

# Sodium and Lithium Environments in Single- and Mixed-Alkali Silicate Glasses. An ab Initio Molecular Orbital Study

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The local coordination environments of alkali cations ( $\text{Li}^+$  and  $\text{Na}^+$ ) in single- and mixed-alkali silicate glasses have been investigated by using cluster model calculations at the Hartree–Fock/6-31G(d) level. The optimized structural parameters obtained for the model clusters are in good agreement with the observed ones. It has been demonstrated that the average coordination number of alkali cations increases in going from Li to Na and that each alkali cation is located in rather individual local sites in both the single- and mixed-alkali clusters. We have further calculated the site-mismatch energies and have shown that a considerable site mismatch is possible to occur during hopping events of alkali cations in mixed-alkali glasses. The present calculated results have elucidated that the molecular orbital overlap or the covalent interaction between alkali cations and their surrounding oxygen atoms plays an important role in structuring individual cations sites, indicating that the physical origin of the mismatch energy in mixed-alkali glasses should not be attributed simply to ion-size differences.

## 1. Introduction

It has been demonstrated that alkali cations in ionic glasses can move through the glass structure to show ionic conduction.<sup>1,2</sup> Such a property of ionic glasses makes them attractive candidates for good ionic conductors, and, therefore, there have been a large number of comprehensive works on the area of ionic-transport properties of glasses to develop highly conductive glassy solid electrolytes. It should be noted, however, that the mechanism of ionic transport in glassy materials has not been fully understood yet. One of the challenging problems of ionic conduction in glasses is the so-called “mixed-alkali” effect.<sup>2–6</sup> The effect is typically manifested by large departures from additivity in dynamical properties during mixing of alkali cations. For example, electrical conductivities in mixed-alkali glasses exhibit minima near equimolar proportions of the two types of alkali cations; the minimum value of ionic conductivity of the mixed-alkali Li/K disilicate glasses is almost 5 orders of magnitude lower than that of either single-alkali glass.<sup>4</sup> Such departures from linearity are also seen in glasses containing  $\text{H}^+$ ,<sup>7</sup>  $\text{Ag}^+$ ,<sup>8,9</sup> and  $\text{Tl}^+$  ions,<sup>10</sup> and the effect should be referred to more generally as the mixed-mobile-cation effect.<sup>2</sup>

Thus far, various theoretical models have been proposed to explain the anomalies in mixed-alkali glasses. The past decade has witnessed great progress in resolving this long-standing problem. Most of the recent theories of the mixed-alkali effect are based on the conducting pathway model, which predicts that ionic transport occurs along the conduction pathway or the percolation channels.<sup>11–22</sup> It has been assumed that for mixed-alkali glasses the conduction pathways consist of a random mixture of the two types of alkali cations and nonbridging oxygens and that the hopping sites are unlikely matched to both alkali cations. Transport of alkali cations of different sizes will mutually interfere when they share the same conducting pathways owing to site-mismatch energies. Ingram<sup>11</sup> referred

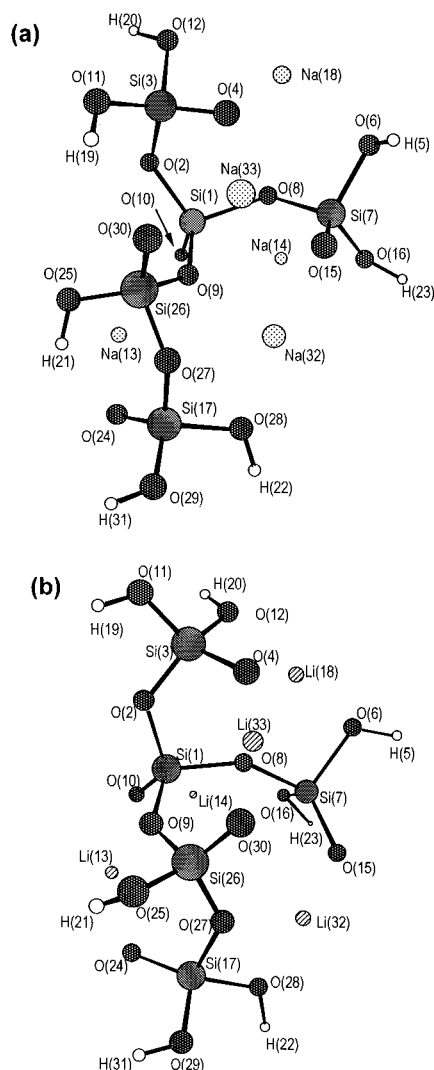
to the effect of site mismatch as the “blocking effect” of foreign cations.

On the basis of the concept, Maass, Bunde, and Ingram<sup>19</sup> have developed a “dynamical structural model.” According to this model, an  $A$  ion will be inclined to jump to a vacancy  $\bar{A}$  previously occupied by an  $A$  ion where the environment is correctly adjusted, but an  $A$  ion declined to jump to a vacant site  $\bar{B}$  previously occupied by a  $B$  ion since the  $\bar{B}$  site has to relax to accommodate an  $A$  ion. They also assumed that if an  $\bar{A}$  or  $\bar{B}$  site is vacant for a period of time  $t_{\bar{A}}$  or  $t_{\bar{B}}$ , it relaxes to some type of interstitial site  $\bar{C}$ , which is adjusted correctly neither to an  $A$  ion nor to a  $B$  ion. Also, if a  $\bar{C}$  site is occupied by an  $A$  or  $B$  ion more than  $t_{\bar{A}}$  or  $t_{\bar{B}}$  time steps, it relaxed to an  $\bar{A}$  or  $\bar{B}$  site, respectively. Maass et al. then performed Monte Carlo simulations to explore the consequence of the dynamical structure model and have shown that the calculated results satisfactorily reproduce the “mobility crossover,” namely the mixed-alkali effect.

In their computer simulations, however, Maass et al.<sup>19</sup> have not calculated mismatch energies but employed the values only as parameters relating to Boltzmann temperatures. In a previous paper, we have attempted to calculate mismatch energies directly by molecular orbital theory using clusters of atoms modeling the local structure of single- and mixed-alkali silicate glasses.<sup>21</sup> Then we have concluded that site mismatch energies are so large that  $\bar{A} \rightarrow \bar{B}$  and  $\bar{B} \rightarrow \bar{A}$  site conversions are difficult to occur and that a site memory effect assumed by Maass, Bunde, and Ingram possibly exists in mixed-alkali glasses. It should be noted, however, that our previous models are rather small; they consist only of two  $\text{SiO}_{3/2}\text{O}^-$  units, and the constituent alkali cations are in contact with one adjacent nonbridging oxygen atom. It is hence probable that the local coordination environments of alkali cations and the effect of structural relaxation in mixed-alkali glasses may not be evaluated in a satisfactory way by using such small clusters.

To calculate site-mismatch energies in mixed-alkali glasses more realistically, we here employ much larger clusters consist-

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**Figure 1.** The optimized geometries of the single-alkali clusters containing (a) five Na atoms and (b) five Li atoms.

ing of five  $\text{SiO}_{3/2}\text{O}^-$  units. As will be shown later, the present clusters reproduce a multiple coordination of alkali cations. Recently, we<sup>23</sup> have shown that the optimized structural parameters, O 1s photoelectron spectrum, and infrared and Raman spectra calculated for the sodium disilicate cluster containing five  $\text{SiO}_{3/2}\text{O}^-$  units at the Hartree–Fock/6-31G(d) level are in good agreement with the respective experimental results, suggesting that the present clusters can provide reasonable structural models of mixed-alkali as well as single-silicate glasses. On the basis of the calculated results, we discuss the local coordination environments of alkali cations in single- and mixed-alkali silicate glasses and present a microscopic basis of a site memory effect proposed in the dynamical structure model.<sup>5,19</sup>

## 2. Models and Computational Procedure

In this work, we first obtain the optimized geometry of the clusters modeling the local structure of sodium and lithium disilicate glasses (see Figure 1). The surface oxygen atoms of the model clusters were terminated by H atoms to satisfy valences. As mentioned previously, these model clusters contain five  $\text{SiO}_{3/2}\text{O}^-$  units connected at the corners by siloxane ( $\text{Si}-\text{O}-\text{Si}$ ) bonds; each  $\text{SiO}_{3/2}\text{O}^-$  unit has three bridging oxygens ( $\text{O}_b$ ), one nonbridging oxygen ( $\text{O}_{nb}$ ), and one  $\text{Na}^+$  or  $\text{Li}^+$  ion as a charge-compensating cation.<sup>24</sup> The geometries of

**TABLE 1: Optimized Si–O Bond Distances (Å) and Si–O–Si Bond Angles (degrees) Calculated for the Single- and Mixed-alkali Clusters at the HF/6-31G(d) Level<sup>a</sup>**

	Na5 <sup>b</sup>	Na4Li <sup>c</sup>	Li5 <sup>d</sup>	Li4Na <sup>e</sup>
Si(1)–O(2)	1.615	1.613	1.630	1.632
Si(1)–O(8)	1.690	1.693	1.662	1.660
Si(1)–O(9)	1.643	1.646	1.628	1.630
Si(1)–O(10)	1.576	1.574	1.589	1.586
Si(3)–O(2)	1.666	1.668	1.649	1.647
Si(3)–O(4)	1.570	1.570	1.576	1.578
Si(3)–O(11)	1.627	1.627	1.628	1.626
Si(3)–O(12)	1.679	1.678	1.678	1.680
Si(7)–O(6)	1.676	1.672	1.681	1.691
Si(7)–O(8)	1.635	1.636	1.627	1.631
Si(7)–O(15)	1.555	1.560	1.539	1.534
Si(7)–O(16)	1.693	1.689	1.704	1.705
Si(17)–O(24)	1.555	1.552	1.556	1.563
Si(17)–O(27)	1.660	1.666	1.663	1.647
Si(17)–O(28)	1.695	1.702	1.684	1.683
Si(17)–O(29)	1.646	1.643	1.641	1.645
Si(26)–O(9)	1.696	1.698	1.684	1.672
Si(26)–O(25)	1.655	1.653	1.641	1.640
Si(26)–O(27)	1.668	1.673	1.670	1.628
Si(26)–O(30)	1.545	1.542	1.550	1.577
Si(1)–O(2)–Si(3)	131.2	130.2	128.0	128.0
Si(1)–O(8)–Si(7)	133.5	130.6	146.6	148.9
Si(1)–O(9)–Si(26)	135.4	138.2	137.0	141.3
Si(17)–O(27)–Si(26)	126.6	124.8	132.3	138.0

<sup>a</sup> For atom labels, see Figures 1 and 2. <sup>b</sup> The single-alkali cluster containing five Na atoms. <sup>c</sup> The single-alkali cluster containing five Li atoms. <sup>d</sup> The mixed-alkali cluster containing four Na and one Li atoms. <sup>e</sup> The mixed-alkali cluster containing four Li and one Na atoms.

the sodium and lithium silicate clusters were completely optimized at the Hartree–Fock (HF) level with the 6-31G(d) split-valence basis set.<sup>25</sup>

We then calculated the optimized geometries of the mixed-alkali clusters and evaluated their site-mismatch energies as follows. First, an Na (a Li) atom in the optimized sodium (lithium) disilicate cluster is replaced by a Li (an Na) atom without changing all the optimized parameters, and the total energy of the nonoptimized mixed-alkali cluster is calculated. Second, we optimized the geometry of this mixed-alkali cluster and obtain its total energy at the stationary point. Finally, the site-mismatch energy is estimated to be the total energy difference between the nonoptimized and optimized mixed-alkali clusters.

All ab initio molecular orbital calculations were carried out using the GAUSSIAN 94 computer program<sup>26</sup> on the CRAY T94/4128 supercomputer.

## 3. Results

### 3.1. Optimized Geometries of Single-Alkali Clusters.

Figure 1 depicts the optimized geometry of single-alkali clusters calculated at the HF/6-31G(d) level. Principal bond distances and bond angles of the single-alkali clusters are listed in Tables 1, 2, and 3. We see from Table 3 that the average Si–O and O–O bond distances and O–Si–O bond angles agree well with the observed ones.<sup>27–30</sup> We also notice from Table 3 that the average total Si–O bond distance of the sodium silicate cluster is slightly longer than that of the lithium silicate cluster, in agreement with the observed tendency. Table 3 shows that the Si– $\text{O}_b$  and Si– $\text{O}_{nb}$  bond distances of the sodium silicate cluster are longer and shorter, respectively, than the corresponding bond distances of the lithium silicate cluster. This indicates that the elongation of the average Si–O bond distance of the sodium silicate cluster above the value for the lithium silicate cluster

**TABLE 2: Principal R–O (R = Li, Na) Bond Distances (Å) of the Single- and Mixed-Alkali Clusters Optimized at the HF/6-31G(d) Level<sup>a</sup>**

	5Na <sup>b</sup>	4NaLi <sup>c</sup>	5Li <sup>d</sup>	4LiNa <sup>e</sup>
R(13)–O(9)	2.641	2.590	2.123	2.124
R(13)–O(10)	2.279	2.290	1.947	1.946
R(13)–O(24)	2.176	2.192	1.778	1.770
R(13)–O(25)	2.731	2.700	3.857	4.342
R(14)–O(8)	2.365	2.391	2.764	2.723
R(14)–O(10)	2.208	2.209	1.783	1.785
R(14)–O(16)	2.391	2.380	1.918	1.917
R(18)–O(4)	2.169	2.169	1.930	1.946
R(18)–O(6)	2.382	2.388	1.984	1.955
R(18)–O(8)	2.687	2.666	2.264	2.305
R(18)–O(12)	2.520	2.530	2.028	1.996
R(32)–O(9)	2.497	2.176	3.859	3.791
R(32)–O(15)	2.220	1.859	1.804	2.191
R(32)–O(27)	2.389	2.115	1.983	3.014
R(32)–O(28)	2.267	1.950	1.987	2.304
R(32)–O(30)	2.652	3.451	3.537	2.292
R(33)–O(4)	2.165	2.163	1.818	1.812
R(33)–O(15)	2.471	2.512	4.574	4.108
R(33)–O(30)	2.220	2.202	1.754	1.795

<sup>a</sup> For atom labels, see Figures 1 and 2. <sup>b,c,d,e</sup> For notations, see Table 1.

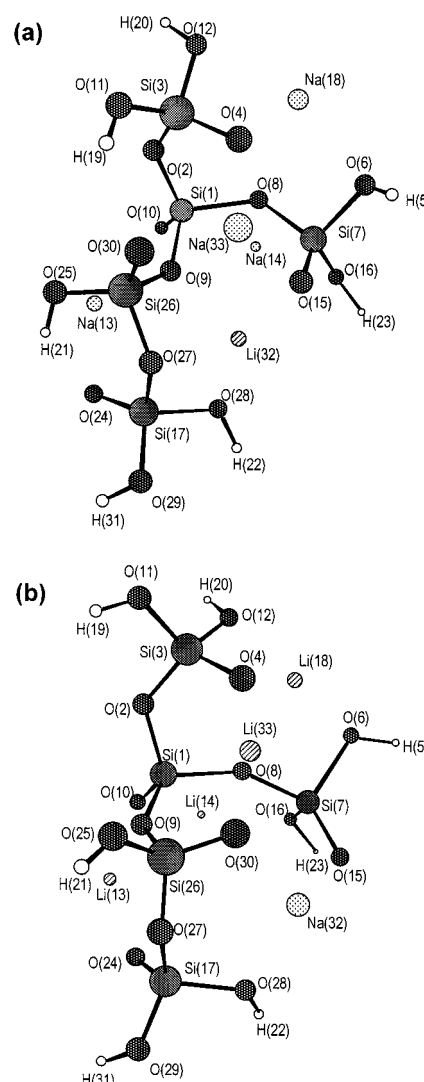
**TABLE 3. Average Si–O, O–O, and R–O Bond Distances of the Model Clusters Calculated at the HF/6-31G(d) Level<sup>a</sup>**

		5Na <sup>b</sup>	4NaLi <sup>c</sup>	5Li <sup>d</sup>	4LiNa <sup>e</sup>
Si–O <sub>b</sub>	calcd	1.663	1.664	1.658	1.654
	obsd	1.636 <sup>f</sup>			
Si–O <sub>nb</sub>	calcd	1.560	1.560	1.562	1.568
	obsd	1.587 <sup>f</sup>			
total Si–O	calcd	1.637	1.638	1.634	1.633
	obsd	1.631 <sup>g</sup>		1.624 <sup>g</sup> , 1.61 <sup>i</sup>	
O–O	calcd	2.670	2.680	2.670	2.669
	obsd	2.66 <sup>g</sup>		2.65 <sup>g</sup> , 2.64 <sup>i</sup> , 2.66 <sup>j</sup>	
Na–O	calcd <sup>k</sup>	2.376	2.384		2.262
	obsd	2.4, <sup>g</sup> 2.3 <sup>h</sup>			
Li–O	calcd		2.025	1.936	1.941
	obsd			2.0, <sup>g</sup> 1.94, <sup>i</sup> 1.97 <sup>j</sup>	

<sup>a</sup> Observed values for the corresponding alkali disilicate glasses are also shown. <sup>b,c,d,e</sup> For notations, see Table 1. <sup>f</sup> Ref 28. <sup>g</sup> Ref 27. <sup>h</sup> Ref 32. <sup>i</sup> Ref 30. <sup>j</sup> Ref 29. <sup>k</sup> Average values for the Na–O bonds less than 3.0 Å. <sup>l</sup> Average values for the Li–O bonds less than 2.5 Å.

results from an elongation of the Si–O<sub>b</sub> distance which overwhelms the contraction of the Si–O<sub>nb</sub> distance on going from Li to Na.

Furthermore, the average Na–O and Li–O bond distances calculated for the single alkali clusters are in excellent accordance with the experimental values<sup>27–30</sup> (see Table 3). The Li<sup>+</sup> ions in the lithium silicate cluster are in contact with 2.8 oxygen neighbors on average, which can be compared well with the observed coordination number of lithium silicate glasses of 2–3.<sup>29,31</sup> It is hence most likely that the present lithium silicate cluster is a reasonable model of the Li coordination environments of actual lithium silicate glasses. On the other hand, as for the sodium disilicate cluster 3–4 oxygen atoms are analyzed at a distance of 2.1–2.7 Å from one sodium atom. Thus the obtained coordination number for the sodium disilicate cluster appears to be smaller than the observed coordination number of around five.<sup>32</sup> This discrepancy may be due to the open structure of the model cluster. However, the present cluster will capture some fundamental features of Na coordination environments in actual sodium silicate glasses, since we have previously confirmed that frequency calculations of the sodium silicate cluster have reproduced satisfactorily the cation-motion vibrational modes that can be found in the far-infrared region.<sup>23</sup>

**Figure 2.** The optimized geometries of the mixed-alkali clusters containing (a) four Na and one Li atoms and (b) four Li and one Na atoms.

### 3.2. Optimized Geometries of Mixed-Alkali Clusters.

Figure 2 shows the optimized geometries of the two types of mixed-alkali clusters; one is the cluster in which an Na site in the sodium disilicate cluster is replaced by a Li ion (which we call model 1), and the other is the cluster in which a Li site in the lithium disilicate cluster is replaced by an Na ion (model 2). The principal bond distances and bond angles of these mixed-alkali clusters optimized at the HF/6-31G(d) level are listed in Tables 1, 2, and 3.

One notices from Figure 2 that no evidence of Na–Li pairs or preferred interaction among unlike cations is seen in the mixed-alkali clusters. This is in agreement with recent spin-echo double-resonance NMR studies of mixed Li/Na silicate glasses,<sup>33</sup> indicating that unlike ion pairs or some type of interaction between dissimilar alkali cations, which were once assumed to explain the mixed-alkali effect,<sup>34–37</sup> will not exist in mixed-alkali glasses.

We also notice from Table 3 that the Li–O bond distances in model 1 and the Na–O bond distances in model 2 are comparable to the Li–O and Na–O bond distances in the single-alkali clusters, respectively. This indicates that the structural relaxation indeed occurs in the mixed-alkali clusters to accommodate the newly introduced minor cation. It should also be worth mentioning that the coordination environments of major



**TABLE 4: Calculated Mismatch Energies Obtained from the Present Cluster Model Calculations**

	mismatch energies (kJ/mol)
$\Delta E_{Na\ on\ \bar{Li}}$	133
$\Delta E_{Li\ on\ \bar{Na}}$	53

alkali cations in the mixed-alkali clusters are hardly altered even when one of the major alkali cations is replaced by another. The above calculated results hence show that the local coordination environments of  $Li^+$  and  $Na^+$  ions are clearly distinct from each other, and the respective coordination environments are substantially unaltered even in the mixed-alkali glasses, in agreement with previous models of the structure of mixed-alkali glasses.<sup>5,19,22</sup>

**3.3. Mismatch energies.** Table 4 lists the calculated site mismatch energies  $\Delta E$  calculated for the present mixed-alkali clusters.  $\Delta E_{A\ on\ \bar{B}}$  means the mismatch energy of an  $A$  ion on a vacant site  $\bar{B}$  previously occupied by a  $B$  ion. As shown in Table 4,  $\Delta E_{Na\ on\ \bar{Li}}$  and  $\Delta E_{Li\ on\ \bar{Na}}$  are calculated to be 133 and 53 kJ/mol, respectively, indicating that a considerable site mismatch is possible to occur in mixed Li/Na silicate glasses. These values are almost comparable to those obtained for much smaller clusters in which each alkali cation interacts only with one adjacent nonbridging oxygen<sup>21</sup> ( $\Delta E_{Na\ on\ \bar{Li}} = 141$  kJ/mol and  $\Delta E_{Li\ on\ \bar{Na}} = 67$  kJ/mol). This correspondence may be fortuitous or may indicate that the potential energy surface in the neighborhood of an alkali site will not change even if the number of its nearby nonbridging oxygens increases.

Tomozawa and Yoshiyagawa<sup>38</sup> have shown that sodium and lithium disilicate glasses have almost the same activation energy for the ionic conductivity ( $\sim 58$  kJ/mol) and that the activation energy in mixed Li/Na disilicate glasses increases to  $\sim 97$  kJ/mol at an alkali ratio of  $\sim 0.5$ . That is, in lithium and sodium disilicate glasses addition of a second alkali increases the activation energy at most by  $\sim 40$  kJ/mol. According to the dynamical structure model by Maass, Bunde, and Ingram,<sup>19</sup> this excess activation energy ( $\sim 40$  kJ/mol) can be regarded as the site-mismatch energy that must be overcome to enable cation migration in mixed Li/Na silicate glasses. It should be noted that the value of  $\Delta E_{Li\ on\ \bar{Na}}$  obtained from the present calculations is in reasonable agreement with the observed one. However, the calculated  $\Delta E_{Na\ on\ \bar{Li}}$  is considerably large in comparison with the observed value. We consider that such a large value of  $\Delta E_{Na\ on\ \bar{Li}}$  can be explained as follows.

In this work, we assumed that an  $Na^+$  ion moves to the position previously occupied by a  $Li^+$  ion to calculate  $\Delta E_{Na\ on\ \bar{Li}}$ . However, it would be difficult for the  $Na^+$  ion to jump to exactly the same position as the  $Li$  site since  $Na^+$  ions are larger than  $Li^+$  ions. In actual mixed Na/Li glasses, the  $Na^+$  ion will jump to the position around the  $Li$  site to avoid a possible steric hindrance between the  $Na^+$  ion and its nearby oxygens (however, the complete structural relaxation cannot be attained until the  $Li$  site relaxes to the  $Na$  site). Thus, the calculated value of  $\Delta E$  will tend to become larger than the observed one, especially when larger ions jump to the sites previously occupied by smaller ions. However, we consider that the present procedure is not far from realistic and is still useful to estimate the mismatch energies from a first principle.

## 4. Discussion

**4.1. Sodium and Lithium Coordination Environments.** As mentioned in section 3.1, the coordination number of  $Na$  in silicate glasses is larger than that of  $Li$ . This change in coordination number can be simply understood in terms of the

**TABLE 5: Mulliken Bond Overlap Populations for R—O (R = Li, Na) Bonds Calculated at the HF/6-31G(d) Level<sup>a</sup>**

	5Na <sup>b</sup>	4NaLi <sup>c</sup>	5Li <sup>d</sup>	4LiNa <sup>e</sup>
R(13)—O(9)	0.069	0.066	0.180	0.170
R(13)—O(10)	0.203	0.257	0.244	0.240
R(13)—O(24)	0.256	0.258	0.375	0.402
R(13)—O(25)	0.152	0.159	0.026	0.010
R(14)—O(8)	0.113	0.109	0.059	0.060
R(14)—O(10)	0.262	0.257	0.320	0.316
R(14)—O(16)	0.144	0.136	0.216	0.222
R(18)—O(4)	0.228	0.224	0.285	0.291
R(18)—O(6)	0.146	0.138	0.182	0.186
R(18)—O(8)	0.077	0.080	0.128	0.128
R(18)—O(12)	0.142	0.141	0.220	0.223
R(32)—O(9)	0.110	0.141(0.113 <sup>f</sup> )	−0.002	0.001(0.004 <sup>g</sup> )
R(32)—O(15)	0.197	0.267(0.240 <sup>f</sup> )	0.313	0.236(0.157 <sup>g</sup> )
R(32)—O(27)	0.241	0.301(0.223 <sup>f</sup> )	0.216	0.095(0.098 <sup>g</sup> )
R(32)—O(28)	0.157	0.217(0.194 <sup>f</sup> )	0.207	0.134(0.102 <sup>g</sup> )
R(32)—O(30)	−0.019	−0.001(−0.013 <sup>f</sup> )	0.037	0.193(0.038 <sup>g</sup> )
R(33)—O(4)	0.203	0.200	0.256	0.254
R(33)—O(15)	0.162	0.142	0.006	0.000
R(33)—O(30)	0.284	0.282	0.401	0.304

<sup>a</sup> For atom labels, see Figures 1 and 2. <sup>b,c,d,e</sup> For notations, see Table 1. <sup>f</sup> These values are the results for the cluster in which the Li(32) atom is located in the Na(32) site in the single-alkali cluster containing five Na atoms. <sup>g</sup> These values are the results for the cluster in which the Na(32) atom is located in the Li(32) site in the single-alkali cluster containing five Li atoms.

difference in the ionic radii between  $Li$  and  $Na$ . However, it is worthwhile to investigate the charge distributions of the clusters since the cation coordination environments are also expected to be influenced by the electronegativities of alkali cations, which will change the electron density of the alkali cation sites of interest. To investigate the charge distributions of the clusters we here carry out a Mulliken population analysis.<sup>39</sup> Since atomic charge is not a quantum mechanical observable, all schemes for computing it are ultimately arbitrary. However, the Mulliken approach, which computes charges by dividing orbital overlap evenly between the two atoms involved, is widely used for qualitative discussions of bonding or for comparing electron distribution in a series of related molecule. The results are tabulated in Table 5.

It is clear from Table 5 that the bond overlap populations  $n$  of  $Li$ —O bonds are considerably larger than those of  $Na$ —O bonds; about half of  $n$  for the  $Si$ —O<sub>b</sub> bonds amount to the value of  $n$  for the  $Li$ —O<sub>nb</sub> bond, indicating that the  $Li$ —O<sub>nb</sub> bonds have strong covalent interactions. It should also be noted that the average  $Li(O_{nb})$  coordination number  $N$  of the lithium silicate cluster ( $N = 1.4$ ) is only slightly smaller than the average  $Na(O_{nb})$  coordination number of the sodium silicate cluster ( $N = 1.6$ ) although the total  $R(O)$  coordination number of the former cluster ( $N = 2.8$ ) is substantially smaller than that of the latter cluster ( $N = 3.6$ ). These results indicate that the  $Li^+$  site will tend to organize the optimum configuration with respect preferably to the nonbridging oxygen atoms rather than the bridging oxygen atoms because of the strong covalent interactions between  $Li$  and O<sub>nb</sub> atoms. Stated in another way, as we go from  $Li$  to  $Na$ , the covalency of the  $R$ —O bonds decreases, and, accordingly, alkali cations will tend to interact with bridging oxygens as well as nonbridging oxygens to increase the total coordination number. It is hence probable that the coordination environments of alkali cations in glasses (optimum coordination number,  $R$ —O bond distance, etc.) will be determined not only by their size but also by the molecular orbital interactions between alkali cations and their surrounding oxygens.

**4.2. Microscopic Basis of a Memory Effect.** We have already shown in the preceding subsection that a molecular

orbital description is necessary to characterize the cation coordination environments in silicate glasses. We here investigate the bond overlap populations associated with a *B* ion on an *A* site in mixed-alkali clusters to analyze the microscopic basis of a cation-site mismatch, or a memory effect.

As shown in Table 5, the values of *n* for the  $\overline{\text{Li}}(\text{on}\overline{\text{Na}}) - \text{O}$  and  $\overline{\text{Na}}(\text{on}\overline{\text{Li}}) - \text{O}$  bonds in the nonoptimized mixed-alkali clusters are quite small in comparison with those for the corresponding bonds in the single-alkali clusters. This indicates that a good energy match between the atomic orbitals of minor alkali cations and their nearby oxygen atoms is not accomplished in the nonoptimized mixed-alkali clusters. However, such a mismatch in orbital energies appears to be improved after the structural relaxation of the mixed-alkali clusters; all the R–O bond overlap populations of the optimized mixed-alkali clusters are comparable to those of the single-alkali clusters. That is, when an *A* site is occupied by a *B* ion, the *A* site will so relax as to maximize the bond overlap populations of the *B*–O bonds. We hence suggest that in mixed-alkali glasses these structural relaxations of the cation sites must occur in every jump process of the mobile cations to yield all the possible molecular orbital overlap; consequently, the relaxation energy will manifest itself in the site mismatch energy. The above considerations probably give a reasonable explanation for the observed fact that the local environment of an alkali cation almost remains intact by the addition of a second alkali and for the excess activation energy of ionic conduction in mixed-alkali glasses.

Thus, the physical origin of the mismatch energy should not be attributed simply to ion-size differences, and the alkali cations in glasses should not be treated simply as positively charged particles; rather, the molecular orbital overlap or the covalent interaction between alkali and oxygen atoms plays an important role in the cation-site mismatch in mixed-alkali glasses.

## 5. Conclusions

We have carried out ab initio molecular orbital calculations on clusters of atoms modeling the local structure of sodium, lithium, and mixed Li/Na disilicate glasses; the geometries of these clusters were completely optimized at the HF/6-31G(d) level. The optimized structural parameters are in good accord with the observed values, indicating that the present single- and mixed-alkali clusters are reasonable models of the corresponding silicate glasses. We have shown that each alkali cation is located in rather distinct local sites in both the single- and mixed-alkali clusters. We have further calculated the site-mismatch energies and have shown that a considerable site mismatch is possible to occur in mixed Li/Na silicate glasses; that is, as has been proposed by the dynamical structure model by Maass, Bunde, and Ingram,<sup>19</sup> an *Na* site has to relax to accept a  $\text{Li}^+$  ion, and vice versa. The calculated mismatch energies are comparable to or rather larger than the observed excess activation energies of mixed Li/Na silicate glasses. On the basis of a population analysis, we then suggest that in mixed-alkali glasses the structural relaxations of the cation sites will occur in every jump process to yield all the possible molecular orbital overlap between alkali cations and their surrounding oxygens. That is, the molecular orbital overlap or the covalent interaction in the cation sites will play an important role in the site mismatch in mixed-alkali glasses.

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