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Evaluation of Various Water Models for Simulation of Adsorption in Hydrophobic Zeolites

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Abstract

We have performed a molecular simulation study on water adsorption in hydrophobic zeolites. The framework structures are truly periodic and therefore the Ewald summation is the natural choice for computing the Coulombic interactions. However, few water models have been parameterized using this method. The adsorption results are extremely sensitive to the water model used, the framework positions in the orthorhombic structure and the atomic charges of the zeolite framework. This work provides insight on the identification of the potential limitations of available force fields and models, and to the point charges used for the zeolite atoms, when they are applied to a highly hydrophobic system. We discuss feasible routes to conciliate simulation and experimental results.

Introduction

Zeolites have nowadays a great importance in industry, as they have wide applications such as catalysis, molecular sieve and gas storage¹. In addition, water is probably the most important molecule on earth, as it is present in most biological and geological proces. Currently, the main use of zeolites in the presence of water is the removal of a wide range of pollutants from water, for example industrial dyes, heavy metals, hydrocarbons and waste oils^{2, 3}. The zeolites selected for this use are usually cheap natural zeolites such as clinoptilolite or mordenite, although synthetic materials have also been used. Interestingly, it has been suggested that water can be present in Mars rocks containing zeolites⁴. Although there are many studies on water in zeolites many of the phenomena related to the presence of water in these structures, such as adsorption or cation exchange, have not been well described nor yet fully understood. Experimental data obtained by different authors or using different techniques lead to different results,

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3 as is the case with adsorption isotherms^{5, 6}. The most likely reason for this void is the
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5 exceptional nature of water. Water is a very simple molecule only composed by three
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7 atoms, and yet its behaviour is quite extraordinary and not completely understood. The
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9 behaviour of water is quite different from what is found for other materials, although
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11 deciding if these properties are anomalous depends on the materials used to compare^{7, 8}.
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17 Classical molecular simulations are normally used to calculate adsorption isotherms and
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19 diffusion in porous materials. In the search for speed and simplicity in the calculations,
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21 simple force fields are desirable. Hydrocarbons and common molecules such as nitrogen
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23 or carbon dioxide adsorbed in zeolites are examples of systems that can easily be
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25 studied with this kind of methods, obtaining adsorption data that match the experimental
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27 data^{9, 10}. Similar approaches have been used for water in zeolites, but with less success¹¹,
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12. This is attributed to the need of long equilibration cycles, and to the fact that small
changes in the potential parameters largely influences the computed values¹³.

Many different water models have been proposed during the last decades in an effort to
reproduce its most important properties. As an example, one single review gathers forty
six different water models¹⁴. None of these models is completely satisfactory when
trying to reproduce simultaneously different properties of water, such as the location of
the density maximum and the critical point. Water models have become more and more
complex with time in a search for correctly predicting the largest number of properties.
Some models include multipoles or polarization in different ways with moderate
success, and it is worth to mention non-atomistic models and models fitted after ab-
initio simulations that are obtaining promising results, as they account for most of the
abnormalities of water¹⁵⁻¹⁷.

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Molecular simulations of water in zeolites generally use simple models for water, mainly SPC and Tip4p. Furthermore, most of the studies concentrate on two types of zeolites, faujasite (FAU) and silicalite (MFI). Most simulation efforts have been focused on the study of the interaction of water with pure siliceous zeolite or alumina exchanged zeolite^{11-13, 18-25}. The first type of zeolite is known to be hydrophobic, while the second is hydrophilic. The interaction between the different atoms is usually modelled with Coulombic interactions plus a simple attractive-dispersive potential such as the Lennard-Jones or Buckingham potentials.

Adsorption and diffusion of water in MFI and FAU type zeolites have been reported by a variety of authors using several models for water. The most popular model is TIP4P²⁶, that has been used by Beauvais *et al.*¹⁸ to describe the location of the sodium cations in FAU in the presence of water, by Di Lella *et al.*¹⁹ to calculate the adsorption isotherms and cation distribution in FAU and MFI, by Trzpit *et al.*²⁰ and by Yang *et al.*²¹ to study water diffusion in MFI or by Cailliez *et al.*²² to study the interaction of water with the possible defects of the zeolite MFI. Desbiens *et al.*^{11, 23} computed adsorption isotherms in MFI with different partial charges for the framework atoms not only with the TIP4P water model²⁶, but also with the TIP5P²⁷, MSPC/E²⁸ and the polarizable DEC²⁹ model. Ramachandran *et al.*¹³ simulated adsorption of water in MFI with TIP4P²⁶ and SPC/E³⁰, trying to reproduce small defects in the framework with extra water molecules. The SPC³¹ water model has been also widely used for adsorption of water in zeolites. Hence, Pellenq *et al.*²⁴ used this model in MFI, including polarization in all the atoms of the system, to study polarization effects, configuration energy and heats of adsorption, and Puibasset *et al.*¹² used this simple model of water in conjunction with a more

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2
3 complex, polarizable potential for the interactions water-zeolite in MFI to study
4 adsorption and formation of water clusters³¹. Other models for water such as TIPS2³²
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6 have also been used by Halasz *et al.*²⁵ to compute the adsorption isotherms of water in
7
8 different faujasites, and similar studies with similar techniques and models have been
9
10 performed in other types of zeolites, for example in zeolite A (LTA)³³, heulandite
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12 (HEU) and clinoptilolite (CLI)³⁴.
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20 The overwhelming majority of water models use a direct pairwise Coulombic
21 interaction truncated at 9 or 10 Angstrom. This may give reasonable results for pure
22 water as a liquid due to a large effective charge screening but prohibits transferability to
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24 multi-component or adsorptive systems where such a screening is absent. Moreover,
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26 zeolites are crystalline materials described by a periodic unit cell. For systems that are
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28 periodic the long-range interactions can be computed exactly up to an arbitrary
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30 precision³⁵. Recently, researchers have become more aware of the special nature of
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32 charge interactions in nanoporous materials. Straightforward truncated, pairwise
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34 Coulombic calculations including methods like the Wolf-method turn out to be non-
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36 transferable to zeolites because of the non-uniform local density (dense framework with
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38 open voids)³⁶. This work provides a simulation study on water adsorption in MFI-type
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40 zeolite using classical force fields to identify the possible limitations of available
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42 methods and force fields parameters when they are applied to this special and highly
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44 hydrophobic system. We also explore possible routes to conciliate simulation and
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46 experimental results.
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58 Simulation details

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3 Adsorption isotherms are calculated in the grand-canonical ensemble, in which the
4 temperature T , the volume V , and the chemical potential μ are kept fixed. The imposed
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6 chemical potential μ is related to the fugacity and can be computed from the equation of
7
8 state for a given pressure. The gas phase was treated as an ideal gas, as the pressures
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10 considered were low. In the case of liquid water, the NIST database³⁷ is used to obtain
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12 the chemical potential. For water, this database covers a validity range for temperatures
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14 from the melting line (lowest temperature 251.2 K at 209.9 MPa) to 1273 K and
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16 pressures up to 1000 MPa. The equation of state for a particular molecular model can be
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18 computed instead, but this calculation is long and is subject to large error bars. Some
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20 studies have shown that the deviation between the calculated and the experimental
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22 chemical potential is negligible in a large range far from the critical conditions¹¹. For
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24 high-density systems, such as liquid water, the probability of successfully inserting one
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26 molecule in the system is very low. For that reason, the insertion/deletion of molecules
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28 in the system were performed using the Configurational-bias Monte Carlo technique
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30 (40% of the MC moves) while other MC moves were attempted during the simulation:
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32 regrowth (20%), rotation (20%) and translation (20%) of a randomly selected molecule.
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34 The maximum translational and rotational displacements were adjusted to achieve an
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36 acceptance probability of 50%. The pore volume in the frameworks was calculated
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38 using the Widom particle insertion method³⁸. The Henry coefficients and heats of
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40 adsorption at zero coverage were computed using MC in the NVT ensemble. The Henry
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42 coefficient is related to the excess chemical potential, which is computed using
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44 Widom's test particle method. More details can be found in ref 38.
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3 For calculating the liquid density of water, the NPT ensemble is chosen. In these
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5 simulations, a fixed number of particles are initially placed in a cubic box
6 with an initial
7 length of 25Å, and then the box length is allowed to change. All the potentials were
8 truncated to different *cutoff* radius and shifted depending on the water model used. At
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10 every moment the box length was at least twice the size of the *cutoff* radius. In our
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12 Monte Carlo simulations, changes in the volume of the system were attempted with a
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14 probability of 10%, while regrowth of the molecule, rotation and translation had a
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16 probability of 30%. The maximum translational and rotational displacements were
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18 adjusted to achieve an acceptance probability of 50%.
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24 Simulations are performed in cycles, and in each cycle MC moves are chosen at
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26 random. The number of MC moves per cycle is equal to the number of particles present
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28 in the system, with a minimum of 20 moves per cycle. More details on the simulation
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30 technique can be found elsewhere^{39, 40}. In the case of calculations of water density or
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32 water adsorbed in zeolites, it has been repeatedly reported that the number of MC or
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34 MD steps necessary for equilibration of the system is unusually large¹³. This is
35
36 especially true when simulating adsorption inside zeolites in the region that is between
37
38 the inflexion point and the saturation zone, as in this region the shape of isotherm is
39
40 very steep. Water molecules interact more strongly with themselves than with the
41
42 zeolite, and form clusters that grow until they fall apart and the process begins again⁴¹.
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44 In this way, to obtain a proper statistic description of the system from the simulation,
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46 the number of cycles has to be large. For the critical zone of the isotherm, up to $5 \cdot 10^5$
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48 initialization cycles are needed; for the other points of the isotherm $1 \cdot 10^5$ initialization
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50 cycles are used and $2 \cdot 10^5$ for production. For the NPT ensemble $5 \cdot 10^4$ initialization
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52 cycles are used and at least $2 \cdot 10^5$ for production.
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3 The model Tip5pEw⁴² is a suitable model for studying adsorption of water in zeolites,
4 because its properties have been refitted using Ewald sums and the adsorption isotherms
5 can be computed with a good precision. There are other models that also have been
6 parameterized with Ewald sums, such as Tip4pEw⁴³, Tip3p-PME⁴⁴, SPC/FW⁴⁵, or
7 SWM4-DP⁴⁶. The last two are flexible water models and therefore their use would
8 increase the simulation time. In any case, flexible water models could be interesting
9 when studying mixtures of water with large molecules or interaction with ions, as it has
10 been shown that flexibility and polarizability can be important in this case^{14, 46, 47}. No
11 hydrolysis is observed in the adsorption of water in zeolites due to the weak interaction
12 of water with the zeolite^{48, 49}, so this effect was not included in our simulations.
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29 Hydrocarbons were modelled using a united atom model, in which CH_x groups are
30 considered as single, chargeless interaction centres with their own effective potential⁵⁰.
31 The bond-stretching, bond-bending and torsion potentials of the alkane, as well as the
32 alkane-alkane and alkane-zeolite potentials, were obtained from a recent
33 parameterisation that accurately describes the adsorption isotherms of alkanes⁵¹. A rigid
34 atomistic model of CO₂ is used⁵² with a bond length of 1.16 Å. Every atom of CO₂ has a
35 partial charge and the dispersive interactions between the molecules are described by a
36 Lennard-Jones potential. The interaction with the zeolite is taken from García-Pérez et
37 al¹⁰. All Lennard-Jones parameters and atomic charges used in this work are listed in
38 Table 1.
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55 To set the crystallographic positions of the atoms of the zeolite, we considered two
56 different X-ray characterizations of silicalite, the first one from Olson et al.⁵³ and the
57 second one from van Koningsveld et al.⁵⁴. Both of them are orthorhombic with space
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3 group Pnma. For both structures, the simulations were performed using eight unit cells
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5 (2x2x2) with periodic boundary conditions, with one size at least twice the *cutoff* radius.
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7 Simulations were performed using a rigid framework⁵⁵. The partial charges of the
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9 framework atoms were taken from the work of Calero et al.³⁹. As the Coulombic
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11 interactions between water and zeolite dominate the adsorption properties of the model
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13 due to the large dipole moment of the water molecules, during our study we test
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15 different charges in the Si atoms, ranging from 0e+ to 3.5e+. To preserve the
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17 **electrostatic neutrality** of the zeolite, every oxygen atom in the zeolite is assigned to half
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19 the charge of the silica atoms (with opposite sign). The Coulombic interactions were
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21 calculated using **the Ewald summation** technique³⁵ with a relative accuracy of 10⁻⁶. The
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23 non-Coulombic interactions of the adsorbates with the framework are dominated by the
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25 dispersive forces between the pseudo-atoms and the oxygen atoms of the zeolite. These
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27 interactions are modelled through an effective Lennard-Jones potential that only takes
28
29 into account the oxygen atoms. The Lennard-Jones parameters of Pascual *et al.* were
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31 implemented⁵⁶ together with Lorentz-Berthelot mixing rules. All Lennard-Jones
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33 potentials were truncated and shifted at a *cutoff* radius of 12Å.
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43 **Results and Discussion**

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46 **Choosing Water Models.** Different researchers have used a wide range of classical
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48 water models trying to describe the different properties of water in zeolites. The bond
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50 length and bond angle of these simple models were usually taken from the experimental
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52 gas phase values, while the interactions were adjusted to reproduce the most important
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54 properties of water and particularly the water density at standard conditions. These
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56 models were fitted for different *cutoff* values for the Coulombic and Lennard-Jones
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58 interactions. We found large differences between simulations that use the Ewald
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3 summation and those that use a direct pairwise potential with spherical *cutoff*⁵⁷. Some
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5 authors claim that particular models of water such as Tip4p/2005⁵⁸ or SPC/Fw⁴⁵ are
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7 better than others when they are compared at the same simulation conditions (cutoff
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9 radius, use of switching functions, method to evaluate the Coulombic energy).
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11 However, it has been shown that the particular simulation conditions are vital for the
12
13 final result of a given simulation⁵⁷. To calculate water properties using one particular
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15 water model, the specific simulation conditions used for the parameterization of that
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17 model should be used. If this is not the case, deviations from the expected behaviour can
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19 be observed, and therefore the former comparison does not make any sense. To
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21 illustrate this point, Figure 1 compares the water density obtained at 1 atm. in the
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23 temperature region that spans from -30°C to 110°C using a variety of models. The
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25 density was computed using Molecular Dynamics simulations in the NPT ensemble
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27 with SPC³¹, Tip4p²⁶, Tip5p²⁷, and Tip5pEw⁴² models for water. Besides the
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29 experimental data, we plot water densities obtained with a) the parameters that were
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31 originally used to fit the particular water model, and b) the same parameters *but* using
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33 Ewald summations and a Lennard-Jones *cutoff* of 12 Å. Most of the models give a
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35 precise estimation of the density at 25°C using the original parameters, as they were
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37 adjusted to reproduce this value. Among the models tested, only Tip5p and Tip5pEw
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39 reproduce the maximum of density around 4°C using the originally reported parameters.
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41 Note that the Tip5pEw is the only model that also matches the experimental density
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43 using conditions other than those considered in the original fitting. This can be easily
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45 explained since Tip5pEw model was originally fitted using Ewald summations and a
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47 variable Lennard-Jones *cutoff* equal to half the box length, which was always close to
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49 12 Å. Furthermore, with Tip5pEw we obtain the best results for the density as a
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51 function of temperature.
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6 Although experimentally the bulk dipole moment of water is reduced upon adsorption
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8 in zeolites, the polarization induced by the zeolite in water is rather small, as well as the
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10 influence of the zeolite in the hydrogen bonds of water⁵⁹. Quantum simulations have
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12 also found problems describing the polarization of water molecules in zeolites²⁴. As
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14 polarity is more important than polarizability in the adsorption of molecules in these
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16 materials, in our study we select the non polarizable Tip5pEw⁴² model for water, that is
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18 simply a Tip5p model parameterized for Ewald sums. Similar models such as
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20 Tip4pEw⁴³, Tip3p-PME⁴⁴, SPC/FW⁴⁵ or SWM4-DP⁴⁶ are also possible candidates,
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22 though some of them are flexible or polarizable and they might give a better description
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24 of some particular properties of the system at a larger computational cost. The SPC,
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26 Tip4p and other similar models can also be used in the study of water adsorption in
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28 zeolites, but due to the importance of the long range interactions, their Ewald-fitted
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30 versions should be used instead.
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39 **Differences between the two characterizations of silicalite.** There are two different
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41 characterizations of the orthorhombic structure of silicalite, one from Olson et al.⁵³ and
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43 another from van Koningsveld et al.⁵⁴. Both structures are similar with slight differences
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45 in the atomic positions. Computing the pore volumes using the Widom insertion
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47 technique lead to 0.166 cm³/g and 0.163 cm³/g for the structures of Olson and van
48
49 Koningsveld, respectively. The two structures differ mainly at the channel intersections.
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51 The maximum deviation between equivalent atoms is lower than 0.37 Å. These
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53 differences have been shown to be important when simulating tight-fitting molecules
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55 such as benzene and xylene, as they can lead to large changes in the computed
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3 properties attributed to the different electrostatic potential felt by the molecules at the
4 intersections⁶⁰.
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10 Water is a small molecule that does not interact strongly with silicalite, so the
11 adsorption in the two structures of MFI is expected to be similar. Figure 2 compares
12 experimental^{23, 61} and simulation data for water adsorption in both MFI structures at 300
13 K. We are using the Tip4p model at the same simulation conditions than previous
14 groups^{11, 19}, assigning a partial charge of $1.4 e^-$ to the silicon atoms of the framework
15 (and therefore a partial charge of $-0.7 e^-$ to the oxygen atoms). Although the adsorption
16 isotherms for both frameworks have a similar shape, for a given loading the pressure
17 differs up to 60 MPa. This large difference between the isotherms calculated in the two
18 different structures is completely unexpected if compared with the isotherms calculated
19 for other molecules of similar size such as propane (Figure 3) and carbon dioxide
20 (Figure 4), that accurately reproduce the experimental data^{10, 62}. Differences between
21 isotherms are minor for the non-polar propane and low for the quadrupolar carbon
22 dioxide, indicating that the discrepancies on the adsorption isotherms for water can be
23 mainly attributed to the water dipole moment. Larger, non-polar molecules such as n-
24 heptane show similar adsorption for both structures at the lower and the higher pressure
25 regions. However, at intermediate pressures the adsorption in the structure of Olson is
26 notably higher than in the van Koningsveld structure. The calculated and experimental
27 isotherms⁶³ are shown in Figure 5. The differences are most likely due to the
28 commensurate "freezing" of n-heptane in the sinusoidal channels. This affects the
29 adsorption at the channel intersections, where the differences between the zeolite
30 structures are the largest⁶⁴.
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3 Similar studies have been performed for other water models. For example, calculated
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5 adsorption isotherms for the flexible models SPCFw and F3C in both structures are
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7 shown in Figure 6. These models showed reduced pressure differences for the
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9 condensation point in the two different characterizations of MFI, since condensation
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11 takes place at low pressures. Apart from this result, large deviations between the two
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13 isotherms are observed as for the other models. Furthermore, the isotherms deviate
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15 significantly from the experimental data. The adsorption isotherms obtained for the
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17 Tip5pEw model are shown in Figure 7. In this case, the differences are much larger than
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19 for the rest of the models tested. The reason is that, for Olson framework, the
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21 condensation takes place at low pressures due to a water phase transition. These results
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23 suggest that the differences originate from the particular behavior of water in this type
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25 of material and not from the details of the force field used. In particular, the large
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27 dipolar moment of water must play an important role in the adsorption. The differences
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29 in adsorption in both characterizations also increase with the dipole or quadrupolar
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31 moment of the molecule, from propane to carbon dioxide and finally water, due to the
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33 large differences in the electrostatic energy at the channel intersections of MFI between
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35 both structures. In all cases, the adsorption capacity in the structure of Olson is larger
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37 than in the structure of van Koningsveld, since the first has a slightly larger pore
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39 volume.
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50 To better understand the sensitivity of water to small changes in the zeolite structure, we
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52 have generated a series of new structures along a path that continuously transforms the
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54 van Koningsveld into the Olson structure. For every generated structure, we have
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56 computed the heats of adsorption of water, carbon dioxide, and propane as shown in
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58 Figure 8. In the case of propane and carbon dioxide, the heat of adsorption remains
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3 practically constant for every structure generated, indicating that the adsorption is barely
4 influenced by small changes in the zeolite structure. This point supports our previous
5 observation that the adsorption isotherms of these molecules in the Olson and van
6 Koningsveld structures do not show large differences. For water, structures which differ
7 less than 0.2 Å from the van Koningsveld have a similar heat of adsorption. However,
8 structures that differ more than this value from the van Koningsveld structure (and
9 therefore closer to the Olson structure) have a significant lower heat of adsorption.
10 Apparently the adsorption of water in the Olson structure is much more sensitive to
11 changes in the atomic positions than the van Koningsveld structure. This could be an
12 indication that the van Koningsveld structure gives a better description of the
13 experimental adsorption isotherm of water in MFI.
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31 To illustrate the importance of the channel intersections of MFI in the adsorption of
32 water, we have calculated the Henry coefficients and heats of adsorption in different
33 locations of the zeolite: straight channels, zig-zag channels and intersections (Table 3).
34 While in both types of channels the values are similar for both structures, in the
35 intersections the differences are quite large. The heats of adsorption for the Olson
36 structure are twice than those for the van Koningsveld structure, and the Henry
37 coefficients are three orders of magnitude larger for the Olson structure. Furthermore,
38 the Henry coefficients indicate that the preferential adsorption sites are the zig-zag
39 channels for the van Koningsveld structure, and the intersections for the Olson
40 structure. This explains the large differences in heat of adsorption found for the whole
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3 The sensitivity of water to the force field parameters can be attributed to the
4 hydrophobic character of all-silica zeolites and not only to the MFI structure, we have
5 performed a parallel study with all-silica DDR, MFI, and LTA zeolites. While MFI is a
6 system of intersecting channels, DDR is formed only by longitudinal channels and LTA
7 is a cage-like structure. For every atom of the structures, we defined a random direction
8 of translation and a random displacement, keeping the size of the unit cell fixed. The
9 maximum displacement was set to be shorter than the maximum difference between the
10 two characterizations of MFI, and a continuous series of structures were generated in
11 line with the previous study. The heats of adsorption of water in the resulting structures
12 are shown in Figure 9. The general trend of the heat of adsorption with the increasing
13 distortion is the same for all structures. It is important to note that the gradient of the
14 curves for all the zeolites considered is similar, which could be indicative of a general
15 behavior for all-silica zeolites. As in the former study, the structures closer to the initial
16 one have a heat of adsorption very similar to the original value, although the
17 displacement at which the drop in the heat of adsorption takes place is shorter.

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41 **Choosing Atomic Charges for the Framework.** The influence of the electrostatic
42 interactions in the adsorption of polar molecules was studied, progressively reducing the
43 point charge of the Si atoms in the structure from $2.05 e^-$ to $0.5 e^-$. To keep the
44 electrostatic neutrality of the structure, the charge of the oxygen atoms were changed
45 accordingly and made equal to half the charge of the silica atoms with opposite sign. In
46 the case of non-polar molecules such as alkanes no effect is observed, as electrostatic
47 interactions between the adsorbed molecules and the framework are not present in the
48 force field. In Figure 4 it is shown that for carbon dioxide a small shift of the isotherm
49 at high pressure is observed when decreasing the silicon charge. This shift can be

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3 explained by the lower interaction of the host molecules with the structure, although the
4 differences on adsorption for the two characterizations remain similar. We found a
5 complete different behavior for the Tip5pEw water model (Figure 7), where the
6 decrease in the silicon charge induces a large shift of the complete isotherm to much
7 higher pressures and reduces adsorption differences between the structures.
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17 The influence of charge and structure was studied for different water models. The Henry
18 coefficients and heat of adsorption of the SPC, Tip3p, Tip4p, Tip5p, Tip5pEw and
19 Tip6p models were calculated for the Olson and the van Koningsveld structures with a
20 partial charge for the silica atoms of $2.05 e^-$, $0.786 e^-$, and $0.5 e^-$. The obtained results
21 are presented in Table 2 showing little differences between different models at the same
22 simulation conditions. This is consistent with our previous assumption that the
23 particular behavior of water in zeolites is due to its large dipole moment. The
24 differences between the Olson and the van Koningsveld structures are remarkable when
25 we use a larger charge for the silicon atoms: there is a difference of one order of
26 magnitude in the Henry coefficient, and the heats of adsorption in the Olson structure
27 are around 50% larger than those in van Koningsveld structure. When we decrease the
28 charge of the silicon atoms, these differences also decrease, indicating again the
29 importance of the electrostatic interactions for the special behavior of water.
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51 The importance of the framework charges in the adsorption of water inspired us to try to
52 fit the water-zeolite interaction parameters, as well as the point charges of the atoms of
53 the framework, aiming to reproduce the experimental adsorption isotherms. However,
54 we failed to find such a set of parameters since the shape of the experimental isotherm is
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3 very steep in the inflexion region, and therefore very sensitive to the parameters of the
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5 interaction potential.
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10 **Conclusions**

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12 The adsorption properties of water in zeolites are difficult to describe both
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14 experimentally and by molecular simulations. The experiments are complicated by the
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16 fact that water adsorbs at very low pressure at the defects. Therefore, the pressure where
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18 the sharp increase in adsorption occurs is sensitive to defects, as well as to the structural
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20 crystallographic positions (in addition to pore blockage/collapse etc.). On the simulation
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22 side, there are only a few water models that are suitably calibrated for studying water
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24 adsorption in zeolites. The Tip5pEw model is calibrated using the Ewald summation
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26 and reproduces well the bulk properties of water. Therefore, it is a suitable candidate to
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28 describe water in a periodic environment, though there is still much uncertainty in the
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30 proper magnitude of the charges, especially of the framework atoms. The dipole
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32 moment of water results in behavior that is completely different from other molecules
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34 with similar size but without dipole moment, so the partial charge of the zeolite atoms is
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36 a critical parameter that has to be chosen carefully. The adsorption of water is also very
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38 sensitive to small changes in the precise location of the zeolite atoms. We provided
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40 evidence that this sensitivity is directly related to the coupling of the dipole of the water
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42 molecules with the electric field induced by the zeolite. Therefore, one has to be
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44 cautious when computing the properties of water and highly polar molecules in these
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46 hydrophobic structures.
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54 **Acknowledgments**

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Table 1 Lennard-Jones parameters and initial partial charges used in this work. Lorentz-Berthelot mixing rules are used for the interaction between water and the zeolite. The water model Tip5pEw has two dummy atoms, labeled as D.

Atom(s)	ϵ/k_B	σ (Å)	q (e ⁻)
Si ³⁹			2.05
O _{zeo} ⁵⁶	93.53	3.0	-1.025
O _{water} ⁴²	89.516	3.097	
H _{water} ⁴²			0.241
D _{water} ⁴²			-0.241
C _{CO2} ⁵²	28.129	2.76	0.6512
C _{CO2} - O _{zeo} ¹⁰	50.2	2.7815	
O _{CO2} ⁵²	80.507	3.033	-0.3256
O _{CO2} - O _{zeo} ¹⁰	84.93	2.9195	
CH ₃ ⁵⁰	108.0	3.76	
CH ₃ - O _{zeo} ⁵¹	93.0	3.48	
CH ₂ ⁵⁰	56.0	3.96	
CH ₂ - O _{zeo} ⁵¹	60.5	3.58	

Table 2 Henry coefficients (a) in $\text{mol}\cdot\text{kg}^{-1}\cdot\text{Pa}^{-1}$ and heats of adsorption (b) in $\text{kJ}\cdot\text{mol}^{-1}$ of water in MFI, calculated with different water models, the two different, orthorhombic characterizations of MFI and different partial charges for the silica atoms of the structure (q). The values in parenthesis indicate the error in the last digits.

a)

q (e ⁻)	Structure	SPC	Tip3p	Tip4p	Tip5p	Tip5pEw	Tip6p
2.05	van K.	2.4×10^{-5} (3)	2.1×10^{-5} (3)	2.0×10^{-5} (3)	2.0×10^{-5} (2)	2.5×10^{-5} (3)	2.2×10^{-5} (2)
	Olson	3.0×10^{-4} (9)	3.7×10^{-4} (1)	1.5×10^{-4} (1.0)	5.2×10^{-4} (5.9)	8.3×10^{-4} (7.2)	1.1×10^{-4} (2)
0.786	van K.	8.0×10^{-7} (1)	8.0×10^{-7} (1)	8.1×10^{-7} (1)	8.1×10^{-7} (1)	9.3×10^{-7} (1)	1.1×10^{-6} (1)
	Olson	1.0×10^{-6} (1)	1.0×10^{-6} (1)	9.9×10^{-7} (1)	1.0×10^{-6} (1)	1.2×10^{-6} (1)	1.3×10^{-6} (1)
0.5	van K.	5.8×10^{-7} (1)	5.8×10^{-7} (1)	6.0×10^{-7} (1)	6.0×10^{-7} (1)	6.9×10^{-7} (1)	8.4×10^{-7} (1)
	Olson	6.3×10^{-7} (1)	6.3×10^{-7} (1)	6.4×10^{-7} (1)	6.5×10^{-7} (1)	7.5×10^{-7} (1)	8.9×10^{-7} (1)

b)

q (e ⁻)	Structure	SPC	Tip3p	Tip4p	Tip5p	Tip5pEw	Tip6p
2.05	van K.	-28.5 (8)	-27.8 (8)	-27.4 (9)	-28.3 (9)	-28.9 (1.0)	-27.1 (8)
	Olson	-41.7 (2.1)	-42.0 (2.6)	-36.6 (5.0)	-44.9 (2.5)	-44.6 (4.3)	-35.0 (1.9)

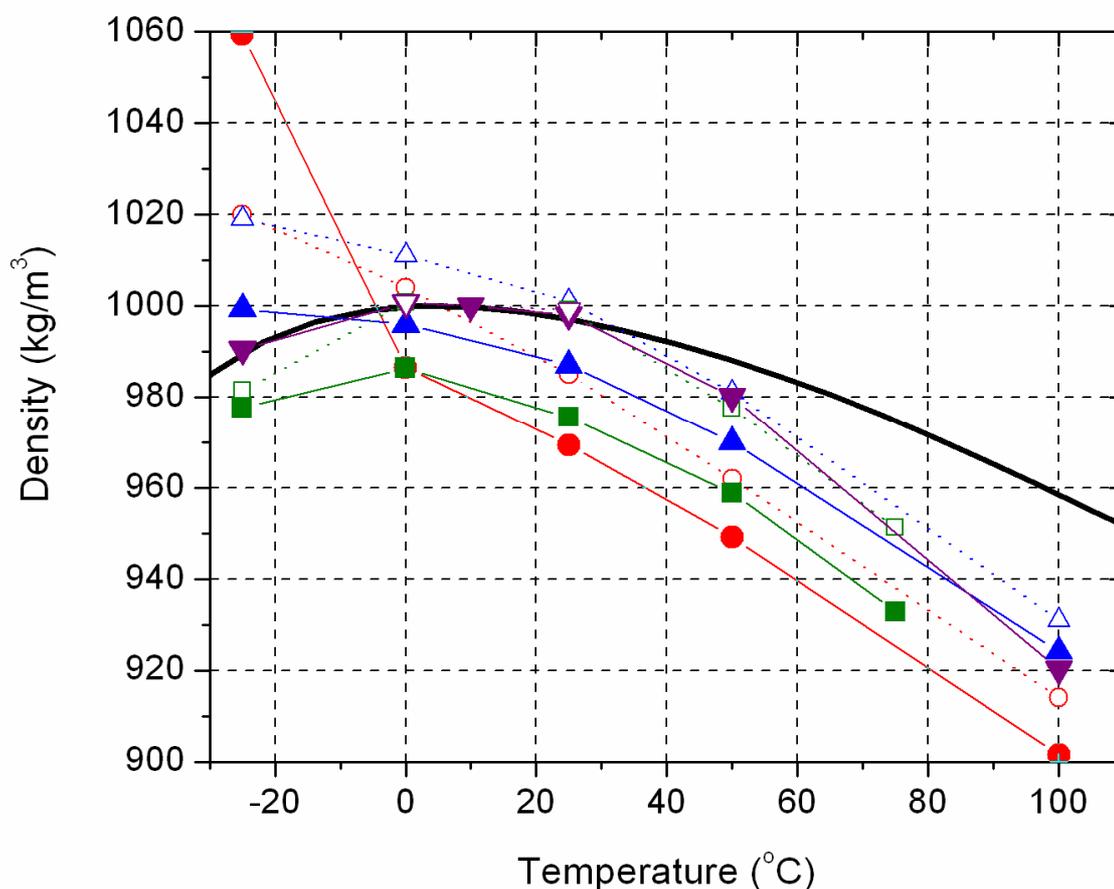
0.786	van K.	-12.8 (1)	-12.8 (1)	-12.8 (1)	-12.8 (1)	-13.2 (1)	-13.6 (1)
	Olson	-13.7 (1)	-13.7 (1)	-13.6 (1)	-13.6 (1)	-14.1 (1)	-14.2 (1)
0.5	van K.	-11.2 (1)	-11.2 (1)	-11.3 (1)	-11.3 (1)	-11.6 (1)	-12.1 (1)
	Olson	-11.5 (1)	-11.6 (1)	-11.6 (1)	-11.5 (1)	-11.9 (1)	-12.3 (1)

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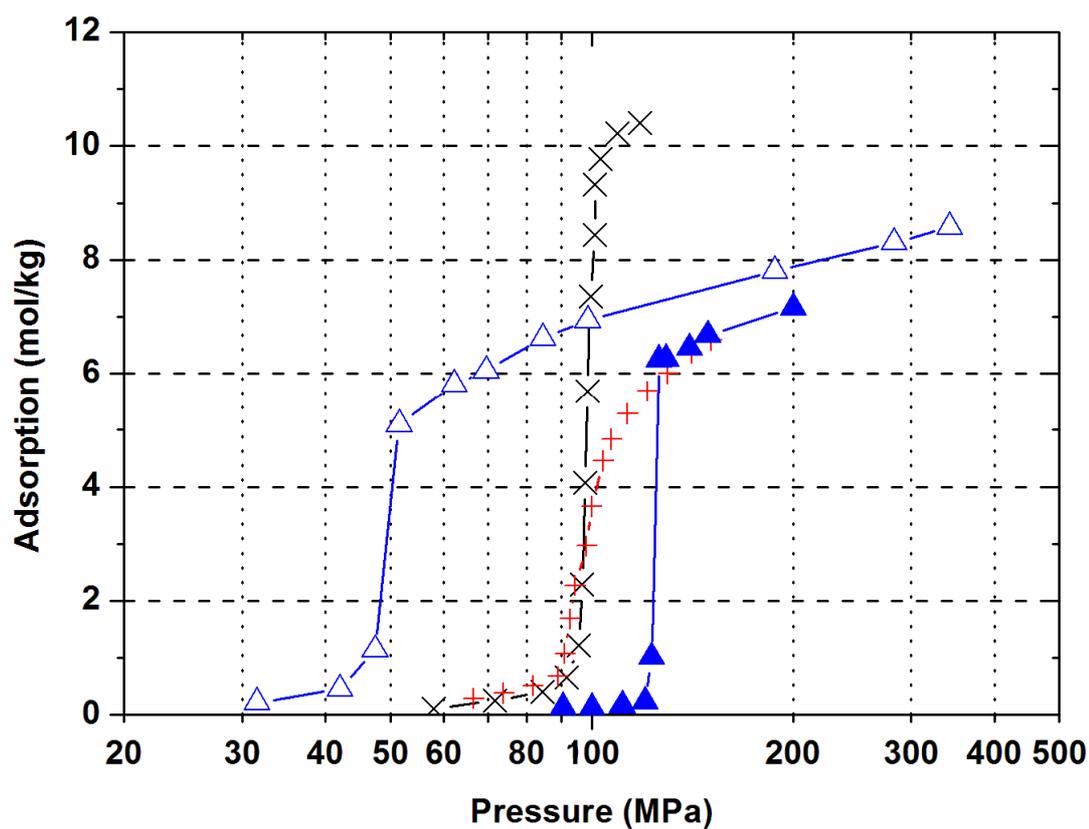
Table 3 Henry coefficients and heats of adsorption of water in MFI, calculated in the Olson and van Koningsveld characterizations of MFI and at different locations in the structure: straight channels, zig-zag channels and intersections. The value obtained for the whole structure is also included for comparison. The values in parenthesis indicate the error in the last digits.

Location	K_H (mol kg ⁻¹ Pa ⁻¹)		ΔH (kJ mol ⁻¹)	
	van Kon.	Olson	van Kon.	Olson
straight channels	6.2x10 ⁻⁶ (6)	1.7x10 ⁻⁵ (1)	-24.7 (6)	-27.8 (2)
zig-zag channels	1.7x10 ⁻⁵ (3)	1.7x10 ⁻⁵ (1)	-30.3 (9)	-28.9 (2.3)
intersections	7.9x10 ⁻⁷ (5)	6.0x10 ⁻⁴ (1.4)	-17.2 (4)	-44.9 (2.1)
Whole structure	2.5x10 ⁻⁵ (3)	5.7x10 ⁻⁴ (1.0)	-28.9 (1.0)	-44.6 (4.3)

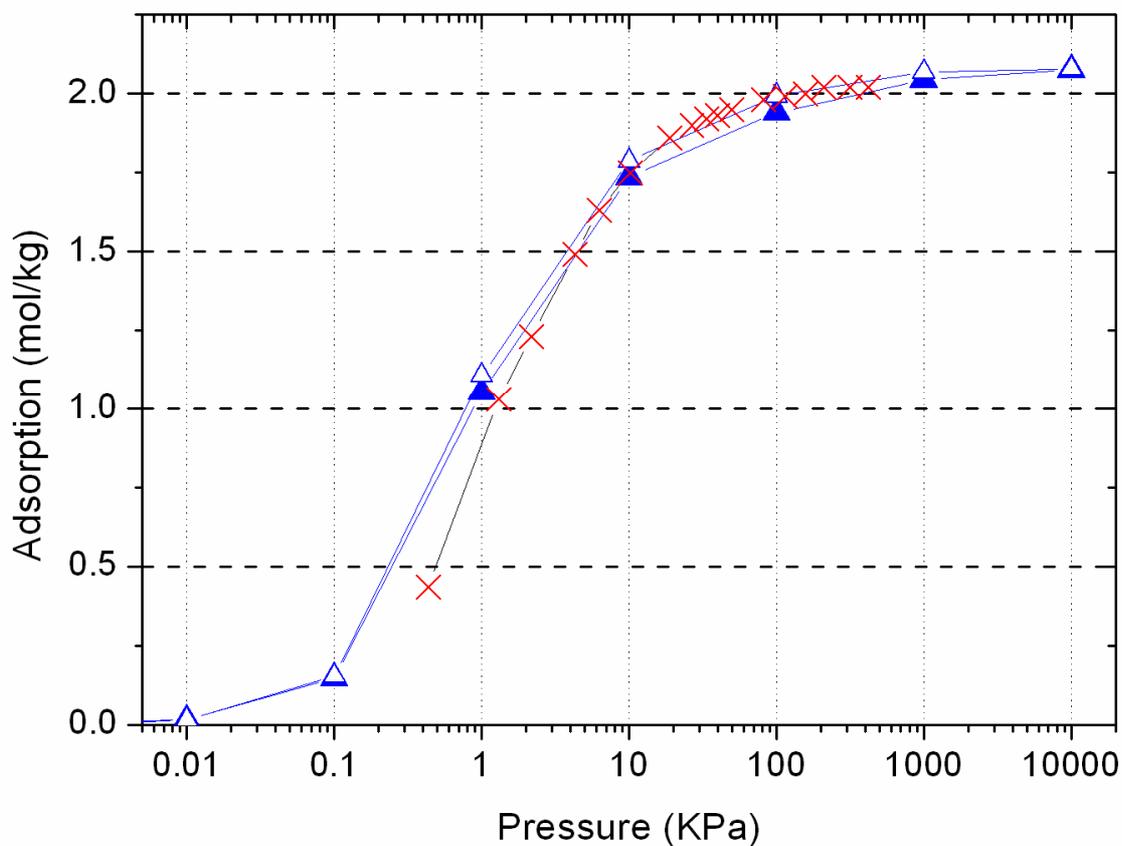
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3 **Figure 1** Experimental³⁷ (black line) and calculated water density as a function of
4 temperature at 1 atm. Simulations were performed using the SPC (●), Tip4p (▲), Tip5p
5 (■) and Tip5pEw (▼) models for water. Simulation data with the original fitting
6 parameters are represented with open symbols, and those using Ewald sums and a
7 Lennard-Jones *cutoff* of 12 Å are represented with solid symbols. Lines are a guide to
8 the eye.
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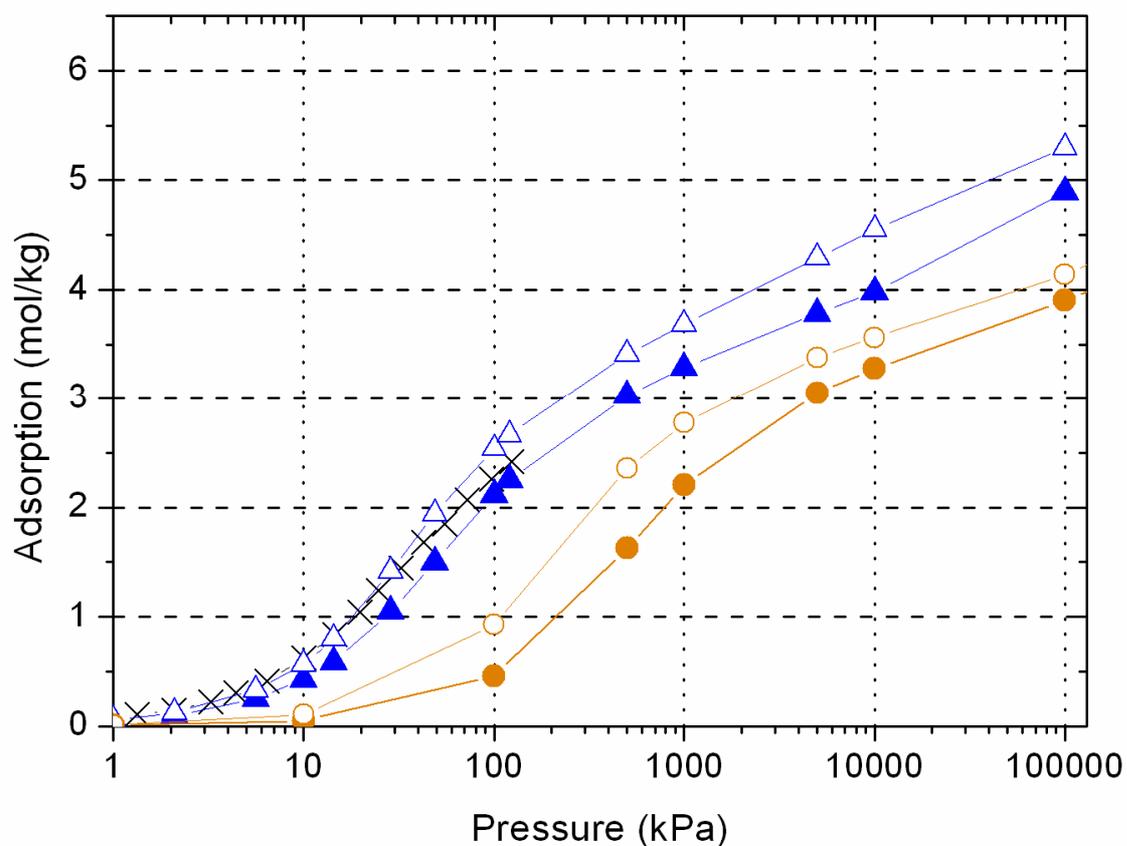
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4 **Figure 2** Experimental^{23, 61} (x and +) and calculated adsorption isotherms of water in
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6 MFI structures at 300 K. Simulations were performed using the Tip4p water model for
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8 the Olson (Δ) and the van Koningsveld (\blacktriangle) structure assigning a partial charge of $1.4 e^-$
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10 to the Si atoms of the framework. The lines are a guide to the eye.
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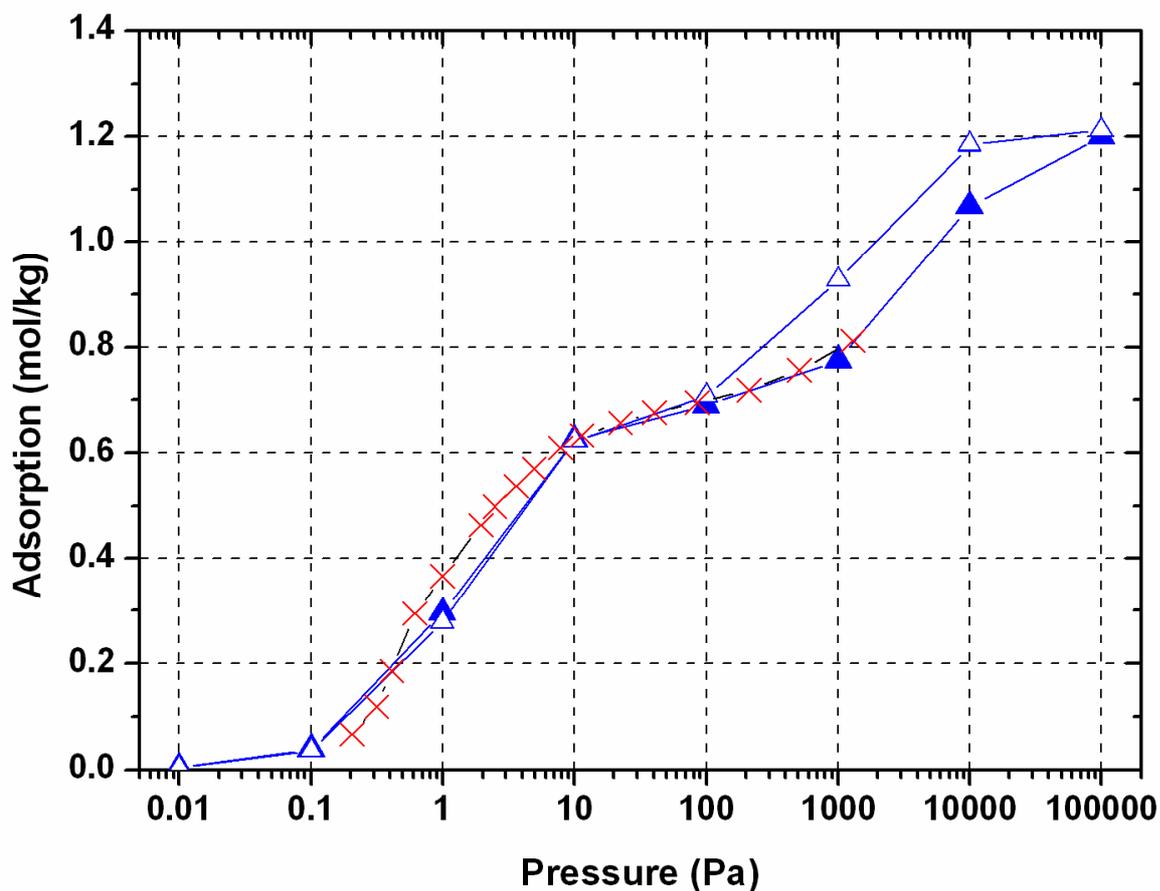
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4 **Figure 3** Experimental⁶² (+) at 303 K and calculated adsorption isotherms of propane in
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6 MFI at 298 K. Simulations were performed using the Olson (Δ) and the van
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8 Koningsveld (\blacktriangle) structures, assigning a partial charge of $2.05 e^-$ to the Si atoms of the
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10 framework. The lines are a guide to the eye.
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3 **Figure 4** Experimental¹⁰ (+) and calculated adsorption isotherms of carbon dioxide in
4 MFI at 273 K. Simulations were performed for the Olson (empty symbols) and the van
5 Koningsveld (solid symbols) structures, assigning partial charges of $2.05e^-$ (\blacktriangle) and
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The lines are a guide to the eye.



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3 **Figure 5** Experimental⁶³ (+) and calculated adsorption isotherms of n-heptane in MFI at
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5 347 K using the Olson (Δ) and the van Koningsveld (\blacktriangle) structure. The lines are a guide
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7 to the eye.
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3 **Figure 6** Calculated adsorption isotherms for water in MFI at 300 K using the SPCFw
4 (▲) and F3C (■) models. Simulations were performed for the Olson (empty symbols)
5 and the van Koningsveld (solid symbols) structures, assigning a partial charge of $2.05 e^-$
6 to the Si atoms of the framework. The experimental isotherms lay at higher pressures
7 and are not shown. The lines are a guide to the eye.
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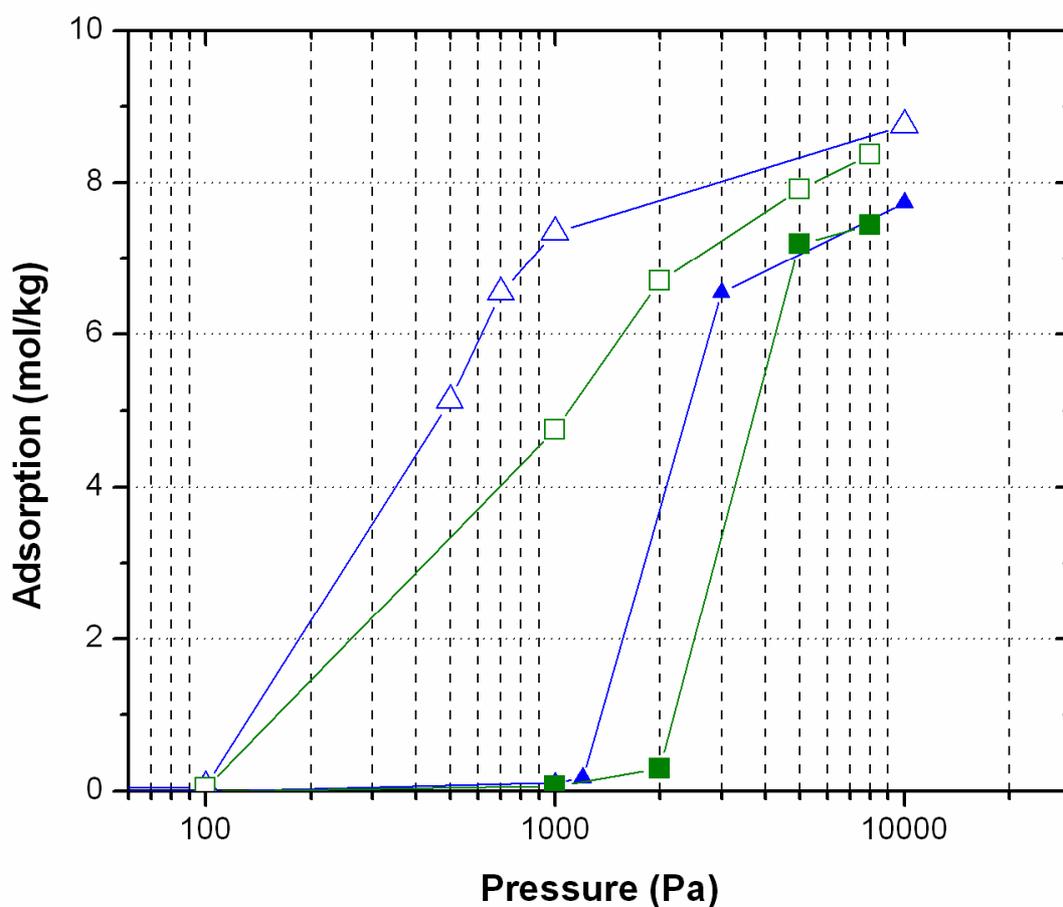
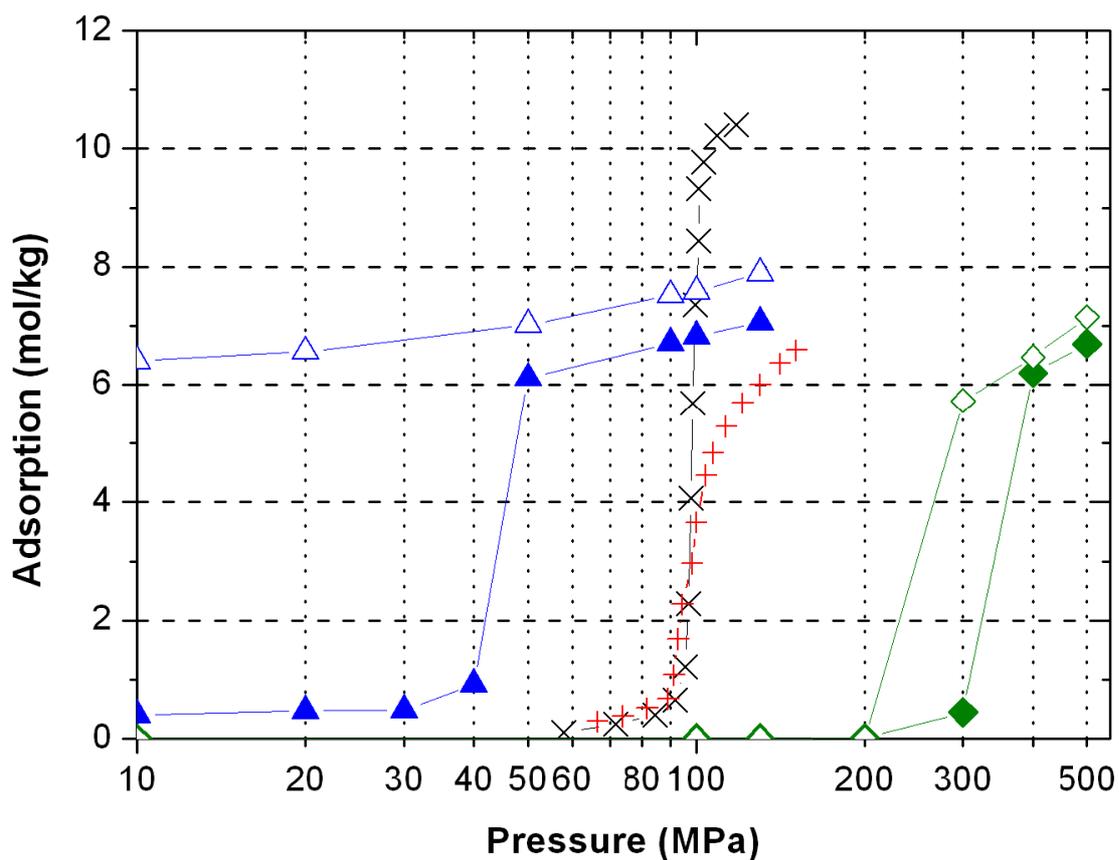
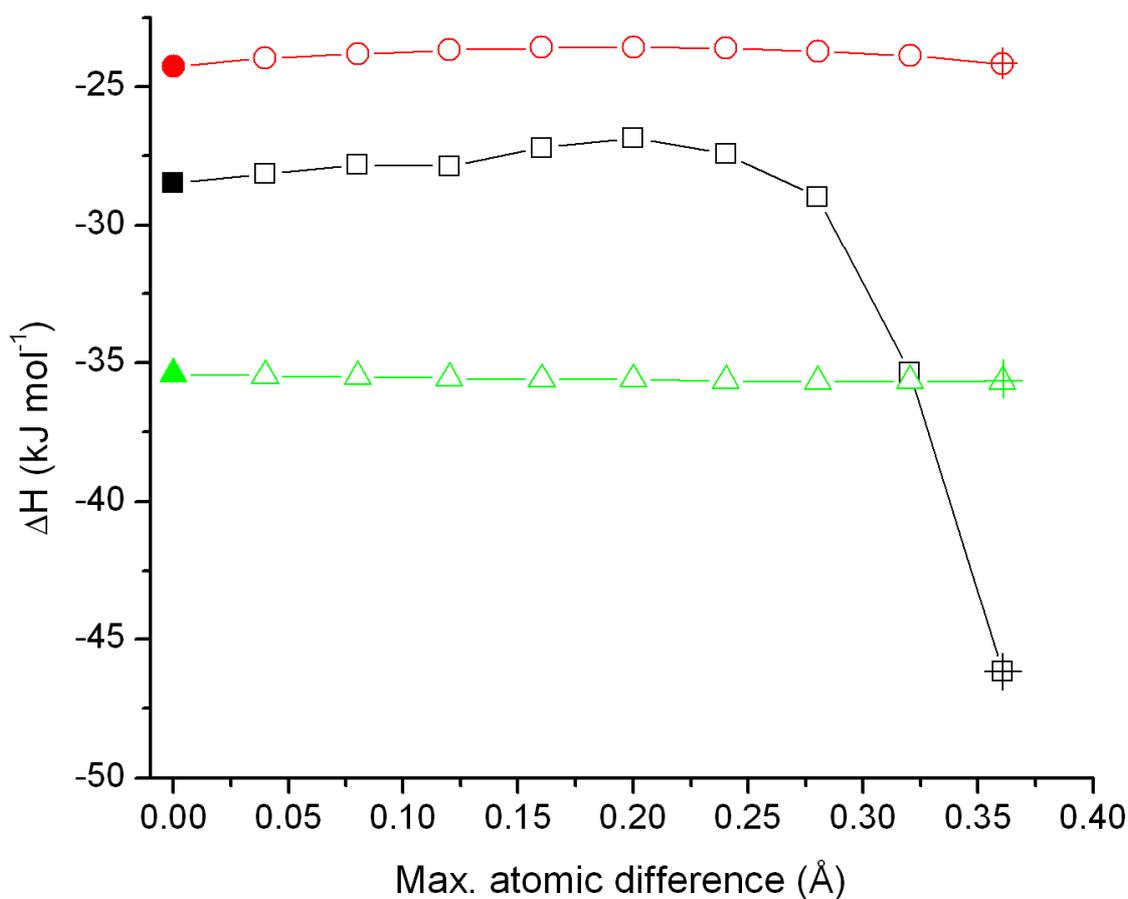


Figure 7 Experimental^{23, 61} (+ and x) and calculated adsorption isotherms for water in MFI at 300 K using the Tip5pEw model. Simulations were performed using the Olson (open symbols) and the van Koningsveld (solid symbols) structure for the framework, assigning a partial charge of $2.05 e^-$ (\blacktriangle) and $0.5 e^-$ (\blacklozenge) to the Si atoms of the framework. The lines are a guide to the eye.

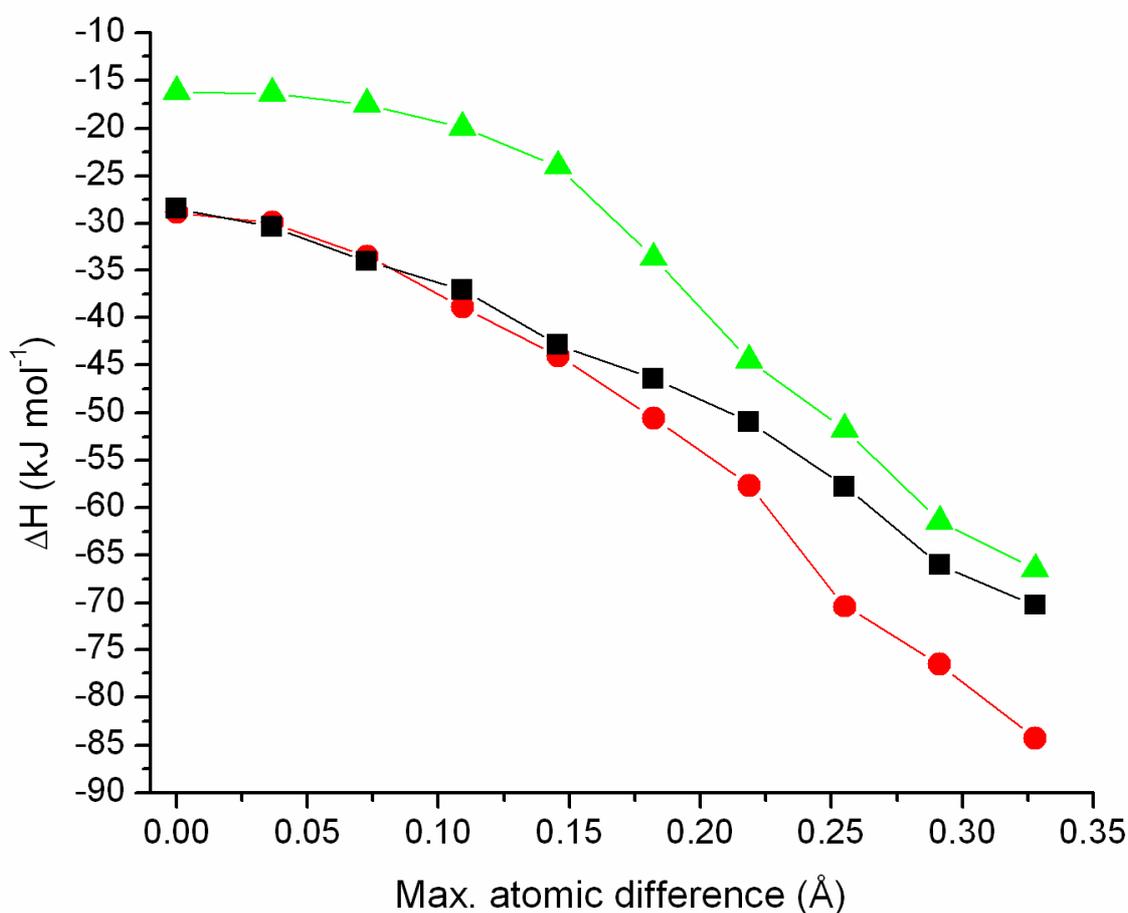


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3 **Figure 8** Calculated heats of adsorption of water (squares), carbon dioxide (circles) and
4 propane (triangles) in different test structures of MFI at 298 K, where the partial charge
5 of the Si atoms of the framework is $2.05 e^-$. The maximum difference between the atom
6 positions of the van Koningsveld and the test structure is represented at the horizontal
7 axis. The generated structures (empty symbols) perform a continuous change from the
8 van Koningsveld (filled symbols) to the Olson structure (crossed symbols).
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Figure 9 Calculated heats of adsorption for water in test structures of pure siliceous MFI (■), DDR (●) and LTA (▲) at 298 K, where the partial charge of the Si atoms of the framework is $2.05 e^-$. The maximum difference between the atom positions of the original and the test structures is represented at the horizontal axis. For each structure, the atoms are progressively displaced independently along a random direction until a random maximum displacement is reached. Random directions and random maximum displacements are generated for each atom.



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