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Dipolar and chemical shift anisotropy relaxation in a solid polymer measured by the NMR coherence time in the rotating frame

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Abstract

In this paper a new approach is proposed to the study of slow dynamics in solid complex systems, such as solid polymer or dense macromolecular aggregates. The peculiar aspect of this method is its ability to separate the relaxation contribution coming from the NMR interactions, which are commonly found in such systems, namely the direct dipolar coupling and chemical shift anisotropy. In this approach, the effect of such interactions on relaxation are, to some extent, separable and observable experimentally vs. temperature and vs. the effective resonant frequency. This is realised by measuring the coherence time in the rotating frame $T_{2\rho}$, which is an unusual NMR parameter whose behaviour is strictly related to the orientation of a tilted rotating frame with respect to the Zeeman field axis. Such an orientation drives the role of the secular part of spin Hamiltonian and makes it controllable experimentally. Thus 'fine' interaction effects, like the chemical shift one, may be observed to overcome the main effect of the stronger direct dipolar interaction.

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1. Introduction

Within the NMR parameters utilised to characterise solid spin systems [1], the so-called relaxation times in the rotating frame are particularly useful. In particular $T_{2\rho}$, the coherence or transverse relaxation time has interesting fea-

tures that apply to the study of solid state relaxometric studies [2,3].

The analysis of the $T_{2\rho}$ behaviour shows that the range of spin dynamics to which $T_{2\rho}$ is sensitive extends to motion slower than that limited by the ordinary weak collision theory [4]. The $T_{2\rho}$ dispersion in the time scale of dynamics, is characterised by an 'ultraslow motion' term which appears as a branch of $T_{2\rho}$ dispersion curve, with a minimum at a frequency associated with the local magnetic field experienced, on average, by spins [5]. The appearance of this term is related to the transformation properties and operations that must be made when

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the reference frame for spin interactions is changed [6]. It is known that these transformations are regulated by elements of Wigner matrices associated with the angles describing the relative orientation between frames. In our case, the frames of interest are the so-called tilted rotating frame (TRF: $x'y'z'$, where $B_e z'$ and B_e is the effective Zeeman magnetic field) and the rotating frame (RF: xyz , where $B_0 z$ and B_0 is the main Zeeman field). The ranks of Wigner matrices involved in the RF–TRF transformation depend by spin interactions: Hamiltonians linear in the spin operator originate first rank transformations in spin–space, while bilinear interactions transform by second rank Wigner elements [7].

Therefore there are particular values of the angle between the Zeeman axes z and z' which cancel the secular parts of the spin interactions in the TRF: by driving opportunely the TRF orientation [8], it is possible to isolate the contribution of the various spin interactions to relaxation.

In this paper we present a very preliminary application of this new approach to solid state NMR relaxation that shows its experimental value and its potential. The results we present in this work, although of qualitative character, show the effect of the secular part of dipolar interaction on the relaxation associated to the weaker interactions like that of chemical shift. In the solid polymer utilised as sample, the cancellation of the secular dipolar term allows the detection of the relaxation associated to chemical shift anisotropy, which shows structures absent in the relaxation by dipolar interaction. We report the example of the $T_{2\rho}(\theta_M, \omega_e)$ behaviour measured in a thermally stressed and unstressed sample of polyethylene (θ_M is the special angle between the axes z and z' which makes null the secular Hamiltonian and ω_e is the effective resonance frequency). In this solid polymer a marked difference is detected by $T_{2\rho}(\theta, \omega_e)$ between the stressed and unstressed sample while small differences are detected by the usual $T_{1\rho}$ relaxation, namely the spin–lattice relaxation time in the RF. This difference may be assigned to mechanisms involving chemical shift anisotropy that normally are difficult to observe by relaxation measurements. A full discussion of such mechanisms is outside the scope of this work and,

furthermore, it could not be made on the basis of the qualitative results presented here. Some indication of the role of the different Hamiltonians can however be given also by these simple data.

2. Theory and experimental results

The transformation from RF to TRF for a generic random spin Hamiltonian can be expressed as

$$\sum_{m=-l}^l (-1)^m A_{lm} F_{l-m}(t) \Rightarrow \sum_{mm'} (-1)^m e^{im'\alpha} d_{m'm}^{(l)} \times (\theta) e^{im\beta} A_{lm} F_{l-m}(t), \quad (1)$$

where the scalar product of irreducible l-rank spherical tensor A_{lm} and F_{lm} , dependent on spin and random coordinates respectively, is projected on TRF by means of the reduced Wigner matrix elements $d_{mm'}$ and rotation operators of angles $\alpha = \omega t$; $\theta = \tan^{-1}((\gamma B_1/(\omega_0 - \omega))$; $\beta = \omega_e t = \gamma B_e t = \gamma [((\omega_0 - \omega)/\gamma)^2 + B_1^2]^{1/2} t$. Here $\omega \cong \omega_0 = \gamma B_0$ is the frequency of the oscillating radio frequency magnetic field $2B_1 \cos \omega t$.

The weak collision approach to relaxation gives for bilinear spin Hamiltonian [9]

$$\frac{1}{T_{2\rho}} \propto \sum_{mm'} (d_{mm'}^{(2)}(\theta))^2 (m' + 2)(3 - m') J(m\omega_0 + m'\omega_e), \quad (2)$$

where $J(m\omega_0 + m'\omega_e)$ is the reduced spectral density of the correlation function $\langle F_{lm}(0) F_{lm}^*(t) \rangle$. For linear spin Hamiltonians the transverse relaxation is given by the equation [10]

$$\frac{1}{T_{2\rho}} \propto \sum_{mm'} (d_{mm'}^{(1)}(\theta))^2 (m' + 1)(2 - m') J(m\omega_0 + m'\omega_e), \quad (3)$$

In both Eqs. (2) and (3), the role of $J(0)$, which is originated by the secular part of Hamiltonian, can be modified by changing the relative orientation between RF and TRF, that is by modifying the ratio between the resonant frequency offset and the radio frequency field intensity [8].

Because $J(0)$ is set up by the condition $m = m' = 0$, it means that the matrix elements

$$\begin{aligned} d_{00}^{(2)} &= -\frac{1}{2}(3 \cos^2 \theta - 1) \\ d_{00}^{(1)} &= \cos^2 \theta \end{aligned} \quad (4)$$

regulate the $J(0)$ role in the case of bilinear ($d_{00}^{(2)}$) or linear ($d_{00}^{(1)}$) interactions. Experimentally this can be made by changing the angle θ from about 54° to 90° which, to some extent, signifies to switch on or off the spin interactions dependently by their rank. In the case of polymers strongly entangled and in absence of quadrupolar interaction, the main spin Hamiltonians affecting the relaxation are the dipolar and the chemical shift ones, which are respectively bilinear and linear in the spin operators.

Our approach to $T_{2\rho}$ measurement is based on the pulse sequence reported in Fig. 1 [8]. The sequence is composed by two radio frequency pulses of length τ_e phase shifted from each other by an angle of 180° . The intensity and resonant offset of the two pulses are set in such a way that an appropriate value of θ is selected and fixed independently by the effective magnetic field and, therefore, measurements with the same θ can be made at different effective resonant frequencies. The phase shift associated with the inversion of the resonant offset produces a rotation of an angle 180° of the z' axis (the second pulse rotates the TRF of an angle $\theta + 180^\circ$ with respect to the z axis) allowing thus a TRF spin echo refocusing. The interval $2\tau_e$ determines the duration of $T_{2\rho}$ evolution, while the time t_w makes the coherence of the signal in the RF to be nullified.

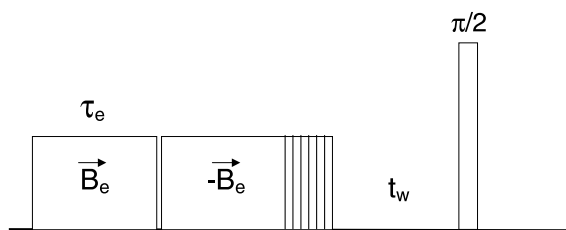


Fig. 1. The $T_{2\rho}(\theta)$ sequence for the rotary echo formation is shown. All the inhomogeneity effects due to the radio frequency field and to the main Zeeman field are therefore eliminated from the signal because of the echo mechanism. The time t_w serves to destroy the coherence signal in RF, so that it must be $t_w \gg T_2$, where T_2 is the coherence time in the RF.

When the pulses are set at $\theta = \theta_M \approx 54^\circ$, the secular part of the dipolar spin interaction is cancelled out and the $T_{2\rho}$ relaxation is associated with the activity of chemical shift anisotropy and to the non-secular terms of dipolar interaction which are sensitive to very slow dynamics [5]. Although it is scaled by a factor $\sqrt{3}$, the chemical shift anisotropy dominates the relaxation mechanisms and, in practice, the ‘magic angle’ relaxation can be attributed to it.

As first experimental result we report in Fig. 2 the $T_{2\rho}$ dependence on θ , at a fixed effective frequency of 60 kHz and room temperature, in a commercial sample of high density polyethylene (HDPE), about 50% crystalline and 50% amorphous, and with a molecular weight of about 5×10^5 . The NMR frequency was 30 MHz on proton. The measurements have been performed by a partially home-made NMR spectrometer based on a Bruker 100/100 electromagnet whose limited stability makes the measurements greatly time spending (about 12 h per point) because of the large number of scan average.

The fit of $T_{2\rho}(\theta)$ made by Eqs. (2) and (3) shows clearly that at $\theta = \theta_M \approx 54^\circ$ the relaxation efficiency is at its lowest value because at this angle the relaxation is produced by the small chemical shift anisotropy contribution described by Eq. (3). The results of Fig. 2 match very well with Eqs. (2) and (3). The condition $\|H_D\| \gg \|H_{CS}\|$, where H_D and H_{CS} are the Hamiltonians of dipolar and chemical shift interactions respectively, is very general in solid systems, but for $\theta = \theta_M$. The maximum ratio between the contribution of the two terms is about two: this confirms the prominent role of the dipolar term in the relaxation. This result is different with respect to that obtained for the dipolar relaxation time in the rotating frame [11,12] because of the explicit dependence of $T_{2\rho}$ by the secular term of interaction.

In Fig. 3 the dispersion of $T_{2\rho}$ for a sample of polyethylene at room temperature is reported for stressed and normal samples. The stressed sample has been heated by a thermal bath at 150°C for 1 h and then cooled, as fast as possible, to 15°C . Also in this case all measurements have been made at room temperature and at 30 MHz on protons.

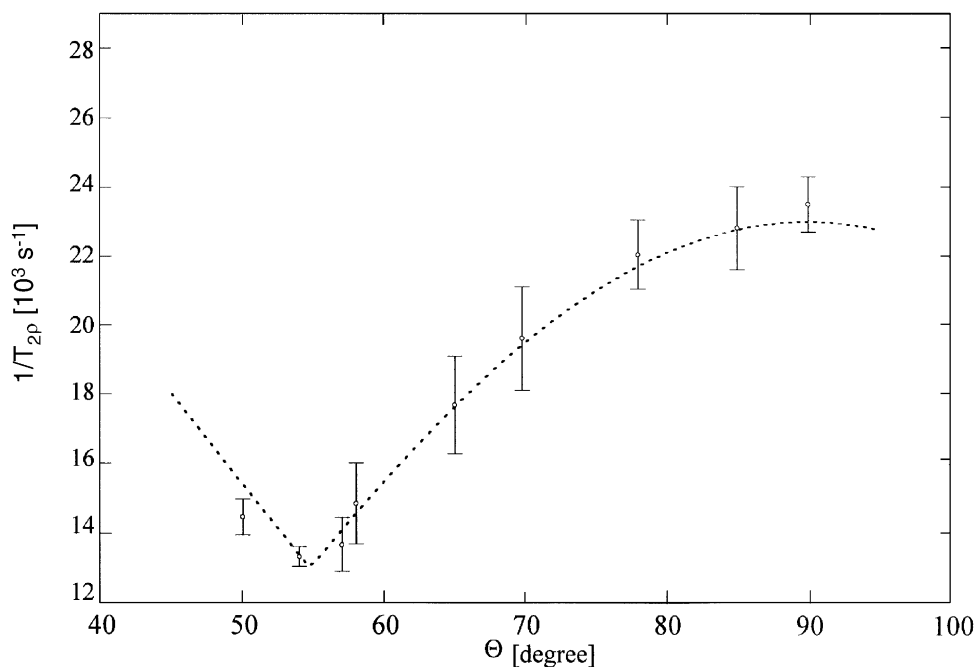


Fig. 2. $T_{2\rho}(\theta)$ at room temperature in a sample of polyethylene at a fixed effective frequency of about 60 kHz.

The data reported in Fig. 3 show that $T_{2\rho}$ is able to detect the change produced by the thermal stress in the solid while the traditional $T_{1\rho}$ measurement made, as usual, at $\theta = 90^\circ$, is not able to detect it (Fig. 4). This evidently because the degrees of freedom related to the activity of chemical shift anisotropy have been modified by thermal stress because of some change in the structure and therefore in the molecular field symmetry. The relaxation from chemical shift anisotropy is normally related to the rotation of CH_2 groups, as in our polymer or, more generally, to the rotation of the termination groups of the polymer chains. It is also evident from Fig. 4 that the degrees of freedom which affect the dipolar relaxation are not changed by the thermal stress, at least for the dynamics range established by the effective frequency to which the measurement has been performed.

3. Conclusions

In this paper we proposed a new tool for studying the slow dynamics in solid complex sys-

tems like polymer melts or macromolecular aggregates. This approach offers the remarkable possibility of following the relaxation effect associated with the different NMR interactions and to follow their evolution also vs. temperature and vs. the effective resonant frequency.

In these spin systems the more common spin couplings are those described by the direct dipolar coupling and chemical shift anisotropy. While the direct dipolar effect on relaxation is that normally observed by $T_{1\rho}$ measurements, the observation of the chemical shift anisotropy relaxation is rare in solids because it behaves as a sort of 'fine' interaction and is normally obscured by the dipolar one. With the approach proposed here, it is possible to study the effect related to the chemical shift anisotropy only, that is independent of the magnitude of the dipolar interaction. Such an occurrence could facilitate the assignment of dynamics to some molecular structure since the two interactions are modulated by a time-dependent perturbation in different ways: typically the rotational diffusion for chemical shift anisotropy and translation for direct dipolar coupling. The direct observation of the

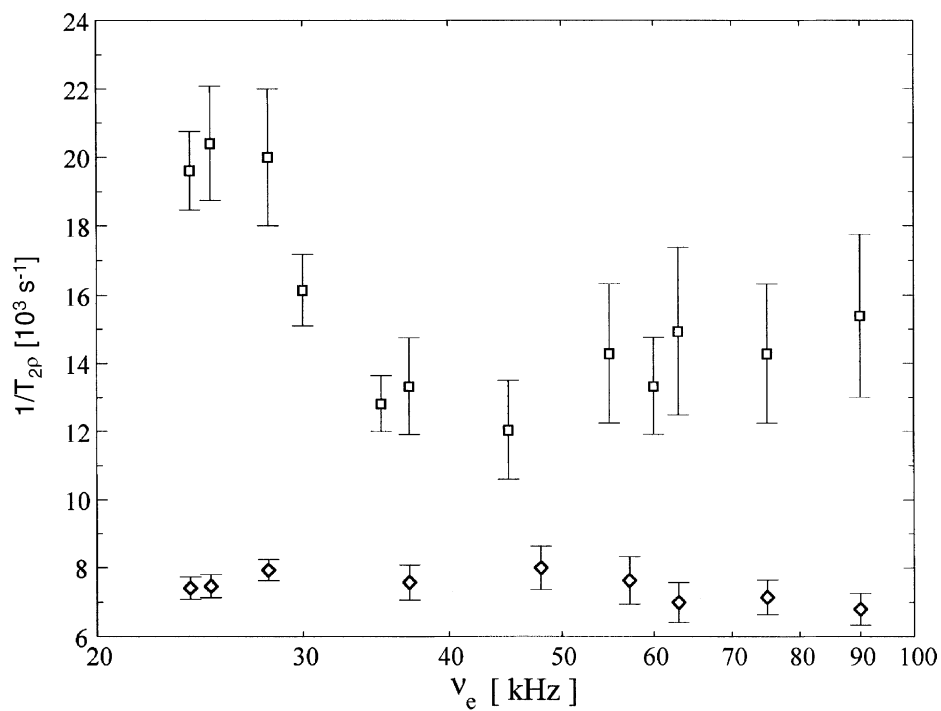


Fig. 3. The dispersion of $T_{2\rho}$ ($\theta \approx 54^\circ$) for two samples of polyethylene is reported. The upper data refer to a normal polyethylene sample while the lower one to a stressed one.

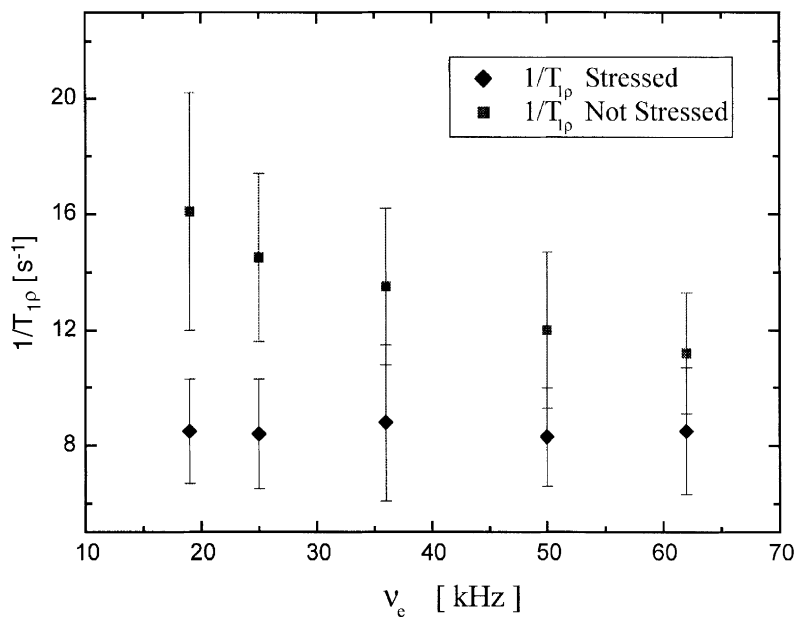


Fig. 4. The dispersion of $T_{1\rho}$ for the samples of polyethylene is reported. The upper data refer to a normal polyethylene sample while the lower one to the stressed one.

chemical shift relaxation in solids therefore gives a direct view of the dynamics/structure events associated to rotation of molecular branch and to its molecular field. This is normally overshadowed by the dynamics/structure events related to dipolar interaction, which are sensitive mainly to dynamics involving motion along the polymer chains.

The results presented in this paper had the main objective of showing the practicability of our method and also to show that some effects normally invisible with the $T_{1\rho}$ relaxation can be observed with $T_{2\rho}$. As an example we report some qualitative results obtained on a polymer submitted to a thermal cycle. The change in some structural parameters is invisible to $T_{1\rho}$ but not $T_{2\rho}$ which shows a marked different behaviour between the stressed and unstressed samples, thanks to the greater sensitivity of the chemical shift anisotropy relaxation with respect to the dipolar one which is dominated by the intensity and orientation of the dipolar field and is weakly sensitive to the symmetry of the molecular field.

Although some indications on the role of the different Hamiltonians have been extracted from the data presented here, the main objective of the

paper was the presentation of a tool which seems very promising for the study of low frequency dynamics and structure of solid state spin system.

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