Molecular Dynamics Simulation Studies of Zeolite A. VIII. Structure and Dynamics of Na^+ ions in a Non-Rigid Dehydrated Zeolite-A Framework

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A molecular dynamics simulation study on the structure and dynamics of Na^+ ions in non-rigid dehydrated Na_{12}-A zeolite framework at 298.15 K was conducted using the same method reported in previous studies on rigid and non-rigid Na_{12}-A zeolite frameworks. The agreement between the experimental and calculated results for the zeolite-A framework atoms of structural parameters for non-rigid dehydrated Na_{12}-A zeolite is generally quite good, and for the adsorbed Na^+ ions the agreement is acceptable. The calculated bond lengths are generally in good agreement with the experimental results and other theoretical data. The calculated IR spectrum by Fourier transform of the total dipole moment autocorrelation function shows two major peaks around 2700 cm^{-1} and 7000 cm^{-1}. The former appeared in the calculated IR spectra of non-rigid zeolite-A framework only system and the latter remains unexplained except, perhaps, indicating a new formation of a vibrational mode of the framework due to the adsorption of Na^+ ions. The peaks above 6200-6800 cm^{-1} in non-rigid dehydrated Na_{12}-A zeolite are much larger than those in non-rigid dehydrated H_{12}-A zeolite.

Introduction

Consideration of the intraframework interaction of zeolite systems is essential when taking account of the energy exchange between the adsorbed molecules and the framework atoms and the dynamical couplings of the sorbate with framework vibrations. This consideration is also important in determining the flexibility of the host lattice. In a previous study,[1] an accurate valence force field for zeolite was presented by Nicholas *et al.* The force field contained terms for bond stretching, bond angle bending, torsional rotational, and non-bonded Lennard-Jones and electrostatic interactions. They found that the force field accurately reproduced the structure and dynamics of silica sodalite through the comparison of theoretical infrared (IR) spectra, radial distribution functions, and mean-square displacements with experimental data.

Recently Faux *et al.*[2] reported MD simulations of fully hydrated and dehydrated Na^+-zeolite 4A with a mobile zeolite framework at 298°K and a steepest descent energy minimization simulation on the dehydrated zeolite. They found that the optimized structure yielded bond lengths, bond angles, and positions of sodium ions in very good agreement with the published X-ray data.[3,4]

In previous studies,[5,6] non-rigid zeolite-A framework was used for molecular dynamics (MD) simulation studies for structures and dynamics of zeolite-A framework atoms[5] and H^+ ions.[6] The first study was on a framework only system, a base case for a consistent study of the role of intraframework interaction on several zeolite-A systems. In addition to the method in our previous studies of rigid zeolite-A frameworks,[7-11] usual bond stretching, bond angle bending, torsional rotational, and non-bonded Lennard-Jones and electrostatic interactions were considered as intraframework interaction potentials.

The second study was on H^+ ions in a non-rigid H_{12}-A zeolite system. Since the structure of H^+ ions in a rigid dehydrate H_{12}-A zeolite framework was studied by our MD simulation method,[11] a comparison of the MD simulation results of these two zeolite systems - rigid and non-rigid - might be interesting: two different structures appeared, depending on the choice of the Lennard-Jones parameter (σ) for the H^+ ion, as observed in the study of rigid dehydrated H_{12}-A zeolite framework, but the ranges of σ were changed for the two structures. It is also found that some of the H^+ ions exchanged sites without changing the number of H^+ ions at each site.

The agreement between experimental and calculated structural parameters for non-rigid dehydrated zeolite A was generally quite good. The calculated IR spectrum by Fourier transform of the total dipole moment autocorrelation function showed two major peaks around 2700 cm^{-1} and 7000 cm^{-1}. The former appeared in the calculated IR spectra of non-rigid zeolite-A framework only system and the latter remained unexplained except perhaps to indicate a new formation of vibrational mode of the framework due to the adsorption of the H^+ ions.

In this paper, continuing our MD simulation studies of zeolite-A systems with rigid zeolite-A framework systems[7-11] and with non-rigid zeolite-A framework systems,[5,6] we present MD simulation of Na_{12}-A zeolite using a non-rigid dehydrated zeolite-A framework. The primary purpose of this study is to test the basic non-rigid zeolite-A framework and several intraframework interactions of Na_{12}-A zeolite framework used in previous studies,[5,6] and to investigate the local structure and dynamics of Na^+ ions in the non-rigid

Na_{12}-A zeolite framework, comparing it with those properties of Na^+ ions in the rigid Na_{12}-A zeolite framework.

In Section II, we present the molecular models and MD simulation method. We discuss our simulation results in Section III and present the concluding remarks in Section IV.

Molecular Models and Molecular Dynamics Simulations

The structure of zeolite-A framework is the same model used in the previous MD simulation study of non-rigid H_{12}-A zeolite system,[6] which is the pseudo cell, $(SiAlO_4)_{12}$, using the space group $Pm\bar{3}m$ (a = 12.2775 A). The Si and Al atoms are assumed to be identical (denoted as T) because the Ewald summation[12] is valid with this assumption. Since the zeolite-A framework is not assumed to be rigid, the framework atoms (T and O) are subject to move according to the equation of motion. For the initial positions of the framework atoms and Na^+ ions, those determined by the X-ray diffraction experiment by Pluth and Smith[3] for the dehydrated Na_{12}-A zeolite system are used.

The interaction potential for the framework atoms is given by the sum of bond stretching, bond angle bending, torsional rotational, and non-bonded Lennard-Jones (LJ) and electrostatic interactions with the Ewald summation,[12] and that for Na^+ ions by the sum of LJ and electrostatic interactions with the Ewald summation.[12] The usual LJ parameters and the electrostatic charges for the Coulomb potential are used from our previous studies[5-11] and are given in Table 1.

The intraframework interaction potentials - T-O bond stretching potential, O-T-O and T-O-T bond angle bending potentials, T-T non-bonded stretching potential, and T-O-T-O torsional rotational potential - are exactly the same ones used in the previous MD simulation study of non-rigid H_{12}-A zeolite system,[6] but are different from those used in the previous MD simulation study of non-rigid zeolite-A only system,[5] except for the T-O-T-O rotational tortional potential, where the equilibrium bond distances and bond angles are the averages of each bond distance and bond angle. The intraframework interaction potentials used in this study are summarized in Table 2. The corresponding forces due to the intraframework interaction potentials are obtained by differentiation with respect to the position vector of each site.[13]

A canonical ensemble of fixed N (number of particles), V (volume of fixed zeolite framework), and T (temperature) is chosen for the simulation ensemble. Gauss's principle of least constraint[14] is used to maintain the system at a constant temperature. The ordinary periodic boundary condition in the x-, y-, and z-direction and minimum image convention are applied for the Lennard-Jones potential with a spherical cut-off of radius equal to half of each simulation box length. Gear's fifth order predictor-corrector method[15] is used to solve the equations of translational motion of the framework atoms with a time step of 2.00×10^{-16} second. The equilibrium properties are averaged over five blocks of 100,000 time steps, for a total of 500,000 time steps after 500,000 time steps to reach an equilibrium state. The configuration of each ion is stored every 5 time steps for further analyses.

Table 1. Lennard-Jones parameters and electrostatic charges used in this study

atom	σ (A)	ε (kJ/mol)	charge(e)
Al(=Si)	4.009	0.5336	0.6081
O(1)	2.890	0.6487	-0.4431
O(2)	2.890	0.6487	-0.4473
O(3)	2.890	0.6487	-0.4380
Na^+	1.776	20.8466	0.55

Table 2. Summary of intraframework interaction potentials used in this study

T-O bond stretching potential : $V(r) = k_r/2\,(r_{T\text{-}O} - r_{eq})^2$, k_r = 250,000 kJ/mol · nm^2 and r_{eq} : T-O(1) = 0.16591, T-O(2) = 0.16531, and T-O(3 or 3') = 0.16688 nm.
O-T-O bond angle bending potential : $V(\theta) = k_\theta/2\,(\theta-\theta_{eq})^2$, k_θ = 0.17605 kJ/mol · deg^2 and θ_{eq} : O(1)-T-O(2) = 108.13, O(1)-T-O(3 or 3') = 111.70, O(2)-T-O(3 or 3') = 107.12, and O(3)-T-O(3') = 110.83 degrees.
T-O-T bond angle bending potential : $V(\theta) = k_{\theta1}/2\,(\theta-\theta_{eq})^2 + k_{\theta2}/2\,(\theta-\theta_{eq})^3 + k_{\theta3}/2\,(\theta-\theta_{eq})^4$, $k_{\theta1}$ = 0.013829 kJ/mol · deg^2, $k_{\theta2}$ = 0.00050542 kJ/mol · deg^3, $k_{\theta3}$ = 0.000005148 kJ/mol · deg^4 and θ_{eq} : T-O(1)-T = 142.08, T-O(2)-T = 164.18, and T-O(3 or 3')-T = 145.55 degrees.
T-T non-bonded stretching potential : $V(r) = k_r/2\,(r_{T\text{-}T} - r_{eq})^2$, k_r = 22,845 kJ/mol · nm^2 and r_{eq} : 0.31381, 0.32747, and 0.31878 nm.
T-O-T-O torsional rotational potential : $V(\phi) = k_\phi/2\,[1 + \cos(3\phi)]$, k_ϕ = -2.9289 kJ/mol.

Results and Discussion

Several potential energies are averaged for 500,000 time steps (100 ps) and are compared with those for the non-rigid H_{12}-A zeolite[6] and for the non-rigid zeolite-A framework only system[5] in Table 3. The adsorption of Na^+ and H^+ ions into the non-rigid zeolite-A framework has affected mostly

Table 3. Average potential energies (kJ/mol) for 500,000 time steps (100 ps)

interaction potential	potential energy		
	Na_{12}-A	H_{12}-A (σ = 0.6A)[a]	framework only[b]
Na^+ - Na^+ LJ potential	-7.5±0.0	0.0	-
Na^+ - Na^+ Coulomb	331.6±0.3	327.3±0.2	-
Na^+ - frame LJ potential	-196.2±0.6	44.5±0.	-
Na^+ - frame Coulomb	-942.8±0.4	-1310.6±0.7	-
frame - frame LJ potential	-185.8±0.2	-188.2±0.1	-187.9±2.1
frame - frame Coulomb	2395.2±1.9	2358.1±0.2	2502.1±4.8
T-O bond stretching	243.6±5.8	236.1±5.5	133.3±8.2
T-T non-bonded stretching	71.3±0.6	55.2±0.3	55.3±3.7
T-O-T bond angle bending	20.1±0.2	22.7±0.1	37.3±2.2
O-T-O bond angle bending	230.0±1.3	276.8±3.9	265.9±9.7
O-T-O-T torsional	-207.5±0.8	-220.9±0.3	-218.4±1.1

[a] Non-rigid dehydrated H_{12}-A zeolite [6]. [b] Non-rigid zeolite-A framework only system [5].

T-O bond stretching and T-O-T bond angle bending energies, since those ions are adsorbed to the O framework atoms. For example, T-T non-bonded stretching energies are nearly unchanged. The difference in the cation-framework atoms Lennard-Jones (LJ) interaction energy of Na_{12}-A and H_{12}-A zeolite systems is most remarkable. Due to the strong cation-framework atoms Coulomb interaction energy and according to the LJ parameters (σ and ε) of cation, the cation-framework atoms LJ interaction energies of Na_{12}-A and H_{12}-A zeolite systems have opposite signs. The difference in the cation-cation LJ energy, nearly the same cation-cation Coulomb energy of both zeolite systems, is again due to the different LJ parameters of cation.

In Table 4, the results of the experimental[3] and calculated structural parameters of non-rigid dehydrated Na_{12}-A zeolite are compared. There are 24 T, 12 O(1), 12 O(2), and 24 O(3) atoms in the pseudo cell. Eight-ring windows are composed of T, O(1), and O(2) atoms, 6-ring of T, O(2), and O(3), and 4-ring of T, O(1), and O(3). The mean crystallographic positions and the mean-square displacement matrices **B** are obtained by referring the values of the individual atoms back to the asymmetric unit by symmetry operations.[16] The elements of the symmetric 3×3 matrix **B** are computed as $u_{ij} = \langle u_i u_j \rangle = \langle r_i r_j \rangle - \langle r_i \rangle \langle r_j \rangle$. The agreement between the experimental and calculated coordinates for the Na_{12}-A zeolite framework atoms is generally quite good as in the case of H_{12}-A zeolite system.[6] Compared with the results for the non-rigid zeolite-A framework only system,[5] the results for framework atoms in the non-rigid dehydrated Na_{12}-A zeolite are closer to experimental findings than those in the non-rigid zeolite-A framework only system except O(2) atom.

Table 4 also shows the results of the experimental[3] and calculated coordinates for Na^+ ions in the non-rigid Na_{12}-A zeolite. Na^+ ions are located at three main sites, referred to as Na_I, Na_{II}, and Na_{III}, corresponding to locations associated with the 6-ring, 8-ring, and 4-ring window sites, respectively. Eight 6-ring, three 8-ring, and twelve 4-ring window sites are found in the pseudo cell. The twelve Na^+ ions in the pseudo cell are distributed as follows: eight at each of the eight 6-ring window sites, three at each of the three 8-ring window sites, and one at one of the twelve 4-ring window sites.

For the adsorbed Na^+ ions, the agreement is poor but quite acceptable. The calculated coordinates for Na^+ ions in the rigid dehydrated Na_{12}-A zeolite are obtained from the results of our previous study for that system.[7] In the comparison of the calculated coordinates for Na^+ ions between the rigid and non-rigid dehydrated Na_{12}-A zeolite frameworks, the results for Na^+ ions in the rigid dehydrated Na_{12}-A zeolite are closer to experimental results than those in the non-rigid dehydrated Na_{12}-A zeolite except Na_{II} type ions. The same trend is seen in calculated bond lengths of the rigid and non-rigid dehydrated Na_{12}-A zeolite frameworks in Table 5. This is due to the fixed framework atoms in the rigid dehydrated Na_{12}-A zeolite system.[7] The anisotropy thermal parameters β_{ij} can be used to visualize the extent of the thermal motions and their anisotropy using the ORTEP computer code.[17]

In Table 5, we compare experimental and calculated bond lengths of non-rigid dehydrated Na_{12}-A zeolite. The calculated bond lengths are in generally good agreement with the experimental ones and the results for rigid dehydrated Na_{12}-A zeolite is much better than those of the non-rigid species except Na_{II}-O bond lengths. The minor disagreement in the

Table 4. Experimental and calculated structural parameters of non-rigid dehydrated Na_{12}-A zeolite (a = 12.2775 A)

atom	x/a	y/a	z/a	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
T									
exp.[a]	0	0.1836	0.3722	38	35	26	0	0	5
cal.	0.0109	0.1835	0.3733	5.2	18.8	17.0	-3.0	-3.1	11.6
cal.[b]	0.0123	0.1792	0.3662	13.2	20.8	19.2	-3.4	-3.3	18.4
O(1)									
exp.[a]	0	0.2275	0.5000	65	76	28	0	0	0
cal.	0.0110	0.2306	0.4862	4.7	14.5	27.7	1.0	0.9	2.2
cal.[b]	0.0044	0.2049	0.4829	1.1	2.4	1.4	-0.5	0.0	0.1
O(2)									
exp.[a]	0	0.2910	0.2910	90	48	48	0	0	22
cal.	0.0110	0.2859	0.2859	5.1	36.6	36.6	-0.8	-0.8	33.3
cal.[b]	0.0108	0.2906	0.2906	66.9	49.5	49.5	17.0	17.0	48.7
O(3)									
exp.[a]	0.1119	0.1119	0.3437	52	52	56	11	3	3
cal.	0.1105	0.1105	0.3480	39.7	39.7	24.3	32.7	16.7	16.7
cal.[b]	0.1065	0.1065	0.3335	21.8	21.8	57.2	33.1	20.6	20.6
Na_I									
exp.[a]	0.1991	0.1991	0.1991	55	55	55	21	21	21
cal.	0.1938	0.1938	0.1938	20.5	20.5	20.5	11.1	11.1	11.1
cal.[c]	0.1965	0.1965	0.1965						
Na_{II}									
exp.[a]	0	0.4290	0.4290	238	177	177	0	0	-64
cal.	0.0426	0.4315	0.4315	139.0	22.4	22.4	-3.3	-3.3	-4.8
cal.[c]	0.0216	0.4601	0.4601						
Na_{III}									
exp.[a]	0.5000	0.2087	0.2087	10	74	74	0	0	-10
cal.	0.4987	0.1966	0.1966	42.0	14.7	14.7	-2.6	-2.6	1.3
cal.[c]	0.4977	0.2101	0.2101						

[a] Experimental results for zeolite A [3]. [b] Non-rigid zeolite-A framework only system [5]. [c] Rigid dehydrated Na_{12}-A zeolite [7].

Table 5. Experimental and calculated bond lengths (A) of non-rigid dehydrated Na_{12}-A zeolite

bond lengths	exp.[a]	cal.	cal.[b]	cal.[c]	JC[d]	FSF[e]
Na_I - O(3)	2.334(3)	2.427(21)	2.329	2.342(315)	2.378	2.41
Na_I - O(2)	2.919(3)	2.756(30)	2.918	2.932(308)	2.993	2.89
Na_{II} - O(2)	2.395(13)	2.558(27)	2.948	-	-	2.44
Na_{II} - O(1)	2.623(7)	2.586(31)	2.910	-	2.456	2.66
Na_{III} - O(3)	2.551(34)	2.379(25)	2.546	2.569(168)	-	2.46
Na_{III} - O(1)	2.573(33)	2.322(32)	2.588	2.590(267)	-	-
Na_I - Na_{III}	3.698(4)	3.744(28)	3.706	4.116(261)	-	-

[a] Experimental results for zeolite A [3]. [b] Calculated from Table 4 for the rigid dehydrated Na_{12}-A zeolite. s[c] Rigid dehydrated Na_{12}-A zeolite [7]. [d] Results by Jackson and Catlow [18]. [e] Results by Faux, Smith, and Forester [2].

calculated bond lengths of Na_I-O and Na_{III}-O between Table 5 in this study and Table 3 in Ref. [7] is probably due to an error in the calculation of bond lengths in Ref. [7], which takes the average of bond lengths between the calculated coordinates of individual Na^+ ions and those of the fixed framework O atoms. In this study, the bond lengths are calculated from Table 4 in which the calculated coordinates for Na^+ ions in the rigid dehydrated Na_{12}-A zeolite are obtained from Table 4 in Ref. [7]. The major error in the calculation of the Na_I-Na_{III} distance is remarkable: 3.706 Å vs. 4.116 Å. This is also due to the calculation of the interionic distance using the calculated coordinates of individual Na_I and Na_{III} type ions. Fortunately, the Na_I-Na_{III} distance does not played an important role in the determination for the electrostatic charge of Na^+ ion.[7] All the bond lengths in our MD simulation studies of the rigid and non-rigid Na_{12}-A zeolite systems are comparable with the lattice energy minimization results by Jackson and Catlow (model e)[18] and the MD simulation results of non-rigid hydrated and dehydrated Na^+-zeolite 4A.[2]

Figures 1 and 2 show mean square displacements (MSD) of framework atoms and Na_I, Na_{II}, and Na_{III} type ions, respectively, in the non-rigid dehydrated Na_{12}-A zeolite. The MSD's of the framework atoms are vibrating but not periodically as in the case of non-rigid zeolite-A framework only system.[5]. The behavior of the MSD's of Na^+ ions is very similar to that of Na^+ ions in rigid dehydrated Na_{12}-A zeolite,[2] but the fluctuation after rapid increase is much smaller. It is also very similar to that of H^+ ions in non-rigid dehydrated H_{12}-A zeolite,[6] but the entire fluctuation is much slower with almost the same magnitude of MSD. This indicates that the dynamics of adsorbed Na^+ ions is very different from that of H^+ ions due to the mass and LJ parameters of Na^+ ion.

The IR spectrum is calculated by Fourier transform of the total dipole moment autocorrelation function.[19] Figure 3 shows the calculated IR spectra of non-rigid dehydrated

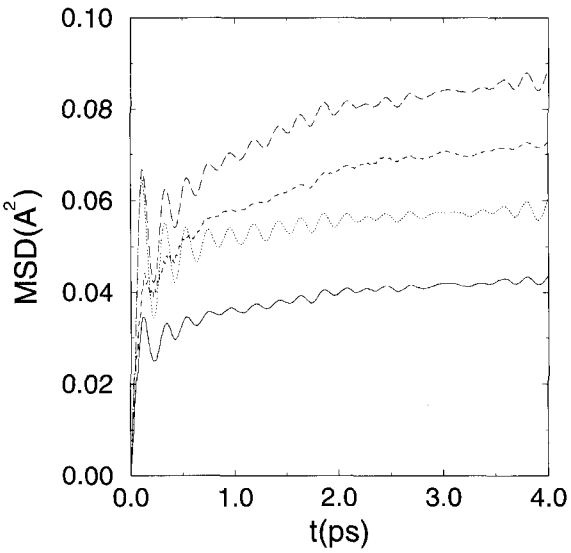

Figure 1. Mean square displacements (MSD) of non-rigid dehydrated Na_{12}-A zeolite framework atoms at 298.15 K, —— for T, ····· for O(1), ------ for O(2), and – – – – for O(3).

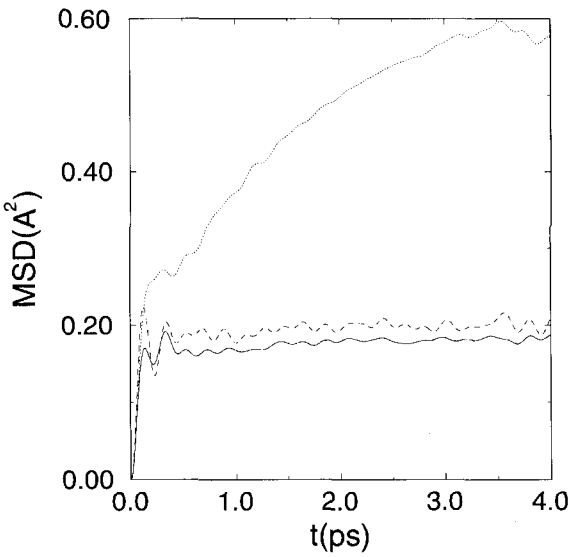

Figure 2. Mean square displacements (MSD) of three types of Na+ ions in non-rigid dehydrated Na_{12}-A zeolite at 298.15 K, —— for Na_I, ····· for Na_{II}, and ------ for Na_{III}.

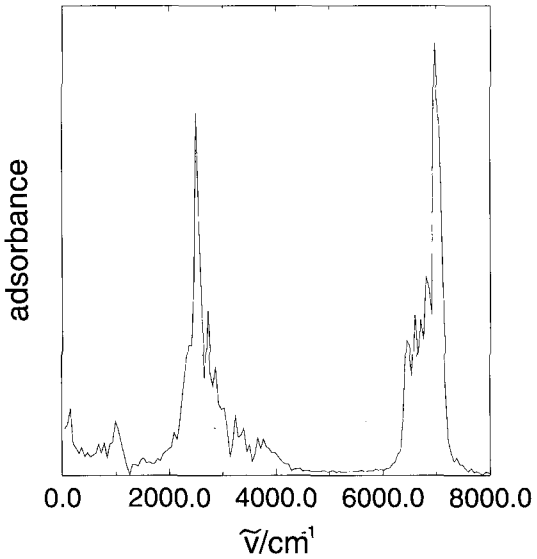

Figure 3. IR spectra of dehydrated Na_{12}-A zeolite at 298.15 K, calculated from the total dipole moment autocorrelation function of non-rigid dehydrated Na_{12}-A zeolite framework.

Na_{12}-A zeolite framework from our MD simulation. There are two major peaks around 2700 cm^{-1} and 7000 cm^{-1} as in the case of non-rigid dehydrated H_{12}-A zeolite. The former appeared in the calculated IR spectra of non-rigid zeolite-A framework only system, and indicating the simple harmonic oscillation of the dipole moment autocorrelation function resulting in a very large sharp peak at 2700 cm^{-1}, which reflects a monotonous dynamical feature of the framework.[5] But here the peak is very distorted, probably due to the effect of the adsorbed Na^+ ions. The latter also appeared in the calculated IR spectra of non-rigid zeolite-A framework only system, which was too small to be considered,[5] but here the corresponding peak is very large, which remains unexplained except perhaps to indicate a new formation of vibra-

tional mode of the framework due to the adsorption of Na^+ ions, which was not observed in non-rigid zeolite-A framework only system.[5] In non-rigid dehydrated H_{12}-A zeolite, the peaks over 6200-6800 cm^{-1} became larger with the increase in σ value for H^+ ion from 0.6 Å to 1.4 Å. Here those peaks are much larger than those in non-rigid dehydrated H_{12}-A zeolite, which indicates that the effect of Na^+ ions on the new formation of the vibrational mode of the framework becomes larger.

Concluding Remarks

A molecular dynamics simulation of non-rigid dehydrated Na_{12}-A zeolite framework was performed at 298.15°K using the usual bond stretching, bond angle bending, torsional rotational, and non-bonded Lennard-Jones and electrostatic interactions for the intraframework interaction potentials. The agreement between the experimental and calculated results for the zeolite-A framework atoms of structural parameters for non-rigid dehydrated Na_{12}-A zeolite is generally quite good, but for the adsorbed Na^+ ions the agreement is somewhat poor. The calculated bond lengths are generally in good agreement with the experimental findings and other theoretical results. The calculated IR spectrum by Fourier transform of the total dipole moment autocorrelation function shows two major peaks around 2700 cm^{-1} and 7000 cm^{-1}. The former appeared in the calculated IR spectra of non-rigid zeolite-A framework only system and the latter remains unexplained except, perhaps, indicating a new formation of a vibrational mode of the framework due to the adsorption of Na^+ ions, which was not observed in non-rigid zeolite-A framework only system. The peaks above 6200-6800 cm^{-1} are much larger than those in non-rigid dehydrated H_{12}-A zeolite.

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