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Fast intramolecular dynamics of triphenyl phosphite investigated by ^{2}H NMR

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Abstract. The first analysis of rapid intramolecular motions of triphenyl phosphite by ^{2}H NMR is presented. The fragile slowing down of the primary relaxation is followed by a solid-echo method. The occurrence of a fast reorientation of the phenyl side groups is demonstrated in the supercooled liquid state, identified as a two-fold flip on the basis of simple lineshape simulations. Coexistence of both static and motionally averaged components in "two phase" spectra indicate a broad distribution of correlation times for this relaxation. This dynamical behavior is shown to persist in the glacial phase.

PACS. 61.25.Em Molecular liquids – 76.60.-k Nuclear magnetic resonance and relaxation – 64.70.Dv Solid-liquid transitions

1 Introduction

First-order structural phase transitions are common in crystalline solids whereas first-order liquid-liquid phase transitions are excessively rare in pure compounds. The existence of liquid polymorphs is beginning to be recognized and a growing interest is devoted to first-order polyamorphic transitions. These phase transitions are principally observed by applying a high pressure [1,2], and are generally associated with a change of density. The evidence of a low-temperature phase in triphenyl phosphite (TPP) at atmospheric pressure [3,4], distinct from the glass, the supercooled liquid and the normal liquid (named the glacial phase) was considered as an original manifestation of polyamorphism, and a real opportunity to analyze such a situation. This glacial phase was obtained *via* a first-order transition from the supercooled liquid state [3–9], either by slow heating from the glass or by maintaining the temperature isothermally above the calorimetric glass transition in the range 210 K–235 K. The opportunity to form the intriguing glacial phase of TPP by a mere variation of temperature has given rise to numerous experimental investigations [3–19] leading to controversial descriptions of the glacial state. Various experimental results (Raman spectroscopy [9,13,15,16], X-ray diffraction [12], inelastic neutron scattering [15] and differential scanning calorimetry [17]) converge into a description of the glacial state in terms of micro- or nanocrystallized domains of the stable crystalline phase, mixed with non-transformed supercooled liquid. The origin and the relative stability of this state were explained from a rapid nucleation rate leading to a heavily nucleated state which frustrates further crystallization [17]. Evidence for rapid nucleation associated with the glaciation process was reported in other works [18,19]. Not so far from this description, Kivelson *et al.* have suggested that the glacial state was apparently amorphous [3–5], and described this phase as a defect-ordered crystal. However the origin of such a picture of the glacial state, emanating from the "frustration-limited domains" (FLD) thermodynamic theory of supercooled liquid [20], is fundamentally different from frustration by high nucleation. The formation of a defect-ordered crystal would be connected with the inability of the system to tile space after the development of a local structure, *versus* to a topological frustration. Demirjian *et al.* [19] have described the glacial state, from NMR experiments interpreted in the frame of the FLD theory, as a plastic crystal composed of domains of nanocrystals. Outside the description of the glacial state as not truly amorphous, Rössler *et al.* claimed that the glacial state is liquid [8,10,21], and the transformation of the supercooled liquid into the glacial state was interpreted as a change of fragility on the basis of dielectric and NMR data. Mizukami *et al.* [11] have also described the glacial state as a highly-correlated liquid from X-ray diffraction, calorimetric, and dielectric measurements. From the high density and diversity of experimental results reported in the literature, emerge intriguing and not yet explained features about the dynamics in the glacial state of TPP. The most intriguing feature is the unusually

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broad dielectric loss in the very low-frequency range. Recent dielectric investigations [22] have revealed that the α-peak (characteristic of the dynamics in the liquid state) was not detected in the glacial state despite the remaining liquid. By heating the glacial state the α-peak is recovered indicating that the original liquid is then present. The analysis of the low-frequency Raman spectrum has revealed similar features [22]. The Rayleigh wing (characteristic of the liquid) disappears during the glaciation process, and is recovered by heating the glacial state. However, it is worth pointing out that characteristic internal bands of the liquid state are observed in the Raman spectrum of the glacial state [16]. Such observations could be interpreted as a change of dynamical properties of the liquid in the glacial state. Another common feature emerging from NMR investigations is the apparent incompatibility of ^{31}P NMR results [8,10] with the description of the glacial state as composed of nanocrystallized domains. However ^{31}P NMR is mainly sensitive to the dynamics of the mass centers of the molecule, and the glacial state is mainly composed of non-transformed supercooled liquid if it is formed in a low-temperature range (210 K–220 K). The use of the deuterium probe can be considered more sensitive to intra-molecular motions in TPP and thus to give a better understanding of reorientations in different states. To get a better insight into the dynamics in the glacial state, ^{2}H NMR experiments were carried out to analyze relaxation processes during glaciation, in the glacial state, and during the conversion of the glacial state into the crystal by heating.

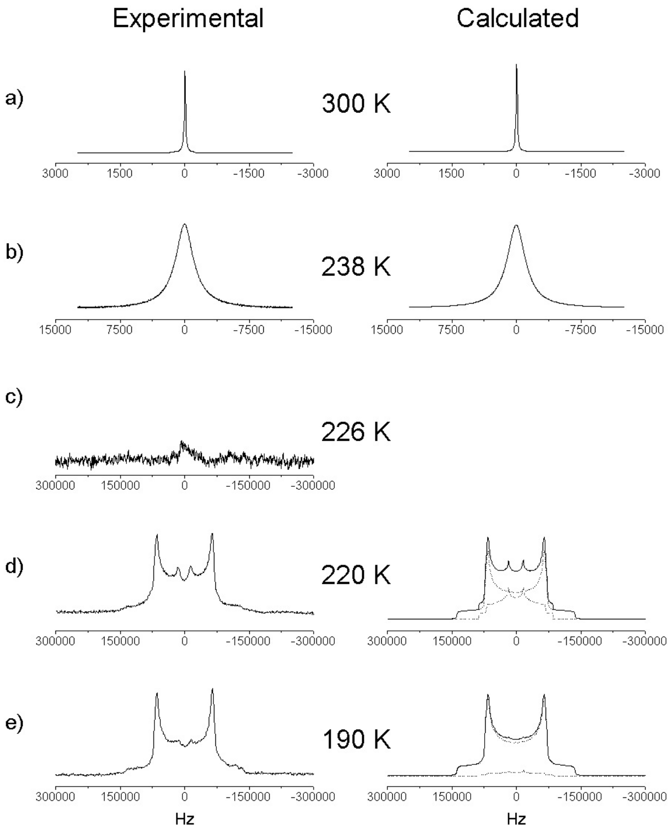

Fig. 1. Left column: ^{2}H NMR spectra of undercooled TPP (quenched down to the observation temperatures at ca. 10 K/min), recorded from a one-pulse (300 and 238 K) or a solid-echo sequence (226, 220 and 190 K). Right column: Refinements of the corresponding experimental spectra using a single Lorentzian line (300 and 238 K), or a combination of two weighted $Q1$ and $Q2$ static quadrupolar lineshapes for spin $S = 1$, with fixed parameters: $Q1$ ($\delta = 137.5$ kHz, $\eta = 0.05$) and $Q2$ ($\delta^* = 86$ kHz $= 5\delta/8$, $\eta^* = 0.6$).

2 Experimental section

Per-deuterated Triphenyl Phosphite was prepared by reacting d$_6$-phenol (Janssen) with phosphorous trichloride (Janssen) under inert atmosphere at room temperature. A final enrichment of about 98% was reached. All experiments were carried out on a Bruker AV400 solid state NMR spectrometer using a Bruker 4mm MAS probe, at 61.42 MHz for ^{2}H. The temperature was monitored with a Bruker BVT 3000 unit, cooling the dried bearing airflow in liquid nitrogen. The gas flow was maintained at sufficiently low pressure to prevent the sample from spinning. With this servo control, heating and cooling rates of about 10 K/min (above 240 K) and about 5 K/min (below 240 K) were obtained. The isothermal temperature stability was observed to be better than 0.2 K. Depending on the liquid- or solid-like aspect of the response, single pulse or solid-echo experiments with $\pi/2$ pulses of 2.6 μs were employed. The pulse spacing for solid-echo experiments was adjusted to 20 μs in order to exceed the approximately 12 μs receiver dead-time. For all experiments conducted on TPP samples in their glassy or glacial phases, fully relaxed spectra were obtained with repetition delays of one second. For experiments on the crystal form, a repetition time of 20 seconds was necessary. The experimental spectra were refined using the DMFIT program [24], with standard static quadrupolar models (assumed to be valid in either the slow or fast limits, and with a systematic 20 Hz Lorentzian broadening) relying only on the two parameters δ (anisotropy) and η (asymmetry) of the quadrupolar tensor defined by [25]:

$$\nu(\theta,\phi) = \pm\frac{\delta}{2}\left((3\cos^2\theta - 1) - \eta\sin^2\theta\cos(2\phi)\right). \tag{1}$$

3 The supercooled liquid

Reference spectra of supercooled liquid TPP at different temperatures were obtained after separate rapid cooling ramps from room temperature (> 10 K/min). Representative samples are displayed in Figure 1, at temperatures ranging from 300 K down to 190 K. At this latter point, the sample was believed to have reached its glassy state. The data show three types of spectra corresponding to three dynamical regimes that follow each other as the temperature is decreased. At high temperatures ($T \geq 230$ K), the spectrum appears as a single Lorentzian line whose width increases upon cooling. In a very narrow temperature window (224–226 K), the ^{2}H NMR signal is hardly measurable, neither by solid-echo nor by the single pulse method. At lower temperatures, the signal reappears and gives rise to broad spectra characteristic of the first order quadrupolar anisotropic broadening. All these low temperature spectra show several discontinuities. The main ones are separated by 128 kHz and are typical of C-D bonds in a static regime. Two additional central discontinuities, distant of 30.3 kHz, can be assigned to a motional averaged component, indicating that a certain proportion of the deuterons are involved in at least one rapid internal anisotropic reorientation. Figure 1b for $T = 220$ and 190 K shows calculated lineshapes to compare with the observed data. These are based on two components: a standard static quadrupolar lineshape ($\delta = 137.5$ kHz, $\eta = 0.05$) assigned to static deuterons and describing the main discontinuities at 128 kHz, and a second component, also based on a static quadrupolar model with parameters $\delta^* = 86$ kHz, $\eta^* = 0.6$, rendering the low frequency peaks at 30.3 kHz. The latter component is assigned to mobile deuterons, and the choice of the lineshape model and its parameters is based on the model of motion explained below.

The three distinct regimes can be interpreted by considering that the mean correlation time of the principal (α) relaxation process dominates the supercooled liquid dynamics, as it slows down on cooling and progressively approaches, matches and crosses the time window of the ^{2}H NMR experiment. In the high temperature window, the Lorentzian shape of the NMR line is an indication of motional averaging of the quadrupolar traceless tensor by an isotropic reorientation of the TPP molecules, in the fast regime ($1/\tau_C \gg \delta$). In this limit, it is possible to extract a model free estimate of the mean correlation time from the linewidth Δ_{FWHM} [26]:

$$\tau_C = \frac{\Delta_{\text{FWHM}}}{2\pi\delta^2_{\text{static}}}\,. \tag{2}$$

In TPP, this estimate is unambiguous, as the measured linewidth is always over 1000 times that measured on D_2O during the standard procedure of compensation of the static field inhomogeneity. The values found for τ_C: 1.3×10^{-8}, 2.4×10^{-8}, 1.3×10^{-7}, 2.8×10^{-7} s respectively at 239, 237.5, 230 and 228 K are in very good agreement with the Vogel-Fulcher model proposed for TPP by Rössler *et al.* [10,21]. This extends over more than one decade the time window in which this is experimentally verified [27,28].

Below 228 K, this mean frequency of isotropic molecular relaxation approaches the quadrupolar static splitting (about 130 kHz). The NMR frequency measured is then only partially averaged by motion, while still many molecules have time to diffuse during the experiment. This phenomenon implies a very rapid loss of coherence in the NMR signal, making it impossible to measure it by a standard echo sequence. This resonance shortening of the homogeneous transverse T_2 relaxation time is a well-known phenomenon often observed in broadline ^{2}H spectroscopy [29,30], unfortunately leading in most cases to a deteriorated signal-to-noise ratio. For that reason, this dynamical window has been recently reinvestigated in the frame of Carr-Purcell-Meiboom-Gill methods [31], offering improved sensitivity [32]. For the supercooled TPP in the range 224 K–227 K, this effect is dramatic, shortening T_2 down to less than 30 μs, making the signal hardly detectable even with a single pulse experiment, due to the NMR probe dead-time. It is worth to note that this temperature range accidentally matches that of the glaciation process in TPP. At lower temperatures, the isotropic α-relaxation becomes slow compared to the NMR signal decay. A quadrupolar lineshape is then measured, which exhibits the characteristic horns of static C-D bonds. Refinement of this component (*cf.* Fig. 1 (right column)) gives an anisotropy parameter of $\delta = 137.5$ kHz with an asymmetry of $\eta = 0.05$. Superimposed to that static spectrum, low frequency discontinuities are visible, indicating the presence of partial motional average, due to a fast relaxational motion distinct from the α-process. Whereas previously reported ^{31}P NMR data [10,21] were mostly sensitive only to global molecular dynamics (as the phosphorous atom is located at the center of the TPP molecule), ^{2}H NMR offers the opportunity to probe the side-group mobility. The simplest dynamical model susceptible to render the position of the observed low frequency peaks is illustrated in Figure 2 (upper part), as a fast 180° flip of the three phenyl rings around their para-O-C bond. This jump implies rapid exchange of the ortho- and meta- C-D bonds, with a flip angle of 120° for the quadrupolar tensor principal axis. If we assume that the remaining para- C-D bond lies on the rotation director, its quadrupolar interaction is not modulated by the ring reorientation. The expected total spectrum in this fast regime model is shown in Figure 2, and consists in the

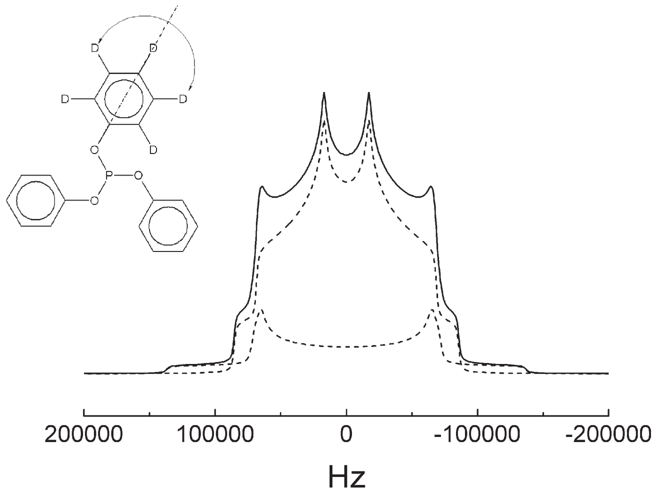

Fig. 2. Upper part: Schematic view of the simple motional model invoked: 180° flip of the side phenyl groups around their O-C bond axis. Bottom: Theoretical lineshape expected from this model: combination of two $Q1$ and $Q2$ static quadrupolar lineshapes for spin $S = 1$, with fixed parameters: $Q1$ ($\delta = 137.5$ kHz, $\eta = 0.05$) and $Q2$ ($\delta^* = 86$ kHz $= 5/8.\ \delta$, $\eta^* = 0.6$), and weighted integrated intensity $Q2/Q1 = 4$.

addition of a static component assigned to the C-D bond lying on the rotation axis and a second component similar to another static one, but with apparent anisotropy $\delta^* = 5\delta_{\text{static}}/8$ ($\delta^* = 85.6$ kHz in the present case) and apparent asymmetry $\eta^* = 0.6$ [25,33]. A ratio of 4 to 1 is expected for the motionally averaged to static integrated intensities, reflecting the number of involved nuclei. Figure 1 (d and e, right column) displays the best fits using these two components at 220 K and 190 K. The parameters $\delta = 137$ kHz , $\eta = 0.05$, then $\delta^* = 85.6$ kHz and $\eta^* = 0.6$ were fixed during the fitting procedure, only the relative intensity of the two components were refined. The experimental separation between the central horns (of about 30 kHz) is in very good agreement with that predicted by the aforementioned model ($\delta^*(1-\eta^*) = 34$ kHz). However, the refined ratio of the narrow and large components is far from 4, and it is temperature dependent, the spectrum becoming almost completely static in the glassy state. This fact shows that only a small number of bonds are actually involved in the observed motion, and that the proportion of static deuterons increases when the sample is further cooled. During the experimental time, the majority of phenyl rings are still, while only a small part are reorienting comparatively very fast ($\tau_C \ll 1/\pi\delta$). In order to account for the data, one must assume the existence of a very broad distribution of correlation times for the phenyl-ring flips. Such apparently "two-phase" temperature dependent spectra characteristic of a wide distribution of correlation times have already been reported in other organic glass formers [33]. This picture of the internal molecular mobility is in agreement with the continuous fading of the central features when cooling down to the glass, indicating that the distribution shifts towards longer times. The measured ratio $W(T)$ between static and dynamic components is then expected to carry information on the static distribution of energy barriers $g(E_A) \propto \frac{\partial W(T)}{\partial T}$ sustending the distribution of correlation times [34]. The completion of such a task would require a systematic experimental study that falls beyond the aim of the present work.

4 Transformation to the glacial phase

We present in this note preliminary results showing how the glaciation process and the final state can be followed by ^{2}H NMR. The glacial states of TPP were obtained through different isotherms after the following temperature cycle: 1) rapid quenching from room temperature (as above), 2) isotherm below T_g (190 K) during 10 to 15 min, 3) rapid heating to the glaciation temperature (216 K < T < 230 K), 4) monitoring of the isothermal transformation, 5) rapid heating to 240 K, and observation for a few minutes at this temperature 6) rapid heating back to room temperature.

Figure 3 displays solid-echo spectra obtained during these isothermal transformations, at different temperatures. The different columns present comparable stages of the evolution for increasing time, although the total durations vary considerably with temperature. During glaciation at 220 K, we waited up to 7 h 30, where no difference with the presented spectrum could be noticed. The presented data have to be assigned to the glacial state after complete transformation. Initially at 228 K, the TPP molecules undergo rapid isotropic reorientations leading to a single (Lorentzian) line in the ^{2}H spectrum. Within only a few minutes, this "thin" line progressively decreases while an apparently static pattern grows. On the basis of these experiments, no remaining liquid with the same dynamical characteristic as the initial supercooled one can be detected at this temperature. The final spectrum displays both features already discussed for the undercooled liquid at lower temperature: static and partially averaged components. These dual features are also present if the glaciation is carried out at other temperatures: at 226 K, due to the very short value of T_2, as already discussed above, the signal of the liquid vanishes. This dynamical coincidence prevents any attempt to quantify the relative remaining part of liquid *versus* solid phase for this temperature. However, it has the advantage that the observed growing lineshape can be assigned with confidence to the actual solid part, here clearly distinct from the supercooled liquid, unless the dynamical properties of this liquid undergo profound changes during the transformation. At 220 K, the lineshape keeps changing for several hours, the main evolution being the repartition between central and edge peaks. The very similarity between the liquid and glacial experimental responses makes it very difficult to distinguish the liquid proportion left at the end of the evolution. For all temperatures, after complete transformation (Fig. 3c), the sample was rapidly heated up to 240 K. Figure 4 shows the evolution of the spectra during this thermal treatment. A very sharp central line appears, about six times broader than that of the supercooled liquid at this temperature. Its intensity progressively decreases during an isothermal rest. The rest of the spectrum reduces to a purely static broad line, with a T_1 spin-lattice relaxation time much longer than that of the glacial or the supercooled phase (more than 2 s). The initial central horns separated by 34 kHz have disappeared, and the resulting spectrum remains unchanged when heating or cooling again. It can therefore be confidently assigned to the stable crystalline form of TPP.

The data in Figure 3 give an image of the nucleation and growth process of a solid phase out of the liquid. Column (c) presents the spectra at the end of the transformation, which can confidently be assigned at 226 and 228 K to a solid component alone, while the one at 220 K probably reflects a mixing of liquid and solid states. We see that the spectrum of the glacial phase presents the same dynamical features encountered in the supercooled liquid (but at lower temperatures), evidenced by both high and low frequency discontinuities (130 and 30 kHz as in the liquid). This indicates that internal motions are present comparable to those in the liquid at lower temperature, described in this paper as 180° flip of the phenyl rings with a distribution of correlation times. Inspection of Figure 3 shows that the final ratio between static and

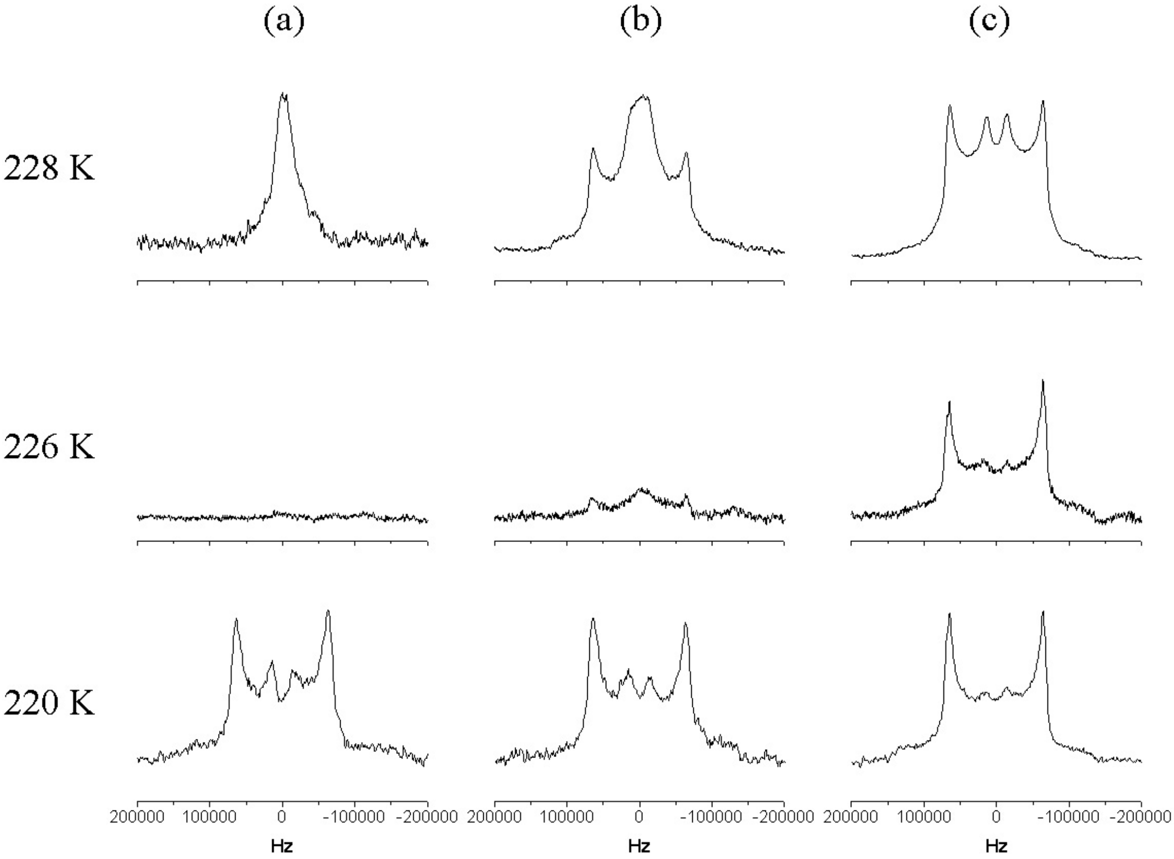

Fig. 3. Evolution of the ^{2}H NMR solid-echo spectra during isothermal glacial transformation of TPP, for three different temperatures. 228 K: (a) $t = 2$ min; (b) $t = 8$ min; (c) $t = 30$ min; 226 K: (a) $t = 5$ min; (b) $t = 20$ min; (c) $t = 1$ h 30 min; 220 K: (a) $t = 5$ min; (b) $t = 2$ h; (c) $t = 5$ h 30. Data at 220 and 226 K were recorded using the same rf-field excitation ($\nu_{rf} \approx$ 96 kHz). In order to prevent the probehead from arcing, the power was reduced to c.a. 60 kHz for the data at 228 K, resulting in a $\pi/2$ pulse length of 4.25 μs. Hence, the excitation might not be quite uniform for this temperature, and the central features of the spectra might be somewhat artificially enhanced.

dynamic parts of the spectra obtained for the glacial state slightly differ for the three temperatures, the central (dynamical) horns being favored at higher temperatures. This is qualitatively in agreement with what is expected if the distribution of correlation times of the phenyl flips in the glacial phase shifts towards shorter values when the temperature is increased. From the ^{2}H NMR results discussed so far, the glacial phase has to be clearly distinguished, at least *via* its dynamical properties, from the supercooled liquid. In order to compare it also with the long-range ordered crystal form of TPP, recrystalisation of the glacial states obtained at 220, 226 and 228 K was made (see Fig. 4).

The transformation from glacial to crystalline phase is very rapid, and occurs quickly upon heating from the glaciation temperature. The NMR central feature indicates that the glacial-to-crystal transition seems to transit through an intermediate at least partial melting, already suspected but not demonstrated by previous broadline ^{1}H NMR studies [19]. This fact suggests that the glacial state obtained after isothermal aging suffers a certain degree of instability *versus* the crystalline form, in agreement with the picture of this phase as an aborted step toward complete crystallization. The inset in Figure 4 displays the spectrum characteristic of the stable crystalline form. At 250 K, it can be fully described by a simple static quadrupolar lineshape, indicating that the phenyl flip encountered in the liquid and glacial phases is either much slower or simply absent in the crystal.

5 Conclusion

We have presented in this note the first ^{2}H NMR study of the local dynamics involved in the supercooled liquid phase of Triphenyl Phosphite, together with a short preview of the quadrupolar broadline signature of the transformation into the glacial state. Mean correlation times for the primary relaxation in the quenched liquid could be extracted from the data, completing within a good agreement those previously reported by other experiments. The

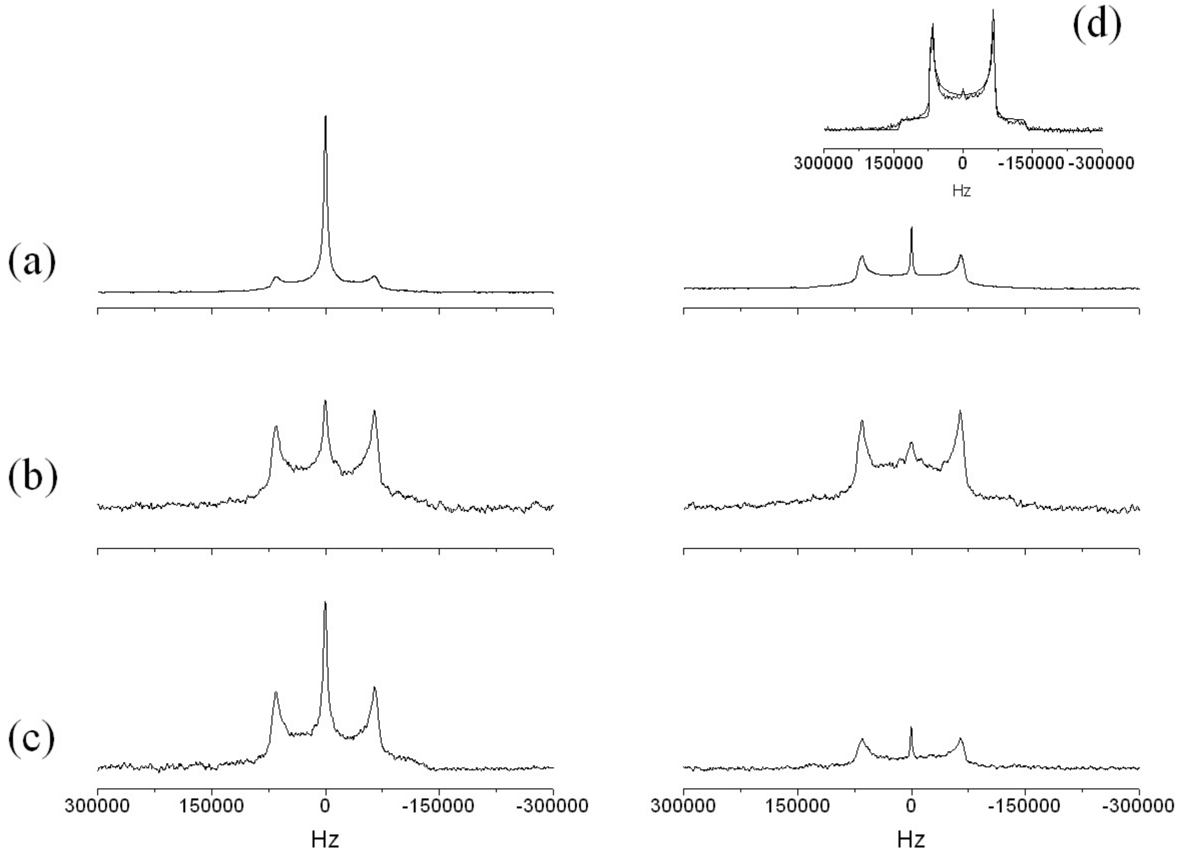

Fig. 4. Evolution of the ^{2}H NMR solid-echo spectra after complete glaciation at (a) 228 K and (b) 226 K and (c) 220 K, when heating rapidly to 240 K. The left-hand column displays the spectra measured right after 240 K is reached, and the right-hand one those obtained after a few minutes. All data were recorded with a relaxation delay of 1 s. The upper inset (d) displays the fully-relaxed spectrum assigned to the stable crystalline phase of TPP, obtained following (b) by heating up to 250 K and waiting for several minutes. Refinement of this spectrum by a static quadrupolar lineshape gives the following parameters: $\delta = 137$ kHz and $\eta = 0.05$.

existence of fast intramolecular motions was also demonstrated, interpreted as 180° flips of the side phenyl rings, and subject to a broad distribution of correlation times. These motions are found also in the glacial state. This molecular agitation not measured in the crystal appears as a dynamical signature of the metastability of the glacial state with respect to the crystal, which is confirmed by the observation of a partial melting of this phase upon heating. The data presented here give a clear image of the side-group fast dynamics of TPP. However, we have to remind that NMR only probes a chemical bond local property, and it is therefore quite insensitive to the actual structural intermolecular static arrangement in the glacial state. In addition, the very particular dynamical window affecting both the supercooled liquid and the glacial state also unfortunately prevents to distinguish unambiguously between pure and mixed phases. However, our new ^{2}H results, and we believe also all previously published NMR data, fully agree with a biphasic picture of the glacial state, which clearly emerges from X-ray, neutron and Raman data. On the other hand, the very slow dynamical properties found in the latter study, evidenced by dielectric and Raman measurements, do not influence our 1D ^{2}H NMR spectra (only sensitive to fast reorientations). This point remains today unexplained. However, as illustrated in this paper, ^{2}H NMR is certainly of considerable interest to bring out new information on the particular problem of slow molecular dynamics. Further investigations in that direction (like 2D slow exchange experiments, stimulated echoes, etc.) will be necessary in a further stage.

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