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Direct Observation of Host−Guest Hydrogen Bonding in the Zeolite NaY/Chloroform System by Neutron Scattering

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Aluminosilicate zeolites have recently been recognized as interesting alternatives to other media such as activated carbons for the sequestration and conversion of halocarbons, for example, methyl chloride,[1] trichloroethylene,[2] and various hydrofluorocarbons.[3] Aluminosilicates and related molecular sieves offer a range of potential advantages, including the possibility of fine-tuning separation processes by utilizing polarity differences between various halocarbons and of tailoring separation processes by harnessing chemically specific host−guest interactions. In contrast to the situation with hydrocarbons in zeolites, relatively little experimental data concerning the behavior of halocarbons in zeolitic materials have been reported so far. Nevertheless, calorimetric[4] and isotherm measurements,[2,5] FTIR/Raman[6] and NMR[7] spectroscopy studies, diffraction work,[8] and generalized force field simulations[9] have been reported on a variety of systems. In view of the growing interest in these systems, we have undertaken a program aimed at developing a better understanding of host−guest interactions in some model zeolite/halocarbon systems.[10−14] In the case of chloroform in zeolite NaY, a variety of interactions appear to be important: $Cl_{sorbate}\cdots O_{framework}$ van der Waals interactions, $Cl_{sorbate}\cdots Na^+$ electrostatic interactions, and $H_{sorbate}\cdots O_{framework}$ hydrogen bonding (H bonding). Diffraction studies on this system[8] have had difficulty in establishing the precise location of chloroform in the supercage of NaY because of substantial disorder arising from the relatively flat conformational energy surface of the system. Experimental evidence for the importance of $H_{sorbate}\cdots O_{framework}$ H bonding in this and other systems containing halocarbons with C−H bonds therefore relies on indirect observations by vibrational spectroscopy. This conclusion is supported by our computer simulations, which draw attention to the substantial positive charge on the H atom in chloroform and the resultant H bonding (Figure 1).[10] In the present study, we show how the differential H pair distribution function (pdf) obtained from neutron scattering contrast measurements on hydrogenous and deuterated chloroform in NaY provides direct support for H bonding and other facets of the host−guest interactions.

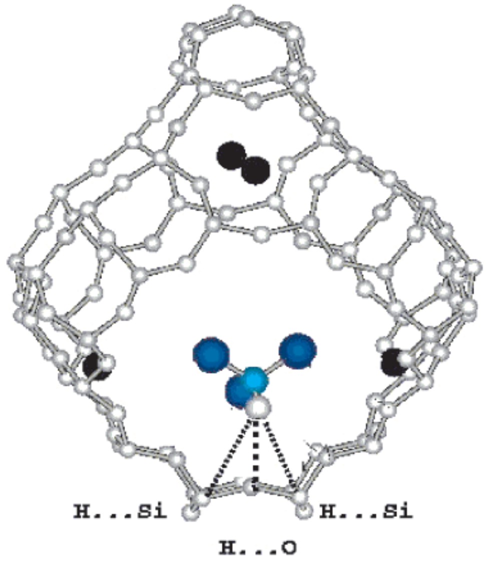

Figure 1. Typical binding geometry of $CHCL_3$ adsorbed in the supercage of NaY according to our computer simulations.[10] Carbon: turquoise; chlorine: blue; hydrogen: gray; sodium: black.

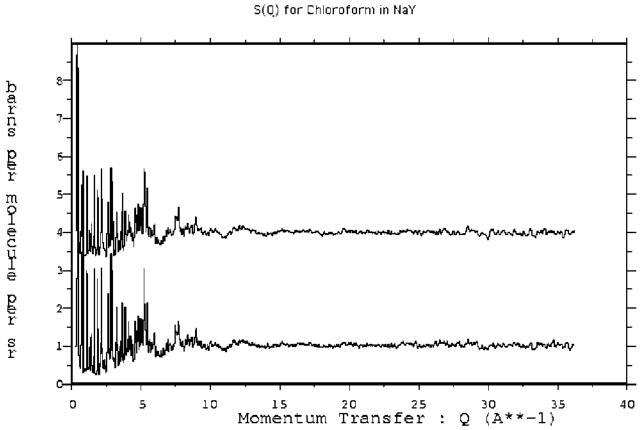

Figure 2. Structure $S(Q)$ for two molecules of chloroform in NaY, $CDCl_3$ (top), and $CHCl_3$ (bottom).

A sample of NaY ($Na_{53}Si_{139}Al_{53}O_{384}$) was dehydrated for 24 h at temperatures up to 400 °C. Approximately 2 g each of the dehydrated NaY was loaded on a vacuum line with two molecules of $CHCl_3$ or $CDCl_3$ per supercage and subsequently sealed in vanadium cans under a helium atmosphere. Neutron diffraction patterns were collected at $T = 20$ K using the GLAD instrument at the Intense Pulsed Neutron Source, Argonne National Laboratory. The complete data treatment leading up to and including the derivation of $G(r)$ was carried out using the programs available for the GLAD diffractometer which are based on the ATLAS suite of programs.[15] Data from all detectors were combined after corrections for scattering from the empty cell, the instrument background, and normalization to a vanadium sample in the standard manner.[16] After making corrections for inelasticity and self-scattering, the total structure factor $S(Q)$ was obtained out to a Q of 37 Å^{-1}; it is shown in Figure 2 for both the normal and deuterated sorbate in NaY (an approximate correction for H scattering was applied to the $CHCl_3$ data). As usual, the total structure factors

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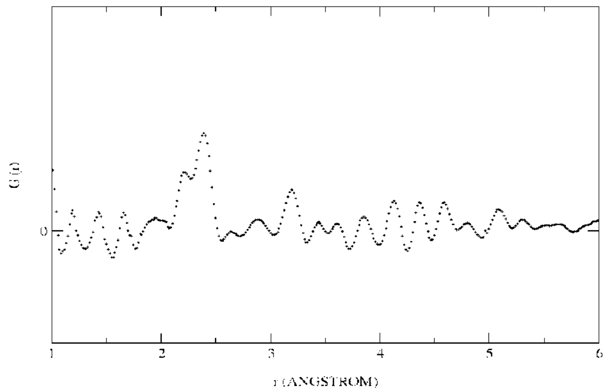

Figure 3. Differential $G(r)$ for the chloroform hdyrogen in NaY (see text).

$S(Q)$ have been normalized to oscillate about a value of 1 at large Q. While the two diffraction patterns appear to be rather similar, the influence on the diffraction peak intensities of the isotopic substitution on the sorbate is quite evident upon close inspection in a number of regions (for example, around $Q \approx 5$ Å^{-1}). The $G(r)$ is then obtained by the Fourier transform of the $S(Q)$,

$$G(r) = 1 + \frac{1}{2\pi^2 r\rho_0}\int \mathrm{d}Q\, Q[S(Q) - 1]\sin(Qr) \qquad (1)$$

where ρ_0 is the average atomic number density.

The total $G(r)$ will contain contributions from all pairs of atoms, both intra- and intermolecular for host and guest. However, in the differential $G(r)$ between $CHCl_3$/NaY and $CDCl_3$/NaY (obtained from the Fourier transform of the difference between the two $S(Q)$ curves), contributions from atom pairs that are identical in both samples are subtracted out, including all host atom pair correlations and those between guest (C and Cl) and host atoms. Only pair correlations of H with the other atoms in the system remain in the differential pdf. A scale factor corresponding to the different scattering cross sections of the two samples has to be applied so that the partial $G(r)$'s that are the same in both samples are subtracted out. This scale factor (1.025 on the $CDCl_3$/NaY data) is rather small because H (or D) constitutes just 2.25 atom % of the sample.

The result of this procedure is shown in Figure 3 for guest−host interatomic distances above 1 Å. The first significant peak, consisting of a doublet at 2.25 and 2.4 Å, contains the principal result of the present study. The shoulder at 2.25 Å can only be ascribed to the CH···O guest−host H-bond distance, whose existence we had postulated earlier on the basis of simulations and spectroscopic studies.[10] It is in remarkable agreement with the result (∼2.3 Å) obtained by the molecular mechanics docking procedure using the force field developed by us.[11] This distance is also close to the mean of tabulated distributions of C−H···O H-bonds involving the chloroform molecule, namely 2.31 Å.[17] The stronger peak at 2.4 Å, with an intensity approximately three times that of the 2.25 Å peak, corresponds to the intramolecular H−Cl distance, expected at 2.35 Å.[18] The presence of both the H-bonding interactions as well as Cl-to-cation interactions was recently deduced from a combined IR and NMR study of chloroform in NaY; at least two adsorption sites were observed with H-bonds of different strengths, being weaker at site II with significant $Cl-Na^+$ interactions.[19] The remaining noticeable feature in the differential PDF is the peak at 3.4 Å, which corresponds to the H to (Si,Al) distance, computed to be also 3.4 Å in our simulation studies. Additional peaks in the differential pdf pattern at larger distances need better statistical accuracy for further interpretation. However, calculations of the total $G(r)$ from crystallography and modeling can, in principle, be used to extract further structural details by direct comparison with the experimental $G(r)$.[20] Previous work, for example on coordination complexes,[21] glasses[22] and polymer electrolytes,[23] has demonstrated the efficacy of isotope contrast pdf methods with neutrons for the study of local structure in disordered systems. The success of the present experiment, and that of a recent study in which isotopic substitution was carried out within the zeolite host,[24] show that variants on this method can be used to address difficult problems in catalytic and related systems. The method should be especially valuable where the local structure at an adsorption site or catalytically active site is not accessible to structural analysis based on long-range ordered structures, or to EXAFS techniques because the absorption edge is at too low an energy.

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References

(1) Zarchy, A. S.; Maurer, R. T.; Chao, C. C. U.S. Patent No. 5 453 113, 1994.
(2) (a) Alvarez-Cohen, L.; McCarty, P. L.; Roberts, P. V. *Environ. Sci. Technol.* **1993**, *27*, 2141. (b) Weber, G.; Bertrand, O.; Fromont, E.; Bourg, S.; Bouvier, F.; Bissinger, D.; Simonot-Grange, M. H. *J. Chim. Phys.* **1996**, *93*, 1412.
(3) Corbin, D. R.; Mahler, B. A. World Patent, W.O. 94/02440, 1994.
(4) Stach, H.; Sigrist, K.; Radeke, K.-H.; Riedel, V. *Chem. Technik.* **1994**, *5*, 278.
(5) (a) Kobayashi, S.; Mizuno, K.; Kushiyama, S.; Aizawa, R.; Koinuma, Y.; Ohuchi, H. *Ind. Eng. Chem. Res.* **1991**, *30*, 2340. (b) Kawai, T.; Yanagihara, Tsutsumi, K. *Colloid Polym. Sci.* **1994**, *272*, 1620.
(6) (a) Xie, J.; Huang, M.; Kaliaguine, S. *React. Kinet. Catal. Lett.* **1996**, *58*, 217. (b) Chintawar, P. S.; Greene, H. L. *J. Catal.* **1997**, *165*, 12. (c) Crawford, M. K.; Dobbs, K. D.; Smalley, R. J.; Corbin, D. R.; Grey, C. P. *J. Phys. Chem.* **1999**, *103*, 431.
(7) (a) Grey, C. P., Corbin, D. R. *J. Chem. Phys.* **1995**, *99*, 16821. (b) Lim, H. P.; Grey, G. P. *Chem. Commun.* **1998**, 2257. (c) Cheung, T. T. P. *J. Phys. Chem.* **1992**, *96*, 5505.
(8) (a) Gameson, I.; Rayment, T.; Thomas, J. M.; Wright, P. A. *J. Phys. Chem.* **1988**, *92*, 988. (b) Kazkur, A. Z.; Jones, R. J.; Couves, J. W.; Waller, D.; Catlow, C. R. A.; Thomas, J. M. *J. Phys. Chem. Solids.* **1991**, *52*, 1219. (c) Kazkur, A. Z.; Jones, R. J.; Waller, D.; Catlow, C. R. A.; Thomas, J. M. *J. Phys. Chem.* **1993**, *97*, 426. (d) Grey, C. P.; Poshni, F. I.; Gualtieri, A. F.; Norby, P.; Hanson, J. C.; Corbin, D. R. *J. Am. Chem. Soc.* **1997**, *119*, 1981.
(9) (a) George, A. R.; Freeman, C. M.; Catlow, C. R. A. *Zeolites* **1996**, *17*, 466. (b) Parise, J. B.; Abrams, L.; Calabrese, J. C.; Corbin, D. R.; Newsam, J. M.; Levine, S., Freeman, C. *Stud. Surf. Sci. Catal.* **1995**, *98*, 248.
(10) Mellot, C. F.; Davidson, A. M.; Eckert, J.; Cheetham, A. K. *J. Phys. Chem.* **1998**, *102*, 2530.
(11) Mellot, C. F.; Cheetham, A. K. *J. Phys. Chem.* **1999**, *103*, 3864.
(12) Mellot, C. F.; Cheetham, A. K.; Harms, S.; Savitz, S.; Gorte, R. J.; Myers, A. L. *J. Am. Chem. Soc.* **1998**, *120*, 5791.
(13) Mellot, C. F.; Cheetham, A. K.; Harms, S.; Savitz, S.; Gorte, R. J.; Myers, A. L. *Langmuir* **1998**, *14*, 6728.
(14) Davidson, A. M.; Mellot, C. F.; Eckert, J.; Cheetham, A. K. *J. Phys. Chem.* **2000**, *104*, 432.
(15) Hannon, A. C.; Howells, W. S.; Soper, A. K. *Proceedings of the Second Workshop on Neutron Scattering Data Analysis*; Johnson, M. W., Ed.; IOP Conf. Series; IOP Publishing: Bristol, 1990; Vol. 107, p 193.
(16) Toby, B. H.; Egami, T. *Acta Crystallogr.* **1992**, *A48*, 336.
(17) Steiner, T. *New J. Chem.* **1998**, *22*, 1099.
(18) Bertagnolli, H.; Leicht, D. O.; Zeidler, M. D.; Chieux, P. *Mol. Phys.* **1978**, *35*, 199.
(19) Bosch, E.; Huber, S.; Weitkamp, J.; Knözinger, H. *Phys. Chem. Chem. Phys.* **1999**, 579.
(20) Egami, T. *Mater. Trans. JIM* **1990**, *31*, 163.
(21) (a) Neilson, G. W.; Enderby J. E. *Proc. R. Soc., London Ser. A* **1983**, *390*, 353. (b) Neilson, G. W.; Enderby, J. E. *J. Phys. Chem.* **1996**, *100*, 1317. (c) Arai, M.; Johnson, R. W.; Price, D. L.; Susman, S.; Gay, M.; Enderby, J. E. *J. Non-Cryst. Solids* **1986**, *83*, 80.
(22) (a) Mao, G.; Saboungi, M.-L.; Price, D. L.; Armand, M. B.; Howells, W. S. *Phys. Rev. Lett.* **2000**, *84*, 5536. (b) Mao, G.; Saboungi, M.-L.; Price, D. L.; Badyal, Y. S.; Fischer, H. E. *Europhys. Lett.* **2001**, *54*, 347.
(23) Turner, J. F. C.; Benmore, C. J.; Barker, C. M.; Kaltsoyannis, N.; Thomas, J. M.; David, W. I. F.; Catlow, C. R. A. *J. Phys. Chem.* **2000**, *104*, 7570.

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