Wideline 2H-NMR Spectroscopy and Imaging of Solids*

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Recent developments, focussing on reduction of the rf excitation power by stochastic excitation, on improvements in sensitivity and excitation bandwidth by magic angle spinning, and on combining wideline spectroscopy with spatial resolution for investigations of spatially inhomogeneous objects are reviewed.

Introduction

The deuteron is a stable isotope of hydrogen with a natural abundance 1.5% and a nuclear spin $I = 1$. Deuterons bound to carbons possess a nuclear quadrupole coupling constant of about 180 kHz, which is strong enough for the quadrupole interaction to dominate all other nuclear spin interactions in the NMR spectrum, yet small enough to calculate the NMR spectrum as a first order perturbation of the Zeeman interaction by the quadrupole interaction. The situation is further simplified for aliphatic deuterons, because their quadrupole coupling tensor is axially symmetric. Then the NMR frequencies corresponding to the observable single quantum transitions ω_+ and ω_- (Fig. 1) [1] show a simple dependence on the angle θ specifying the orientation of the applied magnetic field $\boldsymbol{B}_0$ with respect to the principal Z axis of the quadrupole coupling tensor,

$$\omega_\pm - \omega_0 = \pm \Delta/2 (3\cos^2\theta - 1) = \omega_Q,$$

where ω_0 is the resonance frequency of the isotropic part and Δ measures the anisotropy of the NMR frequency. Thus the NMR frequency of each transition can serve as a protractor to measure angles of molecular orientations. In powders and partially ordered materials the sum of signals weighted by the orientational distribution function is observed and the contributions from the transitions usually overlap in the NMR spectrum. For an isotropic orientational distribution the Pake doublet (Fig. 1, bottom right) is observed.

Changes of this lineshape may result from two effects: 1) The sample exhibits partial molecular order. Then the orientational distribution function can be extracted from the lineshape. 2) The observed deuterons belong to molecular segments which undergo reorientational motion with correlation times τ_c of the order of the inverse linewidth. Typical values for
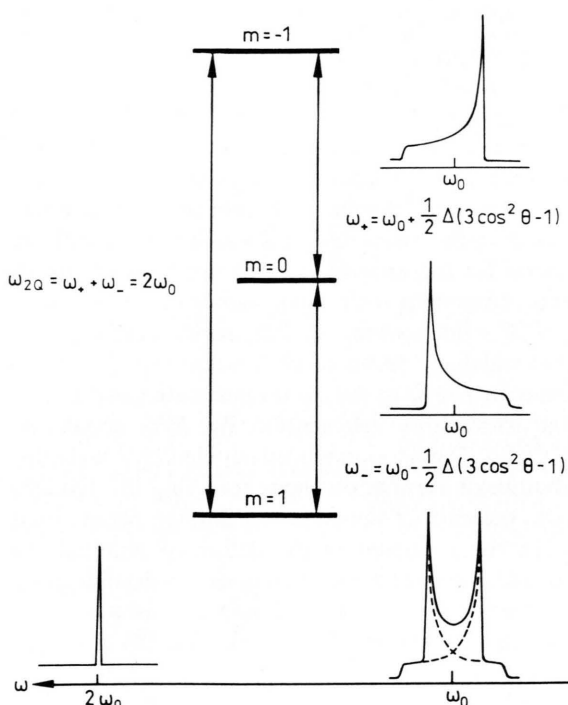

Fig. 1. Energy level diagram and powder lineshapes for deuteron NMR at high magnetic fields. The magnetic quantum number is denoted by m, θ is the angle between the applied magnetic field and the principal Z axis of the quadrupole coupling tensor, and ω_0 is the isotropic resonance frequency. The double quantum transition at frequency $2\omega_0$ can be detected only indirectly. Its resonance is independent of the molecular orientation.

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$\varepsilon = 20\%$

$\varepsilon = 0\%$

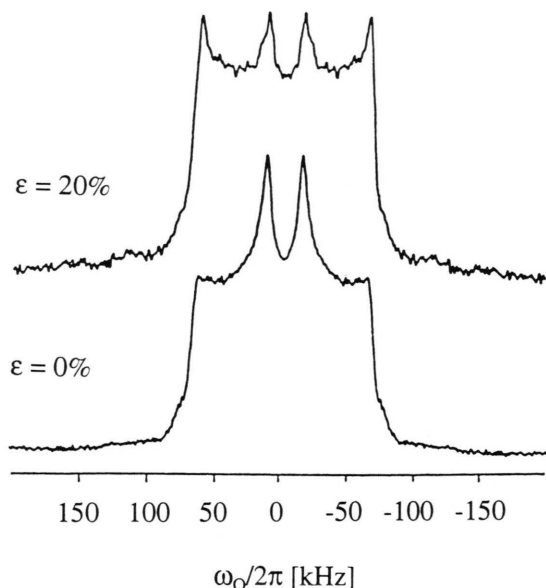|						
150	100	50	0	-50	-100	-150

$\omega_Q/2\pi$ [kHz]

Fig. 2. Spectra of phenyl-deuterated polycarbonate at 253 K before ($\varepsilon = 0\%$) and after ($\varepsilon = 20\%$) deformation by irreversible elongation.

deuterons are 10^{-3} s $> \tau_c > 10^{-5}$ s. A lineshape analysis then provides detailed information about the type and timescale of the motional process. For these reasons, deuteron wideline NMR has become a popular method for the analysis of motion and order in organic compounds such as polymers and liquid crystals [2–7]. For illustration, Fig. 2 [8] depicts partially saturated wideline spectra of phenyl-deuterated polycarbonate at 253 K in the unstrained state ($\varepsilon = 0\%$) and after irreversible deformation by 20% elongation ($\varepsilon = 20\%$). The lineshape is interpreted by a wide distribution of correlation times reflecting the simultaneous presence of slow and fast flipping phenyl rings [9]. In the spectrum of the deformed material the broad features are more pronounced, reflecting an increase in rigidity. It can be interpreted in terms of a fictitious temperature decrease of 10 K [8].

Two-Dimensional Wideline Exchange NMR

Two-dimensional wideline exchange NMR is a technique by which the NMR frequencies ω_Q of initial and final orientations are correlated in case of ultra-slow molecular reorientation [10]. In a three-pulse echo experiment, one-dimensional wideline spectra are acquired at times t_1 and t_2, which are separated by

a time t_m for mixing of longitudinal magnetization components by reorientation on the time-scale of the longitudinal relaxation time T_1. A correlation of both spectra is obtained by using the final magnetization from the frequency encoding period t_1 (initial orientation) as the initial magnetization for the frequency encoding period t_2 (final orientation), however with intermediate storage along the z-axis for magnetization exchange during t_m. In the resultant 2D spectra the conventional 1D wideline spectrum is observed along the diagonal. Signals correlating different initial and final orientations appear in the plane. Characteristic ridges indicate reorientation by discrete jumps, while broad structures indicate diffusive reorientation. From an analysis of such spectra, the distribution $P(\Phi)$ of reorientation angles reached during the mixing time starting from a given initial orientation can be extracted [11, 12].

The use of this technique is illustrated in Fig. 3 [13], showing the phenyl-flip motion in polycarbonate under elastic deformation by applying 3% strain at 233 K. The flip by $\Phi = 180°$ of the phenyl rings results in a reorientation of the quadrupole coupling tensor of the ring deuterons by $\theta = 120°$. As a result of this reorientational jump motion an elliptical ridge pattern appears in the plain of the 2D exchange spectrum (Figure 3 a). But away from the center of the spectrum the ridges are smeared out because the jump angle is illdefined already for the unstrained sample. This jitter is reflected in the corresponding reorientational angle distribution function $P(\Phi)$ (Figure 3 b). Application of a strain of 50 MPa elongates the sample by 3%, and the free volume increases. As a consequence, the jitter of the phenyl flip is approximately doubled (Figure 3 c).

Stochastic Excitation: Hadamard-NMR

Wideline deuteron NMR spectroscopy at high magnetic fields requires radio frequency (rf) excitation power typically in excess of 1 kW for 7 mm diameter coils for uniform excitation of bandwidths of the order of 250 kHz and larger. Echo techniques are used throughout to allow for receiver recovery as well as probe and filter ring down after such strong pulses. Typical deadtimes are 10 μs to 20 μs.

The use of larger samples for increased sensitivity is unfeasible because of the associated increase in rf power, which often cannot be satisfied due to arcing in
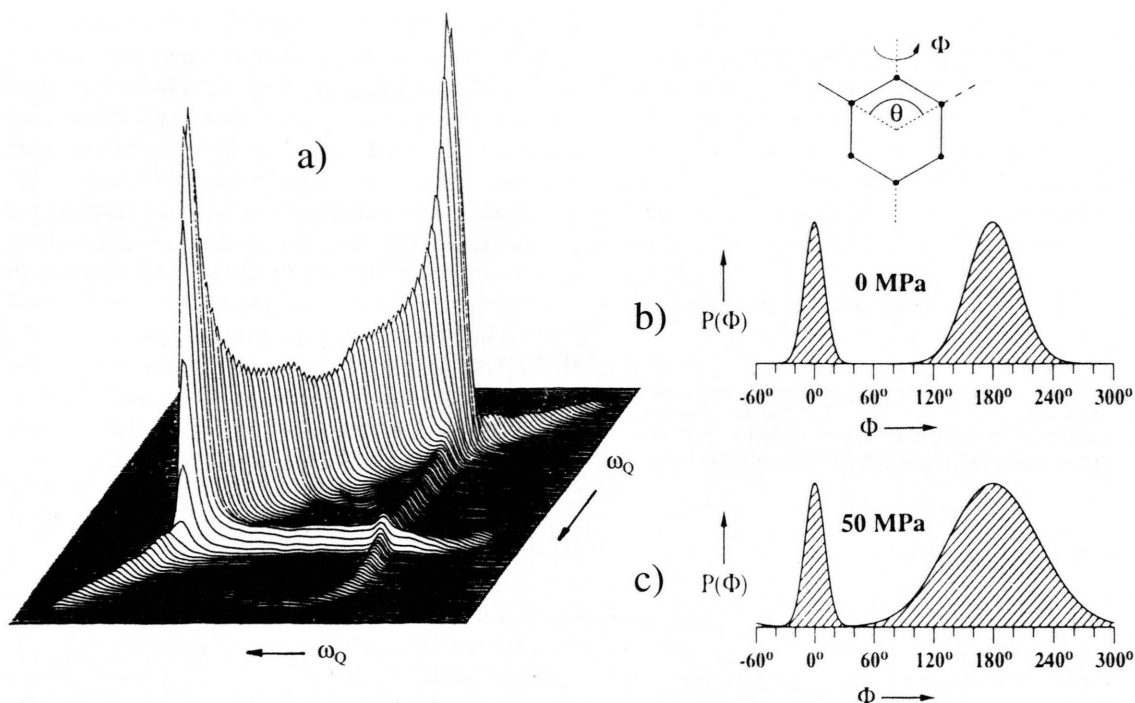
Fig. 3. 2D-exchange spectrum (a) and reorientational angle distribution functions for the phenylring flip of polycarbonate without strain (b) and under elastic deformation (c) by application of a strain of 50 MPa corresponding to an elongation of 3%. Parameters: $T = 233$ K, $t_m = 500$ ms.

the probe and lack of suitable amplifiers. Furthermore, samples with molecular motion in the intermediate exchange regime ($\tau_c \approx 10^{-6}$ s) cannot be investigated because the signal already decays appreciably within the receiver deadtime.

Stochastic excitation is explored in how far it can provide a remedy for both limitations [14]. The rf power is typically decreased by a factor of 1000 compared to pulsed excitation, and the deadtime can be reduced to less than one sampling interval or avoided altogether if transmitter and receiver are decoupled, as for instance in a crossed-coil probe.

In stochastic NMR the rf excitation is applied in a quasi continuous fashion with a random modulation in phase and/or amplitude [15]. For single-coil probes excitation and detection of the response are shared in time, so that the excitation consists of an infinitely long string of randomly modulated rf pulses, and one data point of transverse magnetization is detected in each time window between successive pulses. An interferogram corresponding to a free induction decay signal is derived by cross-correlation of excitation and

response, and Fourier transformation of the interferogram leads to the NMR spectrum. It can be shown that stochastic excitation in magnetic resonance is equivalent to the use of interferometric techniques in optics [16, 17].

When the rf excitation is modulated by samples of random noise, the resulting spectra are contaminated by systematic noise [18]. This, however, can be avoided if pseudo-random noise based on maximum binary length sequences is used for modulation of the excitation instead of truely random noise. Computation of the interferogram by explicit cross-correlation can then be replaced by fast Hadamard transformation of the response [19, 20], and both, Hadamard-NMR and pulsed Fourier NMR provide the same sensitivity.

This is demonstrated in Fig. 4 [14] with deuteron-wideline spectra of hexamethylbenzene [21]. The top spectrum is the Hadamard spectrum, and the middle one is the Fourier spectrum acquired with a quadrupolar echo excitation under the same conditions but with excitation powers of 0.1 W and 1 kW, respec-
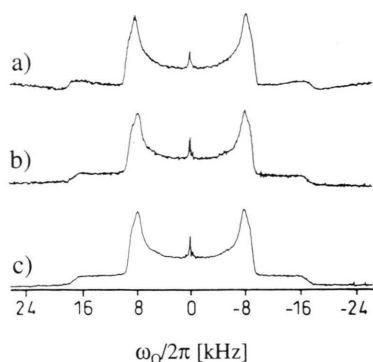
Fig. 4. Deuteron wideline spectra of hexamethylbenzene-d_{18}. a) Hadamard spectrum; filter bandwidth: 500 kHz. b) Quadrupole-echo spectrum; filter bandwidth: 500 kHz. c) Quadrupole-echo spectrum; filter bandwidth: 30 kHz.

tively. The bandwidth of the receiver had been set to 500 kHz, ten times larger than the linewidth in order to avoid filter ringing to allow for rapid sampling of the stochastic response right before each subsequent excitation pulse. But a matched filter can be used with echo excitation, resulting in a corresponding signal-to-noise improvement (bottom). Thus for practical use of stochastic excitation the transmitter and receiver must be decoupled efficiently, for instance by crossed-coil techniques, so that matched filters can be used. This would also remove the baseline distortion in the Hadamard spectrum (top), which results from the time-shift between excitation and detection of the response by a fraction of a sampling interval as required by the time-sharing scheme.
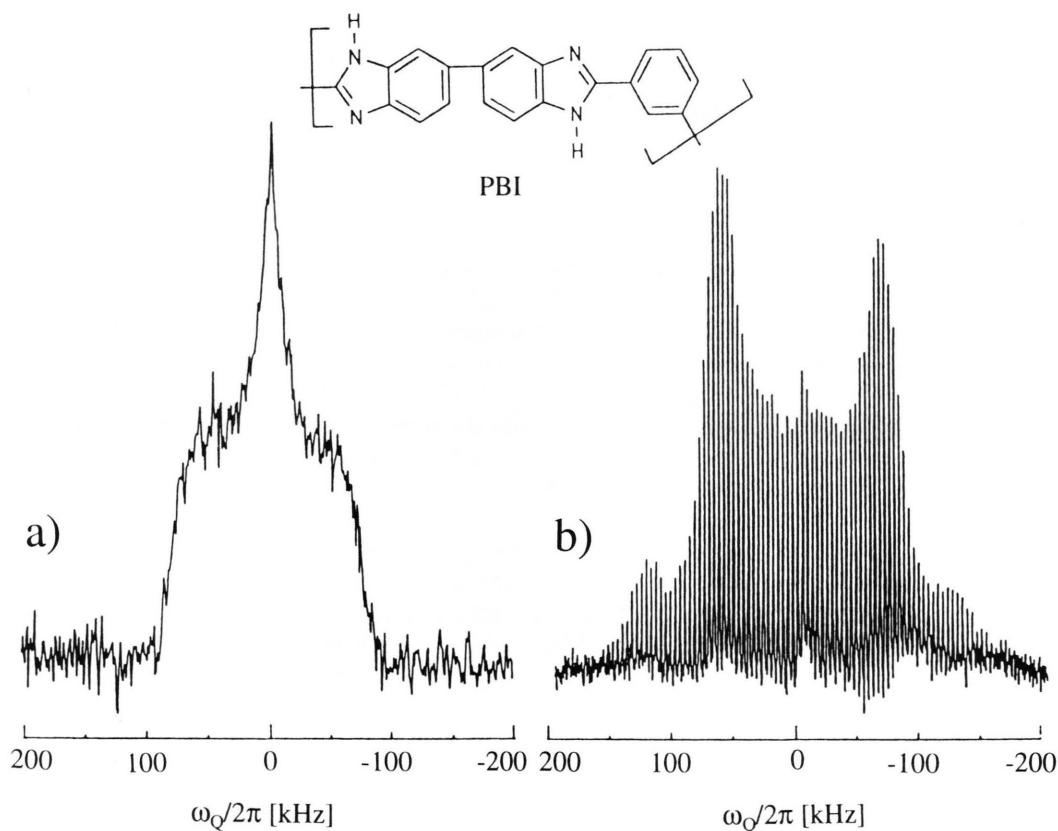

Fig. 5. Deuteron spectra of D_2O in polybenzimmidazole (PBI). a) Quadrupole-echo spectrum with a misleading lineshape due to selective excitation resulting from insufficient rf power. b) MAS spectrum. In addition to an increase in sensitivity, the flip angle of the single-pulse excitation could be decreased below 90° for the sake of narrower pulses to excite the entire spectrum.

Magic Angle Spinning

By magic angle spinning the signal intensity distributed over a wide spectral range of resonance frequencies is focussed into a limited number of narrow spinning sidebands. This results in a dramatic increase in sensitivity, which may be as high as a factor of 200 [22]. Consequently deuterons of rather low concentrations, can be investigated, as for instance on surfaces, water resorbed in polymers, and deuterons in natural abundance.

A comparison of the MAS and the quadrupole echo techniques is given in Fig. 5 [23] for deuterons incorporated in polybenzimidazole (PBI) by drying the polymer and then exposing it to D_2O vapor. A weight increase of 15% and 4% was observed for the samples yielding spectra (a) and (b), respectively. After drying, the deuteron resonance would vanish, indicating the absence of possible deuteron exchange. The solid-echo spectrum (a) produces a lineshape which deviates from the Pake pattern and appears motionally narrowed. The envelope of the MAS spectrum (b), however, traces a Pake pattern of remarkably large bandwidth. This difference in lineshape or envelope, respectively, is an experimental artifact and not due to molecular motion. The available rf power in excess of 1 kW was not high enough to allow for sufficiently narrow 90° pulses required in the quadrupole-echo excitation. Thus the echo excitation was selective. In the MAS measurement a single pulse was used for excitation, and the flip angle could be reduced for the sake of a narrower pulsewidth, so that the entire spectrum could be excited. At the same time the flip angle could be adjusted to the Ernst angle for optimum signal-to-noise ratio.

Instead of displaying a deuteron MAS spectrum with many sidelines (Fig. 6d), it is appealing to plot the sideband envelope (c). It can readily be obtained from Fourier transformation of a single rotary echo (b) chosen from the train of rotary echoes of the MAS free induction decay (FID) signal (a). In fact, the echo decay spectrum compares favorably with the quadrupole echo spectrum (e) apart from some loss of information resulting from partial averaging under the sample rotation. Indeed, such rotary echo spectra preserve some sensitivity with regard to molecular order and mobility, which makes deuteron NMR of static samples such a useful tool [22]. This type of spectral representation can also be applied to 2D Deuteron MAS exchange NMR [24].
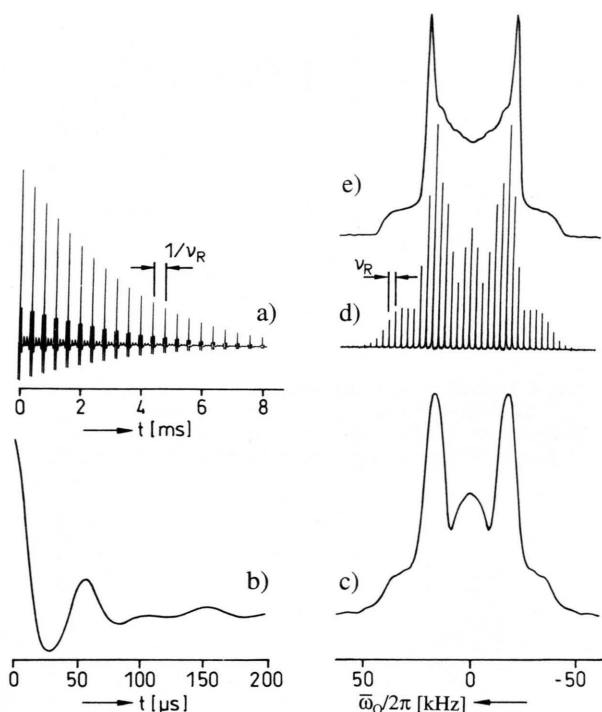

Fig. 6. Time-domain signals and spectra for dimethylsulfone-d_6 at room temperature. a) MAS free induction decay signal (FID). b) Decay of a rotary echo. c) Fourier transform of the rotary echo decay. d) Fourier transform of the MAS FID. e) Quadrupole-echo spectrum of the non-spinning sample.

While the rotary echo transform technique works well for deuteron signals resulting from one chemical shift, a different approach needs to be taken if multiple sites are deuterated in the molecule. Then isotropic chemical shifts and rotary echo spectra displaying the anisotropy of the quadrupole interaction can be separated in a 2D spectrum, which can be derived from the MAS FID or from the sideband spectrum by simple data processing. In this two-dimensional one-pulse (TOP) technique [25] each rotary echo of the MAS FID (cf. Fig. 6a) is written into a separate row of a 2D time-domain data matrix. The 2D Fourier transform of it is the desired spectrum which separates chemical shift and anisotropic interactions on both axes. The spectrum depicted in Fig. 7 has been obtained for polycarbonate, where in addition to the phenyl rings (p, large anisotropy) 5% of the methyl groups (m, narrow anisotropy) have been deuterated as well. The same spectrum can be obtained by mere stacking of the spinning sidebands of the conventional MAS spec-
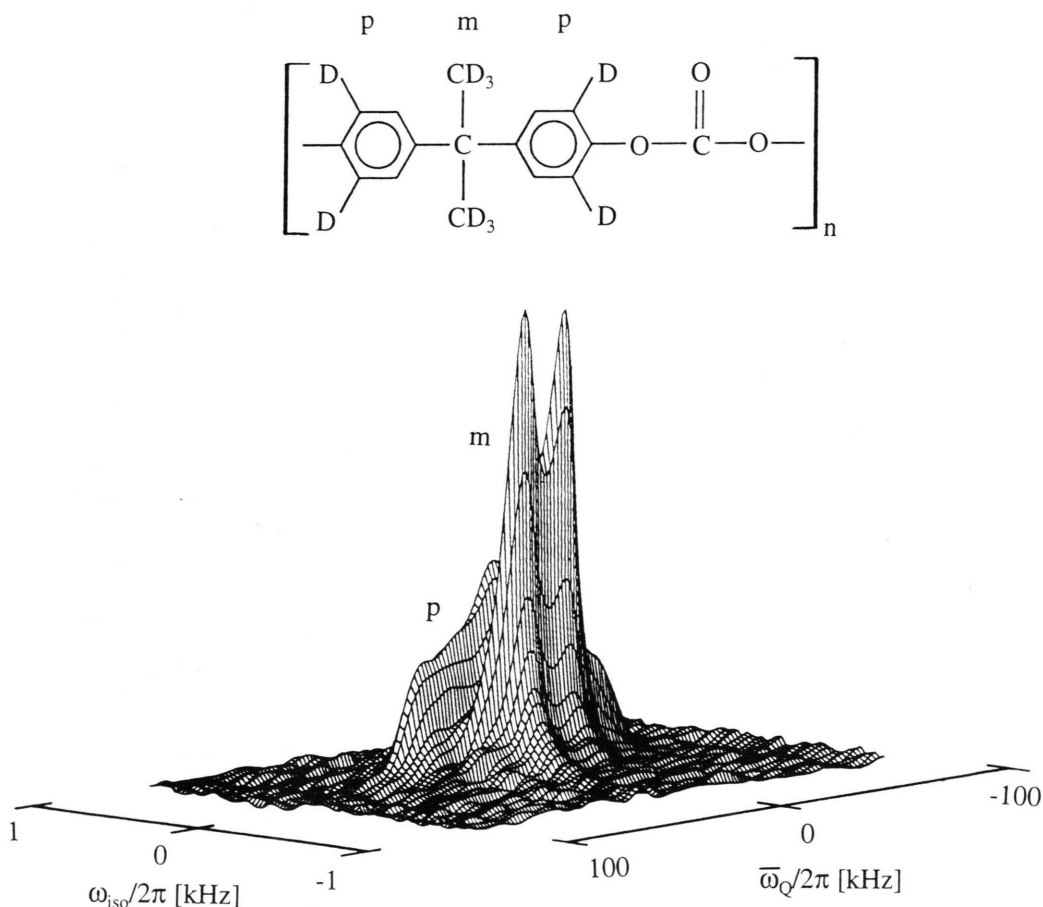
Fig. 7. Two-dimensional one-pulse (TOP) spectrum of polycarbonate which separates the echo-envelope spectra for the methyl (*m*) and phenyl (*p*) resonances.

trum in a 2D fashion. In this case the 2D spectrum is obtained with a single 1D Fourier transformation.

Imaging

In NMR imaging, spatial resolution is achieved by application of magnetic field gradients across the sample. Because the sensitivity and spatial resolution are determinated by the linewidth, it is a particular methodical challenge to access the richness of solid-state deuteron NMR spectroscopy with spatial resolution. Different solutions have been verified experimentally. They are based on the use of echoes from magic angle spinning [26], from spin alignment [27], and from exploitation of the orientation-independent double-quantum transition [1].

Superior spatial resolution is obtained by MAS [26, 28]. Here, however, special hardware is needed, which permits application of gradients rotating in synchronism with the sample [29]. Depending on the speed of sample rotation, dipole-dipole interactions of different strengths are averaged to zero, so that the strength of the interaction enters as a contrast criterium in deuteron MAS imaging in addition to the shape of the rotary echo spectrum. This is shown in Fig. 8 by the example of a spectroscopic image of a composite phantom of ring-deuterated polycarbonate and polystyrene [26]. While the phenylring was fully deuterated in the polystyrene part, only the ortho positions were deuterated in the polycarbonate part of the phantom. Thus the heteronuclear $^1H-^2H$ dipole-dipole interaction of the phenyl deuterons was strong for polycarbonate and weak for polystyrene. The

weak interaction was quenched by MAS, while the strong one was not. Therefore only the polystyrene signals were observed in the spectroscopic image while the polycarbonate magnetization dephased before detection.
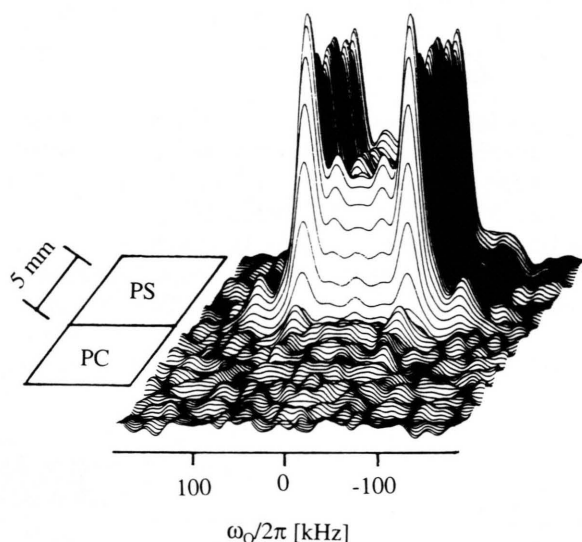

Fig. 8. Spectroscopic MAS image of a composite phantom consisting of ringdeuterated polystyrene and polycarbonate. The polycarbonate signal is suppressed due to the strong deuteron-proton dipole-dipole interaction resulting from partial deuteration of the ring. Along the frequency axis the rotary echo spectrum is displayed.

Similar experiments can be performed on static samples gaining experimental simplicity on the expense of spatial resolution. A particularly robust technique uses the spin alignment technique [27], which has been tested for proton imaging of solids before [30]. Here the signal dephasing by internal spin interactions is rephased for the space encoding period by formation of the alignment echo. Another approach which prevents the signal dephasing altogether exploits the double-quantum evolution during phase encoding [1], because the double-quantum frequency is independent of the molecular orientation and thus corresponds to a narrow line (cf. Figure 1). In addition the effect of an applied gradient on the dephasing of multi-quantum coherence is multiplied by the quantum order, so that the gradient is twice as effective in double quantum imaging.

The use of the technique for investigations of slow molecular motions is illustrated in Fig. 9 by a spectroscopic image of a phantom composed of two pieces of polycarbonate, one without and the other with a dichlorophenylene added as a processing aid. In the lineshape of the section with the additive the broad features are more pronounced, indicating a higher concentration of rigid segments. This is in agreement with the antiplasticising properties of the additive in polycarbonate. Though spectroscopic imaging of deuterons in solid materials is expensive in terms of sample preparation, it is highly rewarding in terms of
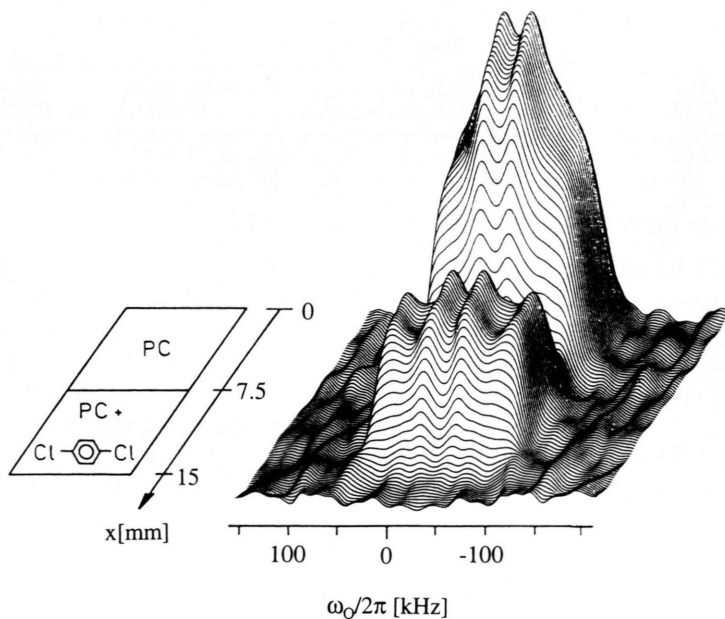

Fig. 9. Spectroscopic double quantum image of a composite phantom of two sections of polycarbonate, one without and one with a low molecular weight additive. The different deuteron lineshapes reflect differences in molecular mobility.

the rich information contents derived from deuteron spectra. Applications are envisioned, for instance in studies of aging, stress, strain, and segmental orientation in polymers.

Summary

One-dimensional wideline deuteron NMR spectroscopy is a well established technique for detailed studies of molecular motion and order. The information contents is further increased by increasing the dimension of the experimental data set in terms of either additional frequency axes, like in 2D exchange NMR, or in terms of additional space axes, like in spectroscopic imaging for investigations of heterogeneous objects. On the other hand, the sensitivity of the technique can markedly be improved on the expense of a slight loss of information by the use of magic angle spinning. Here the conventional spinning sideband spectra can be replaced by their envelopes, which are obtained by Fourier transformation of the rotary echo decay. The use of this form of spectral representation is advantageous for separation of MAS signals from different chemical shifts in a 2D spectrum and for spectroscopic MAS imaging which provides highest spatial resolution.

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