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Conformational Analysis of the Molecular Complexes of Sodium with Methanol and 1,2-Ethanediol: Photoionization and ab Initio Molecular Orbital Studies

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The molecular complexes of the sodium atoms with methanol and 1,2-ethanediol were generated in a flow reactor and studied with photoionization mass spectrometry. The photoionization efficiency spectra of these complexes were measured and the ionization threshold energies were determined by the method of the Watanabe plots. The conformation-dependent bond dissociation energies and ionization energies of these complexes were also calculated by ab initio molecular orbital methods. The photoionization threshold energies of the sodium/methanol complex was determined to be 4.30 ± 0.02 eV, a value in good agreement with the ab initio prediction. Guided by the theoretical results, the experimental photoionization threshold energy of the cyclic conformers of the sodium/1,2-ethanediol complex was determined to be 3.95 ± 0.02 eV and that of the conformers with the concerted intramolecular H-bond was determined to be 4.32 ± 0.01 eV. The bond dissociation energy of the sodium/methanol complex was determined to be 0.28 eV. The interplay of the sodium complexation bonding and the intramolecular hydrogen bonding and its effects on both the bonding energies and the ionization energies of the conformers were discussed. The conformation-dependent physical properties of the corresponding cationic states of these complexes were also reported. Comparisons of the physical and chemical properties among the sodium/1,2-ethanediol, sodium/1,2-dimethoxyethane, and potassium/1,2-ethanediol complexes were emphasized in this study.

1. Introduction

In the past few years, molecular complexes formed between the alkali metal atoms and multifunctional Lewis bases, such as K/ethylenediamine, K/1,2-ethanediol (eo), Na/1,2-dimethoxyethane (DME), and Na/12-crown-4, have been studied in this laboratory.[1−4] The conformation-dependent bond dissociation energies and photoionization threshold energies of these complexes were specifically emphasized in these works. It appears that the general physical properties of these multidentate complexes, whose geometric structures apparently lie between the simplest form of the complexes and the solvated-like higher cluster systems, could be understood and fitted into the general picture of this class of molecular system.[4−11]

Despite the above general relationship of the physical properties among the complexes, by a closer examination of each complex, one would find that the conformation forms, interaction strengths, ionization threshold energies, and other physical properties do vary as either the Lewis base molecule or the alkali metal atom being replaced by even similar elements or compounds. Among the simplest bifunctional Lewis bases, the complex formed from 1,2-ethanediol exhibits the most complicated conformation structures. Apparently, it is a good candidate for a detailed comparison study as the alkali-metal atom of the complexes varied. The rich conformational structure of this type of complexes owing to the interplay of the intramolecular hydrogen bonding of hydroxyl groups and the alkali metal atom bonding is also an interesting subject by itself.[1,2] As for the Lewis base molecules, the Na/DME complex offers a good example for comparison as one changes the Lewis base molecules from the alcohol to the corresponding ether compounds. In these two complexes, the sodium bonds are all in the Na−O form. Along these lines, in this report, the Na/methanol (MeOH) and Na/eo complexes were studied and compared with the K/MeOH, K/eo, and Na/DME systems reported in previous publications.[2,3] The variance and invariance of the physical and chemical properties among these closely related complexes were emphasized in this study.

Since both the neutral and cationic states of the complexes are involved in the present one-photon ionization process, the conformation-dependent geometrical structures and bond energies of Na^+/MeOH and Na^+/eo complexes calculated by the ab initio methods were also reported and compared with those of the corresponding potassium complexes.

2. Experimental Section

The details of the experimental setup, which mainly consists of a photoionization mass spectrometer coupled with a flow reactor, have been described in previous publications.[1−4,12] In the following, only the experimental conditions, which were relevant to the present experiment, are mentioned briefly. The sodium vapor was generated in an oven heated to 616 K. An argon flow, which constituted a partial pressure of about 570 mTorr in the flow reactor, carried the sodium vapor into the flow tube and reacted with diol vapor. Diol was heated to 378 K by an oil bath thermostat and its vapor pressure was regulated by a needle valve with a partial pressure of 30 mTorr in the flow tube. A third flow of argon served as the buffer gas and raised the total pressure in the flow tube to about 2.40 Torr. The final main flow tube was kept at 333 K by circulating water through the insulation compartment. The photoionization efficiency spectra were normalized with the photon number of the laser pulses.

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3. Ab Initio Molecular Orbital Calculations of Na(eo), Na(MeOH), Na$^+$(eo), and Na$^+$(MeOH)

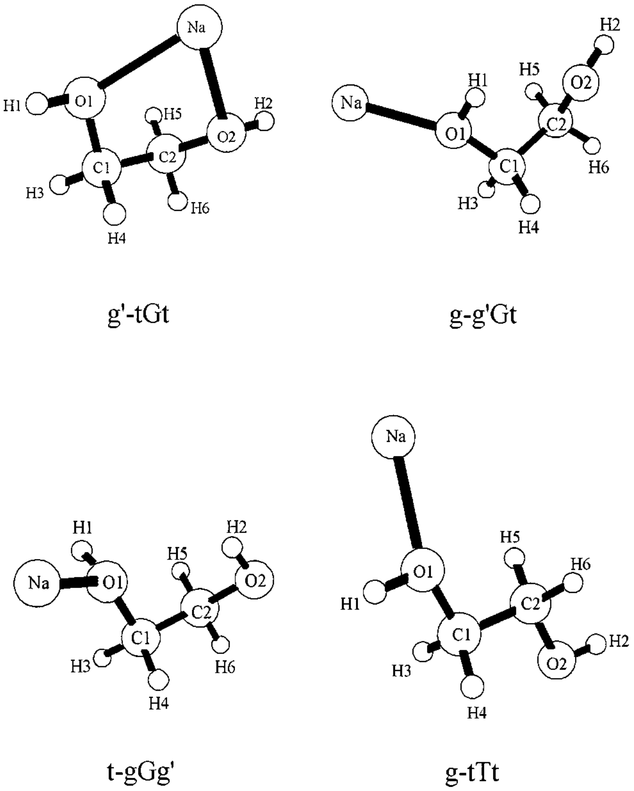
All the ab initio calculations were carried out with the Gaussian 94 program.[13] The geometries and the corresponding harmonic vibrational frequencies were obtained at the MP2(Fu)/6-31G** level. The ionization energies of the neutral complexes were calculated at both the MP2(Fu)/6-311+G(2d,p) and B3PW91/6-311+G(2d,p) levels. The bond dissociation energies of both the neutral and cationic complexes were obtained at MP2(Fu)/6-311+G(2d,p).

In this report, the notation for the conformation of the 1,2-ethanediol was in accord with the convention in the literature.[2,14] The notation for the position of the sodium atom was adapted directly from the potassium case reported previously.[2] Note that when the sodium atom is in eclipse with the neighboring C−H or C−C bond, symbols e°, e, and e′ are specifically employed to designate that the dihedral angles of NaOCC are within the ±10° range of 0°, +120°, and −120°, respectively. The final conformation notation for the sodium complex, for example, would look like g′-tGt, in which g′ indicates the Na position in the dihedral angle of NaOCC, the first t indicates the H position of the first hydroxyl group, which is bonded to the sodium atom in the dihedral angle of HOCC, the G is the dihedral angle of OCCO, and the last t indicates the H position of the second hydroxyl group in the dihedral angle of CCOH.

4. Results and Discussions

4.1. Structures and Bonding of Na(eo) and Na$^+$(eo). Theoretical Results. Since 1,2-ethanediol could be viewed as consisting of two-bonded methanol units, as references, Na(MeOH) and Na$^+$(MeOH) were also studied here. Being similar to the K(eo) complex,[2] the Na(eo) complex could be classified into four general conformational forms according to the conformation relationship between the intramolecular H-bond and the Na bond: (a) a cyclic form where the sodium atom is simultaneously bonding with the two hydroxyl groups and which is designated as the *cy* form; (b) a noncyclic form with the intramolecular H-bond where the oxygen atom of the hydroxyl group is bonding with the Na atom and which is designated as the *int* form; (c) a noncyclic form with the intramolecular H-bond where the electron lone-pair donating oxygen atom is bonding with the Na atom and which is designated as the *int′* form; (d) a straight chain form where only one simple Na-bond is formed and which is designated as the *st* form. Figure 1 shows the four typical Na(eo) conformers that represent each of the four conformational forms: the g′-tGt conformer is in the *cy* form in which an anti-intramolecular H-bond is formed; the g−g′Gt conformer is in the *int* form in which the intramolecular H-bond between H1 and O2 is in concert with the Na-bond through the O1−H1 hydroxyl group; the t-gGg′ conformer is in the *int′* form in which the intramolecular H-bond between H2 and O1 is in competition with the Na-bond for the O1 atom; and the g-tTt conformer is in the *st* form. Note that in the formation of the Na bond there are some degrees of charge polarization in the Na atom due to the electrostatic multipole moments of the hydroxyl groups and/or the charge transfer from the hydroxyl groups to the Na atom.[6−11] In this sense, the intramolecular H-bond and the Na-bond are in concert with each other in the *int* form and are in competition with each other for the lone pair electrons of the same oxygen atom in the *int′* form.

Three stable cyclic conformers, g′-tGt, g′-tGg, and g′-gGg, were located. Their Na atoms are all in the *g′* position. For the noncyclic forms with an intramolecular H-bond, only two conformers g-g′Gt and e-g′Gg were found in the *int* form and also only two conformers t-gGg′ and g-tGg′ were located in the *int′* form. In the case of the straight chain form, if one counted the possible arrangements for the electron lone pairs of the hydroxyl groups in forming the Na-bond, nine distinguishable conformers were obtained. Note that the optical isomer pairs were taken to be equivalent and were not included in this counting. In this report only two representative conformers g-g′Tt and g-tTt were considered for the straight chain form.



g'-tGt g-g'Gt

t-gGg' g-tTt

Figure 1. Schematic diagram of four representative conformers of Na(eo): g′-tGt, g-g′Gt, t-gGg′, and g-tTt.

In general, the primary geometries of the diol moiety in the complex form are very close to those in the free state. Under closer examination some minor geometrical changes could be found. For instance, the bond lengths of C−O whose oxygen is in complexation with the sodium atom usually increase by about 0.01 Å, as compared with the geometries of the corresponding free diol conformers; meanwhile, the bond lengths of the neighboring O−H usually increase by a slight 0.002 Å. Since the interaction strengths of the intramolecular H-bond and the Na-bond are similar, the major geometric changes during the complexation are expected to be the conformation of the hydroxyl groups, i.e., the O−H related dihedral angles. For instance, in the formation of the cyclic conformer g′-tGt, the dihedral angle OCCO decreases from 72° to 61° and that of HOCC decreases from −167° to −177° if compared with those of the free tGt diol. Similarly, for the case of the g′-gGg conformer, the OCCO dihedral angle increases from 47° to 54°, and the H1O1C1C2 dihedral angle increases from 43° to 80°. For the straight chain form, the two hydroxyl groups are both rather far away from each other such that only a simple Na-bond could be formed. In these situations, the conformations of the complex usually do not change much from those of their free states.

Compared with the geometries of the K(eo) complex as reported in a previous publication,[2] there are some similarities and also some variations between these two complexes. The

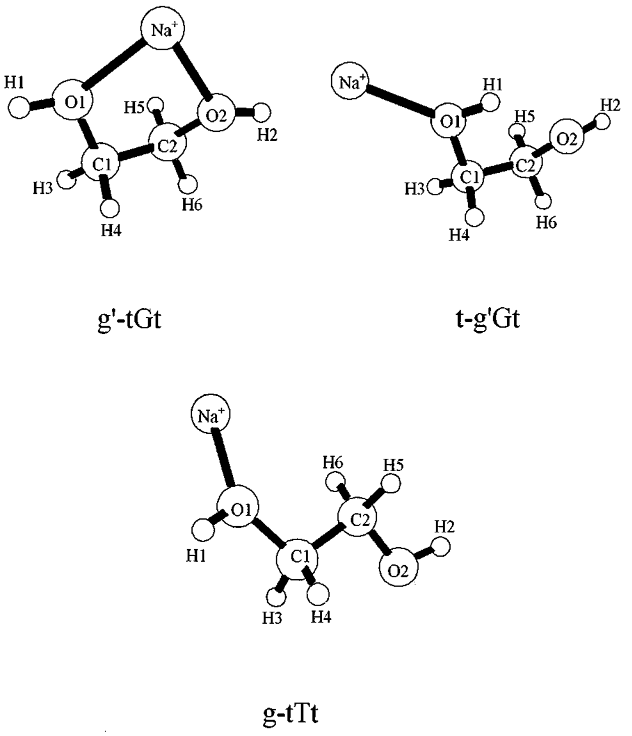


Figure 2. Schematic diagram of three representative conformers of $Na^+(eo)$: $Na^+(g')$-tGt, $Na^+(t)$-g′Gt, and $Na^+(g)$-tTt.

geometric structures of the *cy* and *int′* forms of both complexes are actually quite close to each other. The only appreciable difference is that the K−O bond length is longer than the Na−O bond length by about 0.3 Å. For the other two forms, the sodium and potassium atoms take a quite different conformation position. In the *int* form, the sodium atom is in either the g or e conformation, while the potassium atom only takes the t conformation; and in the *st* form, the sodium atom takes the g conformation, while the potassium atom is in either the e or e° conformation. Apparently, owing to the comparatively larger atomic size, the potassium atom takes the t conformation in the *int* form. The preference of the potassium atom in taking up the e conformation in the *st* form also suggests that the potassium atom has a tendency to form a bond simultaneously with the two electron lone pairs of the hydroxyl group.

In the case of the Na(DME) complex,[3] one would expect that its stable conformers be identical with those of the present Na(eo) system because the bonding capacities of the oxygen with the sodium atom are expected to be similar in both systems. Nevertheless, because the methyl moiety of the methoxy group is much bulkier than the hydrogen moiety of the hydroxyl group, it turns out that either some conformers, such as t-gGg′ and g-tGg′, are too congested to be locally stable or, under some circumstances, different types of conformers could be formed instead. For instance, in contrast to the stable g-tTt conformer of the diol system, the e°-tTt conformer of the dimethoxyethane system is formed, and the Na dihedral angle of the g′-tTg′ conformer of the dimethoxyethane system is −20°, a value quite close to that of the eclipse position. Despite the steric effect, the average Na−O bond length of the diol complex is 2.390 Å which is very close to the average Na−O bond length 2.407 Å of the dimethoxyethane complex.

For the cationic complex only one locally stable conformer was located for each of the *cy* and *int* forms, i.e., $Na^+(g')$-tGt, and $Na^+(t)$-g′Gt. Two representative *st* forms, $Na^+(e)$-g′Tt, and $Na^+(g)$-tTt, were specifically studied here. Their ball-and-stick representations are shown in Figure 2. Apparently, the strong ion−local dipole interaction between the sodium cation and the hydroxyl groups drastically reduces the number of stable conformers as compared with the neutral complex. The primary geometric structures of the diol moiety of the cation are also close to those of the free diol. Compared with the corresponding neutral conformers, the major structural changes of the cationic conformers are those dihedral angles related to the conformations of the hydroxyl groups and also the Na^+−O bond lengths, an expected consequence resulting from the much stronger ion−local dipole interaction.

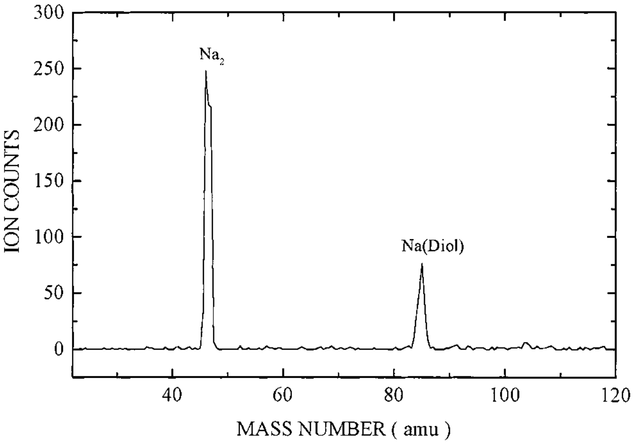


Figure 3. Photoionization mass spectrum of Na(eo) at 248 nm laser radiation.

The geometric parameters and harmonic vibrational frequencies of the neutral and cationic complexes of methanol and 1,2-ethanediol are tabulated in the Supporting Information.

4.2. Photoionization Mass Spectra and Photoionization Efficiency Spectra of Na(MeOH) and Na(eo). Experimental Results. Figure 3 shows the photoionization mass spectrum of the Na flow system in the presence of 30 mTorr of 1,2-ethanediol vapor under 248 nm laser radiation. With a pure sodium flow, the only detected mass signal was Na_2^+. The presence or absence of the $Na^+(eo)$ signal was directly corresponding to the on or off of either the diol vapor or the sodium vapor. This suggested that Na(eo) was formed in the flow tube through the recombination reaction between the Na and diol vapors.

Figure 4a shows the photoionization efficiency spectrum of Na(MeOH). Its corresponding Watanabe plot is shown in Figure 4b. There is only one steplike feature near the threshold ionization region of the spectrum. From the crossing point of two least-squares fitted straight lines the photoionization threshold energy was determined to be 4.30 ± 0.02 eV.

The photoionization efficiency spectrum of Na(eo) and its corresponding Watanabe plot are shown in Figures 5 and 6. The regions corresponding to the first and second ionization thresholds were enlarged and shown in Figure 6a,b. The two ionization threshold energies were determined to be 3.95 ± 0.02 and 4.32 ± 0.01 eV, respectively.

Comparison with the Theoretical Results. Table 1 shows the theoretical vertical and adiabatic ionization energies of the complexes calculated by the HF, MP2, and B3PW91 methods, respectively. Generally speaking, for the diol complex, the HF ionization energies are lower than the corresponding MP2 energies by about 0.15 eV and the MP2 energies are in turn less than the corresponding B3PW91 values by about 0.23 eV. Since it has been demonstrated that the ionization energies calculated by the B3PW91 method are in better agreement with the experimental measurements,[3,4] the B3PW91 ionization

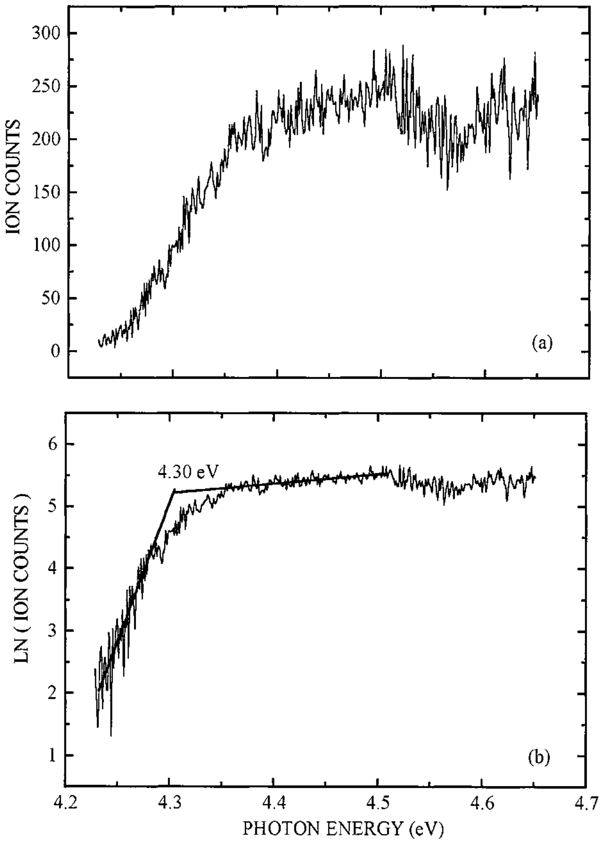


Figure 4. Photoionization efficiency spectrum of Na(MeOH) (a) and the corresponding Watanabe plot (b).

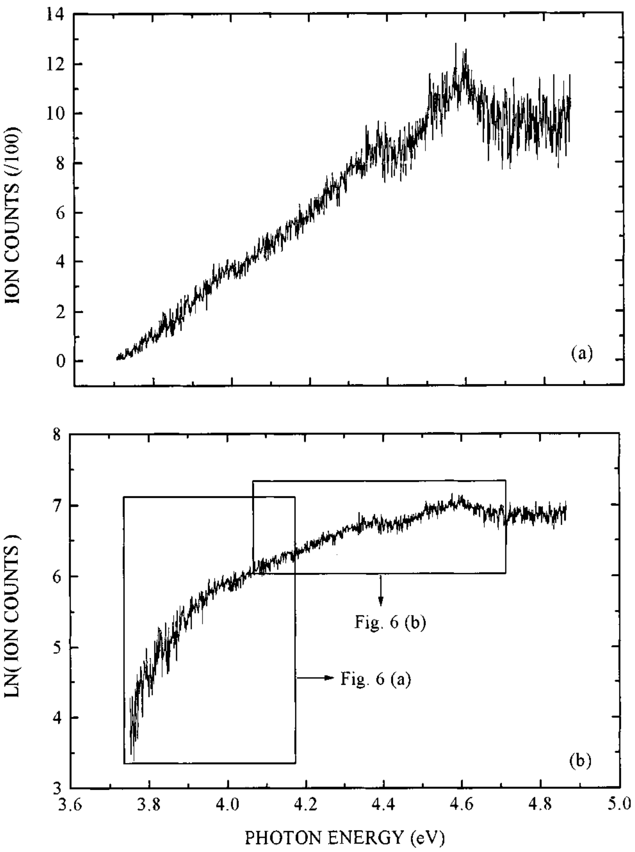


Figure 5. Photoionization efficiency spectrum of Na(eo) (a) and the corresponding Watanabe plot (b).

energies shall be adapted exclusively for the following discussion on the ionization energies. The HF and MP2 ionization energies are served as references.

In the case of Na(MeOH), its theoretical vertical ionization energy of 4.42 eV and adiabatic ionization energy of 4.39 eV are actually quite close to each other. The experimental threshold ionization energy 4.30 ± 0.02 eV is in good agreement with the theoretical prediction. For the diol complex, as shown in Table 1, the theoretical conformation-dependent vertical ionization energies are clustering around four different values. They are in perfect match with the four conformation groups: the *cy* form has an average ionization energy of 4.00 eV; the *int* form is 4.32 eV; the *int′* form is 4.60 eV; and the *st* form is 4.46 eV. It is expected that the *cy* form would have the lowest threshold ionization energy because of the extra stability of the bidentate form in the corresponding cationic state and the *int* form would have the next higher ionization energy because of the additional cooperative interaction between the intramolecular H-bonding and the $Na^+{-}O$ bonding. The follow-ups are the *st* and *int′* forms. It is somewhat unexpected that the *int′* form has the highest vertical ionization energy. Apparently, this higher ionization energy is mainly due to the competitive relation between the intramolecular H-bonding and the $Na^+{-}O$ bonding in the corresponding cationic state. As mentioned previously, the lowest two experimental threshold ionization energies were determined to be 3.95 and 4.32 eV, respectively. Clearly, they are in good agreement with the above theoretical vertical ionization energies of the *cy* and *int* forms, respectively. Additionally, as is going to be discussed in the following subsection, these two forms are also expected to be the major components in the present thermal equilibrium system. The ionization threshold behavior as observed in the lower photon energy range of the photoionization efficiency spectrum was then attributed to the contribution of these two types of conformational forms.

As shown in Figure 6b, in the higher photon energy end, there appears to be one more ionization step at 4.51 eV. This energy is falling right between the average theoretical vertical ionization energies (4.46 and 4.60 eV) of the *st* and *int′* forms, respectively. To further clarify the origin of the spectral feature of this energy region, one could estimate the population ratio of these two conformation forms as follows. Energetically, according to the theoretical adiabatic bond dissociation energies that are going to be discussed in the following section, the *int′* form is more stable than the *st* form by about 0.07 eV. However, entropically, the population ratio of the *st* form to the *int′* form is 9:2 if one counts the conformation number of each species. In short, thermodynamical consideration suggests that neither of these two conformation populations is negligible under the present experimental conditions. The above observations suggest that the general spectral feature around 4.51 eV could be attributed to the contribution of both *st* and *int′* conformers.

Comparison with the Ionization Energies of the Na(DME) and K(eo) Complexes. The threshold ionization energy of the cyclic conformers of Na(DME) has been measured to be 3.80 eV.[3] This is lower than the corresponding threshold ionization energy 3.95 eV of Na(eo) by 0.15 eV. Although the difference is not that significant, it still could be attributed to several contributing factors. Considering only the g′-tGt conformer of both complexes, and with the help of the theoretical bond dissociation energies listed in Table 2, one finds that (a) the bond dissociation energy of Na^+(DME) is larger than that of Na^+(eo) by 0.02 eV, (b) the bond dissociation energy of Na(DME) is lower than that of Na(eo) by 0.03 eV, and (c) the energy difference between the vertical ionization energy and the adiabatic ionization energy of Na(DME) is smaller than that

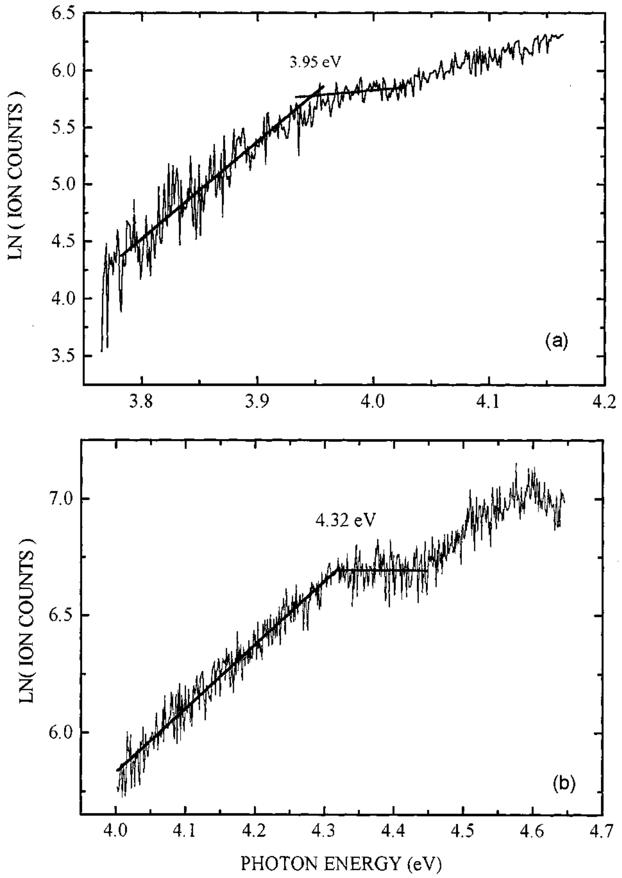


Figure 6. Enlarged Watanabe plot of Figure 5b.

of Na(eo) by 0.02 eV. Taking all these three factors into account, one would find that the ionization energy of the Na(eo) is expected to be higher than that of Na(DME) by 0.07 eV. The additional difference of 0.08 eV between the theoretical estimation and the experimental value could be attributed to the experimental uncertainties and the accuracy of the theoretical calculations. The details of the bond dissociation energies of Na(eo) shall be discussed in the following subsection.

For the sodium and potassium complexes with methanol and 1,2-ethanediol, because the ionization energy of the sodium atom 5.139 eV is much higher than that of the potassium atom 4.339 eV,[15] the ionization energies of the potassium complexes are all lower than those of the corresponding sodium complexes. For these two systems, a more interesting quantity for comparison is the lowering of the threshold ionization energies of the complex with respect to that of the alkali metal atom. The lowering values of the threshold ionization energies for the K(MeOH), *cy* K(eo), and *int* K(eo) complexes are 0.56, 0.94, and 0.74 eV, respectively. The corresponding values for the Na complexes are 0.84, 1.19, and 0.82 eV, respectively. The extra lowering of the Na(MeOH) ionization energy as compared with that of K(MeOH) is mainly due to the comparatively higher Na^+(MeOH) bond energy. On the other hand, the extra lowering of the *cy* Na(eo) and *int* Na(eo) ionization energies as indicated above is not as large as one would expect from the simple point of cationic bonding energies. A closer examination suggests that, for the present diol system, both the comparatively lower bonding energies in the neutral sodium complexes and the relatively larger differences between the vertical and adiabatic ionization energies of the sodium complexes offset the contribution of the extra bonding stability of the corresponding sodium cation complexes.

4.3. Bond Dissociation Energies of Na(eo), Na(MeOH), Na^+(eo), and Na^+(MeOH). Theoretical Results. Table 2 shows the sudden and the adiabatic equilibrium bond dissociation energies of the neutral and the cationic complexes considered in this paper. The methanol complexes are served as references for the diol systems. For the neutral systems, several general trends in the bond dissociation energies among the conformers could be identified: (a) the sudden dissociation energies of the three cyclic conformers are about twice the value of the Na(MeOH) sudden dissociation energy; (b) those with the concerted intramolecular H-bonding are slightly larger than that of the Na(MeOH) value; (c) those with the competitive intramolecular H-bonding are slightly less than that of the Na(MeOH) value; (d) those in the straight chain form are more or less close to the Na(MeOH) value. They indicate that the bonding strength between the sodium atom and the hydroxyl groups of the diol is close to being additive; i.e., the variation of bonding strength is mainly determined by the number of the bonded hydroxyl groups. Nevertheless, for a more accurate account of the general trend of the interaction strengths, the minor perturbation by the intramolecular H-bonding should also be considered. Similar behavior was also observed in the corresponding potassium systems, as reported in a previous publication.[2]

According to the magnitudes of the adiabatic equilibrium dissociation energies with respect to the most stable diol conformer tGg′, the conformers of Na(eo) could be roughly classified into three groups: the *cy* and the *int* forms as the first group, the *int′* form as the second group, and the *st* form as the third group. The similarity of the adiabatic dissociation energies between the *cy* and *int* forms is due to the fact that the single Na-bonding strength is close to the energy difference between the H-bonding and H-antibonding forms of the diol molecule.[16] The conformers of the *int′* and *st* forms are all less stable than those of the first groups. It is expected that at room temperatures the gaseous Na(eo) complex would be mainly composed of the *cy* and *int* forms. As shown in Table 2, the adiabatic dissociation energy with respect to its parent conformation for all the four categories of conformers are close to their sudden dissociation energies. This is in line with the observation that the complexation of the sodium atom does not perturb the conformation of the parent 1,2-ethanediol molecule too much. Nevertheless, for these complexes, the geometrical changes, no matter how minor they may be, always have some effect on this energy difference. For example, the differences are greater for the cyclic conformers as compared to the other conformers. This is manifested in the obvious change of the dihedral angle O1C1C2O2 in the cyclic form category.

For the stable conformations of the Na^+/1,2-ethanediol complex, the conformation-dependent bond dissociation energies follow more or less the general trend of the neutral conformers. Nevertheless, because of the stronger ion−dipole interaction between the sodium cation and the hydroxyl groups, as anticipated, the Na−O1 bond lengths are shorter than those of the neutral ones and the corresponding bond dissociation energies are much larger than those of the neutral counterparts.

Comparison with the Experimental Results and the Bond Energies of K(MeOH), K(eo), and Na(DME). For the sodium complexes considered here, up to date, there was only one experimental measurement on the bond dissociation enthalpy of Na^+(MeOH) that was determined to be 1.15 eV at 660 K.[17] With the help of the ab initio harmonic vibrational frequencies, the bond dissociation energy was corrected to be 1.12 eV. Compared with the corresponding theoretical bond dissociation

TABLE 1: Theoretical Ionization Energies (eV)[a]

		vertical			adiabatic						
	form[b]	HF	MP2	B3PW91	HF[c]	MP2[c]	B3PW91[c]	HF[d]	MP2[d]	B3PW91[d]	exptl
Na → Na$^+$					4.96	5.03	5.27				5.139[e]
Na(MeOH) → Na$^+$(MeOH)		4.03	4.18	4.42	4.01	4.14	4.39				4.30
g′-tGt → Na$^+$(eo)[f]	*cy*	3.54	3.71	3.95	3.40	3.58	3.82	3.40	3.58	3.82	3.95
g′-tGg → Na$^+$(eo)	*cy*	3.63	3.80	4.05	3.35	3.54	3.80	*g*	*g*	*g*	
g′-gGg → Na$^+$(eo)	*cy*	3.57	3.75	4.00	3.28	3.47	3.75	*g*	*g*	*g*	
g-g′Gt → Na$^+$(eo)	*int*	3.96	4.11	4.33	3.37	3.53	3.80	3.89	4.01	4.24	4.32
e-g′Gg → Na$^+$(eo)	*int*	3.95	4.09	4.31	3.33	3.50	3.78	*g*	*g*	*g*	
t-gGg′ → Na$^+$(eo)	*int′*	4.17	4.33	4.56	3.28	3.45	3.75	*g*	*g*	*g*	
g-tGg′ → Na$^+$(eo)	*int′*	4.25	4.40	4.63	3.27	3.45	3.73	*g*	*g*	*g*	
g-g′Tt → Na$^+$(eo)	*st*	4.05	4.20	4.43	3.27	3.38	3.67	3.99	4.14	4.37	
g-tTt → Na$^+$(eo)	*st*	4.11	4.26	4.49	3.24	3.36	3.64	4.02	4.16	4.39	

[a] Calculated at the MP2(Fu)/6-311+G(2d,p)//MP2(Fu)/6-31G** and B3PW91/6-311+G(2d,p)//MP2(Fu)/6-31G** levels. [b] Complex conformations: *cy*, cyclic form; *int*, noncyclic form with the intramolecular H-bond in which the oxygen atom of the hydroxyl group is bonding with the Na atom; *int′*, noncyclic form with the intramolecular H-bond in which the electron lone-pair donating oxygen atom is bonding with the Na atom; *st*, straight chain form. [c] Adiabatic ionization energy with respect to the most stable conformer Na$^+$(tGt). [d] Adiabatic ionization energy with respect to its own conformer state. [e] Reference 15. [f] eo: 1,2-Ethanediol. [g] Blank entries indicate that their neutral parent conformations are not stable in ionic form.

TABLE 2: Theoretical Equilibrium Dissociation Energies (eV) of Na(MeOH), Na$^+$(MeOH), Na(eo), and Na$^+$(eo)[a]

		sudden		adiabatic					
	form[b]	HF	MP2	HF[c]	MP2[c]	ZPEC[d]	HF[e]	MP2[e]	ZPEC[f]
neutral complexes									
Na(MeOH) → Na + MeOH		0.199	0.256	0.193	0.254	−0.021			
g′-tGt → Na + eo[g]	*cy*	0.397	0.488	0.228	0.310	−0.019	0.350	0.455	−0.043
g′-tGg → Na + eo	*cy*	0.370	0.475	0.179	0.274	−0.021	0.326	0.445	−0.039
g′-gGg → Na + eo	*cy*	0.311	0.421	0.112	0.204	−0.014	0.242	0.355	−0.042
g-g′Gt → Na + eo	*int*	0.222	0.279	0.199	0.269	−0.024	0.199	0.269	−0.024
e-g′Gg → Na + eo	*int*	0.212	0.270	0.154	0.231	−0.027	0.192	0.260	−0.020
t-gGg′ → Na + eo	*int′*	0.140	0.216	0.108	0.183	−0.018	0.146	0.212	−0.011
g-tGg′ → Na + eo	*int′*	0.101	0.188	0.095	0.180	−0.014	0.095	0.180	−0.014
g-g′Tt → Na + eo	*st*	0.185	0.249	0.094	0.113	−0.003	0.180	0.246	−0.016
g-tTt → Na + eo	*st*	0.141	0.220	0.065	0.094	0.000	0.132	0.214	−0.017
cationic complexes									
Na$^+$(MeOH) → Na$^+$ + MeOH		1.163	1.155	1.132	1.141	−0.044			
Na$^+$(g′)-tGt → Na$^+$ + eo	*cy*	2.006	1.995	1.772	1.766	−0.046	1.893	1.911	−0.070
Na$^+$(t)-g′Gt → Na$^+$ + eo	*int*	1.384	1.370	1.248	1.294	−0.043	1.248	1.294	−0.043
Na$^+$(e)-g′Tt → Na$^+$ + eo	*st*	1.173	1.165	1.045	1.005	−0.019	1.131	1.138	−0.033
Na$^+$(g)-tTt → Na$^+$ + eo	*st*	1.109	1.125	0.988	0.962	−0.012	1.074	1.095	−0.029

[a] Calculated at the MP2(Fu)/6-311+G(2d,p)//MP2(Fu)/6-31G** level. [b] Complex conformations: *cy*, cyclic form; *int*, noncyclic form with the intramolecular H-bond in which the oxygen atom of the hydroxyl group is bonding with the Na atom; *int′*, noncyclic form with the intramolecular H-bond in which the electron lone-pair donating oxygen atom is bonding with the Na atom; *st*, straight chain form. [c] Adiabatic equilibrium dissociation energy with respect to the most stable conformer of 1,2-ethanediol, tGg′. [d] Zero point energy correction with respect to the most stable conformer of 1,2-ethanediol, tGg′. [e] Adiabatic equilibrium dissociation energy with respect to its own conformer state. [f] Zero point energy correction with respect to its own conformer state. [g] eo: 1,2-Ethanediol.

energy 1.10 eV calculated at the MP2 level, the agreement is very good. Now the experimental ionization energy of Na is 5.139 eV,[15] and the photoionization threshold energy of Na(MeOH) is determined to be 4.30 ± 0.02 eV. Since the difference of the theoretical vertical and adiabatic ionization energies of Na(MeOH) is only 0.03 eV, the experimental adiabatic ionization energy could be well approximated by the present experimental threshold ionization energy. Through the cyclic relation among these energies, the bond dissociation energy of Na(MeOH) was determined to be 0.28 eV. This value could be further corrected to 0.25 eV if the above theoretical energy difference between the vertical and adiabatic ionization energies was taken into account. Compared with the theoretical bond dissociation energy of 0.23 eV as listed in Table 2, the agreement is good. Note that for Na(eo) there were no related experimental measurements reported in the literature.

Comparing the present bond dissociation energies of the neutral sodium complexes with those of the potassium counterparts reported previously,[2] at the HF level, their bond dissociation energies are actually quite close to each other. For instance, at the HF level the equilibrium bond dissociation energy of Na(MeOH) is 0.193 eV, while that of K(MeOH) is 0.172 eV. Both complex systems gain further energy stabilization through the electron correlation as suggested in the MP2 energies. At this calculation level, there are noticeable differences between these two systems; i.e., the correlation energies of the potassium complexes are more stable than those of the corresponding sodium complexes by an average of 0.11 eV, a nonnegligible magnitude if compared with the theoretical equilibrium bond dissociation energies of Na(MeOH) and K(MeOH) calculated at the MP2 level, 0.254 and 0.346 eV, respectively.

For the nature of this type of bonding, it has been generally accepted that electrostatic, charge transfer, and dispersive forces may all have some extent of contribution to its stabilization energy.[5−11,18−20] With the Na(MeOH) and K(MeOH) complexes, the electrostatic interaction energies could be estimated by the dipole−induced dipole interactions. Although the electric polarizability of the potassium atom 43.4 Å^3 is much larger than that of the sodium atom 23.6 Å^3, this factor is more or less compensated by the comparatively longer K−O bond length of the potassium complex such that the electrostatic interaction energies of the two complexes are actually similar to each other. In other words, at either the HF or MP2 calculation level, the electrostatic interaction energies are expected to be similar between the two complexes. As for the contribution of the charge transfer interaction, the Mulliken population analysis indicates that the potassium complex always has a much lower extent of charge transfer than that of the sodium complex. A similar trend was also observed in the natural orbital population, and even in those favorable cases of the sodium complexes, the charge transfer magnitude is only around 0.001 electric charge for each hydroxyl group. In other words, at least, in the case of the potassium complex, the charge-transfer interaction is not important.[21] Since the theoretical electric dipole moment of the methanol calculated at the HF level is always larger than that obtained at the MP2 level under the present basis sets, it is expected that the contribution of dipole−induced dipole interaction calculated at the MP2 level would be less or, in the worst situation, close to that calculated at the HF level. Since the dispersion energy could only be accounted for by going beyond the SCF calculations,[22] it is apparent that the extra stabilization energy of the potassium complex calculated at the MP2 level, as compared with that of the sodium counterpart, is mainly due to the contribution of the dispersion interaction in the potassium complex. Taking the above facts into consideration, for the K(MeOH) complex, one could conclude that the electron correlation energy contributes about half of the complex total stabilization energy, and this energy is mainly due to the dispersion interaction. This observation is in line with an earlier study on the Mg(H_2O) and Ca(H_2O) complexes, which concluded the fact that their bond stability is mainly due to the dispersion energy.[18]

As for the comparison of the bonding energies with the Na(DME) complex, because the relative conformation energies are different between the eo and DME molecules, it makes more sense to compare their sudden bond dissociation energies and/or the adiabatic equilibrium bond dissociation energies in the same conformation state. Since for each one of the Na(DME) conformers, there is always a corresponding or closely related Na(eo) conformer,[3] one could always make comparisons within each conformation pair of these two complexes. It turns out that their sudden dissociation energies are all close to each other to within 0.013 eV and that the adiabatic equilibrium bond dissociation energies within the same conformation state are close to each other to within 0.026 eV, except for the g′-gGg conformer of the Na(DME) complex, in which the steric effect of the methoxy groups strongly distorts the geometry of the complex. In other words, the sodium bonding strengths of these two systems are virtually the same. For these two systems, two major interaction factors (electrostatic and charge-transfer interactions) are expected to be important. The eo and DME molecules could be considered as two coupled units of methanol and dimethyl ether, respectively. The electric dipole moments of methanol and dimethyl ether have been determined to be 1.69 and 1.30 D, respectively.[23,24] Since the Na−O distances of both complexes are quite close to each other, it is expected that the dipole−induced dipole interactions of the Na(eo) system are stronger than that of the Na(DME) system. On the other hand, it is also known that the methyl moiety in the methoxy group of DME has a better electron-releasing capability than that of the hydrogen moiety in the hydroxyl group of eo.[25] It is expected that the charge-transfer interaction would be stronger in the Na(DME) complex. The above observations suggest that the near identical sodium bonding strengths in these two systems are the net result of these two interaction forces acting in a different trend but with a similar change of interaction strength as one varies from the eo to DME molecule.

5. Conclusions

The following conclusions can be drawn from the results of the present photoionization and molecular orbital calculation studies of Na (eo) and Na(MeOH) and their corresponding cationic states.

(a) The conformation-dependent ionization potentials, dissociation energies, and other properties of the Na(eo) and Na(MeOH) complexes were studied by the ab initio molecular orbital calculation methods. The corresponding cationic states were also studied. From the photoionization efficiency spectra and with the guidance of the theoretical results, the photoionization threshold energies of the two most stable conformation forms of Na (eo) were assigned.

(b) For the Na(eo) and K(eo) complexes, the geometric structures of the *cy* and *int′* conformers are quite close to each other. For the other two conformation forms, owing to the comparatively larger size of the potassium atom and the preference of the potassium atom to form a bond simultaneously with the two electron lone pairs of the hydroxyl group, some variations of the stable conformation forms are found. Because the bond energy of Na^+(eo) is much larger than that of the K^+(eo), the lowering of the ionization energies of Na(eo) with respect to the Na atom is always larger than those of the K(eo) complex. The detailed energetic relations regarding the lowering of the ionization energies were discussed. It is also found that, mainly due to the dispersive force, the bond dissociation energies of K(eo) are consistently larger than those of Na(eo).

(c) For the Na(eo) and Na(DME) complexes, there is a general one-to-one conformation correspondence between these two systems. Nevertheless, because the methyl moiety of the methoxy group is much bulkier than the hydrogen moiety of the hydroxyl group, some Na(DME) conformers are either too congested to be locally stable or a different type of conformer is formed instead. The ionization energies and bond dissociation energies of these two complexes are all quite close to each other. Further detailed comparisons also reveal some finer differences between these two systems, and their physical origins were also discussed.

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Supporting Information Available: Supporting Information Available: Six tables that include the structure parameters and harmonic vibrational frequencies of the neutral and cationic sodium complexes discussed in this report. This material is available free of charge via the Internet at http://pubs.acs.org.

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