymer to specific behaviour in both conformational and dynamical aspects that differentiate it from the usual polymers. On the other hand the liquid-crystalline phases are similar when mesogens are in the monomeric state or when they are inserted in a polymeric structure; however the presence of the polymeric backbone and its interactions affects the liquid-crystalline phases in their extent, and in the characteristic long-range correlations and related times. This is true for both the mesogenic groups connected via flexible segments to form the polymeric backbone (main chain liquid-crystalline polymers) and for mesogenic groups pendant from the polymer main chain, again via flexible groups (side chain liquid-crystalline polymers). Between these two situations there is an obvious difference, since in main chain liquid-crystalline polymers long-range order among the polymeric chains has to be observed whereas in the case of side chain liquid-crystalline polymers nothing can be thought about the chain order and long-range correlations only exist among the side mesogenic groups. In the latter case the times involved in collective phenomena are similar to those for monomeric liquid crystals, while in the former case such times occur on a considerably longer time scale. A brief review of these phenomena is given in [1].

Bonding the mesogens in the polymeric chain or as comb-like side chains, anyway, shifts the different liquid crystalline phases towards high temperatures. The polymeric liquid crystal systems show phases with the same order relations as their low molecular weight counterparts, expressed in terms of order parameters, and the different phase transitions are described mathematically by analogous equations.

Only at the glass transition are essential differences met for mesogenic polymers, since it is not a second order transformation. The Ehrenfest equations indeed are not both applicable to this case and then the glass transition appears rather as a freezing-in process [2]. This has the important consequence that anisotropic liquid-crystalline molecular orientation is also frozen in; an anisotropic glass with liquid-crystalline structure is obtained if the liquid crystal is quenched under the effect of orienting electric or magnetic fields [3]. This peculiarity yields a class of materials which is very attractive for application purposes.

2. Interactions on the microscopic scale

2.1. *Generalities*

The wide experience in the study of isotropic and anisotropic molecular motions in normal fluids and solids by the methods of statistical physics, suggests the possibility of extending these studies to phase transitions and to intermolecular interactions modified by the links with the backbone in polymeric fluids and solids. These studies do not present interests from the speculative point of view alone, since knowledge of microscopic intermolecular interactions throws new light on the assessment of macroscopic properties. The effects of long-range order on the exceptional mechanical properties of some polymers and on the organization of biological cells are well known [1]; recently the pronounced anisotropy seems the major factor in obtaining polymeric conductors with good transport properties [4] and liquid-crystalline molecular properties can also play an important role in this field.

The improvements in the availability of advanced theoretical and experimental tools, allow a deeper insight into this polymer class [5, 6]. Among the different techniques, a primary position is held by magnetic resonance spectroscopies that can give direct or indirect information about dynamical behaviour and long-range orientations of mesogenic molecules. In particular proton, deuteron and multipulse magnetic resonance are techniques well recognized in allowing studies of conformational and orientational order and of molecular mobility in different classes of mesogenic polymers [7–11].

2.2. *Electron paramagnetic resonance*

Electron paramagnetic resonance (E.P.R.) spectroscopy seems one of more valuable methodologies in accounting, also in polymeric materials, for the molecular environment and its dynamical evolution. Since the mesogen systems are in general diamagnetic, E.P.R. is useful only when paramagnetic probes (such as nitroxides) are introduced in the materials of interest. Such information is inferred directly from the structure and the shape of the spectra of the paramagnetic probe. In particular we note the following.

(i) The anisotropy of liquid-crystalline materials is related to the orientational order of the materials which is specified, for rigid molecules, by an infinite set of order parameters. Among these order parameters, only the second rank terms are readily measurable [12]. The tendency of the mean molecular orientation, or director, to align along one molecular axis is specified in general by the parameter

$$S = \frac{\langle 3\cos^2\theta - 1\rangle}{2}, \tag{1}$$

where θ is the angle between the director and the molecular axis and the brackets denote the statistical mean for the system. The S parameter undergoes remarkable variations particularly at the phase transitions. The situation is more complicated when we deal, as in the case of polymeric mesogens, with flexible molecules. In this case the conformational variables also affect the orientational order and must be specified in order to characterize completely the anisotropy of the system [10, 13]. The E.P.R. spectrum is a sort of fingerprint of this anisotropy, sensed by the anisotropic magnetic interactions of the paramagnetic molecule. The distribution of lines in the spectrum allows the direct determination of the parameter S.

(ii) In magnetically dilute systems the relaxation phenomena are usually dominated by the modulation of the anisotropic magnetic interactions via the molecular reorientational motions which are characterized by certain correlation times. These times are in general, but specifically in thermotropic systems, dependent on temperature. The study of these spin relaxation processes is then a convincing path to a realistic picture of the molecular dynamics in the systems of interest.

These statements are sound only if the molecular environment and its time evolution is the same for both the paramagnetic systems and the molecules of the mesogenic polymers. This is only true if the paramagnetic centres are connected chemically via stiff bonds to the host polymer (spin labelling [14]); if the parmagnetic systems are only dissolved in the polymer, we are able to extract more information about the solute than about the solvent. In order to obtain effective information a great deal of care has to be spent in the choice of the paramagnetic molecule which must be modelled to the shape of the host system.

Although not numerous, some attempts have been made at studying the molecular environment of polymeric liquid crystals by the E.P.R. method [15–18]. Such studies have allowed measurement, as a function of temperature, of order parameters in both side-chain and main-chain systems. For the former, values comparable with the low-molecular weight mesogens were obtained. For the latter, separate measurements of the micro-order (the mean orientation with respect to a director defined in a molecular domain scale) and macro-order (mean orientation of domain directors in a laboratory frame) were performed. By assuming that the intermolecular motions reflect a brownian rotational diffusion model, two correlation times, $\tau_{R\parallel}$ (related to the diffusional reorientations around the molecular symmetry axis) and $\tau_{R\perp}$ (related to reorientations of the same axis) have been measured, giving values ranging over the large interval 10^{-10}–10^{-6} s, according to the temperature. Such results agree with the extremely wide range of times involved in typical molecular motions of main-chain liquid crystal polymers (up to 10^{-1} s), as measured by multipulse N.M.R. techniques [11].

2.3. *Molecular dynamics by E.P.R. studies*

In fact, E.P.R. spectroscopy gives the most valuable information about the molecular dynamics, just when the molecular motions are strongly slowed down. In this condition, the spectra are similar to that obtained in the rigid limit [18] and their interpretation and connection to the molecular dynamics, except for particular cases [19], require the simulation of spectra by analytical or numerical computation.

A typical path to the calculation of the E.P.R. spectrum, exploits the linear response theory [20], that gives the lineshape as

$$\begin{aligned} I(\omega) &= \operatorname{Re} \mathbb{L}\phi(t) \\ &= \operatorname{Re} \mathbb{L} \frac{\langle S_X S_X(t) \rangle}{\langle S_X S_X \rangle}. \end{aligned} \tag{2}$$

The lineshape is then the Laplace transform of the equilibrium correlation function $\phi(t)$ of the spin observable. The time evolution of the observable of interest S_X is given by

$$\frac{dS_X}{dt} = iLS_X, \tag{3}$$

where the quantum mechanical liouvillian superoperator L is

$$L = \mathscr{H}^{\times} = -[\mathscr{H}, \ldots].$$

The hamiltonian, $\mathscr{H}$, in this case consists of the terms

$$\mathscr{H} = \mathscr{H}_{\mathrm{s}} + \mathscr{H}_{\mathrm{B}} + \mathscr{H}_{\mathrm{i}}, \tag{4}$$

where $\mathscr{H}_{\mathrm{s}}$ is the intramolecular hamiltonian containing the nuclear and electronic spin interactions (which do not depend on the molecular orientation), $\mathscr{H}_{\mathrm{B}}$ denotes the hamiltonian of the degrees of freedom irrelevant for our purposes and $\mathscr{H}_{\mathrm{i}}$ denotes the interactions between $\mathscr{H}_{\mathrm{s}}$ and $\mathscr{H}_{\mathrm{B}}$. By means of the well-known method of the stochastic Liouville equation [21], we can replace the rigorous operator iL of equation (3), with the dynamical operator

$$\Gamma = i\mathscr{H}_{\mathrm{s}}^{\times} + i\mathscr{H}_{\mathrm{i}}^{\times}(\Omega) + \Gamma_{\Omega}^{+}. \tag{5}$$

Here Γ_{Ω} is the operator driving the probability $p(\Omega, t)$ of finding the molecule of interest with orientation Ω at the time t and

$$\frac{\partial}{\partial t} p(\Omega, t) = \Gamma_{\Omega} p(\Omega, t).$$

To lowest order [22], Γ_{Ω} is related to the molecular diffusion properties (intermolecular interactions) via the equation

$$\Gamma_{\Omega} = -\mathbf{M}[\mathbf{D}\mathbf{M}V(\Omega)] - \mathbf{M}\mathbf{D}\mathbf{M},$$

where D is the molecular diffusion tensor, **M** the operator which generates rotations in the molecular frame and $V(\Omega)$ is the potential to be defined for the different cases.

Different methods and algorithms have been developed, starting from the basic stochastic Liouville equation approach, in order to obtain expressions for the simulation of E.P.R. spectra [23–25]. Spectral simulations of radicals either tumbling freely or subject to orienting potentials in the slow motion molecular regime, have been obtained. These methods, effective in several applications, can meet with serious difficulties in characterizing the molecular dynamics of spin labels inserted in polymeric liquid crystals. When the molecular reorientational motions affecting the relaxation processes are further slowed down, the E.P.R. signals become virtually independent of the molecular dynamics and the simulation procedures fail. Furthermore the linewidths can be affected by inhomogeneous broadening due to the superhyperfine interactions with the nuclei of neighbouring atoms. This contribution to the lineshape complicates the treatment and in some applications is taken into account by introducing a residual linewidth.

These difficulties are present in several studies of molecular dynamics in liquid-crystalline polymers. In particular when the temperature is lowered below the glass transition, the molecular motions are so slowed down that they can be detected only by N.M.R. [26] or special spectroscopic techniques. However these residual motions are not insignificant when their effects on magnetic relaxations are thoroughly considered. This statement is demonstrated by recent measurements of E.P.R. spin relaxation in frozen solutions of nitroxide systems in glycerol [27]. The authors measured variations of the relaxation parameters as a function of the temperature near to liquid nitrogen temperature. The values showed changes by orders of magnitude in rather narrow temperature intervals. These unexpected results denote variations of the correlation times of molecular motions affecting the magnetic relaxations round about 10^{-4} s.

The interest of these studies suggests the need for novel techniques capable of escaping these difficulties. One of the most promising techniques recently implemented is two-dimensional electron spin resonance (2D-E.S.E.] [28, 29]. This time-domain E.P.R. technique showed sensitivity to motions with correlation times τ_R of the order of 10^{-4} s and allowed measurements of the homogeneous linewidths of the tempone spin probe in a frozen glycerol–water solution. This kind of experiment gives a nice representation of the map of the linewidth distribution across the whole spectrum; many difficulties are then avoided in the very slow motion regimes.

Apart from its experimental complexity, the 2D-E.S.E. methodology retains two main limitations: (i) the effect of the dead time (depending on the experimental apparatus and, to some extent, unavoidable) that can introduce sensible artifacts in the measurements and is only partially reduced with significant experimental and computational efforts, and (ii) the technique is based on an analysis of transverse relaxation processes of spin packets; accordingly the range of correlation times that can be studied is limited to values τ_R of the order of the transverse relaxation times. Methodologies accounting for times involved in longitudinal relaxation processes could noticeably extend the range of measurable τ_R values since in very rigid materials, longitudinal times are far greater than transversal ones.

3. Non-linear C.W. E.P.R. spectroscopies

Here the features of two C.W. non-linear E.P.R. techniques are discussed. These techniques, the double modulation electron spin resonance (D.O.M.E.S.R.) [30] and the frequency swept longitudinally detected electron spin resonance (L.O.D.E.S.R.) [31] exploit multiple irradiations in low saturation condition and both give direct measurements of the rate of *longitudinal relaxation process*. These methods come out relatively simple and are jointly interpreted, as different aspects of the same physical effect, within the same theoretical framework.

Any difficulty connected with the inhomogeneous line broadening is completely overcome, since contributions to the signal from different spin-packets are found to cancel each other. The relaxation effects, connected to the molecular motions everywhere in the whole spectrum, can be measured. Longitudinal relaxation processes involving extremely long times have been observed, accounting for very slow molecular interactions.

3.1. *Theory*

In the following development the physical system and the radiation fields are treated according to the dressed atom formalism, exploiting the second quantization method [32]. This choice is not strictly necessary but this preference is due to the simplicity of the related formalism and to the easy understanding of the meaning of physical processes involved in each stage of approximation. It has to be pointed out that similar results can be obtained within the usual Bloch-like picture.

For the sake of simplicity the case of a spin system with $S = \frac{1}{2}$ irradiated under E.P.R. conditions by two resonating waves is treated. The extension to the case of different S values or to hyperfine interactions, as well as multiple irradiations, implies only formal complications. The details of the formalism are given in [33]; here only the parts of the treatment useful for the self-consistency of the paper are reported.

The total system, spin and electromagnetic (e.m.) fields are represented by the basis states

$$|m, n_\mathrm{r}, n_\mathrm{s}\rangle \tag{6}$$

which are direct products of the eigenstates of the system and the radiation hamiltonians, with m the quantum number of the spin component parallel to the static field (z axis), n_r and n_s photon occupation numbers for the two e.m. waves. The hamiltonian of the whole system is

$$\mathscr{H} = \mathscr{H}_\mathrm{S} + \mathscr{H}_\mathrm{R} + \mathscr{H}_\mathrm{I}, \tag{7}$$

where $\mathscr{H}_\mathrm{S}$ denotes the Zeeman hamiltonian, $\mathscr{H}_\mathrm{R}$ the radiation hamiltonian and $\mathscr{H}_\mathrm{I}$ the interaction spin-radiation. The problem of resonance signals can be solved with the technique of the statistical operator ϱ. For our purposes ϱ can be divided into a part ϱ_0 accounting for the thermodynamic equilibrium and D which is affected by relaxation processes. The resonance shapes are obtained [34] by solving the linear system of equations

$$\frac{iD_{ij}}{\tau} = [\mathscr{H}, D]_{ij} - \frac{\beta[\mathscr{H}_\mathrm{R}, \mathscr{H}_\mathrm{I}]_{ij}}{\mathrm{Tr}\{\exp[-\beta(\mathscr{H}_\mathrm{S} + \mathscr{H}_\mathrm{I})]\}}, \tag{8}$$

where β is the Boltzmann factor $1/kT$ and τ is the relaxation superoperator. The subscripts i,j refer to states (6). It can be shown [34] that only the D_{ij} terms related to a manifold of nearly degenerate states contribute to the resonances. The succession of states (6) to be considered is then

$$\left.\begin{array}{ll} \ldots|+\tfrac{1}{2}, n_\mathrm{r}+1, n_\mathrm{s}-1\rangle, & |-\tfrac{1}{2}, n_\mathrm{r}+1, n_\mathrm{s}\rangle, \\ |+\tfrac{1}{2}, n_\mathrm{r}, n_\mathrm{s}\rangle, & |-\tfrac{1}{2}, n_\mathrm{r}, n_\mathrm{s}+1\rangle \\ |+\tfrac{1}{2}, n_\mathrm{r}-1, n_\mathrm{s}+1\rangle, & |-\tfrac{1}{2}, n_\mathrm{r}-1, n_\mathrm{s}+2\rangle, \ldots \end{array}\right\} \tag{9}$$

The states (9) are all degenerate if the frequencies of the two waves, ω_r and ω_s, are nearly resonant. In the following, in order to simplify the notation, the states of the succession (9) are labelled by integer numbers, either positive or negative, starting with the correspondence $0 \leftrightarrow |+1/2, n_\mathrm{r}, n_\mathrm{s}\rangle$. According to these choices the matrix representation of hamiltonian (7), that must be used in the equation system (8), is

$$\mathscr{H} = \begin{bmatrix} \ldots & & & & & & & & \\ & \Delta_1 - 2\Delta_2 & \lambda_\mathrm{r} & & & 0 & & & \\ & \lambda_\mathrm{r} & -\Delta_2 & \lambda_\mathrm{s} & & & & & \\ & & \lambda_\mathrm{s} & \Delta_1 - \Delta_2 & \lambda_\mathrm{r} & & & & \\ & & & \lambda_\mathrm{r} & 0 & \lambda_\mathrm{s} & & & \\ & & & & \lambda_\mathrm{s} & \Delta_1 & \lambda_\mathrm{r} & & \\ & & & & & \lambda_\mathrm{r} & \Delta_2 & \lambda_\mathrm{s} & \\ & & & & & & \lambda_\mathrm{s} & \Delta_1 + \Delta_2 & \ldots \\ & & & & 0 & & & \ldots & \ldots \end{bmatrix}.$$

Here $\Delta_1 = \omega_s - \omega_0$, $\Delta_2 = \omega_s - \omega_r$ and λ_r and λ_s are the matrix elements between each pair of eigenstates of $\mathscr{H}_S + \mathscr{H}_R$, of the interactions with r and s waves respectively. A deeper consideration shows that all the states (9) characterized by the same value of the spin quantum number, differ from each other only by the number of related photons; due to the very high number of photons, all such states are then equivalent. This simplifies the solution of system (8) since we can state the recurrence rules

$$D_{ij} = D_{i+2k,j+2k}; \quad D_{i,j+2k} = -D_{i+1,j+2k+1}.$$

Furthermore, for sake of simplicity, by treating the relaxation phenomenologically, the superoperator $1/\tau$ can be specialized into the usual longitudinal $1/T_1$ and transverse $1/T_2$ relaxation rates when the values i and j correspond to the same spin state or not, respectively.

The system (8) contains an infinite number of equations and formally each D_{ij} term is coupled to all the others. However it must be considered that the term D_{ij} corresponds to a transition involving $|i - j|$ photons, as can be seen directly from the states of the basis (9). In consequence we can truncate by neglecting processes involving a number of photons greater than a predetermined number N; this implies disregarding all D_{ij} terms with $|i - j| > N$. By exploiting these recurrence rules we reduce the number of terms D_{ij} of interest. Since in the picture of the statistical operator the observable of interest (in our case a component of the magnetization M_i) is given by $M_i \propto \mathrm{Tr}\{\varrho M_i\}$, consideration of different processes affecting the resonance signal observed on the component M_i implies the calculation of these terms D_{ij} at different orders in the perturbative expansion of the density matrix. Let us examine in some detail the main processes related to the different D_{ij} terms.

First of all it must be pointed out that, due to the conservation of angular momentum, processes involving an odd number of photons correspond to transitions detectable in a transverse direction, while processes involving an even number of photons correspond to transitions detectable in a longitudinal direction. In our scheme, two nearly resonant waves transversally irradiate the spin system and a truncation of the expansion to processes involving more than three photons, allows us to consider the main phenomena observed in E.P.R. spectroscopy.

(i) *Linear processes in terms of the interaction*

These processes are described by the solution of system (8) for D_{01} or D_{12} (according to the observed wave), where the expansion is truncated in first order. The transverse components of the magnetization oscillate at frequencies ω_s and ω_r. This process is the usual E.P.R. resonance, far from saturation.

(ii) *Quadratic processes in terms of the interaction*

These processes involve two photons and are described by the solution of system (8) for D_{02}. The longitudinal component of the magnetization oscillates at the frequency $\Delta_2 = |\omega_r - \omega_s|$. This phenomenon has been reported elsewhere as L.O.D.E.S.R. [35]. It can be observed either with the usual field sweep technique, hence changing the Larmor frequency ω_0, or by changing the frequency Δ_2. The use of recursive methods allows us to obtain an analytic expression for the lineshape for the longitudinal signal S_{LOD} for the case of homogeneously broadened lines [31]

$$S_{\mathrm{LOD}} \propto \lambda_r \lambda_s \left[\frac{1}{(i/T_1) + \Delta_2}\right]\left[\frac{\omega_r}{(i/T_2) + (\omega_0 - \omega_r)} + \frac{\omega_s}{(i/T_2) + (\omega_s - \omega_0)}\right].$$

For inhomogeneously broadened lines, a distribution of Larmor frequencies ω_0^* corresponds to the distribution of spin-packets. By assuming for this distribution the expression $f(\omega_0^*)$, the longitudinal magnetization signal becomes

$$S_{\mathrm{LOD}} \propto \int d\omega_0^* f(\omega_0^*)\lambda_r\lambda_s \left[\frac{1}{(i/T_1) + \Delta_2}\right] \times \left[\frac{\omega_r}{(i/T_2) + (\omega_0 - \omega_r)} + \frac{\omega_s}{(i/T_2) + (\omega_s - \omega_0)}\right]. \tag{10}$$

In the usual E.P.R. or field-swept L.O.D.E.S.R. experiment, the magnetic field is swept over a range comparable with the inhomogeneous distribution and the signal preserves the width caused by $f(\omega_0^*)$. If, on the contrary, a frequency swept experiment is performed, equation (10) shows a resonance occurring in a range of Δ_2 variations comparable with $1/T_1$. If, as observed in many situations, the longitudinal relaxation processes imply times far longer than the transverse ones, the Δ_2 variations span a range where the inhomogeneous distribution does not affect the signal S_{LOD}. By taking into account that experimentally the modulus of this signal is detected, the lineshape is easily related to the longitudinal relaxation rates only; thus

$$|S_{\mathrm{LOD}}| \propto \frac{\lambda_r\lambda_s T_1}{\sqrt{(1 + T_1^2\Delta_2^2)}}. \tag{11}$$

This simple analytical result has been confirmed by numerical solution of the equation system (8); the numerical results [36] confirm that, by assuming $T_1 = 100\,T_2$, the lineshape $|S_{\mathrm{LOD}}|$ is completely independent of the distribution of Larmor frequencies.

(iii) *Cubic processes in terms of the interaction*

These processes correspond to three photon transitions, and so affect the transverse components of the magnetization. Since, in our case, two different waves are present, different processes can occur [36]. Most of them correspond to saturation effects induced in the signal of each wave by the same or by the other wave. Such saturation effects then appear as third order phenomena. There are, however, two other processes, involving three photons, one of one wave and two of the other. These processes correspond to a transition between the levels considered and to oscillations of the transverse components of the magnetization at frequencies $|2\omega_s - \omega_r|$ and $|2\omega_r - \omega_s|$ respectively. In a sense, these processes can be considered as a modification of the usual E.P.R. signal induced by higher order transitions. In our theoretical framework, these effects are calculated by solution of the system (8) for D_{01}, by extending the approximation up to third order. These processes are responsible for the D.O.M.E.S.R. effect observed several years ago [37] and successively interpreted [30, 38]. The main features of this method are:

(1) double modulation of the static magnetic field at frequencies $\omega_m^{(1)}$ and $\omega_m^{(2)}$; variations of the frequency $\omega_m^{(2)}$ induces resonances whenever the condition

$$\omega_m^{(1)} = \frac{p}{q}\,\omega_m^{(2)} \tag{12}$$

is fulfilled, where p and q are integer numbers;

(2) the resonances are extremely narrow even if the sample exhibits wide inhomogeneous line broadenings;

(3) the non-linear character of this effect is evidenced by the measured cubic trend of the D.O.M.E.S.R. signal S_{DOM} versus the irradiating power.

Strictly, the double modulation scheme, due to the equivalence of the field and frequency modulation [39], implies irradiation of the sample by many frequencies. Due to the involved frequency values, for inhomogeneous lines, when condition (12) is approximately fulfilled, we can reasonably suppose that only two spectral components irradiate each spin-packet. This is confirmed by the values of the modulation frequencies typically involved. Within this approximation, the theoretical scheme of double irradiation is valid and matches our purposes well in order to obtain simplified analytical expressions for the D.O.M.E.S.R. phenomenon. A complete theoretical treatment accounting for the full modulation effects is given elsewhere [40].

As we have seen the effects involving processes described by cubic terms in the interaction expansion, are well accounted for by the expression for the term D_{01} of the statistical operator, calculated from the system (8), neglecting all terms involving more than three photons. The analytical results of this calculation are reported; in order to retain consistent notation, the irradiating frequencies involved here are indicated also by ω_{r} and ω_{s}. Such frequencies however, are now two spectral components varying according to the modulation frequencies $\omega_{\mathrm{m}}^{(1)}$ and $\omega_{\mathrm{m}}^{(2)}$; accordingly the quantity Δ_2 is now

$$\begin{aligned} \Delta_2 &= |\omega_{\mathrm{s}} - \omega_{\mathrm{r}}| \\ &= |\omega_{\mathrm{m}}^{(1)} - \omega_{\mathrm{m}}^{(2)}|. \end{aligned}$$

The expression for the transverse component of the magnetization observed, say, at the ω_{s} frequency and proportional to the term D_{01} is

$$M_{\mathrm{tr}}^{(\omega_{\mathrm{s}})} \propto \frac{U + V}{i + (\omega_{\mathrm{s}} - \omega_0)T_2}, \tag{13}$$

with

$$U = \lambda_{\mathrm{s}}\omega_{\mathrm{s}}T_2 - \frac{4\lambda_{\mathrm{s}}^3 T_1 T_2^2 \omega_{\mathrm{s}}}{i + (\omega_{\mathrm{s}} - \omega_0)^2 T_2^2} - \frac{4\lambda_{\mathrm{r}}^2 \lambda_{\mathrm{s}} T_1 T_2 \omega_{\mathrm{r}}}{i + (\omega_0 - \omega_{\mathrm{r}})^2 T_2^2} \tag{14}$$

and

$$V = \frac{2\lambda_{\mathrm{r}}\lambda_{\mathrm{s}}^2 T_1 T_2^2}{i + (\omega_{\mathrm{r}} - \omega_{\mathrm{s}})T_1}\left[\frac{\omega_{\mathrm{s}}}{i + (\omega_{\mathrm{s}} - \omega_0)T_2} + \frac{\omega_{\mathrm{r}}}{i + (\omega_0 - \omega_{\mathrm{r}})T_2}\right]. \tag{15}$$

The usual E.P.R. signal due to the ω_{s} wave is related to one of the transversal components of M and can be inferred directly, at lowest order, from expression (13) by eliminating the cubic terms

$$S_{\mathrm{EPR}}(1) \propto -\frac{\lambda_{\mathrm{s}}\omega_{\mathrm{s}}T_2}{1 + (\omega_{\mathrm{s}} - \omega_0)^2 T_2^2}. \tag{16}$$

By retaining the expansion terms up to third order, the E.P.R. signal becomes

$$S_{\mathrm{EPR}}(3) \propto -\frac{U + \mathrm{Re}\{B\}}{1 + (\omega_{\mathrm{s}} - \omega_0)^2 T_2^2} + \frac{(\omega_{\mathrm{s}} - \omega_0)T_2 \,\mathrm{Im}\{B\}}{1 + (\omega_{\mathrm{s}} - \omega_0)^2 T_2^2}. \tag{17}$$

The D.O.M.E.S.R. signal is observed experimentally, provided that the static field is fixed within the E.P.R. line, as a variation of the usual E.P.R. signal induced by changes of Δ_2. According to the experiment we write the D.O.M.E.S.R. signal as

$$S_{\mathrm{DOM}} = S_{\mathrm{EPR}}(3) - S_{\mathrm{EPR}}(1). \tag{18}$$

From equation (18) we obtain the analytical shape of the D.O.M.E.S.R. signal for the homogeneous case (one only value of ω_0) as

$$S_{\mathrm{DOM}}^{\mathrm{homo}} \propto \frac{\lambda_s^2 \lambda_r \omega_0 T_1 T_2^2}{1 + \Delta_2^2 T_1^2}. \tag{19}$$

Equation (19) shows that the D.O.M.E.S.R. signal, for homogeneous lines, has the usual lorentzian lineshape. *The linewidth however is in this case driven by the longitudinal relaxation processes.* Analytical computations are more difficult for inhomogeneously broadened lines. Some simple cases, but none the less meaningful for the understanding of the D.O.M.E.S.R. phenomenon, can still be studied. Let us consider the case of two spin-packets symmetric with respect to $\omega_r \approx \omega_s$ and separated by one spin-packet linewidth. Under this condition the contribution of each packet is a mixture of absorption and dispersion; when however the contributions are summed the D.O.M.E.S.R. signal becomes

$$S_{\mathrm{DOM}}^{\mathrm{inhom}} \propto \frac{1}{[1 + (\omega_s - \omega_0^*)^2 T_2^2]^2} \frac{\lambda_s^2 \lambda_r \omega_s T_1 T_2^2}{1 + \Delta_2^2 T_1^2}. \tag{20}$$

As we have discussed for the L.O.D.E.S.R. signal, in this case also, the variation of Δ_2 occurs in a range comparable with $1/T_1$, i.e. for values where $|\omega_s - \omega_0^*|$ is essentially constant. Also *when different spin-packets contribute to the signal, the overall lineshape preserves the lorentzian character dominated by the longitudinal relaxation processes.* These meaningful approximate results have been confirmed fully by solving the system (8) numerically [36].

3.2. *A few notes on experiments*

Both the L.O.D.E.S.R. and D.O.M.E.S.R. methodologies have been applied recently to the study of different systems. Measurements aimed chiefly at ascertaining the capabilities of these spectroscopies in studying for the relaxation processes of the materials and to verify that the measured quantities correspond to the same physical phenomenon, according to theoretical expectations. These measurements were concerned with:

(1) a series of dextrose chars pyrolysed at different temperatures and then studied at room temperature; these systems show a very wide range of relaxation times, according to the pyrolysis temperature. In all cases the chars gave broad inhomogeneous E.P.R. lines [41];

(2) frozen solutions of the nitroxide TEMPO in glycerol, measured at different temperatures [42].

In both series of measurements the dependence of the relaxation processes on the external parameters has been easily determined, up to very slow processes. In the cases where measurements with both spectroscopies on samples in identical conditions have been possible, a good superposition of the measured longitudinal relaxation parameters has been obtained and theoretical deductions have been strengthened.

4. Discussion and conclusions

Although the relaxation treatment given here is fairly poor and a more exact theoretical development about the relaxation models is demanded, it is clear that the results of measurements by the non-linear techniques discussed here, are strictly connected to the longitudinal relaxation processes. The experiments and their excellent agreement with the theoretical predictions for both the D.O.M.E.S.R. and L.O.D.E.S.R. spectroscopies enable us to summarize the main features of these methods with some emphasis to their features in the perspective of eventual application to the study of polymeric liquid crystals:

> these methods account for very slow molecular processes affecting the *longitudinal relaxation* in E.P.R. conditions and yield mutually complementary information. In particular the L.O.D.E.S.R. method is very sensitive in a wide range of relaxation, while the D.O.M.E.S.R. is more limited in the range, but more convenient when the relaxation processes become ultra slow and the application of L.O.D.E.S.R. method becomes awkward.
>
> both methods are relatively cheap and simple in the experimental design:
>
> any problem related to inhomogeneous broadening of lines is completely overcome since both the techniques account for the longitudinal relaxation processes of the single spin-packet.
>
> D.O.M.E.S.R. and, in this application, L.O.D.E.S.R. spectrocopies are performed at fixed values of the static field; by changing these values across the whole spectrum, a two-dimensional representation of the longitudinal relaxation processes can be obtained, as observed for the transverse relaxation processes by the electron spin echo technique.

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