

Molecular Complexes between Sodium and Carbonyl Compounds: Photoionization and ab Initio Molecular Orbital Studies

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The molecular complexes formed between sodium and three carbonyl compounds, formaldehyde (fd), acetaldehyde (ad), and acetone (ac), were studied by the ab initio molecular orbital method and photoionization mass spectrometry. In the case of the monosodium complexes, by a search over the global electronic ground state at the MP2/6-31+G(d,p) level, three locally stable minima were located for each of the three complex systems. One of them has the character of a van der Waals interaction and is designated as the complexation-pair state (cp state). The other two are in ion-pair form and are denoted as the ip1 and ip2 states. The nature of the sodium cp bonding with a carbonyl group was compared to the traditional alkali metal atom bonding with a simple Lewis base molecule. At the CCSD(T)/6-311+G(2d,p) level, except for the formaldehyde complex, whose most stable ip state has a small bonding energy, the energies of the other ion-pair states are all found to be slightly higher than the dissociation limit of the neutral dissociation channel. The energies of these three locally stable isomers are actually quite close to each other, with the largest energy separation being only 0.617 eV in Na(ac). For the disodium complexes, only the cp states were considered. The photoionization threshold energies of Na(ad) (cp), Na(ac) (cp), and Na₂(ac) were determined to be 4.23 ± 0.04 , 4.12 ± 0.05 , and 4.34 ± 0.04 eV, respectively. The photoionization threshold energy of Na₂(ad) was estimated to be 4.5 eV. These experimental values are in good agreement with those calculated at the B3PW91/6-311+G(2d,p) level. From the photoionization efficiency spectra of Na(ac) and Na₂(ac), it is suggested that the autoionization process originating from the $\pi^* \leftarrow n$ electronic transition of acetone could contribute to the ionization signal around and beyond the threshold region. The related cationic complexes were also studied theoretically. A unified view of the chemical and physical properties of these three systems is emphasized and discussed.

1. Introduction

In solution, the formation of ion pairs and aromatic ketyl radical anions through the reactions between alkali metal atoms and aromatic carbonyl compounds has been studied intensively by electron paramagnetic resonance (EPR) and UV spectroscopy for quite some time.¹ In the case of aliphatic carbonyl compounds, because their direct interaction with the alkali metal atoms has a stronger tendency to form enolate ions, it was much later that their ion pairs and alkyl ketyl radical anions were generated and studied by the photon photolysis/EPR detection technique.² More recently, it has been demonstrated that the ion-pair states are important in controlling the reactivity in the dimerization reaction of a certain class of carbaldehydes.^{3,4}

Following this line, one would like to know more about the physical and chemical properties of these complexes in their isolated forms. Theoretically, the best-studied system is the Li-(formaldehyde) (Li(fd)) complex;^{5–7} there was only one theoretical report on the Na(formaldehyde) (Na(fd)) and Na(acetone) (Na(ac)) complexes.⁸ Nevertheless, for this class of complexes there is a general picture emerging from these theoretical studies. There exist two types of electronic states that have similar energies but different carbonyl geometries competing for the most stable ground electronic state. One of them is ionic in nature and is called the ion-pair state (ip state). The other has the character of a van der Waals interaction and is called the

complexation-pair state (cp state). For the lithium complex, three local minima with similar energies were obtained. Two of them are in the ip state, and one is in the cp state; the former states are more stable than the latter one.^{5–7} For the sodium/carbonyl complexes, two ground ip states were located in Na(fd), and one ground ip state was found in Na(ac).⁸ The possible cp electronic ground state was not addressed in this Na study. Experimentally, the solvation of the lithium and sodium atoms in the acetone clusters was recently studied by the pick-up molecular beam technique.⁹ The ionization thresholds were measured; that observed for Li(ac) was assigned to the ip state, and that for Na(ac) to the cp state.

In this report, three main issues concerning the sodium/carbonyl systems were addressed. First, it has been well established that the natures of the bonding between the alkali metal atoms and the simple Lewis base molecules containing the hydroxyl, amino, and/or ethereal groups all belong to the same category.^{10–19} For the sodium/carbonyl systems, one would like to know whether the presence of the π and π^* orbitals of the carbonyl group modifies the bonding nature of the cp state. Second, the global electronic ground state consists of two general potential regions. One is dominated by ion-pair interaction, and the other by van der Waals type interaction. A better picture of the energetic relation between their local minima is clearly needed. This relation could help us understand the

possible region of the potential surface probed by the experiments. Third, the photon energy of the $\pi^* \leftarrow n$ electronic transition of the carbonyl compounds is high enough to ionize the sodium/carbonyl complexes around and above the ionization threshold region.^{20–22} Whether this associated autoionization channel contributes to the ionization efficiencies of the sodium complexes is not that obvious. In this paper, both the mono- and disodium complexes were considered. Because the photoionization process involves the neutral and corresponding cationic states, the related cations were also considered. A unified view of the chemical and physical properties of these three systems is emphasized and discussed.

2. Experimental Section

The molecular complexes were generated by a flow reactor system and detected with a photoionization mass spectrometer. The general experiment setup has been described in previous publications.^{14,15,17,19} Here, only an outline of the experimental procedure which is relevant to the present carbonyl systems is given.

The vapors of sodium and carbonyl compounds, which were generated in individual sample cells, were injected into a flow reactor. The molecular complexes formed in the flow reactor were then sampled by a 1 mm orifice and a skimmer in differentially pumped chambers. A molecular beam, which was essentially a thermal beam, was produced and traveled into the ionization chamber. An excimer pumped dye laser, along with a second harmonic generator, was used as the ionization light source. The ions were then selected by a quadrupole mass filter and detected by a Channeltron electron multiplier. Finally, the signals were collected and processed by a fast multichannel scaler and a microcomputer. The laser energy was monitored continuously by a pyroelectric joulemeter. All the photoionization efficiency spectra shown in this report were normalized to the laser photon number.

For the Na/ad and Na/ac systems, the experimental conditions are as follows. The sodium vapor, which was generated by a heated sodium cell, was carried by an argon flow of about 0.65 Torr pressure and injected into the main flow reactor. The main flow reactor was kept at 316 K by a thermostat. Acetaldehyde or acetone (purity >99%) was degassed, and its vapor was directly introduced into the flow reactor through a liquid sample cell. Their pressures were maintained at approximately 120 mTorr. By the introduction of additional argon flow as a buffer gas, the total pressure of the flow reactor was kept at around 2.4 Torr.

For the Na/fd system, the formaldehyde vapor was obtained by heating solid paraformaldehyde polymer in a 373 K silicone oil bath. The signals of the complexes were searched by varying the experimental conditions, such as the formaldehyde vapor pressure, the pressure of the carrier gas, the pressure of the buffer gas, the flow reactor temperature, and the photon energy. Nevertheless, neither a Na(fd) nor a Na₂(fd) signal was observed in the present experimental setup.

3. Ab Initio Molecular Orbital Calculations

All ab initio molecular orbital calculations were carried out by using the Gaussian 94 package.²³ The geometries of the molecular complexes were optimized at the MP2(full)/6-31+G(d,p) level. The geometric parameters and harmonic vibrational frequencies were tabulated in the Supporting Information. The follow-up single-point energies were calculated at the MP2(full)/6-311+G(2d,p), CCSD(T,full)/6-311+G(2d,p), and B3PW91/6-311+G(2d,p) levels.

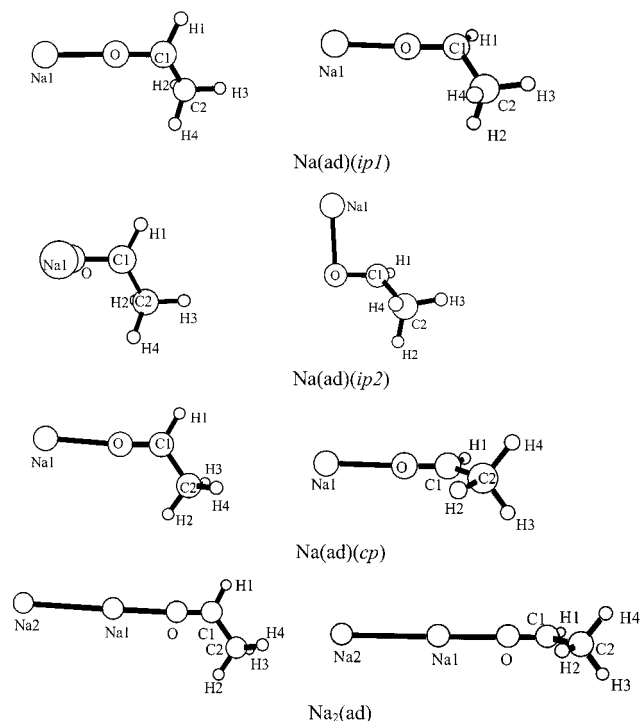


Figure 1. Ball-and-stick representations of the Na(ad) and Na₂(ad) complexes. Both the top and side views are shown side by side. The Na/fd and Na/ac systems have similar structures.

4. Results and Discussion

4.1. Structures and Bonding. Mono- and disodium complexes of formaldehyde, acetaldehyde, and acetone, as well as their corresponding cationic complexes, were considered.

(a) *Neutral Monosodium Complexes.* Three local minima were located at the MP2(full)/6-31+G(d,p) level over the global electronic ground state for each of the three Na(fd), Na(ad), or Na(ac) complexes. Two of them are ion pair in nature and the third one is basically a weak van der Waals type bonding without any appreciable charge redistribution. They were denoted as ip1, ip2 (ion pair), and cp (complexation pair), in the ordering of increasing energy stability according to the MP2 and CCSD(T) calculations. The first three molecular drawings in Figure 1 show ball-and-stick representations of the three local minima of Na(ad). The general geometric structures and charge distributions of Na(fd) and Na(ac) are similar to those of Na(ad). The Mulliken charge population analysis calculated at the MP2 level suggests that for the ip1 and ip2 states, the Na atom possesses appreciable net positive charge; meanwhile, there is a large negative charge enhancement in the adjacent oxygen and carbon atoms as compared with the parent molecule. For instance, in the case of Na(fd), the Mulliken charges on the Na, O, and C atoms are 0.84, -0.77, and -0.21 *e*, respectively, for the ip1 state and -0.09, -0.29, and 0.11 *e*, respectively, for the cp state. Note that for the free fd molecule, the O and C charges are -0.33 and 0.11 *e*, respectively. Apparently, the charge distributions of these two states are completely opposite to each other in that the positive end of the ip1 state is at the Na atom and that of the cp state is at the C atom. The dipole moments of the ip1 and cp states are 8.85 and 6.39 D, respectively. Although their magnitudes are close to each other, as the Mulliken charge distribution suggests, their main polarization directions are opposite to each other. For the present three complex systems, the overall electron density distributions of the sodium atom and the carbonyl moieties in the ip1 and ip2

states are similar to each other. However, for the cp state there is only a small negative charge enhancement in the sodium atom. The geometric parameters of Na(fd), Na(ad), and Na(ac), along with those of their parent molecules, are tabulated in the Supporting Information.

The theoretical geometry parameters of these three carbonyl parent compounds are in good agreement with the experimental values.^{24–26} For fd, the theoretical r_{CO} , r_{CH} , and $\angle\text{HCH}$ values are 1.223 Å, 1.098 Å, and 116.6°, respectively; the corresponding experimental values are 1.2078 ± 0.003 Å, 1.1161 ± 0.007 Å, and 116.5 ± 0.7°, respectively.²⁴ In the case of ad, for its methyl group the theoretical r_{CH} and r_{CC} are 1.090 and 1.499 Å, respectively; the corresponding experimental values are 1.086 and 1.501 Å, respectively. For the -CHO group, the theoretical r_{CO} , r_{CH} , $\angle\text{CCH}$, and $\angle\text{CCO}$ values are 1.226 Å, 1.103 Å, 115.8°, and 124.4°, respectively; the corresponding experimental values are 1.216 Å, 1.114 Å, 117.5°, and 123.9°, respectively.²⁵ Finally, for the ac molecule the theoretical r_{CO} , r_{CC} , r_{CH} , $\angle\text{CCC}$, and $\angle\text{HCC}$ values are 1.230 Å, 1.510 Å, 1.090 Å, 116.6°, and 109.9° (average), respectively; the corresponding suggested experimental values are 1.215 Å (assumed), 1.515 ± 0.005 Å, 1.086 ± 0.010 Å, 116.2 ± 1°, and 110.3 ± 1°, respectively.²⁶ The above-reported experimental values were obtained through the analysis of the microwave spectra of the isotopic substituted species.

For all three carbonyl complexes, the ip1 state is in a linear shape in which the sodium atom is lying collinearly to be within 4° with the carbonyl group. The ip2 state is in an L-shape in which the sodium atom is nearly perpendicular to the carbonyl group. In the same complex, except for the NaOC angle, the geometric parameters of ip1 and ip2 are actually quite close to each other. In the formation of the ip states, the geometries of the carbonyl moieties undergo quite substantial structural changes from their parent form. More specifically, for the ip1 and ip2 states of Na(fd), the out-of-plane bending angles between the HCH plane and the C–O bond are 27.5° and 28.8°, respectively. In the case of Na(ac), the bending angles between the CCC plane and the C–O bond are 38.7° and 38.6°, respectively. For Na(ad), the bending angles between the CCO plane and the (O)CH bond are 33.6° and 34.2°, respectively. The C–O bond lengths of the free carbonyl compounds are all around 1.23 Å. In the ip states, they increase to about 1.33 Å. In summary, the main general geometric trend among the ip states is that the O–Na bond distance of the ip1 state is shorter than that of the ip2 state by about 0.1 Å.

The C–O bond length and the out-of-plane bending angle of the $^1\text{A}_2(\text{n},\pi^*)$ excited state of formaldehyde have been determined to be 1.3232 Å and 34.01°, respectively,²⁷ and the corresponding approximate values for the $\text{S}_1(\text{n},\pi^*)$ state of acetaldehyde were reported to be 1.343 Å and 33.5°, respectively.^{28–30} There were no detailed experimental geometric parameters available for the $\text{S}_1(\text{n},\pi^*)$ state of acetone, except that it is known to be in a generally pyramidal shape.³¹ Clearly, the general geometric parameters of the S_1 excited states of the carbonyl compounds are similar to those of the corresponding ip states of the sodium complexes. Additionally, the singly occupied molecular orbitals (SOMOs) of the ip states are of π^* character. In short, as has been suggested in the literature,^{7,8} for the ip1 and ip2 states of the present systems the unpaired electron occupies the empty antibonding π^* orbitals of the carbonyl compounds. Nevertheless, there are still differences between their SOMOs. In the ip2 state, the hybridized sp orbital of the sodium atom interacts with the π^* antibonding orbital of carbonyl compounds. In the ip1 state, however, the sodium atom

not only interacts with the carbonyl compound's π^* antibonding orbital but also mixes to some degree with the C–O σ bond orbital of the carbonyl compound.

The above geometries of ip1 and ip2 of Na(fd) are in good agreement with those calculated at MP2/6-31G* as reported in the literature.⁸ The ip1 state of Na(ac) also has been calculated at HF/3-21G* by the same authors. Their r_{NaO} and r_{CO} values are 1.8935 and 1.3490 Å. Compared with the present values of 1.983 and 1.332 Å, the variations are in line with the general trend between these two levels of calculations.

In contrast to the ip states, the carbonyl moieties undergo only very minor changes in the formation of the cp states. The sodium atom is collinear with the carbonyl group in Na(fd)(cp) and Na(ac)(cp). In the case of Na(ad)(cp), the sodium atom is slightly off in the cis position with respect to the carbonyl hydrogen atom. Because the observed orientation of the acetaldehyde dipole moment is in the same general cis position,²⁵ one could reason that the sodium atom is attracted to the carbonyl O atom by the local electric dipole of the acetaldehyde and forms the Na(ad)(cp) state. The theoretical dipole moments of fd, ad, and ac calculated at the MP2/6-31+G(d,p) level are 2.54, 2.91, and 3.08 D, respectively. They are in good agreement with the experimental values of 2.32, 2.69, and 2.90 D, respectively.^{24–26} This general trend of the dipole moment could be attributed to the electron-donating capability of the methyl groups on the carbonyl carbon. At the MP2/6-31+G(d,p) level, the Mulliken charge populations at the sodium atoms of Na(ac)(cp), Na(ad)(cp), and Na(fd)(cp) are -0.104, -0.098, and -0.088 e , respectively. The magnitude of the Mulliken charge population depends on the size of the basis set, and it increases as the basis set gets larger. Nevertheless, for the present sodium complexes, the charge population feature persists even at lower basis sets such as 6-31G*. Additionally, the general charge population trend from the lithium to potassium complexes, in which the lithium complexes show a significant extent of the charge-transfer population whereas the potassium complexes carry a negligible Mulliken charge-transfer character, also supports the conclusion that the present sodium complexes are an intermediate case in the charge-transfer interaction. All these observations suggest that the dipole-induced dipole and charge-transfer interactions are contributing to the formation of the complexation bond and that the bonding nature of the cp states is similar to those of the conventional alkali metal atom–Lewis base molecule complexes reported previously. The presence of the occupied π and unoccupied low-lying π^* orbitals of the carbonyl compounds exerts no obvious effects on the bonding of the cp state.

(b) *Neutral Disodium Complexes.* Only the most stable disodium forms were considered. As a representative, the geometric structure of Na₂(ad) is shown at the bottom panel of Figure 1. In general, the geometric parameters of disodium complexes are similar to those of the monosodium cp states if one compares their related molecular fragments. Mulliken population analysis suggests that the electronic properties of the most stable disodium systems are essentially the same as those of the monosodium systems in the cp state. Because of a stronger dipole-induced dipole interaction, the Na–O bond lengths of these disodium complexes are all shorter than those of their monosodium counterparts by about 0.05 Å. The Na–Na bond distances of the complexes are longer than that of the free disodium molecule by an average of 0.028 Å. Note that the theoretical Na₂ bond length is 3.153 Å and the experimental value is 3.0788 Å.³²

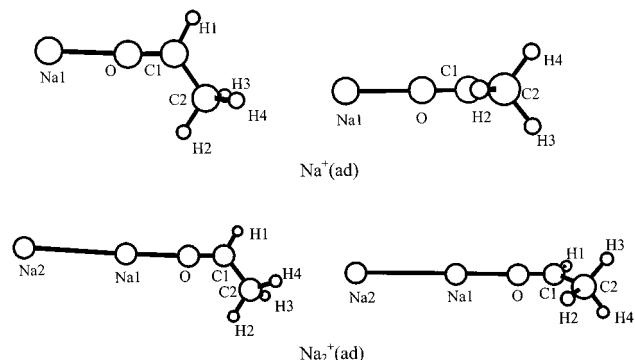


Figure 2. Ball-and-stick representations of the $\text{Na}^+(\text{ad})$ and $\text{Na}_2^+(\text{ad})$ complexes. Both the top and side views are shown side by side. The $\text{Na}^+(\text{fd})$ and $\text{Na}^+(\text{ac})$ systems have similar structures.

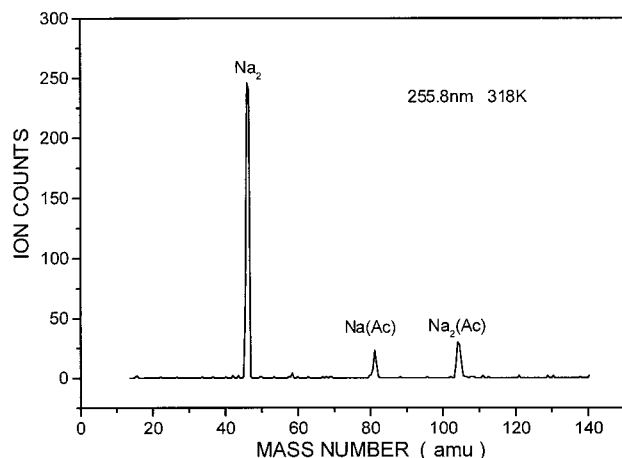


Figure 3. Photoionization mass spectrum of Na/ac at 255.8 nm laser radiation.

(c) *Cations.* Figure 2 shows the geometric structures of $\text{Na}^+(\text{ad})$ and $\text{Na}_2^+(\text{ad})$. The related formaldehyde and acetone systems have similar general geometric structures. Except for the $\text{Na}-\text{Na}$ and/or $\text{Na}-\text{O}$ bond lengths, the geometric structures of the mono- and disodium cationic complexes are close to those of the neutral counterparts in the cp state. For the monosodium cations, owing to the strong ion-dipole interaction, the $\text{Na}-\text{O}$ bond distances are shorter than those of the neutral counterparts by an average of 0.15 Å. For the same reason, the $\text{Na}-\text{O}$ bond lengths of the disodium cations are also shorter than those of the neutral counterparts by about 0.06 Å. The $\text{Na}-\text{Na}$ bond lengths of the disodium cations are longer than those of the corresponding neutral complexes by about 0.46 Å, a quantity that is close to the difference of the bond lengths between the Na_2 and Na_2^+ molecules, 0.5 Å. Note that the theoretical Na_2^+ bond length is 3.653 Å and the experimental value is 3.60 Å.³³

4.2. Photoionization Mass and Efficiency Spectra and Theoretical Ionization Energies. 4.2.1. Experimental Results.

(a) *Na/ac Complexes.* Figure 3 shows the photoionization mass spectrum of the Na/ac system at 255.8 nm laser radiation. At this photon energy, the ion signals of Na_2 , $\text{Na}(\text{ac})$, and $\text{Na}_2(\text{ac})$ were observed. The $\text{Na}(\text{ac})$ and $\text{Na}_2(\text{ac})$ signals would disappear immediately if either acetone or sodium vapor was terminated. Figures 4 and 5 show the photoionization efficiency spectra and the corresponding Watanabe plots of $\text{Na}(\text{ac})$ and $\text{Na}_2(\text{ac})$, respectively. Their threshold ionization energies were determined to be 4.12 ± 0.05 and 4.34 ± 0.04 eV, respectively. The $\text{Na}(\text{ac})$ ion signal starts to appear as the photon energy reaches ~ 4.0 eV and then increases steadily to the threshold ionization region around 4.1 eV. Afterward, the signal increases

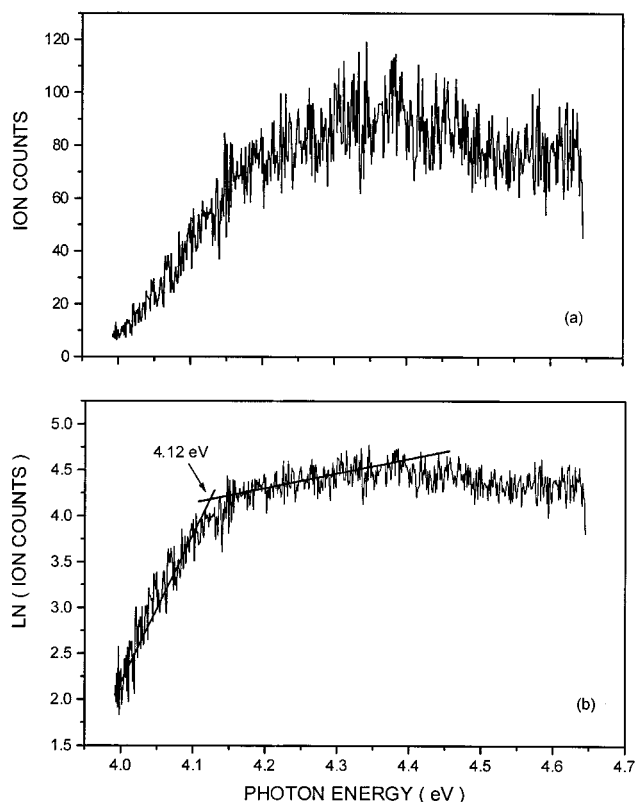


Figure 4. (a) Photoionization efficiency spectrum of $\text{Na}(\text{ac})$ and (b) the corresponding Watanabe plot.

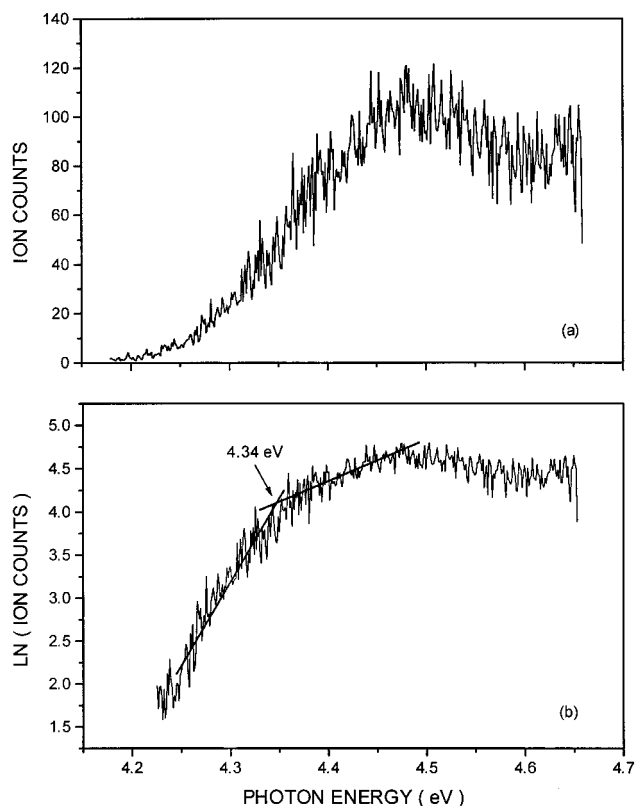


Figure 5. (a) Photoionization efficiency spectrum of $\text{Na}_2(\text{ac})$ and (b) the corresponding Watanabe plot.

at a slower rate until reaching a local maximum at ~ 4.4 eV. It decreases slightly as the photon energy increases further. In the case of $\text{Na}_2(\text{ac})$, as shown in Figure 5, the ion signal appears at a photon energy of ~ 4.25 eV and steadily increases until it

reaches the threshold region at 4.34 eV. Beyond the threshold, it rises again at a slower rate and reaches a local maximum at around 4.45 eV. Afterward, the ion signal decreases slightly up to ~ 4.6 eV.

For the alkali metal atom complexes formed by the simple Lewis base molecules such as hydroxyl, amino, or ethereal compounds, it has been observed that the ionization efficiency spectra around and beyond the threshold regions are all flatter than those of the acetone case.^{14,15,17,19} The present spectra seem to suggest that some additional ionization channels are contributing to the ionization signal around and beyond the threshold region. One plausible source could be the autoionization process originating from the $\pi^* \leftarrow n$ electronic transition of acetone. Its excitation energy at half-height of the maximum absorption falls in the 4.13–4.96 eV range.²⁰ The rationalization is as follows. The sodium atom continuous absorption cross section at the ionization threshold is 0.130 Mb,³⁴ and the maximum acetone $\pi^* \leftarrow n$ absorption cross section is 0.052 Mb at around 4.5 eV.²⁰ For the weakly bonded Na(ac)(cp) complex at zero-order approximation, one could estimate that the straight ionization cross section of the complex is 0.13 Mb and the upper bound of the autoionization cross section is 0.052 Mb if the photon energy is higher than the threshold ionization energy. It has been established that, depending on the photon energy, the $S_1(n,\pi^*)$ state is coupled to the nearby triplet state T_1 and also to the ground electronic state S_0 .^{20,35} From the fluorescence decay rate constants of acetone, it has been suggested that the rapid decrease of the fluorescence decay time at around 4.04 eV is due to the onset of the photodissociation on the potential surface of the triplet state.³⁵ Because of the relatively much longer lifetime of the S_1 state in the low photon energy regime, it is expected that the autoionization process is more important. As photon energy reaches 4.25 eV and beyond, which is the energy of the above 4.04 eV plus the bonding energy of Na(ac)(cp), 0.21 eV, because of the competition of the photodissociation channel, the higher the excess photon energy gets, the less efficient the autoionization process becomes. Following the same argument, for the $Na_2(ac)$ molecule one could estimate that the above turning-on photon energy is located at about 4.43 eV. These two estimated energies are higher than their corresponding threshold ionization energies of 4.12 and 4.34 eV and are also close to the positions of the maximum ion signals. This evidence, although still indirect, supports the possible contribution of the autoionization process in the present systems. For a more definite description of the ionization cross section of these systems, further detailed studies are needed.

For the monosodium mass spectrum, if the photon energy is higher than 4.84 eV, energetically it is possible that the photoionization of $Na_2(ac)$ could generate an energy-rich $Na_2^+(ac)$ cation that might further dissociate into the sodium atom and the $Na^+(ac)$ cation. As shown in Figure 4, this onset energy is much higher than the energy range considered in this report. The above energetic relations of the complexes are discussed in section 4.3.

(b) *Na/ad Complexes.* As in the case of the Na/ac system, the Na(ad) and $Na_2(ad)$ signals were observed in the photoionization mass spectra. In the present experiment, the $Na_2(ad)$ signal was only about one-third of that of Na(ad), and their overall signals were weaker than those of Na/ac.

As shown in Figure 6, the photoionization threshold energy of Na(ad) was determined to be 4.23 ± 0.04 eV. Because of a poor S/N ratio, the ionization threshold energy of $Na_2(ad)$ could only be estimated to be 4.5 eV. The ion signal of Na(ad) increases steadily from around 4.09 eV to the threshold region.

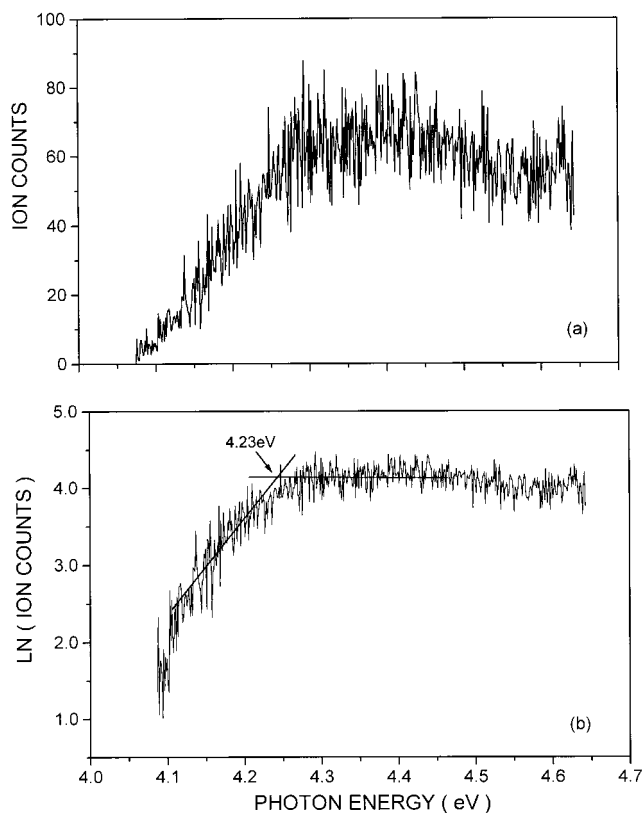


Figure 6. (a) Photoionization efficiency spectrum of Na(ad) and (b) the corresponding Watanabe plot.

Afterward, the signal holds more or less constant, and then after passing ~ 4.46 eV, it decreases slightly. In contrast to the acetone case, the photoionization efficiency spectrum is more similar to those of the simple Lewis base molecules in the literature. In other words, for the acetaldehyde system, there were no clear spectral features that suggest the possible involvement of the autoionization originating from the expected $\pi^* \leftarrow n$ transition.

At half-height of the maximum absorption, acetaldehyde has a photon absorption range from 3.95 to 4.77 eV.²¹ It has been demonstrated that as the photon energy reaches 3.94 eV and beyond, the fluorescence decay rate constants increase drastically.^{36–38} This has been attributed to the opening of the triplet state dissociation channel. Following the general argument of the acetone case, one would expect that the dissociation process could compete effectively with the autoionization process if the photon energy reached 4.10 eV, in which the bonding energy of Na(ad), 0.16 eV, has been added. The threshold ionization energies of Na(ad) and $Na_2(ad)$, 4.23 and 4.5 eV, are well above this value. Along this line, it is suggested that the absence of the possible autoionization spectral feature for the acetaldehyde system could be attributed to the competition of the dissociation channel over the triplet state potential in this photon energy range.

4.2.2. Theoretical Ionization Energies and Comparison with Experimental Measurements. Table 1 shows the theoretical vertical and adiabatic ionization energies of the sodium complexes. The discussion of this section was centered on the B3PW91 results.

(a) *Na/ac Complexes.* The theoretical vertical ionization energies of Na(ac)(ip1) and Na(ac)(ip2) are 4.58 and 5.19 eV, and the adiabatic ionization energies are 3.60 and 3.64 eV, respectively. The large differences between these two ionization energies are consistent with the substantial structural differences between the stable cationic state and the ip neutral states. The

TABLE 1: Ionization Energies of Na, Na₂, and Sodium Complexes^{a,b}

species	vertical (eV)			adiabatic (eV)			expt
	HF	MP2	DFT	HF	MP2	DFT	
Monosodium							
Na → Na ⁺				4.94	5.03	5.27	5.139 ^c
Na(fd)(ip1) → Na ⁺ (fd)	4.39	4.52	4.97	3.43	3.82	4.22	
Na(fd)(ip2) → Na ⁺ (fd)	5.19	5.28	5.82	3.46	3.98	4.43	
Na(fd)(cp) → Na ⁺ (fd)	3.90	4.10	4.30	3.88	4.08	4.29	
Na(ad)(ip1) → Na ⁺ (ad)	4.13	4.29	4.73	3.00	3.43	3.84	
Na(ad)(ip2) → Na ⁺ (ad)	4.84	4.97	5.43	3.00	3.58	3.96	
Na(ad)(cp) → Na ⁺ (ad)	3.78	3.97	4.16	3.76	3.96	4.14	4.23 ^d
Na(ac)(ip1) → Na ⁺ (ac)	3.95	4.17	4.58	2.73	3.21	3.60	
Na(ac)(ip2) → Na ⁺ (ac)	4.61	4.79	5.19	2.68	3.31	3.64	
Na(ac)(cp) → Na ⁺ (ac)	3.70	3.89	4.07	3.68	3.88	4.05	4.12 ^d
Disodium							
Na ₂ → Na ₂ ⁺	4.09	4.66	4.96	3.97	4.56	4.87	4.895 ^e
Na ₂ (fd) → Na ₂ ⁺ (fd)	3.45	4.10	4.35	3.36	4.02	4.29	
Na ₂ (ad) → Na ₂ ⁺ (ad)	3.38	4.03	4.27	3.28	3.95	4.20	4.5 ^d
Na ₂ (ac) → Na ₂ ⁺ (ac)	3.33	3.98	4.21	3.24	3.90	4.15	4.34 ^d

^a fd = formaldehyde, ad = acetaldehyde, ac = acetone. ^b Calculated at the HF/, MP2/, and B3PW91/6-311+G(2d,p)//MP2/6-31+G(d,p) levels, respectively. ^c Reference 45. ^d This work. ^e Reference 46.

similarity of the adiabatic ionization energies of the two ip states is also consistent with the closeness of the bond dissociation energies of these two states, which is discussed in section 4.3.

In contrast, the difference between the theoretical vertical and adiabatic ionization energies of Na(ac)(cp), 4.07 and 4.05 eV, is rather small. This is consistent with the relatively small structure variations between Na(ac)(cp) and Na⁺(ac). Similarly, the difference between the vertical and adiabatic ionization energies of Na₂(ac), 4.21 and 4.15 eV, is also small. This is also in line with the minor structure change from Na₂(ac) to Na₂⁺(ac).

In the photoionization efficiency spectra, there were no apparent spectral features that could be attributed to the ip states as predicted in the theoretical calculations. This observation is consistent with the negative bond dissociation energies for the ip1 and ip2 states at both the MP2 and B3PW91 calculation levels, discussed in section 4.3. As shown in the table, the experimental threshold ionization energies of Na(ac)(cp) and Na₂(ac) are in good agreement with the theoretical vertical ionization energies.

The ionization threshold energy of Na(ac) also has been measured to be 3.88(3) eV by a pick-up beam technique.⁹ Compared with the present experimental ionization threshold energy of 4.12 ± 0.05 eV and the theoretical adiabatic ionization energy of 4.05 eV, the value is apparently on the low side. One possible reason is that the two experiments are probing two different regions of the potential surface. The present flow reactor produces sodium complexes at room temperature. Its population is at thermal equilibrium, and the most probable population is at the lowest energy state. However, the pick-up beam technique generates a much colder sodium cluster through an associative collision process. It is plausible that the sodium clusters could be trapped significantly in metastable states near the neutral dissociation limit, like the ip states of Na(ac). As discussed in section 4.3, their energies are close to the dissociation limit. The theoretical adiabatic ionization energies of the ip1 and ip2 states of Na(ac) are 3.60 and 3.64 eV, respectively. The difference in the above ionization threshold measurements could be just the result of the involvement of the ip states.

(b) *Na/ad Complexes.* The theoretical vertical ionization energies of Na(ad)(ip1) and Na(ad)(ip2) are 4.73 and 5.43 eV.

In comparison with the theoretical adiabatic ionization energies, 3.84 eV for Na(ad)(ip1) and 3.96 eV for Na(ad)(ip2), the large difference between these two types of ionization energies is consistent with the large geometrical variation between the stable cationic and neutral cp states. On the other hand, the theoretical vertical ionization energy of Na(ad)(cp), 4.16 eV, is close to the adiabatic ionization energy, 4.14 eV. The small variation is consistent with the minor structure change from Na(ad)(cp) to Na⁺(ad). Similarly, the variation between the vertical and adiabatic ionization energies of Na₂(ad) is only 0.06 eV.

The experimental ionization threshold energy of Na(ad), 4.23 ± 0.04 eV, is in good agreement with the theoretical vertical ionization energy of Na(ad)(cp), 4.14 eV. There were no apparent spectral features that related to the ionization of the ip states. This is in line with the negative bond dissociation energies of the ip states at both the MP2 and B3PW91 calculation levels. The estimated experimental ionization threshold energy of Na₂(ad), 4.5 eV, is in reasonably good agreement with the theoretical vertical ionization energy, 4.27 eV.

(c) *Na/fd Complexes.* The theoretical vertical ionization energies of Na(fd)(ip1) and Na(fd)(ip2) are 4.97 and 5.82 eV, and the corresponding theoretical adiabatic ionization energies are 4.22 and 4.43 eV, respectively. The large difference between these two types of energies is in line with the large geometric variation from the stable neutral complexes to the cations. In contrast, the theoretical vertical and adiabatic ionization energies of Na(fd)(cp) are 4.30 and 4.29 eV, respectively. The small variation is consistent with the small structure change from Na(fd) to Na⁺(fd). Similarly, the variation between the vertical and adiabatic ionization energies of Na₂(fd) is also small, only 0.06 eV.

In summary, the orderings of the vertical or adiabatic ionization energies of the three systems in either the monosodium cp states or the disodium complexes are Na(fd) > Na(ad) > Na(ac) and Na₂(fd) > Na₂(ad) > Na₂(ac). In contrast, the extent of the variation between vertical and adiabatic ionization energies among the same monosodium or disodium complexes is virtually the same. The Na(ac)(cp) has the lowest ionization energy because the interaction between the sodium cation and acetone is the strongest among the three complexes, as is also the case for Na₂(ac).

4.3. Equilibrium Bond Dissociation Energies. The equilibrium bond dissociation energies (D_e) and vibration zero-point energy corrections (ZPEC) are listed in Table 2. The bond dissociation energy (D_0) could be obtained through the relation $D_0 = D_e + \text{ZPEC}$. The enthalpy of the bond dissociation, ΔH_T^0 , could be calculated by the well-established method of statistical mechanics. In this report, the ZPEC and the thermal energy correction were calculated under the harmonic oscillator approximation at the MP2(full)/6-31G+(d,p) level. According to the recommended scaling factors calculated by MP2(fc)/6-31G(d,p) (the closest calculation level to the present report), which are 1.0229 for the low-frequency vibration mode, 0.9608 for ZPEC, and 1.0084 for the vibrational thermal correction,³⁹ the accuracy of the harmonic oscillator approximation is adequate for the present purpose. For some simple ion cluster systems, the good agreement between the theoretical enthalpies of reactions and the measured values also supports the adequacy of the present calculations despite some large amplitude vibrational modes involved.⁴⁰ The present theoretical uncertainty of ΔH_T^0 is mainly determined by the computed accuracy of D_e .

(a) *Neutral Complexes.* As shown in Table 2, some general trends appear in the bond dissociation energies of the monosodium complexes: (i) The bond dissociation energies of each

TABLE 2: Equilibrium Bond Dissociation Energies (eV) of Neutral Sodium Complexes^{a-c}

reactions	HF	MP2	CCSD(T)	DFT	ZPEC ^d
Monosodium					
Na(fd)(ip1) → Na + fd	-0.303	-0.124	-0.104	0.007	0.012
Na(fd)(ip2) → Na + fd	-0.278	0.032	0.057	0.223	-0.002
Na(fd)(cp) → Na + fd	0.142	0.132	0.148	0.078	-0.029
Na(ad)(ip1) → Na + ad	-0.556	-0.337	-0.295	-0.164	0.010
Na(ad)(ip2) → Na + ad	-0.558	-0.199	-0.151	-0.049	0.003
Na(ad)(cp) → Na + ad	0.199	0.183	0.202	0.131	-0.028
Na(ac)(ip1) → Na + ac	-0.705	-0.431	-0.359	-0.263	0.006
Na(ac)(ip2) → Na + ac	-0.754	-0.330	-0.269	-0.222	0.003
Na(ac)(cp) → Na + ac	0.249	0.234	0.258	0.181	-0.029
Disodium					
Na ₂ → Na + Na ^e	-0.015	0.502	0.720	0.607	-0.010
Na ₂ (fd) → Na ₂ + fd	0.309	0.303	0.319	0.208	-0.047
Na ₂ (ad) → Na ₂ + ad	0.377	0.367	0.385	0.276	-0.042
Na ₂ (ac) → Na ₂ + ac	0.435	0.429	0.448	0.333	-0.039

^a fd = formaldehyde, ad = acetaldehyde, ac = acetone. ^b Calculated at the HF/, MP2/, CCSD(T)/, and B3PW91/6-311+G(2d,p)//MP2/6-31+G(d,p) levels, respectively. ^c Negative bond energies mean that the complex energies are located above the dissociation energy limit of the neutral fragments. ^d Zero-point energy correction. ^e The experimental value is 0.745 eV (ref 42).

individual cp state calculated by the HF, MP2, CCSD(T), and B3PW91 methods are close to each other. Their stability ordering among the three species is Na(ac)(cp) > Na(ad)(cp) > Na(fd)(cp). For the carbonyl systems, the electron correlation is not that important in the forming of the cp states. (ii) For each individual ip state, the relative bonding stability is in the order of HF < MP2 < CCSD(T) < DFT. Except for the ip2 state of Na(fd) calculated by the MP2 and CCSD(T) methods and the ip1 and ip2 states of Na(fd) calculated by the DFT method, which have a rather small stabilization energy, the remaining ip states all lie above the dissociation energy limit for the neutral fragments. (iii) For a given species, the ip2 state is more stable than the ip1 state at the MP2, CCSD(T), and DFT levels, and the cp state is always the most stable state at all the calculation levels. (iv) For the cp states, the ordering of the bonding stability is Na(ac) > Na(ad) > Na(fd), whereas for each of the two ip states, the bonding stability is in reverse order at all the calculation levels.

In the complex formation between the sodium atom and simple Lewis base molecule, it has been established that the major interaction energy is due to the dipole-induced dipole interaction and the charge transfer from the Lewis molecule to the sodium atom.¹⁰⁻¹⁹ For the cp states of the present carbonyl complexes, it is known that the electric dipole moments of the three free carbonyl compounds are in the ordering of ac > ad > fd. One would expect that the dipole-induced dipole interaction strength would follow the same ordering. According to the Mulliken charge population analysis as discussed in section 4.1, the acetone complex has the largest charge-transfer character. Apparently, despite the presence of the π bonding, the bonding of the present cp states is in line with the general bonding properties of the traditional bonding between the sodium atom and simple Lewis base molecules. The stability ordering of the cp states among the three carbonyl systems could also be rationalized accordingly.

For the stability of the ip states, a gain of 0.20–0.48 eV extra energy stabilization as one moves from the HF calculation level to the CCSD(T) level suggests that the electron correlation is very important for this charge-transfer state. The bond energy difference between the MP2 and CCSD(T) calculations is at most 0.072 eV for the ip2 state of Na(ac). This suggests that

the MP2 and CCSD(T) levels are adequate for the present systems. At the B3PW91 level, depending on the complexes, the energy stability increases further by about 0.05–0.17 eV when compared with those of the CCSD(T) calculation. Note that the conventional DFT methods usually overestimate the interaction energies of the charge-transfer complexes.⁴¹ Furthermore, as listed in Table 2, the equilibrium bond dissociation energies of Na₂ calculated at the HF, MP2, CCSD(T), and B3PW91 levels are -0.015, 0.502, 0.720, and 0.607 eV, respectively. Compared with the experimental value of 0.745 eV,⁴² the CCSD(T) calculation yields the closest result. In this report, the bond dissociation energies calculated at the CCSD(T) level are reckoned to be the best values and are employed solely for the following energy discussion.

For either the linear or the L-shaped form of the ip state, the Na–O bond distances are close to each other, and the Na Mulliken charge population, which has a positive value, decreases from Na(fd) to Na(ac). Because the ip states of Na(fd) have the highest energy stability and those of Na(ac) show the least energy stability among these three complexes, the above variation of the Na atom charge populations suggests that the electrostatic interaction is the major factor in determining the relative energy stability of these ip states.

Experimentally, in fluid solutions it has been shown that the main species observed are either the aliphatic ketyl radical anions or the ion-pair states.^{2,3} No complexation-pair states were observed. To the contrary, the present theoretical results suggest that the cp states are always more stable than the ip states. Because the ip states could be more readily stabilized than the cp states by just adding one polar solvent molecule to the present monosodium complex, it is expected that in fluid solvents, especially in the polar ones, the most stable state would be the ip state instead of the cp state as discussed in this report.

In the case of the disodium complexes, the bond dissociation energy is about twice that of the monosodium cp counterpart at the HF, MP2, and CCSD(T) levels, and their order of bonding strength is the same as that of the corresponding monosodium cp state, that is, Na₂(ac) > Na₂(ad) > Na₂(fd). For this series of sodium complexes, it has been suggested that a good portion of the bonding strength is dipole-induced dipole interaction in nature. The electric dipole polarizability of the sodium atom is 24.3 Å³, and the electric dipole polarizability along the internuclear axis of the sodium molecule is 52.2 Å³.⁴³ Assuming that the interaction distances in the mono- and disodium systems are close to each other, one would expect that the induction stabilization energy of Na₂ is about twice that of Na. The good agreement between the above two general trends is in line with the current understanding that the dipole-induced dipole interaction is an important factor for the Na bonding in the carbonyl compounds. Note that for the disodium complexes, the extent of the charge transfer from the carbonyl compound to Na₂ is close to that of the corresponding monosodium complexes.

(b) *Cationic Complexes.* Table 3 shows the bond dissociation energies of the monosodium and disodium cationic complexes. For these systems dominated by ion-dipole interactions, the MP2, CCSD(T), and B3PW91 bond dissociation energies are in very good agreement with each other. For instance, in the case of Na⁺(ad) the equilibrium bond dissociation energies are 1.254, 1.267, and 1.263 eV at the MP2, CCSD(T), and B3PW91 levels, respectively. There is about a 0.05–0.13 eV energy difference as one goes to the HF level. The percentage contribution of the electron correlation effect to the bonding energy is not that important for these cationic complexes.

TABLE 3: Equilibrium Bond Dissociation Energies (eV) of Cationic Sodium Complexes^{a,b}

reactions	HF	MP2	CCSD(T)	DFT	ZPEC ^c
Monosodium Ions					
Na ⁺ (fd) → Na ⁺ + fd	1.206	1.081	1.094	1.060	-0.054
Na ⁺ (ad) → Na ⁺ + ad	1.378	1.254	1.267	1.263	-0.047
Na ⁺ (ac) → Na ⁺ + ac	1.508	1.388	1.402	1.406	-0.043
Disodium Ions					
Na ₂ ⁺ → Na ⁺ + Na ^d	0.957	0.970	0.972	1.006	-0.007
Na ₂ ⁺ (fd) → Na + Na ⁺ (fd)	0.674	0.728	0.733	0.731	-0.011
Na ₂ ⁺ (fd) → Na ₂ ⁺ + fd	0.923	0.840	0.856	0.785	-0.057
Na ₂ ⁺ (ad) → Na + Na ⁺ (ad)	0.640	0.693	0.699	0.687	-0.011
Na ₂ ⁺ (ad) → Na ₂ ⁺ + ad	1.104	0.977	0.994	0.944	-0.050
Na ₂ ⁺ (ac) → Na + Na ⁺ (ac)	0.616	0.668		0.658	-0.010
Na ₂ ⁺ (ac) → Na ₂ ⁺ + ac	1.167	1.086		1.058	-0.045

^a fd = formaldehyde, ad = acetaldehyde, ac = acetone. ^b Calculated at the HF/, MP2/, CCSD(T)/, and B3PW91/6-311+G(2d,p)// MP2/6-31+G(d,p) levels, respectively. ^c Zero-point energy correction. ^d The experimental value is 0.9886 eV (ref 33).

Additional support for this type of system is the experimental bond energy of Na₂⁺, 0.9886 eV,³³ which is in good agreement with the theoretical values of 0.970, 0.972, and 1.006 eV calculated at the MP2, CCSD(T), and B3PW91 levels, respectively.

The Na⁺ and Na₂⁺ bonding energy to the carbonyl compounds increases as one goes from fd to ac. This is in line with the general trend that ac has the largest dipole moment and electric dipole polarizability, whereas fd has the smallest values. Both the ion-dipole and ion-induced dipole interactions contribute to the stability of these complexes.

Experimentally, the enthalpy of dissociation for Na⁺(ac) has been measured to be 1.445 ± 0.009 eV over a temperature range of 640–680 K.⁴⁴ With the theoretical thermal energy correction for the bond dissociation enthalpy, -0.006 eV at 660 K, the experimental bond dissociation energy D_0 of Na⁺(ac) is 1.439 ± 0.009 eV. This value is slightly higher than the theoretical bond dissociation energy of 1.359 eV calculated at the CCSD(T) level. Nevertheless, considering the experimental difficulty in handling acetone under comparatively high-temperature conditions and also the moderate size of the molecular system in the calculations, the agreement is considered to be good.

With the bond dissociation energy of the cationic complex, one could calculate the bond dissociation energy of the corresponding neutral complex by the following relation:

$$D_0(\text{Na}(\text{ac})) = \text{IP}(\text{Na}(\text{ac})) + D_0(\text{Na}^+(\text{ac})) - \text{IP}(\text{Na}) \quad (1)$$

The above relation is exact if the adiabatic ionization energy of Na(ac) is employed. For the cp states of the present systems, because the geometric structures of the neutral and cationic states are similar to each other, the experimental threshold ionization energy is a good approximation to the adiabatic ionization energy. With the experimental ionization energy of Na, 5.139 eV,⁴⁵ the experimental bond dissociation energy of Na⁺(ac), 1.439 eV, and the adiabatic ionization energy of the neutral complex approximated by the present experimental threshold energy of 4.12 ± 0.05 eV, the bond dissociation energy of Na(ac)(cp) is 0.42 eV. Taking the energy difference of 0.02 eV between the theoretical vertical and adiabatic ionization energies of Na(ac)(cp) into account, one obtains a refined value of 0.40 eV for the Na(ac)(cp) bond dissociation energy. Compared with the theoretical value of 0.258 eV, apparently, the agreement is not satisfactory.

On the other hand, following the above procedure, one may check the internal consistency of the theoretical bond dissociation energies by starting from the Na⁺(ac) theoretical bond dissociation energy of 1.359 eV instead. Along with the above sodium atom ionization energy, the experimental threshold ionization energy of Na(ac)(cp), and the energy difference between its vertical and adiabatic ionization energies, the final bond dissociation energy of Na(ac)(cp) becomes 0.32 eV. The 0.06 eV difference from the theoretical value of 0.258 eV is close to the quoted experimental error of the threshold ionization energy of Na(ac)(cp), 0.05 eV. The internal consistency of the neutral and cationic bonding energies of Na(ac) is reasonably good. In other words, the present theoretical bond dissociation energy of Na⁺(ac) is likely to be a more accurate value and the experimental result may be slightly overestimated by about 0.08 eV.

5. Conclusion

Three molecular complex systems, sodium/formaldehyde, sodium/acetaldehyde, and sodium/acetone were studied theoretically. In the monosodium case, three locally stable minima were located for each of the three systems over the ground electronic state; two of them were identified as ion-pair states, and the third as a complexation-pair state. There were no other local minima located at the present calculation level. In the case of disodium complexes, only the global minimum states were studied. Their physical and chemical properties are similar to those of the monosodium cp state, with the disodium acting as a unit. For the cp states of the monosodium and disodium carbonyl compounds, despite the presence of the π and π^* orbitals of the carbonyl group, the nature of the bonding is in the same category as that between the alkali metal atoms and the simple Lewis base molecules. In the monosodium systems, the energy separations among the three local minima are quite close to each other. Because of the differences in the charge distribution, adding an additional polar solvent molecule to the system could readily alter their relative stability. On the other hand, these closely spaced stable states could be simultaneously probed in a thermal sodium atom/carbonyl molecule collision process.

The photoionization mass spectra and photoionization efficiency spectra of the sodium/acetaldehyde and sodium/acetone systems were measured. The general features of the spectra were discussed, and the corresponding photoionization threshold energies were determined accordingly. Only the complexation-pair states were observed. These are consistent with the theoretical predictions that their ion-pair states are all lying either very close to or slightly above the dissociation limit of their neutral fragments. The photoionization thresholds determined are in good agreement with the theoretical values at the B3PW91/6-311+G(2d,p) level. It is suggested that the additional spectral features in the Na/ac photoionization efficiency spectra are due to the possible contribution of the autoionization process originating from the $\pi^* \leftarrow n$ electronic transition of the carbonyl compounds.

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

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