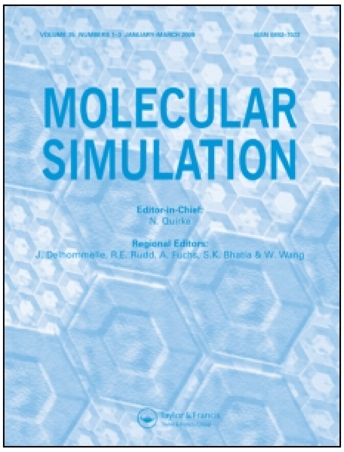

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Investigation of the electronic and dynamic properties of sodium and caesium exchanged zeolite by MO and MD simulations

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INVESTIGATION OF THE ELECTRONIC AND DYNAMIC PROPERTIES OF SODIUM AND CAESIUM EXCHANGED ZEOLITE BY MO AND MD SIMULATIONS

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For the pyrochemical reprocessing of spent metallic fuels in molten salt baths it is of importance to investigate the electronic and dynamic properties of the negative elements like Cs in aluminosilicates framework. The molecular orbital simulation has been performed on three types of clusters and 4A-zeolite frameworks with exchangeable alkali-ions containing as significant fission products in order to estimate the geometry optimization, the vibrational frequency factors and the electric densities, etc. These quantum chemical results enable us to conclude that the most stable structure is consistent with the X-ray results. Moreover, the obtained infrared spectrum was reproduced by the experimental results. Furthermore, the molecular dynamics simulation for Na-A and Cs-A zeolites has been carried out at 673 K in order to investigate the dynamics of Na^+ and Cs^+ ions in Na-A and Cs-A zeolite frameworks. These results revealed that Na I ion in β-cage was more stable than the other Na ions in Na-A zeolite and Cs I ion in α-cage was maintained stability in Cs-A zeolite in consideration of the self-diffusion coefficients.

Keywords: Caesium; Cluster; Electronic properties; Dynamics; MD simulation; MO simulation

INTRODUCTION

Recently, in order to separate the significant electronegative fission products such as Cs, we have been developed the pyrochemical treatment process [1] combining

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both the successive countercurrent electromigration [2,3] with a molecular dynamics (MD) simulations [3–8] from a standpoint of the estimation of the maximal concentration, and the electrochemical techniques [9–13]. In a previous paper, as another candidate for the processes to function as inorganic ion exchangers, we discussed MD simulation study for the order of the adsorption selectivity with the mean squares displacements (MSD) and the normalized velocity autocorrelation functions (VCF) for electronegative elements in the sodalite and zeolite-A frameworks at 673 K [14]. This result revealed that the multivalent cations were independent of the ionic radius and more stable than the monovalent ones in Na-A zeolite. Most simulation work on zeolite systems has been employed by MD methods, because the advantage of MD could be obtained not only static but also dynamic properties. On the other hand, few Molecular Orbital (MO) simulation study were reported so far, although it was important to survey the electronic properties of each cluster (α, β and γ) in zeolite frameworks as for the quantum chemical viewpoints. In this paper, the main attention was given in the investigation of electronic structure in zeolite frameworks and dynamic behaviors of Cs^+ and Na^+ ions in the Na-A and seven-twelfths Cs-exchanged zeolites by both MO and MD methods. The electronic structure was discussed in view of the different semi- and non-empirical quantum chemical methods. We calculated the electronic properties with the PM3 [15], AM1 [16], MNDO [17,18], MINDO/3 [19,20], MSINDO [21,22], CNDO/2 [23,24], INDO [25], CNDO/2S [26], INDO/2S [27] and the EHT [28,29] method. The non-empirical results with the vibrational frequency calculated at the $\mathrm{ZPE} + \mathrm{MP2}/6-311++\mathrm{G}^{**}//\mathrm{HF}/6-311++\mathrm{G}^{**}$ level of *ab initio* theory have been compared with the corresponding experimental values.

COMPUTATIONAL METHODS

(a) Molecular Orbital Simulation

The MOPAC3.0 package [30] has been employed for the MINDO/3, MNDO, AM1, and PM3 calculations as semi-empirical quantum chemical methods. On the other hand, all *ab initio* calculations have been performed using GAUSSIAN98 suite of quantum chemical routines [31] as non-empirical quantum chemical methods. *Ab initio* methods including correlation as well as zero point energy (ZPE) and employing medium-sized basis sets ($\mathrm{ZPE} + \mathrm{MP2}/6-311++\mathrm{G}^{**}//\mathrm{HF}/6-311++\mathrm{G}^{**}$) allow calculation of vibrational frequencies which agree nicely with the corresponding measured values.

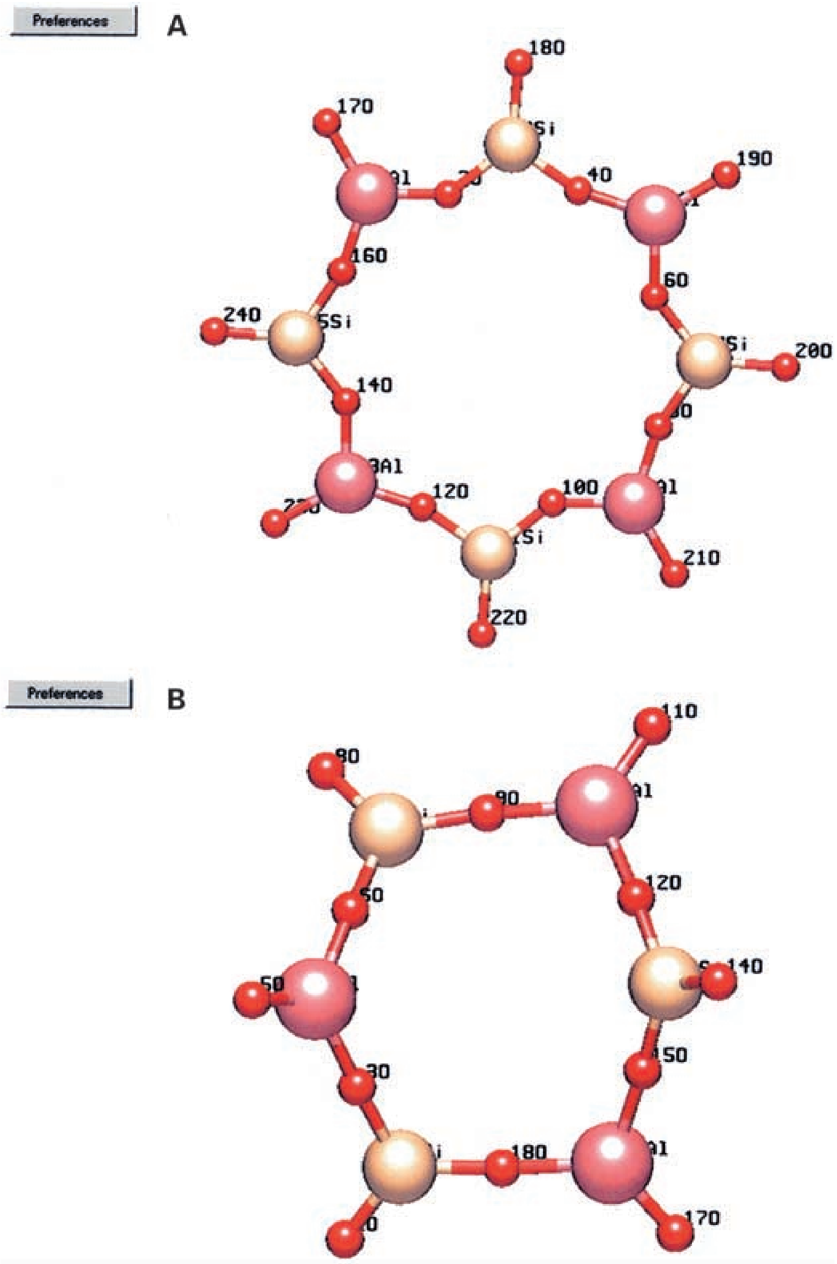
(b) Molecular Dynamics Simulation

Na-A zeolite framework is modeled by the pseudo cell, $(AlSiO_4)_{12}$ and the *Pm3m* space group which contains three kinds of $12Na^+$ ions (Na I, Na II, Na III). Cs-A zeolite framework is similar to the space group of Na-A which has three different of $7Cs^+$ ions (Cs I, Cs II, Cs III) and $5Na^+$ ions (Na I). The framework atoms are fixed in the space at the positions determined by X-ray diffraction experiment of [32] and [33] for the Na-A ($Na_{12}Al_{12}Si_{12}O_{48}$) and Cs-A zeolite ($Cs_7Na_5Al_{12}Si_{12}O_{48}$), respectively. For MD simulation of the zeolite system, 840 particles were employed with the initial position data. Interatomic potential functions consist of Colombic, short-range repulsion, van der Waals attraction, and Morse potential terms applied only to the interactions among aluminum, silicon and oxygen. Because of the small charge of Al and Si in zeolite framework estimated from the above-mentioned quantum chemical study, the applied MD of zeolite is following partially ionic potential model:

$$\begin{aligned}\Phi_{ij} &= \frac{z_i z_j e^2}{4\pi\varepsilon_0 r_{ij}} + f_0(b_i + b_j)\exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) - \frac{c_i c_j}{r^6} \\ &\quad + D_{ij}\{\exp[-2\beta_{ij}(r_{ij} - r_{ij}^*)] - 2\exp[-\beta_{ij}(r_{ij} - r_{ij}^*)]\} \qquad (1)\end{aligned}$$

TABLE I Potential parameters for MD simulation of $Na_{12}Al_{12}Si_{12}O_{48}$ and $Cs_7Na_5Al_{12}Si_{12}O_{48}$

Ion	*Number*	Z(e)	M	a/(Å)	b/(Å)	c(kJ$^{1/2}$Å^{3}mol$^{-1/2}$)
$Na_{12}Al_{12}Si_{12}O_{48}$, *Pm3m*, $a = 12.28$ Å						
Na I	80	1.000	22.99	1.388	0.120	10.000
Na II	30	1.000	22.99	1.388	0.120	10.000
Na III	10	1.000	22.99	1.388	0.120	10.000
Al	120	2.250	26.98	1.022	0.080	0.000
Si	120	2.400	28.09	0.942	0.090	0.000
O	480	− 1.4125	16.00	1.908	0.150	20.000
Ion pair	$D(10^{-19}$J)	β	r*(Å)			
	Al–O	44.00	2.00			
	Si–O	74.00	2.00			
$Cs_7Na_5Al_{12}Si_{12}O_{48}$, *Pm3m*, $a = 12.32$ Å						
Cs I	30	1.000	132.90	2.272	0.080	25.000
Cs II	20	1.000	132.90	2.272	0.080	25.000
Cs III	20	1.000	132.90	2.272	0.080	25.000
Na I	50	1.000	22.99	1.022	0.120	10.000
Al	120	1.800	26.98	1.022	0.080	0.000
Si	120	2.400	28.09	0.942	0.090	0.000
O	480	− 1.300	16.00	1.908	0.150	20.000
Ion pair	$D(10^{-19}$J)	β	r*(Å)			
	Al–O	44.00	2.00			
	Si–O	74.00	2.00			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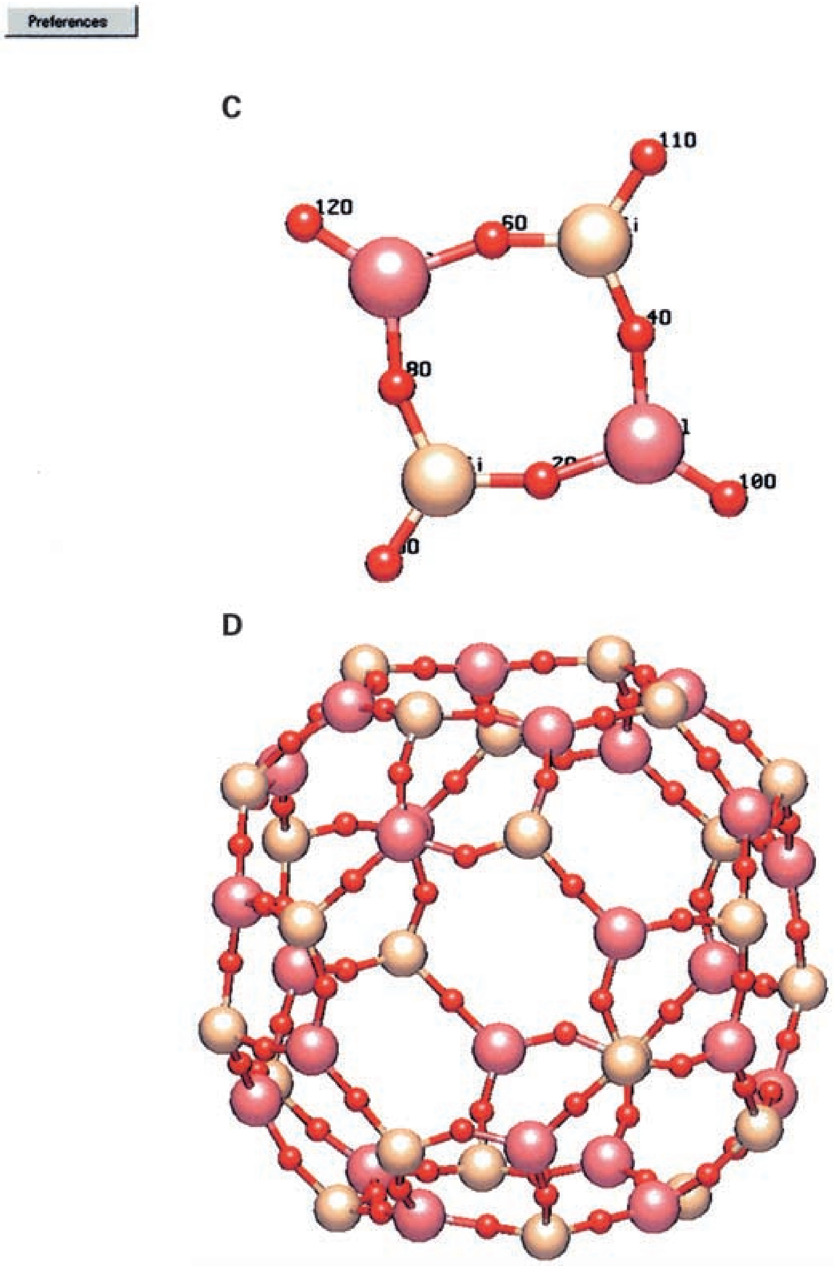

FIGURE 1 The structure of each cluster consists of zeolite framework employed for the MO calculation. (a) α cage, $[Al_4Si_4O_{16}]^{4-}$, 8ring, Na II site, (b) β cage, $[Al_3Si_3O_{12}]^{3-}$, 6ring, Na I site, (c) γ cage, $[Al_2Si_2O_8]^{2-}$, 4ring, Na III site, (d) total structure of zeolite framework.

TABLE II The calculated electric densities and charges of each cluster consists of zeolite framework

No.	*Element*	*Charge*	*Electric density*
(a) α cage, $[Al_4Si_4O_{16}]^{4-}$, 8-ring, Na II site			
1	Al	0.783	2.217
2	O	−0.799	6.799
3	Si	1.592	2.408
4	O	−0.793	6.793
5	Al	0.766	2.234
6	O	−0.800	6.800
7	Si	1.591	2.409
8	O	−0.796	6.796
9	Al	0.765	2.235
10	O	−0.797	6.797
11	Si	1.589	2.411
12	O	−0.794	6.794
13	Al	0.765	2.235
14	O	−0.799	6.799
15	Si	1.585	2.415
16	O	−0.813	6.813
17	O(Al)	−0.827	6.828
18	O(Si)	−0.928	6.928
19	O(Al)	−0.833	6.833
20	O(Si)	−0.929	6.929
21	O(Al)	−0.833	6.833
22	O(Si)	−0.929	6.929
23	O(Al)	−0.835	6.835
24	O(Si)	−0.932	6.932
(b) β cage, $[Al_3Si_3O_{12}]^{3-}$, 6-ring, Na I site			
1	Si	1.587	2.413
2	O	−0.819	6.819
3	Al	0.781	2.219
4	O	−0.815	6.815
5	Si	1.597	2.403
6	O	−0.815	6.815
7	Al	0.780	2.220
8	O	−0.818	6.818
9	Si	1.587	2.413
10	O	−0.816	6.816
11	Al	0.786	2.214
12	O	−0.817	6.817
13	O(Si)	−0.931	6.931
14	O(Al)	−0.807	6.807
15	O(Si)	−0.933	6.933
16	O(Al)	−0.806	6.806
17	O(Si)	−0.932	6.932
18	O(Al)	−0.809	6.809
(c) γ cage, $[Al_2Si_2O_8]^{2-}$, 4-ring, Na III site			
1	Si	1.554	2.446
2	O	−0.811	6.811
3	Al	0.745	2.254
4	O	−0.811	6.811
5	Si	1.554	2.446
6	O	−0.810	6.811
7	Al	0.744	2.256
8	O	−0.811	6.811

TABLE II – *continued*

No.	*Element*	*Charge*	*Electric density*
9	O(Si)	− 0.906	6.906
10	O(Al)	− 0.771	6.771
11	O(Si)	− 0.906	6.906
12	O(Al)	− 0.771	6.771

where r_{ij} is an interatomic distance and f_0 is a constant. Parameters, z, a, b and c, are for atomic species, and D_{ij}, β_{ij} and r_{ij}^{*} are for Al–O and Si–O pairs. All the potential parameters employed for the sodium and caesium occluded zeolites are tabulated in Table I. The Ewald method [34] was applied for the calculation of the Coulomb forces; the cutoff distance in real space was $L/2$, and the reciprocal lattice vectors $|n^2|$ were counted up to 27. The convergence parameter α was $5.6/L$ and the time step 2 fs. At the beginning, MD runs were performed with the constant temperature method following by Woodcock's suggestion [35]. After constant temperature, 673 K, runs of several thousand steps, these were switched to constant energy runs. From the runs during more than 10^4 time steps using Verlet's Algorithm after attainment of equilibrium, the self-diffusion coefficients were estimated from the MSD and VCF.

RESULTS AND DISCUSSION

(a) Semi- and Non-empirical MO Calculation

The zeolite consists of three types of clusters which are α ($[Al_4Si_4O_{16}]^{4-}$, 8ring), β ($[Al_3Si_3O_{12}]^{3-}$, 6-ring) and γ ($[Al_2Si_2O_8]^{2-}$, 4-ring) shown in Fig. 1 (a–c). The obtained charge and electric densities for each cluster by MO calculation were presented in Table II. The obtained electric densities were smaller than the theoretical ones. The total structure of zeolite framework shown in Fig. 1(d) were employed for the estimation of the geometrical optimization. The most stable structure was specified in Table III compared with the corresponding X-ray results [33] and they show a good coincidence. Then the vibrational frequency for the infrared spectrum were estimated from the Gaussian package. The calculated results were shown in Fig. 2 together with the experimental ones and the corresponding signs were assigned in Table IV which could be reproduced experimental results by MO calculation.

TABLE III The most stable structure of the sodium and caesium exchanged zeolite framework by molecular orbital methods based on the geometry optimization for comparison with the X-ray data [33]

Bond length (Å)	*X-ray* [33]	*MO*
(Si, Al)– O(1)	1.662	1.658
(Si, Al)– O(2)	1.666	1.662
(Si, Al)– O(3)	1.665	1.660
Cs(1)– O(1)	3.401	3.346
Cs(1)– O(2)	3.582	3.412
Cs(2)– O(3)	3.114	2.992
Cs(3)– O(3)	3.187	3.077
Na–O(3)	2.424	2.216
Bond angle (deg.)	*X-ray [33]*	*MO*
O(1)– (Si, Al)– O(2)	107.1	107.6
O(1)– (Si, Al)– O(3)	111.0	112.2
O(2)– (Si, Al)– O(3)	109.0	106.8
O(3)– (Si, Al)– O(3)	109.6	110.9
(Si, Al)– O(1)– (Si, Al)	144.9	142.0
(Si, Al)– O(2)– (Si, Al)	159.4	163.1
(Si, Al)– O(3)– (Si, Al)	147.0	144.3
O(3)– Cs(2)– O(3)	81.5	79.4
O(3)– Cs(3)– O(3)	79.3	76.8
O(3)– Na(1)– O(3)	113.9	118.7

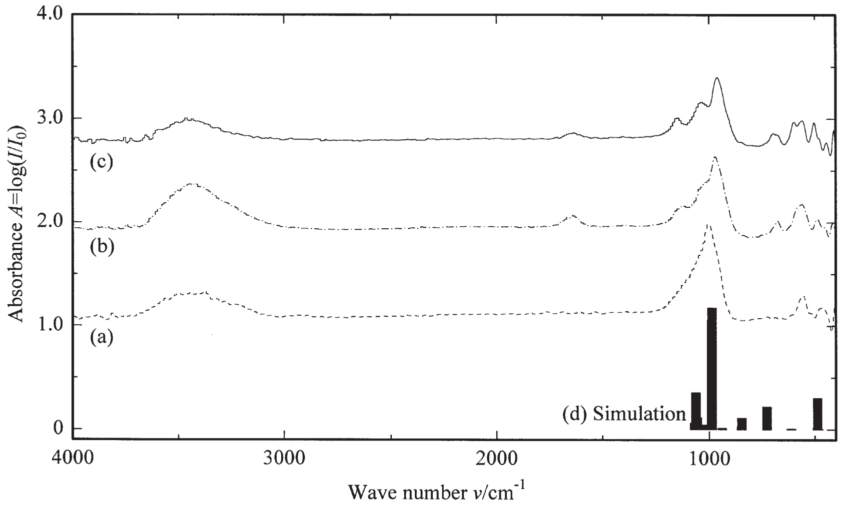

FIGURE 2 Relationship between the experimental infrared spectrum and the simulated vibrational frequency results, (a) 4a powder zeolite after dehydration; broken line, (b) zeolite in LiCl–KCl at 673 K for 24 h; chain line, (c) caesium occluded zeolite in LiCl–KCl at 673 K in Ar atmosphere; solid line, (d) simulation results; bar chart.

(b) Na-A Zeolite, $Na_{12}Al_{12}Si_{12}O_{48}$ in MD

Zeolites are microporous aluminosilicates with relatively rigid anionic frameworks which contain exchangeable cations and generally removable and replaceable guest molecules such as water and organic compounds. The framework of zeolite-A [36] is generated by placing a cubic double 4-ring units (D4R, $Al_4Si_4O_{16}$) in the centers of the edges of a cube of edge 12.3 Å. This arrangement produces truncated octahedral units centered at the corners of the cube. Each corner of the cube is occupied by a truncated octahedron (β cage) enclosing a cavity with a free diameter of 6.6 Å. The center of the unit cell is a large cavity (α cage) which has a free diameter of 11.4 Å. Entry into the α cage cavity is possible through six 16-membered $Al_4Si_4O_8$ rings (called 8-ring), mean free diameter of which is approximately 4.2 Å. Each β cage cavity is surrounded cubically by eight α cage through a 2.2 Å 12-membered $Al_3Si_3O_6$ 6-ring. In Na-A zeolite, 12 Na ions are in the pseudo cell, eight of them, Na I are located near the corner of the oxygen 6-rings on the 3-fold axis, and three Na ions, Na II, are randomly distributed to the 4-fold degenerated positions displaced about 1.2 Å from the center of the oxygen 8-rings. The remaining Na ion, Na III, is located near the opposite oxygen 4-ring.

The MSD and VAC for three types of Na ions in Na-A zeolite frameworks with time steps are displayed in Fig. 3 (a) and (b), respectively. As shown in Fig. 3(a), it could be readily seen that Na II and Na III ions in zeolite is highly mobile and exchangeable. The VCF are oscillating continuously, decaying rapidly to zero and having different depth and position of the first peaks, which indicates random

TABLE IV The results observed from the IR spectrum of the salt occluded zeolites

v (cm^{-1})	*Sign*	*Exchanged cation*
(a) 4a power zeolite after dehydration (broken line)		
465	Si(Al)− O bend	Na
557	Double 4-rings	Na
997	external linkages or internal tetrahedra asym. stretch.	
(b) 4a powder zeolite in LiCl−KCl at 673 K for 24 h (chain line)		
483	Si(Al)− O bend	Li
562	Double 4-rings	Na
674	Si(Al)− O sym. stretch.	Na
970, 1044, 1118	external linkages or internal tetrahedra asym. stretch.	
(c) caesium occluded zeolite in LiCl−KCl at 673 K in Ar atmosphere (solid line)		
446	–	
504	–	
557	double 4-rings	Na, Cs
600	double 4-rings	Li
690	Si(Al)− O sym. stretch.	K
960, 1024, 1150	external linkages or internal tetrahedra asym. stretch.	

movings, back and forth, cages with different speeds. The behavior of the MSD's is common: that of short, rapid increase and then that of slow, flat changes, which also indicates random moving in closed cages, but of different sizes. The self-diffusion coefficients of Na^+ ions were calculated from the MSD and the VAC

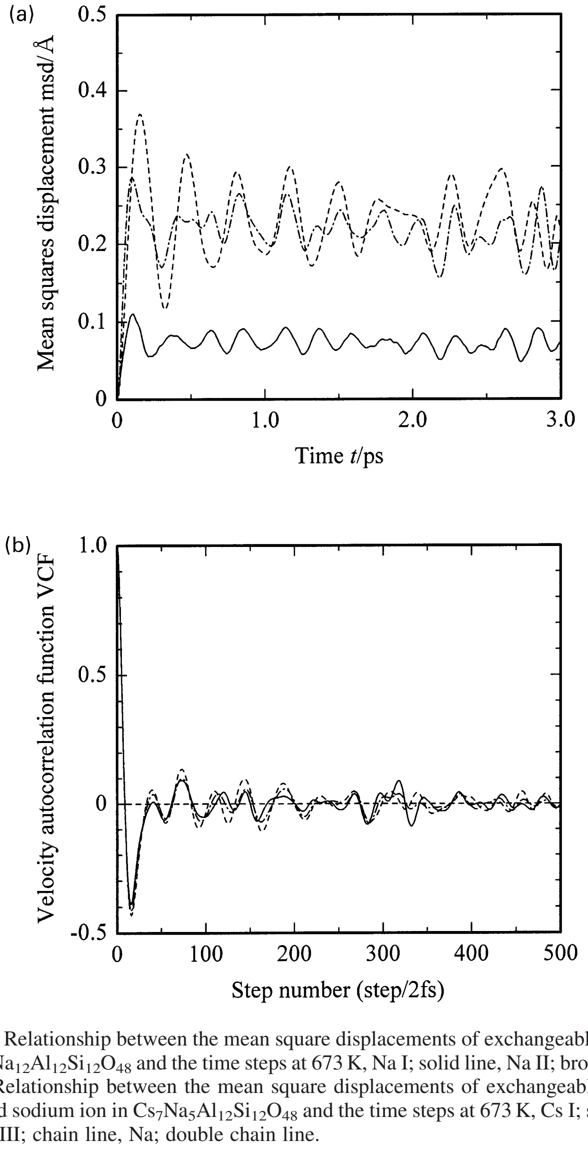

FIGURE 3 (a) Relationship between the mean square displacements of exchangeable three kinds of sodium ions in $Na_{12}Al_{12}Si_{12}O_{48}$ and the time steps at 673 K, Na I; solid line, Na II; broken line, Na III; chain line. (b) Relationship between the mean square displacements of exchangeable three kind of caesium ions and sodium ion in $Cs_7Na_5Al_{12}Si_{12}O_{48}$ and the time steps at 673 K, Cs I; solid line, Cs II; broken line, Cs III; chain line, Na; double chain line.

using the Einstein expression Eq. (2a) [37] and Eq. (2b), respectively:

$$D = \frac{1}{6}\frac{1}{\mathrm{d}\tau}\langle\{r_i(t+\tau) - r_i(t)\}^2\rangle \tag{2a}$$

$$D = \frac{1}{3}\int_0^\infty \mathrm{d}t\langle v_i(t)v_i(0)\rangle \tag{2b}$$

as given in Table V. The results obtained with the simulation predict that in Na-A zeolite the order of the self-diffusion coefficients for three kinds of Na ions would be the following order.

$$D_{\mathrm{Na\,I}} < D_{\mathrm{Na\,III}} < D_{\mathrm{Na\,II}} \tag{3}$$

This behavior means that Na I ion are relatively stable in Na-A zeolite than Na II and Na III ions, which is consistent with the simulated results [38,39] used by other potential parameters.

(c) Cs-A Zeolite, $Cs_7Na_5Al_{12}Si_{12}O_{48}$ in MD

The crystal structures of hydrated ($a = 12.32$ Å) and seven-twelfths Cs^+-exchanged molecular sieve zeolite A, $Cs_{0.58}Na_{0.42}[AlSiO_4]$-A, stoichiometry $Cs_7Na_5Al_{12}Si_{12}O_{48}$ per unit cell, have been investigated by MD methods. Caesium ions are located at three distinct crystallographic sites in each structure. Three Cs^+ ions lie at the centers of the 8-oxygen rings at sites of D_{4d} symmetry, filling that equipoint; these ions are approximately 0.3 Å further from their nearest framework oxygen neighbors than the sum of the appropriate ionic radii would indicate. The remaining four Cs^+ ions are associated with the 6-oxygen rings and lie on unit cell threefold axes. Because each Cs^+ ion is too large to lie in the plane of its nearest 6-ring neighbors, all four are found near but off that

TABLE V Self-diffusion coefficients calculated from the mean squares displacements and the velocity autocorrelation functions for exchangeable sodium and caesium ions

Exchanged ion	*Ionic radius* (pm)	*MSD*	*VAC*
(a) $Na_{12}Al_{12}Si_{12}O_{48}$		D (10^{-6}(cm^2/s))	D (10^{-6}(cm^2/s))
Na I	117.0	1.24	1.79
Na II	117.0	5.30	4.81
Na III	117.0	3.82	4.46
(b) $Cs_7Na_5Al_{12}Si_{12}O_{48}$			
Cs I	172.0	0.87	1.54
Cs II	172.0	3.17	3.01
Cs III	172.0	4.42	3.45
Na I	117.0	2.47	2.14

position. Three Cs^+ ions are recessed approximately 2.0 Å into the large cavity from that plane, and one is located in the sodalite unit approximately 2.15 Å from the plane of its nearest framework oxygen neighbors. To minimize electrostatic repulsions, these latter four Cs^+ ions are probably associated with four

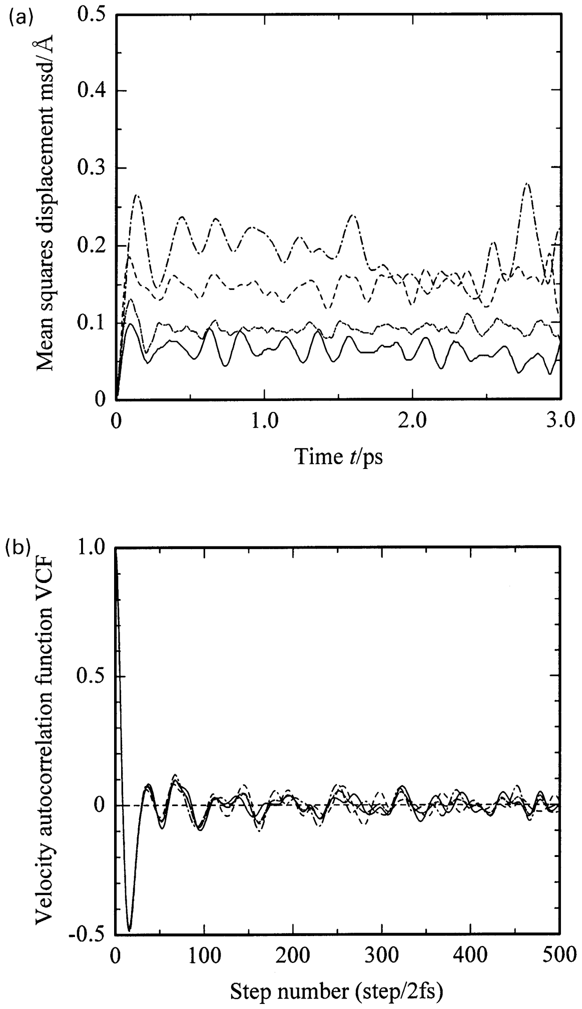

FIGURE 4 (a) Relationship between the normalized velocity autocorrelation functions of exchangeable three kinds of sodium ions in $Na_{12}Al_{12}Si_{12}O_{48}$ and the step numbers at 673 K, Na I; solid line, Na II; broken line, Na III; chain line. (b) Relationship between the normalized velocity autocorrelation functions of exchangeable three kinds of caesium ions and sodium ion in $Cs_7Na_5Al_{12}Si_{12}O_{48}$ and the step numbers at 673 K., Cs I; solid line, Cs II; broken line, Cs III; chain line, Na; double chain line.

tetrahedrally placed 6-rings in each unit cell or sodalite unit; the exchangeable limit observed appears to be related to this structural feature. In each structure, positions for only four of the five Na^+ ions were found; these are near the centers of those remaining four 6-rings not associated with Cs^+ cations.

The MSD and VAC for three types of Cs ions and Na ion in Cs-A zeolite frameworks with time steps are displayed in Fig. 4 (a) and (b), respectively. As shown in Fig. 4 (a), we would readily understand that Cs II and Cs III ions in Cs-A zeolite is highly mobile and exchangeable. The self-diffusion coefficients of each ion were calculated from the MSD and the VAC using Eq. 2(a) and (b), respectively as presented in Table V. The results obtained with the simulation predict that in Cs-A zeolite the order of the self-diffusion coefficients for three kinds of Cs ions and Na ion would be as follows.

$$D_{\mathrm{Cs\,I}} < D_{\mathrm{Na\,I}} < D_{\mathrm{Cs\,II}} < D_{\mathrm{Cs\,III}} \tag{4}$$

A series of the simulated results revealed that Cs II and Cs III ions are relatively more mobile and replaceable than Cs I and Na I, and Cs I and Na I ions are relatively stable in Cs-A zeolite than Cs II and Cs III ions. Finally, our calculated results were demonstrated that Cs ions in α-cage are more stable than Na ions, and Na ions in β cage are more stable than Cs ions.

CONCLUSION

We investigated the electric properties of each cluster and the geometric optimization of the total structure of zeolite frameworks. The obtained parameters for structure were in good agreement with the X-ray experimental results. In addition, the self-diffusion coefficients of three kinds of Na in Na-A zeolite and Cs in Cs-A zeolite estimated from MD simulation at 673 K together with the mean squares displacements and normalized velocity autocorrelation functions. The gained self-diffusion coefficient of Na I ion in Na-A zeolite is smaller than that of Na II and Na III ions, which means that eight Na I ions are stable, and three Na II ions and Na III ion could be exchangeable and replaced the other ions easily. On the contrary, the obtained self-diffusion coefficients of the eight Cs I ions are smaller than those of the other Cs II and Cs III ions and Na I ion in Cs-A zeolite. A series of simulated results were demonstrated that the Cs I ions were more stable than Na ions because the large ionic radius of Cs was equivalent to the space in α-cage.

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