The carbon chemical shift tensor in polyoxymethylene

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The complete chemical shift tensor of the carbons in crystalline polyoxymethylene is determined via the two-dimensional dipolar correlated ^{13}C chemical shift NMR technique. The orientation of the tensor is determined by the local tetrahedral symmetry of the $C_2H_2O_2$ unit and not by the overall symmetry of the helical chains. In an accompanying paper this shift tensor is used to study ultraslow motions in polyoxymethylene.

I. INTRODUCTION

Many spin interactions in a solid are described by a tensor. As tensor interactions are related to molecular and crystal axes, the information contained in such a tensor interaction can be used to obtain geometrical information about the molecule or crystal being studied. It is well known, e.g., that the magnetic dipole interaction between two spins is coaxial with the internuclear axis of the two interacting nuclei. Knowledge of the complete tensor of the dipolar interaction between a ^{13}C and a ^{1}H, for instance, yields quantitative information about the C–H distance and the orientation of the C–H axis, with respect to the molecule.

The first technique to record dipolar modulated ^{13}C spectra of solids, the 2D separated local field (SLF) experiment, was proposed by Waugh[1] and applied to single crystals and oriented polymers by his co-workers.[2–4] Here, dipolar modulation refers to the fact that ^{13}C FIDs are collected during the detection period of the 2D experiment, which are phase modulated by the dipolar interaction of the ^{13}C spin with surrounding protons. Stoll *et al.*[5] were the first to use the technique in powders. They analyzed the spectra after a single Fourier transform, leaving the dipolar modulation in the timespace. Linder *et al.*[6] showed that it is advantageous to apply a complete two-dimensional Fourier transform of the acquired signals, thus obtaining very characteristic 2D powder patterns.

Munowitz *et al.*[7–10] applied this technique, which separates the chemical shift and heteronuclear dipolar interactions into samples spinning at the magic angle. As both interactions are inhomogeneous, the resulting two-dimensional spectrum consists of a set of spinning sidebands. The analysis of these 2D spinning sideband spectra can also give the geometrical information one wants to obtain. Schaefer *et al.*[11] used the experiment of Munowitz *et al.* to detect the averaging of dipolar interactions, in that way, obtaining information about molecular motions in the kHz regime. This has been applied to various polymers.

Another example of the use of a tensor interaction will be treated in the accompanying paper. There the chemical shift tensor of ^{13}C spins is used to detect and analyze slow molecular rotations. Via a novel two-dimensional solid state NMR experiment, it can be determined for such a case about what axis the rotations take place and about what angle. One piece of information, however, is needed before the motion can be analyzed: the orientation of the chemical shift tensor of the particular ^{13}C spin, relative to the molecular axes. Most conveniently, this can be determined from single crystal studies, at least when single crystals are available. For the system described in the next paper, polyoxymethylene, single crystals of sufficient dimensions cannot be obtained. Fortunately, the two-dimensional SLF solid state NMR technique allows the determination of a complete ^{13}C chemical shift tensor, including the orientation relative to molecular axes, even for noncrystalline material.[6] With this technique the orientation of the ^{13}C chemical shift tensor is determined relative to the dipolar ^{13}C–^{1}H tensor interaction. Since the orientation of the latter is known, the ^{13}C chemical shift tensor can be determined relative to molecular axes. Here we apply this technique to polyoxymethylene, in order to be able to analyze slow molecular motions in this polymer, as described in the next paper.

II. EXPERIMENTAL

The pulse scheme used to obtain spectra which correlate heteronuclear dipolar interactions and chemical shielding anisotropy is shown in Fig. 1. Multiple pulse decoupling (MREV-8, $\pi/2$ pulse length 1.6 μs, cycle time 28.8 μs) was used for homonuclear proton decoupling during t_1. The scaled heteronuclear ^{13}C–^{1}H dipolar interaction and the anisotropic chemical shift modulate (in phase) the signal detected during t_2. As proton decoupling is applied during t_2 only the anisotropic chemical shift is effective during this detection period.

For a semicrystalline polymer like polyoxymethylene the presence of the NMR signal from amorphous parts of the material interferes with the dipolar correlation spectrum of the crystalline regions. The amorphous signal is eliminated by the pulse sequence of Fig. 1 by making use of the vastly different spin–lattice relaxation times T_1 for the amorphous and crystalline carbons.[12] At 75 MHz, the carbon frequency of the CXP 300 spectrometer used for this experiment, the amorphous carbon T_1 is 90 ms, while the crystalline T_1 is 18 s. After cross polarization the total magnetization (amorphous + crystalline) is flipped to the $-z$ axis from where the amorphous part of the magnetization rapidly relaxes to the $+z$ axis. At the point where this magnetization passes through zero another $\pi/2$ pulse is applied which brings the crystalline magnetization in the xy plane from where the evolution period for the 2D experiment starts.

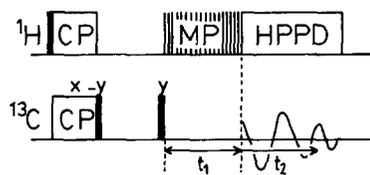The double-resonance probe was equipped with a hori-

FIG. 1. Pulse scheme to obtain a 2D dipolar chemical shift correlated spectrum of the crystalline parts of polyoxymethylene, free from the signal of the amorphous regions.

zontal coil (ϕ = 6 mm) of flat copper wire. The sample used in the experiment was a cylindrical (5×11 mm) piece of polyoxymethylene (Hostaform-C from Hoechst).

III. THE STRUCTURE OF POLYOXYMETHYLENE

Polyoxymethylene, with chain structure $(-CH_2O-)_n$, is the polymerization product of formaldehyde. It is rather difficult to grow large crystals of the polymer, but some x-ray studies of small single crystals have been made. The stable form of POM has trigonal symmetry, with the chains arranged in a helical conformation. Within a single crystal only helices with the same handedness are found, with right or left handedness equally probable. Huggins[13] proposed the 9/5 model, meaning that the unit cell consists of chains with nine CH_2–O monomer units in five turns of the helix. Uchida and Tadokoro[14] refined this to a 29/16 model. Both helices are so similar, however, that it is difficult to decide which model is the most reasonable.[15] The local tetrahedral symmetry of the CH_2O_2 unit appears to be hardly distorted by the helix formation (O–C–O bond angle $\sim 111°$). The H–C–H angle is 109° and the C–H bond length is 1.09 Å. The H–C–H plane makes an angle of 55° with the helix axis.[14] This information about the proton positions allows us to find the orientation of the chemical shift tensor within the molecule.

Bulk-crystallized POM has a spherulitic structure, consisting of crystalline lamellae connected to each other by amorphous material. The lamellae, in which the molecular chains are folded, are approximately 100 Å thick.[16] The crystallinity is approximately 60%. A detailed description of a spherulitic structure in crystalline polymers is given by Sharples.[17]

Proton-decoupled ^{13}C spectra of a static sample of bulk-crystallized POM at room temperature show separate signals of the crystalline and the amorphous phase.[18] Because the glass temperature of the amorphous phase is below room temperature, a lot of motion exists in this part of the polymer. In fact, there is so much motion in the amorphous material that the chemical shift anisotropy is largely averaged, which results in a fairly narrow line in the NMR spectrum. For the rigid crystalline regions in the sample we observe a structured line determined by the chemical shielding anisotropy. From this line shape the principal values of the chemical shift tensor were found to be: σ_{xx} = 67 ppm, σ_{yy} = 86 ppm, and σ_{zz} = 111 ppm.

IV. EXPERIMENTAL RESULT AND SIMULATION OF THE DIPOLAR CHEMICAL SHIFT CORRELATED SPECTRUM

The dipolar correlated chemical shift spectrum for the crystalline regions of polyoxymethylene, as obtained with

the pulse program of Fig. 1, is shown in Fig. 2(a). We have to find the relative orientation of the carbon chemical shift tensor by simulation of this spectrum for different assumed relative orientations of the ^{13}C–^1H dipolar and ^{13}C chemical shift tensors.

A general description of the calculation of powder resulting from experiments correlating tensorial interactions is given by Linder et al.[6] Here we describe the specific case of the correlation of the heteronuclear dipolar interaction to the chemical shielding anisotropy in a CH_2 group of polyoxymethylene. During the evolution period t_1, the strong homonuclear ^1H–^1H is suppressed by multiple pulse decoupling. Thus, the relevant Hamiltonian for the ^{13}C spins is determined by the chemical shift H_{CS} and the heteronuclear dipolar interaction H_D. During the detection period normal high-power proton decoupling is applied so that only the ^{13}C Zeeman interaction remains:

$$H^{(1)} = H_{CS} + CH_D ,$$
$$H^{(2)} = H_{CS} , \tag{1}$$

where C represents the scaling factor due to the homonuclear decoupling. Of course it is possible to remove the influence of H_{CS} during t_1 by applying a π pulse in the middle of the evolution period, as has been described by Stoll et al.[5] But the effect of H_{CS} during t_1 can also be calculated, therewith avoiding the need of an accurately adjusted π pulse in the experiment.

Evaluation of the Hamiltonians $H^{(1)}$ and $H^{(2)}$ gives us the resonance frequencies during evolution and detection period, thus allowing the calculation of the total 2D powder
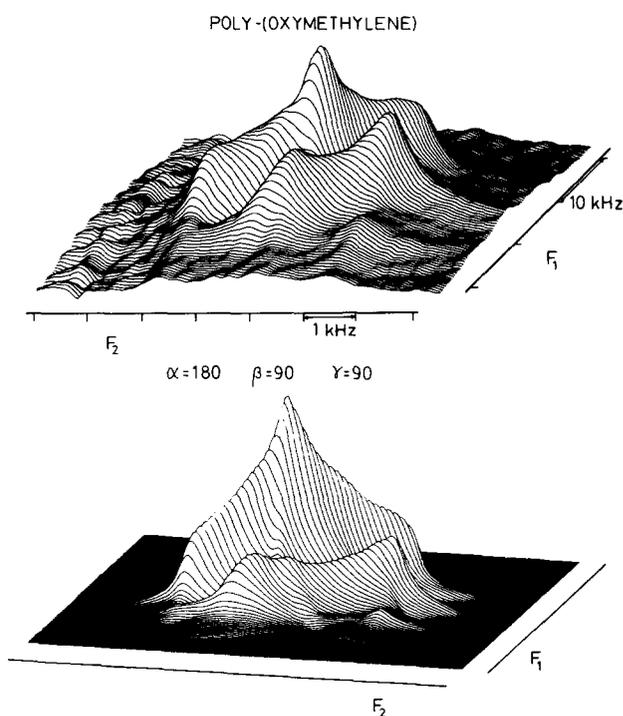
POLY-(OXYMETHYLENE)

α = 180° β = 90° γ = 90°

FIG. 2. (a) 2D dipolar correlated ^{13}C spectrum of crystalline polyoxymethylene obtained with the pulse scheme of Fig. 1. MREV-8 ($\pi/2$ pulse length 1.6 μs, cycle time 28.8 μs) was used during t_1. 400 scans were accumulated for 34 t_1 values. In t_1 a cosine filter was applied prior to Fourier transformation. (b) Simulation of spectrum (a) with the orientation of the chemical shift tensor in POM (see the text), α = 180°, β = 90°, γ = 90°.

pattern. Summing over all transitions (i and j), with resonance frequencies $\omega_i^{(1)}(\theta,\varphi)$ and $\omega_j^{(2)}(\theta,\varphi)$, we get

$$
S(\omega_1,\omega_2) = \sum_i \sum_j \int_0^{2\pi} \int_0^\pi g_i^{(1)}[\omega_1 - \omega_i^{(1)}(\theta,\varphi)] g_j^{(2)}
$$
$$
\times [\omega_2 - \omega_j^{(2)}(\theta,\varphi)] \sin\theta d\theta\, d\varphi , \qquad (2)
$$

where θ and φ are the polar angles that describe the orientation of randomly distributed microcrystals with respect to the external magnetic field. The line shapes are denoted by the functions g.

The resonance frequency of a certain ^{13}C spin, relative to the frequency γB_0, during the evolution period depends on the eigenstates of the two connected protons and on the orientations of the chemical shielding and dipolar tensors with respect to the external field:

$$
\omega_1^{(1)} = \omega_{CS}(\theta,\varphi) + C\,[\omega_{D1}(\theta,\varphi,\alpha,\beta,\gamma)
$$
$$
+ \omega_{D2}(\theta,\varphi,\alpha,\beta,\gamma)] ,
$$
$$
\omega_2^{(1)} = \omega_{CS}(\theta,\varphi) + C\,[\omega_{D1}(\theta,\varphi,\alpha,\beta,\gamma)
$$
$$
- \omega_{D2}(\theta,\varphi,\alpha,\beta,\gamma)] , \qquad (3)
$$
$$
\omega_3^{(1)} = \omega_{CS}(\theta,\varphi) - C\,[\omega_{D1}(\theta,\varphi,\alpha,\beta,\gamma)
$$
$$
- \omega_{D2}(\theta,\varphi,\alpha,\beta,\gamma)] ,
$$
$$
\omega_4^{(1)} = \omega_{CS}(\theta,\varphi) - C\,[\omega_{D1}(\theta,\varphi,\alpha,\beta,\gamma)
$$
$$
+ \omega_{D2}(\theta,\varphi,\alpha,\beta,\gamma)] .
$$

During the detection period we simply find

$$
\omega^{(2)} = \omega_{CS}(\theta,\varphi) . \qquad (4)
$$

Here θ and φ are the polar angles which orient the external magnetic field in the principal axis system of the chemical shielding tensor. α, β, and γ are the Euler angles relating the dipolar interaction to the principal axis system of the CS tensor. The expression for ω_{CS} is easily obtained by transforming the Hamiltonian H_{CS} from the principal axis system to the laboratory frame over the Euler angles φ, θ, 0:

$$
\omega_{CS}(\theta,\varphi) = \omega_{XX} \sin^2\theta\cos^2\varphi + \omega_{YY}\sin^2\theta\sin^2\varphi
$$
$$
+ \omega_{ZZ}\cos^2\theta , \qquad (5)
$$

with $\omega_{XX} = \gamma B_0 \sigma_{XX}$, etc. In order to obtain expressions for ω_{D1} and ω_{D2} for the two protons, we have to evaluate the dipolar Hamiltonian H_D in the laboratory frame. To get similar expressions for both protons we define a local axis system (LOC) in the CH_2O_2 unit whose z axis is the bisector of the H–C–H angle and the y axis perpendicular to the H–C–H plane (Fig. 3). To come from the principal axis system of the dipolar interaction (D-PAS) to this axis system, one has to rotate over an angle $\tfrac{1}{2}\delta$ about the y axis for proton 1 and $-\tfrac{1}{2}\delta$ for proton 2 ($\delta =$ H–C–H angle $= 109°$). As we like to determine the orientation of the chemical shielding tensor within the molecule, we transform from this local axis system to the principal axis system of the chemical shielding tensor (CS-PAS) over the Euler angles α,β,γ. These angles α,β,γ are thus the unknown parameters which we want to recover from the simulated spectra. The last step is then to transform from the CS-PAS to the laboratory frame (LAB) over angles φ, θ, 0:
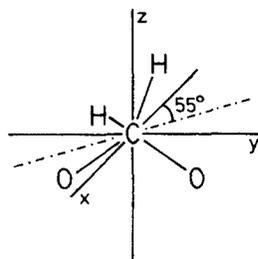

FIG. 3. Local axis system LOC in the CH_2O_2 unit. The O–C–O plane is chosen as the yz plane, and the H–C–H plane as the xz plane. The helix axis (- - -) makes an angle of 55° with the H–C–H plane.

$$
D\text{-PAS} \xrightarrow{0,\pm(1/2)\delta,0} LOC \xrightarrow{\alpha,\beta,\gamma} CP\text{-PAS} \xrightarrow{\varphi,\theta,0} LAB ,
$$

$$
H_D = \sum_m D_{m,0}^2\,\varphi,\theta,0 \sum_{m'} D_{m',m}^2(\alpha,\beta,\gamma)
$$
$$
\times D_{0,m'}^2(0,\pm\delta/2,0)\gamma_C\gamma_H\hbar^2 r_{CH}^{-3}I_z S_z . \qquad (6)
$$

Some algebra eventually yields the contributions of the dipolar interactions to the resonance frequencies during t_1:

$$
\omega_{D1,2} = -\tfrac{1}{2}\gamma_C\gamma_H\hbar r_{CH}^{-3}\{1 - 3[A\sin(\pm\tfrac{1}{2}\delta)
$$
$$
+ B\cos(\pm\tfrac{1}{2}\delta)]^2\} , \qquad (7)
$$

with

$$
A = \sin\theta\,[\cos\alpha\cos\beta\cos(\varphi+\gamma) - \sin\alpha\sin
$$
$$
\times(\varphi+\gamma)] + \cos\theta\cos\alpha\sin\beta
$$

and

$$
B = -\sin\theta\sin\beta\cos(\varphi+\gamma) + \cos\theta\cos\beta .
$$

Before we can calculate the 2D powder pattern from these resonance frequencies using Eq. (2), there is still one point to consider, namely the line shape for each resonance. This depends on the type of modulation and how the data are Fourier transformed. In this case we have to do with phase modulation, i.e., the phase of the signal detected during t_2 is a linear function of length of evolution period t_1. Successive complex Fourier transforms with respect to t_2 and t_1 gives the following line shape of mixed absorption and dispersion signals:

$$
S(\omega_1,\omega_2) \sim \{A_1(\omega_1)A_2(\omega_2) - D_1(\omega_1)D_2(\omega_2)
$$
$$
+ i[A_1(\omega_1)D_2(\omega_2) + D_1(\omega_1)A_2(\omega_2)]\} \qquad (8)
$$

with

$$
A_i(\omega_i) = \frac{T_2}{1 + T_2^2(\omega_i - \omega)^2}
$$

and

$$
D_i(\omega_i) = \frac{T_2^2(\omega_i - \omega)}{1 + T_2^2(\omega_i - \omega)^2} .
$$

Generally an absolute value calculation is performed on such a signal, i.e., the square root of the sum of the squares of the real and the imaginary signal is calculated.

The presence of dispersion mode signals lowers the resolution of a powder spectrum, and can even lead to the disappearance of certain ridges in a 2D powder pattern. Pure absorption mode spectra can be achieved by performing a second experiment for each t_1 value with an additional $^{13}C\,\pi$ pulse at the end of the evolution period and coaddition of the thus obtained FID to the FID of the original experiment.[19] The limited number of lines in a pulse program on a Bruker
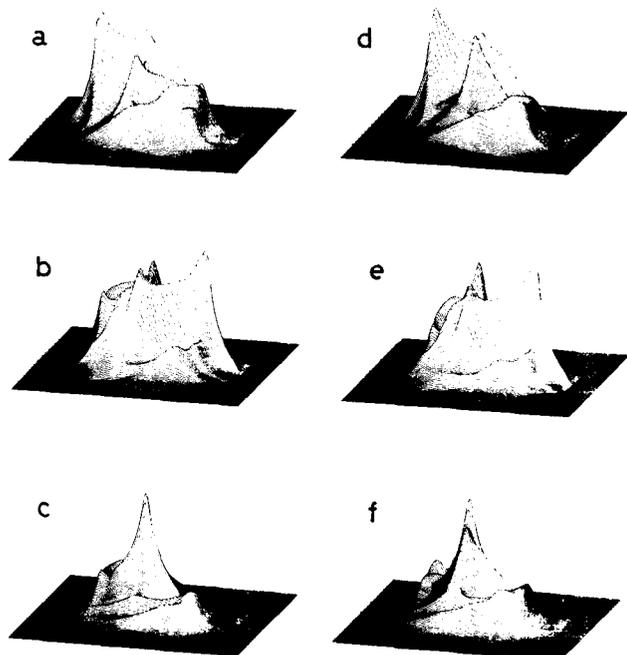
FIG. 4. The simulated spectra for the six possible orientations of the shift tensor for which one principal axis is parallel to the helix axis and another in the O–C–O plane. (a) $\alpha = 55.2°$, $\beta = 0°$, $\gamma = 0°$, σ_{22}//helix, σ_{33}//OCO; (b) $\alpha = 55.2°$, $\beta = 90°$, $\gamma = 0°$, σ_{22}//helix, σ_{11}//OCO; (c) $\alpha = 55.2°$, $\beta = 90°$, $\gamma = 90°$, σ_{11}//helix, σ_{22}//OCO; (d) $\alpha = -34.8°$, $\beta = 0°$, $\gamma = 0°$, σ_{11}//helix, σ_{33}//OCO; (e) $\alpha = -34.8°$, $\beta = 90°$, $\gamma = 0°$, σ_{33}//helix, σ_{11}//OCO; (f) $\alpha = -34.8°$, $\beta = 90°$, $\gamma = 90°$, σ_{33}//helix, σ_{22}//OCO.

FIG. 6. Simulated spectra for two orientations of the shift tensor that differ by 10°. (a) $\alpha = 180°$, $\beta = 90°$, $\gamma = 90°$, the same orientation as in Fig. 2(b). (b) $\alpha = 170°$, $\beta = 90°$, $\gamma = 90°$.

CXP-300 with Z70 pulse programmer, however, does not allow this in a straightforward way. Thus we have to calculate the effect of dispersion mode signals in our spectrum. This is legitimate because the experimental spectrum in Fig. 2(a) shows, despite of dispersive signals, characteristic features which should allow the recovery of the orientation of the chemical shift tensor.

The 2D spectra were calculated in a rectangular grid of 100×100 frequency values (ω_1, ω_2). Generally 90 000 sampling points were evaluated over a whole sphere. The spectrum thus calculated is subsequently convoluted with the line shape function described in Eq. (8) followed by an absolute value calculation, resulting in a spectrum that can be compared to the experimental one.

From the structure of polyoxymethylene one expects the orientation of the chemical shielding tensor to be determined either by the local tetrahedral symmetry of the CH_2O_2 unit or by the overall symmetry of the helix (or even by both). Simulation of these possibilities gives very different 2D powder patterns, and the right solution is easily de-
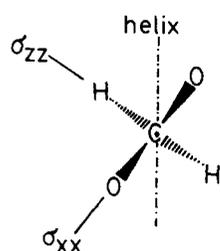

FIG. 5. Projection of the local CH_2O_2 unit in polyoxymethylene showing the orientation of the chemical shift tensor in the molecule, obtained by transforming the axis system in Fig. 3 over the Euler angles 180, 90, 90. The Y axis points perpendicular to the plane of the drawing.
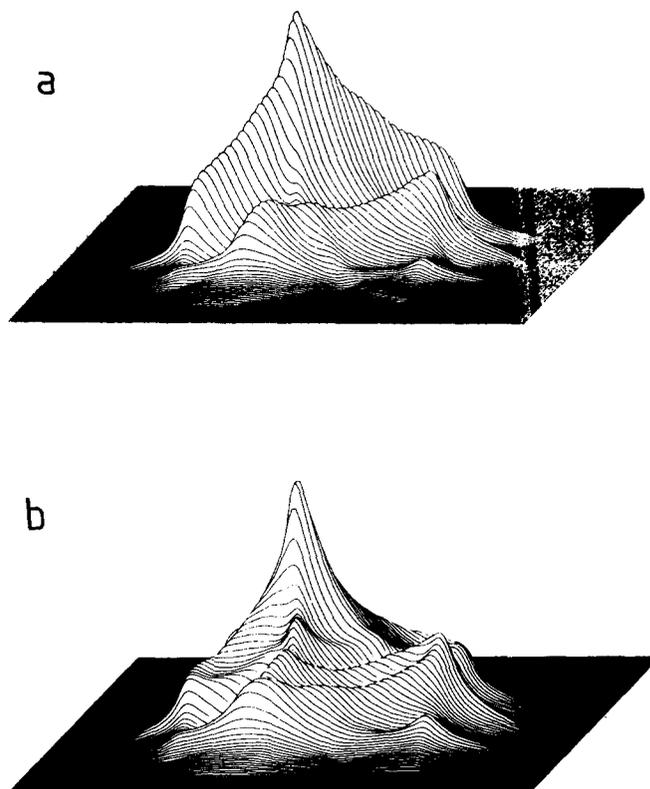
termined. Figure 4 shows the calculated spectrum for the six possible orientations of the carbon tensor for which one principal axis is parallel to the helix axis and another in the OCO plane. It is clear that none of these simulated spectra even resembles the experimental spectrum of Fig. 2(a).

Figure 2(b) shows the simulated spectrum for which the chemical shielding tensor orientation is determined by the local tetrahedral symmetry of the CH_2O_2 unit. Here $\alpha = 180°$, $\beta = 90°$, $\gamma = 90°$, the z axis is oriented perpendicular to the O–C–O plane, the y axis is located within the O–C–O plane and bisects the O–C–O angle. The X axis is of course perpendicular to the Y and Z axis (Fig. 5). For this orientation the agreement between the experimental and the simulated spectrum is more than satisfactory.

By varying the angles α, β, γ in little steps we were able to determine the accuracy of this experiment. If one of the angles is changed by more than 5° the resulting spectrum diverts clearly from the experimental spectrum, see Fig. 6. This means, taking experimental variations into account, that the accuracy must be better than 10°.

V. CONCLUSIONS

The dipolar correlated ^{13}C chemical shift NMR technique can be used to determine rather accurately the orientation of a chemical shift tensor in a semicrystalline polymer like polyoxymethylene. The orientation is completely determined by the local symmetry.

ACKNOWLEDGMENTS

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