

Computer Simulations of Water in Zeolites

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Abstract

The complex topic of water in zeolites is viewed from completely different points: On the one hand, quantum chemical calculations at the Hartree-Fock and MP2 levels have been performed to investigate water-silicalite interaction as well as the energy barrier and water orientations during diffusion into and in the silicalite. The silicalite-water pair potential has been developed using 1.000 ab initio data points. The results indicate how water molecules move and turn during movement through the center of the silicalite pore. The energy barriers for water molecules to enter the pore and to diffuse from one channel to the other channel have been examined. It was found that water molecules enter and leave the pores preferably by pointing its dipole vector towards the center of the cavity. Calculations have been performed using extended 6-31G and 6-31G* basis sets with BSSE (basis set superposition error) corrections. On the other hand we present molecular dynamics simulations with a well established empirical water model [1] in the natural zeolite chabazit. Both the water molecule and the zeolite lattice are modelled flexible. The diffusion and the configuration of the water molecules inside the zeolite are examined.

1. Introduction

As water plays a strong and essential role as well for absorption as for catalytic properties of zeolites [2,3], the water-zeolite interaction is of great interest. Water molecules facilitate the exchange of the charge-compensating cations, essential for the industrial catalysts. In addition, all naturally zeolites are hydrated. The only available data on the water-silicalite interactions are experimental measurements by Flanigen et al. [4] and Vigne-Maeder et al. [5] which reported the initial isostatic heat of adsorption of 6 kcal/mol and the mean heat of adsorption of the first four water molecules of 9.6 kcal/mol, respectively. Vigne-Maeder et al. has also reported that an average water-silicalite interaction at 300 K is -12.5 kcal/mol and the approximated energy barrier for diffusion through the intersection between the straight and the zig-zag channels of the silicalite is 8 kcal/mol. The aim of this study is to use quantum chemical calculations at the Hartree-Fock(HF) and MP2 levels to determine the water-silicalite interactions in order to understand water

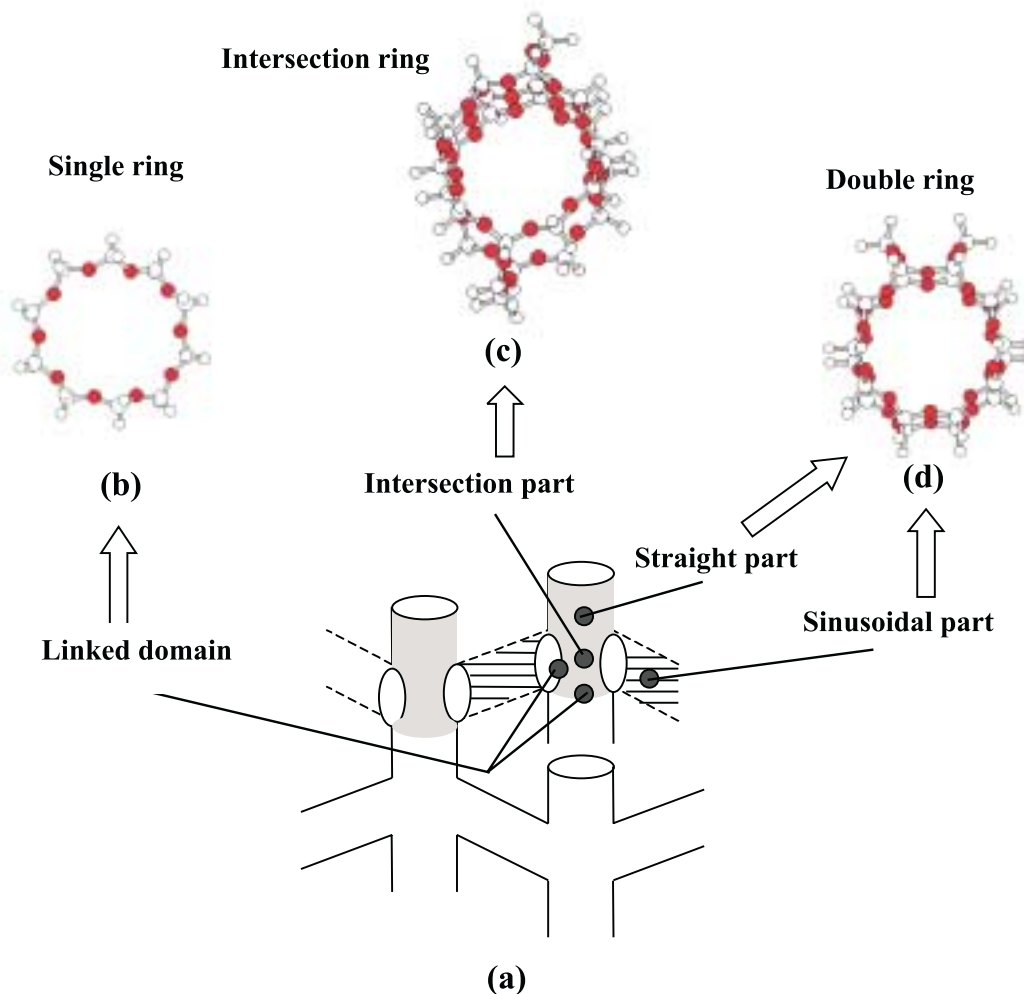


Figure 1. Schematic representations of the (a) silicalite crystal structure, (b) linked domain, (c) straight and sinusoidal channels and (d) intersection more details see text

orientation, preferable binding sites and energy barriers during the movement into and in the silicalite pores. In addition, 1,000 ab initio data points have been fitted to an analytical form. The obtained pair potential was, then, used in molecular dynamics simulation.

The natural zeolite chabazit is of special interest for the research about diffusion because of its anisotropic structure. The diffusion of water in chabazit was measured by Bär and Kärger [6] and they found an anisotropy of the diffusion, which does not fit to the crystal structure of chabazit. For this part of the study a well established empirical water model [1] is used. Vibrations are taken into account as well for the lattice as for the water molecule.

2. Computational details

2.1. Quantumchemical calculations

Ab initio calculations at the HF and the MP2 levels have been performed for the water-silicalite system using extended 6-31G and 6-31G* basis sets [7,8]. Experimental geometries of water [9] and silicalite [10] have been used and kept constant throughout the

calculations. An error due to the unbalance of the basis set, BSSE, has been also examined and taken into consideration. All calculations are performed using the G98 program [11]. The silicalite crystal structure was represented by three fragments (Figures 1b-1d), called single, double and intersection rings. The sinusoidal channels and the main part of the straight channels of the crystal (Figure 1a), in which their inner surfaces are almost identical, were represented by the double 10-oxygen membered ring (Figure 1d). This fragment (mentioned later, for simplicity, as double ring0) consists of 30 O and 22 Si atoms. The bigger fragment (35 O and 29 Si atoms) contains parts of the sinusoidal and the straight channel. It is used to represent the intersection and named intersection ring (Figure 1c). Note that, the remaining valence orbitals of the silicon atoms of both fragments are filled up by hydrogen atoms. To investigate the energy barrier via the diffusion from the intersection to the straight or to the sinusoidal channels, the water-silicalite interaction in the linked domain has been also calculated. The selected fragment is the 10-oxygen membered ring (Figure 1b).

Numerous configurations of water molecules have been generated inside the three fragments shown in Figure 1. To search for the optimal binding site, interactions between water and silicalite for each fragment have been calculated outside and inside the windows.

2.2. MD-simulations

The molecular dynamics simulations use the BJD-model [1], a flexible valence force water model. The zeolite chosen for this work is chabazite, a natural zeolite, which is especially interesting for diffusion because of its anisotropic structure. The calculations are done with flexible framework. The interaction potentials are taken from the literature: For the lattice vibrations, the model of Suffritti and Demontis [12] is used. The missing interactions are taken from Probst et al. [13].

As a starting point for the zeolite lattice, data from the X-ray diffraction study of Smith and Rinaldi [14] is used. Before starting the simulation, the lattice is relaxed with respect to the model for lattice vibrations which is used.

Due to the very fast intramolecular vibrations of the water molecules, a very short time step, $\delta t = 0.25$ fs had to be used. The simulation run was 2000000 steps long, simulating 0.5 ns. The MD-box is orthogonal, with $x = 26.4$ Å, $y = 22.683$ Å and $z = 30.2$ Å, containing 6 rhombic unit cells with 39 water molecules. In the preceding thermalization period, the temperature is controlled to produce a well defined physical starting situation at $T = 300$ K. During the evaluation period of the run, no additional thermalisation takes place.

The program is written in Fortran90 and the simulations were carried out on HP J5600.

3. Results and discussion

3.1. Optimal Method and Optimal Diffusion Path

The calculated results indicate clearly that the correlation (MP2) method and the BSSE correction do not play an essential role in predicting the geometry of the system. However, in order to increase the reliability of the interaction energies, all data points reported in this study are the results of the HF calculations with BSSE corrections. In addition, the effect of the small framework fragment on the interaction energy dominates at long distances (outside the channel) and is negligible in the region around the optimal

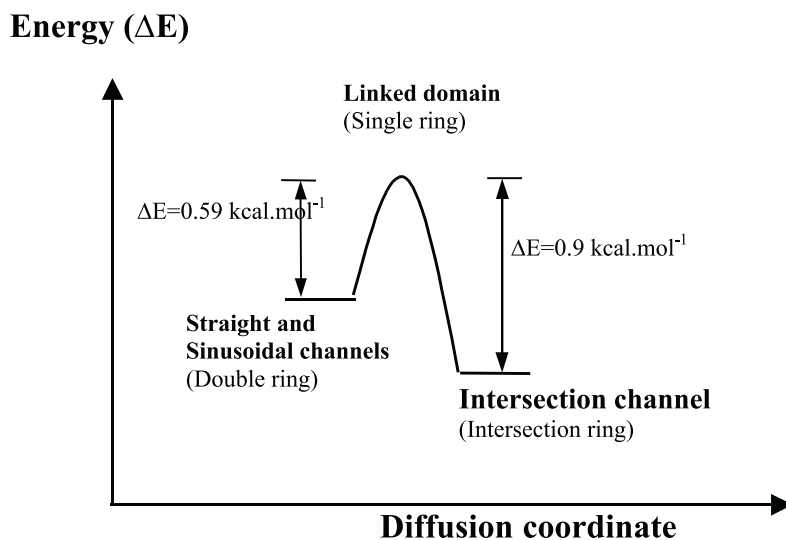


Figure 2. Changes of the water-silicalite interaction energy via the diffusion in the silicalite channels

distances (inside the channel). It is interesting to note here, therefore, that diffusion of water molecule through center of the window of the silicalite is a kind of rolling movement. The molecule must move and turn in order to find the optimal route. In addition, water enters and leaves the pores by pointing its dipole vector towards the center of the cavity.

Another energetically favourable pathway for a water molecule to move in the silicalite channel, is a kind of site hopping. It can attach to a specific binding site on the window first. Then it enters the pore, finds the next binding site and moves from one to the next site along the inner wall of the channel. Ab initio data show that

- the first binding site for a water molecule before entering the silicalite channel is to coordinate to the oxygen atom of the linked domain to form a single hydrogen bond outside the pore
- it makes no significant difference for a water molecule to enter the pore along the inner wall of the sinusoidal or straight channels, or the intersection, and
- moving of water molecule along the inner wall of the channels is less preferable than that through center of the pore.

3.2. Energy Barrier to Enter and to Cross the Channels

To investigate the energy barriers for water molecules to enter the silicalite channels, the most stable water-silicalite interaction energies inside and outside the pores have been examined and compared. The energy data indicates clearly, that water molecules must bind to the oxygen membered ring on the window first, to enter the pore of the silicalite via the linked domain (represented by the single ring). The situation is different for the

intersections. I.e., no difference has been found for water molecules between moving along the central line or starting binding to the window before entering into the silicalite via this channel. The energy difference between the two processes lies within the thermal fluctuations at room temperature. Similar investigation has been used to examine the energy barriers for water molecules to move from one channel to the other inside the silicalite. With the most stable interaction energy for encapsulation of a water molecule in the three channels, the diffusion process was schematically drawn in Figure 2. The barrier is placed at the linked domain which is represented by the single ring (Figures 1a and 1b). The amount of energy required to move from the straight or the sinusoidal channel to the intersection and back is 1.72 and 2.93 kcal/mol which is equivalent to the mean kinetic energy at a temperature of about 800 K and 1440 K, respectively. These values are much smaller than that of 8 kcal/mol yielded from the development of the water-silicalite potential map using the empirical method [5].

3.3. Ab initio Silicalite-Water Pair Potential

To develop the silicalite-water pair potential, based on ab-initio SCF calculations, the experimental geometry of silicalite and the water molecules was treated as rigid throughout the calculations. The water molecule was placed at numerous positions inside the fragments. The obtained 1,000 SCF data points were fitted to an analytical function of the form:

$$\Delta E(W, S) = \sum_{i=1}^3 \sum_{j=1}^{288} \left(\frac{A_{ij}^{ab}}{r_{ij}^6} + \frac{B_{ij}^{ab}}{r_{ij}^{12}} + \frac{C_{ij}^{ab}}{r_{ij}^8} + \frac{q_i q_j}{r_{ij}} \right) \quad (1)$$

where 3 and 288 denote the numbers of atoms of water (W) and the silicalite (S) lattice, respectively. A_{ij} , B_{ij} and C_{ij} are fitting constants and r_{ij} is the distance between an atom i of water and an atom j of silicalite, q_i and q_j are the atomic net charges of the atoms i and j in atomic units, obtained from the population analysis of the isolated molecules. Superscripts a and b on the fitting parameters have been used to classify atoms of equal atomic number but different environment conditions, for example oxygen and silicon atoms of silicalite in the different channels. The third polynomial term (C_{ij}/r_{ij}^8) was added in order to obtain better numerical fitting. The silicalite-water fitting parameters were summarized in Table 1.

Table 1 Final optimization parameters for the atoms of water interacting with the atoms in different channels (subscripts sd and st denote sinusoidal and straight channels, respectively) of the silicalite lattice (energy in kcal/mol, distance (r_{ij}) in Å and atomic net charges (q) in atomic unit).

i	j	q_i	q_j	A(Å ⁶ kcal./mol)	B (Å ¹² kcal/mol)	C (Å ⁸ kcal/mol)
O	Si _{sd}	-0.86629	1.56986	-18023.70045	-2548026.49363	241557.06465
O	Si _{st}	-0.86629	1.67270	6035.98387	117801.34659	-21871.06318
O	O _{sd}	-0.86629	-0.78493	7592.37634	275412.63747	-50145.22438
O	O _{st}	-0.86629	-0.83653	-1605.57745	-26996.92676	8135.57650

i	j	q_i	q_j	A(Å ⁶ kcal./mol)	B (Å ¹² kcal/mol)	C (Å ⁸ kcal/mol)
H	Si _{sd}	0.43314	1.56986	-7525.63685	-192955.39323	2074.08326
H	Si _{st}	0.43314	1.67270	-8362.88299	-100800.83750	34694.38682
H	O _{sd}	0.43314	-0.78493	503.177431	-282.15505	-396.99593
H	O _{st}	0.43314	-0.83653	2074.08323	5641.19273	-5018.41068

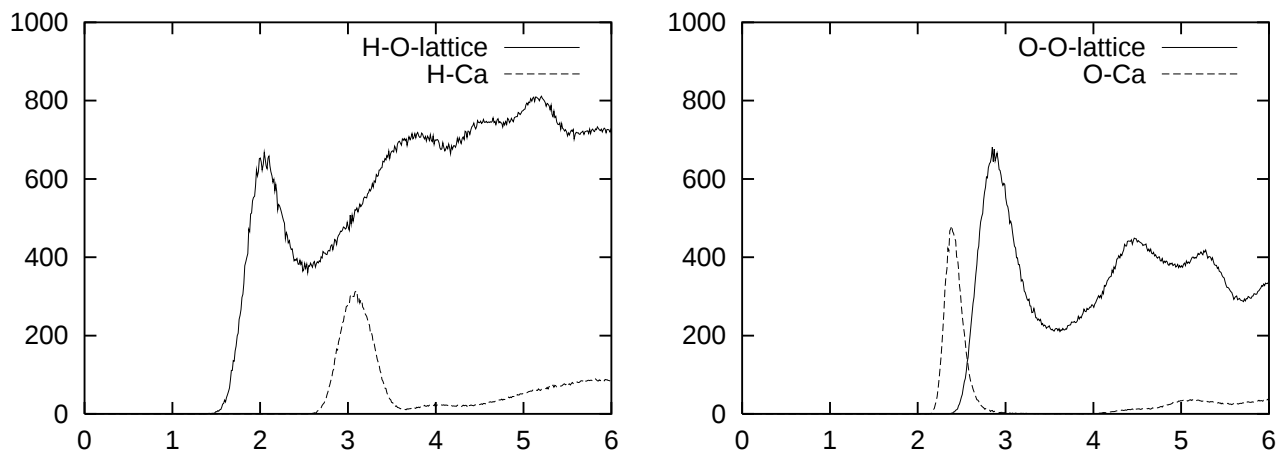


Figure 3. Radial distribution function of the water atoms with the lattice oxygen and the calcium in arbitrary units over the distance in Å

3.4. MD-Simulations

The MD simulations which have been performed so far, turned out to be too short to determine the diffusion coefficient with a good reliability, For the elements of the diffusion tensor this is valid even more. Up to now the diffusion coefficient can be only approximated as $D \approx 3 * 10^{-11} m^2/s$ with an error of up to 100 %. Therefore longer simulations will be performed to improve the reliability of the results and to analyse the anisotropy of the diffusion.

The structures of the radial distribution functions (rdf's) give some insight in the coordination of the guest molecules in the zeolite framework. The rdf $O(H_2O)-Ca$ shows only one peak, indicating, that there is only one hydration shell around the Ca-Ion. This can be seen in den H-Ca-rdf as well. The rdf of the water atoms with the framework oxygen show some more peaks, but those are probably caused by the next oxygen atoms in the framework and by a second hydration shell. The fact, that the Ca-water rdfs show only

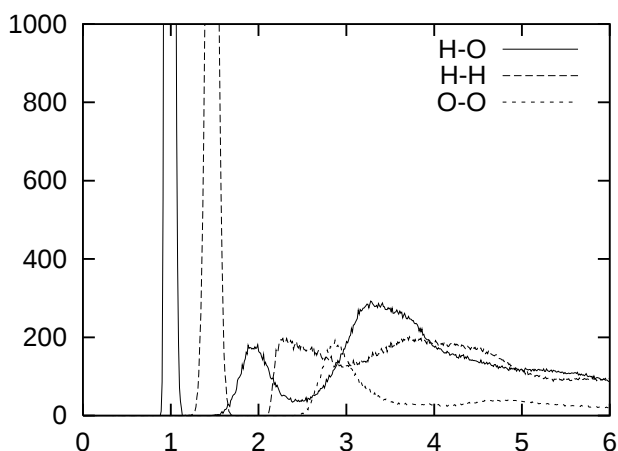


Figure 4. Radial distribution function of the the water atoms with each other in arbitrary units over the distance in Å

one peak, means, that the water molecules are at this low loading in the middle of the two Ca-Ions in each cavity. For the water-water rdfs the peaks can be easily identified for a coordination of just two atoms. Only the O-O-rdf shows a slight second peak, indicating a higher order of coordination.

4. Acknowledgements

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