Quantum chemical calculation of infrared spectra of acidic groups in chabazite in the presence of water

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The changes in the spectra of the acidic group in chabazite are studied by quantum chemical calculations. The zeolite is modeled by two clusters consisting of eight tetrahedral atoms arranged in a ring and seven tetrahedral atoms coordinated around the zeolite OH group. The potential energy and dipole surfaces were constructed from the zeolite OH stretch, in-plane and out-of-plane bending coordinates, and the intermolecular stretch coordinate that corresponds to a movement of the water molecule as a whole. Both the anharmonicities of the potential energy and dipole were taken into account by calculation of the frequencies and intensities. The matrix elements of the vibrational Hamiltonian were calculated within the discrete variable representation basis set. We have assigned the experimentally observed frequencies at ~ 2900, ~ 2400, and ~ 1700 cm^{-1} to the strongly perturbed zeolite OH vibrations caused by the hydrogen bonding with the water molecule. The ABC triplet is a Fermi resonance of the zeolite OH stretch mode with the overtone of the in-plane bending (the A band) and the overtone of the out-of-plane bending (the C band). In the B band the stretch is also coupled with the second overtone of the out-of-plane bending. The frequencies at ~ 3700 and ~ 3550 cm^{-1} we have assigned to the OH stretch frequencies of a slightly perturbed water molecule. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1709896]

I. INTRODUCTION

Zeolites in their hydrogenated form are very important catalysts for many reactions in petrochemistry that require Brønsted acidity. During the last decade, adsorption of water on zeolites has been extensively studied both experimentally[1–8] and theoretically[9–20] in order to understand the nature of the interaction of basic molecules with the Brønsted sites in the zeolites. The reaction can be studied by infrared spectroscopy because the frequencies of the vibrations of the zeolite hydroxyl group will change upon interaction with the water molecule. When water is adsorbed on H-ZSM-5,[1–6,21] HY,[7] H-MOR,[4] or chabazite[22] a triplet of bands appears at 2872–3000, 2403–2515, and 1700 cm^{-1}, known also as an ABC triplet. This triplet is accompanied by two peaks at 3700 and 3550 cm^{-1}. The A and B bands have been interpreted by Marchese et al. as an asymmetric and a symmetric OH stretch of a protonated water molecule, and the C band as a H–O–H bending vibration. This model does not explain the two peaks above 3550 cm^{-1}. Theoretical models have been made by representing the zeolite by clusters consisting of several tetrahedral atoms,[9–17] and a hydrogen-bonded water molecule was found to be a minimum on the potential energy surface and a protonated water molecule to be a transition state. The molecular dynamics of water in sodalite[18] and H-SAPO-34 (Refs. 19 and 20) has shown that a single water molecule is hydrogen bonded to the acidic site. Molecular dynamics (MD) simulations give contradicting results for the protonation of water in zeolites. Nusterer et al.[18] have shown for sodalite and Jeanvoine and

Ángyán[19] for H-SAPO-34 that when two water molecules are adsorbed a proton transfer from the zeolite to the water cluster can take place. Termath et al.[20] have shown that three water molecules are needed to form a protonated water cluster. Benco et al.[23] have, however, observed protonated water when performing MD simulations of a single water molecule in gmelinite. Experiments with ^{18}O-substituted water molecules[3,8] also support the model for hydrogen-bonded complexes because the positions of the bands in the ABC triplet did not change. If the vibrations of the water molecule were involved in the ABC triplet, the frequencies are expected to be shifted because of the change of the reduced mass.

The fingerprint of a hydrogen-bonded hydroxyl group is the broadening of the OH stretch band. In liquids this has been explained[24–26] as a coupling of the OH stretch mode with the intermolecular mode OH···adsorbate. The appearance of two or three bands has been explained with a Fermi resonance of the downward-shifted OH stretch with upward-shifted OH bending modes. Pelmenschikov et al.[9,10] have proposed this model to hold also for the spectra of acidic zeolites interacting with basic molecules.

Quantum chemical calculations can help by assigning these frequencies. The common way to calculate infrared frequencies is the harmonic approach. Such an approach is not adequate to describe the idea of Fermi resonance, which is between the fundamental of the OH stretch and the two overtones of the OH bendings.[27] This requires at least a cubic coupling term. Moreover, the large shift of the OH stretch itself is also caused in large part by anharmonicities in the potential energy surface. In the present work we have calcu-

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lated the frequencies of the zeolite OH group with and without water using anharmonic potential energy and dipole surfaces that have been constructed from the zeolite OH stretch, in-plane bending, out-of-plane bending, and the water molecule center of mass. We will show that the anharmonic coupling of the zeolite OH stretch mode with the in-plane and out-of-plane bending modes results in states in which the first excited state of the stretch is mixed with the first overtone of the in-plane bending and with the first and second overtones of the out-of-plane bending. In the ABC triplet the main contribution in the A band is from the overtone of the in-plane bending, in the B band this is the stretch, and in the C band this is the overtone of the out-of-plane bending.

II. COMPUTATIONAL DETAILS

A. Electronic structure calculations

We model the zeolite by two clusters that have the topology of chabazite.[28] One of the clusters is an 8T ring and the other represents an intersection of two 8T ring (see Fig. 1). We will refer to the latter as an open 7T cluster. The clusters have been terminated by hydrogen atoms, positioned at 1.47 Å (Si–H) and 1.55 Å (Al–H) along the Si–O bond. The ground-state electronic structure calculations are based on density functional theory using the B3LYP (Ref. 29) functional implemented in GAUSSIAN98 (Ref. 30). A mixed basis set has been used: 6-311+G* on the oxygen atom of the water molecule, all oxygen atoms in the open 7T cluster, and oxygen atoms O_1, O_2, and O_3 in the 8T ring, and 6-31G** on Al, Si, the rest of the oxygen atoms in the 8T ring, the acidic proton, and the protons of water. To reduce the computational costs the STO-3G basis set has been used on the dangling hydrogens. The geometry constraint of the real zeolite structure has been mimicked by fixing the terminating hydrogens at their initial positions. The rest of the clusters has been fully optimized.

B. Dynamics

The hydrogen bond between the water molecule and acid site leads to a flat potential energy surface along the zeolite hydroxyl bond. The anharmonicities are large and from a one-dimensional calculations we have estimated an anharmonic downward shift of the zeolite OH stretch frequencies in the interval of 466–551 cm^{-1}. Previous theoretical studies[13,17,31] have shown a protonated water molecule to be a transition state that connects two almost equivalent hydrogen-bonded minima with the activation energy being 15–26 kJ/mol. Such a low activation energy should be treated as a double-well potential. The two minima in these studies correspond to O_2 and O_3 in Fig. 1. We have used larger clusters including the neighboring Si tetrahedron. As a consequence, we could no longer find a stable situation with a proton on O_2. The water proton can move to the zeolite framework, but to O_1 and not to O_2. Proton transfer between oxygen atoms O_1 and O_3 in the same 8T ring (see Fig. 1) will result in an acid group from a Si tetrahedron rather than an Al tetrahedron, which is not a stable configuration as observed also by Haase $et\ al.$[32] To realize a proton exchange between the oxygen atoms O_1 and O_3 from the Al tetrahe-
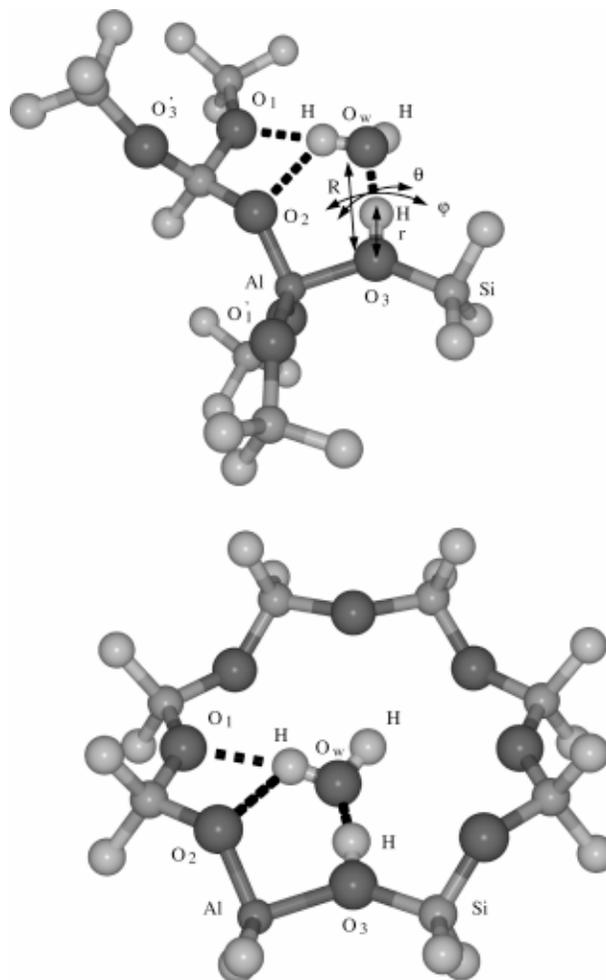

FIG. 1. Equilibrium structures of water adsorbed on the 7T cluster and 8T ring and a schematic representation of the internal coordinates used to compute the spectra. O_x and O'_x, where $x=\{1,3\}$, are symmetrically equivalent. The coordinates are defined as follows: the zeolite OH stretch coordinate r, the zeolite in-plane bending φ, the out-of-plane θ, and the water center-of-mass coordinate R, which is the distance between the center of mass of the water molecule and the O_z atom.

dron the water molecule has to be moved from one 8T ring to another, which we expect to be a reaction with a high activation energy. Therefore, we think that we have a single well-defined minimum for a hydrogen-bonded water molecule.

We have focused on the OH vibrations in the zeolite before and after adsorption of water, because these vibrations are the most affected by the interaction between the water molecule and acid site. To compute the infrared spectra for all OH vibrations at least seven internal coordinates are needed: the zeolite stretch, in-plane and out-of-plane bending, the water symmetric and asymmetric stretch and bending, and the water center of mass. A complete potential energy surface will be very costly to calculate. In the complex of water with zeolite the geometry of the water molecule is slightly changed compared to an isolated water molecule. The hydrogen bond between the water molecule and acidic proton causes a drastic decrease of the zeolite OH stretch frequency. Due to this large shift, we do not expect that there will be significant coupling between the internal coordinates

of the water molecule and the zeolite OH group, so we have treated them separately.

We have used two sets of coordinates for calculating the infrared spectra: one for obtaining the potential energy surface and the other for solving the Schrödinger equation for the vibrations. The potential energy and dipole surfaces for the zeolite OH vibrations were expressed in the internal coordinates shown in Fig. 1. These form the first set of coordinates. They allow an accurate and relatively simple description of these surfaces. The zeolite OH stretch coordinate describes the movement of the oxygen and hydrogen atoms along the equilibrium zeolite OH bond. For the zeolite OH group two bending modes can be defined. If we consider the Si–O–Al plane, then the in-plane bending coordinate describes the tilting of the zeolite OH group in that plane and the out-of-plane bending coordinate describes the tilting of the zeolite OH group in a plane perpendicular to the Si–O–Al plane and containing the zeolite OH bond. The oxygen and hydrogen atoms have been moved along these coordinates for these three vibrations while conserving the center of mass of the zeolite OH group. The rest of the atoms from the zeolite clusters have been kept fixed at their equilibrium positions. The fourth coordinate corresponds to the movement of the water molecule along the $O_z\cdots O_w$ bond while keeping all internal coordinates of water fixed.

For the water molecule we have included the OH stretch vibrations and the bending coordinate that is the variation of the H–O–H angle. The hydrogen and oxygen atoms were moved along these coordinates while keeping the center of mass of the water molecule fixed.

The potential energy and dipole surfaces were fitted by a polynomial of coordinates $\{q_k\}$ that are the changes of the internal coordinates. The potential energy for the zeolite OH group plus the water center of mass is given by

$$V(q_1,\ldots,q_4)=\sum_{i_1,\ldots,i_4} c_{i_1,\ldots,i_D}\prod_{k=1}^{4} q_k^{i_k}, \tag{1}$$

with

$$q=(\Delta r,\sin \Delta \varphi,\cos \Delta \theta,\Delta R), \quad 0\leqslant\sum_{k=1}^{4} i_k\leqslant n. \tag{2}$$

In these expressions $c_{i_1,\ldots,i_D}$ are coefficients, n is the order of the polynomial, Δr is the deviation of the zeolite OH bond distance from the equilibrium structure, $\Delta \varphi$ is the change of the in-plane angle φ, $\Delta \theta$ is the change of the out-of-plane angle θ, and ΔR is the change of the distance between the zeolite oxygen atom and the center of mass of the water molecule (see Fig. 1).

The values of the internal coordinates should cover the area where the wave functions of interest have non-negligible amplitudes. For each coordinate separately we have used 15 points and performed a fit of the one-dimensional potential energy (see below). With this fit we determined for each coordinate separately the vibrational ground and excited states as explained below. We then reduced the 15 points to 5 in such a way that the ground state and several excited states were reproduced. These 5 points have been used further for the construction of the multidi-

mensional grid. For all OH stretch vibrations the points correspond to distances of 0.8, 0.9, 1.0, 1.25, and 1.4 times the equilibrium OH bond distance r_0. For the zeolite OH stretch coordinate in complexes with water an extra point at $1.55r_0$ was added because of the flatness of the potential energy surface. The potential energy along the zeolite bending coordinates is steeper for the complex with water compared with the bare zeolite. The zeolite in-plane bending coordinate was obtained by changing the angle φ by $0°,\pm21°,\pm49°$ and $0°$, $\pm14°,\pm35°$ for the bare zeolite and after adsorption of water, respectively. The water bending coordinates have been changed by the same values as the in-plane bending of the zeolite in the complex with water. The potential energy for the out-of-plane bending is flat around the equilibrium position and steepens at relatively large values of θ. To incorporate this feature we needed 7 points for the out-of-plane bending coordinate for the bare zeolite corresponding to changes of the angle θ of $0°,\pm20°,\pm40°,\pm60°$ and 5 points for the complex with water, $0°,\pm20°,\pm45°$. For the water center-of-mass stretch the distance between the zeolite oxygen atom the water center of mass was changed by -0.35, -0.15, 0, 0.25, and 0.5 Å.

The fit of the three-dimensional potential energy and dipole surfaces for the bare zeolite was done on a grid constructed of the zeolite OH stretch and in-plane and out-of-plane coordinates. For the four-dimensional fit for the complex with water the grid was done in the same way as for the bare zeolite with an additional coordinate of the water center-of-mass stretch. The frequencies of the water molecule were calculated separately from those of the zeolite OH group. A two-dimensional fit was done for the two OH stretch coordinates and one-dimensional fit for the bending coordinate.

We are interested in obtaining a good description of the ground state and a relatively small number of excited states. Therefore, we have given greater weight to grid points with lower energy. The weights are calculated as

$$w_i=\frac{e^{-fE_i}}{\sum_{j=1}^{M}e^{-fE_j}}, \tag{3}$$

where M is the number of the grid points and f is an energy scale factor such that the root-mean-square error of the fit is smaller than $1.10^{-3}E_h^{-1}$. The value of f was $125E_h^{-1}$. In the multidimensional calculations we have excluded the points for which more than two coordinates take an extreme value. The three-dimensional potential energy was fitted with 167 points and the four-dimensional potential energy for the complex with water with 513 points. The x, y, and z components of the dipole surface each were fitted using the same procedure and the same weight factors w_i as applied to the corresponding potential energy points. The determination of the coefficients $c_{i_1,\ldots,i_D}$ is a liner problem, and the coefficients were found using singular value decomposition.[33]

The Schrödinger equation is usually solved using the variational principle. In this method the total wave function is expanded as a linear combination of an n-dimensional orthonormal basis set. To find the eigenvalues of the vibrational Hamiltonian we have used the Hermite discrete vari-

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able representation (DVR) basis set $\{\chi_{\alpha_k}^{(k)}(x)\}$, and for the characterization of the eigenstates we have used harmonic oscillator eigenfunctions (Hermite functions) $\{\varphi_k(x)\}$. The coordinates of these functions are Cartesian coordinates (see below). The Hermite functions are characterized by the ratio of the reduced mass and force constant. The force constants were derived from the curvature at the equilibrium structure in the direction of the internal coordinate. The DVR basis set is given by

$$\chi_\alpha(x) = \sum_{i=1}^{n} w_\alpha^{-1/2} \varphi_i^*(x_\alpha) \varphi_i(x), \quad \alpha = 1,2,...,n, \quad (4)$$

where w_α and x_α are the weights and quadrature points, obtained from the Gauss–Hermite quadrature.[33,34] The DVR and Hermite functions are related by a unitary transformation, and we can always switch between them. Thus we can write a function $\Psi(x)$ as

$$\Psi(x) = \sum_{i=1}^{N} a_i \varphi_i(x) = \sum_{\alpha=1}^{N} b_\alpha \chi_\alpha(x), \quad (5)$$

with

$$a_i = \sum_{\alpha=1}^{N} b_\alpha \langle \varphi | \chi_\alpha \rangle.$$

The multidimensional wave function we expand in products of one-dimensional DVR basis sets:

$$\Psi(x_1,...,x_D) = \sum_{\alpha_1=1}^{n_1} \cdots \sum_{\alpha_D=1}^{n_D} a_{\alpha_1,...,\alpha_D} \prod_{k=1}^{D} \chi_{\alpha_k}^{(k)}(x_k), \quad (6)$$

where x_k are Cartesian coordinates (the second set of coordinates) and n_i is the number of quadrature points along the ith coordinate. In all calculations we have used 13 DVR points along each coordinate. The Cartesian coordinates make calculation of the vibrational wave function easier than internal coordinates. They are defined as follows. The unit vector $\bar{\mathbf{x}}_r$ is along the equilibrium zeolite OH bond, the unit vector $\bar{\mathbf{x}}_\varphi$ is perpendicular to $\bar{\mathbf{x}}_r$ and is in the Si–O–Al plane, and the unit vector $\bar{\mathbf{x}}_\theta$, is perpendicular both to $\bar{\mathbf{x}}_r$ and the Si–O–Al plane. The displacements are then written as $x_r\bar{\mathbf{x}}_r + x_\varphi\bar{\mathbf{x}}_\varphi + x_\theta\bar{\mathbf{x}}_\theta$, where x_r, x_φ, and x_θ are the Cartesian coordinates. Evaluating the Hamilton matrix elements within the DVR basis set makes it possible to express the kinetic energy operator in Cartesian coordinates without cross terms. The kinetic energy matrix elements are

$$\langle \chi_{\alpha_1}^{(1)} \cdots \chi_{\alpha_D}^{(D)} | \hat{T} | \chi_{\beta_1}^{(1)} \cdots \chi_{\beta_D}^{(D)} \rangle$$

$$= -\sum_{k=1}^{D} \frac{1}{2m_k} \left\langle \chi_{\alpha_1}^{(1)} \cdots \chi_{\alpha_D}^{(D)} \left| \frac{\partial^2}{\partial x_k^2} \right| \chi_{\beta_1}^{(1)} \cdots \chi_{\beta_D}^{(D)} \right\rangle \quad (7)$$

$$= -\sum_{k=1}^{D} \frac{1}{2m_k} \left\langle \chi_{\alpha_k}^{k} \left| \frac{\partial^2}{\partial x_k^2} \right| \chi_{\beta_k}^{(k)} \right\rangle \prod_{k' \neq k} \delta_{\alpha_{k'}\beta_{k'}}. \quad (8)$$

The resulting matrix is sparse because of the δ's. When evaluating the potential energy matrix we have transformed the Cartesian coordinates into the coordinates we have used to fit the potential energy, and then we have calculated the

value of the potential energy at the DVR points. If x_r, x_φ, and x_θ are DVR points for the zeolite OH stretch and in-plane and out-of-plane bending, respectively, then the coordinate transformation is

$$r = \sqrt{x_r^2 + x_\varphi^2 + x_\theta^2} + r_0, \quad (9)$$

$$\cos\theta = \frac{x_\theta}{r}, \quad (10)$$

$$\sin\varphi = \frac{x_\varphi}{\sqrt{r^2 - x_\theta^2}}, \quad (11)$$

with r_0 being the equilibrium OH bond distance for each system. The water center-of-mass coordinates do not change. The potential matrix for the vibration of the zeolite OH bond is then

$$\langle \chi_{\alpha_i}^{(x_r)} \chi_{\alpha_j}^{(x_\varphi)} \chi_{\alpha_k}^{(x_\theta)} | \hat{V} | \chi_{\beta_i}^{(x_r)} \chi_{\beta_j}^{(x_\varphi)} \chi_{\beta_k}^{(x_\theta)} \rangle$$

$$= V(r_{\alpha_i}, \sin\varphi_{\alpha_j}, \cos\theta_{\alpha_k}) \delta_{\alpha_i\beta_i} \delta_{\alpha_j\beta_j} \delta_{\alpha_k\beta_k}. \quad (12)$$

We have computed the integrated absorption coefficients by applying Fermi's golden rule and Boltzmann distribution at a given temperature T. The integrated absorption coefficients are then given by

$$S_{nm} = \frac{N_A \Delta E}{6\epsilon_0 \hbar^2 c^2} \sum_{i=x,y,z} |\langle \psi_n | \mu_i | \psi_m \rangle|^2 \frac{e^{-E_n/kT} - e^{-E_m/kT}}{\sum_{j=1}^{M} e^{-E_j/kT}}. \quad (13)$$

In this expression S_{nm} is the absorption coefficient of the transition from state $|\psi_n\rangle$ to state $|\psi_m\rangle$, ΔE is the energy difference between the states, E_j is the energy of the state $|\psi_j\rangle$, μ_x, μ_y, μ_z are the components of the dipole, $\hbar$ is Planck's constant divided by 2π, k is the Boltzmann constant, N_A is Avogardo's number, ϵ_0 is the electrical permittivity of vacuum, c is the speed of light, and M is the number of states. The spectra have been generated by convolution of the Dirac δ function with a normalized Gaussian curve of width of 10 cm^{-1} multiplied by the absorption coefficient. All spectra have been computed at a temperature of 298.15 K. Each energy level is characterized by the quantum number of the Hermite functions. The first quantum number is for the zeolite stretch, the second for the in-plane bending, the third for the out-of-plane bending, and the fourth for the water center-of-mass stretch. A transition between the levels is denoted by an arrow. The harmonic frequencies have been calculated with the harmonic part of the potential energy in Cartesian coordinates.

III. RESULTS AND DISCUSSION

A. Zeolite cluster without water

There are two stable proton position in chabazite for the acidic proton: O_1 and O_3. We have studied adsorption of water on both proton sites,[35] and we have found that a more stable complex is formed with the proton position O_3 than O_1. In this paper all calculations for the bare zeolite clusters and complex with water have been done for the proton attached to O_3.

TABLE I. The calculated anharmonic and harmonic frequencies (ω) in cm^{-1} and absorption coefficients (S) in km/mol of the zeolite OH group without water. The transition shows the quantum number of the Hermite function in the involved states. The first quantum number refers to the stretch, the second to the in-plane bending, and the third to the out-of-plane bending.

| | 7T cluster | | | | 8T cluster | | | |
| | Anharmonic | | Harmonic | | Anharmonic | | Harmonic | |
Transition	ω	S	ω	S	ω	S	ω	S
000→001	377	65.1	381	72.0	421	64.2	375	60.0
001→002	400	19.9	381	22.9	445	16.3	375	19.6
002→003	440	4.2	381	5.6	464	2.6	375	4.8
000→002	777	11.6	762	0.0	867	7.0	750	0.0
000→010	1018	231.9	1023	224.3	1054	296.9	1075	283.5
000→020	2048	4.0	2046	0.0	2108	2.4	2150	0.0
000→100	3610	169.1	3821	177.0	3550	155.7	3843	158.3

The computed anharmonic and harmonic frequencies of the bare zeolite clusters are listed in Table I. The anharmonic spectra are shown in Figs. 2(a) and 3(a). The infrared frequencies of the bending modes are difficult to be observed experimentally because they are below 1100 cm^{-1}, a region where the skeletal vibrations are. However, these modes have been identified using neutron spectroscopy.[36–39] The frequency for the out-of-plane bending has been found in the interval of 320–420 cm^{-1} and the one for the in-plane bending in the interval of 1052–1080 cm^{-1} depending on the Al concentration. The lower values are for higher Si/Al ratio. The frequencies we have calculated for the bendings of the 8T ring are in a very good agreement with the experiment. Those of the 7T cluster are about 40 cm^{-1} lower. We have
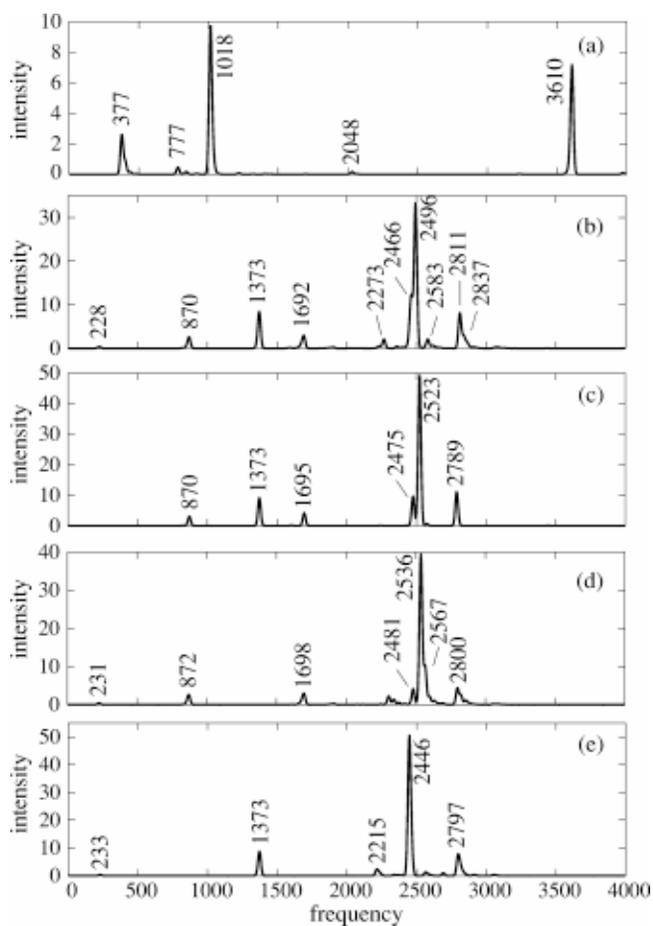

FIG. 2. Calculated infrared spectra of the zeolite OH group in the 7T cluster before (a) and after (b) adsorption of water. In the spectra (c)–(e) different coordinates have been fixed. In spectrum (c) this is the water center-of-mass stretch, in (d) the in-plane bending, and in (e) the out-of-plane bending. The frequencies are in cm^{-1} and the intensities in km/mol.
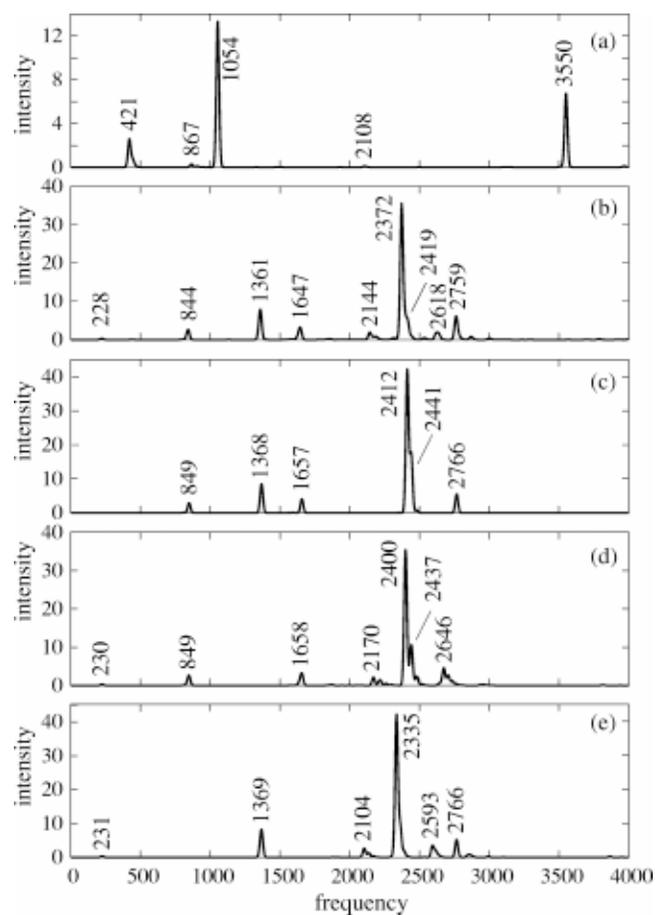
FIG. 3. The calculated infrared spectra of the zeolite OH group in the 8T ring before (a) and after (b) adsorption of water. In the spectra (c)–(e) different coordinates have been fixed. In spectrum (c) this is the water center-of-mass stretch, in (d) the in-plane bending, and in (e) the out-of-plane bending. The frequencies are in cm^{-1} and the intensities in km/mol.

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calculated for the OH stretch in the 8T ring a frequency of 3574 cm^{-1} and for the 7T cluster of 3609 cm^{-1} using one-dimensional surfaces. The value of the stretch frequency in the 8T ring is in a good agreement with the experimental frequency of 3579 cm^{-1} for chabazite.[22] The corresponding value in the 7T cluster is 60 cm^{-1} higher and falls in the interval where the OH stretch frequency of H-ZSM-5 (Ref. 4) and mordenite (Ref. 4) is found. When the bending modes were included the stretch frequency was decreased 24 cm^{-1} for the 8T ring and did not change for the 7T cluster. This is an indication that there is a slight coupling between the stretch and bendings of the acid group in the 8T ring.

The anharmonicity can affect both the position and spacing between the energy levels. The frequency of the stretch is lowered by the anharmonicity by 221 and 293 cm^{-1} for the 7T cluster and 8T ring, respectively. The anharmonic frequency of the bendings in the 7T cluster are slightly shifted to lower values compared to the harmonic values. In the 8T ring the anharmonic frequency for the out-of-plane bending is 46 cm^{-1} higher than the harmonic one. For the in-plane bending the anharmonic frequency is always lower than the harmonic. The potential energy surface along the out-of-plane bending steepens at larger amplitudes. This results in increasing the separation between the energy levels. Therefore the frequency of the hot bands (the transition between the subsequent excited state) is increased. Due to thermal population, the transition from the first excited state to the second excited state has a significant intensity, 19.9 and 16.3 km/mol, compared to the intensity of the fundamental transition, 65.5 and 64.2 km/mol, for the 7T cluster and 8T ring, respectively. Also the first overtone (000→002) can be seen.

Meijer *et al.* have calculated anharmonic spectra of the zeolite OH group using a three-dimensional surface with the coordinates of the hydrogen atom[40] and a six-dimensional surface with the coordinates of the oxygen and the hydrogen atoms.[41] For the hydrogen out-of-plane bending coordinate they have found a negative second derivative. We have calculated the spectra of the OH group in the 7T cluster, fitting the potential energy using Cartesian coordinates and not internal coordinates, and we have also found the equilibrium structure to be a maximum for the out-of-plane coordinate. The frequencies were 374 (out-of-plane), 1004 (in-plane), and 3187 (stretch) cm^{-1}. The frequencies of the bendings are in a good agreement with their calculations, and the frequency of the stretch is somewhat lower. This in an indication of a strong coupling between the high-energy mode (the stretch) and the low-energy modes, especially the out-of-plane bending, when Cartesian coordinates are used for fitting the potential energy surface. Our calculations show that a three-dimensional potential energy surface gives good agreement with the experiment provided that the center of mass is fixed and a reduced mass of the OH group and internal coordinates are used.

B. Zeolite cluster with water

Water in the 7T cluster. The equilibrium structure of water adsorbed on the 7T cluster corresponds to a hydrogen-bonded complex. The adsorption energy of the complex is −67.3 kJ/mol. A strong bond is formed between the water

oxygen atom and the acidic proton, an $O_w \cdots H_z$ distance of 1.586 Å. One of the water protons forms a weak hydrogen bond with the oxygen atoms from the Al and neighboring Si tetrahedrons. The distances between the water hydrogen atom and the oxygen atoms are 2.345 and 2.031 Å, respectively. The hydrogen bond between the oxygen atom from the water molecule and acid site weakens the zeolite OH bond. The zeolite OH bond distance increases from 0.969 to 1.013 Å.

The zeolite OH stretch frequency is then redshifted compared to the frequency of the isolated OH group in the zeolite. The bending vibrations correspond to a movement perpendicular to the hydrogen bond, and therefore in the complex with water these movements are more restricted. The potential energy surfaces for the bendings in the complex are steeper than those for the bare zeolite, and the corresponding frequencies are blueshifted. Using the harmonic part of the four-dimensional (4D) potential energy surface, we have calculated harmonic frequencies for the zeolite stretch of 2982 cm^{-1}, for the in-plane bending 1391 cm^{-1}, for the out-of-plane bending 880 cm^{-1}, and for the water center-of-mass stretch 224 cm^{-1}. In these calculations we have used only the coordinates of the zeolite OH group. We have also calculated the harmonic frequencies for the whole system including the vibrations of the framework. The frequency from the normal-mode analysis for the zeolite OH stretch was 62 cm^{-1} lower than that from the 4D potential energy surface. The frequencies of the bendings were 39 and 8 cm^{-1} higher for the in-plane and out-of-plane bendings, respectively. Theoretically calculated harmonic frequencies of water adsorbed on zeolites[13–16] fall in the interval of 2635–2953 cm^{-1} for the zeolite OH stretch, 1357–1471 cm^{-1} for the zeolite in-plane bending, and 1104–1109 cm^{-1} for the zeolite out-of-plane bending. The harmonic frequencies we have calculated fall in these intervals with exception of the frequency of the zeolite out-of-bending vibration, which in our calculation is lower. The comparison of the harmonic frequencies obtained from the 4D potential energy surface and the normal-mode analysis shows that there is no significant harmonic coupling between the vibrations of the zeolite OH bond and the framework.

The calculated spectrum including anharmonicities is shown in Fig. 2(b). The zeolite OH stretch frequency is further shifted because of the anharmonicity and is found at about 2500 cm^{-1}. The anharmonic shift of the bending frequencies is only several wave numbers. After hydrogen bond formation the frequency of the out-of-plane mode undergoes a shift of 490 cm^{-1} and that of the in-plane bending a shift of 350 cm^{-1}. Due to these shifts, the energy level of the zeolite OH stretch becomes situated between the overtones of the out-of-plane bending (at 1692 cm^{-1}) and the in-plane bending (at 2811 cm^{-1}). The Fermi resonance occurs with both bending modes yielding the *ABC* triplet. In Table II the frequencies and largest coefficients of the basis functions of the four states that are involved in the Fermi resonance are listed. The peak at 1692 cm^{-1} corresponds to the overtone of the out-of-plane bending mode, and we assign it to the *C* band. The peak at 2811 cm^{-1} corresponds to the overtone of the in-plane bending which we assign to the *A* band. The

TABLE II. The frequencies, largest coefficients, and quantum number of the basis function of the states that correspond to a Fermi resonance in the spectrum of water adsorbed on the 7T cluster. The Hermite functions are ordered as for the zeolite OH stretch, in-plane bending, out-of-plane-bending, and water center-of-mass coordinate, respectively.

| 1692 cm^{-1} | | 2466 cm^{-1} | | 2496 cm^{-1} | | 2811 cm^{-1} | |
Function	Coeff.	Function	Coeff.	Function	Coeff.	Function	Coeff.
0020	−0.752	0030	+0.424	1000	+0.532	0200	−0.585
0040	−0.420	1000	−0.395	0030	+0.310	1000	−0.359
1000	+0.203	0050	+0.327	0050	+0.244	0400	−0.337
0060	−0.171	0111	+0.273	0200	−0.225	1001	−0.330

resonance of the stretch with the overtones of the out-of-plane bending does not occur only with the first overtone, but also with the second overtone. This results in two peaks at 2466 and 2496 cm^{-1}. In the latter also the overtone of the in-plane bending is involved. These peaks we assign to the B band. The spectrum in Fig. 2(b) shows a number of additional peaks besides those in Table II. These peaks have a more complex origin. The frequency at 2273 cm^{-1} results from a difference transition from an already exited level of the hydrogen bond to the level that is characterized by the wave function corresponding to the frequency of 2496 cm^{-1} listed in Table II, in which the main contribution is from the zeolite OH stretch mode. A difference transition from the already excited hydrogen bond to the level we have assigned to the A band results in a frequency of 2583 cm^{-1}. Also combination modes can be observed in which the transition is from the ground state to a state that corresponds to the A band also with an excited hydrogen bond. The frequency of this transition is at 2837 cm^{-1}.

To check the influence of the different coordinates on the calculated spectra we have calculated the spectra while fixing the hydrogen bond, in-plane, or out-of-plane bendings. These spectra are shown in Figs. 2(c)–2(e). When the hydrogen bond is fixed the spectrum contains fewer peaks because the difference and combination bands with the hydrogen bond mode are absent. The frequency of the B band is shifted to a somewhat higher frequency and that of the A band to a somewhat lower frequency. When the in-plane bending is fixed we observe additional splitting of the B band. The frequency at 2567 cm^{-1} originates from the transition from a level of an excited hydrogen bond to a level in which both the zeolite OH stretch and hydrogen bond are excited (0001→1001). There is a peak in the region of the A band (at 2800 cm^{-1}) that does not originate from a Fermi resonance, but is the 0000→1001 combination transition. In the spectrum with the fixed out-of-plane mode the peak that corresponds to the C band disappears and the B band consists of one peak only.

The polarity of the zeolite OH bond is increased by the interaction with water. Consequently, the frequencies not only shift, but there is also an increase of the intensity of the spectrum with adsorbed water compared to the bare zeolite. The intensity of the overtones is also increased because the overtone energy levels are mixed with the OH stretch.

Compared to the experimentally observed frequencies for the B and C bands the calculated frequencies agree within a few tens of wave numbers. The frequency of the A band that we have calculated is lower, 60 cm^{-1}. Zecchina et al.[4]

have reported frequencies for the zeolite in-plane bending of 1352 cm^{-1} and for the out-of-plane bending of 870 cm^{-1}. The theoretically calculated frequencies are again in a good agreement with the experiment. Although the positions of the peaks from the ABC triplet are in very good agreement with the experiment, the intensity of the B band is higher then the intensity of the A band, whereas in the experimental spectra these bands have approximately equal intensity. This shows that the intensities of the peaks are much more sensitive to the coupling of the coordinates than the frequencies.

When constructing the potential energy we have moved only the oxygen and hydrogen atoms. The frequencies of the bending modes are in the region where the skeletal vibrations are observed and they are expected to be coupled to them. This may lead to further splitting within the A and B bands, which may increase the intensity of the difference and combination bands, and therefore the width of the bands will be more pronounced.

Water in the 8T ring. Water forms stronger hydrogen bonds with the acidic proton in the 8T ring compared to the 7T cluster. The adsorption energy of the complex is −78.8 kJ/mol. The distance between the water oxygen atom and the acidic proton is 0.02 Å shorter than that in the 7T cluster. The water proton is situated at distance of 2.551 and 2.104 Å from the oxygen atoms of the Al and the neighboring Si tetrahedra, respectively.

We have calculated the harmonic frequencies from the 4D potential energy surface at 2914 cm^{-1} for the zeolite OH stretch, 1381 and 857 cm^{-1} for the in-plane and out-of-plane bendings, respectively, and 223 cm^{-1} for the hydrogen bond. The harmonic frequencies of the zeolite OH stretch from the normal-mode analysis were 95 cm^{-1} lower than those from the 4D potential energy surface. For the bending vibrations the difference is 57 and 25 cm^{-1} for the in-plane and out-of-plane bendings, respectively, with the normal frequencies being higher than the 4D frequencies. The difference between the harmonic frequencies obtained from the 4D potential energy surface and the normal-mode analysis is at maximum of 4%. Therefore, we can assume that the 4D potential energy surface is a valid approximation for describing the vibrations of the zeolite OH vibrations.

The calculated spectra including anharmonicities are shown in Fig. 3. The main difference between the four-dimensional spectra of water adsorbed on the 7T cluster and 8T ring is the position of the B band. For the 8T ring it is 120 cm^{-1} lower compared to that for the 7T cluster. The band at 2372 cm^{-1} originates from a transition from the ground state

TABLE III. The frequencies, largest coefficients, and quantum number of the Hermite function of the states that correspond to a Fermi resonance in the spectrum of water adsorbed on the 8T cluster. The basis functions are ordered as for the zeolite OH stretch, in-plane bending, out-of-plane-bending, and water center-of-mass coordinate, respectively.

1647 cm^{-1}		2372 cm^{-1}		2419 cm^{-1}		2759 cm^{-1}	
Function	Coeff.	Function	Coeff.	Function	Coeff.	Function	Coeff.
0020	−0.756	1000	−0.672	0030	−0.523	0200	+0.694
0040	−0.423	2000	−0.301	0050	−0.407	0400	+0.400
1000	+0.209	1001	+0.260	0010	+0.318	1000	−0.255
0060	−0.171	0200	+0.206	1010	+0.256	1002	−0.186

to the state in which the stretch and overtone of the in-plane bending are mixed (see Table III). The band at 2419 cm^{-1} is a transition from the ground state to the second overtone of the out-of-plane bending mainly. Because the contribution of the stretch in this state is less than that for the 7T cluster, the intensity of this peak is smaller than the intensity in the 7T cluster. Also in the A band the contribution of the OH stretch is smaller than compared to the corresponding state in the 7T cluster and the intensity of the A band is smaller. The separation between the A and B bands is 487 cm^{-1}, which is somewhat larger than the separation between these bands for the 7T cluster, 415 cm^{-1}. The band that is at 2618 cm^{-1} has a different origin than the band at 2583 cm^{-1} in the spectra for the 7T cluster. There this was the 0001→0200 difference band, and here this is the combination band 0000→1001.

Smith et al.[22] have reported frequencies for the A band at 2879 cm^{-1} and for the B band at 2403 cm^{-1}. They have assigned these bands to a protonated water molecule. In our model we have shown that the A and B bands appear because of a Fermi resonance between the stretch and first overtone of the in-plane bending. In the theoretical spectra the frequency of the A band is somewhat lower.

We have obtained good agreement between the adsorption energies and geometries of methanol adsorbed on the 8T rings and periodic calculations using PW91 density functional.[42] The comparison of the theoretically computed infrared spectra of water adsorbed on the 8T ring with the experimental spectra for chabazite is an additional argument that the 8T ring is a good model for the acid site in chabazite. Comparing the results for the open 7T cluster with theoretical calculations from the literature[14,31,43] for water adsorbed on clusters representing an acid site in H-ZSM-5, we see that the adsorption energy of −67.3 kJ/mol is in the reported range of from −53.1 to −92.5 kJ/mol. The zeolite OH bond distance in our calculations is 0.01 Å shorter than that reported by Zygmunt et al.[14] and 0.01 Å longer than that found by Ryder et al.[31] The intermolecular bond distance between the water oxygen atom and the zeolite acid proton we have found to be 0.02 Å (Ref. 14) and 0.13 Å (Refs. 31 and 43) shorter. The difference between the coordination of the water molecule in our calculations and the calculations mentioned above is the presence of an extra oxygen atom so that the water molecule forms a bifurcated and not a single hydrogen bond with the zeolite cluster. Based on the agreement between the theoretical anharmonic frequencies and the experiment and the agreement of the adsorption energies and geometries with previous calculations, we hypothesize that the open 7T cluster is representative of the adsorption of water in H-ZSM-5. We think that this might be explained by the influence of the backbone of the ring in the 8T cluster. The interaction between water and the acid site involves only the neighboring Si tetrahedrons, but we think that it is enhanced by the proximity of the zeolite oxygen atoms from the rings. This occurs in the 8T cluster, but not in the open 7T cluster. In real systems this then should occur in narrow-pore zeolites like chabazite, and not in wide-pore zeolites like H-ZSM-5, and the calculations for the 8T ring should agree with the experiments on chabazite and the calculations for the 7T cluster with the experiments on H-ZSM-5, which is indeed what we find.

The water molecule. The model for the interaction between a protonated water molecule and the zeolite is not able to explain the appearance of the two bands at 3700 and 3550 cm^{-1}. If the water molecule is hydrogen bonded to the zeolite, then these bands may originate from the asymmetric and symmetric stretch vibrations of a slightly perturbed water molecule. We have calculated for the asymmetric and symmetric stretches for an isolated water molecule anharmonic frequencies of 3756 and 3637 cm^{-1}, respectively. The value for the asymmetric mode is in a good agreement with the experiment,[44] and the value for the symmetric mode is 20 cm^{-1} lower. When the water molecule interacts with the zeolite, one of the water hydrogen atoms forms a weak hydrogen bond with the oxygen atoms from the zeolite. The corresponding OH bond is slightly elongated: 0.973 and 0.977 Å in the 7T cluster and 8T ring, respectively. The OH bond distance of the hydroxyl group of water that is not involved in an interaction with the zeolite is 0.962 and 0.964 Å, respectively. In the complex with water the OH stretch vibrations of water are decoupled, because one of the water protons forms a second hydrogen bond with the zeolite, which is, however, much weaker than the first one. The anharmonic stretch frequency of the unperturbed OH bond was calculated at 3714 and 3697 cm^{-1} for the 7T cluster and 8T ring, respectively. The frequency of the OH group involved in a hydrogen bond with the zeolite was calculated at 3407 and 3470 cm^{-1} for the 7T cluster and 8T ring, respectively. These values are lower than the experimental values and indicate that the secondary hydrogen bond of water with the zeolite cluster is somewhat stronger.

The bending mode of the water molecule is shifted by ca. 30 cm^{-1} in the complex with water because of the weak hydrogen bond. The calculated values were 1614 cm^{-1} for
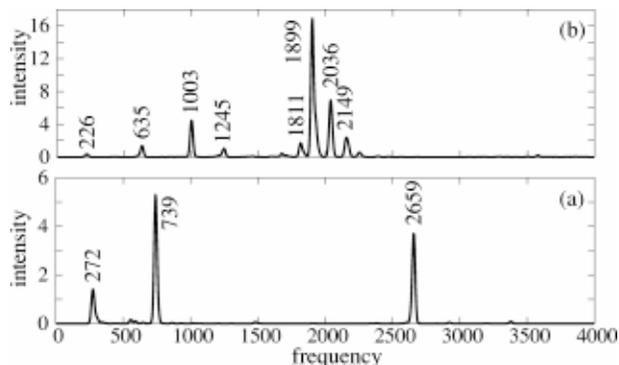
FIG. 4. The calculated infrared spectra of the zeolite OD group in the 7T cluster before (a) and after (b) adsorption of water. The frequencies are in cm^{-1} and the intensities in km/mol.

both clusters. In the experiment this frequency is found at 1628 cm^{-1}.

C. Isotope effect

The potential energy does not change when an atom is substituted by an isotope of the same element. The frequency of the vibrations changes because the reduced mass is changed. When the hydrogen atom in the zeolite OH group is replaced by a deuterium atom the frequency undergoes a shift of ca. 1000 cm^{-1} because the reduced mass of the OH group is decreased by a factor of almost 2. In the harmonic approximation the ratio between the frequencies of the OD and OH groups is approximately 0.728 ($\approx 1/\sqrt{2}$). Experimentally,[2,3,6] the OD stretch frequency of a bare zeolite is observed in the interval of 2659–2670 cm^{-1}. The frequencies we have calculated are in a very good agreement with the experiment (see Figs. 4 and 5). The ratio ω_{OD}/ω_{OH} was found to be 0.737–0.744. The frequency of the in-plane bending was reported by Pelmenschikov et al.[10] at 894 cm^{-1}. We have calculated frequencies of 739 and 771 cm^{-1} for the 7T cluster and 8T ring, respectively. The potential energy surface for the in-plane bendings is nearly harmonic, and the calculated shift of the frequency after H→D substitution follows the harmonic approximation rule. In the complex of water in the 7T cluster the peaks from the Fermi resonance

between the OD stretch and in-plane bending are at 1899 and 2036 cm^{-1}. The bands at 1811 and 2149 cm^{-1} are difference and combination transitions from coupling with the hydrogen bond, respectively. The same feature was found for the zeolite OD bond in the 8T ring. Consistently with the higher acidity of this group compared to that in the 7T cluster, the frequencies are 40 cm^{-1} lower. These peaks are difficult to observe experimentally because they fall in the regions where the overtones of the zeolite skeletal vibrations are. Also their intensity is decreased by a factor of almost 2 compared to the spectra of the zeolite hydroxyl groups. Parker et al.[2] have observed a broad band with a maximum around 2150 cm^{-1} and another relatively narrow band at 1900 cm^{-1}. For adsorption of CD$_3$CN on (Ref. 10) the corresponding bands were found at 1875 and 2060 cm^{-1} with the low-frequency band having larger intensity. The frequencies of the in-plane bendings were calculated at 999 and 1003 cm^{-1} and are in good agreement with the experimental[10] value of 988 cm^{-1}.

Overall, the spectra of the zeolite OD groups show that the shift of the frequencies for the isotope-substituted group are smaller when the anharmonicities are large.

IV. CONCLUSIONS

In the present work we have calculated the infrared spectra of water adsorbed on zeolites including anharmonicities. We have assigned the experimentally observed frequencies at ~2900, ~2400, and ~1700 cm^{-1} to the strongly perturbed zeolite OH vibrations caused by the hydrogen bonding with the water molecule. Anharmonicities are very important as they account both for the large redshift of the stretch frequency of the weakened by the hydrogen bond zeolite OH bond and the coupling between the stretch and bending modes. We have shown that the ABC triplet is a Fermi resonance of the zeolite OH stretch mode with the overtone of the in-plane bending (the A band) and the overtone of the out-of-plane bending (the C band). In the B band the stretch is also coupled with the second overtone of the out-of-plane bending.

The water molecule is slightly affected by the interaction with the zeolite acid site. The two OH stretch vibrations were found to be decoupled. The frequency of the OH bond that forms a weak hydrogen bond with the zeolite oxygen atoms was calculated at 3407 and 3470 cm^{-1} for the 7T cluster and 8T ring, respectively. The corresponding frequency of the free OH bond was calculated at 3697 and 3714 cm^{-1}.

The positions of the frequencies of the ABC triplet were found to be in very good agreement with the experiment. Therefore, we conclude that clusters consisting of several T atoms describe reasonably well the interaction of water with the acid site. There is still room for improvement of the width of the bands. We have shown that peaks around the center of the A and B bands rise up from difference and combination modes with the low-frequency mode of the intermolecular mode.
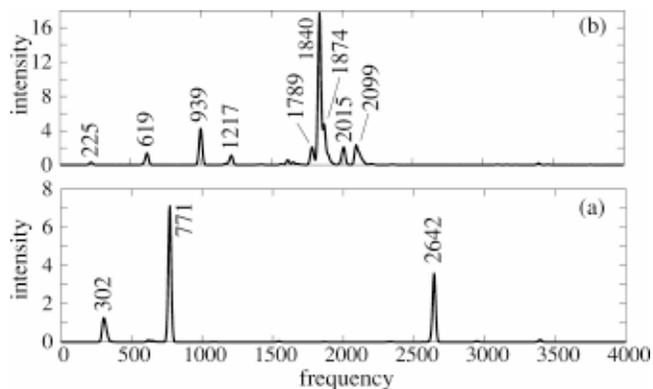

FIG. 5. The calculated infrared spectra of the zeolite OD group in the 8T ring before (a) and after (b) adsorption of water. The frequencies are in cm^{-1} and the intensities in km/mol.

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