Variable-Angle Three-Dimensional Exchange Nuclear Magnetic Resonance Spectroscopy for the Study of Molecular Motion in Complex Solids

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Abstract: Although molecular motions are responsible for many of the macroscopic properties observed in solids, especially in polymers, methods for studying these processes in all but the simplest systems are scarce. In the present study we introduce a three-dimensional nuclear magnetic resonance experiment for characterizing ultraslow molecular motions in complex solid systems. The technique extracts dynamic information by resolving the two-dimensional exchange distributions that can be observed in spectra of static samples, according to the isotropic chemical shifts of individual molecular sites. These three-dimensional correlations are achieved by processing signals arising from a fast-spinning solid sample using two independent macroscopic axes of rotation as extraction parameters, an approach which becomes practical due to the simple scaling behavior of anisotropic chemical shifts with respect to the axis of sample rotation. The principles involved in this new spectroscopic technique are discussed, and the method is illustrated with an application to the analysis of motions in isotactic polypropylene.

High-resolution nuclear magnetic resonance (NMR) spectra of solids can currently be obtained for most magnetically active nuclei, thanks to the development of various spin- and spatial-averaging techniques.[1] These methods are designed to provide NMR spectra in which only the isotropic components of the local spin interactions are reflected, thereby extending several applications of solution NMR to the analysis of solids. However, when the anisotropic parts of NMR interactions, such as the chemical shift and the quadrupolar couplings, are averaged out, valuable details about the structure and dynamics of the system under observation are also generally lost. This loss is particularly regrettable when the attempt is made to understand the mechanical properties of polymeric materials in terms of local molecular reorientations,[2] which can generally be characterized by analyzing the line shapes arising from the chemical shift anisotropy (CSA) of individual spin-$^1/_2$ sites.[3] For example, in cases where the motions involve relatively simple or well-defined dynamics, fitting CSA powder patterns over a range of temperatures provides an accurate description of the geometry and thermodynamics of the process.[4] For more complex dynamic processes involving distributions of jump angles or rates, or with dynamic processes occurring too slowly to introduce significant changes in an NMR spectrum, anisotropies can be used to analyze molecular motions if they are incorporated into a solid-state version of the two-dimensional (2D) exchange NMR experiment initially proposed by Jeener *et al.*[5,6] In the resulting pulse sequence (Figure 1), spins are excited and allowed to evolve during a time t_1 under

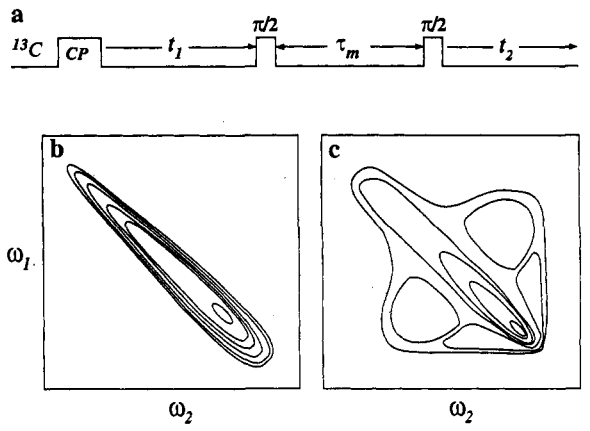

Figure 1. Basic pulse sequence of the conventional 2D solid-state exchange NMR experiment (a). ^{13}C magnetization is created by cross-polarization from protons at the beginning of the experiment; two $\pi/2$ pulses separated by a mixing period are then used to correlate the chemical shift frequencies during intervals t_1 and t_2. Line shapes generated by the solid-state 2D exchange NMR experiment are characteristic of the motion involved. The sharp ridge which arises from a static system, schematically represented in part b, is distributed by molecular motions over a considerable region of the (ω_1,ω_2)-domain (c). Features in this correlation distribution carry valuable information about the dynamic process.

the effects of their initial chemical shifts ω_1. This spectral information is subsequently stored along the z-axis of the rotating frame by a radio-frequency (rf) pulse during a mixing period τ_m while molecular reorientations take place, and finally, the magnetization is returned to the (x,y)-plane of the rotating frame and allowed to evolve at chemical shift frequencies ω_2 during a later time t_2. Regular increments in t_1 and conventional signal sampling during t_2 afford a 2D distribution $S(t_1,t_2)$, whose Fourier transformation with respect to the extraction vector (t_1,t_2)

$$I(\omega_1,\omega_2) = \int\int S(t_1,t_2)\exp[i(\omega_1 t_1 + \omega_2 t_2)]\,dt_1\,dt_2 \quad (1)$$

yields a spectrum reflecting the joint probability distribution that spins at a given initial orientation with respect to the external magnetic field have undergone molecular reorientations during

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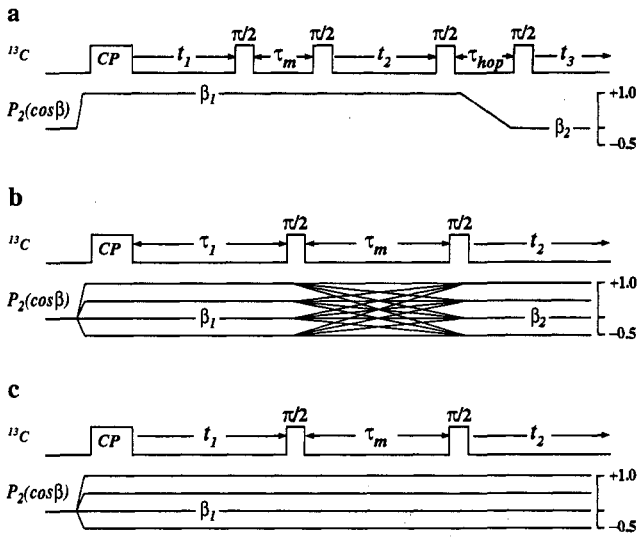

Figure 2. Three approaches toward isotropically resolved exchange correlation spectra. (a) A "conventional" 3D sequence using three evolution times and involving two storage periods, the first to allow exchange and the second to allow the rotor axis to hop to the magic angle. (b) A high-resolution 3D VACSY NMR approach in which these mixing steps are combined to yield an experiment with only one storage period. After initial excitation, spins are allowed to evolve during a fixed time τ_1 at various angles β_1. Spin-packets are stored and recalled by $\pi/2$ pulses; signals are subsequently sampled during t_2 as a function of independent spinning angles β_2. (c) A high-resolution 3D VACSY sequence which does not require a change in the spinner axis. In this experiment independent sets of 2D exchange data are recorded at a series of different spinning angles.

the mixing period τ_m.[7] If no molecular motions have occurred during the mixing, equal anisotropic chemical shifts during t_1 and t_2 will confine the signal to a sharp ridge lying along the main diagonal of the (ω_1,ω_2)-plane (Figure 1b). Molecular reorientations during τ_m, however, will give rise to significant off-diagonal CSA peaks (Figure 1c) whose frequencies and intensities can be interpreted to yield the exact details of the motions.

The presence of these anisotropic spectral features, on which the experiment relies, confines the applications of this 2D solid-state exchange approach to relatively simple or isotopically enriched systems.[8] In general, its use as a tool for the analysis of complex unlabeled systems will be complicated by overlap among the broad anisotropic line shapes which arise from chemically inequivalent sites. Spectral resolution may be improved if the experiment is carried out on a sample which is rotating slowly about the magic axis;[9] under certain conditions this approach can then be applied to the study of more complex systems,[10] although this is achieved at the expense of a considerable increase in the complexity of the observed spectra.

A general way to avoid these limitations would be to separate the full 2D exchange distributions yielded by the sequence shown in Figure 1, according to the individual isotropic chemical shift of each site. Three possibilities for extending the exchange spectra to include a third isotropic dimension are depicted in Figure 2. In Figure 2a we show how this may be accomplished by conventional multidimensional NMR methods by simply adding an extra dimension to the experiment corresponding to evolution under the isotropic chemical shift interaction. In this example, a normal 2D exchange experiment is performed on a spinning sample with the rotor axis parallel to the B_0 field ($\beta_1 = 0°$). The magnetization is then stored while the rotor is hopped to the magic angle ($\beta_2 = 54.74°$) where isotropic evolution occurs during t_3. Although the extension of the experiment to three dimensions is straightforward, it involves significant losses in the signal intensity; the extra storage of the magnetization reduces the signal by a factor of $1/\sqrt{2}$, and T_1 relaxation further reduces magnetization during the hopping–storage delay.

We have recently reported a variable-angle correlation spectroscopy (VACSY) technique which yields isotropic–anisotropic correlation spectra using a series of variable-angle spinning (VAS) experiments in place of hopping.[11] In this article, we show how this approach can be incorporated into exchange experiments to eliminate the necessity for a second storage period and its associated signal losses. The next section describes the principles of obtaining 3D VACSY exchange NMR spectra. We then present applications to ^{13}C NMR analysis of molecular motions in isotactic polypropylene and discuss some of the potential advantages of this new experiment.

Theory

The goal of the present high-resolution exchange NMR experiment is to obtain a spectral distribution $I(\omega_1^a,\omega_2^a,\omega^i)$ in which CSA frequencies ω^a at times t_1 and t_2 appear correlated, as well as separated along a third dimension according to the isotropic chemical shifts ω^i of individual sites. This isotropic separation can be conveniently achieved if the sampling occurring during the acquisition period t_2 of the conventional static 2D exchange NMR experiment is replaced by a set of VAS signal acquisitions. Indeed, upon fast spinning about an axis inclined at an angle β with respect to the external magnetic field, the rotating-frame phases ϕ of nuclear magnetizations evolve in time according to

$$\phi(\beta,t) = \omega^i t + \omega^a P_2(\cos\beta)t \qquad (2)$$

where

$$P_2(\cos\beta) = (3\cos^2\beta - 1)/2 \qquad (3)$$

is the second-order Legendre polynomial of $\cos\beta$. The spinning angle β allows one to control the relative contributions of isotropic and anisotropic interactions to the total phase acquired by the spins. Thus, interpolation of a 2D set of time-domain VAS data over a regular grid followed by Fourier transformation with respect to the extraction vector $(t,P_2(\cos\beta)t)$ yields a 2D spectral distribution where full static CSA powder line shapes ω^a appear resolved according to the isotropic frequencies ω^i.[11] By appending this variable-angle correlation spectroscopy (VACSY) procedure to the conventional 2D exchange NMR sequence, it becomes possible to separate the broad signals arising from different exchanging sites according to their isotropic frequencies as well as to extract the anisotropic chemical shift frequencies of the spins immediately after the mixing period, without introducing an additional segmentation of the time axis.

The complete 3D exchange NMR experiment also requires chemical shift anisotropies to be monitored at an initial time t_1. Although full static CSA interactions could be retrieved from the final correlation spectra if the sample were spun at an angle $\beta_1 = 0°$ or not rotated at all during this period, severe technical problems, involving a special rf coil assembly in the first case and a stop-and-go approach in the second, are associated with these options. It is possible to avoid these complications if the spin system is allowed to evolve during a *fixed* initial interval τ_1 as a function of *variable* spinning angles β_1. A scheme of the complete 3D sequence resulting from independent τ_1- and t_2-VAS evolutions is shown in Figure 2b. The set of signals acquired using this sequence is given by the weighted average

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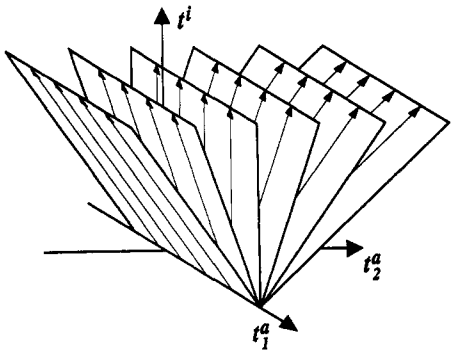

Figure 3. Non-Cartesian sampling of the (t_1^a,t_2^a,t^i)-space occurring during the high-resolution 3D VACSY sequence shown in Figure 2b. Arrows indicate the actual data detection involved in each VAS acquisition; β_1 determines the initial position of the system along the t_1^a-axis, and β_2 controls its evolution in the (t_2^a,t^i)-plane. Interpolation of these data over a regular grid followed by 3D Fourier transformation affords a resolved 2D exchange correlation spectrum for each site in the system.

$$S(\beta_1,\beta_2,t_2) = \int\int\int I(\omega_1^a,\omega_2^a,\omega^i)\exp(-i\omega^i\tau_1)\exp\{-i[\omega_1^a P_2(\cos\beta_1)\tau_1 + \omega_2^a P_2(\cos\beta_2)t_2 + \omega^i t_2]\}\,d\omega_1^a\,d\omega_2^a\,d\omega^i \quad (4)$$

The first exponent in this expression, arising from isotropic evolution during τ_1, only introduces a first-order phase distortion of the peaks along the isotropic frequency domain and has no effect on the final position of the signals. Fourier transformation with respect to the extraction components $t_1^a = P_2(\cos\beta_1)\tau_1$, $t_2^a = P_2(\cos\beta_2)t_2$, and $t^i = t_2$, therefore, leads to the isotropically resolved joint probability distributions of having spins evolving with an anisotropic shift ω_1^a during τ_1 and with an anisotropic shift ω_2^a during t_2.

Figure 3 illustrates the roles played by the experimental variables (β_1, β_2, t_2) in the sampling of the (t_1^a,t_2^a,t^i)-space. Processing the array available from the complete 3D VACSY exchange experiment requires interpolation of the sampled data onto a regular grid of points in the (t_2^a,t^i)-plane; Fourier transformation along t_1^a however is straightforward, provided that the $\{\beta_1\}$ angles are chosen so as to generate constant increments in the value of $P_2(\cos\beta_1)$. The "spin-warp" sampling which then occurs along t_1^a shares several useful features with its NMR imaging counterpart sequence,[12,13] and therefore we choose it over other alternatives for encoding the initial frequencies of the chemical shift anisotropies. One of its main advantages stems from the possibility of changing the sign of $P_2(\cos\beta_1)$. τ_1-evolution frequencies can then be modulated using both positive and negative scaling factors so as to generate a time-domain echo which helps to remove phase distortions in the anisotropic exchange patterns. Moreover, as VAS spin-warp NMR only encodes the full static anisotropies, it maximizes the information being sought without spreading the resonances according to their (redundant) isotropic chemical shifts.

This version of the 3D VACSY exchange experiment allows us to obtain the 3D anisotropic–isotropic correlation information by combining the rotor hop and exchange mixing periods. Although this procedure is simpler than the one shown in Figure 2a, a sudden mechanical movement of the sample rotor is still necessary. The next logical simplification removes the hop altogether, by constructing the 3D anisotropic–isotropic correlations from a series of 2D VAS exchange experiments, as shown in Figure 2c. This latter method, a natural 3D exchange version of the VACSY experiment, appears to be the simplest experimental approach to achieving isotropically separated exchange spectra, but it involves more elaborate data processing. These results will be presented in a future publication.[14]

Experimental Section

Natural-abundance ^{13}C cross-polarization NMR spectra were recorded at 7.07 T on a home-built spectrometer based on Tecmag pulse programmer and data acquisition systems. Samples were spun using a Doty Scientific 7-mm spinner assembly installed inside a dynamic-angle spinning probehead system described elsewhere in detail.[15] The angles of sample spinning were controlled using a stepping motor located at the base of the probe. Since the main axis of the rf coil coincides with the axis of sample rotation, spinning angles $\{\beta\}$ were restricted to the $-0.5 \le P_2(\cos\beta) \le 0.5$ range. The complete 3D VACSY exchange sequence requires changing the spinning angles from β_1 to β_2 during the mixing period; this axis hopping however only involves a small fraction (<10%) of the times normally needed to monitor exchange (≥500 ms) and therefore has no effect on the overall duration of the experiment. Hartmann–Hahn matching conditions were achieved at rotating fields of ca. 60 kHz, and the relative rf phases of the transmitter pulses shown in Figure 2b were cycled to select the $+1 \rightarrow 0 \rightarrow -1$ coherence-transfer pathway for the ^{13}C spins.

A set of 31 different spinning angles $\{\beta_2\}$ were used during the t_2 acquisition, chosen as described in eqs 10–12 of ref 11 for $P_{2max} = -P_{2min} = 0.5$ and twice the spectral width along the ω_2^a-axis as compared to the isotropic dimension. Thirty-one β_1-orientations were also used to encode the anisotropic frequencies during τ_1, chosen according to

$$P_2(\cos\beta_1)_i = -0.5 + (i-1)/30; \quad i = 1, ..., 31 \quad (5)$$

This choice places all the t_2-VAS acquisitions along a regular grid in t_1^a; spectral widths along the ω_1^a-domain are then determined by the duration of the evolution time τ_1. Once the complete 3D set $S(\beta_1,\beta_2,t_2)$ was acquired, we transferred it to a Stardent 3000 Titan computer for further processing. Data were interpolated into a regular array of 128 × 64 × 31 points in (t^i,t_2^a,t_1^a)-space, weighted, and zero-filled to a 128^3-cube. 3D Fourier transformation afforded the final high-resolution exchange NMR spectra.

Results and Discussion

The potential applications of the 3D VACSY exchange NMR sequence illustrated in Figure 2b were explored by analyzing the motional behavior of isotactic polypropylene (iPP, $[-CH_2CH(CH_3)-]_n$). This polymer exhibits sharp X-ray diffraction peaks arising from well-defined crystalline regions in which two symmetry-related polypropylene chains are helically arranged, each one possessing three monomers per unit cell.[16] Dielectric and mechanical measurements have revealed several relaxation phenomena in the crystalline regions of iPP; at room temperature, motions of ca. 10^0–10^2 Hz involving molecular reorientations are responsible for the so-called α-relaxation process.[17] Spiess and co-workers recently explored the nature of these motions at 380 K by analyzing the 2D ^2H exchange NMR spectrum of an iPP sample in which methyl hydrogens had been synthetically replaced by deuterons.[18] The results observed in these studies led the authors to conclude that methyl groups in iPP undergo discrete 3-fold 120° jumps about the main axis of the polymer helix, exchanging the quadrupolar tensor of each methyl among three sites whose principal axes are 113° apart.

The rates of these jumps are too slow to introduce appreciable distortions in the room-temperature ^{13}C CSA line shapes of either the >CH–, $-CH_2-$, or $-CH_3$ carbon atoms, all of which can be resolved in the 2D VACSY isotropic–anisotropic correlation spectrum of iPP shown in Figure 4. The main deviation from an

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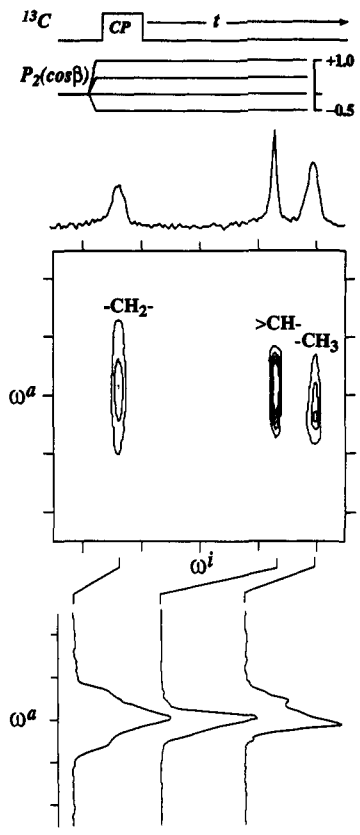

Figure 4. 2D isotropic–anisotropic VACSY ^{13}C NMR spectrum of isotactic polypropylene, obtained using the sequence shown for 31 different spinning angles β. The 1D plot above the 2D spectrum shows the projection of the data onto the isotropic axis, while those below are the anisotropic ^{13}C NMR line shapes resolved for the three different sites of isotactic polypropylene. All markers are 1 kHz apart.

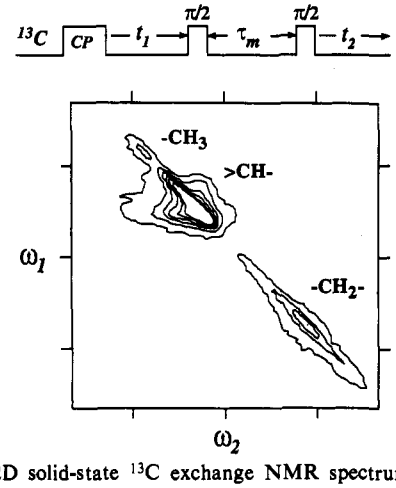

Figure 5. 2D solid-state ^{13}C exchange NMR spectrum of isotactic polypropylene recorded on a static sample using the sequence shown. Forty-eight t_1-points and a mixing period τ_m = 1 s were used to acquire the data; markers are 1 kHz apart.

ideal powder pattern appears in the case of the methyl carbon signal, although this irregularity is probably due to a superposition of carbon signals arising from crystalline regions and more mobile amorphous domains.[19] The presence of molecular motions however is clearly evident in the static 2D ^{13}C exchange NMR spectrum of iPP, which shows significant ridges departing from the main diagonal (Figure 5). Individual powder patterns in this spectrum overlap significantly, thus precluding the extraction of accurate angular or dynamic information about the intervening

(19) Similar distortions are observed in the ^2H NMR pattern shown in Figure 7 of ref 18.

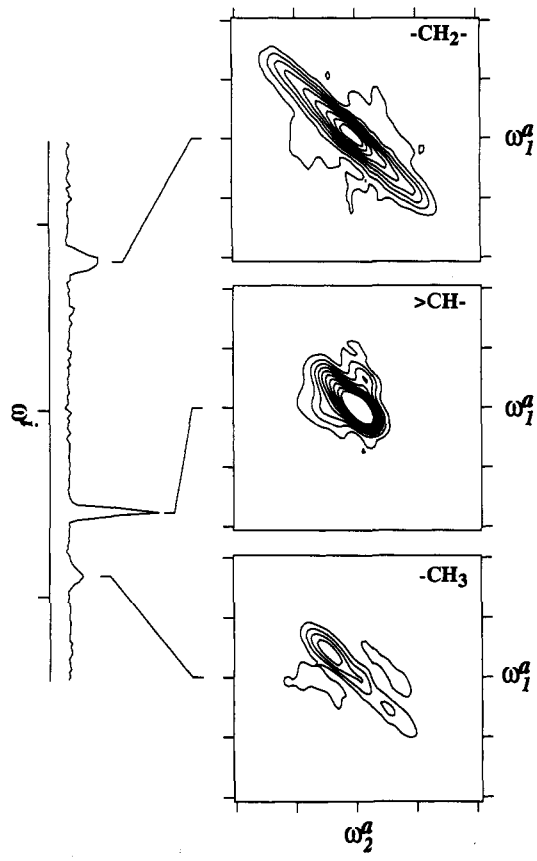

Figure 6. Results of the high-resolution 3D VACSY exchange NMR experiment (τ_m = 1 s) applied to isotactic polypropylene. The total acquisition time for the experiment was 5 days. The 1D plot on the left is the isotropic projection of the full 3D set; the 2D ($\omega^a{}_1$,$\omega^a{}_2$)-correlation spectra on the right correspond to slices extracted at the isotropic shifts of the different sites. All markers are 1 kHz apart.

process. The high-resolution 3D VACSY exchange NMR approach described above makes possible the separation of these exchange correlation spectra according to the chemical nature of each site. Results from such an experiment are illustrated in Figure 6, which shows a plot of the 1D spectrum obtained after projecting the 3D set onto the ω^i-axis, together with 2D exchange distributions corresponding to anisotropic slices extracted from the 3D spectrum at the isotropic shifts of individual iPP resonances. Relative peak intensities in this 3D spectrum deviate from the patterns observed in conventional CPMAS NMR due to relaxation during τ_m; along their main diagonals, however, the resolved 2D exchange distributions show typical CSA powder line shapes which are essentially identical to those available from the isotropic–anisotropic NMR spectrum shown in Figure 4.

Off-diagonal peaks and broadened diagonal ridges reveal the presence of molecular motions for all three sites of iPP. It is possible to correlate this spectral information with the helical jumps observed in the ^2H NMR study, provided that the magnitudes and local molecular orientations of the individual chemical shift tensors are known. Principal components are immediately available from the singularities observed in the anisotropic line shapes resolved for each site of iPP. Tensor orientations can be obtained for the methyl and methylene carbons on the basis of symmetry arguments. Since for both sites CSA line shapes are essentially axial, the z-orientations of these principal axis systems can be placed along the C–CH_3 bond in the first case and along the C–H bond in the second. For the methylene carbon, whose CSA asymmetry parameter is 1, we place the orientation of the principal axis system following guidelines arising from single-crystal and theoretical studies:[20] the z-axis of the tensor bisects the H–C–H bond angle, and the y-axis is located in the C–CH_2–C plane perpendicular to the C–H bonds.

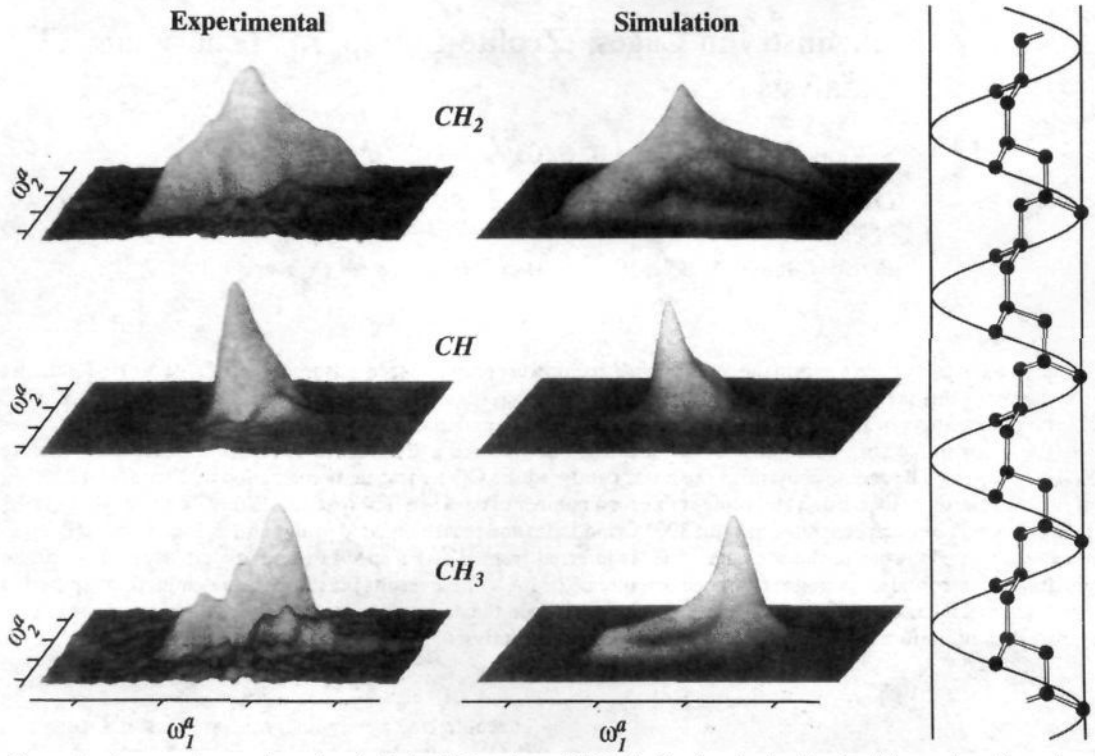

Figure 7. Comparison between the experimental and calculated 2D exchange NMR distributions obtained for the different sites of isotactic polypropylene. Simulations were obtained as described in the text, by assuming 120° jumps of the polypropylene helix, whose carbon backbone is outlined by the scheme shown to the right of the spectra.

These tensor parameters and the known geometry of crystalline iPP are used to calculate the chemical shift frequencies of each type of carbon atom in a monomer for a given orientation of the polymer chain. The resonance frequencies of the three exchange-related positions for each carbon atom can be evaluated by rotating the tensors 120° about the main axis of the helix. Complete 2D exchange ^{13}C NMR spectra for each carbon are then simulated by averaging the orientation of the polymer helix over a set of powder angles, the only remaining parameter in the fit being the ratio τ_c/τ_m between the motional correlation time and the mixing time used in the experiment. Figure 7 compares the experimental 2D ^{13}C exchange NMR plots that can be resolved for each iPP site with simulated spectra obtained by assuming $\tau_c \gg \tau_m$. There is good agreement between these calculated exchange distributions and the experimental spectra for all carbon atoms in the monomer. The main deviations from the expected pattern appear for the methyl signal; the distortions in the experimental plot however are very similar to the ones observed in the static powder line shape of the $-CH_3$ carbon (Figure 4) and are therefore probably unrelated to molecular reorientations occurring during the mixing period.

Conclusion

Extracting chemical information from anisotropic line shapes in multisite systems has been a long-standing challenge in solid-state NMR. In the present study we have illustrated a 3D experiment that achieves this goal by correlating and resolving chemical shift anisotropies at different times, thus making possible detailed studies of motional processes in complex systems without having to use synthetic isotope enrichment. Since this high-resolution technique achieves the separation of 2D exchange distributions using a single storage period, there is not the loss in signal that would arise due to an extra storage period or to relaxation during the hop delay. From a spectroscopic point of view it is worth noting that the present experiment relies not only on the time-domain segmentation conventionally associated to multidimensional NMR but also on the extraction of anisotropies using spinning angles as Fourier parameters. This possibility arises as a consequence of the scaling behavior of chemical shift interactions in solids with respect to the angle of the rotation axis. We are currently exploring additional applications of these VACSY principles, in particular to the incorporation of dipole–dipole interactions into these types of NMR acquisition schemes.

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