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Short Communication

Dynamic disorder in stable and metastable thiophene. II. Non Lorentzian nuclear relaxation and glass transition

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Résumé. — Nous avons effectué une étude du thiophène cristallin par relaxation magnétique nucléaire du proton. Nos résultats montrent qu'aussi bien dans les séquences de phases stables que métastables, la réorientation dans le plan moléculaire ne peut être décrite par un seul temps de corrélation. Ce phénomène de relaxation nucléaire non lorentzien est interprété en termes d'une distribution de temps de corrélation, et en termes de la description, mathématiquement équivalente, des puits de potentiels inégaux. Notre conclusion est que le phénomène observé constitue une signature, au plan dynamique, des systèmes susceptibles d'être vitrifiés.

Abstract. — A study of the proton nuclear relaxation of crystalline thiophene has been undertaken. Our results demonstrate that, in both the stable and the metastable phase sequences, the in-plane molecular reorientation does not have a single correlation time. This non Lorentzian nuclear relaxation is discussed in terms of a distribution of correlation times and in terms of the mathematically equivalent model of unequal potential wells. We conclude that the observed relaxation feature is the dynamical fingerprint for glass-forming materials.

Introduction.

The first part of this work published earlier [2], has revealed an in-plane dynamic disorder of the thiophene (C_4H_4S) molecule in both the stable and the metastable crystalline phase sequences. In addition, the proton n.m.r. second moment calculations, based on structural data, has shown that the many different allowed local configurations were energetically inequivalent. Our suggestion that this behaviour could be related to the existence of the glass transitions observed at very low temperature is examined here in the light of a proton magnetic resonance study.

Experimental.

The thiophene samples studied here had the same origin as those used in our previous work [2]. The nuclear spin relaxation times were measured, at 25 and 80 MHz, using a Bruker SXP spectrometer. T_1 have been obtained using the inversion-recovery method. The temperature was controlled to better than 1 K. The precision of the T_1 data is estimated to be $\pm 5\%$.

Results.

The temperature dependences of T_1 in the metastable and stable phase sequences are plotted in figures 1 and 2 respectively (see part I of this work for the appropriate thermal treatment that enables us to study these sequences independently). The existence of a single minimum in each phase sequence can obviously be attributed to the in-plane molecular motion already revealed in our earlier lineshape study [2]. No appreciable discontinuity can be observed at the various phase transitions, except for the first order II-III transformation in the stable sequence. This again agrees with our previous findings [2].

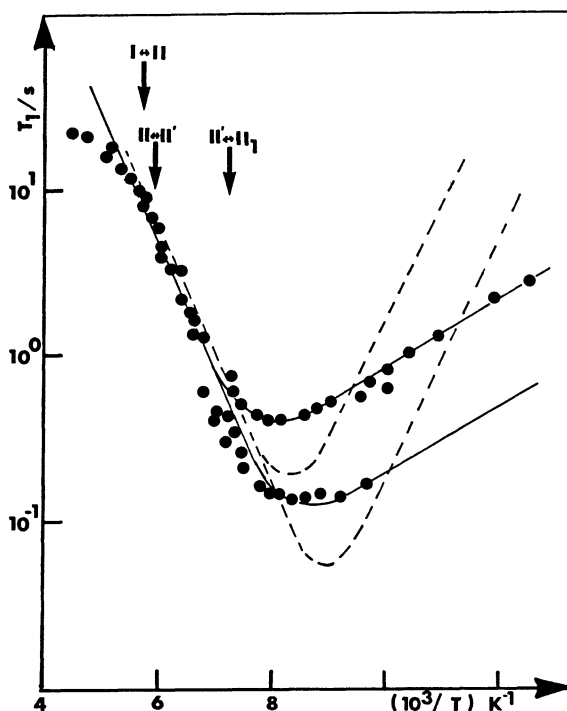


Fig. 1.— Proton spin-lattice relaxation times (T_1) versus $1/T$ plot for thiophene in the metastable phase sequence : (•) experimental data at 25 and 80 MHz ; (---) computed T_1 values with the Lorentzian model (B.P.P. theory) ; (—) computed T_1 with Noack's calculation [6] using a Davidson and Cole distribution of correlation times with $a = 0.27$ (see text). The phase transition temperatures are indicated by arrows (details on the phase diagram are given in part I of this work [2]).

The prominent feature of these T_1 data is the departure from the well-known Lorentzian (single correlation time) Bloembergen-Purcell and Pound (B.P.P.) relaxation theory [3]. The computed T_1 values using an exponential correlation function (Lorentzian spectral density) is shown in figures 1 and 2 and illustrate the deviations of the data from the predictions of the B.P.P. theory :

1) an asymmetry is observed in the slopes of T_1 vs. $1/T$ on the two sides of the minima. The ratio of the cold to the hot side slopes is 0.28 in the metastable sequence and 0.60 in the stable one ;

2) at low temperature (cold side of the minima), the frequency dependence of T_1 is ω_0^m with

$m = 1.24$ (metastable sequence) and $m = 1.60$ (stable sequence), instead of the predicted value of $m = 2$ [4];

3) the T_1 values at the minima are longer than expected for the Lorentzian model by a factor of approximately 3 to 4.

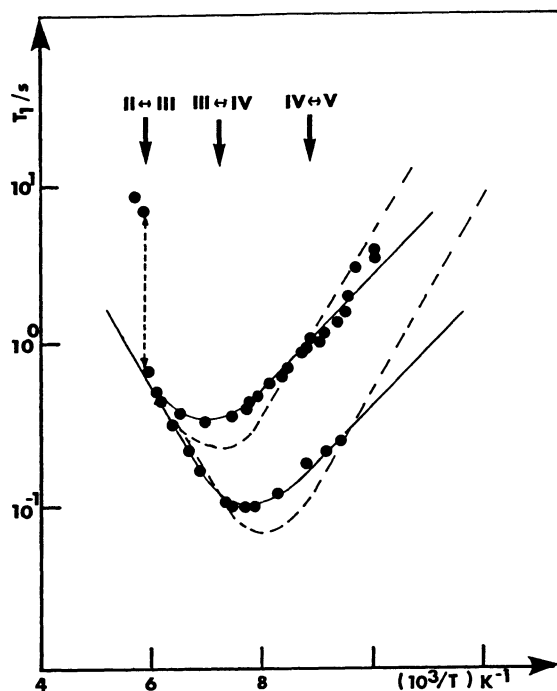


Fig. 2.— Proton spin-lattice relaxation times (T_1) versus $1/T$ plot for thiophene in the stable phase sequence : (●) experimental data at 25 and 80 MHz ; (---) computed T_1 values with the Lorentzian model (B.P. theory) ; (—) computed T_1 with Noack's calculation [6] using a Davidson and Cole distribution of correlation times with $a = 0.60$ (see text). The phase transition temperatures are indicated by arrows (details on the phase diagram are given in part I of this work [2]).

A good fit to the data has been obtained here with the use of the Davidson and Cole [5, 6] distribution of correlation times $g(\tau)$:

$$g(\tau) = \begin{cases} \{(\sin a\pi)/\pi\} \{\tau/(\tau_0 - \tau)\}^a & \tau < \tau_0 \\ 0 & \tau > \tau_0 \end{cases} \quad (1)$$

a is the width of the distribution ($a = 1$ in the limit of a single correlation time).

The best fit obtained for thiophene is shown in figures 1 and 2.

A particular (and useful) result from the Davidson and Cole distribution is that [7] the ratio of the hot side to the cold side slopes is equal to " a ". The cold side frequency dependence of T_1 being ω_0^{1+a} . This agrees fairly well with experiment, using $a = 0.27$ for the metastable sequence, and $a = 0.60$ for the stable one.

Molecular motion and glass transitions.

In some previous works on glassy crystalline materials [8-10], we have expressed the idea that the thermodynamic glass transition must be correlated with the freezing of a large amplitude molecular motion. By "freezing", we mean that the characteristic time of the motion, which progressively increases while lowering the temperature, becomes longer than the time-scale of the specific heat experiment ($\sim 10^5$ s). Our present data on thiophene agree with this hypothesis, since an extrapolation to low temperature, using an Arrhenius activated law with the measured apparent activation energy of 15.3 kJ mol^{-1} (hot side slope of the $\ln T_1$ vs. $1/T$ line), predicts the occurrence of a thermodynamic glass transition at 41.6 K in the stable phase sequence and 40.7 K in the metastable one. The actual glass transitions have been observed at 42 and 37 K respectively [11].

We now turn to the possible connection between the occurrence of glass transition and the observed non Lorentzian n.m.r. relaxation.

An alternative explanation for the non-Lorentzian relaxation data such as those observed in this work has been provided by Look and Lowe [12], Anderson [13] and Polak and Ailion [14]. These authors have interpreted their data as arising from molecular motion occurring between energetically non equivalent sites. Such a model seems *a priori* relevant to describe the orientational disorder in a molecular crystal for which the usual Frenkel model of jumps between definite orientations has been successfully applied in a previous X ray scattering study [16]. Anderson [13] has treated a model of jumps between minima in the threefold potential where two minima have equal depth and the third may have higher or lower potential energy by an amount of Δ ($\Delta > 0$ for higher and $\Delta < 0$ for lower energy). Polak and Ailion [14] have reported relaxation rates in solid trans, trans, mucodinitrile for which the asymmetry parameter Δ is positive. In this case, the molecules spend a greater fraction of time in the low energy orientation and this produces smaller orientational fluctuations which leads to very long T_1 and an asymmetry in the temperature dependence of $\ln T_1$ opposite of what is observed here. In contrast, the thiophene relaxation behaviour can be accounted for by considering $\Delta < 0$. In this case, a partial reorientation still occurs between the lower energy minima. This incomplete rotational process leads to T_1 values larger than predicted by the usual B.P.P. theory but still of the same order or magnitude (see Refs. [13 ; 15]). Moreover, the asymmetry of the temperature dependence of $\ln T_1$ now results in a smaller slope at low temperature (see Ref. [14], Eqs. (6a, b)) in agreement with our observations. A simple model with only one asymmetry parameter has been shown to account for all the unexpected features observed in thiophene [15]. However, the fit is quantitatively poorer than the one described here using a distribution of correlation times. As shown by X ray scattering [16], a physically more feasible model would imply 20 inequivalent potential wells. Since hardly any information is available on the relative depth of the minima we did not try to improve our fit by adding arbitrarily chosen asymmetry parameters. We assert however that a good fit to the data can be achieved using such an appropriate model since the unequal potential wells model is formally equivalent to the more phenomenological distribution of correlation times. Indeed a molecular motion occurring between energetically non equivalent sites will produce a non exponential decay of the autocorrelation function $\phi(t)$ describing the motion [17]. This in turn leads to a non Lorentzian density function $J(\omega)$. Since a non exponential decay of $\phi(t)$ can be viewed as the Laplace transform of a distribution of correlation times :

$$\phi(t) = \int d\tau g(\tau) \exp(-t/\tau) \quad (2)$$

both descriptions of the non Lorentzian relaxation behaviour are then mathematically equivalent.

The unequal potential wells model provides a simple rule for predicting the occurrence of a non Lorentzian relaxation behaviour : if the symmetry group of the allowed molecular orientations is not a subgroup of the molecular symmetry group (or *vice versa*), or, if it is so, when the respective symmetry axes of these two groups do not coincide, a non Lorentzian behaviour will be observed. This explains why such behaviour is observed in thiophene but not in benzene, in cyclohexanol but not in cyclohexane and in azaferrocene but not in ferrocene. A non Lorentzian n.m.r. behaviour clearly indicates that some molecular degree of freedom can be frozen-in through an appropriate thermal treatment.

This "departure from molecular symmetry" rule was borrowed from Szwarc [18] who, independently, suggested it as a clue to account for secondary glass transitions in molecular crystals. This parallel between n.m.r. dynamic relaxation features and the thermodynamic glass transition phenomenon leads us to conclude that the observed non Lorentzian relaxation is nothing else than a dynamical fingerprint for glass-forming materials.

Thiophene has proved to be an excellent model-system for studying such a complicated phenomenon as glass transition. A further insight into the local disorder should be provided by neutron scattering experiments and molecular dynamics simulations.

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