A High-Resolution ^{17}O NMR Study of Siliceous Zeolite Faujasite

L. M. Bull,[†] A. K. Cheetham,[‡] T. Anupold,[§] A. Reinhold,[§]
A. Samoson,[§] J. Sauer,[⊥] B. Bussemer,[⊥] Y. Lee,[||] S. Gann,[||]
J. Shore,[||] A. Pines,[||] and R. Dupree*,[#]

Institut des Matériaux de Nantes, Laboratoire de Chimie
des Solides, 2 rue de la Houssinière, B.P. 32229
44322 Nantes, Cedex 3, France
Materials Research Laboratory, University of California
Santa Barbara, California 93106
Institute of Chemical Physics and Biophysics
Akadeemia Tee 23, Tallinn, Estonia and the National
High Magnetic Field Laboratory, 1800 East Paul
Dirac Drive, Tallahassee, Florida
Humboldt-Universität, Institut für Chemie
Berlin, D-10117, Germany
Materials Sciences Division
E.O. Lawrence Berkeley National Laboratory
1 Cyclotron Road, Berkeley, California 94720
Department of Chemistry, University of California
Berkeley, California 94720
Physics Department, University of Warwick
Coventry CV4 74L, U.K.

Received December 19, 1997

^{29}Si and ^{27}Al solid-state NMR have already played a vital role in the characterization of technologically important zeolites,[1] but relatively few ^{17}O NMR studies have been performed.[2] ^{17}O is only 0.037% in natural abundance, it is expensive to isotopically enrich, it has a small magnetic moment, and the electric field gradient is relatively large so the static and magic-angle spinning (MAS) line shapes are often broad and featureless. Nevertheless, using high magnetic field strengths (11.7−16.9 T) and state-of-the-art double rotation probes, we have obtained high-resolution ^{17}O NMR spectra in which, for the first time, all crystallographically inequivalent oxygen sites in a zeolite have been resolved. In addition, we present an assignment of the spectrum based upon quantum mechanical chemical shift and field gradient calculations.

^{17}O has a nuclear spin of $I = {}^5/_2$ so the observed NMR line shape of the central transition and its relative peak position are determined by the quadrupole coupling constant, C_q, the asymmetry parameter of the electric field gradient tensor, η, and the quadrupolar and chemical shift tensors, all of which are dependent upon the coordination of the oxygen and the type of bonding in which it is participating.[3] The potential of ^{17}O NMR to study silicates[4] and zeolites[2] has been demonstrated using MAS and variable angle spinning techniques. Chemically distinct environments such as Si−O−Si and Si−O−Al were distinguished in several zeolites, but individual sites could not be resolved. High-resolution ^{17}O NMR spectra of condensed silicates[5,6] have been obtained by techniques such as double rotation (DOR)[3] and dynamic angle spinning (DAS).[3]

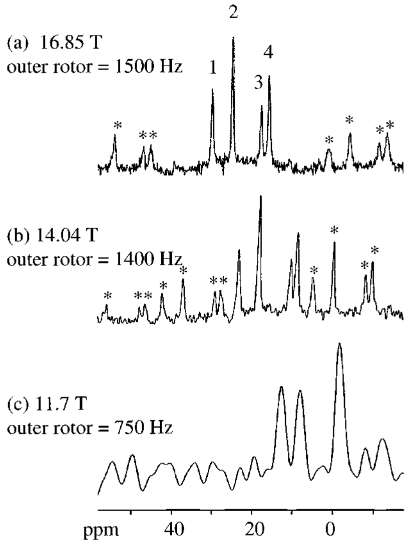

Figure 1. ^{17}O double rotation NMR spectra of Sil-Y. Spinning sidebands are indicated by an asterix. Spectra are all referenced to H_2O at 0 ppm. The peak notation used in the rest of the paper is shown above spectrum a.

Assignments of ^{17}O spectra have been made by using correlations between C_q and η and the Si−O−Si bond angle.[4,6] These semiempirical correlations, based on either quantum mechanical calculations[7] or the Townes−Dailey model,[8] have predicted relationships where C_q is expected to increase, and η to decrease, with Si−O−Si bond angle. However, with the limited amount of data in the literature currently it is uncertain whether these correlations are quantitatively reliable. There have also been numerous attempts to calculate field gradients in various materials.[9] Ab initio density functional theory calculations have been performed on the mineral forsterite[10] where electric field gradients within about 5% of the absolute experimental values were obtained for ^{25}Mg and ^{17}O.

Sil-Y was chosen for investigation by ^{17}O NMR for several reasons: (i) it adopts the same topology (FAU) as zeolites X and Y, which are used widely as acid catalysts and separating media, (ii) the structure has been determined from neutron diffraction with high accuracy,[11] (iii) the framework does not contain aluminum or charge compensating cations that could cause chemical shift dispersion, and (iv) due to its structural simplicity (one crystallographically distinct Si site and four crystallographically distinct oxygen sites), it is an excellent sample for calculating the ^{17}O NMR chemical shifts and field gradients.

The static and MAS ^{17}O NMR spectra of $^{17}O_2$(g) enriched Sil-Y are broad and featureless, as expected.[12] Under DOR conditions the second-order quadrupolar interaction is averaged, resulting in the observation of high-resolution spectra, where the observed shifts in ppm, δ_{obs}, for ^{17}O are determined by the field independent isotropic chemical shift, δ_{iso}, and the field dependent isotropic second-order quadrupolar shift, δ_q. δ_q is determined by the values

---

[*] To whom correspondence should be addressed.

[†] Institut des Matériaux.

[‡] University of California, Santa Barbara.

[§] Institute of Chemical Physics and Biophysics.

[⊥] Humboldt-Universität.

[||] E.O. Lawrence Berkeley National Laboratory and University of California, Berkeley.

[#] University of Warwick.

(1) Engelhardt G.; Michel, D. *High-Resolution Solid-State NMR of Silicates and Zeolites*; Wiley: Chichester, 1987.

(2) Yang, S.; Park, K. D.; Oldfield, E. *J. Am. Chem. Soc.* **1989**, *111*, 7278−7279.

(3) Chmelka, B. F.; Zwanziger, J. W. *NMR Basic Principles and Progress*, 33; Springer-Verlag: Berlin, 1994; pp 79−124.

(4) Schramm, S.; Oldfield, E. *J. Am. Chem. Soc.* **1984**, *106*, 2502−2506.

(5) Mueller, K. T.; Wu, Y.; Chmelka, B. F.; Stebbins J.; Pines, A. *J. Am. Chem. Soc.* **1991**, *113*, 32−38.

(6) Grandinetti, P. J.; Baltisberger, J. H.; Farnan, I.; Stebbins J. F.; Werner, U.; Pines, A. *J. Phys. Chem.* **1995**, *99*, 12341−12348.

(7) Tossell, J. A. *J. Non-Cryst. Solids* **1990**, *120*, 13−19.

(8) Townes, C. H.; Dailey, B. P. *J. Chem. Phys.* **1949**, *17*, 782.

(9) Palmer, M. H.; Blair-fish, J. A. *Naturforsch. A* **1994**, *49*, 137−145.

(10) Winkler, B.; Blaha, P.; Schwarz, K. *Am. Min.* **1996**, *81*, 545−549.

(11) Hriljac, J. A; Eddy, M. M; Cheetham, A. K.; Donohue, J. A.; Ray, G. A. J. *Solid State Chem.* **1993**, *106*, 66−72.

(12) Enrichment of Sil-Y was performed by dehydrating under high vacuum (10^{-4} Torr) at 500 °C for 12 h, and then sealing in a quartz tube under 1/3 atm of $^{17}O_2$(g). The tube was heated to 750 °C for 24 h. All spectra were collected in a synchronous fashion [Samoson, A.; Lippmaa, E. *J. Magn. Reson.* **1989**, *84*, 410].

S0002-7863(97)04300-X CCC: $15.00

Table 1. Observed ^{17}O NMR Shifts, P_Q, C_q, and η Values for the Four Oxygen Peaks in Sil-Y[a]

	obsd shifts (ppm) ±0.2				δ_{iso} (ppm)	P_Q (MHz)	from DAS C_q (MHz)	η
	$\delta_{7.07T}$	$\delta_{11.7T}$	$\delta_{14.04T}$	$\delta_{16.85T}$	±0.3	±0.02	±(0.03)	±0.05
peak 1	−48.8	12.8	23.2	30.5	47.3	5.15	5.14	0.1
peak 2	−53.8	7.9	18.2	25.5	42.3	5.15	5.10	0.3
peak 3	−69.6	−1.1	10.4	18.5	37.2	5.43	5.39	0.2
peak 4	−67.9	−1.1	8.8	16.5	34.8	5.32	5.28	0.2

[a] The peak notation is the same as in Figure 1.

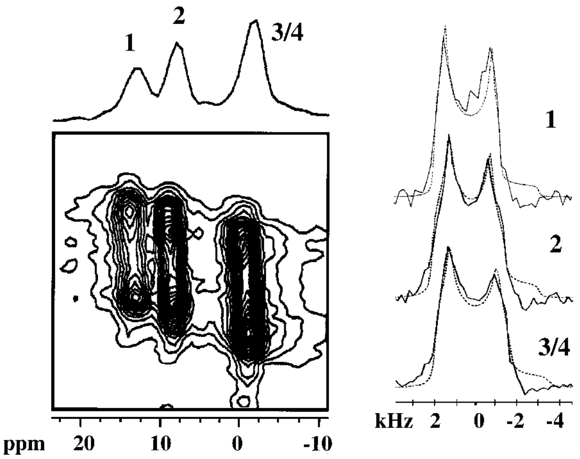

Figure 2. Two-dimensional ^{17}O DAS NMR spectrum of Sil-Y and its projections onto the isotropic and anisotropic axes obtained at a field strength of 11.7 T.

of C$_q$, η, and the Larmor frequency. From the field dependence of δ_{obs} one can determine δ_{iso} and P_Q, ($P_Q = C_q(1 + \eta^2/3)^{1/2}$). Figure 1 shows the ^{17}O DOR spectra of Sil-Y collected at field strengths of 11.7, 14.04, and 16.85 T. Spectra were also collected at 7.07 T, but are not shown. At the two highest fields all four crystallographically distinct oxygen sites in the zeolite are clearly resolved. The significant enhancements in resolution observed at higher fields arise primarily because the field dependence of the quadrupolar shift partially cancels the chemical shift dispersion at 11.7 T. The values of the isotropic chemical shift and P_Q are given in Table 1. η could not be obtained from simulating the intensities of the spinning sidebands as these intensities are affected by chemical shift anisotropy.[13] Not surprisingly, as the bonding is very similar at each site and the range of Si−O−Si bond angles is only 10°, these parameters cover only a small range and therefore cannot be used directly for assignment purposes.

A 2-D DAS experiment can possibly provide additional information, stretching the spectrum into the second, anisotropic dimension, where C_q and η can then be obtained from simulations. A magic-angle detected 2-D DAS spectrum,[3] which is shown in Figure 2, was measured at a field strength of 11.7 T over 2 weeks. Due to the overlap of the two high-field lines and the limited signal-to-noise, simulations of the anisotropic slices were constrained by the P_Q values obtained from the DOR measurements. The results of these fits are shown in Figure 2, and the electric field gradient parameters are given in Table 1.

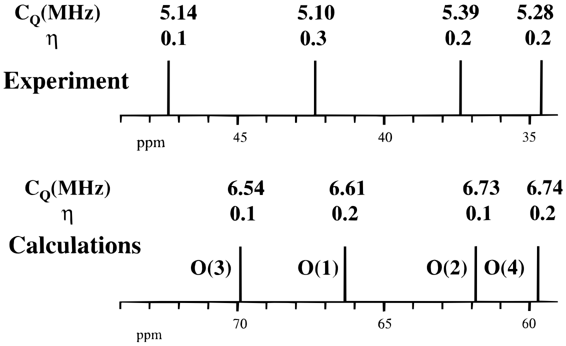

Figure 3. The assignment of the ^{17}O NMR spectrum of Sil-Y using quantum mechanical cluster calculations. The peak positions are the genuine chemical shifts without any field dependent quadrupole effects.

The assignment of the ^{17}O NMR spectrum is an even more challenging problem than resolving the different oxygen sites as all four sites have the same multiplicity. Therefore, we performed electric field gradient and chemical shift calculations for each oxygen site based on the method of Bussemer et al.[14] The structure was optimized by using an ab initio parametrized shell model potential[15] with a triple-ζ polarization basis for oxygen and a double-ζ polarization basis for Si.[14,16] From this structure, clusters of four complete coordination spheres of silicon and oxygen around each oxygen site were terminated with hydrogen atoms. The field gradient tensor was obtained with the moloch module of the TURBOMOLE program,[17] with V_{xx}, V_{yy}, and V_{zz} being obtained from the diagonalized tensor. The ^{17}O NMR isotropic chemical shifts were calculated with the CPHF-GIAO method.[18] The values of δ_{iso}, C_q, and η are shown in Figure 3.

The calculated values of C_q are consistently larger than those determined experimentally. This arises mainly from the use of cluster models instead of periodic calculations, but it is believed that the relative sizes of C_q will be representative of the system, especially for Sil-Y where the asymmetric unit is small relative to the size of the cluster, and all the oxygen sites have a similar environment. It is well-known that the absolute value of the chemical shift is also difficult to obtain due to the uncertainty of referencing to H_2O. However, we are confident that the sequence of lines is correctly predicted because it was unchanged when (1) different reference structures were used, (2) the basis sets on all of the atoms were extended to triple-ζ polarization, (3) the cluster size was varied, and (4) electron correlation was included into the calculations when the DFT method was used.[19]

From the electric field gradient and chemical shift calculations, we find that the range of calculated chemical shifts (10.2 ppm) is very close to the range of experimental values (12.5 ppm). In addition, the peaks at highest frequency (O(1), O(3)) have the lowest calculated and experimentally observed C_q values, and the calculations correctly predict that peak 2, corresponding to site O(1), has the largest asymmetry parameter. Consequently, we would assign the ^{17}O NMR spectrum of Sil-Y according to Figure 3 using the calculated chemical shifts. Compared to the common practice of correlating solid-state NMR shifts with bond valency or to the nature of neighboring atoms, this work takes shift interpretations to a new level of complexity. In particular, subtle differences in the local structure have been detected experimentally and these have been interpreted by quantum-chemical calculations.

Acknowledgment. This work was supported by the MRSEC Program of the National Science Foundation under award No. DMR-9632716. R.D. would like to acknowledge the EPSRC (UK). A.S., T.A., and A.R. are supported by a NATO linkage grant (1 1312 0154) and would like to acknowledge the Estonian Science Foundation. Use of the facilities at the National High Magnetic Field Laboratory, Florida, is greatly appreciated. We would also like to thank Dr. J. Donahue for synthesizing the sample of Sil-Y and Dr. V. Moravetski for helpful discussions.

JA9743001

---

(13) Samoson, A.; Sarv, P.; van Braam Houckgeest, J. P.; Kraushaar-Czarnetzki, B. *Appl. Magn. Reson.* **1993**, *4*, 171.

(14) Bussemer, B.; Schröder, K.-P.; Sauer, J. *Solid State Nucl. Magn. Reson.* **1997**, *9*, 145−156.

(15) Schröder, K.-P.; Sauer, J. *J. Phys. Chem.* **1996**, *100*, 11043−11049.

(16) Moravetski, V.; Hill, J. R.; Eichler, U.; Cheetham, A. K.; Sauer, J. *J. Am. Chem. Soc.* **1996**, *118*, 13015−13020.

(17) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165−169.

(18) Häser, M.; Ahlrichs, R.; Baron, H. P.; Weis, P.; Horn, H. *Theor. Chim. Acta* **1992**, *83*, 455−470.

(19) Bussemer, B.; Sauer, J. To be submitted for publication.