Additional Information

Evidence of Hydronium Formation in Water-chabazite Zeolite Using Inelastic Neutron Scattering Experiments and $ab\text{-}initio$ Molecular Dynamics Simulations

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Abstract

A combined study of Inelastic Neutron Scattering and ab-initio Molecular Dynamic simulations has been performed in order to study the the water-acid site interaction in zeolite chabazite with a ratio Si/Al=16 that corresponds to 2 protons/u.c. with two different water coverages with the number of water molecules being lower and higher than that of proton sites. These results have provided a clear picture of the water-acid site interaction and it has been demonstrated that there are two regimens of water adsorption, which depend on the water loading. i) At low water coverage (water/acid site ~ 0.5), the main interaction between water and the zeolitic acid sites are established through hydrogen bond and there is no proton transference to water. ii) At relatively

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high water loading (water/acid site $\sim$ 3), it has been observed the clustering of water molecules and hydronioum cations formed by the complete transference of the zeolitic proton to the water molecules. The formation of water-hydronium clusters interacting with oxygen atoms of the zeolite framework provides the stabilization energy needed for the protonation of water molecules confined in the cavities of chabazite. These results are the experimental evidence obtained from INS of proton transfer from the zeolitic acid site and the hydronium formation and are in agreement with a previous computational study[18] and very recent Solid State NMR spectroscopy studies.[19]

The inspection of the low energy bands (translational and optic modes) and librational bands of the experimental results allows to obtain information about the H-bond network of the hydronium-water cluster.

INTRODUCTION

Zeolites are among the most successful microporous materials used for catalysis and separation,[1,2] particulary for refining processes[3] due to the combination of acid properties and the presence of structured channel systems of dimensions very close to many widely used reactants. Zeolites show a very high thermal and chemical stability[4] and their large structural and compositional variety facilitates the possibility of fine tuning their adsorption and catalytic properties. In addition, their polar properties (hydrophobicity/hydrophilicity) can be modified by selecting the appropriate chemical composition and concentration of structural defects in the framework.[5] For instance, at ambient pressure, highly polar zeolites could adsorb up to 30 wt% of water, whilst no water is adsorbed in pure silica zeolites.[6] For these reasons, zeolites appear as suitable systems for the study of confined liquids. Since nearly 20 years ago, there is controversy on which conditions are necessary for acid zeolites to protonate water. One of the early Inelastic Neutron Scattering (INS) studies on water adsorbed at low loading in H-mordenite tentatively assigned to hydronium ions, hydrogen-bonded water, and free hydroxyl groups the observed vibrational bands.[7] In this work the presence of hydroxonium ions was derived from the presence of two peaks at 1385 and 1670 cm^{-1}, which were assigned respectively to the symmetric and antisymmetric bending modes of this species. In what concerns the low water loading conditions, the early work of Wakabayashi $et\ al.$ using FT-IR spectroscopy on H-ZSM-5 confirmed the H-bonded adsorption.[8] However the nature of the species formed for high loading conditions has been a matter of debate for a long period. The interaction of water molecules with Brønsted acid sites in a microporous solid acid catalyst, SAPO-34 (with CHA topology), was studied by powder neutron diffraction and infrared spectroscopy,[9] and the results showed that two species were mainly present: An H_3O^+ ion and the water molecule hydrogen-bonded to the acid site of the zeolite. Ab-initio simulations of water adsorbed showed that the proton affinity of the water trimer is large enough to achieve the protonation in HSAPO-34.[10,11] Concerning another type of zeolites, Jobic $et\ al.$[12] stated that hydroniums were not observed upon water adsorption on

ZSM-5 using theoretical calculations and INS, while Jentys *et al.*[13] based on IR spectroscopic results conclude the opposite, and some doubts remain about the number of water molecules that participate in the formation of hydronium cation. Zecchina *et al.*[14] studied by means FTIR spectroscopy the neutral and ionic hydrogen bonded complexes on ZSM-5. The study concluded that at low dosages the interaction of H_2O with the zeolite the water was H-bonded to the zeollite. However at higher dosages these species were transformed into $H^+(H_2O)_n(n_{average} = 3 - 5)$ ionic species. Interaction of water on cluster models of Brønsted acid sites of zeolites was investigated by ab-initio quantum chemical methods.[15] The authors found for the 1:1 cluster (one water molecule per SiO(H)Al) the water molecule H-bonded to the acid site of the zeolite. However for the 2:1 complex (2 water molecules per SiO(H)Al), both H-bonded or hydronium formation, are minima on the potential energy surface. The difference between the 1:1 and 2:1 complex was rationalised by the larger proton affinity of the water dimer compared with the water monomer. So after all these studies a key point has been established: the proton affinity of single H_2O molecule is not the only parameter that should be considered when evaluating the presence of neutral or protonated adsorbed species. Two more important criteria are the ratio between adsorbed H_2O molecules and Brønsted sites as well as the way in which the zeolite micropore can stabilize water clusters.

The early experiments based on IR spectroscopy on the zeolite beta underlined the formation of a doublet at about 2885 and 2463 cm^{-1} which was assigned to symmetric and asymmetric stretching modes of hydronium ions.[16] However the spectra becomes really complex for high H_2O loading, since the hydration is accompanied by a growth of a triplet caused by a Fermi resonance effect between $\nu(O_{zeolite} - H......O_{water})$ vibrations and $2\delta(O_{zeolite} - H......O_{water})$ that overlaps with the characteristic signatures of stretching modes of hydronium ions. Based on FTIR results on H-SSZ-13 (with CHA topology), Bordiga *et al.*[17] found that at low loading, water is H-bonded to the acid site of the zeolite. However, at higher loading there is a transformation into $H^+(H_2O)_n$ with $n_{average} = 3 - 5$.[17] Quantum calculations on the same zeolite were performed by Vener *et al.*[18] and the results showed

that at increasing loading, protonated water clusters become increasingly more stable due to the large proton affinity of the largest clusters. A very recent study combining NMR spectroscopy and ab-initio Molecular Dynamic simulations has shown for the first time an experimental evidence of the conditions in which hydronium cations are stable in hydrated H-ZSM5 zeolites, indicating that: hydrogen bonds between water molecules and the tetrahedrally coordinated aluminum in the zeolite lattice weaken with the formation of hydronium ion-water clusters, H_2O molecules form strong hydrogen bonds with H_3O^+ and an increase the mobility of protons.[19]

For this study a combined study using INS and *ab-initio* Molecular Dynamics simulations (AIMD) was performed. Among vibrational spectroscopies, INS presents very appropriate features for our task. This technique is mainly sensitive to vibrations involving hydrogen atoms because of their much higher incoherent cross-section (σ_{inc}) compared to other elements. As a consequence, INS is well suited for investigating hydrated compounds, as water vibrations can be observed on a wide spectral range, even in regions where signals from the framework atoms would dominate the spectra in other vibrational techniques, for instance IR or Raman spectroscopy. This would allow to overcome the interpretation of the complex spectra of IR spectroscopy and explore the low energy part of the spectra that can give information about the H-bond network since is strongly indicative of the coordination of the water molecule, i.e. the number of H-bonds formed. Another important feature is that the INS intensities are directly related to atomic displacements which can be computed from empirical force fields or from ab-initio quantum chemical methods. The chabazite structure used for this study contains only one crystallographic T (T = Si, Al) site and four O atoms,[20] making it and ideal candidate for the INS study of adsorbed molecules, since computational approaches can be applied at relatively low computing cost. In the present work we have proceeded as follows: first of all the use of the same chabazite structure (CHA) as in previous results, but in this work with a higher Si/Al ratio (Si/Al = 16) in order to have less protons per unit cell (2 protons/u.c.). This will allow us to study in a simple system two water load-

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ings, with the number of water molecules being lower and higher than that of proton sites. Similarly, we will study the homogeneous and heterogeneous distribution of water molecules per acid site, respectively.

MATERIALS AND METHODS

Sample preparation. Chabazite zeolite with Si/Al ratio of 16 (SSZ-13) was synthesized according to a procedure based on the Verified Syntheses of Zeolitic Materials of the International Zeolite Association (http://www.iza-online.org/synthesis/default.htm), following the method reported previously.[21] In particular, aluminium hydroxide (57% Al_2O_3, Aldrich) was added to an aqueous solution containing sodium hydroxide and N,N,N, trimethyl-1-adamantamonium hydroxide (ROH)(O.52M). Then, amorphous silica (Aerosil 200, Degussa) was also added to the mixture and homogenized for one hour. The molar composition of the gel was the following: $10 \, Na_2O : 2.5 \, Al_2O_3 : 100 \, SiO_2 : 4400 \, H_2O : 20 \, ROH$. The crystallization was carried out in Teflon lined stainless steel autoclaves at 433 K under rotation during 4 days. The zeolite was recovered by extensive washing with deionized water followed by drying at 373 K. The crystallinity of the sample was checked by means of X-ray diffraction (XRD) that showed the characteristic XRD pattern of highly crystalline CHA zeolite (Figure S1 of SI). The sample was further calcined at 853 K for removing the occluded organic material and submitted twice to ion exchange treatments with NH_4Cl followed by calcination at 773 K in order to exchange the Na cations by protons. The structural integrity of the zeolite was preserved after calcination and ion exchange treatments as indicate the corresponding XRD pattern (Figure S1) and the BET surface are the micropore volume obtained from the N_2 adsorption isotherm (see SI).

The chemical composition of the zeolite was determined by ICP on a Varian 715-ES ICP-Optical Emission Spectrometer giving a Si/Al ratio of 16 and Na/Al of 0.30 in the as-prepared zeolite, and the same Si/Al ratio and a negligible amount of Na in its protonic

form (Na/Al=0.01). Chabazite zeolite was also characterized by means of ^{27}Al and ^{29}Si MAS NMR spectroscopy and the results can be found in the SI.

In the following we will refer to the sample under study Chabazite with Si/Al=16 as CHA16. Two hydration states were prepared: low and high loading, with 0.87 weigth % (1 molecule/u.c.) and 5.0 weigth % (6 molecules/u.c.) of water, respectively.

Inelastic Neutron Scattering experiment. INS spectra were measured at 10 K in the range of energy transfers from 1 to 200 meV with an energy resolution of $\Delta E/E \sim$ 2% using the Lagrange neutron spectrometer installed at the hot source of the high-flux reactor at the Institute Laue-Langevin in Grenoble.[22,23] This energy range was obtained by combining the mosaic Cu(220) monochromator for the intermediate energy range, with the elastically bent Si(111) and Si(311) monochromators for the lower energy range. The energy transfer was calculated by subtracting 4.5 meV, the constant final energy of the PG analysers, from the energy of the incoming neutrons selected with the different monochromators. The background spectrum from the cryostat and an empty sample holder was measured separately and then subtracted from the raw INS spectrum of the sample. In the extent that the final wavevector, k_f, where $k \equiv 2\pi/\lambda$, is much smaller than the incident wavevector, k_i (and therefore high Q), the observed intensity is directly proportional to the Generalized Density of States (GDOS), that is the hydrogen partial density of states, $g_H(E)$ in the case of hydrogenated materials.

Computational details: Normal modes calculation. The theoretical VDOS(ω) was calculated using the direct method on the basis of first-principles calculations. Calculations were performed on a unit cell with formula $Si_{34}Al_2O_{72}H_2$ in order to have a Si/Al = 17 close to the experimental one (Si/Al=16) and an integer number of hydroxyls, SiO(H)Al, that corresponds to two hydroxyl groups, SiO(H)Al, per unit cell. The cell parameters were fixed to those provided by the International Zeolite Association.[20] The calculations were performed on the relaxed structure by using the DMol^3 *ab-initio* simulation package in Materials Studio software[24] and the eigen modes were obtained from the dynamical matrix.

All electronic functions were calculated at the Γ point and the dynamical matrix for any point in reciprocal space was generated and diagonalised to compute phonon eigenmodes i. The double numerical plus-d-function basis set (DND) all-electrons basis set was used for all the calculations. The DND basis set includes one numerical function for each occupied atomic orbital and a second set of functions for valence atomic orbitals, plus a polarization d-function on all atoms. Perdew-Burke-Ernzerhof parametrization of the generalized gradient approximation (PBE-GGA) was used in all the calculations.[25,26] The corresponding DFT quantum chemical calculations provide information on the frequencies of normal modes of the given systems and the amplitudes of the atomic displacements from the equilibrium positions. The calculated neutron scattering spectra can be approximated as $\sim g_H(E)$.

Computational details: *ab-initio* **Molecular Dynamics Simulations.** In *ab-initio* Molecular Dynamics (AIMD) simulations, the atoms are moved according to classical Newton's mechanics whereas the interatomic forces acting between atoms are computed according to quantum mechanics, solving from first-principles the electronic structure for a given set of atomic positions and then calculating the resulting forces on each particle. In this case, the vibrational spectra can be extracted from MD trajectories, via the Time Fourier Transform of the velocity-velocity autocorrelation function:

$$g(\omega) = \sqrt{\frac{1}{2\pi}} \int_{-\infty}^{\infty} e^{i\omega t} \sum_i \frac{\langle \vec{v}_i(t)\vec{v}_i(0)\rangle}{\langle \vec{v}_i(0)\vec{v}_i(0)\rangle} dt \qquad (1)$$

where the function $\frac{\langle \vec{v}_i(t)\vec{v}_i(0)\rangle}{\langle \vec{v}_i(0)\vec{v}_i(0)\rangle}$ is the velocity-velocity autocorrelation function (VAF), calculated from a chosen initial time (t=0) for the MD trajectory and for each atom of the system i, along all three components of the velocity $\vec{v}_i$. The AIMD simulations were performed using CASTEP code.[27] All calculations use optimised ultrasoft pseudopotentials generated with the Perdew-Burke-Ernzerhof (PBE)[26] functional within the generalized-gradient approximation (GGA). We used a plane-wave cut-off energy of 500 eV. For the calculations the same cells as for the normal modes calculations were used. Optimized structures were used

as input for the production of AIMD trajectories. They were firstly thermal equilibrated at 300 K in the NVT ensemble over 4 ps with a 1.0 fs timestep. The equilibration run was followed by a production run of 10 ps, performed also in the NVT ensemble at 300 K. The density of states (DOS) was then computed as time-Fourier transform of the velocity auto-correlation function (VACF) computed from the coordinates of each step of the trajectories, as implemented in the nMOLDYN program.[28]

Details of the crystallographic models used for the calculations. The calculated unit cell has the formula $Si_{34}Al_2O_{72}H_2$ in order to have a $Si/Al = 17$ close to the experimental one ($Si/Al=16$). Two models were initially used for the ab-initio calculations. The main difference between the models is that in model 1 (M1) the two protons are placed on the crystallographic oxygens O2H and O3H, both pointing to a 8-ring, and in model 2 (M2) the protons are placed on O1H and O3H, pointing to a 6-ring and 8-ring respectively. These structures were used for all the calculations for this system and subsequent hydrated versions of this system were studied from models produced from the above structures.

Ab-initio Molecular Dynamics simulations were performed on two hydrated models : i) low loading, with 1 water molecule per unit cell, corresponding to 0.87 weigth % and will be called '1W', and ii) high loading, with 6 water molecule per unit cell, corresponding to 5.0 weigth % that will be called '6W'. These loadings can also be converted into water molecules per 'cha' cage by taking into account that there are 3 cavities per unit cell (see Figure S4 in SI).

RESULTS AND DISCUSSION

Dehydrated chabazite. Figure 1 shows the comparison between the measured INS results of the dehydrated CHA16 and hydrogen partial density of states, $g_H(E)$, from the normal modes calculations for the two models, M1 and M2. The comparison between the models and the experimental spectrum does not allow us to disclose completely any of the models.

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Since with a unique unit cell is difficult to reproduced the low energy modes that are a combination of the zeolite framework relaxation and the out-of plane bending modes, the choice of M2 is based on the better reproduction of the in plane Si-OH wag (at ~ 1100 cm^{-1}) that suggests that the proton distribution in chabazite is in majority the M2 configuration.

From the frequency analysis of the vibrational bands is possible to identify the characteristic bands: at ~ 400 cm^{-1} the hydroxyl hydrogen wag out of the plane of the Al-O-Si bridge in the lattice, at ~ 800 cm^{-1} the riding mode of the Si-OH bond stretch and at ~ 1100 cm^{-1} the hydroxyl hydrogen wag in the plane of the Al-O-Si bridge in the lattice. The position of these vibrational bands are close to the ones identified on the LTA with different Si/Al ratios.[29,30]
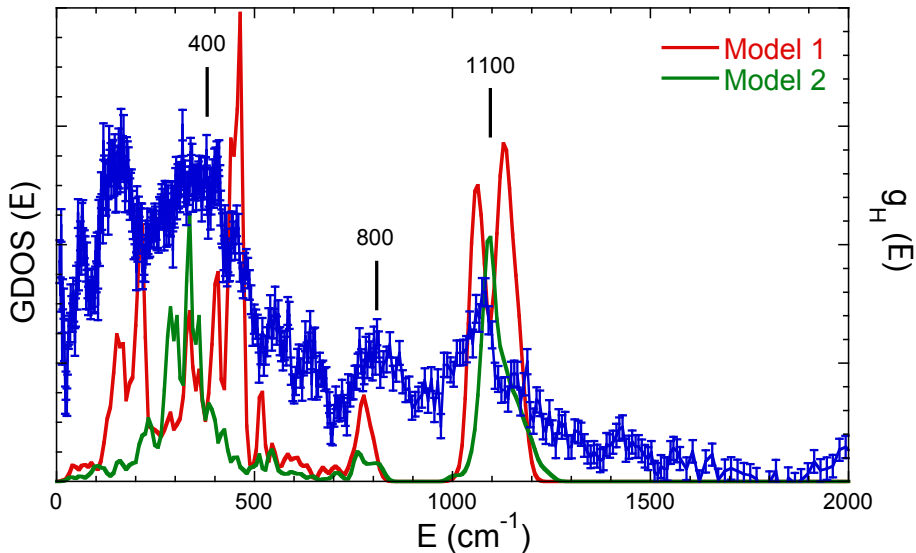

Figure 1: *Comparison of the experimental results for the dehydrated CHA16 with the Hydrogen partial density of states, $g_H(\omega)$, from the normal modes calculations for the two models described in the text.*

Low water loading chabazite (CHA-6W, 6 water/u.c., 5% weight water; 3 water/acid site).

The disorder induced in the system by the introduction of water molecules cannot be reflected by using DFT calculations since several unit cells should be used for the calculation. For that reason this disorder was introducing with anharmonicity effect by performing AIMD

simulations at 300 K for the hydrated systems. Since for the dehydrated zeolite another calculation method was employed (DFT calculations) a comparison of the density of states obtained by two different methods (DFT and AIMD) is shown in the SI.

Figure 2 shows the model used for the calculations of the hydrated zeolite with one water molecule (CHA16-1W). For the location of the water molecule the total energy of the system was calculated, and the minimum was found when the water molecule is H-bonded to the Brønsted site of the zeolite.
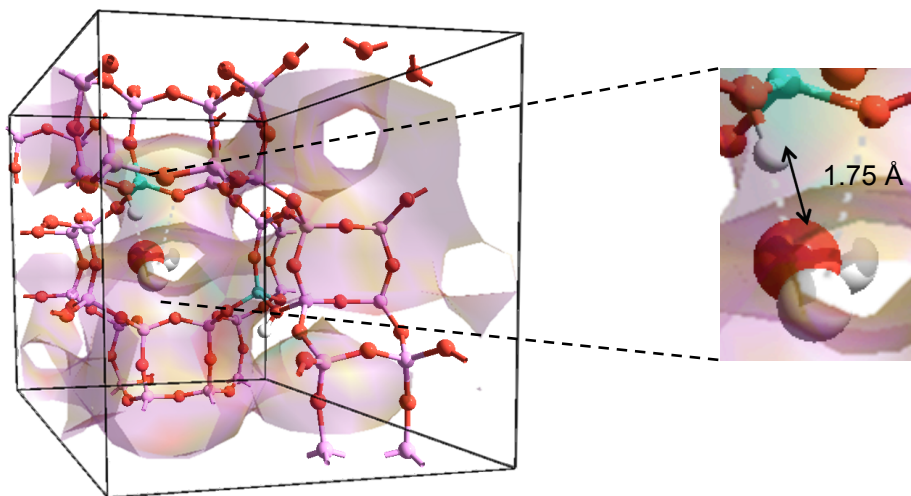

Figure 2: *Model of CHA16 with one water molecule (1W) H-bonded to the zeolitic OH group. The dashed grey lines represent H-bonding in the system. Si = pink, O = red, Al = blue, H = white*

As it can be seen in Figure 2, obtained from energy minimization, water binds to a Brønsted site within the pore. This shows the water docks to the acidic protons, at a distance $d(H_{zeolite}......O_{water}) = 1.75$ Å, as is illustrated in the zoom of Fig. 2, but one of the water hydrogens form a H-bond with a framework [non hydroxyl] oxygen, increasing the stability of the water in that bonding site. The above model was used for the AIMD simulations.

For the calculation of the density of states (DOS), three different species were considered: two hydrogen in structural hydroxyls (OH non coordinated and OH coordinated with the

water molecule) and the hydrogens of the water molecule (1W). From the velocity-velocity autocorrelation of these two species (Eq. 1) their partial density of states were obtained. The results, together with the total hydrogen density of states g_{allH}, are shown in Figure 3 for the CHA16-1W. This allowed us to identify the characteristic bands that are [approximately] at: 400 cm^{-1} [Brønsted site hydrogen wag out of the plane of the Al-O-Si bridge in the lattice], 500 cm^{-1} [synchronous asymmetrical water wag], 1050 cm^{-1} [Brønsted site hydrogen not coordinated to water wag in the plane of the Al-O-Si bridge in the lattice] and 1400 cm^{-1} [Brønsted site hydrogen (coordinated to water) wag in the plane of the Al-O-Si bridge in the lattice]. The INS results of CHA16-1W is superimposed with the calculated DOS. The fingerprint region of the three spectra overlap very well, apart from the region around 800 cm^{-1} that corresponds to the second harmonic of the peak at 400 cm^{-1} that overlaps with the riding mode of the Si-OH bond stretch of the dehydrated zeolite.
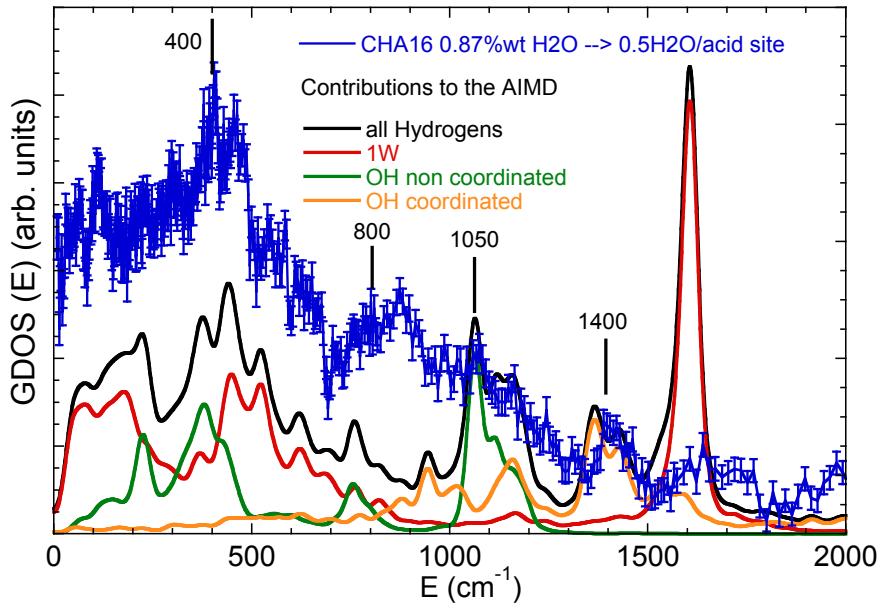

Figure 3: *Comparison of the experimental results for the CHA16-1W (0.87 % weight) and with the Hydrogen partial density of states, $g_H(\omega)$, from the ab-initio molecular dynamics simulations.*

To further validate this work and confirm the water H-bond to the zeolitic SiO(H)Al, potential energy surfaces (PES) were calculated. Figure 4 shows the PES for the proton transfer between water molecule and the chabazite at different distances from the hydroxyl oxygen of the zeolite (O_z) to the oxygen of the water/hydronium (O_w). The PES shows that the proton transfer occurs more favourably at O-O distance equal to 2.5 Å, with an activation barrier of 15 kJ/mol. The process is endothermic, and hence the reverse reaction is always preferred, showing in this case 5 kJ/mol as barrier.
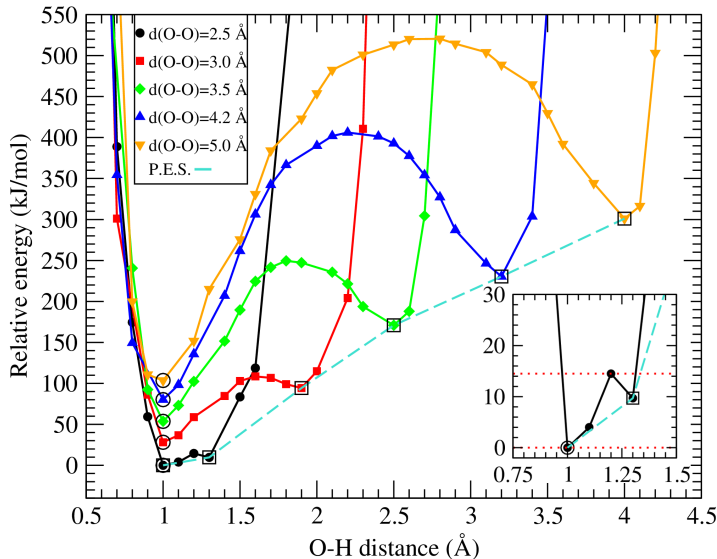

Figure 4: *PES of proton transfer from hydronium [squared minima on the right] back to the chabazite [circled minima on the left.] The distances in the legend shows the distance between the hydroxyl-oxygen of the zeolite (O_z) and the oxygen of the water/hydronium (O_w). The curve at d(O-O)=2.5 Å (highlighted in the inset) shows that the proton can be transferred to water with a barrier of 15 kJ/mol, and the reverse process requires only 5 kJ/mol.*

High water loading chabazite (CHA-6W, 6 water/u.c., 5% weight water; 3 water/acid site). Figure 5 shows the comparison of the INS spectra of the three systems under study: the dehydrated chabazite, with 0.87 % and 5 % weight of water. The spectrum of ice-h is shown as well on Figure 5 for comparison. Since the scattering cross section of the Hydrogen atoms is very large in comparison with the other atoms, it can be estimated that the scattered intensity comes from the Hydrogen atoms. The experimental results shown in Figure 5 are the spectra normalised to the amount of Hydrogens in the samples: 2, 4 and

14 for the dehydrated, 0.87 % and 5 % chabazite, respectively. As it can be observed, the intensity of the characteristic vibrational bands of water (librational bands at 550 cm^{-1} and bending modes at 1600 cm^{-1}) increase with the hydration state of the sample.
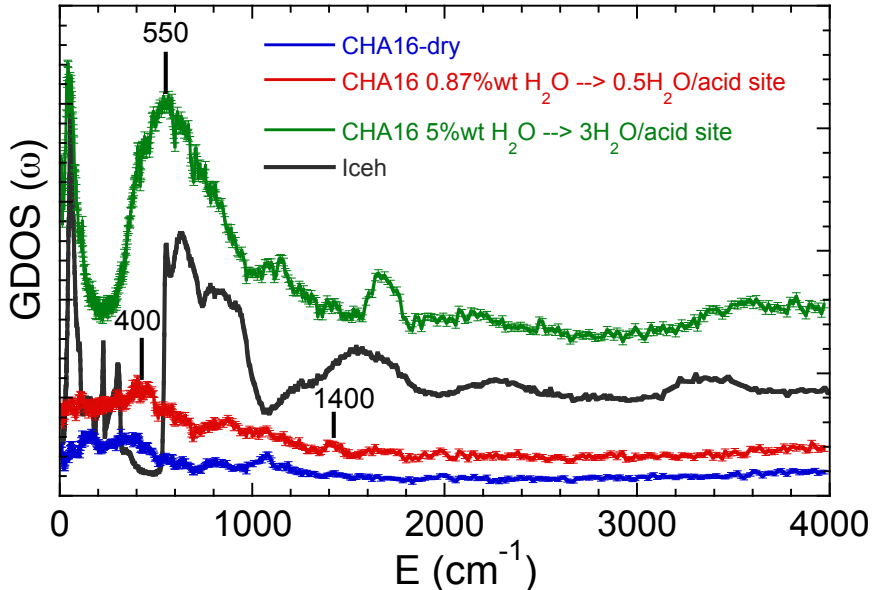

Figure 5: *Comparison of the measured generalized density of states for CHA16-dry (dehydrated CHA16), 1W (0.87 % weight) and 6W (5 % weight). The spectra of Ice-h is also shown for comparison taken from Reference.*[32]

From Figure 5, it can be observed two main differences. i) The librational band of the 0.87 % sample is shifted to lower energy (400 cm^{-1}) than that of the 5% sample (550 cm^{-1}). This shift is originated by the overlap of two contributions that were described with the analysis of the AIMD trajectories (Figure 3): the librational band of the water molecule ($\sim$ 450 cm^{-1}) and the OH wag out of plane of the non-coordinated SiO(H)Al ($\sim$ 400 cm^{-1}). ii) The other difference is the change of intensity of vibrational band appearing at 1400 cm^{-1}, corresponding to the OH wag in plane of the coordinated SiO(H)Al with water.

In order to identify the spectral changes on the experimental results, AIMD simulations were performed. Figure 6 shows a snapshot of the AIMD simulation with a representation of a 2 × 2 × 1 unit cell in order to clearly visualize the positions of the Al atoms, one in the 8-ring and the other on the 6-ring. From the very beginning of the simulation two protons

were transferred from the zeolite and two hydroniums were formed (a snapshot of the AIMD simulations is shown in Figure 6). This result is in agreement with the study of the stability of the proton in zeolites with the presence of water molecules (monomers and dimers)[13] and with a recent study combining NMR and MD simulations.[19] Such a cluster appears to be stable during the time of our simulations, where the H-bond can be continously formed between the water molecules, the hydronium cations and the zeolitic oxygens. Therefore for the calculation of the DOS, two different species were considered: the hydrogens of the two hydronium molecules ($2H_3O^+$) and the hydrogens of the four water molecules (4W). From the velocity-velocity autocorrelation of these two species (Eq. 1) their partial density of states were obtained. The results, together with the total hydrogen density of states g_{allH}, are shown in Figure 7. The vibrational bands of the calculated spectra corresponding to the hydronium are: at 900 cm^{-1} for the librational bands, 1200 cm^{-1} for the symmetric and 1600-1700 cm^{-1} for the antisymmetric bending modes of these hydronium species. The latter values are close to the ones found in literature by means of IR and Raman spectroscopy of hydronium ions.[31] The width of the librational band measured experimentally cannot be reproduced with the AIMD simulations since this depends on the local organization of the water molecules. Since one unit cell has been simulated, is not possible to simulate the different water configurations that can be observed in a such disorder system.
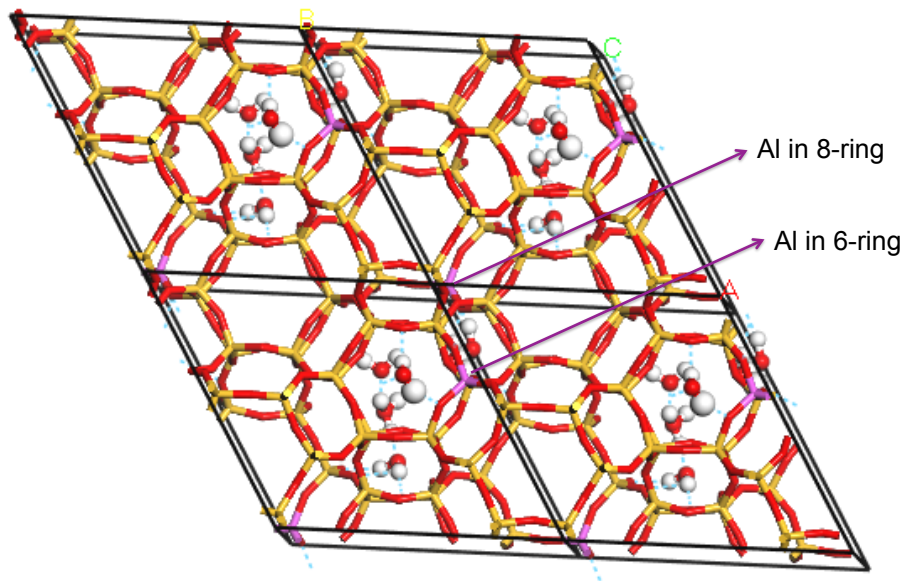
Figure 6: *Snapshot of the AIMD simulations of CHA16-6W with a representation of a 2 × 2 × 1 unit cell showing the formation of hydronium ions. Hydrogen atoms from the zeolite leading to hydronium cations are highlighted with a larger size (only one is visible due to the orientation on the unit cell).*

Figure 6 shows a snapshot of the AIMD simulation with a representation of a 2 × 2 × 1 unit cell in order to clearly visualize the positions of the Al atoms, one in the 8-ring and the other on the 6-ring. From the simulations of CHA16-6W, it can be observed that a 4-water cluster is formed, which contributes to stabilize the two hydroniums. This result is in agreement with the study of the stability of the proton in zeolites with the presence of water molecules (monomers and dimers)[13] and with a recent study combining NMR and MD simulations.[19] Such a cluster appears to be stable during the time of our simulations, where the H-bond can be continously formed between the water molecules, the hydronium cations and the zeolitic oxygens.
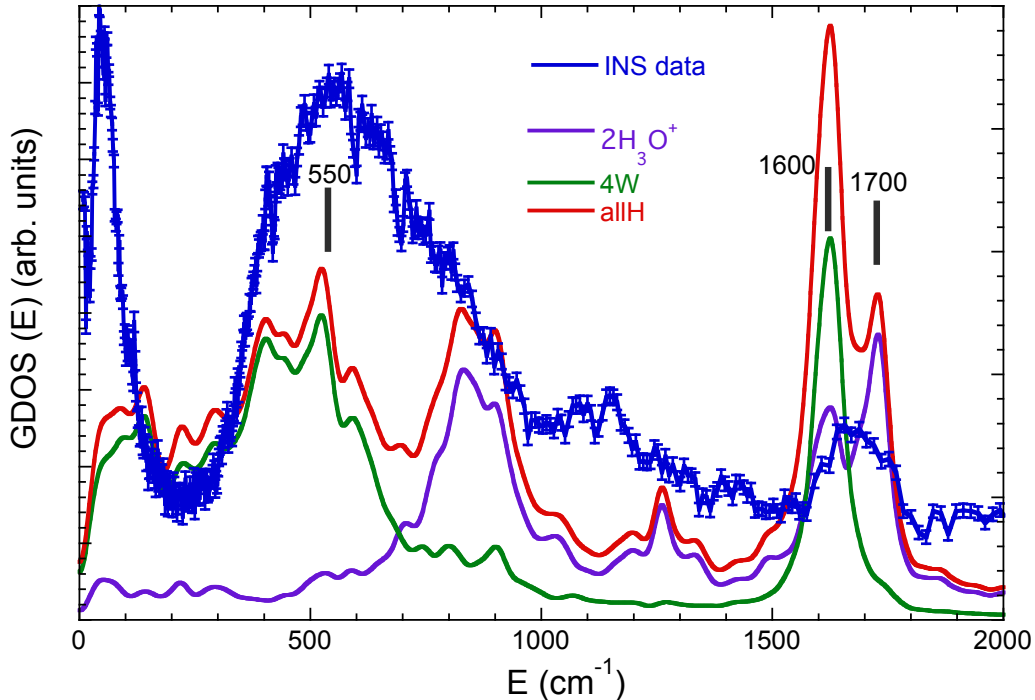
Figure 7: *Comparison of the experimental results for the CHA16 with 6 water molecules and with the Hydrogen partial density of states, $g_H(\omega)$, from the ab-initio molecular dynamics simulations.*

A close inspection to Figure 7 shows that the band at 1600-1700 cm^{-1} increases its intensity as the H$_3$O$^+$ species become increasingly present and that overlaps with the water bending modes. Our AIMD calculations show that: at low water content when no hydroniums are present only a peak at 1600 cm^{-1} is present (Figure 3), whilst at larger water content when hydroniums are formed, two close peaks at 1600 and 1700 cm^{-1} are formed (Figure 7), resulting in an increased intensity of the overall band, in agreement with the INS experimental spectra. It should be noted that the intensity of the calculated intensity of the bands appearing at $\sim$ 1600 cm^{-1} is very high when compared with the experimental one. From Eq. 4 of SI it can be observed that the intensity of the vibrational bands is damped by an exponential term, the Debye Waller factor, that depends on two factors: the temperature and the momentum transfer, Q. The experiment is performed at low temperature in order to decrease as maximum the thermal agitation of the atoms, however the momentum transfer

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on a inverse geometry instrument as Lagrange with $\mathbf{k_i} \gg \mathbf{k_f}$ is $\mathbf{Q} \approx \mathbf{k_i}$. This means that high energies implies high Q values and therefore the exponential term will damp the intensity of the vibrational bands appearing at higher energies.

An inspection of the low energy bands (translational and optic modes) and librational bands of the experimental GDOS of CHA16-6W (Figure 5) allow to obtain information about the network of H-bonds. The broadening of the translational band at $\sim 49\,\mathrm{cm}^{-1}$ and the absence of the H-bonds stretching (if compared with the spectrum of Ice-h) appears as a consequence of the disorder of the water molecules in the cluster.[32,33] Since the large water loading refers to 6 water molecules/u.c., and all water molecules locate in the same cavity (Figure 6), this results in an effective loading of 6 water molecules/cavity. This corresponds to a water density of 0.5 g/cm^3 (half the density of bulk water), giving a large mobility of water molecules inside the cavity which can be the origin of the observed broadening of the translational band. And as a consequence of this geometrical aspects the librational band appears at lower energies, $\sim 450\,\mathrm{cm}^{-1}$ that is characteristic of water molecules forming three H-bonds,[34] if compared with the position on the ordered phase Ice-h ($\sim 550\,\mathrm{cm}^{-1}$) forming four H-bonds.

In order to check the validity of the model M2 as the one that better describe the system, AIMD simulations were performed as well on the model M1. As it was observed on the evolution of the trajectories during the simulation time, the location of the proton determines the cluster of the water molecules and the proton transfer. When using the M1 only one proton is transferred in such a way that there is one proton hydrogen bonded to one water molecule, and another proton that is transfer to the water cluster. In this case the H-bond network created by the cluster is relatively weak and this can be observed by the position of the librational band of the water molecules that appears at lower energy (~ 350 cm^{-1}) that the experimental one. The decomposition of the calculated density of states with the different contributions is shown in SI. When using the M2 two protons are transferred to the water cluster and a stronger H-bond is created and the calculated librational band

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reproduce the experimental results. This appears as another argument to use the M2 model for simulating the hydrated structure.

The AIMD simulations allowed us to perform a detailed analysis of the stretching spectral region and isolate the contribution of the different especies from the signal. Figure 8 shows the comparison of the two hydrated systems, 1 W and 6 W, with the different species: 1 water molecule (1W) for CHA16-1W and 2 hydroniums ($2H_3O^+$) and 4 water molecules (4W) for CHA16-6W. The stretch frequency of the water molecule of CHA16-1W has a main vibrational band at ~ 3750 cm^{-1} that corresponds to an isolated water molecule. The water molecule is H-bonded to the proton of the zeolite, but the hydrogens are not H-bonded. However in CHA16-6W the stretching frequency of the water molecules appears at lower energies since the molecules are forming a ring through the H-bonds with the oxygens of the water molecules (O_W) and with the oxygens of the zeolite framework (O_z) and can be seen in Figure 6.
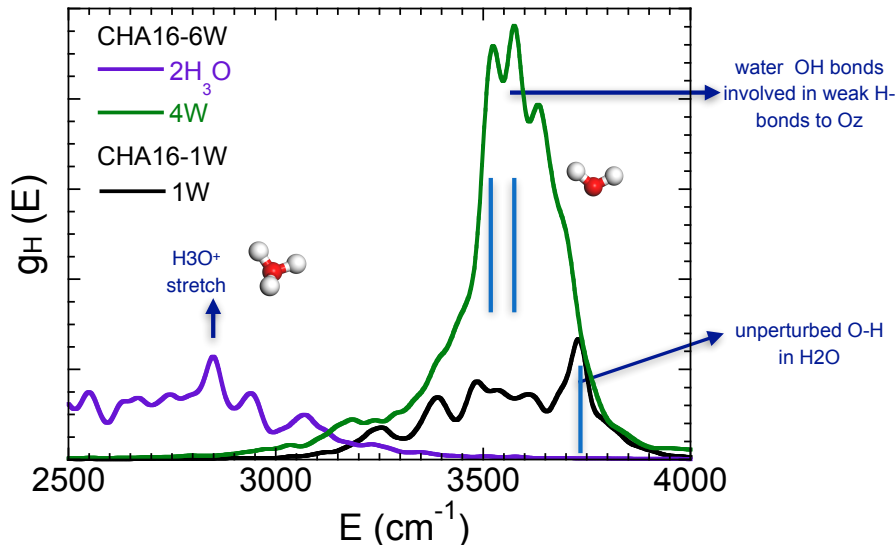

Figure 8: *Zoom at the stretching region of the density of states obtained from the trajectories of the AIMD simulations of CHA16 with two hydration states: 1W and 6W.*

CONCLUSIONS

The combination of INS and Molecular dynamic simulations, with highly crystalline zeolite samples, has allowed to provide a clear picture of the water-acid site interaction in zeolite chabazite (Si/Al=16). It has been demonstrated that there are two regimens of water adsorption, which depend on the water loading. i) At low water coverage (water/acid site $\sim$ 0.5), the main interaction between water and the zeolitic acid sites are established through hydrogen bond and there is no proton transference to water. ii) At relatively high water loading (water/acid site $\sim$ 3), it has been observed the clustering of water molecules and hydronioum cations formed by the complete transference of the zeolitic proton to the water molecules.

These conclusions were based on the good agreement between the INS experiments and the theoretical calculations from which the assignation of bands can be obtained and allowed to give accurate information about the state of water and Brønsted acid sites. One signature of the presence of hydronium ions has been found in the increased intensity of the band at 1600-1700 cm^{-1} (antisymmetric bending mode), where the contribution near 1700 cm^{-1} is due to the hydronium ions as confirmed by ab initio molecular dynamics. It seems that in the high water loading, the formation of water-hydronium clusters interacting with oxygen atoms of the zeolite framework provides the stabilization energy needed for the protonation of water molecules confined in the cavities of chabazite.These results are the experimental evidence obtained from INS of proton transfer from the zeolitic acid site and the hydronium formation and are in agreement with a previous computational and very recent Solid State NMR spectroscopy studies.[18,19]

The inspection of the low energy bands (translational and optic modes) and librational bands of the experimental results allows to obtain information about the network of H-bonds. The broadening of the translational band in CHA16-6W and the absence of the H-bonds stretching (if compared with the spectrum of Ice-h) appears as a consequence of the disorder of the water molecules in the cluster given the high mobility in the cavity. The

librational band of the water molecules in the calculated spectrum appears at lower energies, $\sim 450\,\mathrm{cm}^{-1}$ that is characteristic of water molecules forming three H-bonds,[34] if compared with the position on the ordered phase Ice-h (sharp band band at $\sim 550\,\mathrm{cm}^{-1}$) forming four H-bonds.

The combined study shown in this work based on INS and AIMD simulations has been used first, to validate the model for the calculations, and second to obtain information about the H-network of the water molecules. This kind of study can be particularly useful for understanding the influence of the geometry of the cavity and the Al position in the framework on the H-bond network of the hydronium-water cluster.

ASSOCIATED CONTENT

Supporting Information

Details of sample characterization: X-ray diffraction spectra and ^{27}Al and ^{27}Si MAS NMR spectra, the Inelastic Neutron Scattering experiment, the model used for the calculations and comparison of AIMD simulations, DFT calculations and INS results.

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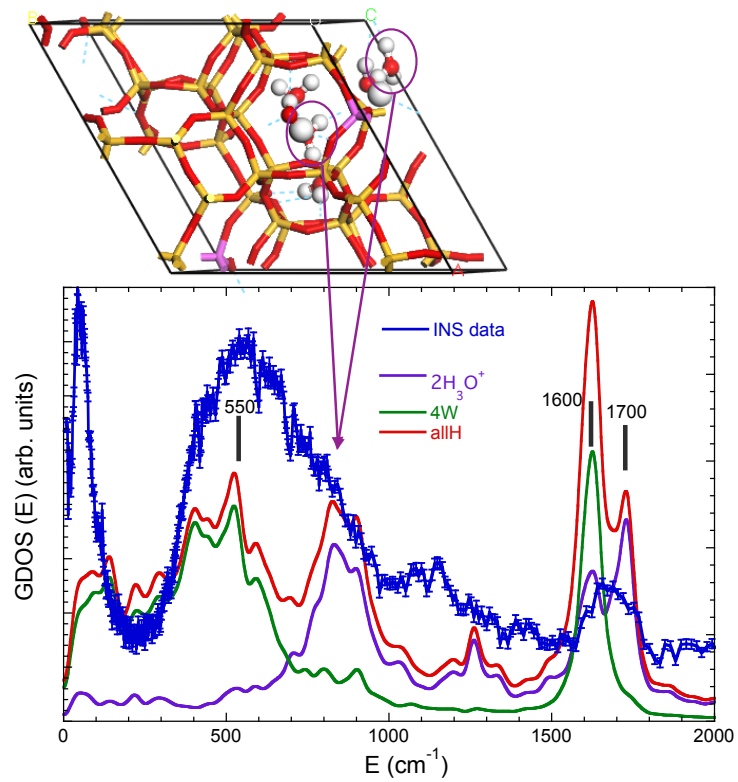The authors declare no competing financial interest.

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References

(1) Weckhuysen, B.M.; Yu, Jihong. Recent advances in zeolite chemistry and catalysis. *Chem. Soc. Rev.* **2015**, 44, 7022-7024.

(2) Jia, W.; Murad, S. Separation of gas mixtures using a range of zeolite membranes: A molecular-dynamics study. *J. Chem. Phys.* **2005**, 122, 234708.

(3) Primo, A.; Garcia, H. Zeolites as catalysts in oil refining. *Chem. Soc. Rev.* **2014**, 43, 7548-7561.

(4) Sousa-Aguiar, E.F. (2016). Zeolites and Zeolite-Like Materials (Eds. Sels. B.F.; Kustov, L.M.) Ch. 6, 270.

(5) Kawai, T.; Tsutsumi, K. Evaluation of hydrophilic-hydrophobic character of zeolites by measurements of their immersional heats in water. *Colloid Polym Sci.* **1992**, 270, 711-715.

(6) Derouane, E.G. (2007). Catalysts for Fine Chemical Synthesis, *Microporous and Mesoporous Solid Catalysts.* Volume 4, 47.

(7) Jobic, H.; Czjzek, M.; van Santen, R. A. Interaction of Water with Hydroxyl Groups in H-Mordenite: A Neutron Inelastic Scatterlng Study. *J. Phys. Chem.* **1992**, 96, 1540-1542.

(8) Wakabayashi, F.; Kondo, J.N.; Domen, K.; Hirose, C. FT-IR Study of $H_2^{18}O$ Adsorption on H-ZSM-5: Direct Evidence for the Hydrogen-Bonded Adsorption of Water. *J. Phys. Chem.* **1996**, 100, 1442-1444.

(9) Smith, L.; Cheetham, A.K.; Morris, R.E.; Marchese, L.; Thomas, J. M.; Wright, P. A.; Chen, J. On the Nature of Water Bound to a Solid Acid Catalyst. *Science* **1996**, 271, 799-802.

(10) Jeanvoine, Y.; Ángyán, J.; Kresse, G.; Hafner, J. On the Nature of Water Interacting with Brønsted Acidic Sites. Ab Initio Molecular Dynamics Study of Hydrated HSAPO-34. *J. Phys. Chem. B* **1998**, 102, 7307-7310.

(11) Termath, V.; Haase, F.; Sauer, J.; Hutter, J.; Parrinello, M. Understanding the Nature of Water Bound to Solid Acid Surfaces. Ab Initio Simulation on HSAPO-34. *J. Am. Chem. Soc.* **1998**, 120, 8512-8516.

(12) Jobic, H.; Tuel, A.; Krossner, M.; Sauer, J. Water in Interaction with Acid Sites in H-ZSM-5 Zeolite Does Not Form Hydroxonium Ions. A Comparison between Neutron Scattering Results and ab Initio Calculations. *J. Phys. Chem.* **1996**, 100, 19545-19550.

(13) Jentys, A.; Warecka, G.; Derewinski, M.; Lercher, J.A. Adsorption of Water on ZSM-5 Zeolites. *J. Phys. Chem.* **1989**, 93, 4837-4843.

(14) Zecchina, A.; Geobaldo, F.; Spoto, G.; Bordiga,S.; Ricchiardi,G.; Buzzoni,R.; Petrini, G. FTIR Investigation of the Formation of Neutral and Ionic Hydrogen-Bonded Complexes by Interaction of H-ZSM-5 and H-Mordenite with CH_3CN and H_2O: Comparison with the H-NAFION Superacidic System. J. Phys. Chem. **1996**, 100, 16584-16599.

(15) Krossner, M.; Sauer, J. Interaction of Water with Brønsted Acidic Sites of Zeolite Catalysts. Ab Initio Study of 1:1 and 2:1 Surface Complexes. *J. Phys. Chem.* **1996**, 100, 6199-6211.

(16) Pazé, C.; Bordiga, S.; Lamberti, C.; Salvalaggio, M.; Zecchina, A.; Bellussi, G. Acidic Properties of H-β Zeolite As Probed by Bases with Proton Affinity in the 118-204 kcal mol^{-1} Range: A FTIR Investigation. *J. Phys. Chem. B* **1997**, 101, 4740-4751.

(17) Bordiga, S.; Regli, L.; Lamberti, C.; Zecchina, A.; Bjørgen, M.; Lillerud, K.P. FTIR Adsorption Studies of H_2O and CH_3OH in the Isostructural H-SSZ-13 and H-SAPO-34: Formation of H-Bonded Adducts and Protonated Clusters. *J. Phys. Chem. B* **2005**, 109, 7724-7732.

(18) Vener, M.V.; Rozanskay, X.; Sauer, J. Protonation of water clusters in the cavities of acidic zeolites: $(H_2O)_n$ H-chabazite, n = 14. *Phys. Chem. Chem. Phys.* **2009**, 11, 1702-1712.

(19) Wang, M. *et al.* Genesis and Stability of Hydronium Ions in Zeolite Channels. *J. Am. Chem. Soc.* **2019**, 141, 3444-3455.

(20) Baerlocher, Ch.; McCusker, L.B. , Database of Zeolite Structures: http://www.iza-structure.org/databases/

(21) Zones, S.I.; Van Nordstrand, R.A.Novel zeolite transformations: The template-mediated conversion of Cubic P zeolite to SSZ-13. *Zeolites* **1988**, 8, 166-174.

(22) Ivanov, A.; Jiménez-Ruiz, M.; Kulda, J. IN1-LAGRANGE the new ILL instrument to explore vibration dynamics of complex materials. *Journal of Physics: Conference Series* **2014**, 554, 012001.

(23) https://doi.ill.fr/10.5291/ILL-DATA.7-05-456

(24) http://accelrys.com/products/materials-studio

(25) Perdew, J.P.; Chevary, J.A.; Vosko, S.H.; Jackson, K.A.; Pederson, M.R.; Singh, D.J.; Fiolhais, C. Atoms, molecules, solids, and surfaces: Applications of the generalized

gradient approximation for exchange and correlation. *Physical Review B* **1992** 46, 6671-6687.

(26) Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77, 3865-3868.

(27) http://accelrys.com/products/datasheets/castep.pdf

(28) Calandrini, V.,; Pellegrini, E.,; Calligari, P.,; Hinsen, K.,; Kneller, G.R., *nMoldyn - Interfacing spectroscopic experiments, molecular dynamics simulations and mod- els for time correlation functions. JDN 2011*, **2011** 12, 201.

(29) Lemishko,T.; Valencia,S.; Rey, F.; Jiménez-Ruiz, M.; Sastre, G., Inelastic Neutron Scattering Study on the Location of Brønsted Acid Sites in High Silica LTA Zeolite. *J. Phys. Chem. C* **2016**, 122, 24904-24909.

(30) Lemishko,T.; Jiménez-Ruiz, M.; Rey, F.; Valencia,S.; Blasco, T.; Vidal Moya, A.; Sastre, G., Inelastic Neutron Scattering Study of the Aluminum and Brønsted Site Location in Aluminosilicate LTA Zeolites. *J. Phys. Chem. C* **2018**, 120, 11450-11454.

(31) Williams, J.M.; *The Hydrogen Bond*, Schuster, P., Zundel, G., Sandorfy, C., Eds.; North-Holland: Amsterdam, 1976; p 655.

(32) Li, J. Inelastic neutron scattering studies of hydrogen bonding in ices *J. Chem. Phys.* **1996**, 105, 6733-6755.

(33) Li, J.; Kolesnikov, A.I. Neutron spectroscopic Investigation of dynamics of water ice. *J. Mol. Liquids* **2002**, 100, 1-39.

(34) Eckert, J. Computational study of inelastic neutron scattering vibrational spectra of water clusters and their relevance to hydration water in proteins. *Biochem Biophys Acta* **2017**, 1861, 3564-3572.

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