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The presence of long-lived spin states in organic solids with rapid molecular motions

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Abstract

For organic solids with sufficiently mobile molecular segments, the application of a long and weak pulse ($\gamma B_1/2\pi \sim 100$ Hz) can yield inverted sharp peaks with linewidths of ~100 Hz in the ^{1}H NMR spectra, and the use of multi-frequency weak pulses can excite multiple inverted sharp peaks. For these compounds, the normal ^{1}H free induction decay (FID) of a static sample contains a slowly decaying part, which can be detected by acquisition delay up to about 2 ms. The presence of highly mobile molecular segments can also be identified by using a "dipolar filter."

Keywords: Proton NMR; Solids; Rapid motions; Weak pulse; Acquisition delay; Dipolar filter

1. Introduction

In our recent nuclear magnetic resonance (NMR) studies, we have found that the application of multi-frequency weak pulses to nematic liquid crystals can be used for the storage [1] and processing [2–4] of binary information at the molecular level. The principle of this technique is that a weak pulse can produce inverted sharp peaks at the applied frequencies, which can be set arbitrarily over the entire spectral range of ~25 kHz for the liquid crystal sample. To further explore this interesting phenomenon, we have examined whether organic solids would show similar responses to weak pulses, and the basic properties of the compounds that exhibit such behavior.

In both liquid crystals and ordinary organic solids, there are large proton–proton dipolar interactions. As a result, their ^{1}H nuclear magnetic resonance (NMR) spectra are very broad, having linewidths of tens of kHz. Liquid crystals are characterized by the presence of orientational order but lack of long-range positional order; therefore, intermolecular dipolar interactions are averaged to zero. In most organic solids, the molecules have both positional and orientational order, and the only important motions are small-amplitude vibrations; both intramolecular and intermolecular dipolar interactions are significant.

Two techniques have been used to reduce the ^{1}H linewidth of organic solids. The first is magic-angle spinning (MAS) [5] when the sample is spun rapidly along an axis forming the magic-angle $\theta = \tan^{-1}\sqrt{2} = 54.74°$, second-rank tensor interactions can be averaged out if the spinning rate is high enough compared to the static interactions (when both are expressed in Hz). Because ^{1}H–^{1}H dipolar interactions are in the order of several tens of kHz, it requires very high spinning rates to resolve the proton peaks of different functional groups [6]. Another approach is the use of multiple pulses to create a time-averaged Hamiltonian for which homonuclear dipolar interactions are reduced as much as possible [7–9]. The combination of the two techniques (combined rotation and multiple pulse spectroscopy, CRAMPS) [10] can result in resolvable ^{1}H peaks for different functional groups in many organic solids using moderate spinning rates.

Although the ^{1}H peaks of organic solids are usually very broad, a tiny fraction of the free induction

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decay (FID) may have a much longer decaying time, so that a few relatively narrow ^{1}H NMR peaks (of the order of 10^2 Hz) with very low intensities can be observed with acquisition delay [11]. Interpretations on the origin of these peaks are controversial [11–14]. Nevertheless, we have found that this phenomenon is much more pronounced for organic solids with rapid molecular motions. More importantly, it is related to the unusual effect that the application of long and weak pulses can produce inverted sharp peaks, which was previously observed for liquid crystals [1–4,15] and isotropic solutions [16]. The results are reported here.

2. Experimental

All chemicals were purchased from Aldrich. According to the manufacturer, the compound poly(vinyl stearate) has an average molecular weight M_w of about 90,000 Da and a T_g of 45 °C; the compound poly(maleic anhydride-*alt*-1-tetradecene) has an average M_w of about 9000 Da, an average M_n of about 7300 Da, and a T_g of 65 °C. Tertrabutylammonium bromide, obtained from Aldrich Chemicals, was recrystallized in chloroform. A piece of twin single crystals of about 20 mm in length, 1 mm in thickness, and 3 mm in width was used for the experiments.

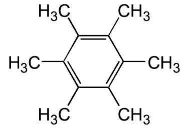
Tetrapropylammonium (TPA) silicalite was synthesized in the following way [17]. 0.215 g NaOH (5.4 mmol) and 1.46 g TBA bromide (5.5 mmol) were dissolved in 2.98 g of water (166 mmol). 10.88 g tetraethyl orthosilicate (5.2 mmol) was then added. The two-layered liquid was stirred vigorously for 2 h. The two liquid phases became one, and some precipitate appeared. The whole mixture was transferred to an autoclave, which was heated at 160 °C for 3 days. The resulting solid was filtered and washed many times with distilled water. Finally, it was dried overnight at 90 °C.

All NMR experiments were carried out at 400.0 MHz and 20 °C on a Varian INOVA-400 NMR spectrometer. For most experiments, an indirect detection ("liquid state") probe manufactured by Narolac, for which the 90 ° pulse width of a "hard pulse" was 3.6 µs, was used without sample spinning. The powder samples were put in 5 mm (o.d.) glass tubes. Some of the samples (TPA bromide, TPA silicalite, and di-*tert*-butyl oxalate) were further dried in vacuum overnight at room temperature and then tightly capped. The MAS experiments were carried out using a Varian MAS probe with 6 mm (o.d.) rotors.

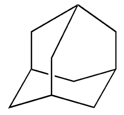
For all spectral displays, an exponential multiplication factor (line broadening) of 10 Hz was used in the Fourier transform, but the linewidth measurements were carried out without exponential multiplication.

3. Results

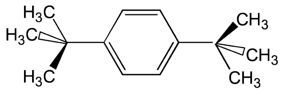
The effect of applying weak pulses (defined as having $\gamma B_1/2\pi \sim 100$ Hz hereafter) to a number of organic solids was investigated. As expected, compounds with no or insignificant rotational motions (for example naphthalene and cholesterol, respectively) did not show any ^{1}H NMR signal distinguishable from the background (observed using an empty sample tube). On the other hand, compounds that contain molecules or molecular segments with significant fast rotations did respond to weak ^{1}H pulses similar to liquid crystals. The structures of the compounds studied in this work are shown in the following, and the molecular motions of these compounds in the solid state will be compared in Section 4.



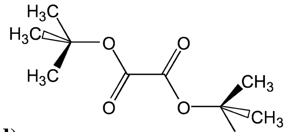
(a) Hexamethylbenzene



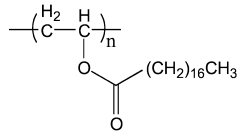
(b) Adamantane



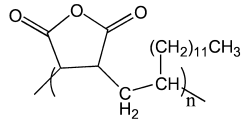
(c) 1,4-Di-*tert*-butylbenzene



(d) Di-*tert*-butyl oxalate



(e) Poly(vinyl stearate)



(f) Poly(maleic anhydride -*alt*-1-tetradecene)

$(CH_3CH_2CH_2)_4N^+\ Br^-$

(g) Tetrapropylammonium bromide

$(CH_3CH_2CH_2)_4N^+\ Si_xO_y^-$

(h) Tetrapropylammonium silicalite

$(CH_3CH_2CH_2CH_2)_4N^+\ Br^-$

(i) Tetrabutylammonium bromide

The ^{1}H NMR spectra obtained by applying strong and weak pulses to compounds **a**–**f** are shown in Fig. 1. The spectra of compounds **g**, **h**, and **i** exhibit characteristics similar to those of 1,4-di-*tert*-butylbenzene and di-*tert*-butyl oxalate (Figs. 1c and d) and are not shown, but other experiments on these compounds will be discussed later. The spectra of rubber (in the form of 3 mm width rubber bands manufactured by Alliance Rubber) show the same features as those of poly(maleic anhydride-*alt*-1-tetradecene) (Fig. 1f), except that its linewidth is smaller (1.1 kHz instead of 3.1 kHz); since rubber is not regarded as a genuine solid, it will not be further considered.

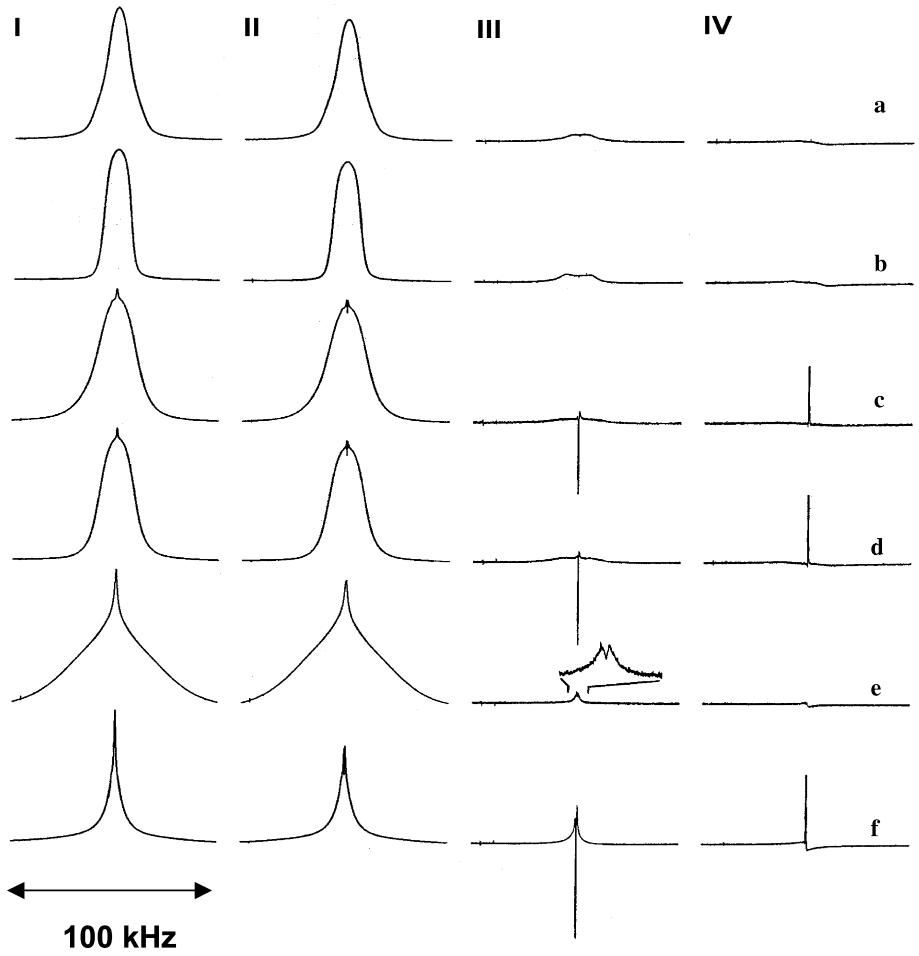


Fig. 1. ^{1}H spectra obtained from the application of strong and weak pulses. Column I: strong only; column II: weak followed by strong; column III: weak only, vertical scale 20×; column IV: strong followed by weak, with $\pm 90°$ phase shift and phase cycling for the weak pulse, vertical scale 20×. The alphabetical labeling of these spectra corresponds to those given in the structural formulae. Strong pulse: $\gamma B_1/2\pi = 69$ kHz, duration = 3.6 μs; weak pulse: $\gamma B_1/2\pi = 82$ Hz; duration = 8.0 ms. For the inset in III-(e), spectral width = 10 kHz, vertical scale 100×.

The spectra in columns II and III of Fig. 1 indicate that a weak pulse applied at the resonance frequency "rotates" part of the z-magnetization to the xy plane. Although the pulse is very weak ($\gamma B_1/2\pi = 82$ Hz), the transfer of magnetization covers the entire spectral range of each compound. However, it is not uniformly distributed, and there are obvious indentations in the center of the spectra (Fig. 1, column III). The most striking feature is the appearance of a sharp inverted peak (linewidth ~100 Hz) at the irradiating frequency (Fig. 1c–f, column III). This sharp peak is very prominent for six of the nine compounds studied, but is barely visible for poly(vinyl stearate), and is not present (beyond the background signal) for adamantane and hexamethylbenzene. When a weak pulse is used in spin-locking experiments (Fig. 1, column IV), the broad components appear as a weaker dispersion signal, but the sharp peak becomes an absorptive signal. These results indicate that the presence of z-magnetization is not an absolute requirement for the weak pulse to produce magnetization in the xy plane.

The effect of the width of weak pulses on the ^{1}H spectra is shown in Fig. 2. For adamantane (Fig. 2b) and hexamethylbenzene (spectra not shown), a broad component having the same width as that in the normal spectrum can be observed for pulse width less than 10 μs because short pulses are broadband regardless of their power. An indentation appears in the middle of the spectrum when the pulse width is increased to about 100 μs, but the spectral pattern and amplitude do not change when the pulse width is further increased (for pulse width = 10 ms, there is a very small sharp peak at the center of the spectrum, but it is indistinguishable from that obtained by using an empty sample tube). The broad component also develops quickly for di-*tert*-butyl oxalate (Fig. 2d) and other compounds, but the narrow component develops more slowly, starting to appear after about 100 μs. Finally, the inverted sharp peak appears for pulse width exceeds 3 ms. The linewidths of the two positive components are 18.3 and 0.65 kHz, and that of the inverted component is 92 Hz.

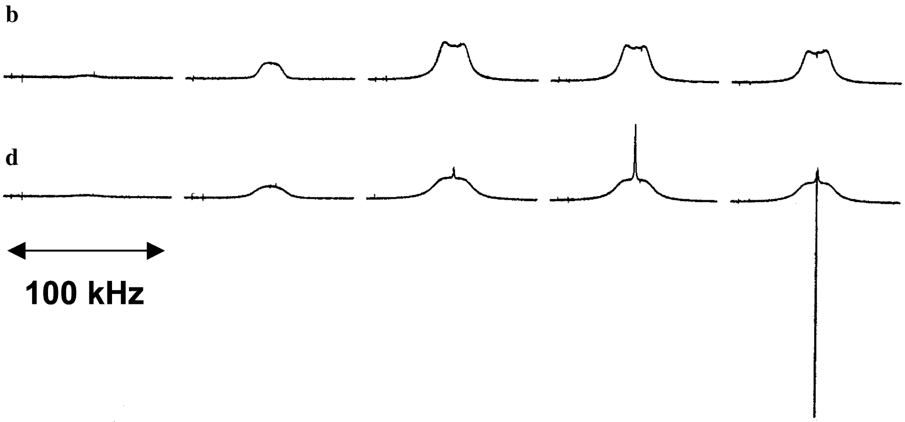


Fig. 2. ^{1}H spectra obtained from the application of a weak pulse with $\gamma B_1/2\pi = 82\,\mathrm{Hz}$ for different durations: 10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}, and 10^{-2} s, respectively, from left to right. (b) Adamantane; (d) di-*tert*-butyl oxalate. The alphabetical labeling of these spectra corresponds to those given in the structural formulae.

To further examine the features of the narrow components in compounds with rapid molecular motions, the method of delayed acquisition was used. Technically it is the same as cutting off the initial fast-decaying part of the FID obtained by using a single strong pulse before carrying out Fourier transform. For many organic solids without MAS, a few narrow peaks can often be detected with an acquisition delay of about 100 μs, but their intensities quickly diminish with longer delay times [11–14]. This is the case for adamantane, hexamethylbenzene, and to a lesser extent, poly(vinyl stearate) (Figs. 3a, b, and e, respectively). On the other hand, di-*tert*-butyl oxalate, 1,4-di-*tert*-butylbenzene, and poly(maleic anhydride-*alt*-1-tetradecene) show many overlapping narrow peaks that persist to much longer acquisition delays, up to about 2 ms (Figs. 3c, d, and f, respectively). It should be noted that the second group of compounds gives inverted narrow peaks upon the application of weak pulses, but the first group does not (Fig. 1).

It is well known that normally the peak height of an NMR signal varies with the pulse duration as a slightly damped sine function, as shown in Fig. 4 for a liquid sample (data represented by solid squares). However, upon the application of a weak pulse, the heights of the sharp peaks of the solids studied show a different dependence on the pulse width: although they oscillate with the same periodicity as the liquid sample, the peaks are always negative, and have different damping factors for different compounds. The data for 1,4-di-*tert*-butylbenzene are similar to that for di-*tert*-butyl oxalate, and those for TPA bromide are similar to that for TPA silicalite; they are not shown to avoid overcrowding. The linewidths of the inverted peaks do not vary systematically with the length of the weak pulse, but increase approximately linearly when $\gamma B_1/2\pi$ increases from 82 to 166 Hz.

To investigate the effect of MAS, two compounds that contain only methyl protons, hexamethylbenzene and di-*tert*-butyl oxalate, were studied. At a spinning rate of 6 kHz, the ^{1}H spectrum of hexamethylbenzene shows three pairs of spinning sidebands, and its linewidth is reduced from 13.4 to 0.88 kHz. Upon the application of a weak pulse, the spectrum shows only a small central peak a linewidth of 0.99 kHz. At the same spinning rate, the linewidth of di-*tert*-butyl oxalate is reduced from 17.4 to 1.09 kHz for a strong pulse. However, the application of a weak pulses produces a narrow inverted peak in addition to the broader central peak (linewidth 1.12 kHz), and the intensity of the inverted peak oscillates with the pulse width up to about 80 ms (Fig. 5). These results are similar to those obtained for the corresponding static samples (Figs. 1 and 2), except that the broad component appears more prominently in the MAS spectra because of the large reduction in its linewidth.

To determine whether intermolecular dipolar coupling has any effect on the response to the application of weak pulses, we compare the ^{1}H spectra of TPA bromide and TPA silicalite. In TPA bromide, the tetrapropylammonium cations are not too far apart, and there are extensive intermolecular dipolar couplings. The normal ^{1}H spectrum obtained with a strong pulse is neither Gaussian nor Lorentzian, and has a linewidth of 65 kHz at half height (Fig. 6I-g). In TPA silicalite, the TPA ions are trapped inside silicalite cages similar to those in the zeolite ZSM-5 (other tetraalkylammonium ions are not as good a template as TPA for the formation of cages) [18]. The TPA cations are not freely rotating in the cages [19], but are located quite far from one another [20] so that intermolecular interactions are very small. As a result, the normal ^{1}H spectrum shows a single peak that is almost Lorenztian and has a much smaller width than the TPA bromide signal (Fig. 6I-h;

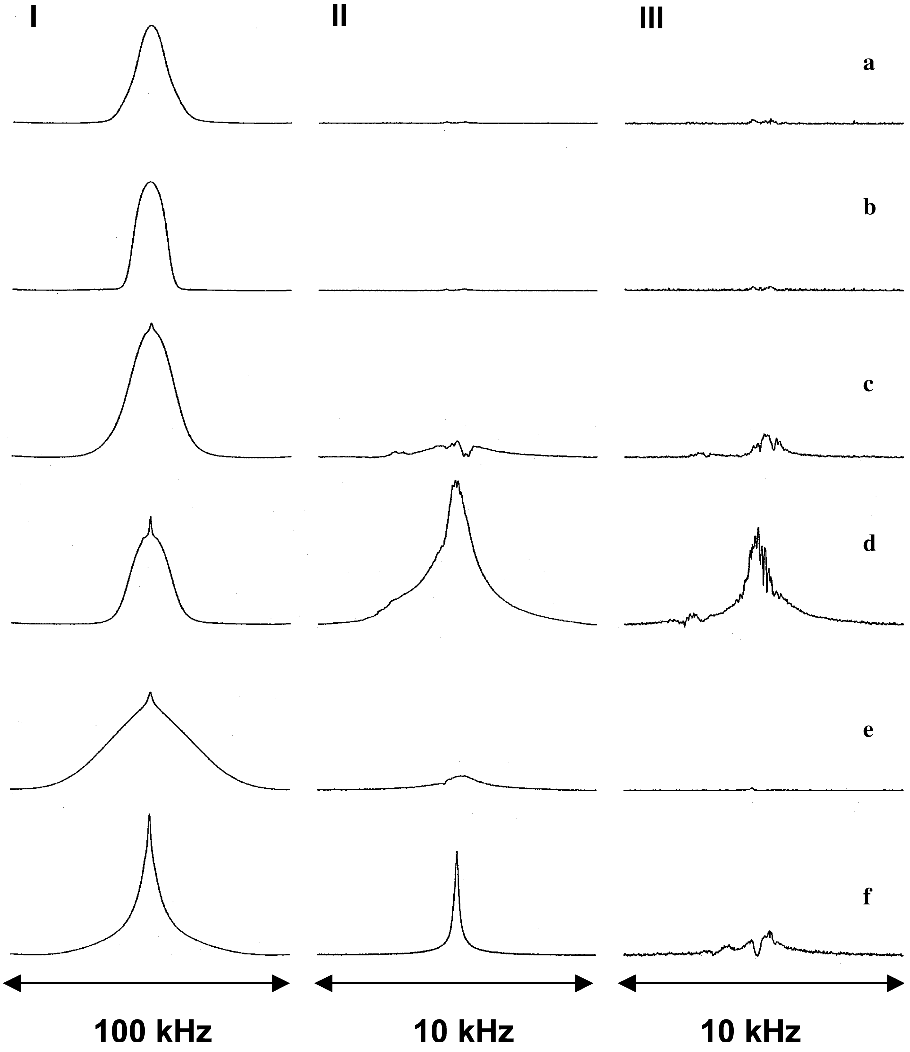


Fig. 3. ^{1}H spectra of static samples obtained from the application of a strong pulse ($\gamma B_1/2\pi = 69$ kHz) with different delay times for data acquisition after the pulse: column I: 2 μs; column II: 1 ms, absolute value mode, vertical scale 100×; column III: 2 ms, absolute value mode, vertical scale 500×. The number of scans was 2000. The alphabetical labeling of these spectra corresponds to those given in the structural formulae.

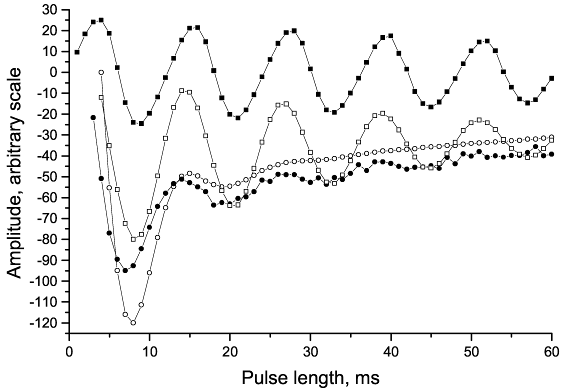


Fig. 4. The dependence of the amplitudes of the sharp peaks on the duration of a weak pulse with $\gamma B_1/2\pi = 82$ Hz. ■, a liquid (5% dioxane in $CDCl_3$); □, di-*tert*-butyl oxalate; ●, tetrapropylammonium silicalite; and ○, poly(maleic anhydride-*alt*-1-tetradecene)

linewidth = 5.4 kHz). However, the linewidths of the inverted sharp peaks produced by the application of a weak pulse are about the same for TPA bromide (120 Hz) and TPA silicalite (110 Hz). To compare the response of the two solids in more detail, a multi-frequency weak pulse, which contains 7 harmonics with the same amplitudes and 400 Hz apart for the adjacent frequencies, was applied. For both compounds, seven sharp peaks appear at the irradiating frequencies (Fig. 6, column II). Although the relative amplitudes of the peaks for TPA silicalite are slightly larger than those for TPA bromide, the profiles of the sharp peaks and the spectral range that they can be observed (<3 kHz) are similar for the two compounds. Initially, the unusual response of liquid crystals to weak pulses was attributed to the presence of long-lived spin states resulting from extensive dipolar interactions in spin clusters which do

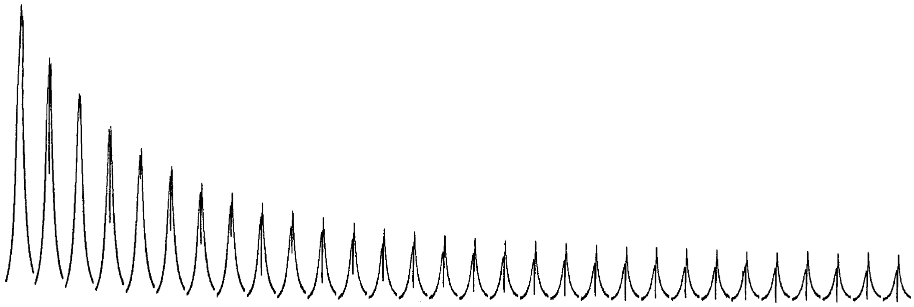


Fig. 5. ^{1}H spectra of di-*tert*-butyl oxalate with MAS at 6.0 kHz. A weak pulse with $\gamma B_1/2\pi = 80$ Hz was applied for durations ranging from 5 to 150 ms in increments of 5 ms each, from left to right. Spectral width = 4 kHz each.

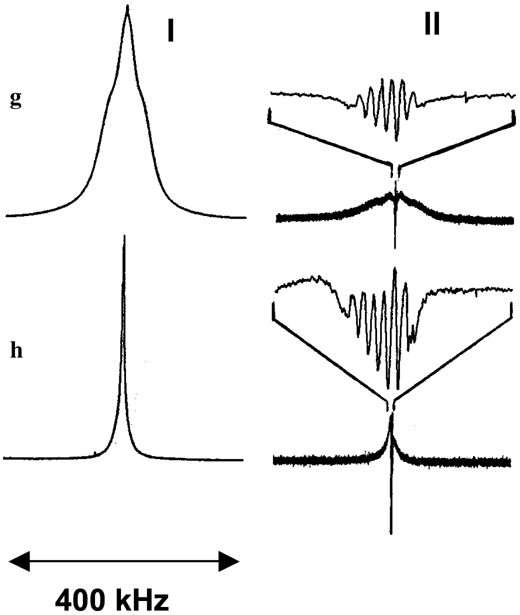


Fig. 6. ^{1}H spectra obtained from the application of (I) a strong pulse ($\gamma B_1/2\pi = 69$ kHz) for 3.6 μs and (II) a weak 7-frequency pulse for 10.0 ms; vertical scale 10×. Each of the seven harmonics in the weak pulse has the same amplitude ($\gamma B_1/2\pi = 148$ Hz) and is separated by 400 Hz from the next harmonic. (g) Tetrapropylammonium bromide; (h) tetrapropylammonium silicalite. Spectral width of the insets = 10 kHz. The alphabetical labeling of these spectra corresponds to those given in the structural formulae.

not interact with each other [1], and little attention was paid to the role of fast segmental motions. However, because the results of TPA bromide and TPA silicalite are only slightly different, we now conclude that the absence of intermolecular dipolar interactions is not a necessary condition for the observation of the inverted sharp peaks; on the other hand, fast molecular motions must be present.

In "hole burning" experiments [21,22], weak pulses are used to selectively saturate or invert part of a powder spectrum created by strong pulses, in essence tagging spins at a particular orientation. To ascertain that the unusual response of these compounds to weak pulses is not due to the polycrystalline nature of the samples, a single crystalline sample of tetrabutylammonium bromide was studied. The ^{1}H NMR spectra obtained by applying a strong pulse to the two types of crystals of the same compound are different (Figs. 7a and b). When a weak 8-frequency pulse is applied to the single-crystalline tetrabutylammonium bromide, eight inverted peaks appear at the irradiating frequencies (Figs. 7c and d), just like the polycrystalline samples of tetrapropylammonium salts (Fig. 6).

For another study of the effect of rapid motions on the ^{1}H NMR of solids, we used a pulse sequence called "dipolar filter" devised to study mobile components in polymers [23,24]. The multiple pulse sequence was designed to select the magnetization for protons with small dipolar interactions as a result of partial averaging due to high molecular mobility. The spectra for 1,4-di-*tert*-butylbenzene are shown in Fig. 8. It can be seen that the broad component is indeed filtered away by the multiple pulse, and the effect is more pronounced when the mixing time (the delay time between the dipolar filter and the detection pulse) decreases. The most interesting result is the modulation of the narrow components to show equally spaced peaks with separations equal to the reciprocal of the mixing time (the modulation is not observed for mixing time larger than 20 ms because the peaks are too close together to be resolved). These characteristics of the spectra do not change appreciably when the spacing between the pulses in the dipolar filter was varied between 5 and 100 μs, and the number of pulse cycles in the filter varied between 4 and 40. Di-*tert*-Butyl oxalate shows the same spectral features. The results for TPA bromide, TPA silicalite, and poly(maleic anhydride-*alt*-1-tetradecene) are similar, but the modulation is less prominent. Poly(vinyl stearate) has a very weak narrow component, and hexamethylbenzene and adamantane have none. These results mirror the effect of weak pulses shown in Fig. 1 and the effect of acquisition delay shown in Fig. 3. However, we cannot give a quantitative interpretation of the effect of spectral modulation as a function of mixing time in the dipolar filter (Fig. 8, column I).

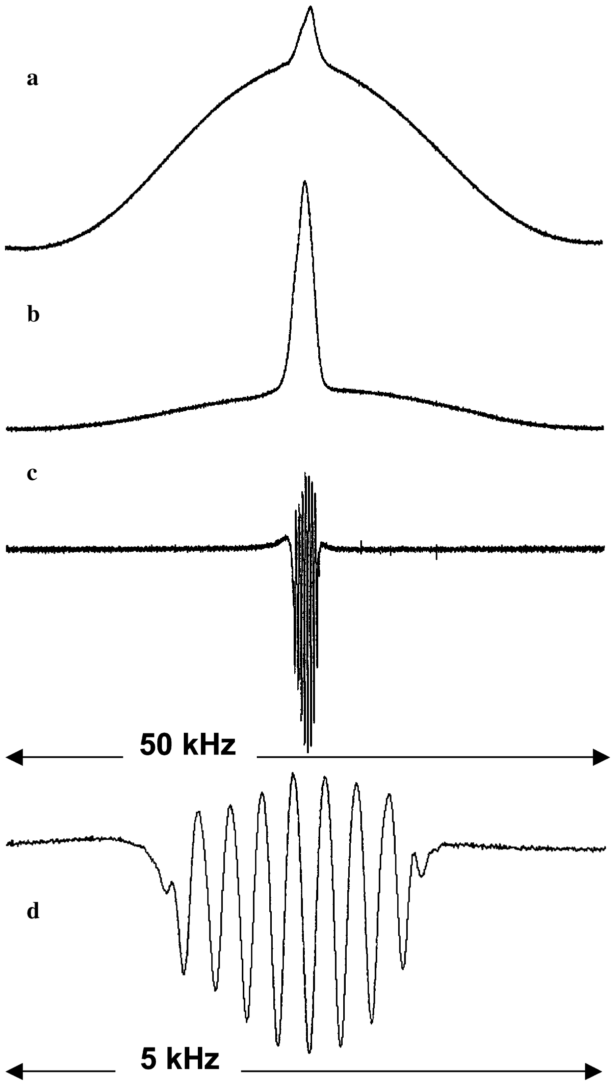


Fig. 7. ^{1}H NMR spectra of tetrabutylammonium bromide. (a) Spectrum of a polycrystalline sample obtained with a strong pulse ($\gamma B_1/2\pi = 69$ kHz); spectral width = 50 kHz. (b) Spectrum of a single crystalline sample obtained with a strong pulse ($\gamma B_1/2\pi = 69$ kHz); spectral width = 50 kHz. (c) Spectrum of the same sample obtained with an 8-frequency weak pulse (250 Hz apart; total $\gamma B_1/2\pi = 600$ Hz). (d) Expansion of the spectrum in (c).

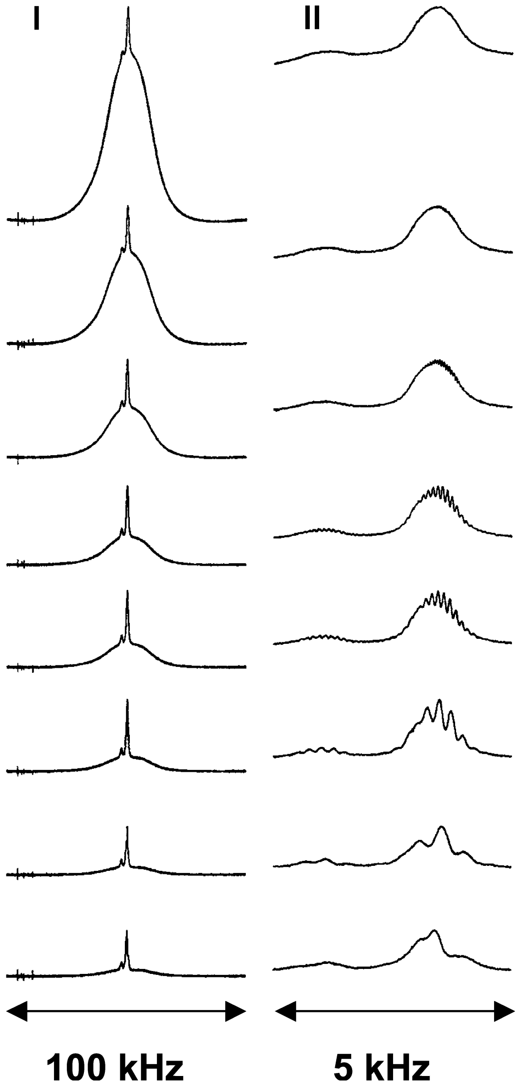


Fig. 8. ^{1}H spectra of 1,4-di-*tert*-butylbenzene obtained by using the "dipolar filter" sequence [23,24] (spacing between pulses = 24 μs; number of cycles = 10; and mixing time in ms = 80, 40, 20, 10, 8, 4, 2, and 1, from top to bottom). Column II: the narrow components displayed in an expanded scale.

4. Discussion

The features exhibited in the spectra shown in Figs. 1–8 are special for solids with appreciable molecular or segmental motions. These motions are briefly discussed in the following.

Adamantane is a "plastic solid" in which the molecules undergo rapid rotations with a rotational barrier of 27 kJ mol^{-1} [25]. At room temperature, there is no orientational order, and the intramolecular dipolar interactions are averaged to zero. However, the overall positional order is maintained, so that there are still extensive intermolecular dipolar interactions. In hexamethylbenzene, the six methyl groups rotate rapidly down to about 70 K [26]; above 170 K the benzene ring also undergoes rotation about the 6-fold axis, and the barrier of rotation is 28 kJ mol^{-1} [26]. The tertiary butyl group in many *tert*-butyl compounds is also a "double rotor": each methyl group rotates rapidly along the C–C bond, and the whole *tert*-butyl group also rotates rapidly along the C–X bond with a rotational barrier of 24 kJ mol^{-1} [27,28]. Poly(vinyl stearate) and poly(maleic anhydride-*alt*-1-tetradecene) are both comb-like polymers with glass transition temperature (T_g) above room temperature. In poly(vinyl stearate), the side chains are more or less "crystalline" [29], with small-amplitude segmental motions. In poly(maleic anhydride-*alt*-1-tetradecene), the malonic anhydride moiety in the backbone forces the pendant groups to be quite far apart from their neighbors, so that the side chains do not exhibit crystallinity below T_g [29]. This situation is quite unusual, and the solid is described as "having a 'glassy' polymer backbone suspended in a sea of molten side-chains" [29]. The alkyl chains in tetraalkylammonium salts are also quite mobile in the solid state, and undergo significant motions at room temperature [30].

Among the nine compounds studied, six show inverted sharp peaks upon the application of long and weak pulses (with $\gamma B_1/2\pi \sim 100\,\text{Hz}$ for more than a few milliseconds; Figs. 1, 2, and 5–7). For this group of compounds, spectra obtained using strong pulses with long acquisition delay (up to about 2 ms; Fig. 3) show overlapping narrow components, indicating the presence of long-lived spin states. On the other hand, although there are also rapid internal motions in hexamethylbenzene, adamantane, and poly(vinyl stearate), the dipolar-filter experiments show that their molecular segments have less overall mobility. As a result, their responses to the applied weak pulse are less prominent and do not show inverted peaks. This is particularly evident when the responses of the two comb-like polymers to weak pulses (Figs. 1e and f, respectively) are compared.

The responses of compounds **c**, **d**, **f**, **g**, **h**, and **i** to weak pulses (Figs. 1, 2, and 5–7) are similar to those of liquid crystals [1–4,15]. However, it must be pointed out that there is an important difference between the solid phase and the liquid crystalline phase. Liquid crystals possess the unique property of having large intramolecular ^{1}H–^{1}H dipolar couplings (up to 10^4 Hz) and fast rotations (albeit anisotropic), so that weak pulses can produce inverted peaks over the whole spectral range (~25 kHz). Molecules in solids have positional ordering, so that the molecular mobility is limited even in the presence of fast molecular or segmental rotations; as a result, sharp inverted peaks can only be observed in a fraction of the total spectral range (Figs. 6 and 7).

In recent experiments, sharp inverted peaks have also been observed in isotropic liquids by applying weak RF irradiation to broad signals which arise from extensively overlapping peaks [16]. A numerical analysis showed that the inverted peak can be considered as a cumulative effect of the long and weak pulse acting on many transitions that are slightly off resonance on both sides of the irradiating frequency; the only role of the J couplings (or dipolar couplings in liquid crystals) is to produce a large number of peaks that overlap with each other. For organic solids having sufficiently mobile molecular segments, the presence of overlapping narrow peaks (linewidth about 10^2 Hz) can be observed with acquisition delay (Figs. 3c, d, and f). This is consistent with the above interpretation, but a more quantitative analysis is necessary to have a better understanding of the observed phenomena.

Acknowledgment

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