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The ^{129}Xe Chemical Shift Tensor in a Silicalite Single Crystal from Hyperpolarized ^{129}Xe NMR Spectroscopy

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The NMR chemical shift of adsorbed ^{129}Xe is known to depend on the size and shape of the void space, the chemical composition of the absorbent, and the nature and concentration of coadsorbed molecules.[1] Although a great deal of experimental data have been accumulated, the relationship between the ^{129}Xe chemical shift and the size and shape of the voids, and its dependence on temperature and loading levels, still is not well understood.[1] In addition, the ^{129}Xe NMR signals often are averaged by fast exchange between sites and even with the gas phase, and thus cannot be assigned to a particular site or to structural features.[2] Another problem is to account for the various contributions to the observed chemical shift, in particular those arising from Xe−Xe interactions. Significant theoretical insights have been accomplished with the computation of isotropic Xe chemical shifts in zeolites where very good agreement was achieved between calculation and experiment.[3] These calculations in fact provide much more information than can be tested experimentally since the calculated shift tensors have to be averaged for comparison with the experimentally observed isotropic spectra. Thus the tensor components and their sensitivity to local structure remain untested.

To make progress, we need experimental ^{129}Xe chemical shift tensors, ideally unaffected by exchange or Xe−Xe interactions. Such spectra have been observed in closed cell systems such as inclusion compounds,[1,4] and in a few open systems with noncubic crystal symmetry such as channel zeolites,[5] aluminophosphates,[2,6] and organic zeolite mimics,[7] where the effects of exchange and Xe−Xe interactions can be excluded or controlled. Furthermore, although the principal components of the chemical shift tensor obtained from powder spectra can sometimes be referred to the crystal axes on the basis of symmetry,[4] more often this referencing of the shift tensor orientation can be done only from data on large single crystals. NMR spectra of ^{129}Xe in the voids of single crystals have not been reported, because of low sensitivity, the need for large crystals, and technical problems such as rotating a gas-loaded sample about crystal axes. The dramatic increase in sensitivity of hyperpolarized (HP) relative to thermally polarized (TP) Xe now makes single-crystal studies feasible.[8] Here we report the first determination of a ^{129}Xe chemical shift tensor obtained from rotation patterns of a single crystal of silicalite using HP Xe produced in a continuous flow system.[10] The very low partial pressure of HP Xe used not only facilitates crystal rotation in an open system but also minimizes Xe−Xe interactions[9] and exchange with the gas phase. We also report measurements on silicalite powder as a function of temperature.

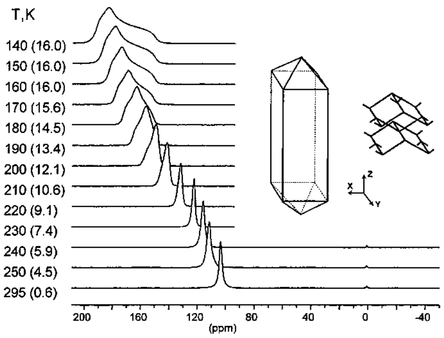

Figure 1. ^{129}Xe NMR spectra of continuous flow HP Xe adsorbed in silicalite powder as a function of temperature. Estimated concentrations of adsorbed xenon in atoms per unit cell (see ref 19c) are shown in parentheses. Inset: Channel orientations in a silicalite crystal.

Silicalite is an aluminum-free version of the synthetic zeolite ZSM-5.[14,15] Below 340 K the unloaded silicalite is monoclinic,[16,17] space group $P2_1/n$, with unit cell parameters $a = 20.107$ Å, $b = 19.879$ Å, $c = 13.369$ Å, $\alpha = \beta = 90^{o}$, $\gamma = 90.67^{o}$[15], and above 340 K it is orthorhombic, *Pnma*, with $a = 20.07$ Å, $b = 19.92$ Å, $c = 13.42$ Å. Its silica framework defines a porous network with two types of cross-linked channels: (a) straight channels parallel to the *y*-axis and (b) sinusoidal channels running in the *x* direction in planes parallel to the [010] face (Figure 1). The channels have roughly elliptical free-space cross sections with axes ranging 5.2−5.8 Å.[15] The reduced dimensionality of the channels affects a number of properties, e.g., Xe diffusion is

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(10) ^{129}Xe NMR spectra were obtained at 110.7 MHz (Bruker DSX-400 spectrometer), using a single-axis goniometer probe (Morris Instruments Inc.) modified to allow a flow of HP Xe over the crystal. Silicalite crystals were synthesized according to ref 12 and calcined at 800 K. HP Xe[11] was produced with an apparatus described in ref 13, based on the design of ref 11c, with the optical pumping cell in the fringe field of the spectrometer magnet. The gas mixture, containing 7.6 Torr of Xe polarized to 4−5%, was delivered at 150−200 cm^3/min to the sample region via plastic tubing. Three similar crystals (~0.5 × 0.5 × 1 mm) were each glued by one of three visually orthogonal crystal planes to a glass capillary that was then fixed in the goniometer of the probe. The orientation of the crystals was observed using X-ray diffraction.

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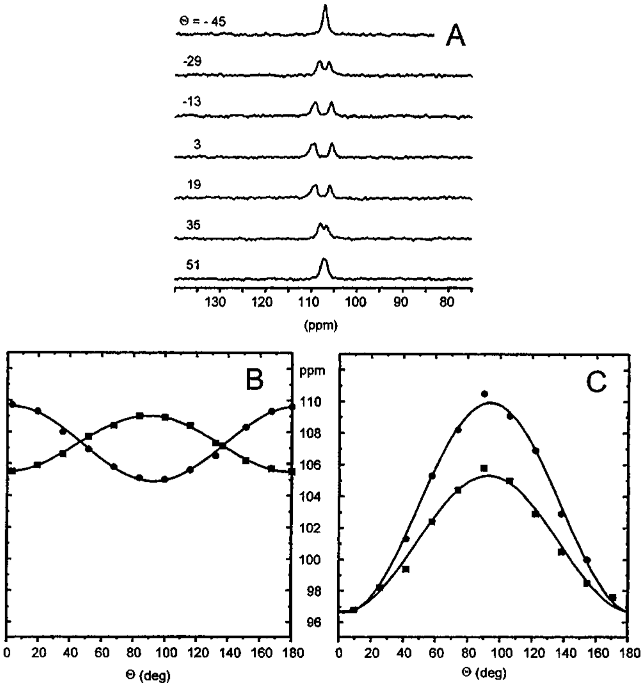

Figure 2. HP ^{129}Xe NMR results for single crystals of silicalite at 295 K: (A) spectra ($\pi/2$ pulses, 512 scans each, 5 s delay) and (B) chemical shifts versus crystal orientation, Θ, about the *z* axis, perpendicular to the magnetic field. (C) Chemical shifts versus Θ about the second orthogonal orientation. The third orthogonal orientation gave an identical pattern.

anisotropic.[18,19] Similarly, each type of channel should impart a characteristic anisotropic chemical shift to a resident xenon atom, as observed in the linear channels of ALPO-11 and other materials.[6,7] However, since a xenon atom is expected to exchange rapidly between the two channel types, the net result will be a single averaged shielding tensor.

The variable temperature HP ^{129}Xe spectra for Xe in a powder of micrometer-sized silicalite crystallites clearly show chemical shift anisotropy of increasing magnitude below 230 K (Figure 1). The anisotropy even changes sign at 180−190 K. These changes are not unexpected,[5a,6c,7] since although the partial pressure of Xe in the gas stream remains constant (7.6 Torr), the amount of Xe adsorbed and its residence time will both increase with decreasing temperature. Xe−Xe interactions will therefore increase on cooling, and together with dynamic averaging over different sites this results in temperature-dependent line shapes. Similar anisotropies have been observed previously using TP Xe, but only for large crystallites with the channels completely filled with Xe.[5b] The change from isotropic to anisotropic line shapes appears to indicate the point where exchange with the gas phase is no longer dominant for this particular size of crystallite.

HP ^{129}Xe NMR single-crystal rotation patterns at 295 K (Figure 2) clearly show an orientation-dependent chemical shift, with a 12 ppm range for rotation around the crystal *x* or *y* axes and about 5 ppm for rotation about the *z* axis. The anisotropy indicates that for these millimeter-sized crystals, exchange with the gas phase is no longer a significant factor. The small line widths (<100 Hz) allow an accurate determination of the chemical shifts to be made. TP ^{129}Xe NMR experiments would be highly impractical, since it would take 800−2000 times longer (a conservative estimate) to obtain spectra of similar quality.

It is very interesting that two separate lines are observed for each orthogonal orientation. Simple crystallographic considerations and a knowledge of the diffusion coefficients rule out an assignment of the line pairs to different xenon sites, so it must be concluded that they originate in microscopically different regions, between which exchange must be slow on an NMR time scale. Crystal twinning is one possible explanation, and this was confirmed by X-ray diffraction.[20] Twinning is very common in crystals where two lattice parameters are similar, as in silicalite. Single crystals of orthorhombic silicalite transform reversibly at 340 K into twinned monoclinic crystals with a 1:1 volume ratio.[15−17] The situation can be viewed as an alternation of the (010) layers in the crystal with respect to the *x* direction. The size of the twin domains can be more than 50 unit cells[16] (~1000 Å). In this type of twinning, however, the orientations of the channels remain the same, so there should still only be one resonance. A different situation arises if during crystallization the (001) layers at some point continue growing after turning 90°around the *z* axis, leading to alternating domains with the *x* and *y* axes swapped. In this case, the entire channel system is rotated by 90°,[18] and if the domains are sufficiently large, there will be two Xe resonances whose rotation patterns are 90° out of phase. This is consistent with the experimental observations (Figure 2).[20]

Table 1. Components of the ^{129}Xe Chemical Shift Tensors (ppm) in Silicalite at 295 K Obtained from the Single-Crystal Rotation Patterns

δ_{xx}	δ_{yy}	δ_{zz}	δ_{xy} (δ_{yx})	$\delta_{xz} = \delta_{zx}$	$\delta_{yz} = \delta_{yz}$	δ_{iso}[a]
105.2	110.0	96.5	0.2	0.5	−0.7	103.9
109.3	105.6	96.5	0.0	0.4	−0.3	103.8

[a] An isotropic chemical shift for silicalite of 104.0 ppm was reported previously.[1,5b]

The chemical shift tensors, determined from analysis of the rotation patterns[21] of the two lines, are coincident within experimental error, except that the orientations of the δ_{xx} and δ_{yy} components are switched (Table 1). Since the absolute directions of the *x* and *y* axes in the crystal cannot be defined because of the twinning, unfortunately it is not possible to assign definite directions to all of the tensor components. However, it can be concluded that the most shielded component δ_{zz} is parallel to the *z* direction in the crystal. The tensor is nonaxial, consistent with the crystal symmetry. It reflects interaction of the Xe with the silicalite framework but as a complicated function of dynamic averaging over all accessible sites and surfaces.

In conclusion, we report the first observation of the ^{129}Xe NMR of xenon adsorbed in a single crystal, made possible by the use of HP Xe. The two signals observed for each orthogonal crystal orientation are assigned to xenon in twinned regions of the silicalite crystal, and the chemical shift tensor is derived. The information is a critical first step in providing high-quality experimental data for comparison with calculated values. In addition, it is clear that information can be obtained on the nature of crystal growth and twinning, with the possibilities of studying domain sizes and transport processes. Higher levels of polarization would lead quite naturally to the ability to examine smaller crystals.

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