

The heterogeneity of the hydroxyl groups in chabazite

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Two different clusters that have the topology of chabazite but different shapes have been used as a model for the Brønsted sites in chabazite. One of the clusters consists of eight tetrahedral atoms (8T) arranged in a ring and the other represents an intersection of two 8T rings. The adsorption of water and methanol on the two stable proton positions in chabazite has been studied using the B3LYP functional. The coordination of water and methanol with respect to the zeolite fragments were found to be similar, but with methanol situated closer to the acid site than water. The anharmonic zeolite OH stretch frequencies were found to be in the range of 2170–2500 cm^{-1} and 1457–2074 cm^{-1} in the presence of water and methanol, respectively. As a measure of the acidity of the bridging hydroxyl groups in chabazite the shift of the zeolite OH stretch frequency upon adsorption has been used. We have found that the proton attached to the oxygen atom O_1 to be more acidic than the proton attached to the oxygen atom O_3 . Also, in the closed ring clusters the zeolite hydroxyl groups are more acidic than in the open clusters. This is not due to a steric effect as the orientation of the adsorbates with respect to the zeolite site is very similar for both clusters. The anharmonicities of the zeolite O–H bond account for about 40% in the redshift upon the adsorption of water or methanol. © 2003 American Institute of Physics. [DOI: 10.1063/1.1628221]

I. INTRODUCTION

The two major factors of the hydrogen form of zeolites that determine their wide range of application as a catalyst are the bridging hydroxyl groups, which determine the catalytic activity, and their porous structure, which determines the shape selectivity. The selectivity is a property that can be measured by the distribution of the end products. The activity can be determined by measuring the rate of the reaction. The mechanism is much more difficult to be studied, however, as it is difficult to observe reaction intermediates and transition states. The hydroxyl groups in zeolites have an acidic character. One way to assess the acidity is to look at the changes in the IR spectra after adsorption of basic molecules such as water and methanol. The interaction with the adsorbates weakens the zeolite OH bond and the corresponding frequency is redshifted. The larger the shift the more acidic is the zeolite hydroxyl group. The question then is what the influence is of a particular zeolite structure on the acidity of the bridging hydroxyl groups.

The adsorption of water and methanol has been studied both on clusters^{1–18} representing a small part of the zeolite and in periodic calculations^{19–26} including the zeolite crystal structure. The role of the zeolite structure on the activation of methanol has been studied in periodic approach but the conclusions are somewhat contradictory. Comparing the adsorption energy and the geometry of methanol on different zeolites Haase *et al.*²⁶ have concluded that the zeolite framework does not have a decisive influence on either the adsorption energy or the geometry. Stich *et al.*²⁵ have concluded that protonation of a single methanol molecule may

occur depending on the zeolite framework. Instead of comparing different zeolite frameworks one can also compare different hydroxyl groups within the same zeolite structure. An example of a zeolite with different hydroxyl groups is chabazite. In the IR spectra two different proton positions are observed²⁷ with a difference in the OH stretch frequencies of 24 cm^{-1} . As there is only one possible Si→Al substitution the protons are bound to oxygen atoms from the same Al tetrahedron. The T–O bond distances are within the narrow interval of 1.599–1.617 Å and the T–O–T bond angle within 144.8–150.0°. In spite of the similarity of the structural parameters the two hydroxyl groups have a different crystallographic environment.

In this paper we have addressed the problem of the effect of the zeolite crystal structure in two ways. Chabazite is modeled with two clusters of different size and shape. The adsorbates, water and methanol, have different basicity and size. We will show that upon the adsorption of water and methanol the two zeolite hydroxyl bonds are strongly perturbed but to a different extent. The acid proton H_1 , observed at higher frequency in the spectra of chabazite, was found to be more acidic than the proton H_3 . The adsorption of methanol in one of the clusters affects the zeolite OH stretch frequency so much that it shifts to the region of 1600 cm^{-1} . Including anharmonicities when calculating the frequency of the zeolite OH stretch vibration is essential. We have found that the contribution of the anharmonicity to the shift of the fundamental frequency can be several hundreds of wave numbers.

II. COMPUTATIONAL DETAILS

The framework of zeolites is built from corner-sharing Al and Si tetrahedra. The crystal structure of pure silica form

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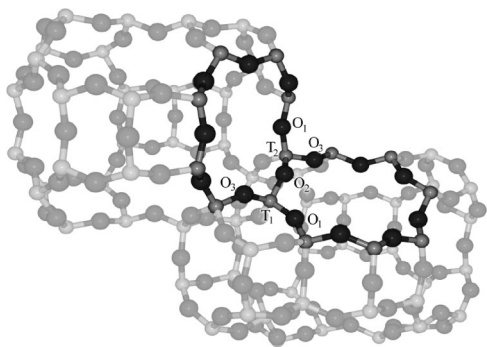


FIG. 1. The intersection of two cages in the crystal structure of chabazite. T_1 and T_2 are part of two 8T rings, which belong to different cages.

of chabazite²⁸ is shown in Fig. 1. The unit cell contains 12T atoms with only one T atom in the asymmetric part. Every T atom is a member of two 8T, three 4T, and one 6T rings. An 8T ring has four T atoms which form a plane, two paired T atoms above, and two paired T atoms below that plane. Substituting a Si atom with an Al atom leads to a formally negatively charged system which can be neutralized by attaching a H atom to the oxygen atoms from the Al tetrahedron. The Al atom was placed in the T_1 position. We have considered protonation of the oxygen atoms O_1 and O_3 which are part of different 8T rings. If the hydrogen atom is bonded to oxygen atom O_1 then within the 8T ring containing that oxygen atom the Al atom is situated in-plane. For the hydrogen atom attached to O_3 the Al atom is out-of-plane.

We model the zeolite with a cluster representing an intersection of two 8T rings in the structure of chabazite, denoted further in this paper as an open 7T cluster (see Fig. 2). The cluster has been terminated by hydrogen atoms, positioned at 1.47 Å along the Si–O bond. The ground state

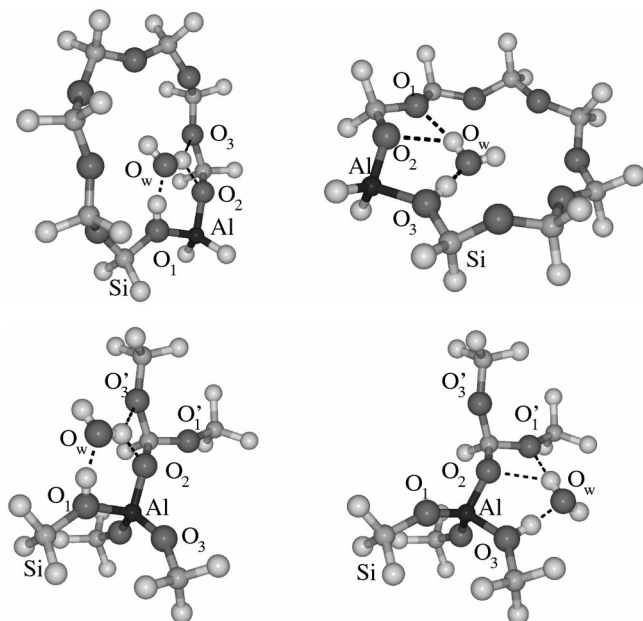


FIG. 2. The calculated adsorption modes of water with the zeolite protons H_1 and H_3 in the closed 8T rings and the open 7T clusters. The projection and the numbering of the oxygen atoms corresponds to Fig. 1. O_x and O'_x , where $x = \{1,3\}$, are symmetrically equivalent.

electronic structure calculations are based on density functional theory using the B3LYP²⁹ functional implemented in GAUSSIAN 98.³⁰ A mixed basis set has been used; 6-311+G* on all oxygen atoms and 6-31G** on Al, Si, C, the acid proton and the protons of methanol and water. To reduce the computational costs a STO-3G basis set has been used on the dangling hydrogens. The geometry constraints of the real zeolite structure has been mimicked by including the terminating hydrogen atoms with fixed Cartesian coordinates at the initial positions. The rest of the cluster has been fully optimized. We have also studied the adsorption of water on 8T rings (see Fig. 2), represented in the same way as described in Ref. 18. To assess the basis set superposition error (BSSE) we have carried out counterpoise calculations.^{31,32} We have used a PW91 and DZVP2 basis set on all atoms in the 8T ring¹⁸ and we have not found significant differences in the geometry and the harmonic frequencies when the STO-3G and DZVP2 basis sets were used on the dangling H atoms. Cluster calculations as described above have been shown to give good results for the interaction of molecules with zeolites.^{1–18}

In the calculations of the shifts of the frequency of the zeolite OH stretch vibration the anharmonicity has been included. This has been done by representing the potential energy in the 1-dimensional vibrational Hamiltonian by a polynomial:

$$H = T + V(r) = \frac{1}{2\mu} p^2 + c_0 + c_1 \Delta r + c_2 \Delta r^2 + c_3 \Delta r^3 + c_4 \Delta r^4, \quad (1)$$

where μ is the reduced mass and Δr is the change of the zeolite OH bond distance. The oxygen and hydrogen atoms have been moved along the OH bond while keeping the center of mass fixed. For the zeolite cluster without adsorbates the coefficients c_i have been obtained by fitting five points. The bond distances were 0.8, 0.9, 1.0, 1.2, and 1.4 times the equilibrium distance r_0 . For the zeolite with adsorbed water or methanol an extra point at 1.55 r_0 was added because of the flatness of the potential energy surface. The fit error for the potential energy surface of the complexes was in the range $1.99\text{--}2.53 \times 10^{-4} E_h$. The harmonic frequencies have been calculated with the quadratic part of the polynomial expression of the potential energy. As the equilibrium structure is a minimum of the potential energy surface, the coefficient c_1 is zero and the harmonic frequency is given by $\omega^h = \sqrt{2c_2\mu}^{-1}$. To find the eigenvalues of the vibrational Hamiltonian including anharmonicities we have expanded the vibrational wave function as a linear combination of Hermite functions³³ up to 12th order. The width of the Hermite functions is determined from the reduced mass and the force constant, $(\hbar^2/2c_2\mu)^{1/4}$. The coefficients were determined using the linear variation principle. The elements of the Hamiltonian matrix could be calculated exactly for the Hamiltonian (1). We have also compared one-dimensional (1-D) harmonic calculations with normal mode calculations with all degrees of freedom of the clusters to show that there is no harmonic coupling between the OH stretch and other modes.

TABLE I. Proton affinity, selected geometry parameters, and O–H vibrational excitation of the zeolite clusters. The vibrational frequencies ω^h and ω_{0-1} are the harmonic and the anharmonic fundamental, respectively, and ω_{0-2} is the anharmonic overtone. Energies in kJ/mol, bond lengths in Å and frequencies in cm^{-1} . A zero point energy correction is included.

		PA	O _z –H	Al–O _z	Si–O _z	ω^h	ω_{0-1}	ω_{0-2}
O ₁	{ 8T ring	1282	0.970	1.959	1.731	3868	3601	6980
	{ 7T cluster	1248	0.968	1.932	1.719	3895	3629	7036
O ₃	{ 8T ring	1284	0.972	1.938	1.708	3843	3574	6925
	{ 7T cluster	1256	0.969	1.883	1.717	3877	3609	6997

Anharmonic coupling terms are neglected here because they affect the frequency of the OH stretch much less than the terms in 1.^{34–36}

III. RESULTS AND DISCUSSION

A. Zeolite cluster without adsorbate

In previous calculations¹⁸ we have studied all the possible acid proton positions. The experimentally found²⁷ and theoretically predicted^{18,20,37–40} preferred positions for the acid protons in chabazite are oxygen atoms O₁ and O₃. In the present study we will concentrate on them.

The difference in the relative stability of the two acid proton positions in the open 7T clusters is 8.1 kJ/mol in favor of the proton H₃. This energy difference is by 5.4 kJ/mol larger than what we have found for the cluster of an 8T ring.¹⁸ The relative stability of the acidic protons is in agreement with other cluster calculations using 13T atoms⁴¹ and an embedded 5T cluster.⁴² In periodic calculations^{20,37,39,41} the H₁ proton position becomes more stable. As can be seen from Table I the proton affinities of the oxygen atoms show a strong dependence on the choice of the cluster. Compared to the 8T rings the proton affinity of the open 7T clusters are lower by 28–34 kJ/mol. When the H atoms attached to the Al atom in the 8T ring were replaced by OSiH₃ groups, the proton affinities were increased by 10 and 4 kJ/mol for oxygen atoms O₁ and O₃, respectively. Brand *et al.*⁴³ have found a strong dependence of the deprotonation energies not only on the size but also on the shape of the clusters. Our results agree with this observation. Although the absolute values of the proton affinity changes for the different clusters, the oxygen atom O₃ has a higher proton affinity than the oxygen atom O₁ for all cluster approximations. Experimental data for the deprotonation energies of chabazite are not available. Based on periodic calculation Haase *et al.*²⁶ have found a value of 1196 kJ/mol for the H₁ proton position. Embedding 2T clusters Brändle *et al.*⁴⁴ have reported 1277 kJ/mol and 1258 kJ/mol for H₁ and H₃ proton positions, respectively. Compared to our results, the difference in the proton affinity of the two oxygen atoms is larger, 17 kJ/mol, and in their calculations the oxygen atom O₁ has a higher proton affinity than the oxygen atom O₃. Using a different embedding method Naslusov *et al.*⁴² have found the proton affinity of the O₃ oxygen atom to be higher by 6 kJ/mol than that of the O₁ oxygen atom. They have reported deprotonation energies of 1250 and 1256 kJ/mol for the proton positions H₁

and H₃, respectively. These values are only by 2 kJ/mol lower than the corresponding values we have calculated for the open 7T cluster.

The way the Al atom is terminated influences the Al–O bond distance for a greater extent than the OH bond distance (see Table I). When instead of H atoms OSiH₃ groups are used to terminate the Al atom, the Al–O(H) bond distance is by 0.027 Å and 0.055 Å shorter for O₁ and O₃, respectively. The OH bond distance is shortened by 0.003 Å for the O₃ atom. The Al–O(H) distance for the H₃ proton position in the open 7T cluster agrees very well with the periodic calculations^{26,39} and embedded 2T clusters.⁴⁴ The corresponding distance for the H₁ proton position in our calculation is longer by 0.025 Å. Greatbanks *et al.*⁷ have also found a slight increase of the Al–O(H) and OH distances when embedding a 3T cluster.

The calculated harmonic and anharmonic frequencies are also presented in Table I. The anharmonicities have the following effect on the vibrational energy levels. They shift the energy levels to lower energy and decrease the distance between the levels. As can be seen from Table I the anharmonic frequencies for the fundamental transition ω_{0-1} are by 266–269 cm^{-1} lower compared to the harmonic ones. For the 8T rings the frequency of the stretch vibrations of the zeolite hydroxyl groups are 3601 cm^{-1} and 3574 cm^{-1} , for the proton positions H₁ and H₃, respectively. These values are in excellent agreement with the experimental values²⁷ of 3603 cm^{-1} and 3579 cm^{-1} . For the open 7T cluster the frequency is shifted 35 cm^{-1} upwards for the H₃ proton position. The near IR spectrum provides information about the overtones of the OH stretch vibration. In a harmonic approximation the frequency of the overtone is a multiple of the fundamental frequency. The experimental values^{45,46} of the first overtone of HZSM-5 are at 7077 cm^{-1} and 7065 cm^{-1} . These values are smaller than twice the fundamental frequency, which shows that indeed the separation between the first and the second excited states is smaller than the separation between the ground and the first excited states. We have calculated somewhat lower frequencies for the overtones, which indicates that the anharmonicity of the OH bond is larger in our theoretical model.

Nevertheless the difference in the relative proton stability between our models for the acidic site and the periodic calculations, we have found in an agreement with the experiment and the periodic calculations the OH stretch frequency of the H₁ proton to be higher than that of the H₃ proton. Shah

TABLE II. Adsorption energy and selected geometry parameters of water adsorbed on the clusters. Energies in kJ/mol, bond lengths in Å. A zero point energy correction is included. H_w^f denotes the hydrogen atom from the water molecule which is not involved in hydrogen bonding the the zeolite cluster.

		E_{ads}	O_1-H	O_2-H	O_3-H	O_w-H_z	O_w-H_w	$O_w-H_w^f$
O_1	8T ring	-66.5	1.026	2.034	2.561	1.533	0.976	0.964
	7T cluster	-68.2	1.016	1.882	2.495	1.568	0.982	0.962
O_3	8T ring	-78.8	2.104	2.551	1.020	1.566	0.973	0.964
	7T cluster	-67.3	2.031	2.345	1.013	1.586	0.977	0.962

et al.^{20,37} have calculated anharmonic frequencies of 3590 and 3565 cm^{-1} for the H_1 and H_3 proton position, respectively. Jeanvoine *et al.*³⁹ have reported somewhat lower anharmonic frequencies. The differences between our cluster calculations and the periodic calculations is not only the way the acidic site is modeled but also in the periodic calculations the PW91 density functional and plane waves as a basis set were used. We have shown¹⁸ that the PW91 functional gives longer OH bond distances and lower harmonic frequencies compared to the B3LYP functional. We expect that the lower anharmonic frequencies obtained in the periodic calculations are mainly due to the density functional. Ugliengo *et al.*⁴⁷ have calculated the anharmonic frequency of 3624 cm^{-1} for the H_1 proton position which is in a very good agreement with that of the open 7T cluster in the present study. They have used B3LYP and a localized basis set in a periodic approach.

B. Zeolite rings with adsorbates

1. Water

Energies. The adsorption energies and the geometries of a water molecule interacting with the zeolite clusters are shown in Table II. For both cluster types the water complex with the acid proton H_3 is more stable. The difference in the adsorption energies of the water molecule within the 8T ring is 10 kJ/mol in favor of the adsorption complex with the acid proton H_3 . For the open 7T clusters the difference almost disappears. All values for adsorption energies listed in Table II are within the range of previous theoretical studies,^{8,10,14,17,19} from -45.6 to -92.5 kJ/mol.

Geometries. Selected geometrical parameters characteristic for the complexes between water and the zeolite active site are listed in Table II. The water coordination is depicted in Fig. 2. In both adsorption complexes a strong hydrogen bond is formed between the zeolite proton (H_z) and the oxygen atom (O_m) of water (see Table II and Fig. 2). We will refer to it as a primary hydrogen bond. One of the hydrogen atoms of the water molecule forms a bifurcated hydrogen bond with the oxygen atoms of the zeolite cluster. This hydrogen bond will be referred as a secondary hydrogen bond. The zeolite oxygen atom closest to the water proton in the complex of water with the acid proton H_1 is O_2 which belongs to the Al tetrahedron, whereas for the complex with the acid proton H_3 this is the oxygen atom O_1' from the neighboring Si tetrahedron. The backbone of the ring is not present in the open 7T clusters. When one goes from the open 7T cluster to the closed 8T ring the $O_w \cdots H_z$ distance decreases for both acid proton positions. This goes along

with the lengthening of the O_z-H_z bond distance. The water proton in the open 7T cluster is closer to the zeolite oxygen atoms than in the 8T ring. Similar strengthening of the primary hydrogen bond and weakening of the secondary hydrogen bond was found by Greatbanks *et al.*⁷ when embedding a 3T cluster. They have found an $O_w \cdots H_z$ distance shortened by 0.07 Å and an O_z-H_z bond distance elongated by 0.05 Å. We do not observe such great changes in the coordination of the water molecule as the cluster we consider includes the neighboring Si tetrahedron, which makes it more flexible. In the open 7T cluster and in the closed 8T ring the fragment of the zeolite the water molecule interacts with includes the same number of oxygen atoms and the reorientation of the water molecule is less pronounced. For comparison the $O_w \cdots H_z$ distance is shortened by 0.04 Å and the O_z-H_z is elongated by 0.01 Å for the complex with the acid proton H_1 . Tajima *et al.*⁹ have also observed a similar trend of strengthening of the primary hydrogen bond when extending a 3T cluster to an 8T ring of H-form zeolite. It is difficult to compare the absolute values as in their calculations the zeolite fragment was treated as a rigid anion framework. With regard to the distance between the water molecule and the zeolite proton and the zeolite hydroxyl bond distance, our results differ from previous theoretical calculations.^{7,8,10,17,19} We have found water to be closer to the zeolite proton compared to the adsorption modes found by Ryder *et al.*¹⁷ and Zygmunt *et al.*¹⁰ and further from the zeolite proton in comparison with Krossner *et al.*⁸ and Nusterer *et al.*¹⁹ The zeolite hydroxyl bond distance was found to be shorter.

Frequencies. The interaction between the water molecule and the acid site is via a hydrogen bond, which weakens the zeolite hydroxyl bond. As can be seen later from Table IV, the zeolite OH stretch vibration frequencies are shifted to lower values compared with the frequencies for the isolated zeolite clusters. Already in the harmonic approximation the shift is 629–880 cm^{-1} . The smaller shift is for the adsorption complex with the acid proton H_3 in the open 7T cluster and the upper shift is for the one with the acid proton H_1 in the 8T ring. Along with the weakening of the zeolite OH bond the potential energy surface flattens which is expressed in increasing the difference between the harmonic and anharmonic frequencies. We have calculated anharmonic frequencies for the zeolite OH stretch vibration in the presence of water in the range of 2170–2500 cm^{-1} . The frequencies for the acid proton H_3 in the 8T ring are close to the experimental value²⁷ of 2403 cm^{-1} in the spectra of hydrated H-SSZ-13. The frequency for the same proton in the open 7T cluster is close to the experimental value^{10,48,49} of

TABLE III. Adsorption energy and selected geometry parameters of methanol adsorbed on the clusters. Energies in kJ/mol, bond lengths in Å. A zero point energy correction is included.

		E_{ads}	$\text{O}_1\text{-H}$	$\text{O}_2\text{-H}$	$\text{O}_3\text{-H}$	$\text{O}_m\text{-H}_z$	$\text{O}_m\text{-H}_m$
O_1	8T ring	-68.4	1.062	2.090	2.394	1.422	0.975
	7T cluster	-74.5	1.029	2.022	2.376	1.509	0.976
O_3	8T ring	-75.3	2.107	2.383	1.046	1.472	0.974
	7T cluster	-74.0	2.084	2.330	1.029	1.520	0.975

2480 cm^{-1} of the B band in the spectrum of water adsorbed on HZSM-5. The anharmonicity of the zeolite OH bond is larger for the 8T rings compared to the open 7T clusters. For the isolated OH stretch vibrations we have calculated a difference between the harmonic and anharmonic frequencies of 266–269 cm^{-1} . In the presence of water we have found that the difference almost doubles.

The two proton position in the 8T ring and the open 7T cluster have different environments which affects the adsorption geometry of the complex with water and the OH stretch vibration frequencies. When the backbone of the ring is removed the frequencies are shifted upwards for both acid positions. The shift for the acid proton H_1 is 240 cm^{-1} , whereas for H_3 it is 154 cm^{-1} . The difference in the deprotonation energies of the two protons in the 8T ring is only 2 kJ/mol and it increases to 8 kJ/mol for the open 7T cluster. It is a too small difference to say which of the two zeolite protons is more acidic. However, if we compare the frequencies of the two OH bonds in the 8T ring, we will find a difference of 180 cm^{-1} . For the open 7T cluster the corresponding difference is 94 cm^{-1} . Therefore we draw the conclusion that the proton position H_1 is more acidic as its frequency in the presence of water is at a lower value.

C. Methanol

Energies. The adsorption of methanol within the 8T rings has been extensively discussed in Ref. 18. In this paper we want to point out the differences in the geometry and the IR frequencies when methanol is adsorbed on an open 7T cluster and on a closed 8T ring. The adsorption energies and the geometries of a methanol molecule interacting with the zeolite clusters are listed in Table III. For both clusters representing the zeolite active site the most stable configuration is with the H_3 proton position. The adsorption energy for the proton position H_1 is larger for an open 7T cluster than for an 8T ring by 7 kJ/mol. For the proton position H_3 the it is other way around but by only 1 kJ/mol. Similar to water, methanol adsorbed on the open 7T cluster shows almost the same adsorption energies.

We have calculated a proton affinity of methanol of 754 kJ/mol and water of 686 kJ/mol. As methanol is more basic than water one expects that methanol will interact stronger with the acid site. Indeed when water and methanol were co-adsorbed on HZSM-5⁵⁰ the TPD and the IR spectra have shown the pure adsorption of methanol only. The difference in the adsorption energies, we have calculated, are in agreement with this observation though they differ only by 5 kJ/mol.

Geometries. The coordination of methanol and water in

the open 7T clusters and the 8T rings is similar (see Figs. 2 and 3). The adsorbate OH bond distances are very alike with the exception of the complex with the acid proton H_1 in the open 7T cluster. There the water proton is the closest to the zeolite cluster and the corresponding OH bond distance in water is the longest. The major difference between the methanol and water complexes is the strength of the primary hydrogen bond. As the adsorption energies suggest methanol to be bounded stronger to the acid proton, in terms of geometry this is expressed in a shorter $\text{O}_m\cdots\text{H}_z$ distance. The influence of the backbone of the ring on the geometries of the methanol coordination in the rings follows the same trend as for water, but it is more pronounced. For both acid proton positions the $\text{O}_m\cdots\text{H}_z$ distance in the 8T ring is shorter than the one in the open 7T cluster and the corresponding zeolite hydroxyl bond distance is longer. The $\text{O}_m\cdots\text{H}_z$ distance is shortened by 0.087 Å and 0.048 Å for the proton positions H_1 and H_3 , respectively. The zeolite OH bond distance is elongated by 0.033 Å for the proton H_1 and by 0.023 Å for the proton H_3 .

Frequencies. The calculated harmonic and anharmonic frequencies are listed in Table IV. As methanol forms a

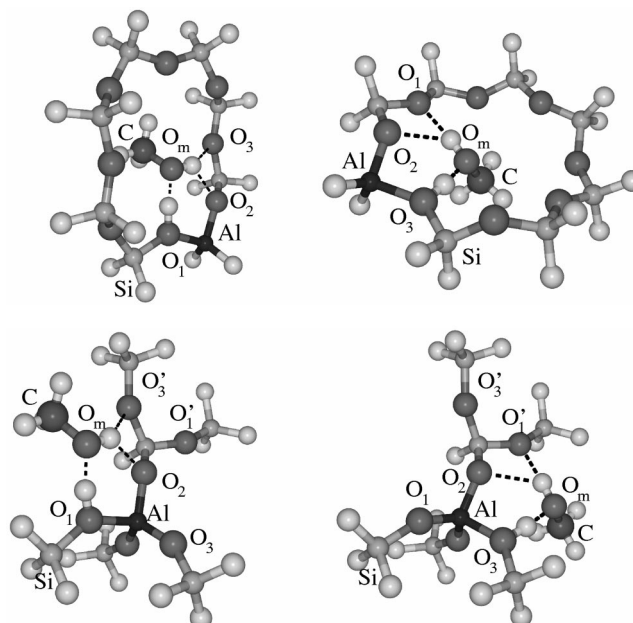


FIG. 3. The calculated adsorption modes of methanol with the zeolite protons H_1 and H_3 in the closed 8T rings and the open 7T clusters. The projection and the numbering of the oxygen atoms corresponds to Fig. 1. O_x and O'_x , where $x=\{1,3\}$, are symmetrically equivalent.

TABLE IV. The anharmonic (ω^{anh}) and the harmonic (ω^h) frequencies, and their difference for the zeolite OH stretch vibrations with adsorbed water and methanol on the different clusters. In parentheses the harmonic frequencies from a normal mode analysis including the framework vibrations are given. The frequencies are in cm^{-1} .

		Water			Methanol		
		ω^{anh}	ω^h	$\omega^{\text{anh}} - \omega^h$	ω^{anh}	ω^h	$\omega^{\text{anh}} - \omega^h$
O_1	{ 8T ring	2170	2721(2697)	551	1457	2165(2119)	708
	{ 7T cluster	2410	2876(2853)	466	2060	2649(2625)	589
O_3	{ 8T ring	2350	2840(2819)	490	1686	2404(2384)	718
	{ 7T cluster	2504	2980(2920)	476	2074	2657(2637)	583

stronger hydrogen bond with the zeolite, the frequencies are expected to be even more redshifted compared to water. In harmonic approximation the shift is in the interval of $952\text{--}1436\text{ cm}^{-1}$. Similar to water the lower shift is for the acid proton H_3 in the open 7T ring and the upper shift for the acid proton H_1 in the closed 8T ring. When anharmonicities are included the frequencies are further decreased. For the 8T ring the anharmonic zeolite OH stretch vibration frequency is 1457 cm^{-1} for the proton H_1 and 1686 cm^{-1} for the proton H_3 . This shows that the stretch vibration can be lowered so much that it falls in the region where the bending vibration of water is, which is generally the mode assignment for frequencies in that region. In the power spectra of a single methanol molecule adsorbed on chabazite Stich *et al.*²⁵ have found for the OH vibrations only a peak at about 1600 cm^{-1} . In their MD simulations they have observed a formation of methoxonium cation but in the power spectra the asymmetric and symmetric OH stretch frequencies were missing. The band at about 1600 cm^{-1} has been assigned to the bending vibration of a protonated methanol molecule. As Stich *et al.* have done the calculations in a periodic approach, thus the crystal structure of chabazite is included, our results for the frequencies in the 8T ring can be compared with theirs. The hydrogen bond between the acid proton and methanol weakens the zeolite hydroxyl bond in such an extent that the potential energy becomes very flat. The anharmonicities are large and even for physisorbed methanol a band at about 1600 cm^{-1} can be observed, which is a strongly perturbed OH stretch vibration. The frequencies for the open 7T cluster are shifted upwards for the proton H_3 by 603 cm^{-1} and for H_1 by 388 cm^{-1} . This shows that potential energy surface depends very much on the shape of the cluster representing the zeolite active site.

The interaction of methanol with the acid proton H_1 is influenced strongly by the addition of the backbone of the ring both in terms of the adsorption energies and geometries. In the 8T ring and the 7T cluster the Al atom has different surroundings. In order to check whether the observed differences are also due to the different termination of the Al atom we have carried out calculations on an 8T ring with Al atom terminated by OSiH_3 groups. The adsorption energy was found to be -82.5 kJ/mol , 14.2 kJ/mol larger in absolute value, whereas the geometry related to the coordination of the methanol molecule changed not more than 0.007 \AA . The harmonic frequency of the zeolite OH stretch was only by 2 cm^{-1} lower. When H atoms were used to terminate the Al

atom in the 7T cluster the adsorption energy has decreased only by 0.9 kJ/mol . The zeolite OH bond distance was increased by 0.002 \AA and the $\text{O}_m \cdots \text{H}_z$ distance was decreased by 0.011 \AA . The harmonic frequency of the zeolite OH stretch was decreased by 36 cm^{-1} . As has been shown in other theoretical studies^{2,5} by extending open clusters the interaction energy changes while the geometry changes little. We conclude that we can compare the 7T cluster and 8T ring although the Al atom has different surroundings. The main changes in the geometry and the frequencies are caused by the inclusion of the backbone of the ring.

BSSE. Usually the BSSE correction energy is calculated for the equilibrium structure. For the water and methanol complexes in the 8T ring the BSSE was found to be in the range of $18.0\text{--}26.1\text{ kJ/mol}$ whereas for the 7T cluster the values are by 10 kJ/mol lower, $10.8\text{--}12.3\text{ kJ/mol}$. We have calculated BSSE corrected anharmonic frequencies for the methanol complex with the H_3 proton in the following way. For each geometry we have calculated the BSSE correction energy and added it to the total energy and then perform the fit. The BSSE correction was 22.9 kJ/mol for the shortest distance and 24.8 kJ/mol for the longest distance. The difference is only 2 kJ/mol . The anharmonic frequency was increased by 22 cm^{-1} . This shift falls in the range of $10\text{--}40\text{ cm}^{-1}$ found by Silvi *et al.*⁵¹ for hydrogen bonded dimers and a hydrogen bonded NH_3 to the silanol groups.⁵² The shift caused by the inclusion of the BSSE is much smaller than the shift resulting from including the anharmonicity. Therefore it will not influence the comparison and the conclusions made in this paper.

Anharmonicities. As can be seen from Table IV, the anharmonicity of the zeolite OH stretch vibrations for both water and methanol in the 8T rings are larger than in the open 7T clusters. Methanol forms a stronger hydrogen bond with the zeolite hydroxyl group and the frequencies are more red shifted than the ones with water, and the effect of the anharmonicity is stronger. It is interesting to see what fraction of the total shift of the zeolite OH stretch vibration frequency is due to the anharmonicity. This can be done by dividing the total shift of the frequency minus the shift in the harmonic approximation by the value of the total shift. For water on all clusters $38\text{--}43\%$ and for methanol $33\text{--}38\%$ is due to anharmonicities. Although the absolute value of the shift caused by the anharmonicity in the presence of methanol is larger, its contribution to the total shift is smaller or equal to that for water.

The anharmonic shifts are rather large. Del Bene *et al.*⁵³ have also found a very large anharmonic shift (more than 1000 cm^{-1}) for the Br–H stretch mode in the complex with ammonia. In their study both hydrogen bonded and protonated complex were local minima along the Br–H bond. When water or methanol is adsorbed on the acidic site for both cluster models the potential energy surface has only one minimum when the hydrogen and the oxygen atoms are moved along the O–H bond.

That the OH stretch mode is not coupled to the other modes can be seen as follows: The harmonic frequencies obtained from the 1-D potential energy surface and from a normal mode analysis including framework vibrations are quite close (see Table IV). Also the atomic displacements of the normal mode vibrations show that there is only one mode with appreciable displacement of the oxygen atom and the hydrogen atom of the OH group, and that there is hardly any displacement of other atoms for that mode. So we have a very well defined OH stretch vibration.

The role of the crystal structure. Methanol is a larger molecule than water and one may think that the hydrogen bond between methanol and the zeolite OH group is strengthened because the backbone of the ring pushes methanol towards the acid site. The methyl group of methanol, however, is not in the ring but on both cluster types the orientation of methanol in respect to the zeolite site is very similar. Therefore the steric effect can be excluded. The ring structure enhances the interaction between the adsorbates and the zeolite. This is probably due to an electrostatic effect that increases the basicity of water and methanol.

IV. CONCLUSIONS

In this paper we have studied the adsorption of water and methanol on two different clusters that have the topology of chabazite but a different shape. In the 8T rings the adsorbates are stronger bound than in the 7T rings. The proton position H_3 is more favorable than the H_1 position. The interaction between the acid site and the adsorbates is via a hydrogen bond. The distance between the adsorbate oxygen atom and the zeolite proton was found to be 1.533–1.586 Å for water and 1.422–1.520 Å for methanol.

The zeolite OH stretch vibration frequencies have been calculated including anharmonicities. Without adsorbates the two proton positions in chabazite are very much alike, both with regard to the OH bond distance and the OH stretch vibration frequency. The presence of water and methanol makes them more distinguishable as can be seen from the zeolite OH stretch frequencies of the 8T rings. This difference between the frequencies of the protons H_1 and H_3 is 180 cm^{-1} when water is adsorbed and 229 cm^{-1} in the case of methanol. The backbone of the ring strengthens the hydrogen bond between the adsorbates and the zeolite hydroxyl group. The zeolite OH bond is weakened and the anharmonicities become more important. Their contribution to the total shift of the zeolite OH stretch frequency can be up to 43%. In the case of methanol adsorbed in the 8T rings the zeolite OH bond is so much weakened that the stretch frequency gets close to 1600 cm^{-1} , where the bending fre-

quency of a water like fragment is observed. Thus, a frequency around 1600 cm^{-1} does not necessarily mean that the protonation of methanol has occurred.

The comparison between adsorbed water and adsorbed methanol has shown that the backbone of the ring has a larger influence on the adsorption geometry and frequency of the zeolite OH bond in the case of methanol. In order to get a quantitative agreement of the calculated and experimental frequencies, at least the zeolite OH in-plane and out-of-plane bending coordinates have to be included. Such multidimensional studies are in progress. Finally, our results seem to indicate that the electronic structure calculations give good potential energy surfaces, and that deviations from normal mode analyses are due to the neglect of anharmonicities.

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