J. Am. Chem. Soc. **1994**, *116*, 5315–5323

A Combined Structural Study Using NMR Chemical-Shielding-Tensor Correlation and Neutron Diffraction in Polycrystalline Methanol

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Received December 2, 1993[⊗]

Abstract: A structural study by solid-state NMR and neutron diffraction is presented for the two crystalline phases of methanol. The temperature dependence of the α-phase structure from 1.5 to 145 K shows a variation of the relative orientation of the hydrogen-bonded chains. Results of the first investigation of the β-phase by neutron diffraction are given. Independent structural information is obtained by spin-diffusion powder NMR spectroscopy, where the relative orientation of the carbon-13 chemical shielding tensors for both phases is determined. By combination of the NMR and diffraction results, the orientation of the carbon-13 chemical shielding tensor in a molecular coordinate system can be determined. It is found that the most shielded axis of the tensor is tilted from the C–O bond direction toward the proton of the hydroxyl group by 7.0° and 5.5° in the α-phase and β-phase, respectively. This tilt fully reconciles the results from NMR and diffraction methods, and the disagreement between NMR and X-ray results in the β-phase found by Tycko and Dabbagh (Tycko, R.; Dabbagh, G. *J. Am. Chem. Soc.* **1991**, *113*, 3592–3593) is resolved. For the α-phase, the agreement between NMR and neutron diffraction results is significantly improved by taking into account the tilt as well as the temperature dependence of the structure.

1. Introduction

Nuclear magnetic resonance (NMR) has become an important tool for the investigation of molecular structures in the liquid and solid phases. The most informative parameter is the nuclear dipole–dipole interaction that allows accurate measurements of internuclear distances in solids, particularly in combination with suitable isotope substitutions.[1-5] In the liquid phase, dipolar interactions are accessible through the nuclear Overhauser effect, and structure determinations based on NMR had a major impact on molecular biology.[6-8] The strict and simple relation between the measured dipolar coupling vectors and molecular geometry is the key for the success in these applications.

The chemical shielding anisotropy (CSA) and the quadrupolar coupling tensors also contain structural information which, however, cannot be extracted as straightforwardly because there is no a priori relation between their principal axes system and the crystallographic structure. Given that such a relation can be established by combining NMR with neutron or X-ray diffraction or possibly by correlation with dipolar interaction tensors, the three orientational angles provide a powerful tool for investigating molecular properties. Luckily, it is often found that one of the principal axes is approximately parallel to an internuclear vector. A set of empirical rules has been derived for orientation of CSA tensors in the molecular frame.[9] In contrast, dipolar interactions are, in the absence of anisotropic motion, described by an axially symmetrical tensor and yield only a single orientational angle.

This work focuses on the structure of the two crystalline phases of methanol (CH_3OH)[10,11] and on the relative orientations of the carbon CSA tensors as well as their orientation in the molecular frame. The α-phase is stable below 156 K, and the β-phase exists between 159 K and the melting point at 175.4 K. Dilatation measurements indicate that the transition from the β-phase into the α-phase occurs in two steps:[12] a first-order transition takes place at 159 K and a second-order transition at 156 K. The structure between the two temperatures has not yet been characterized.[10] On rapid cooling of the liquid below 100 K, methanol freezes into a glass[13,14] which transforms into the α-phase when warmed above 130 K.[15] In the two crystalline phases, methanol is hydrogen bonded and forms infinite parallel chains.[10,11]

Tauer and Lipscomb characterized the β-phase with X-ray diffraction using a single crystal at 163 K.[11] Based on the observed reflections, three space groups *Cmcm*, *Cmc*2$_1$, and *C*2*cm* are possible. Deviations from the group of highest possible symmetry, *Cmcm*, which lead either to *Cmc*2$_1$ or *C*2*cm*, are not reflected in the C and O coordinates but refer exclusively to the proton positions that are not accurately known from the X-ray study. Four molecules are present in the orthorhombic unit cell of dimensions a = 6.43 Å, b = 7.24 Å, and c = 4.67 Å. All C–O bonds appear to be parallel and confined to planes perpendicular

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to the crystallographic axis *a*. This planarity is probably a consequence of motional averaging.

Because no single crystals of the α-phase were available, Tauer and Lipscomb could not obtain a reliable structure of that phase. However, a recent powder neutron diffraction study of Torrie et al.[10] clarified the structure of α-methanol. The unit cell contains four molecules related to one another by twofold screw axes. The crystal structure was found to be orthorhombic with cell dimensions a = 4,8728 Å, b = 4.6411 Å, and c = 8.8671 Å at 15 K and belongs to the space group $P2_12_12_1$.

Tycko and Dabbagh[16,17] have recently recorded two-dimensional (2D) ^{13}C spin-diffusion NMR spectra of methanol in the α-phase, β-phase, and glassy phase. From such experiments information about the relative orientation of the ^{13}C CSA tensors can be obtained.[18,19] In the interpretation of their measurements, Tycko and Dabbagh assumed that the ^{13}C CSA tensor in methanol is coaxial with the C–O bond and concluded that their NMR experiments support the structure of α-methanol proposed by Torrie et al.[10] However, they called in question the structure of β-methanol proposed by Tauer and Lipscomb[11] since the 2D NMR spectrum shows that the angle between the most shielded principal axes of the CSA tensors deviates from the angle between the C–O bond directions determined by Tauer and Lipscomb.

For methyl groups, empirical relationships between the principal axis system of the ^{13}C CSA tensor and the molecular fixed coordinate system have been derived.[9,20] The axis corresponding to the most shielded principal component of the carbon CSA tensor lies along the C_3 axis of the methyl group and the remaining two principal components are often nearly degenerate. However, deviations of a few degrees from this arrangement were found in single-crystal studies.[9] If structural information is to be obtained from NMR measurements alone, the orientation of the CSA tensors in a molecular frame of reference is needed.

In principle, the relative orientation of the ^{13}C CSA tensor with respect to the heteronuclear dipolar interaction within the methyl group can be determined by NMR using the separated local field experiment.[21,22] Because the dipolar interaction is unambiguously related to the molecular geometry, this procedure offers a possibility for orienting the chemical shielding anisotropy in the molecular frame of reference. However, a small deviation of the CSA tensor from the C_3 axis manifests itself only in a weak broadening of the two-dimensional quartet structure of the separated local field experiment. A similar broadening is also expected from dipolar interactions between the carbon and the proton spins that do not belong to the same methyl group as the carbon. The disentanglement of these two effects can be an obstacle in measuring the orientation of the carbon CSA tensor in methyl groups. Quantum mechanical calculations of the ^{13}C shielding tensor of methanol in the gas phase using the IGLO method[23] yielded deviations of the CSA principal axis from the C_3 symmetry axis of the methyl group of 0.3° and 0.8° for two different basis sets for the molecule in the staggered conformation and 2.7° in the eclipsed conformation.

In this contribution, we present a structural analysis which combines neutron diffraction and CSA tensor correlation by 2D spin-diffusion powder NMR spectroscopy.[18,19] We describe the dependence of the crystal structure of α-methanol on temperature. The investigations with neutron diffraction confirmed the α-phase structure at 15 K given in ref 10 and the geometry of the C and O network in the β-phase proposed in ref 11. The refinement of the deuteron positions of β-methanol led to the space group $Cmc2_1$ instead of $Cmcm$ found for the heavy atoms alone.[11] Moreover, the orientation of the CSA tensor in the molecular frame is determined from the 2D NMR spectrum using information about the relative orientation of the molecules from crystallographic measurements. In the α- and β-phase, the most shielded direction of the CSA tensor is, within experimental error, contained in the plane defined by the carbon and the hydroxyl group and deviates from the C–O bond by 7.0° ± 1.8° and 5.5° ± 1.5°, respectively, pointing toward the hydroxyl group. These deviations, together with the temperature dependence of the crystal structure, account for the apparent deviations described in ref 16 and fully reconcile the diffraction studies and the NMR measurements in the two phases.

2. Experiments and Data Processing

1. Powder Neutron Diffraction Measurements. The neutron diffraction measurements were performed on the Double-axis-Multi-Counter (DMC) diffractometer at the reactor Saphir of the Paul Scherrer Institute (PSI) in Würenlingen.[24] The diffractometer was operated in high-resolution mode for two measurements in the α-phase at 15 and 145 K with a neutron wavelength of 1.6984 Å and in high-intensity mode with a wavelength of 1.7037 Å for all other measurements.

Deuterated methanol (CD_3OD; isotopic purity >99.5%) was purchased from Fluka Chemie (Switzerland) and used without further purification. To avoid the formation of large crystallites upon cooling to 77 K, which would distort the powder diffraction patterns, methanol was sprayed in small portions under a nitrogen/helium atmosphere into a vanadium can immersed in liquid nitrogen. The solid that formed in the can was mechanically ground before more liquid was added. The sample was quickly transferred into the precooled ILL-type cryostat and was annealed at 145 K to eliminate any possible β-phase component. The annealing was continued for 4 h until no more changes were noticed in the diffraction profile.

Full diffraction profiles of the α-phase were collected successively at 145, 100, 60, 15, and 1.5 K. The diffraction patterns measured at 145 and 15 K are shown in Figure 1. After completion of the temperature series, a second profile at 145 K was recorded. The results of the first measurement were accurately reproduced. In order to obtain a stable powder diffraction profile of the β-phase, the sample was annealed at 168 K for 3 h before a full diffraction profile was recorded within 4 h (Figure 2). A control measurement at the end indicated that no significant crystallite growth had taken place in the β-phase at 168 K.[10]

2. Neutron Diffraction Data Analysis for α-Methanol. For structural refinement, a modified Rietvield analysis program by Wiles and Young[25] was used with the neutron scattering lengths published by Sears.[26] The space group $P2_12_12_1$ was taken from ref 10 and the nuclear coordinates as well as the dimensions of the unit cell therein were used as initial guess for the least squares refinements. At the first stage, the overall scale factor, six parameters which describe the background, the zero point of the scattering angle, the peak shape parameters (U, V, W, asymmetry),[25] the parameters of the unit cell, the 18 fractional coordinates, and an isotropic temperature factor for each atom, in all 38 parameters, were optimized by least-squares fitting. This initial attempt led to isotropic temperature factors larger than 7 Å^2 at 145 K for the methyl deuterons. The fit was improved by introducing anisotropic temperature factors for these three deuterons. The optimization of 53 parameters yielded at 145 K a weighted profile agreement factor (R_{wp}) of 3.92%, whereas the goodness-of-fit criterion (χ^2) reached 4.30. The differences

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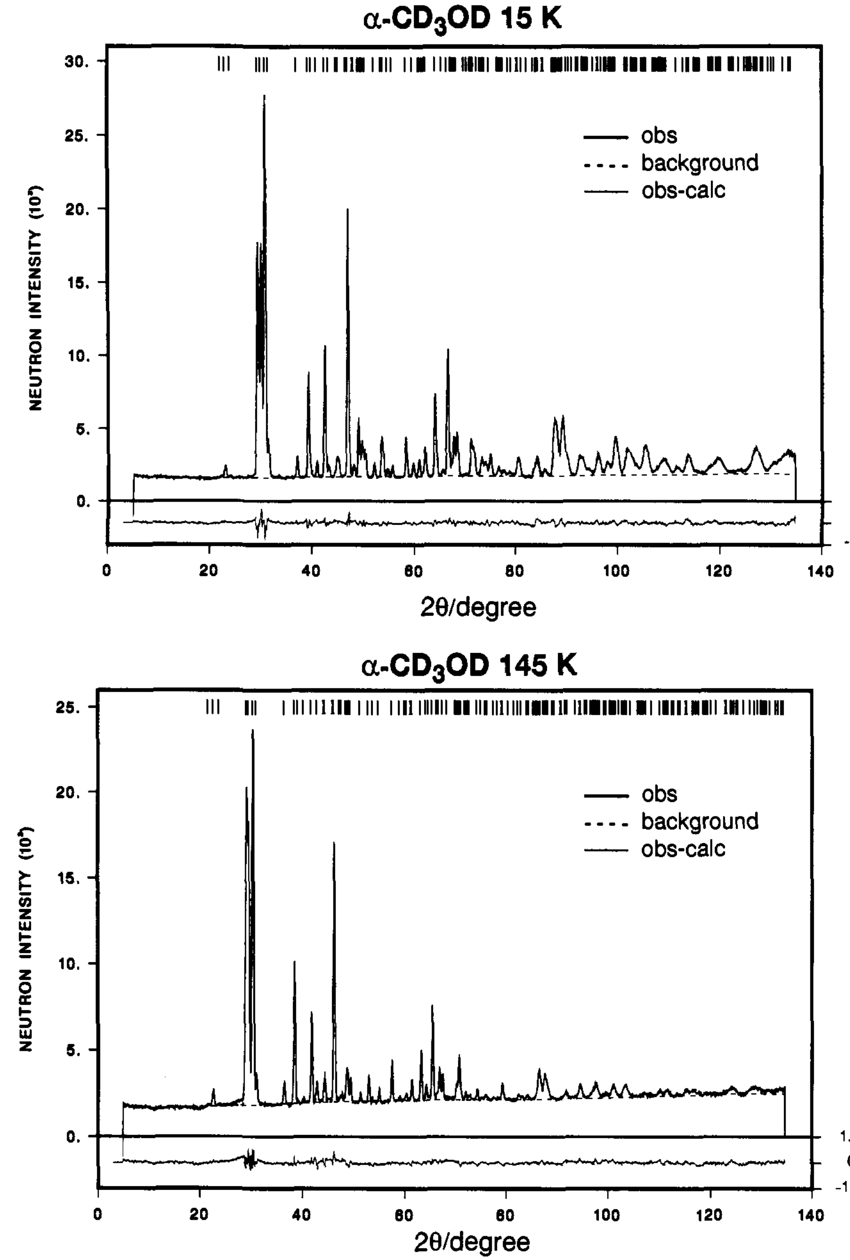

Figure 1. Powder neutron diffraction profiles of α-CD_3OD at 15 and 145 K measured with 1.6984-Å neutrons. The background profile and the difference between observed and calculated profiles are included.

between observed and calculated profiles at 15 and 145 K are displayed in Figure 1 and the structural parameters are listed for all investigated temperatures in Table 1. The errors indicated for neutron diffraction results are standard deviations for the positional parameters and should be multiplied by a factor of approximately 3 to give a more realistic estimate of the errors as discussed in refs 10 and 27.

3. Neutron Scattering Data Analysis for β-Methanol. The analysis of the diffraction profile of β-methanol was performed with the same program as the one used for the α-phase. The dimensions of the orthorhombic cell and the space group *Cmcm* proposed by Tauer and Lipscomb[11] account for all peak positions, but the symmetry elements of *Cmcm* restrict severely the possible deuterons positions. For instance, the averaged position of the deuterium involved in the hydrogen bond is constrained at $(0, {}^1/_2, {}^1/_2)$, the equidistant locus between two oxygens. Comparing the location of these hydrogen-bonded deuterons in the α-phase with those found in other hydrogen-bonded substances[28] with O···O distances similar to the one of methanol, 2.7 Å, an asymmetric position is more likely. Therefore, an attempt was made to describe the crystal by a space group with lower symmetry. From the observed reflections Tauer and Lipscomb[11] concluded that three space groups were possible: *Cmcm*, $Cmc2_1$, and *C2cm*. *C2cm* imposes the same restriction on the hydrogen bonds as *Cmcm*, while the symmetry operators of $Cmc2_1$ allow for four methanol molecules per unit cell with asymmetric hydrogen-bonds. The hydroxyl group, the carbon, and one deuterium of the methyl group are located at the special position $(0,y,z)$ with a 4-fold multiplicity, and the two remaining deuterons occupy the equivalent general positions (x,y,z) and $(\bar{x},y,z)$ with an 8-fold multiplicity.[29] Hence the methyl group can adopt either a staggered or an eclipsed conformation with respect to the hydroxyl group.

Since our unit cell parameters deviate by less than 0.6% from the ones measured by Tauer and Lipscomb,[11] we adopted the fractional coordinates of C and O they determined from single-crystal X-ray diffraction. A refinement was attempted with 22 parameters, including the zero point of the scattering angle, the dimensions of the cell, the overall scale factor, the peak parameters

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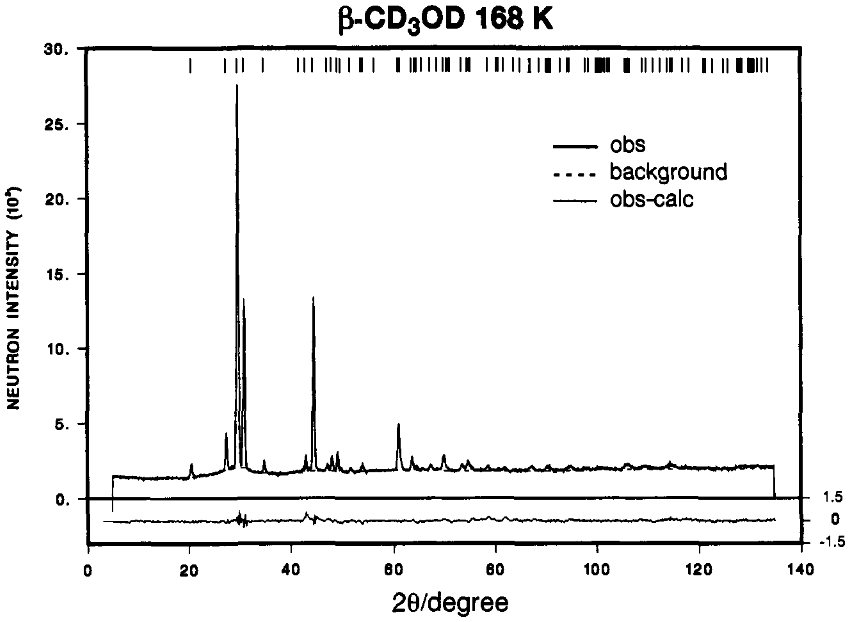

Figure 2. Powder neutron diffraction profile of β-CD_3OD at 168 K measured with 1.7037-Å neutrons. The background profile and the difference between observed and calculated profiles are included.

(U, V, W, asymmetry),[25] seven independent coordinates for the positions of the deuterons, and six isotropic temperature factors. The resulting isotropic temperature factors for the oxygen and for the deuterons of the methyl group were very high ranging from 8 to 11 Å^2. Therefore, we introduced additionally 11 asymmetry parameters to describe the thermal motion of these atoms. The resulting thermal ellipsoids extend predominantly in the plane of the methyl deuterons with root mean square values for the displacement up to 0.82 Å. This feature might indicate the presence of further conformations in addition to the staggered one. We considered this possibility in a new refinement with staggered and eclipsed rotamers. To keep the number of variables low, we assumed identical isotropic temperature factors for all methyl deuterons and confined their positions to a plane perpendicular to (010). The relative population of the staggered and eclipsed conformations was introduced as a variable. The thermal motion of the oxygen was described anisotropically, whereas all other temperature factors were assumed to be isotropic. The difference between the observed and calculated profiles under these conditions is shown in Figure 2.

If all constraints used so far in the refinement are lifted, except for the one of equal isotropic temperature factors for the deuterons of the methyl group, thereby increasing the number of free parameters from 23 to 34, the goodness-of-fit does not improve significantly. Moreover, the molecular geometry is distorted in an implausible manner: the C–D bond lengths vary between 0.94 and 1.22 Å and the D–C–D bond angles between 101° and 119° with large uncertainties. Thus, the evaluation of the powder neutron diffraction data requires constraints obtained from other measurements because of the moderate number of resolved peaks compared to the number of parameters in the model. Combining our experimental data with the results of Tauer and Lipscomb[11] led to a reasonable molecular geometry (Table 2) with good *R* factors. This adds to the validity of the C–O structure in ref 11.

4. 2D Spin-Diffusion Powder NMR Measurements. ^{13}C-labeled methanol (99%) was purchased from CIL Isotopes (USA) and CH_3OH from Fluka Chemie (Switzerland). Both liquids were used without additional purification. All measurements were performed on a home-built spectrometer operating at 220 MHz proton resonance. Nitrogen was used as cryogen in a home-built probe head. The 2D spin-diffusion experiment[18] follows the general scheme of 2D exchange spectroscopy.[6,30] It starts with a preparation period in which the carbons are cross-polarized from the protons. During the evolution period proton decoupling is applied. The mixing period is flanked by two $\pi/2$ pulses between which spin diffusion takes place correlating spin resonances which originate from the same microcrystallite. During the detection period, proton decoupling is again applied. The resulting 2D spectra can be considered as a pair correlation map of those resonance lines that belong to the same microcrystallite. The rf-field strengths on the proton and carbon channels were matched at 50 kHz.

^{13}C-enrichment increases the signal-to-noise ratio of the experiment and the spin-diffusion rate constant. However, at the same time, the spectral resolution decreases due to enhanced ^{13}C–^{13}C dipolar interactions. Instrumentally limited measurement times at 145 K made the use of a 99% enriched sample necessary to achieve sufficient sensitivity. At 168 K the ^{13}C abundance was chosen to be 20%, still large enough to obtain equilibrated spectra in approximately 10 s and leading to substantially better resolution than fully enriched samples. Spectra obtained for samples of natural isotopic abundance using the same experimental parameters did not show any off-diagonal intensity. Therefore, it is assured that the off-diagonal intensity observed for the labeled samples arises solely from spin diffusion, and contributions due to motional reorientation of CSA tensors can be excluded.

5. Analysis of NMR Data for α-Methanol. 2D spin-diffusion tensor correlation spectra at 145 K of $^{13}CH_3OH$ are shown in Figure 3 for mixing times (τ_m) of 0 and 600 ms. After a mixing time of 600 ms, the 2D spectrum has reached a steady state. From the control measurement with vanishing mixing time, the homogeneous peak broadening in the 2D spectrum and the principal components of the CSA tensors can be obtained. All 1D sections perpendicular to the 2D diagonal showed, within experimental error, Gaussian profiles of identical width. Therefore we used a homogeneous 2D Gaussian peak shape in the 2D spectra simulations. Its full width at half height was fitted to 410 ± 15 Hz (7.4 ± 0.3 ppm), and the principal components of the CSA tensor obtained by least-squares fitting are $\sigma_{11} = -74 \pm 2$ ppm, $\sigma_{22} = -68 \pm 2$ ppm and $\sigma_{33} = -8 \pm 2$ ppm relative to TMS. These values agree well with previous measurements.[23,31] Since the entire 2D spectrum for $\tau_m = 0$ ms can be fitted by a single

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Table 1. Structural Parameters of Deuterated α-Methanol from 1.5 to 145 K Obtained by Neutron Diffraction Measurements[a]

	T (K)				
	1.5	15	60	100	145
a, Å	4.8820(2)	4.8845(2)	4.8982(2)	4.9179(3)	4.9426(3)
b, Å	4.6469(3)	4.6364(3)	4.6396(3)	4.6479(4)	4.6569(3)
c, Å	8.9042(5)	8.9076(5)	8.9375(4)	8.9876(6)	9.0675(7)
C x	0.1879(8)	0.1857(8)	0.1943(7)	0.1982(10)	0.2025(16)
y	0.5005(17)	0.5105(14)	0.5026(16)	0.5091(17)	0.5062(34)
z	0.1039(5)	0.1048(5)	0.1016(4)	0.1011(5)	0.1008(9)
B, Å^2	0.818(1)	0.927(1)	0.823(1)	0.827(1)	2.82(15)
O x	0.4497(5)	0.4486(7)	0.4512(6)	0.4521(9)	0.4511(16)
y	0.4789(12)	0.4760(12)	0.4737(11)	0.4725(16)	0.4701(22)
z	0.1788(4)	0.1772(4)	0.1786(4)	0.1786(5)	0.1812(7)
B, Å^2	0.19(7)	0.46(7)	0.78(8)	1.61(11)	3.77(22)
D_1 x	0.4872(11)	0.4864(13)	0.4852(11)	0.4862(14)	0.4789(20)
y	0.6664(8)	0.6642(9)	0.6633(8)	0.6569(11)	0.6553(15)
z	0.2280(5)	0.2280(5)	0.2289(5)	0.2301(7)	0.2313(8)
B, Å^2	1.48(9)	1.73(10)	1.92(0)	2.91(14)	3.65(18)
D_2 x	0.1631(15)	0.1687(10)	0.1614(16)	0.1638(22)	0.1587(30)
y	0.3208(17)	0.3150(15)	0.3195(15)	0.3217(22)	0.3127(31)
z	0.0341(8)	0.0313(5)	0.0354(8)	0.0411(13)	0.0507(21)
β_{11}	0.027(4)	–0.008(2)	0.040(6)	0.072(8)	0.088(10)
β_{22}	0.017(2)	0.023(3)	0.033(3)	0.058(5)	0.073(8)
β_{33}	0.007(2)	0.008(1)	0.017(2)	0.028(3)	0.052(4)
β_{12}	–0.019(3)	0.006(1)	–0.015(4)	0.001(5)	–0.007(7)
β_{13}	–0.011(2)	–0.002(1)	–0.009(1)	–0.014(3)	–0.004(2)
β_{23}	–0.007(2)	–0.004(2)	–0.018(3)	–0.034(3)	–0.028(6)
D_3 x	0.0262(7)	0.0256(8)	0.0286(7)	0.0342(10)	0.0429(15)
y	0.5175(11)	0.5081(12)	0.5197(12)	0.5237(20)	0.5374(20)
z	0.1876(4)	0.1878(4)	0.1847(4)	0.1820(6)	0.1756(9)
β_{11}	0.014(2)	0.021(2)	0.020(2)	0.026(3)	0.044(4)
β_{22}	0.045(4)	0.055(4)	0.081(4)	0.118(7)	0.065(2)
β_{33}	0.009(1)	0.010(1)	0.008(1)	0.012(1)	0.024(2)
β_{12}	0.003(4)	–0.050(4)	0.012(5)	–0.001(7)	0.008(7)
β_{13}	–0.001(1)	–0.001(1)	0.001(1)	0.005(1)	–0.004(2)
β_{23}	–0.010(1)	0.003(2)	–0.006(2)	–0.007(3)	–0.013(3)
D_4 x	0.1741(13)	0.1719(15)	0.1809(14)	0.1857(16)	0.1983(22)
y	0.6972(18)	0.6968(15)	0.7007(18)	0.7037(23)	0.6821(34)
z	0.0385(8)	0.0410(7)	0.0387(7)	0.0392(9)	0.0376(14)
β_{11}	0.010(4)	0.053(4)	0.010(4)	0.019(5)	0.060(8)
β_{22}	0.040(3)	0.050(4)	0.053(4)	0.080(7)	0.154(11)
β_{33}	0.015(1)	0.012(1)	0.013(1)	0.018(2)	0.020(2)
β_{12}	–0.015(3)	0.004(3)	–0.004(3)	0.011(4)	–0.020(6)
β_{13}	–0.003(2)	–0.016(2)	–0.005(5)	–0.010(2)	–0.018(3)
β_{23}	0.011(2)	0.021(2)	0.011(3)	0.016(3)	0.048(5)
R_p, %	2.87	3.14	2.40	2.64	2.98
R_{wp}, %	3.48	3.92	3.05	3.39	3.82
R_e, %	2.00	1.74	1.06	1.98	1.84
χ^2	3.03	5.10	8.32	2.93	4.30

[a] a, b, c: lattice parameters. x, y, z: fractional coordinates. B: isotropic thermal parameter. β_{ij}: anisotropic temperature factor parameters. R_p, R_{wp}, R_e: R-factor of the profile, weighted R-factor of the profile, expected R-factor. χ^2: goodness-of-fit criterion.

set of principal components, all CSA tensors in a unit cell have identical principal components, within experimental accuracy.

A quantitative analysis of the near-equilibrium 2D spin-diffusion spectrum with $\tau_m = 600$ ms allows one, in principle, to determine the distribution of the relative CSA tensor orientations within a microcrystallite. In general a three-dimensional distribution function $P(\alpha_{CSA},\beta_{CSA},\gamma_{CSA})$ is required, where α_{CSA}, β_{CSA}, and γ_{CSA} are the Euler angles as defined in ref 20. However by assuming axially symmetric CSA tensors, the distribution function can be reduced to a one-dimensional function $P(\beta_{CSA})$ where β_{CSA} measures the angle between the unique axes of the tensors. For α-methanol, the difference between the principal components σ_{11} and σ_{22} is less than the homogeneous line width so that the 2D line shape in the spin-diffusion spectra is insensitive to the asymmetry and the simplification is justified. A distribution function represented by 31 discrete values for β_{CSA} was fitted to the experimental spectrum using the procedure described in ref 32. The resulting distribution function is displayed in Figure 3d.

Table 2. Structural Parameters in Deuterated β-Methanol at 168 K Obtained by Combining X-ray and Neutron Diffraction Data As Explained in the Text

R_{exp}, %	2.11
R_p, %	2.83
R_{wp}, %	3.79
χ^2	2.75
lattice parameters, Å	
a	6.4033(10)
b	7.2005(8)
c	4.6481(9)

Atomic Position Coordinates and Isotropic Thermal Parameters B, Å^2

	x	y	z	B
C	0.0	0.214	0.250	7.25(32)
O	0.0	0.411	0.250	
D_1	0.0	0.4697(9)	0.4258(18)	3.43(17)
D_{2t}	0.0	0.1794(6)	0.0479(28)	6.12(23)
D_{3t}	0.1336(10)	0.1794(6)	0.1048(21)	6.12(23)

Anisotropic Thermal Factor Parameters of the Oxygen

β_{11}	β_{22}	β_{33}	β_{23}
0.118(8)	0.017(3)	0.021(6)	–0.027(3)

Bond Lengths, Å

C–O	1.419
O–D_1 (intramolecular)	0.918(8)
O···D_1 (intermolecular)	1.736(8)
C–D_2	1.01(2)
C–D_3	1.04(2)

Bond Angles, deg

D_1–O–C (intramolecular)	120.2(5)
D_1···O–C (intermolecular)	118.2(3)
D_2–C–O	103.9(3)
D_3–C–O	103.3(3)
D_2–C–D_3	119.5(9)

6. Analysis of NMR Data for β-Methanol. The measurements in β-methanol were performed at 168 K on a 20% ^{13}C-labeled sample. A mixing time τ_m of 12.5 s was used to obtain a steady-state spectrum. The 2D spectrum is shown together with one for $\tau_m = 0$ s in Figure 4. Inspection of 1D sections perpendicular to the diagonal of the spectrum of Figure 4a indicates that the homogeneous peak width depends on the resonance frequency of the spin packets, in contrast to the finding for the α-phase. From these sections a frequency-dependent Gaussian width was determined. The full width at half height of the peak reaches a minimum of 190 Hz in the center of the powder line shape and is maximal, 239 Hz, at the most shielded value σ_{33}. By taking into account this non-uniform broadening, the principal components of the CSA tensor were found as $\sigma_{11} = -73 \pm 2$ ppm, $\sigma_{22} = -61 \pm 2$ ppm, and $\sigma_{33} = -8 \pm 2$ ppm relative to TMS. It has been suggested in ref 16 that the increase of the asymmetry of the shielding tensor in the β-phase, compared to the α-phase, may result from a rapid dynamical averaging process in the β-phase, within a plane perpendicular to the least shielded principal axis. A detailed discussion of the orientation of the averaged CSA tensor in the molecular frame is postponed to the next section.

In priciple, the asymmetric CSA tensor in the β-phase would require a three-dimensional distribution function $P(\alpha_{CSA},\beta_{CSA},\gamma_{CSA})$ for the analysis of the 2D spin diffusion spectrum. From the almost diagonal appearance of the 2D spin-diffusion spectrum of Figure 4b, it is obvious that only small β_{CSA} values can contribute to the observed spectrum. Otherwise intensity further away from the diagonal of spectrum would be present. If β_{CSA} approaches zero, the rotations by α_{CSA} and γ_{CSA} take place about the same axis and only the sum $(\alpha_{CSA} + \gamma_{CSA})$ is relevant. As an approximation, we set $\alpha = 0°$ and fit to the experimental spectrum the distribution function $P(\beta_{CSA},\gamma_{CSA})$. It is sufficient to restrict the range of β_{CSA} to $0° < \beta_{CSA} < 20°$ while γ_{CSA} varies in the range $-90° < \gamma_{CSA} < 90°$. A distribution function with 10 and 11 discrete values for β_{CSA} and γ_{CSA}, respectively, was used. The result of the fit shown in Figure 4d has two maxima located at $\gamma_{CSA} = 0°$ and $\beta_{CSA} = 0°$ and 11°.

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(32) Hagemeyer, A.; Brombacher, L.; Schmidt-Rohr, K.; Spiess, H. W. *Chem. Phys. Lett.* **1990**, *167*, 583–587.

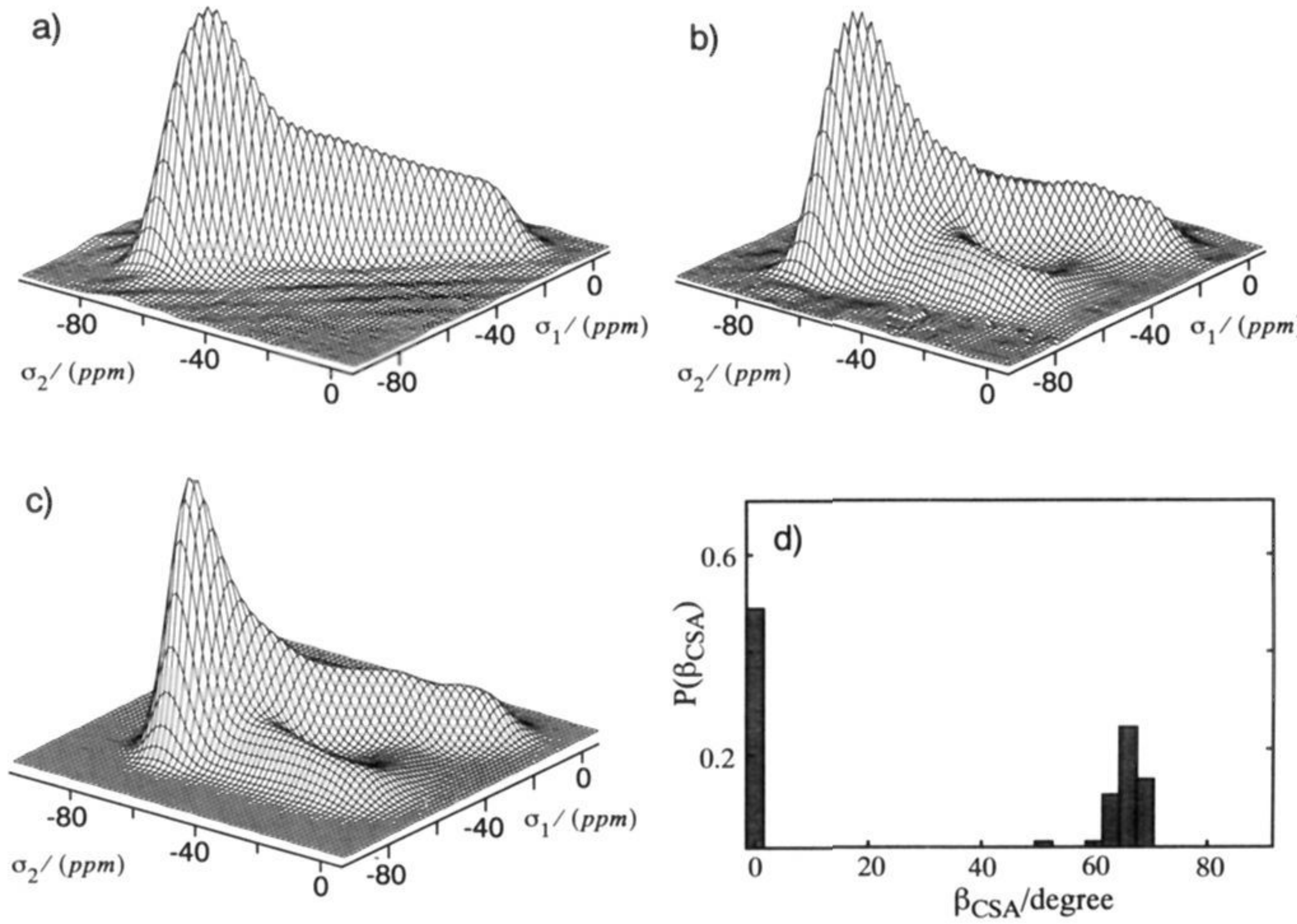

Figure 3. 2D powder ^{13}C NMR spin-diffusion spectra at 145 K of α-$^{13}CH_3OH$, 99% ^{13}C labeled, with mixing times of (a) 0 and (b) 600 ms. The shielding σ_1 and σ_2 are relative to TMS. (c) Computer-simulated fit to the experimental spectrum in part b. The ^{13}C CSA tensor is assumed to be axially symmetric and a distribution function for the angle β_{CSA}, represented by 31 independent amplitudes, is fitted to (b). The CSA principal components and a uniform Gaussian broadening are determined from the spectrum in part a and used as fixed parameters in the fitting procedure. The distribution function $P(\beta_{CSA})$ obtained from the fit is shown in part d.

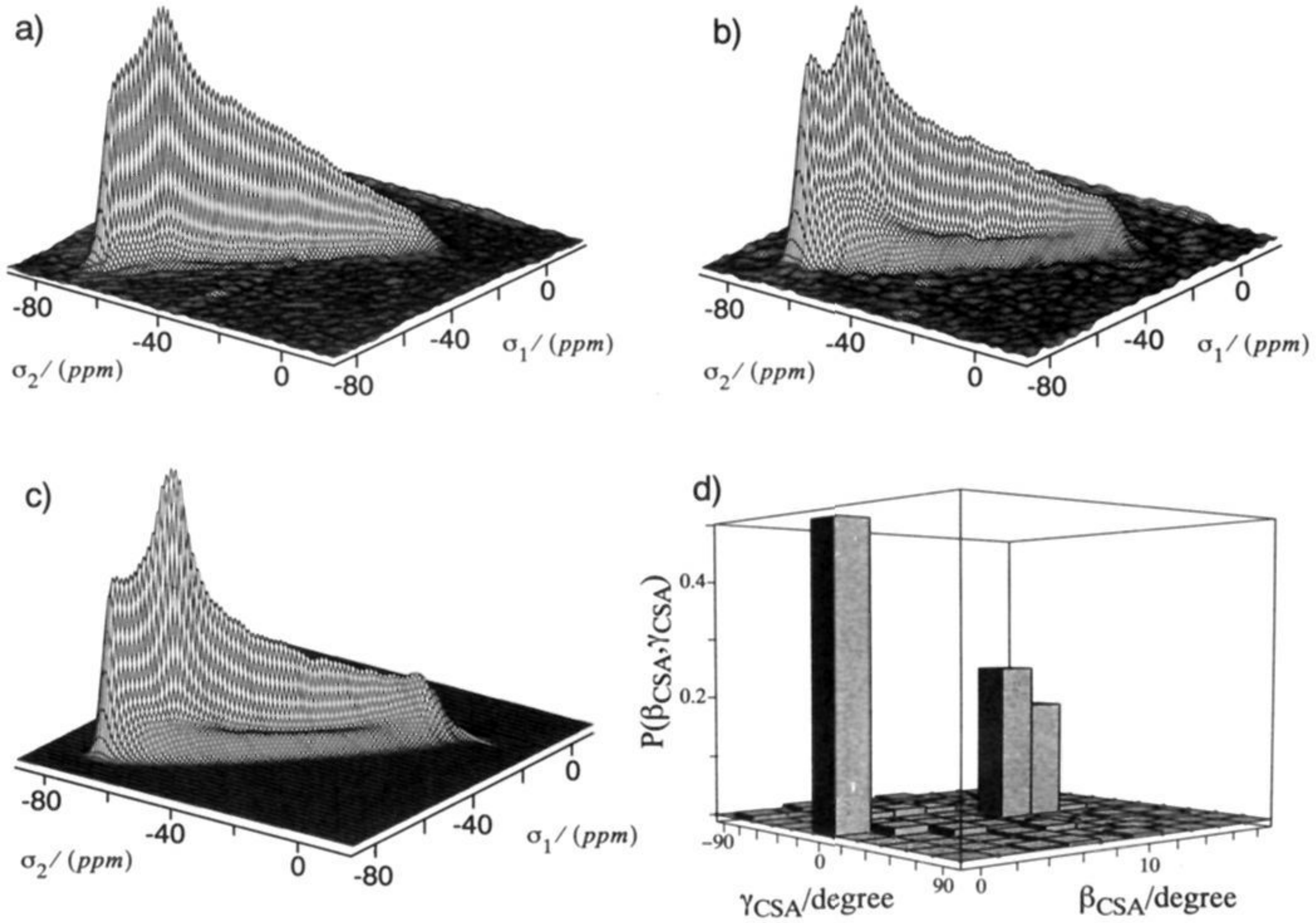

Figure 4. 2D powder ^{13}C NMR spin-diffusion spectra at 168 K of β-$^{13}CH_3OH$, 20% ^{13}C labeled, with mixing times of (a) 0 and (b) 12.5 s. The shieldings σ_1 and σ_2 frequencies are indicated relative to TMS. (c) Computer-simulated fit to the experimental spectrum in part b. The CSA principal components and the non-uniform Gaussian broadening are determined from the spectrum in part a and used as fixed parameters. The two-dimensional angular distribution function $P(\beta_{CSA},\gamma_{CSA})$ obtained from the fit to the spectrum in part b is shown in part d.

The small systematic deviation between the computed and the measured 2D spin-diffusion spectra, especially visible along the diagonal near the least shielded part (Figure 4), can be explained by cross-polarization and T_1 effects. Though the measured powder pattern did not show any critical dependence on the cross-polarization time in Hartmann–Hahn experiments,[33] the intensity at σ_{11} was always about 8% too high relative to the one at σ_{22} when compared with a theoretical pattern. In addition, T_1 relaxation during the mixing time of the 2D experiment is found to be orientation dependent and the spin packets at σ_{22} are selectively attenuated. The two effects act in parallel, favoring the intensity at σ_{11} with respect to the one at σ_{22}. The quality of the extracted Euler angles, of β in particular, is not strongly affected by this kind of distortion since its distribution is mainly

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(33) Hartmann, S. R.; Hahn, E. L. *Phys. Rev.* **1962**, *128*, 2042–2053. Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569–590.

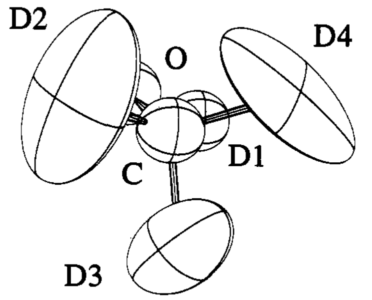

Figure 5. Molecular structure of deuterated α-methanol at 145 K. The thermal ellipsoids account for the 50% probability of finding a nucleus within their volumes. The thermal factors of C, O, and D_1 were assumed to be isotropic.

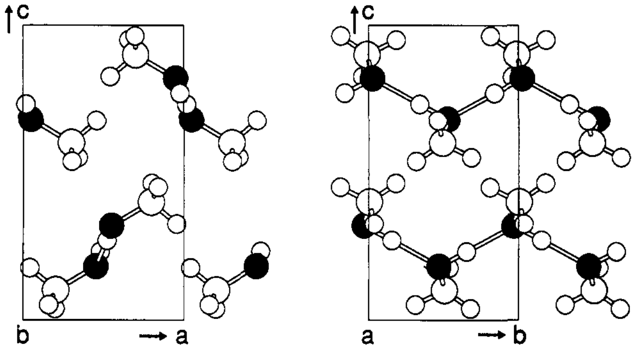

Figure 6. Crystal structure of deuterated α-methanol determined at 145 K by neutron diffraction.

determined by the ellipticity of the outer diagonal ridges in the 2D spectrum.[34]

Table 3. Angles between C–O Bonds in Deuterated α-Methanol Obtained by Neutron Diffraction

T/K	$\phi_1{}^a$	$\phi_2{}^a$	$\phi_3{}^a$
1.5	8.0	55.9	55.3
15	12.7	54.7	52.9
15 (ref 10)	12.3	51.3	49.7
60	10.7	58.2	57.1
100	13.1	59.6	57.9
145	13.4	62.6	60.9

[a] ϕ_1 refers to the C–O bonds within the same hydrogen-bonded chain, ϕ_2 and ϕ_3 to C–O bonds in different chains.

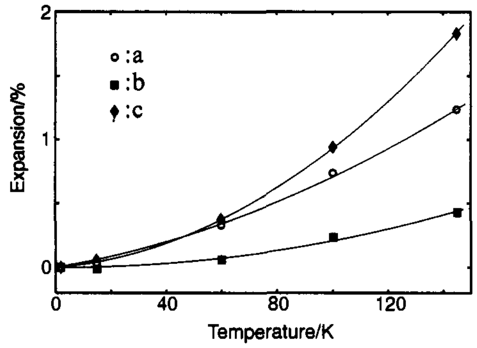

Figure 7. Thermal expansion of the orthorhombic unit cell parameters *a*, *b*, and *c* of deuterated α-methanol from 1.5 to 145 K. The expansion is given in percent deviation from the value at 1.5 K. The lines are quadratic functions fitted to the experimental points.

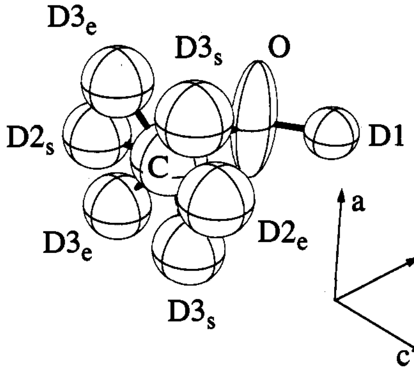

Figure 8. Molecular structure of deuterated β-methanol at 168 K. The ellipsoids account for the 50% probability of finding a nucleus within their volumes. Only the thermal motion of the oxygen is described anisotropically. The staggered (s) and eclipsed (e) deuteron positions are shown simultaneously.

3. Discussion of the Results

1. Crystal structure of α-Methanol. In Figure 5 the molecular structure obtained from the analysis of the neutron data at 145 K is displayed with thermal ellipsoids that account for the 50% probability of finding the nucleus within their volume. The ellipsoids of the methyl deuterons indicate a large amplitude vibration about an averaged position that represents the staggered conformation. The structural parameters of the α-phase as a function of temperature are listed in Table 1. The crystal structure of α–methanol consists of infinite hydrogen-bonded chains (Figure 6), as described in ref 10. The molecular geometry at 15 K is in excellent agreement with that proposed by Torrie et al.[10] Even the tilt of 4.0(5)° of the C–O bond from the 3-fold axis of the methyl group in the direction of the deuterium trans to the hydroxyl group is within the experimental error equal to the value of 3.1(6)° measured in ref 10. The tilt angle decreases to about 2° when the temperature is raised to 145 K. The only significant deviation of our structural parameters at 15 K from those of Torrie et al.[10] at the same temperature is the longer C–O bond length: 1.445(6) Å in comparison to 1.407(6) Å. Since the relative orientations of the C–O bonds of the four molecules of a unit cell will be of primary interest for comparison with the relative orientation of the CSA tensors, their temperature dependences are listed in Table 3. The parameter ϕ_1 stands for the angle between C–O bonds of molecules belonging to the same hydrogen-bonded chain whereas ϕ_2 and ϕ_3 denote the angles to C–O bonds in another chain. The angle ϕ_1, which monitors structural changes within a hydrogen-bonded chain, is almost constant from 15 to 145 K but temperature alters significantly the orientation between chains, with a maximum change of 8°. Figure 7 displays the variations of the unit cell parameters as a function of temperature. The largest changes of 1.24% and 1.83% occur along the directions *a* and *c*, respectively. These directions are perpendicular to the axes of the hydrogen-bonded chains and thus suggest that reorientations of the chains and not changes within a chain dominate the temperature dependence of the crystal structure.

The NMR measurements, where identical principal components for all CSA tensors were found, confirm that the carbon sites are related by symmetry operations. The relative orientation of two CSA tensors is characterized, in the α-phase, by a single Euler angle as discussed above. From Figure 3d it is seen that at least two sites must exist in the unit cell and that their CSA tensors are related by a rotation of about 66°. From neutron diffraction, we know that there are four molecules per unit cell. Thus we can conclude that two pairs of nearly coaxial CSA tensors are present. This arrangement requires a special relative orientation of the crystallographic symmetry axis and the principal axis of the symmetric CSA tensor. This property is exploited below to determine the orientation of the principal axis in the molecular (or crystallographic) coordinate system.

2. Crystal Structure of β-Methanol. The crystal structure of β-methanol was found to belong to the space group $Cmc2_1$ with four molecules per unit cell. Figure 8 shows the molecule with the thermal ellipsoids for staggered and eclipsed conformations

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(34) Schmidt, C.; Blümich, B.; Spiess, H. W. *J. Magn. Reson.* **1988**, *79*, 269–290.

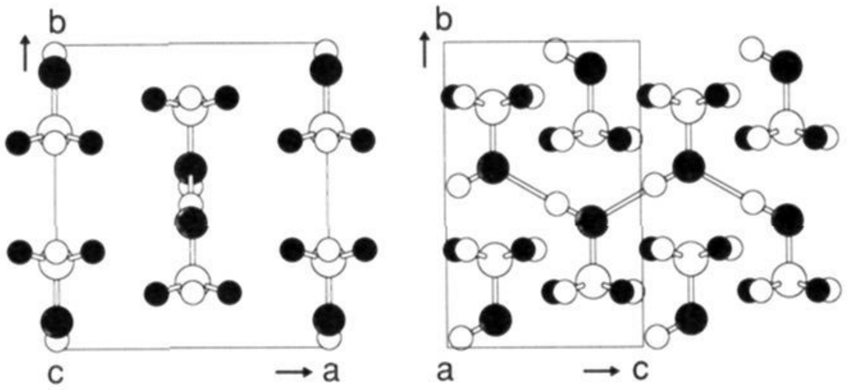

Figure 9. Crystal structure of deuterated β-methanol at 145 K. The open methyl deuteron representations correspond to the staggered and the shaded ones to the eclipsed conformations.

of the methyl group. The structure refinement yielded populations of 0.64(2) and 0.36(2) for the staggered and eclipsed rotamers, respectively.

It has already been pointed out by Tauer and Lipscomb[11] that all oxygen atoms and hydrogen bonds of the same chain are in a planar (100) trigonal arrangement (Figures 8 and 9 and Table 2). The X-ray diffraction data indicate an anisotropic thermal ellipsoid of the oxygen extended along the (100) axis (Figure 8). The dynamical origin of the disorder is established by several NMR studies.[16,35,36] The root mean square vibrational amplitude along the (100) direction reaches 0.47 Å. The increase of the intramolecular C–O–D_1 angle from 104.7° in the α-phase at 145 K to 120.2° in the β-phase at 168 K diminishes sterical contacts between the hydroxyl and the methyl group and is compatible with a larger population of the eclipsed conformation. A further consequence of the strong anisotropic motion of the oxygens is a short intramolecular O–D_1 bond length of 0.92(1) Å, compared to 0.97(1) Å in the α-phase at 145 K. In contrast, the hydrogen-bonded O···D_1 distances are similar in the two phases: 1.71(1) Å in the α-phase at 145 K and 1.73(1) in the β-phase at 168 K.

In the NMR tensor-correlation spectra a single Euler rotation different from the identity is resolved. Therefore two pairs of coaxial CSA tensors must exist in the unit cell, related by the Euler rotation (0°,11°,0°). All CSA tensors have, within experimental error, identical principal components, suggesting that the sites are related by a symmetry operation. As for the α-phase, the NMR and diffraction constraints can be simultaneously fulfilled when the CSA tensor is in a special orientation with respect to the molecular axis system.

3. Orientation of the Carbon CSA Tensor in the Molecular Frame. In this work we measured by neutron diffraction the crystal structures of fully deuterated methanol and extracted the relative orientations of the ^{13}C CSA tensors by NMR from protonated samples. When combining the results of both measurements to extract the orientation of the CSA tensor in the molecule, we have to assume a negligible isotopic effect on the structure. The difference between C–H and C–D bond lengths is generally less than 1%. For example, one finds a difference of 0.3% in the case of CH_4 and CD_4.[37] The isotopic effect on the separation of hydrogen-bonded oxygen atoms depends on the O···O distance. The largest variation, about 1%, occurs at 2.50 Å, whereas the change is less than 0.1% at 2.67 Å.[28] The O···O distances are 2.68(1) Å in the α-phase at 145 K and 2.66(1) Å in the β-phase of methanol at 168 K, ranking methanol among the substances for which the isotope effect on the O···O separation is expected to be very small. The variations in positional parameters of all atoms for substances subject to large changes in the O···O distance such as squaric acid[38] or potassium dihydrogenphosphate[39] do not exceed 1 pm. A comparison of our results with the structure published by Tauer and Lipscomb[11] shows that perdeuteration of the β-phase at 168 K does not change the lattice parameters by more than 0.6%. These facts suggest that the isotopic effect is sufficiently small not to affect the conclusions drawn from our measurements.

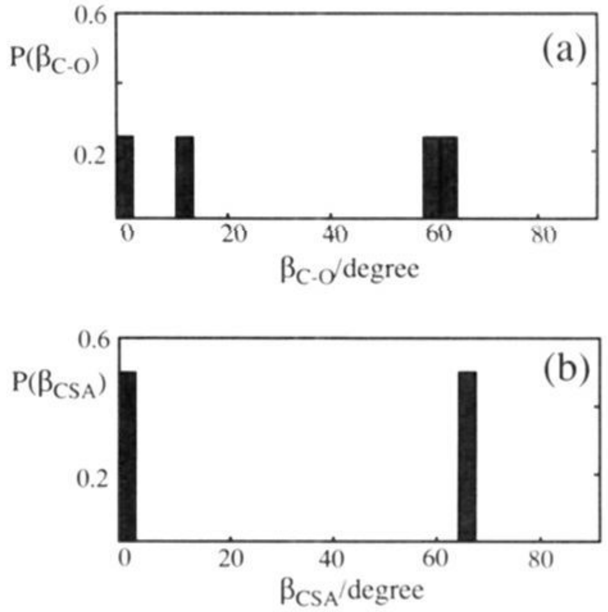

Figure 10. (a) Distribution of the angle β_{C-O} between the C-O bonds in α-methanol at 145 K based on crystallographic information. (b) Distribution of the angle β_{CSA} between the axially symmetric ^{13}C CSA tensors of α-methanol at 145 K obtained by least-squares fitting of the orientational angles θ and ϕ to the 2D NMR spectrum of Figure 3b based on crystallographic information. The optimum values are $\theta = 7.0°$ and $\phi = 1.0°$.

The distribution of the angle between C–O bonds (β_{C-O}) in α-methanol at 145 K listed in Table 3 is graphically represented in Figure 10a. This distribution deviates from that of the β_{CSA} angle between the unique axes of the symmetric ^{13}C CSA tensors extracted from the NMR data shown in Figure 3d. In particular, the difference between the intrachain $\beta_{C-O} = 13.4°$ and $\beta_{CSA} = 0°$ angles indicates a deviation of the most shielded axis of the CSA tensor from the C–O bond. Table 3 shows that in addition to this deviation there is a strong temperature dependence of the crystal structure that prohibits the comparison of data recorded at different temperatures.

The three screw axes of the space group $P2_12_12_1$ of α–methanol ensure an identical orientation of the carbon CSA tensor in the molecular frame for all four sites and allow one to orient unequivocally the CSA tensors in their molecular frames by a single set of angles. Since the small asymmetry of the CSA tensor is neglected, only two angles are necessary to describe its orientation in the molecular coordinate system. The angle θ measures the deviation of the tensor axis from the C–O bond and ϕ is the rotation angle about the C–O bond measured from the COH_1 plane (Figure 11a). These two angles were determined by fitting the experimental 2D NMR spectrum of Figure 3b by a computed spin-diffusion spectrum originating from four CSA tensors that are related to the crystal structure by the two fitted parameters θ and ϕ. At 145 K, we obtained $\theta = 7.0° \pm 1.8°$ and $\phi = 1° \pm 10°$. The resulting distribution of the four β_{CSA} angles between the unique axes of the CSA tensors is displayed in Figure 10b. The two distributions of the β_{CSA} angle of Figure 3d and 10b are essentially equal, only the peak centered at 66° is broader when obtained exclusively from NMR data. The differences between the distributions of β_{CSA} and β_{C-O} result from the deviation of the CSA tensor axis from the C–O bond direction.

The four carbon and oxygen atoms in the unit cell of β-methanol occupy special positions within symmetry planes perpendicular to the crystallographic axis *a*. Hence one of the two least shielded axes of the CSA tensors must lie along the *a* axis, and any rotation relating two CSA tensors has to take place about that axis. Moreover, the C–O bonds are parallel and related to one another by 2-fold screw axes or glide planes. Under these conditions only two orientations in the three-dimensional distribution $P(\alpha_{CSA},\beta_{CSA},\gamma_{CSA})$ have a non-vanishing probability: (0°,0°,0°)

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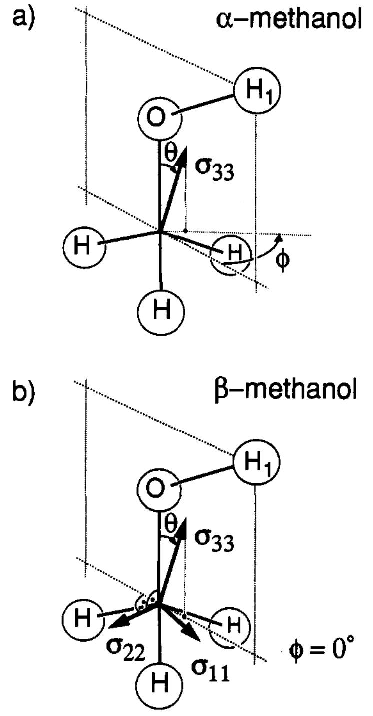

Figure 11. Position of the ^{13}C CSA tensor in the molecular frame of methanol. The angles θ and ϕ orient the most shielded axis in the molecule. (a) In α-methanol, the small asymmetry of the CSA tensor is neglected and least-squares fitting leads to $\theta = 7.0° \pm 1.8°$ and $\phi = 1.0° \pm 10°$. (b) In β-methanol, the symmetry of the crystal constrains ϕ to 0° and the principal axis, associated with the component σ_{22}, is perpendicular to the COH_1 plane. The angle θ amounts to $5.5° \pm 1.5°$.

and $(-\gamma_{CSA},\beta_{CSA},\gamma_{CSA})$ here γ_{CSA} can amount to 0° or 90° corresponding to a rotation about the principal axis associated with the component σ_{22} or with σ_{11}. The results of the least-squares analysis presented in Figure 4d, where no symmetry restrictions were used, fit the requirements of the space group. A renewed analysis of the experimental spectrum of Figure 4b including the symmetry constraints yields $\beta_{CSA} = 11.0° \pm 3.0°$ and $\gamma_{CSA} = 0°$. From these results, the orientation of the CSA tensor in the molecule can be derived directly. Since the most shielded axis of the CSA tensor has to lie in the plane of symmetry, $\phi = 0°$ (Figure 11b) and the space group requires $\theta = \pm\beta/2$, it follows that $\theta = \pm 5.5° \pm 1.5°$. In addition, since $\gamma_{CSA} = 0°$, the principal axis, associated with the component σ_{22}, lies perpendicular to the COH_1 plane. In view of the results for the α-phase and bearing in mind that the most shielded CSA axis is normally in the direction of the highest electron density, the θ value of $-5.5°$ can be safely ruled out. We conclude that the most shielded axis is tilted from the C–O bond by 5.5° in the direction of the hydroxyl group. Because of the fast motional averaging in β-methanol, the Euler angles define the orientation of the averaged CSA tensor with respect to the averaged molecular structure. Since the excursions from the averaged structure are small (root mean square excursion: 0.47 Å) and take place predominantly perpendicular to the C–O–H plane, the angle θ is not significantly affected by the conformational dynamics.

4. Conclusions

The experimental results obtained for crystalline methanol confirm that correlation of ^{13}C chemical shielding tensors through spin diffusion in static powder samples provides an accurate method for measuring their relative orientations.[18] A precision better than 2° is achievable. Such measurements can yield valuable information about the structure of solids and complement the well-established diffraction methods. Particularly useful is the possibility of selective isotopic labeling as it offers a means to focus on the desired information. However, one should bear in mind that the principal axes of CSA tensors do not necessarily coincide with internuclear vectors and thus do not allow a straightforward deduction of bond directions unless the orientation of the CSA tensors is known from other sources.

The combination of crystallographic data and 2D spin-diffusion NMR provides an accurate method for positioning CSA tensors in a molecular frame that does not require the use of single crystals. Following this scheme, we found that the most shielded principal axis of the nearly symmetric ^{13}C CSA tensor in α- and β-methanol is tilted from the C–O bond in the direction of the hydroxyl group by $7.0° \pm 1.8°$ and $5.5° \pm 1.5°$, respectively. This tilt explains the apparent differences between the NMR and X-ray diffraction results in the β-phase described by Tycko et al.[16] Furthermore, the unaccounted differences between the calculated and measured spectra for the α-phase in ref 16 (see Figures 1c,d and 2c,d in ref 16) can be explained by taking into account the tilt and the temperature dependence of the structure.

The similar tilt directions and tilt angles in the two crystalline phases suggest that the orientation of the ^{13}C CSA tensor in methanol is predominantly a molecular property. The gas-phase IGLO calculations yielded tilt angles of 0.3° and 0.8° for two different basis sets for the staggered conformation, which dominates in the two crystalline phases.[23] These values deviate significantly from the values found in this study. Whether this is due to the different molecular structures in the gas phase and the solid phase or whether it results from an inadequate theoretical treatment is not known at this moment.

The structural variations of the α-phase were monitored from 1.5 to 145 K. The dominant feature consists of a rotation of the hydrogen-bonded chains about their axis. The maximum reorientation in the mentioned temperature range is about 8°.

The neutron diffraction study of β-methanol at 168 K corroborates the unit cell parameters and the atomic positions obtained from the single-crystal X-ray diffraction study by Tauer and Lipscomb,[11] even if the scarcity of reflections in the measured neutron diffraction profile prevents a fully independent structure refinement. The deuteron positions, measured by neutron diffraction, provide valuable additional information. The space group $Cmc2_1$ gives a physically more sensible description of the system than $Cmcm$, proposed by Tauer and Lipscomb, because the deuterons involved in hydrogen bonds are not symmetrically localized between two oxygen atoms. According to our measurements, the methyl group in β-methanol does not reside exclusively in staggered conformations as in α-methanol. At 168 K, the eclipsed rotamers are populated to 36%. This may be related to the pronounced anisotropic thermal motion of the oxygen atoms along the 100 axis.

Acknowledgment. We are indebted to Prof. J. Dunitz and Dr. G. Seyfang at ETHZ for their advice on isotopic effects. We also thank M. Koch at LNS for his technical support and M. Tomaselli at ETHZ for the stimulating discussions. This project was supported by the Swiss National Science Foundation and by the Aluminium Fonds, Neuhausen.