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# Associative ionization of excited sodium species with various ligands: assessing relative bonding strengths of ion–ligand interactions

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## Abstract

Associative ionization reactions of excited sodium species with water, acetonitrile (CH<sub>3</sub>CN), benzene (C<sub>6</sub>H<sub>6</sub>), acetone [(CH<sub>3</sub>)<sub>2</sub>CO], diethylether (Et<sub>2</sub>O), ethanol (CH<sub>3</sub>CH<sub>2</sub>OH), methanol (CH<sub>3</sub>CH<sub>2</sub>OH), ammonia (NH<sub>3</sub>), 1-propanol (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH), *n*-butyl alcohol (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH), and dimethoxyethane (DME) were investigated under thermal conditions using a fast flow reactor. This is the first reported heteronuclear associative ionization reaction of excited sodium species with these ligands. The measurements reported herein allow for an assessment of the relative extent of interaction of sodium ions with benzene compared to the above mentioned ligands. Particularly significant are the comparative studies of water and benzene, which provide evidence that the binding energy of Na<sup>+</sup> with benzene exceeds that with water. (Int J Mass Spectrom 204 (2001) 247–253) © 2001 Elsevier Science B.V.

**Keywords:** Associative ionization; Clusters ions; Sodium bonding energies; Excited sodium species

## 1. Introduction

The elucidation of the influence of solvation on ion–molecule reactions is of importance to physical chemistry [1]. With gas-phase cluster experiments, the degree and nature of the solvent can be varied in which the properties of the solvated species may have characteristics that are between those of the gas and condensed phase [2]. In recent years, there has been a growing interest in the significance of cation– $\pi$  interactions as an important noncovalent intermolecular force in biological systems [3]. Studies of Na<sup>+</sup>–ligand

complexes have been of long-standing interest in our research group, stemming from investigations into the effects of solvation on the thermochemical properties of ion–neutral association reactions [4,5]. Also, the interaction of organic molecules with alkali metal ions, such as sodium ions, is important in the catalytic properties of mixed metal oxide materials [6–8]. Currently, there exists considerable debate concerning the binding energies of sodium ions with different ligands [5,9–11]. We seek to shed light on this controversy by investigating the associative ionization reactions of excited sodium species with a wide range of ligands in order to obtain a relative binding energy scale. One approach is through investigation of the

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extent of associative ionization between excited atoms and ligands.

Associative ionization (Hornbeck-Molnar process) is an unique ionization process that occurs when an electronically excited atom or molecule,  $A^*$ , collides with a species,  $B$ , leading to the formation of an ionized association complex [12]:



For reaction (1) to occur, the ligand,  $B$ , has to be capable of forming a strong bond with the ion,  $A^+$ , and the energy of the excited species,  $A^*$ , must be relatively near its ionization potential. Interestingly, such ionization processes have been proposed to be involved within interstellar clouds [13]. New experimental methods are being developed in order to investigate this process with hopes of a better understanding of radiation chemistry and plasma physics [14]. A number of early studies relevant to our investigations have been published by Herman and Cermák [15–17] who reported associated Hg ion complexes formed in associative ionization reactions with metastable Hg. Also reported were complexes of carbon monoxide with sodium formed by associative ionization reactions. Ion–molecule reactions have been investigated in the formation of neutral sporadic Na layers [18].

## 2. Experimental

Experiments are conducted in a fast-flow reactor affixed with a high-pressure ion source. The details of this apparatus and experimental procedure have been described in previous publications [19–21] and only a brief outline is presented here. In the source, excited sodium species are generated by resistively heating a platinum filament (32 gauge) coated with a 1:2:1  $\text{NaNO}_3:\text{SiO}_2:\text{Al}_2\text{O}_3$  mixture [22]. Excited sodium species are carried into the flow tube by a continuous flow of 7000 sccm (standard cubic centimeter per minute) of a helium buffer gas which is maintained at a selected pressure ( $\sim 0.3$  Torr). The source is maintained at a higher pressure ( $\sim 20$  Torr) than the flow tube by a copper diaphragm (inner diameter = 2.95

mm hole) affixed between the source and flow tube. Approximately 30 cm downstream of the source, a selected concentration of reactant gas is introduced through a reactant gas inlet. Excited sodium species and the neutral reactant gas are allowed to react for several milliseconds before a small fraction of reactant and product ions are sampled through an orifice, scanned by a quadrupole mass spectrometer, and detected by a channeltron electron multiplier.

For determination of the relative extent of interaction, benzene was first used as the reference reactant gas while a similar concentration of the reactant ligand gas was separately added afterwards at a concentration between  $0.24 \times 10^{13}$  and  $1.15 \times 10^{13}$  molecules/cm<sup>3</sup>. In each experiment, the addition of ligand reactant gas was undertaken three times at scan times of two minutes to obtain a reliable ion concentration of the formed sodium–ligand ion complex. The average value of the ratio of  $\sum_n I_n(\text{Na}^+\text{L}_n)$  to  $\sum_n I_n(\text{Na}^+\text{B}_n)$  ( $I_n$  denotes ion concentration,  $L$  is ligand,  $B$  is benzene,  $n$  is the number of ligands attached to the sodium ion) was calculated for each set of experiments. Under current experimental conditions, sodium ion clusters contained no more than two ligand species. For the purposes of comparison, another series of experiments were performed in which the cluster ions were generated by the introduction of the ligand reactant gas directly into the source region. This effected similar reactions with the excited sodium species in the high-pressure region of the source.

We attempted to obtain a constant and reproducible concentration of the excited sodium species based on the ion signal of the  $\text{Na}^+(\text{benzene})$  by adjusting the filament current (temperature) under conditions where  $1.14 \times 10^{13}$  molecules/cm<sup>3</sup> of benzene reactant gas was added to the flow tube. The filament current for each set of experiments was adjusted to a fixed value of  $8.0 \pm 0.2$  A.

## 3. Results and discussion

The experimental results presented in Table 1 list the ratio of  $\sum_n I_n(\text{Na}^+\text{L}_n)$  to  $\sum_n I_n(\text{Na}^+\text{B}_n)$ , i.e. the

Table 1  
Relative extent of interaction of Na<sup>+</sup> binding energies as determined in the flow tube

Ligand	Average value of $\sum_n I_n$ [Na <sup>+</sup> (ligand) <sub>n</sub> ] to $\sum_n I_n$ [Na <sup>+</sup> (benzene) <sub>n</sub> ]
DME	1.131 ± 0.041
Benzene	1.000 ± 0.033
Et <sub>2</sub> O	0.816 ± 0.018
1-Propanol	0.738 ± 0.027
Ethanol	0.733 ± 0.016
Acetone	0.713 ± 0.034
CH <sub>3</sub> CN	0.601 ± 0.031
<i>n</i> -butyl alcohol	0.559 ± 0.022
CH <sub>3</sub> OH	0.155 ± 0.006
NH <sub>3</sub>	0.035 ± 0.003

ratio of sodium ion–ligand cluster signal to sodium ion–benzene cluster signal. Although we are unaware of any other similar studies of the formation of Na<sup>+</sup>–ligand complexes arising from reactions of the excited alkali metal species with the ligands under study in our investigation, the origin of the clusters is well understood from prior investigations of associative ionization. Referring to Fig. 1, it is clear that the interaction of the band of Rydberg states with a ligand having a sufficiently strong bond with the derived ion, will undergo associative ionization.

The cross section of associative ionization reactions will be influenced by two factors (see Fig. 1). First is the manifold of Na\* states which cross with the Na<sup>+</sup>–ligand curve that will give rise to associative ionization. We assume that for associative ionization to occur the Na\*–ligand curve lies above the Na<sup>+</sup>–ligand curve and the internuclear separation is smaller than  $R_e$  (the crossing point between the two curves). Thus the deeper the well, the more states will contribute to the product ion formation. The second factor is the magnitude of  $R_e$ , i.e. the internuclear separations where the excited neutral system curve lies above the ion curve and spontaneous ionization may occur. The fact that the cross section for associative ionization between a polyatomic molecule and a state-selected single Rydberg state increases with increasing  $n$  has been observed experimentally [23]. In collisions between K\* [specific (*nd*) Rydberg states] and polyatomic molecules (water, hydrogen

sulfide, methanol, propanol, dimethylether, acetone, etc.), the cross section increased with  $n$ , for  $9 \leq n \leq 15$ . The authors ascribed this increase to “differences in electric dipole moments and complexities” of the target molecules. A closer inspection shows that the cross section increases with both dipole moments and polarizabilities of the concerned particles, but not proportionally. The shape of the potential energy curve of the K<sup>+</sup>–ligand system and the crossing position with the K\*–ligand potential energy curve is a more likely explanation of the increased size of the cross section of individual states. Preliminary calculations (HF/6-31G\*) of the ionic potential energy curve for the Na<sup>+</sup>–water system [24] and  $R_e$ , from calculated data, showed that the ratios of the cross sections for  $n = 9–13$ , is calculated to be proportional to  $R_e^2$ , are those for K\*(*nd*)–water as presented in [23] (see Table 2). The cross section for associative ionization appears to be not only influenced by the populations of the reacting excited states, but also by the position of  $R_e$  (width of the well).

However, one may assume that the ion–ligand potential energy curves determined primarily by elec-

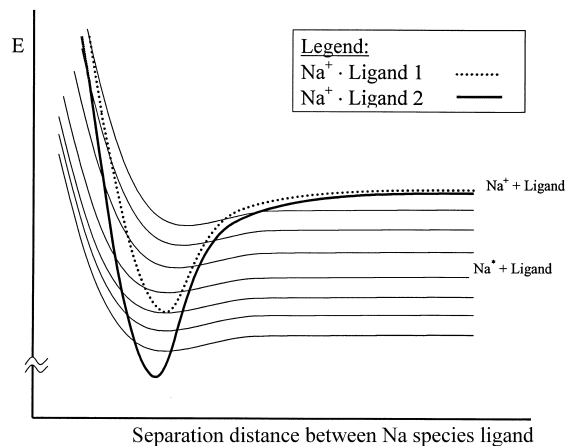


Fig. 1. Schematic diagram of the potential energy curves describing associative ionization. The excited sodium species approaches the ligand along the potential energy curve Na\* + ligand where at a transition point, an electron is released from the Na\* + ligand curve to Na<sup>+</sup> + ligand curve. The bond energy of Na\* + ligand 2 is larger than the bond energy of Na\* + ligand 1.  $R_e$  is the internuclear separations where the excited neutral system curve lies above the ion curve and spontaneous ionization may occur. Adapted from [17].

Table 2

Ratios of cross sections for Na\*(*nd*)-water and Na\*(*nd*)-benzene; note: error in K\*-molecule cross sections about 50%

<i>n</i>	IP-E <sub>e</sub> (ev)	<i>R<sub>e</sub></i> (Å)		Relative cross section		
		Water	Benzene	Na*( <i>nd</i> )-water	Na*( <i>nd</i> )-benzene	K*( <i>nd</i> )-water <sup>a</sup>
8	4.92	5.40	5.12	0.87	0.78	
9	3.89	5.80	5.55	1.0	0.92	1.0 (3.9 × 10 <sup>-12</sup> cm <sup>2</sup> )
10	3.14	6.15	5.90	1.12	1.03	1.7 (6.7 × 10 <sup>-12</sup> cm <sup>2</sup> )
11	2.60	6.45	6.20	1.24	1.14	1.48 (5.8 × 10 <sup>-12</sup> cm <sup>2</sup> )
12	2.18	6.95	6.55	1.44	1.27	1.51 (5.9 × 10 <sup>-12</sup> cm <sup>2</sup> )
13	1.86	7.65	7.05	1.74	1.48	1.74 (6.8 × 10 <sup>-12</sup> cm <sup>2</sup> )

<sup>a</sup> See [23].

trostatic forces (and thus containing both terms dependent on polarizability and dipole moment), will be rather similar. Differences will exist only for very large internuclear separations (very high *n*), in the case of both polar and nonpolar ligands. As an extreme case, the relative cross sections for Na<sup>+</sup>-water (water:  $\mu = 1.84$  D,  $\alpha = 1.45$  Å<sup>3</sup>) was compared to Na<sup>+</sup>-benzene ( $\mu = 0$  D,  $\alpha = 10.4$  Å<sup>3</sup>); the potential energy curve for Na<sup>+</sup>-benzene was calculated to be similar to Na<sup>+</sup>-water [24]. See columns five and six in Table 2. IP-E<sub>e</sub> of column 2 is the calculated difference between the ionization potential of sodium and the electronic energy of the specific excited state of sodium. Although associative ionization cross sections depend on the width of the well, relative contributions will not vary for similar potentials.

The ratios of the two intensities derived from the experiments reported herein provide a measure of the distribution of energy states that can be accessed through the ligand-excited atom interaction, and hence are proportional to the relative extent of interaction of the respective systems being compared. In order to obtain a meaningful comparison in the present work, one ligand is chosen as the reference system and experiments with other selected ligands are made successively. Therefore, differences in the heating of the filament are effectively solved by this method. In principle, the values of the ratio are a direct measure of the relative extent of interaction of all the ion-ligand complexes to each other if there is a continuous and reproducible density of electronic states of the excited sodium species in the reaction region. Based on this assumption, referring to Table 1,

the order of the relative extent of interaction of sodium to each ligand are found to be dimethyloxyethane (DME) > benzene > Et<sub>2</sub>O > 1-propanol > ethanol > acetone > acetonitrile > *n*-butyl alcohol > methanol > ammonia. The trend of the relative extent of interaction of these ligands is generally consistent with the bond energies reported in the literature and presented in the second column of Table 3. Using the heated filament method, we cannot be certain that the distribution of energy levels are uniform, and so the ratios must be viewed individu-

Table 3

Experimental Na<sup>+</sup>-ligand binding energies; values listed in column 2 are  $-\Delta H^\circ$  values, which are nearly equivalent to the bonding energy (0.5 kcal/mol), DME = (CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), Et<sub>2</sub>O = (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>O; ligands are listed in decreasing order of relative extent of interaction as determined from these experiments.

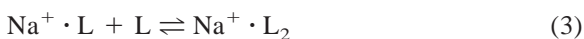
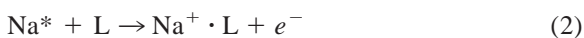
Ligand	Literature <sup>a</sup> (kcal/mol)	Armentrout and Rodgers <sup>b</sup> (kcal/mol)
DME	46.7	3.78 ± 0.9
Benzene	27.5 ± 1.5	21.1 ± 1.0
Et <sub>2</sub> O	30.5 ± 0.3	
1-Propanol		25.8 ± 1.0
Ethanol		24.4 ± 0.9
Acetone	32.9 ± 0.2	31.2 ± 1.0
CH <sub>3</sub> CN	(28.6–32.9) <sup>c</sup>	
<i>n</i> -butyl alcohol		26.1 ± 1.1
CH <sub>3</sub> OH	26.1 ± 0.2	21.9 ± 1.4
NH <sub>3</sub>	28.6 ± 0.4	24.4 ± 1.3
H <sub>2</sub> O	23.2	22.6 ± 1.8
CO <sub>2</sub>	15.4	
Ar		15.4

<sup>a</sup> See [5,9,30].<sup>b</sup> See [10].<sup>c</sup> Determined using the flowing afterglow technique [4].

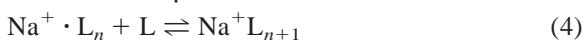
ally, namely considering which systems have stronger or weaker interactions with a selected ligand compared to the  $\text{Na}^+$ –benzene reference system. It is important to note that the measurements made in the flow tube were found to be independent of the concentration of the ligand, demonstrating as expected that the associative ionization is a function of the strength of the interaction potential and not dependent on the reaction kinetics.

Several other reactant gases than those listed in Table 1 were studied but were found not to react in the flow tube with excited sodium species. These include water, argon, carbon dioxide, and ethylene. Argon, carbon dioxide, and ethylene were added into the flow tube through a reactant gas inlet undiluted from their respective lecture bottles. Water vapor was added to the flow tube via a heated reactant gas inlet, which is located 30 cm downstream of the source, by heating a closed vessel containing water to boiling, and flowing a controlled amount of a helium carrier gas across the water sample. Adding water through the reactant gas inlet did not allow for reactions with excited sodium species, and thus we infer that this lack of ionization of sodium is due to the comparatively weak binding energy of water to the sodium ion.

We have in the past used the same technique to produce sodium water cluster ions using a fast flow reactor coupled to a high pressure ion source [4,25–27].  $\text{Na}^+(\text{H}_2\text{O})_n$  cluster ions were formed by reactions between sodium species and a specific amount of water vapor introduced in the source. When a reactant gas is added to the ion source, excited sodium species are effectively depleted, which leads to the formation of cluster ions by the following reaction mechanism:



⋮



L is the reactant gas that is added to the source. When the reactant gas is added in the source, all of the excited sodium species are depleted, leading to the

formation of  $\text{Na}^+ \cdot \text{L}$ . This cluster ion,  $\text{Na}^+ \cdot \text{L}$ , can then cluster with the remaining reactant gas leading to larger cluster ions. Sodium ions were not detected when there was no reactant gas added into the helium buffer gas.  $\text{NH}_3$ , and  $\text{CH}_3\text{OH}$  were used as reactant gases and were found to associate with sodium ions within the source, as well [4].

Sodium species formed by the thermal evaporation of a heated filament are formed in excited states and thus the respective Rydberg states of fairly long lifetime are formed. The radiative lifetime of the Rydberg states increases with the third power of the principal quantum number [28]. The drift time from the ion source to the interaction region is in the neighborhood of a millisecond and thus the population of the lower lying excited states will be considerably depleted before the atoms reach the interaction region where the reactant gas inlet is located.

The population of the Na excited states will also be influenced by collisional quenching, especially in the high-pressure region of the ion source. The cross section for collisional quenching of Rydberg states by  $n, l$ -changing and  $l$ -mixing processes is known to increase with  $n$  (for  $4 < n \leq 10$  by a factor of about 10) and then to decrease very slowly for  $n > 10$  [29]. Thus, long-lived Rydberg states of  $\text{Na}^*$  in the reaction zone may be expected to be depleted by radiative transitions (short lifetimes,  $n < 5$ ) and by collisional quenching ( $n > 8$ ) by the helium buffer gas ( $10^5$  collisions).

In order to shed further light on the relative strength of the interaction of water compared to benzene with  $\text{Na}^+$ , we conducted another series of experiments in which the reactant gas (benzene or  $\text{H}_2\text{O}$ ) was added into the source region in individual separate experiments. Under these conditions, the short residence time ensured the survival of higher Rydberg states of sodium, enabling interaction with the surrounding ligand molecules. Under these conditions, experiments did display the formation of sodium cluster ions that is a result of associative ionization of excited sodium species with the respective reactant gas [see reactions (2)–(4)]. However, the ratio of  $\text{Na}^+$ –water to  $\text{Na}^+$ –benzene was far less than one, providing further evidence that the bonding

Table 4

Relative extent of interaction of Na<sup>+</sup> as determined in the source; ligands are listed in decreasing order of relative extent of interaction as determined in the flow tube

Ligand	Average value of $\Sigma_n I_n[\text{Na}^+(\text{ligand})_n]$
CH <sub>3</sub> OH	11 960 ± 22%
NH <sub>3</sub>	7 732 ± 27%
D <sub>2</sub> O	4 997 ± 22%

energy of benzene to Na<sup>+</sup> is considerably greater than that for H<sub>2</sub>O. This finding is consistent with the bond energy values tabulated in column two of Table 3 and the failure to detect the Na<sup>+</sup>·H<sub>2</sub>O ions with reactions of the lower energy Rydberg states present in the flow tube. The helium buffer gas effectively quenches the higher energy states of the excited sodium by the time that is required for the excited sodium species to reach the reactant gas inlet.

NH<sub>3</sub>, D<sub>2</sub>O, and CH<sub>3</sub>OH were added to the source in individual separate experiments under the same filament conditions. The total Na<sup>+</sup>(L)<sub>n</sub> ion intensity was found to increase in the following order: Na<sup>+</sup>(D<sub>2</sub>O)<sub>n</sub> < Na<sup>+</sup>(NH<sub>3</sub>)<sub>n</sub> < Na<sup>+</sup>(CH<sub>3</sub>OH)<sub>n</sub>. See Table 4. This result is consistent with findings obtained by adding the ligand gas at the reactant gas inlet where the lower energy states of excited sodium exist. Acetone, benzene, and water were also added to the source in another series of individual separate experiments under the same filament conditions. The order of Na<sup>+</sup>(L)<sub>n</sub> ion intensity was found to increase as follows: Na<sup>+</sup>(H<sub>2</sub>O)<sub>n</sub> < Na<sup>+</sup>(acetone)<sub>n</sub> < Na<sup>+</sup>(benzene)<sub>n</sub>. See Table 5. These source experiments are consistent with the experiments performed in the flow tube and with the trend of binding energies given in the second column of Table 3. The relative

Table 5

Relative extent of interaction of Na<sup>+</sup> binding energies as determined in the source

Ligand	Average value of $\Sigma_n I_n[\text{Na}^+(\text{ligand})_n]$
Benzene	4322 ± 15%
Acetone	4063 ± 4%
H <sub>2</sub> O	1901 ± 12%

extent of interactions between Na<sup>+</sup>(acetone) and Na<sup>+</sup>(benzene), determined in these experiments, are very similar. From repetitive experimental sets of data, we would occasionally see a reversal of relative extent of binding but the average of total set of experiments would show Na<sup>+</sup>(benzene) to be more strongly bonded than Na<sup>+</sup>(acetone). In the high-pressure mass spectrometry experiments, the binding energy of Na<sup>+</sup>(acetone) and Na<sup>+</sup>(benzene) are relatively large and are closer to each other in strength, whereas Na<sup>+</sup>(H<sub>2</sub>O) would not be expected to have as large a binding energy. The source experiments are not consistent with the guided ion beam mass spectrometry results presented in the third column of Table 3. Experiments performed using the guided ion beam mass spectrometer would predict the binding energy of Na<sup>+</sup>(benzene) to be comparable to Na<sup>+</sup>(H<sub>2</sub>O).

#### 4. Conclusions

We have provided new insights into the thermochemistry of sodium ions with various ligands. The fact that we did not observe associative ionization of sodium in interactions with water in the flow tube provides further evidence that water binds to sodium ions weakly compared to species like benzene. The stronger binding of sodium ions to benzene relative to water is in agreement with the findings of Kebarle and co-workers who studied the binding of potassium ions with water and benzene [30,31]. In this paper, we have avoided concluding that our findings establish the exact order of bonding of sodium ions to various ligands. Instead, we take the approach of providing the scientific community with some interesting findings that need to be considered in conjunction with the differing findings of binding energies reported between experimental groups at various laboratories as well as the differing binding energies found by various theoreticians.

In the process of studying excited sodium species with various ligands, we investigated other alkali metals (lithium, potassium, and cesium). These alkali metal ions were prepared in a similar manner as the

sodium filament. We found that lithium and potassium filaments produced excited species, whereas cesium did not. In the lithium experiments, H<sub>2</sub>O, benzene, acetone, and CH<sub>3</sub>CN were added separately to the source. Lithium was found to undergo associative ionization with acetone and CH<sub>3</sub>CN, but not with H<sub>2</sub>O or benzene. We believe that this finding is due to the stronger binding energies of Li<sup>+</sup> with acetone (45 kcal/mol) and CH<sub>3</sub>CN (43 kcal/mol) compared to H<sub>2</sub>O (34 kcal/mol) and benzene (38 kcal/mol) [32,33]. The relative extent of interaction as found by the lithium source experiments follow the same order of binding energies determined by ion cyclotron resonance spectroscopy. Finally, the ionic composition of the atmosphere may be affected by associative ionization processes occurring by the presence of meteoritic sodium with atmospheric species that have a strong binding affinity to sodium ions.

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