Host/Guest Interactions and Femtosecond Scale Proton Exchange in a Zeolitic Cage

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We present a first-principles computer simulation study of the sodium hydroxosodalite dihydrate $Na_8[Al_6Si_6O_{24}](OH)_2 \cdot 2H_2O$. We have found that a fast proton exchange occurs, on the femtosecond scale, between two OH^- encapsulated in the cavities (β-cages) of the sodalite. The hosted species, formally two $O_2H_3^-$ groups not directly linked to the framework, show a correlation with the motion of the sodalite framework, indicating a nonthermal coupling between the zeolitic host and its molecular guests. The presented results are in agreement with experimental data.

Introduction

By intracage chemistry researchers refer to the physicochemical processes that occur in the cavities belonging to the lattices of the natural or synthetic crystals known as zeolites (literally boiling stones). Zeolites, beyond the geophysical relevance of the natural species, are technologically strategic materials, and their use and scope have been in continuous growth since the first synthetic crystal appeared.

We present here a study of one such intracage process: the fast exchange, on the 10^{-15} s scale, of an H^+ between two OH^- ions physisorbed in one of the most common zeolitic cavities, the β-cage of a sodalite crystal.

The exchange process involves molecular species hosted but not chemically linked to the walls in the cages of the crystal. Nevertheless a proton's jumps are correlated to the motion of the atoms forming the crystal, showing that there is coupling between guest chemicals and their crystalline host.

Zeolites form a class of porous crystalline aluminosilicates[1] of relevant technological interest.[2,3] At the microscopic level, zeolites have been the subject of several studies, mainly from the structural point of view. Such crystals are formed by a regularly connected network of corner-sharing SiO_4 tetrahedra that do not completely fill the space, but leave some empty and regular space, cavities, of molecular size. Moreover, zeolites generally have AlO_4 to SiO_4 substitutions, giving rise to a charged network, the framework, whose charge is balanced by extraframework ions, mainly alkaline and alkaline-earth cations. Besides naturally occurring zeolites, there is a wealth of synthetic structures[4] with different chemical composition. Zeolites frameworks show different topologies,[5] originating structures with a rich variety of cavities that in turn form a complementary *empty* framework made up of cages and channels: here molecules are quantitatively sieved from mixtures or extraframework ions exchanged,[2] and here guest (adsorbed) molecules undergo catalytic-like reactions.[3] It can be said that the chemistry in the *empty* framework, actually that of its guests, is influenced by the *filled* aluminosilicate framework in a peculiar way (*intracage chemistry*). It is this influence that can, and is, technologically exploited.

While the structure of most frameworks is generally well-known, guest species are characterized with lower accuracy. Moreover, the understanding of host/guest interactions is still in its infancy. In this respect modern computer simulations can give positive contributions, in particular the Car Parrinello first-principles molecular dynamics[6] due to its capability to tackle chemical events. So far, few examples of applications of this method in the zeolites field have appeared in the literature, and they were mostly devoted to the study of adsorbates bonded to the frame,[7] or to the study of the size quantization effect,[8] which is another important issue in zeolite-based technologies.[9]

Details of Calculations

Here we present results from a first-principles simulation of sodium hydroxosodalite dihydrate, $Na_8[Al_6Si_6O_{24}](OH)_2 \cdot 2H_2O$, where the molecular guests are not chemically or hydrogen bonded to the sodalite cages. Experimental data for this system have been reported,[10] where results were obtained from neutron and X-ray scattering and IR and NMR spectroscopies, for both the protonated and deuterated forms at 170 K. We refer to these data as the experimental data.

In our calculations of the protonated form, we have adopted the experimental lattice parameters and symmetry, a cubic cell of 8.87 Å, with periodic boundary conditions, The simulated cell contains 8 Na^+, 6 Al^{3+}, 6 Si^{4+}, 28 O^{6+}, and 6 H^+ ions and 224 electrons. Electron−electron interaction is calculated within a (gradient-corrected) density functional approximation,[11] while norm-conserving nonlocal pseudopotentials[12] were used for the (valence only) electron−ion interactions. Wave functions were expanded in plane waves up to a cutoff of 60 Ry (electron density up to 240 Ry). A time step of 0.12 fs was used for the integration of the equations of motion and a fictitious[6] mass of 500 au was used for the wave function coefficients while physical masses were used for the ions. After equilibration, we have followed the dynamics of the system for about 2.5 ps at an average temperature of 150 K. Energy was conserved within 10^{-5} au.

Results

Figure 1 shows the pair distribution functions, $g(r)$, that represent the probability of finding an ion at a given distance from another, calculated for the framework oxygens with the other framework atoms (Al, Si) and with the extraframework cations Na. The comparison with the $g(r)$'s obtained from the experimental coordinates, also reported in Figure 1, shows that the sodalite structure is well reproduced. The aluminosilicate framework forms polyhedral cages (two truncated octahedra per cell), each containing four Na cations forming a tetrahedron. The sodalite cages (β-cages) are the building blocks of many technologically important zeolites.[9]

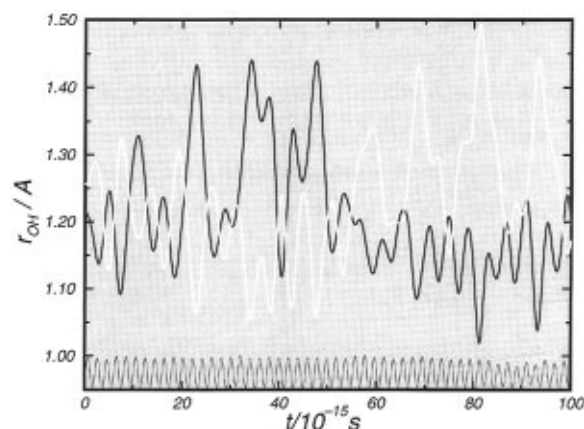**4488** *J. Phys. Chem. B, Vol. 101, No. 23, 1997*

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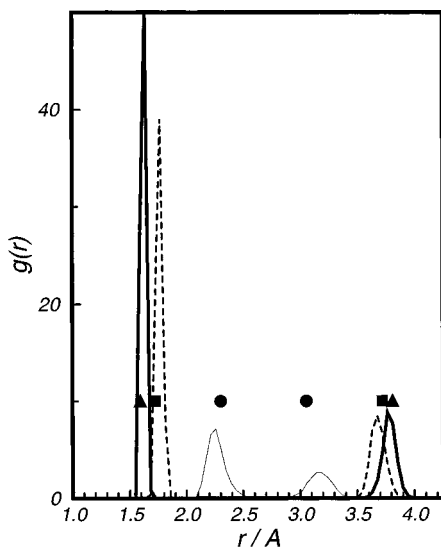
Figure 1. Pair distribution functions $g(r)$ for framework oxygens O(1) with Al, Si, and Na atoms. Thick line refers to O−Si $g(r)$, dashed line to O−Al, thin line to O−Na. Full circles refer to the peaks' positions of the O−Na $g(r)$ calculated from experimental crystallographic coordinates, full triangles to O−Si, full squares to O−Al. All distances in angstroms.

Figure 2. Calculated distances between one H(1) and its first O(2) neighbors (thick white and thick black lines). Thin black line, calculated distance of one O(2)−H(2) pair. Distances in angstroms, time in femtoseconds.

Figure 3. Snapshot of one $O_2H_3^-$ with its Na_4 tetrahedron. Large white spheres represent Na, small white spheres H(1) and H(2) atoms, dark spheres O(1) atoms. H(1) is in the picture's center.

Experimental structural data show that each $O_2H_3^-$ complex is enclathrated in one Na_4^{+4} tetrahedron, and no hydrogen bond among guest hydrogens and framework oxygens has been found. Two crystallographically different groups of H (or D) are present, one formed by two atoms, labeled H(1), and the other by four, labeled H(2), one of which, H(1), is highly disordered. Formally each complex is composed of one OH$^-$ ion and one H_2O molecule. Each oxygen in the complex, labeled O(2) (O(1) are those of the framework), is surrounded by two Na$^+$, one H(2), and one H(1); the last is shared between two O(2). However the oxygen−oxygen distance is very short, being 2.29 and 2.36 Å for the deuterated and nondeuterated sodalites respectively.
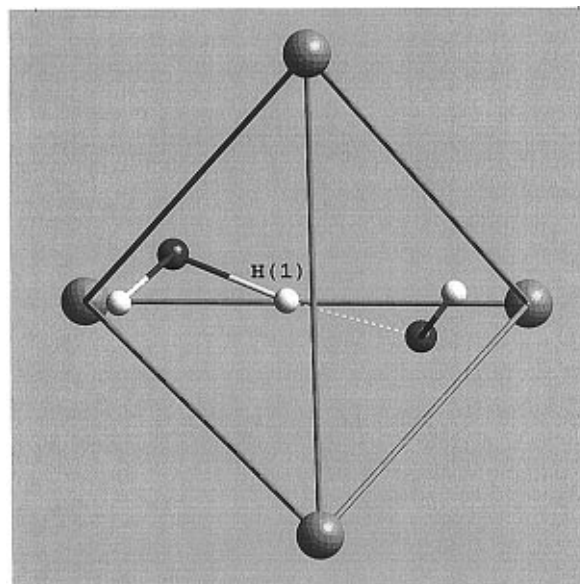
The experimental IR spectra present interesting features in the frequency regions typical of water: just one stretching (3640 cm^{-1} for OH and 2685 cm^{-1} for OD) and no bending mode of the H_2O molecule is detected. Moreover, a broad band around 1500 cm^{-1} is observed in the nondeuterated sample and assigned to the H(1) motion. This band is attributed to a strong hydrogen bond within the complex.

Our results fit with these experimental findings. The complex's oxygens are in the right positions separated on average by 2.41 Å, and we have found that each $O_2H_3^-$ is formed by two stable OH$^-$ with a third proton H(1) that undergoes a fast exchange between the two OH$^-$ groups in $O_2H_3^-$. The exchange mechanism accounts for the disorder in the crystallographic positions of the H(1) protons. Figure 2 shows the calculated distances of one H(1) from the two nearest extraframework oxygens O(2) as a function of time. It is clear that H(1) jumps from one oxygen to the other. Also shown in Figure 2 is one of the O(2)−H(2) distance oscillations: the two motions are different with the exchange time scale of the order of femtoseconds. Figure 3 shows a snapshot of one Na_4^{4+} tetrahedron with the enclathraded $O_2H_3^-$ representing a configuration when the jumping H(1) proton is close to one oxygen.

The minima in the O(2)−H(1) distances, of about 1.1 Å, indicate weak OH bonds. This means that a water molecule is not only distorted in the sodalite but has a too short mean life to be instrumentally detected, so the bending mode and the splitting in symmetric and asymmetric stretching modes typical of stable water molecules are not present in the IR signal. The simulated vibrational spectrum is shown in Figure 4: in the water stretching zone only one band is present around 3400 cm^{-1}, in qualitative agreement with the experimental pattern.

It would be of interest to know whether the proton exchange and the connected weak OH bond breaking and forming process are due to a purely thermal effect or whether there is correlation between $O_2H_3^-$ and the charged zeolite framework dynamics. Thermal coupling has been shown to exist for methane adsorbed in silicalite,[13] an all-silica zeolite with a neutral frame. There, due to host/guest stochastic collisions, the framework acts as heat reservoir for the sorbed molecules. Moreover, recent classical simulations[14] have shown that vibrational energy relaxation of a diatomic oscillator is favored at frequencies near the zeolite framework oscillation modes, indicating a dynamical host−guest coupling.

We have calculated some partial spectra from the velocities of different groups of atoms in our sample. The resolution in partial spectra[15] allows, apart from an easy way of assigning the various bands, inspection of when the motion of different atoms is correlated. The comparison with the total calculated spectrum reveals some important details. The H(1)'s partial

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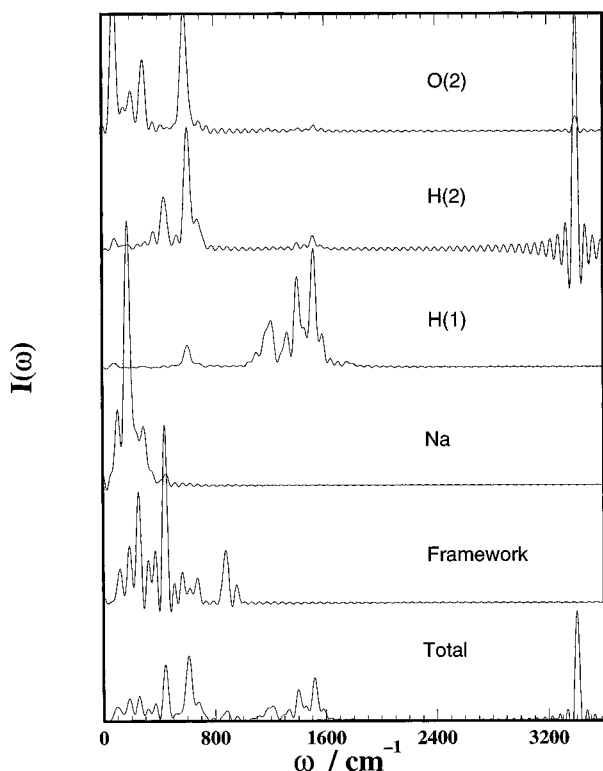
Figure 4. Calculated vibrational spectra. All spectra are normalized to 1. Partial spectra are shifted upward. Frequencies in cm^{-1}, intensities in arbitrary units.

spectrum (see Figure 4) shows that the high-frequency stretching mode is missing and that the group of peaks in the range 1000–1800 cm^{-1} should be assigned to the exchanging protons and correspond to the broad 1500 cm^{-1} absorption found experimentally. Moreover, the 3400 cm^{-1} absorbtion band is shared only by the O(2) and H(2) atoms, indicating that this mode is decoupled from the other modes in the sample. Other interesting features emerge from the partial spectra in the far-IR region. There, different groups of atoms present several bands at the same frequencies. This implies that the motion of the various groups (framework atoms, extraframework cations and anions) is correlated. This finding is not surprising if we recall the charged nature of the involved species: long range electrostatic interactions couple the electric field oscillations generated by the various groups of atoms. Thus, the physisorbed O$_2$H$_3^-$ anion is coupled to the sodalite dynamics at well-defined energy

ranges; this kind of host/guest correlation, clearly nonthermal, possibly copes with the above mentioned heat reservoir effect to drive the femtosecond scale process described here, *i.e.* a rapid bond transfer from one oxygen to the other in the O$_2$H$_3^-$ system.

In summary, we have studied the dynamics of a molecular guest in a zeolitic cage via a first-principles simulation obtaining results in agreement with experiments. We have found that a physisorbed molecular complex is involved in a femtosecond scale proton exchange and that such a process is coupled with the sodalitic framework dynamics.

References and Notes

(1) Gottardi, G.; Galli, E. *Natural Zeolites*; Springer-Verlag: Berlin, 1985.

(2) Breck, D. W. *Zeolites molecular sieves*; John Wiley: New York, 1974.

(3) Weitkamp, J. *Proceedings of the Ninth International Zeolite Conference*; von Ballmoos, R., Higgins, J. B., Treacy, M. M. J., Eds.; Butterworth-Heinemann: London, 1992; pp 13–46.

(4) Kessler, H. *Proceedings of the Ninth International Zeolite Conference*; von Ballmoos, R., Higgins, J. B., Treacy, M. M. J., Eds.; Butterworth-Heinemann: London, 1992; pp 47–92. Lewis, D. W.; Willock, D. J.; Catlow, C. R. A.; Thomas, J. M.; Hutchings, J. M. *Nature* **1996**, *383*, 604.

(5) Meier, W. M.; Olson, D. H. *Atlas of zeolite structure types*, 3rd ed.; Butterworth-Heinemann: London, 1992.

(6) Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, *55*, 2471.

(7) Campana, L.; Selloni, A.; Weber, J.; Pasquarello, A.; Papai, I.; Goursot, A. *Chem. Phys. Lett.* **1994**, *226*, 245. Campana, L.; Selloni, A.; Weber, J.; Goursot, A. *J. Phys. Chem.* **1995**, *99*, 16351. Filippone, F.; Buda, F.; Iarlori, S.; Moretti, G.; Porta, P. *J. Phys. Chem.* **1995**, *99*, 12883. Nursterer, E.; Bloch, P. E.; Schwarz, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 175. Nursterer, E.; Blochl, P. E.; Schwarz, K. *Chem. Phys. Lett.* **1996**, *253*, 448. Shah, R.; Payne, M. C.; Lee, M.-H.; Gale, J. D. *Science* **1996**, *271*, 1395.

(8) Monnier, A.; Srdanov, V.; Study, G.; Metiu, H. *J. Chem. Phys.* **1994**, *100*, 6944. Ursenbach, P.; Madden, P. A.; Stich, I.; Payne, M. C. *J. Phys. Chem.* **1995**, *99*, 6697.

(9) Ozin, G. A.; Kuperman, A.; Stein, A. *Angew. Chem., Int. Ed. Engl.* **989**, *28*, 359. Stein, A.; Ozin, G. A. *Proceedings of the Ninth International Zeolite Conference*; von Ballmoos, R., Higgins, J. B., Treacy, M. M. J., Eds.; Butterworth-Heinemann: London, 1992; pp 93–125.

(10) Wiebcke, M.; Engelhardt, G.; Felsche, J.; Kempa, P. B.; Sieger, P.; Schefer, J.; Fisher, P. *J. Phys. Chem.* **1992**, *96*, 392.

(11) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, 1989. Becke, A. D. *J. Chem. Phys.* **1992**, *96*, 2155. Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(12) Troullier, N.; Martins, J. L. *Phys. Rev. B* **1991**, *43*, 1993.

(13) Demontis, P.; Suffritti, G. B.; Fois, E.; Quartieri, S. *J. Phys. Chem.* **1992**, *96*, 1482.

(14) Demontis, P.; Suffritti, G. B.; Tilocca, A. *J. Chem. Phys.* **1996**, *105*, 5586.

(15) Madden, P. A. In *Liquids, Freezing and Glass Transition*; Hansen, J. P., Levesque, D., Zinn-Justin, J., Eds.; Elsevier Scince Publishers: Amsterdam, 1991; pp 548–627.