Chem. Rev. **2000,** *100,* 4023−4037

Charge Separation in Molecular Clusters: Dissolution of a Salt in a Salt−(Solvent)$_n$ Cluster

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Received January 12, 2000

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A. Introduction

The scope of this paper is to review experimental and theoretical studies on charge separation in mixed salt−polar solvent clusters.

Since the development of supersonic jets, molecular clusters have been widely used to monitor the evolution of matter properties from isolated molecules to the condensed phases.[1,2]

Among the solvation processes, charge separation induced by solvents is one of the simplest and most important processes in nature. Solvation effects on atoms,[3−15] molecules,[16,17] or ions [18−117]—and particularly alkali-metal cations[67−76,83−91,97−99,108−112] and halogen anions[21−40,83−84,86−98,100,102−107,114−116]—have long been studied in clusters to follow step by step the variation of physical and chemical properties of a system as the number of solvent molecules increases.

The related subject of intermolecular charge transfer in van der Waals complexes (donor−acceptor complexes excited on the one part (A*−D or A−D*) where the electron is transferred with formation of an ionic A^-−D^+ species) has already been recently reviewed and will not be treated here.[117,118] Bichromophores, in which the donor and acceptor are linked by a rigid, semirigid, or flexible aliphatic bridge (D−B−A), represent the exact intermediate between inter- and intramolecular electron transfer. Electron transfer processes in isolated jet-cooled bichomophores, which have received thorough attention, have been extensively reviewed recently.[119−122]

However, little work has at present been devoted to solvation of simple ion pairs or salts in clusters where a neutral molecule which has an ion pair structure in the ground state (Na^+Cl^-, for example) separates into two solvated ions: Na^+−(solvent)$_m$···Cl^-−(solvent)$_p$. The acronyms CIP, for Contact Ion Pair, and SSIP, for Solvent-Separated Ion Pair, will refer to structures where the positive and negative ions stay in contact (Na^+Cl^-−(solvent)$_n$) and structures where the two ions are separated by solvent molecules Na^+−(solvent)$_m$···Cl^-−(solvent)$_p$.

This process is very fundamental in nature and plays an important role in environmental and atmospheric chemistry, both in the formation and chemistry of aerosols[123−129] and in the mechanism of cloud saturation using silver salts to make rain.[130−133] It also has more practical interests, especially for cooking.

There has been a lot of fascinating work on charge separation in solutions, which will not be presented here, except for comparisons with clusters. In particular, in all schoolbooks, it is written that NaCl in water separates into Na^+ and Cl^- ions surrounded by water molecules. From simple saturation concentration arguments, it can be derived that at 300 K about nine water molecules per salt molecule are necessary to dissolve NaCl in water and only about five for NaI. On the other hand, coordination numbers (which correspond to the number of solvent molecules in the first solvation shell of an ion in solution) have been derived for a sodium cation in water and a Cl^- or I^- anion in water: for Na^+ the coordination number is 4 or 6 depending on the concentration;[134,135] for Cl^- or I^- it is 6.[29,135,136]

All these estimates correspond to mean values over a macroscopic ensemble at room temperature. From the coordination numbers quoted above, it seems that

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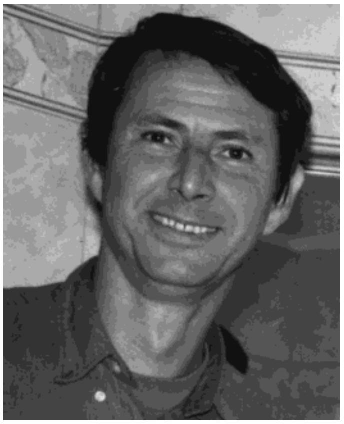
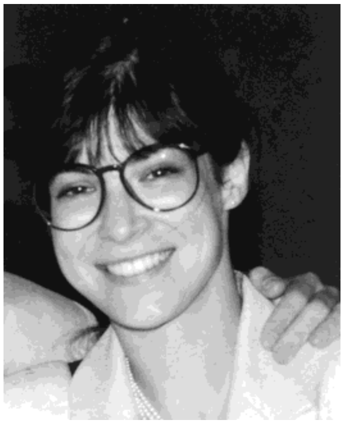
10.1021/cr990059s CCC: $35.00

Claude Dedonder-Lardeux, born in France in 1950, graduated in chemical physics at the University of Orsay in 1976, working on energy transfer between aromatic molecules. Her "thèse d'état" was on photodissociation of polyatomic molecules. She is presently Research Director at the CNRS and works on chemical reactivity and solvation effects in molecular clusters.

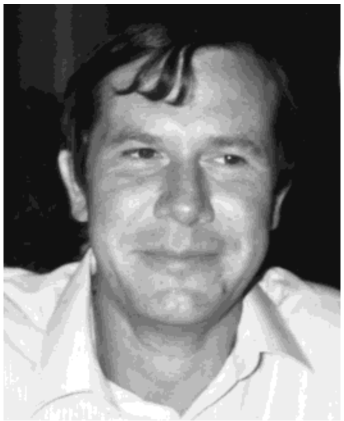
Gilles Grégoire was born in 1972 near Paris and obtained his Ph.D. in Physics from the University Pierre et Marie Curie of Paris in 1999, working on the charge separation of NaI in polar solvent clusters. His research interests focus on solvation and reactivity in molecular clusters using time-resolved experiments.



Christophe Jouvet, born in France, in 1954, graduated in physics at the University of Orsay, with a Ph.D. in 1980 (electronic relaxation of glyoxal in a supersonic jet), and his "thèse d'état" was completed in 1985 (reactivity and electronic relaxation in mercury van der Waals complexes). He spent one year in 1981 as a postdoctoral fellow at the James Franck Institute (University of Chicago) with Prof. S. A. Rice and worked with Prof. J. P. Simons at the University of Nottingham in 1987. He is Research Director at the CNRS, working in the field of van der Waals complexes and molecular clusters.



Séverine Martrenchard, born in 1969 in France, obtained her Ph.D. in chemical physics from the University of Orsay in 1993, studying the solvation and reactivity in molecular clusters. Her main interest is the study of ion–molecule reaction in clusters using multiphoton ionization or one photon with synchrotron radiation. She is presently "chargée de recherches" at the CNRS.



Daniel Solgadi, born in 1948 in Algeria, was "directeur de recherches" at the CNRS. He studied organic chemistry at the University of Orsay, where he obtained his Ph.D. in 1973, studying the chemical reactivity of brominated compounds and completed his "thèse d'état" in 1976 on relations between molecular structure and reactivity. He started to work in the field of mass spectrometry and photoelectron spectroscopy in organic chemistry, and then moved to the chemical physics world to work first on photodissociation dynamics and afterward on chemical reactivity in clusters. D. Solgadi died on Feb 10, 2000. He was for more than 10 years not only the most enthusiastic but also the friendliest co-worker of the authors above.

charge separation could well be observed in rather small clusters, but temperature effects may affect this expectation. We may ask the simple questions: What happens on the microscopic scale? How many solvent molecules will be necessary to dissociate the salt in a separated ion pair? Will this solvated ion pair be stable, or will the cluster break? What governs the charge separation: energy, entropy, ...? This is exactly the same line as followed in the case of excited-state proton transfer, where a number of studies have been devoted to the characterization of the mechanism in molecular clusters in model cases such as phenol or naphthol solvated by water or ammonia.[137−161]

For simple systems, two main aspects have been studied in this field, the charge separation of salt and the acid dissociation. We will here focus on the first case, where the cluster can be considered as purely a solvent stricto sensu, and no chemical reaction occurs in the charge separation process. In the case of acids,[162−175] a proton is released that reacts with the solvent molecules, for example, to form the hydronium ion when water is the solvent. This makes the interpretation more complicated, and in particular the role of tunneling cannot be neglected.

Moreover, in the case of salts, the absorption (in particular for NaI, which has a low energy and quasi-stable excited state) is optically accessible by laser and information about charge separation can be gained through laser spectroscopy.

B. Methodology

a. Experimental Aspects

Experimental studies involving step by step solvation in molecular clusters rely on mass spectroscopic detection to analyze the cluster size. Therefore, many studies have been done on either positively charged or negatively charged solvated clusters. When the charge separation in a neutral cluster is studied, an ionization step is necessary.

Only a few experiments have been done on neutral clusters containing a salt molecule, and in each case the ionization scheme is different. Three techniques have been used: laser desorption/ionization from a liquid beam,[176,177] ionization and charge separation through cluster impact on a surface,[178] and conventional multiphoton ionization starting from neutral salt−(solvent)$_n$ clusters.[179−181]

In the first type of experiment, a liquid beam is introduced into vacuum[182−187] and irradiated with an ultraviolet laser. Ions are ejected from the liquid surface and detected by a time-of-flight mass spectrometer.[176,177,187]

The second experiment uses a beam of neutral clusters of polar molecules, which, after collision with a surface, produce fragment ions, either positive or both positive and negative depending on the polar molecule used.[178,188−192]

In the last case, resonance-enhanced multiphoton ionization (REMPI) of neutral salt−(solvent)$_n$ clusters, analyzed by time-of-flight mass spectrometry, is used to question the nature of the electronic states of the salt and the evolution with cluster size. A conventional experimental setup for REMPI can be divided into three parts: generation of clusters in a supersonic expansion, excitation and ionization of the clusters with lasers (either one or two colors can be used with nanosecond, picosecond, or femtosecond time resolution), and detection of the ions (parents and fragments).[179−181] The difficulty in such an experiment is to produce cold molecular clusters doped with a salt molecule. This was overcome by adding a small oven after the normal pulsed nozzle. Two types of ovens have been used so far. In the first case, a pickup cell heated at 600 °C is located 1 cm downstream from the valve and NaI is pushed by an argon flow into the ionization region of the mass spectrometer. Only very small cluster sizes can be observed with this setup.[193] In the second setup, a small oven is attached to the valve and the carrier gas flow (helium or argon) passes through the oven heated at 450 °C before expansion through a 1 mm aperture hole. Under these conditions, larger clusters (up to $n = 60$) can be produced in the expansion.[179]

b. Theoretical Aspects

Theoretical investigations on salt−(solvent)$_n$ clusters have been conducted through many models: ab initio methods,[194−196] or mixed ab initio/model potential[197] for small clusters, Monte Carlo growth methods[198−201] or Molecular Dynamics Simulations for larger ones.[202−204] In the latter procedure the temperature effect can be taken into account but the potentials used have to be simpler than full ab initio potentials.[197−202]

C. REMPI Studies of Salt Dissolution

a. What Are the Changes Expected?

What changes are expected, especially on the spectroscopic properties of the system when dealing with REMPI studies, which can reveal the charge separation process?

Let us take as an example the prototype NaI system to illustrate these expectations. The relevant potential energy curves for the isolated molecule are presented in Figure 1a: in alkali-metal halides, the ionic Na^+I^- ($X\ ^1\Sigma_0{}^+$) ground state crosses the covalent $\Omega = 0^+$ and $\Omega = 1$ excited states correlating to the asymptotic Na $^2S_{1/2}$ + I $^2P_{3/2}$ limit (the crossing point, represented by a black point in the figure, is located at an internuclear distance of 7 Å in NaI). For symmetry reasons, only the $\Omega = 0^+$ state is coupled to the ground state. When the interaction is strong, as in NaI, a trapping well is formed, which is represented here by the adiabatic A state. In a classical REMPI experiment, an initial pump pulse (λ_{pump}) excites NaI to the A state, which can be probed

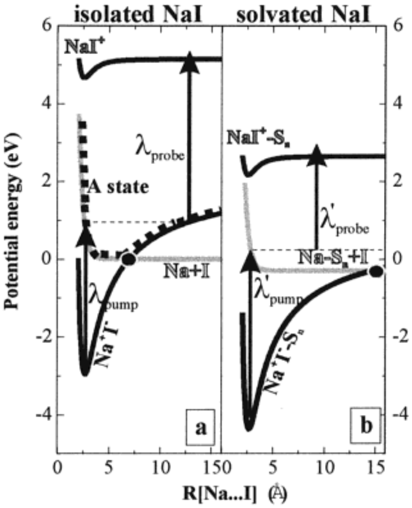


Figure 1. Scheme of the evolution of sodium iodide potential curves from the isolated molecule (left) to NaI solvated by a few polar molecules (right). In the solvation process, the ground and ionic states are more stabilized than the first excited state, leading to a large blue shift of the A ← X absorption transition and a red shift of the D_0 ← A transition. Another consequence of the different stabilization of the ground and excited states is that the crossing point will be at larger internuclear distance and the coupling between the two diabatic states will then be very weak. A fast dissociation along the covalent curve is then expected, leading to the production of Na−(solvent)$_m$ + I−(solvent)$_p$ fragments.

by ionization with a second laser pulse (λ_{probe}) to the NaI^+ state correlating to the $Na^+ + I$ limit. This A state is one of the benchmark cases for studying the wave packet evolution.[205]

1. Solvation-Induced Transition Shifts

Let us first assume that, in small clusters, there is no charge separation, i.e., that NaI stays as a contact ion pair, Na^+I^-, in the ground state. The solvation energy is expected to be greater for the ion state because the interaction will be charge−dipole and for the ground state which has a strong dipole moment (9.2 D)[206] than for the excited covalent A state. This leads to a strong stabilization of the Na^+I^-−(solvent)$_n$ ground state with respect to the excited state, together with a destabilization of the excited state with respect to the ion state. In other words, there will be a large blue shift of the A ← X absorption transition and a red shift of the D_0 ← A transition.

Another consequence of the different stabilization of the ground and excited states is that the crossing point will be located at larger internuclear distance (see Figure 1b). The coupling between the two diabatic states will then be very weak, and we expect a fast dissociation along the covalent curve, leading to the production of fragments: Na−(solvent)$_m$ + I−(solvent)$_p$ as long as the time scale of the laser pulses is greater than the dissociation time, which has been calculated to be around 200 fs for NaI−H_2O.[204] As the number of solvent molecule increases, the ion pair state will cease to cross the excited state, which will then become purely repulsive as calculated for the liquid.[207]

2. Oscillator Strengths

In a crude approximation the A ← X transition is due to an electron transfer from the I^- (in the Na^+I^- (X) ground state) toward the sodium atom in its ground 3s state (in the NaI A covalent excited state). The transition moment is proportional to the overlap of the electronic wave functions of I^- and Na (3s $^1S_0$) and is therefore expected to be strongly dependent on the Na···I interatomic distance. As long as the NaI molecule stays as a contact ion pair, the transition probability may be little affected. However, if charge separation occurs, and especially when solvent molecules insert between the two ions, the transition probability will decrease considerably as shown in Figure 2. This suggests that vanishing excitation efficiency might be considered as an indication of charge separation in the cluster.

b. Spectroscopic Characterization

The evolution of the A ← X transition with solvation has been measured for NaI−(solvent)$_n$ clusters, with the solvent being water, ammonia, and acetonitrile,[180] and two main points arise.

(i) The first solvent molecule induces a strong blue shift of the A ← X transition of the order of 1 eV (0.8 eV for NH_3, 1.1 eV for water and CH_3CN). The electronic shift is in agreement with theoretical calculations.[204]

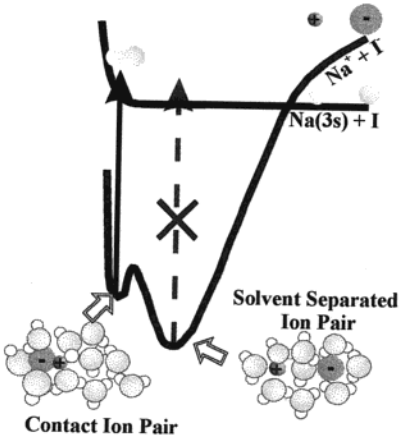


Figure 2. Expected potential curves for NaI in a large cluster: the two configurations CIP and SSIP have similar energies. In the CIP conformation, the transition from the ground state to the first excited state is allowed. In the SSIP structure, the transition moment, which corresponds to an electron transfer from I^- to Na^+, is expected to be smaller due to the presence of solvent molecules between the two ions.

(ii) For each solvent, there is only a weak dependence of the absorption region on cluster size for $n > 1$. The weak size dependence of the NaI−(solvent)$_n$ absorption threshold is more unexpected as compared to the case of Na−(solvent)$_n$ clusters, where the ionization potential decreases with the cluster size, at least for the small complexes. In these clusters, since the Na···solvent intermolecular distances in the ground and ionic states are similar, ionization corresponds more or less to an adiabatic transition, and the enthalpy change between the two states can thus be determined by the measurement of the ionization potential. But in the bare NaI molecule, the Na···I equilibrium distances in the ground and excited states are strongly different, 2.72 and around 4.5 Å, respectively, and the Franck Condon region is localized on the repulsive wall of the excited state. The A ← X transition thus corresponds to a vertical transition, and the enthalpy change between the NaI ground and excited states cannot be accessed.

All the structures calculated for salts in clusters in the ground state[194−197,199−201] have outlined a slight enhancement of the Me^+−X^- equilibrium distance even if the two ions stay in contact. This implies that the Franck−Condon region will move to larger NaI internuclear distances, allowing an excitation transition to a lower part of the repulsive wall of the excited state. This effect could cancel more or less the expected blue shift of the A ← X transition with the cluster size for $n > 1$ and might explain the weak size dependence in the absorption threshold.

c. Mass Spectra

Mass spectra have been recorded for different salts, NaI, RbI, CsI, and different solvents, water, ammonia, acetonitrile, methanol, dimethyl ether.[179−181,208]

For each solvent, several mass spectra have been reported for different backing pressures of the buffer gas (argon or helium). As an example of characteristic results, the mass spectra obtained for CsI with two solvents, H_2O and CH_3CN, are shown in Figure 3.

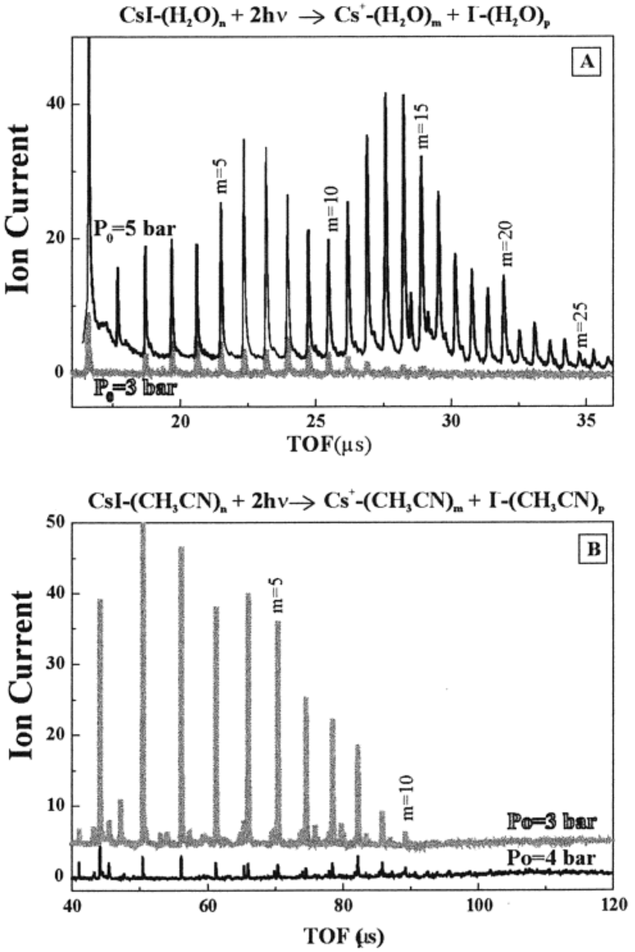


Figure 3. Typical mass spectra obtained after two-photon ionization of salt−(solvent)$_n$ clusters. Here the salt is CsI, the carrier gas is helium, the laser wavelength is 235 nm and the oven temperature is 300 °C. A) When water is the solvent, an increase of the backing pressure from 3 bar (bottom) to 5 bar (top) induces an increase in the signal, and the mean cluster size shifts to larger masses. (B) When CH_3CN is the solvent, at low pressure (3 bar), $Cs^+(CH_3CN)_m$ clusters up to $m = 10$ are detected (top). At higher pressure (4 bar), the signal vanishes and no larger clusters are observed (bottom). Large clusters are probably present in the expansion but not excited.

concentration).[179,208] This is illustrated in Figure 3b for $CsI-(CH_3CN)_n$ clusters, which can be compared to the $CsI-(H_2O)_n$ clusters presented in Figure 3a. In the latter clusters, for the lower pressure (helium, 3 bar), the ion current intensity decreases with the cluster size from 8 water molecules to the largest detected ions, i.e., $n = 15$. When the backing pressure is raised to 5 bar, the mean cluster size is shifted to larger masses, $n = 14$, the ion current intensity increases, and $Cs^+-(H_2O)_n$ ions can be observed up to 30 water molecules. Conversely, for $CsI-(CH_3CN)_n$ clusters, the ion current is larger at the lower pressure and only clusters up to $n = 10$ are clearly observed. The increase in backing pressure only leads to a global decrease of the signal on all masses, and clusters larger than $n = 10$ are no more clearly detected than at lower pressure.

A common feature to all the spectra recorded is that MeI^+-(solvent)$_n$ clusters are never observed (Me stands for Na, Rb, or Cs). This is due to the dissociative character of the excited state and the decrease of the coupling in the avoided crossing, leading to the disappearance of the quasi bound state. Thus, only Me^+-(solvent)$_n$ fragments are detected.

The spectra are characterized by rather different mass distributions when different solvents are used under similar experimental conditions. For water clusters as well as for methanol clusters, large fragments are observed: $Na^+-(H_2O)_n$ are observed up to $n = 60$ [179], $Cs^+-(CH_3OH)_n$ up to $n = 25$. The maximum cluster size is in this case limited by the expansion conditions due to experimental problems (limitation of the backing pressure, clogging of the valve and the nozzle, ···).

When ammonia, acetonitrile, or dimethyl ether is the solvent, no large clusters can be observed, whatever the conditions (higher backing pressures and

Usually, increasing the backing pressure before the supersonic expansion will induce a shift of the cluster size distribution to larger masses. As a matter of fact, by changing the backing pressure, the ion product distribution Me^+-(solvent)$_n$ coming from the ionization of $MeI-$(solvent)$_n$ should be shifted to larger mass peaks, while the ion current intensity of the lighter masses should decrease. This is clearly observed for water clusters.[181] However, for ammonia, dimethyl ether, or acetonitrile clusters, by doubling the backing pressure, the ion current intensity of the lighter masses decreases as expected but no heavier ions are detected.

Since the photon energy is sufficient to ionize the fragments,[6,14] this result outlines the decrease of the A ← X excitation efficiency in large ammonia, acetonitrile, or DME clusters. As already stated, this may be seen as an indication of charge separation of the salt within the clusters; i.e., a few solvent molecules insert between the two ions.

It is however intriguing that charge separation would occur in ammonia and acetonitrile for a small number of solvent molecules (7 for $NaI-CH_3CN$, 10 for RbI and $CsI-CH_3CN$, and around 10 for $NaI-NH_3$) and would not occur in water even in clusters containing as many as 60 molecules. The numbers given above are just indicative; they correspond to the last peak clearly seen in the mass spectra, but the parent cluster can be larger: in the excitation of the salt occurring on a dissociative state, a large amount of energy is released in the cluster, which may lead to evaporation of one or two solvent molecules.

The difference between solvents might be due to the cluster structure: water forms strong hydrogen-bonded networks, and the salt molecule might stay on the surface of these clusters, while acetonitrile and DME are aprotic solvents, where the salt can be inside. Ammonia clusters also form hydrogen bonds, but weaker than in water clusters, and MeI could be inside the cluster in this case also: this is what is found for a sodium atom interacting with water and ammonia.[108,109] This question of different cluster structures favoring or not charge separation may be addressed in two ways: through theoretical investigation of cluster structure, and through the photodissociation dynamics of $MeI-$(solvent)$_n$ clusters,

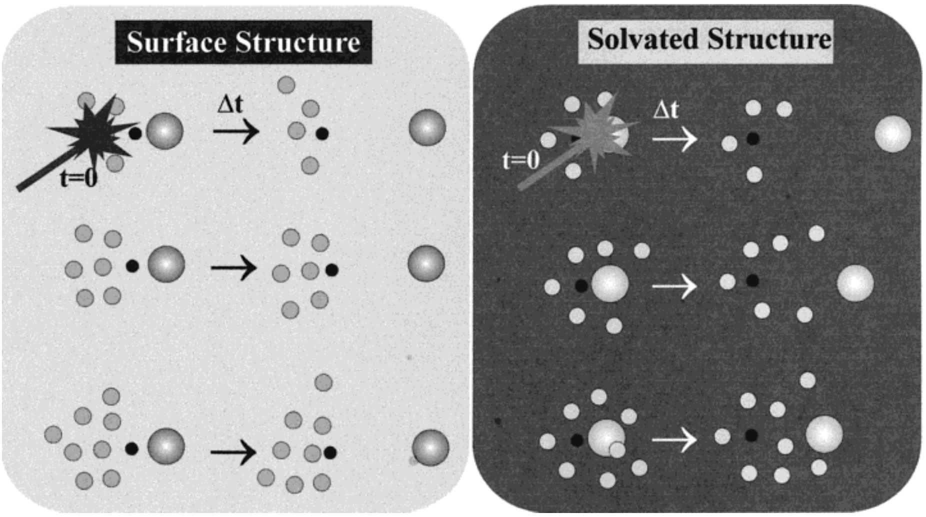


Figure 4. Effect of the cluster structure on the excited-state dissociation of a salt molecule. For small sizes, two kinds of clusters seem to exist. Left: For clusters with surface structure, the salt dissociation is not strongly modified by the solvent (water case). Right: For more solvated structures, the solvent perturbs the dissociation.

where a different behavior is expected if the solute is inside or on the surface of the cluster. In the latter case, the photodissociation dynamics should not depend too much on the cluster size, while in the former case, each solvent molecule will interact closely with the solute and the cluster size dependence should be very pronounced as illustrated by the scheme in Figure 4.

d. Photodissociation Dynamics as a Structural Probe

What are the dynamical processes probed in femtosecond experiments? Let us point out a few important points on femtosecond pump−probe experiments with ion detection in particular when clusters are studied.

(i) In all pump−probe experiments, the time evolution signal observed can only reflect the dynamics in the probed excited state. Time constants of all processes occurring in the final state, in this case the ionic state, cannot be directly addressed by this method.

(ii) A dynamical process occurring in an excited state will only be observable in the ion signal if there is some variation of the ionization cross section. This is a tautology. However, evaporation processes are known to play a major role in the ion states of clusters, and one has to be aware that if similar processes are occurring for sizes $n - 1$, n, and $n + 1$, evaporation may completely mix up the assignment of an observed mass peak to a neutral precursor, especially if there is no variation of the ionization cross section with cluster size.

(iii) A last point which has to be kept in mind is that the time evolution of the ion signal reflects not only the excited-state dynamics but also the way to probe it. In other words, the excited-state dynamics may look completely different if different probe schemes are used.[209]

In the femtosecond dissociation studies of NaI in a solvent cluster, no $\mathrm{NaI^+{-}(solvent)}_n$ ions are detected in the time-of-flight mass spectrometer, as on the nanosecond time scale, and no recurrences on the $\mathrm{Na^+{-}(solvent)}_n$ signals can be seen, conversely to what has been observed for the bare NaI molecule.[180,181] This is in agreement with the expectation of excitation located on the repulsive wall of the $\mathrm{NaI{-}(solvent)}_n$ excited state: a few femtoseconds after the pump pulse, the kinetic energy transferred on the NaI coordinate, which will be conserved in the ion state after ionization, first induces the lengthening of the NaI bond in the $\mathrm{NaI{-}(solvent)}_n$ parent. As the avoided curve crossing occurs at large internuclear distance where the ionic−covalent coupling (V_{12}) is very weak, there will be a complete bond breaking of $\mathrm{NaI(A){-}(solvent)}_n$ into $\mathrm{Na{-}(solvent)}_n$. Thus, excitation of NaI within the cluster should lead to a rapid decrease of the parent population ($\mathrm{NaI^*{-}(solvent)}_n$) and a correlated increase of the fragment population ($\mathrm{Na{-}(solvent)}_n$).

But this is not the end of the process. The excitation process brings around 1 eV of excess energy in the clusters: in $\mathrm{NaI{-}H_2O}$, with a 250 nm pump laser wavelength, the excess energy has been evaluated to be 1.6 eV, with 1.2 eV in the NaI coordinate and the rest in the solute−solvent coordinate,[204] and the amount of excess energy should decrease with the cluster size (as the ground state is more stabilized than the excited state, for the same photon energy the excess energy should become smaller as the cluster size increases). If the dissociation is seen as an impulsive bond rupture between sodium and iodine, around 80% of the excess energy will be carried out by the Na atom colliding with the solvent cluster and will be redistributed as internal energy in the $\mathrm{Na{-}(solvent)}_n$ clusters. Hot fragment clusters are thus produced in the excitation/dissociation process, which will have to evaporate solvent molecules to cool down. This is illustrated in the upper part of Figure 5, where the excitation laser induces rupture of the NaI bond and evaporation of solvent molecules. The lower part of Figure 5 illustrates the ionization step: at very short delay times between excitation and ionization, a hot $\mathrm{NaI{-}(solvent)}_n$ can be ionized but the energy in the cluster will lead to the $\mathrm{Na^+{\cdots}I}$ bond rupture, leaving a hot $\mathrm{Na^+{-}(solvent)}_n$ cluster which can further evaporate a neutral solvent mono-

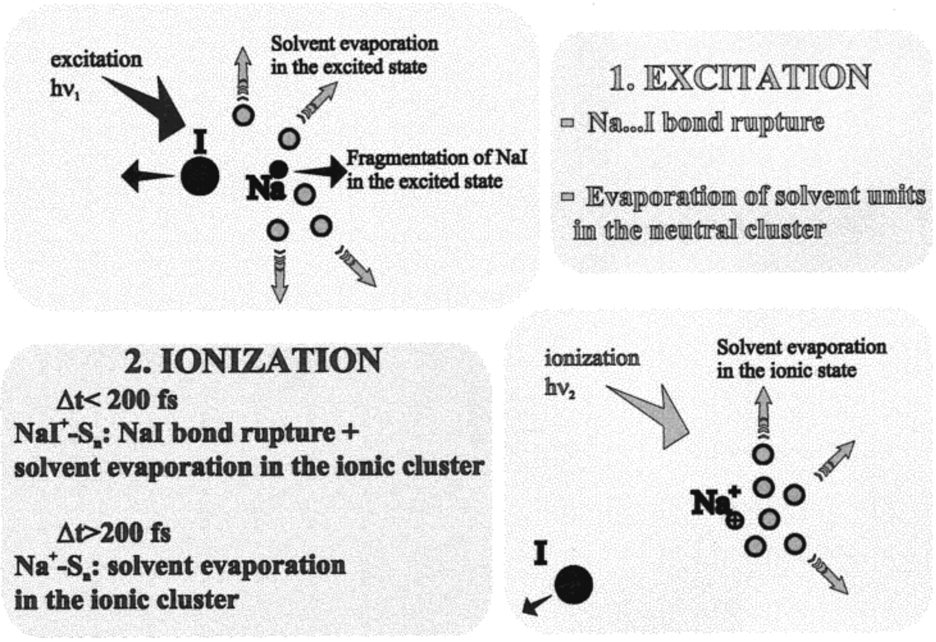


Figure 5. Scheme of the femtosecond dissociation of the salt in a polar cluster. Top: The pump laser excites the salt within the cluster into a dissociative state with a large excess energy. Hot fragments are produced, which will evaporate monomer units to cool. Bottom: At short delay times between the pump and probe, a hot NaI−(solvent)$_n$ can be ionized, but the energy in the cluster will lead to the Na$^+$···I bond rupture, leaving a hot Na$^+$−(solvent)$_n$ cluster which can further evaporate a neutral solvent monomer. At longer delays between the pump and probe, a hot Na−(solvent)$_n$ cluster will be ionized which will also tend to evaporate in the ionic state.

mer. At longer delays between the pump and probe, a hot Na−(solvent)$_n$ cluster will be ionized which will also tend to evaporate in the ionic state.[180]

From the femtosecond study of the evaporation of one NH$_3$ from hot NaI−(NH$_3$)$_n$, using a one-photon ionization step (305 nm),[180] it has been clearly demonstrated that when a bond rupture (NaI dissociation, solvent evaporation) can happen in both the excited state and in the ionic state, the following law must be applied: *The evaporation dynamics is observed only if the ionization cross section changes with cluster size.*

Indeed, starting from a NaI−(solvent)$_{n+1}$ excited cluster, two pathways lead to the detection of the same final ionic fragment Na$^+$−(solvent)$_n$: the AID (for absorption ionization dissociation)[210−212] and ADI (absorption dissociation ionization)[213−215] channels already proposed in the study of ammonia clusters. To understand the observed signal, the relative efficiencies of these two channels have to be compared. If the ionization cross section is independent of the cluster size, the evaporation in the ionic state hides the dynamics in the excited state, and the resulting ion signal will be constant in time. Conversely, when the ionization cross section increases with the cluster size, the time-dependent signal recorded on the Na$^+$−(solvent)$_n$ ion exhibits an exponential decay, reflecting the higher contribution of the ionized hot neutral population at size $n + 1$ as compared to the cold neutral population at size n.[180]

The dynamics observed on the Na$^+$−(NH$_3$)$_{n=2-6}$ masses as a function of the time delay between the pump and probe lasers in the case of resonant two-photon ionization with the same pump wavelength and the probe set at 610 nm is presented in Figure 6B. The probe energy is exactly the same as in the previous case (one 305 nm probe photon), but the signal on the Na$^+$−(NH$_3$)$_n$ masses exhibits biexponential decays with different time constants, on the order of 200 fs and 20 ps,[181] as can be clearly seen on the right side of Figure 6 for the cluster $n = 4-6$.

The signals for water, Na$^+$−(H$_2$O)$_{n=4-7}$, have been reported in Figure 6A. A small rise time is observed that decreases with the cluster size, without any particular dynamics afterward, the signal remaining constant on the time scale of the experiment. As pointed out above, this corresponds to absence of variation of the ionization cross section with the cluster size.

This can be related to a different aggregation of the water molecules to the cluster for sizes $n \geq 4$. Instead of arranging around the NaI molecule, the water molecules rather stick on the water cluster side, at the opposite of the solute. In such a structure, the solvation effects on the NaI and Na excited states should be rather small and no size effect on the ionization cross section is expected to occur. Therefore, the femtosecond dissociation experiments seem to indicate that the salt stays out of the water cluster whereas for ammonia the salt tends to be encapsulated in the ammonia cluster. This effect might be due to the method of producing the clusters and is certainly also linked to the temperature of the cluster.

D. Charge Separation Studied in a Liquid Beam

Charge separation has also been studied in the case of salts, NaI and CaI$_2$, in ethanol solutions, through evaporation of cluster ions from the surface of a liquid beam.[176,177]

A solution of NaI in ethanol is expanded in the vacuum, and the interaction with a pulsed laser at

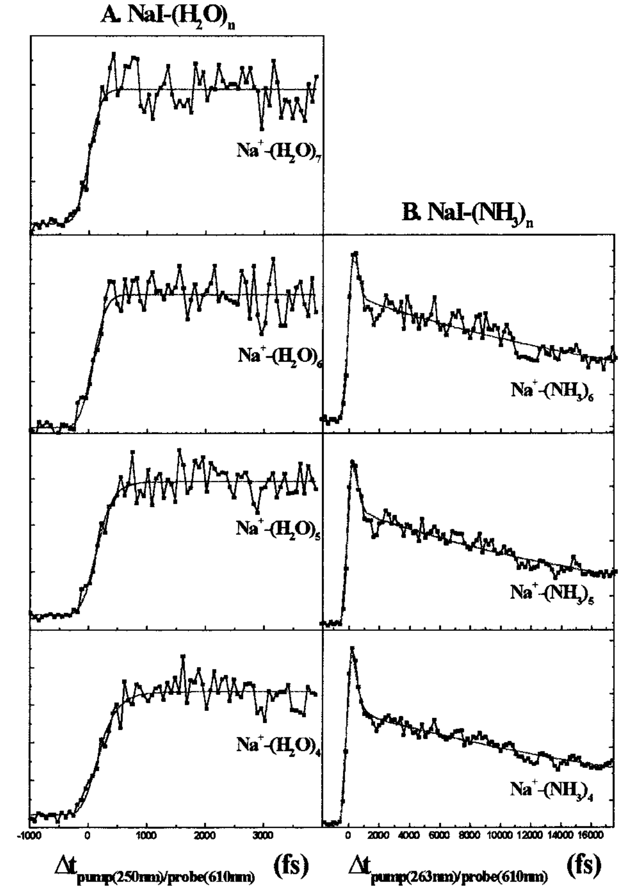


Figure 6. Femtosecond dynamics of NaI bond rupture in two different solvents. The probe wavelength is set at 610 nm for the two experiments, while the pump wavelength is changed to ensure the same amount of excess energy in the excited state for the two different solvent clusters: it is 245 nm for water clusters and 263 nm for ammonia clusters. The helium backing pressure is 3 bar for both experiments, and the oven temperature is 450 °C. Since there is competition between the ionization/dissociation and the dissociation/ionization processes, the excited-state dynamics is observed only if the ionization cross sections change with the cluster size. (A) NaI−$(H_2O)_n$ clusters: Nearly no time evolution is observed, indicating that the ionization cross section is independent of the cluster size. The salt stays on the cluster surface. (B) NaI−$(NH_3)_n$ clusters: Two decays, assigned to the NaI bond rupture (200 fs) and to the evaporation of one NH_3 molecule (20 ps), are observed. Here the ionization cross section changes with the cluster size. The salt is surrounded by solvent molecules.

220 nm leads to the observation of $Na^+(ethanol)_n$ or $Na^+(NaI)_m(ethanol)_n$ clusters. The maximum size observed is $n = 5$ ethanol molecules, much smaller than what has been observed in the REMPI experiment. The cluster size distribution decreases as the laser power increases, but the ion signal increases. Surprisingly the $Na^+(NaI)_m(ethanol)_n$ mean size is independent of the NaI concentration in the liquid.[176]

For CaI_2 in ethanol solution, the ions ejected from the liquid beam surface are mainly $CaI^+(ethanol)_n$, $n = 1-7$, $CaOEt^+(ethanol)_n$, $n = 2-9$, and H^+-$(ethanol)_n$. Solvated Ca^{2+} cations, although present in solution, are not observed because $Ca^{2+}(ethanol)_n$ nascent clusters dissociate into $CaOEt^+(ethanol)_p$ and $H^+(ethanol)_q$ fragments by Coulomb explosion.[177]

What mechanism can lead to the formation of these clusters? In this case, ion pairs are already present in the solution. The evaporation of charged clusters is linked to the accumulation of charges on the surface of the liquid beam. It has been considered that the photons are absorbed by the solvated I^-, the 220 nm photon corresponding to the absorption to the CTTS (charge transfer to solvent) band. If this process occurs in the vicinity of the surface, the electron can be ejected to the vacuum, leading to a strong increase of the concentration of the positive charges (solvated Na^+, CaI^+, or Ca^{2+}) in the solvent. In this Coulomb ejection scheme, the nascent cluster size is limited to the number of ethanol molecules in the first solvation shell of the cation ($n = 6$ for Na^+, $n = 7$ for CaI^+), and can undergo unimolecular dissociation. In the case of CaI_2 in solution, Ca^{2+}-$(ethanol)_n$ nascent clusters dissociate into $CaOEt^+$-$(ethanol)_p$ and $H^+(ethanol)_q$ fragments by Coulomb explosion.

For ions ejected from a NaI solution in ethanol, the size distribution appears to shift to smaller sizes with the laser power. This implies that the nascent cluster ion, $Na^+(EtOH)_n$, gains internal energy from the laser through ionization−recombination cycles mediated by solvated electrons as described below: in the ethanol solution, NaI is partly dissociated in $Na^+ + I^-$. Under irradiation, I^- releases an electron into ethanol (solvated electron, e_{sol}).[216] The solvated electron is likely to recombine with iodine within a picosecond time scale to regenerate I^- in releasing the recombination energy to the solution. The regenerated I^- is excited again by absorption of a photon and then releases an electron, etc. The excitation−recombination cycles release the photon energy (5.65 eV) into the solution as heat within the duration of a single laser pulse, resulting in an increase of the internal energy of the nascent cluster ion. The scheme of the energy transmission via the excitation−recombination cycles is supported further by the result of inefficient transmission of the photon energy to solutions in which no solvated electron is present, such as ethanol solutions of phenol, aniline, ...[217] In this type of solution the cluster size distribution remains unchanged with laser power.

A mechanism similar to that proposed for the NaI−$(solvent)_n$ clusters produced in a supersonic expansion could also be also postulated: a first photon could excite NaI in solution in the vicinity of the surface. NaI would dissociate, leading to the evaporation of solvated sodium atoms, and a subsequent photon might ionize the cluster. In this case, only small clusters are expected to be emitted from the surface, the excess energy in the bond rupture being on the order of 1 eV. The ion signal should then be proportional to the number of photons, but the cluster size should be nearly independent of the laser power: this was not verified experimentally.

In light of the mechanism proposed for liquid beam experiments, the implication of the CTTS absorption in free clusters studied through REMPI experiments has to be discussed. If in the small complexes the CIP is certainly the dominant species, for larger clusters, the charge-separated complexes should be present in the case of acetonitrile clusters, for example. In this case, excitation to the CTTS band is probably possible.

Is the excitation cross section of the CTTS band comparable to the NaI excitation cross section? The absorption cross section of the CTTS can be estimated to be on the order of 2×10^{-17} cm^2 from the photoionization work on $I^-(H_2O)_n$.[25] The absorption cross section of free NaI has been measured to be quite similar at 300 nm.[218] The solvated contact ion pair should have a similar absorption cross section, although the transition is strongly shifted toward high energy. Thus, in clusters, the CIP and the SSIP can both absorb with equivalent efficiencies, the former to the NaI−(solvent)$_n$ excited state and the latter to the CTTS band.

At what wavelength is the CTTS absorption located? In an acetonitrile solution the I^- CTTS band has been measured at 5 eV,[219] whereas it is at 5.45 eV in water. In small $I^-(H_2O)_n$ complexes, this band is red shifted,[25] and therefore, the CTTS band could well be accessed in experiments using lasers between 4.5 and 5 eV. In the liquid phase, the free electron conduction band is 1.5 eV above the CTTS band and the energy to remove an electron from the cluster should be smaller (0.5 eV for $I^-(H_2O)_4$). However, in the SSIP clusters, the Coulomb attraction has to be overcome, which can still be fairly large. If it is assumed that the electron in the CTTS band is about 4 Å from the Na^+ core, the energy required for ionization will be 3.5 eV, which is accessible with the wavelengths used in REMPI experiments. As mentioned above, there is a very fast recombination reaction (1 ps for Cl^- in water[220]) of the electron with the nearby halogen atom to the ground-state anion. This effect will lead to an important energy release in the cluster and will induce rapid evaporation in the cluster. Therefore, the signature of the CTTS excitation in a cluster will be its absence in the mass spectrum.

So the absence of large Me^+(solvent)$_n$ fragments when acetonitrile or ammonia is the solvent can be interpreted as due to an inefficient absorption of the clusters with SSIP structures, or alternatively, if the CTTS band can be accessed, the clusters will be so hot that they will evaporate and be detected at much smaller masses. Experimental results do not allow settling this issue at the present time.

E. Surface Impact Charge Separation

Another method to study charge separation in clusters is to perform surface impact ionization. The scattering of neutral clusters of polar molecules (H_2O, SO_2, NO, NH_3, ⋯) with low incident velocities from surfaces is known to produce the emission of positively and negatively charged fragments, even though the kinetic energy per molecule is smaller than the molecular ionization potential.[178] Clusters issued from a supersonic expansion collide with a surface (SiO_2) which can be covered with alkali-metal atoms or salt molecules. When alkali-metal atoms are present on the surface, positively charged fragments containing an alkali-metal atom are observed when the clusters are large enough (around 20) for NH_3, H_2O, and SO_2. In this latter case, due to the strong electronic affinity of the clusters, SO_2^- negatively charged clusters are observed. The yields of both charged species are comparable. The key to the charge separation in the cluster seems to be the pickup of a neutral alkali-metal atom, which immediately ionizes in the cluster, followed by the delocalization of the valence electron in the cluster and the subsequent collision-induced fragmentation of the cluster into charged species. Water or ammonia clusters are not able to stabilize the delocalized electron, leading to a much weaker anion signal than in the case of SO_2 clusters. In the case of water clusters, another mechanism, the autoprotolysis of water, may also be active in the charge separation process.[178,191,192]

The ability of other metal atoms to induce surface impact ionization of SO_2 clusters has been tested by doping the surface. Although ex situ surface analysis confirmed the presence of Fe, Ni, Mn, and Cr, exclusively K and Na atoms caused the observed strong signal. However, an indium-loaded surface seemed indeed to produce the corresponding $In^+(SO_2)_n$ ions, thus indicating that the metal atom must have a low ionization potential.

To study further the charge separation process, the surface was covered with NaCl. Neither strong $Na^+(SO_2)_n$ peaks nor any chlorine-carrying anions could be observed. This shows that dissolution of salts does not occur on the time scale of cluster impact, and confirms that atoms in their neutral states are inducing the ionization of fragmenting clusters. This work shows that, although the cluster temperature is probably high (it can be expected to be on the order of 400 K[221]), the salt molecule does not dissociate into an ion pair. A possible interpretation may be that the barrier to penetrate into the cluster is very high as mentioned in ref 201. Another phenomenon, the calefaction effect, might be involved: as demonstrated in ref 221, the contact of the cluster and the surface is not necessarily very good since a monolayer of free monomers can be trapped between the cluster and the surface.

F. Theoretical Investigations

Theoretical investigations have been conducted through many models to obtain the structures and equilibrium between the CIP and SSIP on various systems. The most studied system is the $Me^+X^-(H_2O)_n$ cluster system (where Me is an alkali-metal and X a halogen atom).

a. Salts in Liquid Water

In a condensed phase, the ion association process may be described in terms of an equilibrium between two states for the associated ions: contact ion pair (CIP) and solvent-separated ion pair (SSIP). The interconversion between the two states for singly charged ions in a pair at room temperature would involve passing over a free energy barrier.[135,207,222−238] The resulting potential curve for an ion pair in solution is shown in Figure 7 with the two minima, CIP and SSIP, separated by a barrier. Barrier cross-

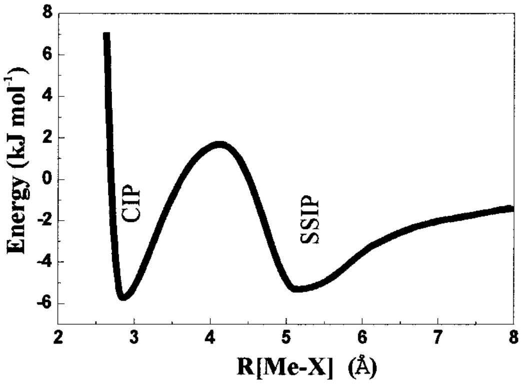


Figure 7. Typical calculated potential of mean force for a salt, MeX, in liquid water adapted from refs 135 and 231 (Me corresponds to an alkali metal and X to a halogen atom). The SSIP and CIP structures are more stable than the two separated ions.

ing may be considered as an activated process driven by solvent fluctuations. The presence of this free energy barrier is the result of cancellation between the bare interionic attraction and the reaction field provided by the solvent that tends to separate the two ions. At short distances, the final shape of the potential of mean force depends mainly on the local structure of the solvent surrounding the ion pair. From the microscopic point of view, the SSIP ↔ CIP process involves expelling solvent molecules from the region lying between the two ions, into the bulk solvent.

The energetics of barrier crossing in the bulk have been the subject of many investigations using molecular dynamics simulations, the potential used for water being either the simple point charge (SPC) model or more sophisticated potentials including polarization. For NaCl in water, the barrier height is calculated to be on the order of 10 ± 2 kJ mol^{-1} and the stabilities of both the CIP and the SSIP are comparable, both being stabilized by 5 kJ mol^{-1} relative to the infinitely separated ions. The role of the polarization is not very important in the qualitative point of view.[135]

At the opposite, at large concentrations, it seems that the stability of clusters formed of two anions and two cations has to be taken into account. These dimers represent one-fourth of all the ions of the solution.[236]

The excited-state dynamics of the CIP structure, in relation to the cluster experimental results, has also been studied through the photodissociation of NaI in liquid water: the short time dissociation products are atoms; they could convert to ions on the millisecond time scale by activated electron transfer. However, the radiative lifetime is shorter, ruling out this mechanism.[207]

b. Salts in Water Clusters

1. Molecular Dynamics Simulations

In clusters, D. Laria and R. F. Fernandez-Prini did MD simulations on the solvation of ion pairs by a few water molecules (8, 12, 16, 32) at 200 K:[202] the potential used for the water interaction was the simple point charge (SPC) model. The potential of mean force has been calculated, and the free energy barrier that in solution characterizes the equilibrium between CIP and SSIP is seen for large enough clusters: In $KCl(H_2O)_n$, the equilibrium distance is 0.3 nm for $n = 4$, 8, which corresponds to the CIP structure. A second minimum begins to appear at $R = 0.4$ nm for $n = 16$ and is more pronounced for $n = 32$. H_2O accumulates close to the central plane of the ion pair, and at the ends of the cluster only when n is large. It seems that the stabilization of the SSIP configuration is mainly due to the difficulty of squeezing out solvent molecules into the bulk solvent as the (local) solvent density increases due to the fact that solvent molecules are more closely packed around the ion pair.

The same authors revisited the system using the SPC/POL potential (which includes water polarization) in water clusters up to 64 molecules including also NaCl and KCl.[203] The polarization effects are not negligible. In particular ionic solvation is reduced; i.e., the solvent tends to occupy a larger volume (enhancement of the hydrogen-bonded structure, leading to a segregation of the solute), and the solvent structure around the solute becomes asymmetric.

The stability of $Cl^-{-}Cl^-$ in a SPC water cluster has also been investigated. These clusters are remarkably stable; e.g., 64 water molecules are sufficient to transform the repulsion between the bare ions into an effective attraction that extends to 25 Å. Also important is the size of the dissociation barrier of the charged aggregates; the energy required to split the two ions ranges from roughly 8 kJ mol^{-1} for $n = 8$ to 50 kJ mol^{-1} for $n = 64$.

$NaI(H_2O)_n$ clusters have been calculated using both SPC and a polarizable five-site water model. In the first publication the photodissociation of NaI attached to only one water molecule has been modeled in comparison with the same dynamics in the liquid and in comparison with experiment.[204] At the equilibrium geometry the dipole moment of the molecule is reversed between the ground and the excited states. In the excitation of $NaI{-}H_2O$, the water molecule, which is initially aligned with the dipole moment of the ground state, feels a strong reversed dipole. This leads to a destabilization of the cluster: at the same time, the NaI bond rupture starts and the water molecule is ejected with a large amount of rotational energy. All these processes occur within 2 ps, which is in agreement with experimental results, although evaporation processes from larger clusters contaminate these latter ones.

For larger clusters, the potential of mean force for the ground state has been investigated, in particular, the appearance of the NaI CIP and SSIP structures in clusters. For the SCP potential the results obtained are very similar to those of Laria et al. (see Figure 8). The ion pair is stable with respect to dissociation in free ions even in very large clusters, the opposite of what is observed in liquids, where the two ions can separate freely.[201] This behavior should be expected. Even for large clusters, the separation of the two ions will lead finally to the formation of two separated clusters, $I^-(H_2O)_n$ and $Na^+(H_2O)_m$, which will still be interacting through the Coulomb

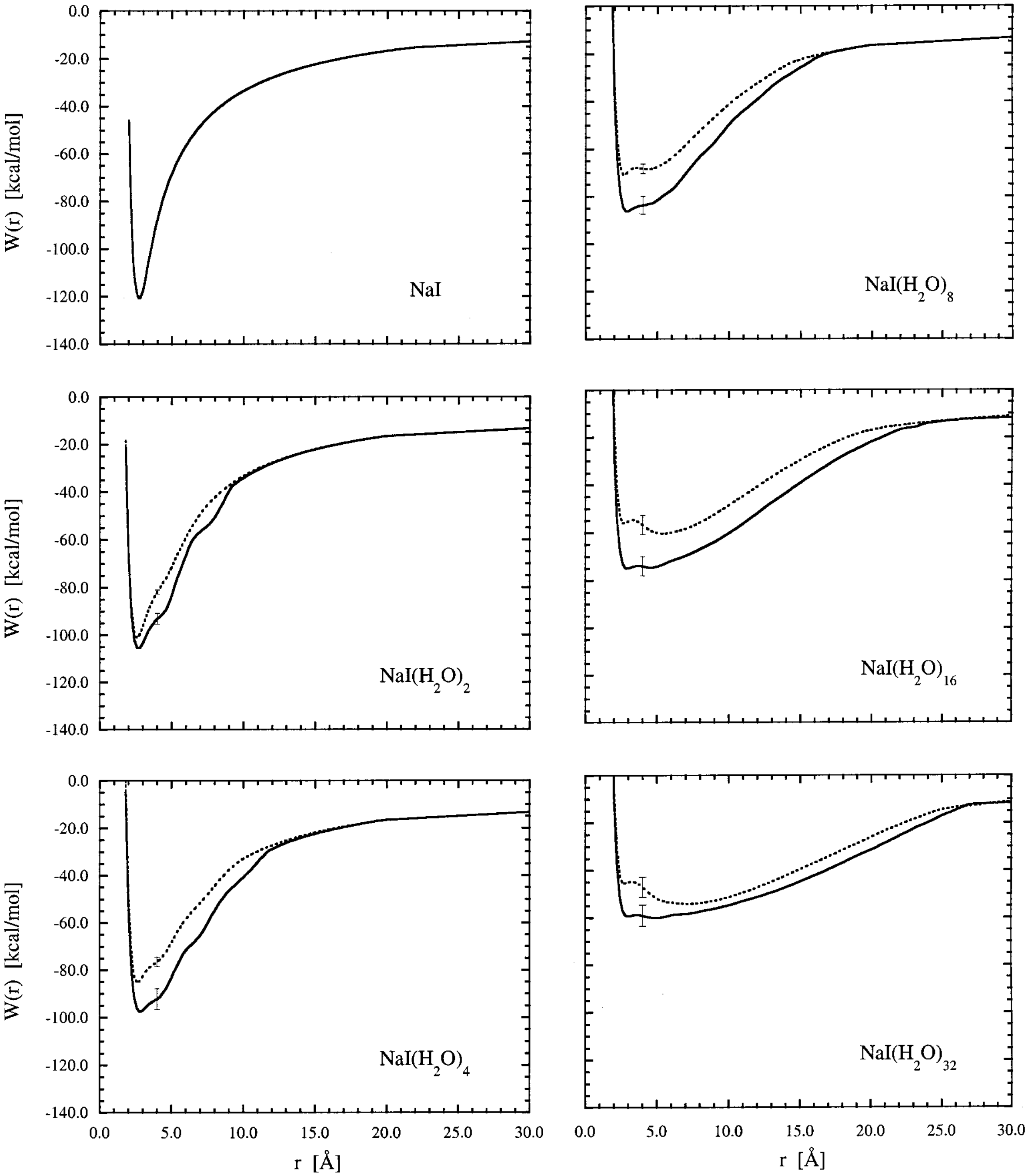


Figure 8. Potential of mean force for NaI in water clusters at 300 K. Reprinted with permission from ref 199. Copyright 1995 Elsevier. Solid line: Polarizable five-site water model potential (OPCS) (see ref 115). Dotted line: TIP4P water potential[237] supplemented with the optimized potentials for liquid simulations (OPLS).[238]

attraction acting at infinite distance in the vacuum.

At shorter distances, two minima, which can be associated with the CIP and SSIP structures, are seen for $n = 16$ and up (see Figure 8). The effect of the polarization is very large, especially for the CIP structure, which is lowered by roughly 20 kcal mol^{-1}, and for the barrier, which for $n = 16$ decreases from 2.8 to 1.3 kcal mol^{-1}. The SSIP structure is less favored when the polarization is included in the calculation.

At 300 K the equilibrium between CIP and SSIP is strongly displaced toward the SSIP. The SSIP structure is 2 times more favored for $n = 16$ and 10 times for $n = 32$.

In relation to the experimental interpretation that, in the SSIP structure, the absorption will not be allowed, leading to absence of detection of clusters with SSIP structures in the mass spectrum, the oscillator strengths have been calculated. The first comparison for the 1−1 complex shows that the electronic oscillator strength decreases for SSIP by a factor of 3 as compared to that for CIP (for NaI−H_2O at $R_{NaI} = 2.8$ Å, the oscillator strength is $f = 0.13$, whereas for $Na^+\cdots H_2O\cdots I^-$ with $R_{NaI} = 6$ Å, $f = 0.04$).

The authors also mention, although not yet fully documented, the tendency for NaI−$(H_2O)_n$ to have surface structures: as the cluster grows, water molecules more likely bind to each other rather than to the solute.

These two latter conclusions are in excellent agreement with the previous interpretation of the experimental results.

2. Ab Initio Methods/Most Stable Structures

The molecular dynamics method requires a fairly simple potential but allows one to take into account the entropy effects that certainly have a very important role in the solvation effect. However, these effects are also strongly dependent on the intermolecular potentials, and a reliable description of the interaction energy requires a very elaborated potential energy function. An extensive exploration of large systems cannot be easily done with high-level ab initio techniques, and is therefore limited to small systems, but large systems are benchmarks for other methods. The approach between the ab initio techniques and molecular dynamic simulations is to develop accurate semiempirical potentials specifically tailored for these clusters which involve three different types of interactions, ion−ion, ion−solvent, and solvent−solvent. This approach allows the exploration of the potential energy surface through Monte Carlo methods for fairly large systems.

All these methods represent complementary approaches to complicated systems that cannot be fully calculated.

Ab initio supermolecule calculations have been performed for $n = 1-3$ water with NaCl.[194] It has been shown that the NaCl internuclear distance increases from 2.42 Å (gas-phase value) to 2.63 Å for 2 water molecules with correspondingly decreasing vibrational frequency. For larger systems, up to 10 water molecules, mixed methods were used to explore the different minima of the potential energy surface.[197] The number of isomers increases rapidly with the number of molecules, but on average the NaCl distance increases from 2.59 Å for $n = 4$ to 3.17 Å for $n = 10$ (the minimum which presents the largest internuclear distance is found at 4.2 Å), with a charge on the sodium which varies from 0.8 to 0.95. All these structures can still be considered as CIP structures; the SSIP structure is far from being energetically favored for these small sizes.

However, a more recent ab initio calculation concludes that $NaCl-(H_2O)_6$ is the first cluster size where solvent-separated and contact ion pairs are isoenergetic, with a 3 kcal mol^{-1} barrier between the two structures.[196]

Contradictory results are found with Monte Carlo simulations on $NaCl-(H_2O)_n$ and $LiCl-(H_2O)_n$, at room temperature, which seem to show that ions separate, abruptly for LiCl from $n > 3$, with a more regular increase of the Na^+Cl^- distance for NaCl, leading to a water-shared ion pair where the first three or four water molecules tend to sandwich between the ions and the next attach to the cation.[199] The discrepancy between these results could be due to the different potentials used to model water.

c. NaI in Acetonitrile Clusters

The charge separation of NaI clustered with acetonitrile molecules has been studied, using a model potential specially devised for the $NaI-(CH_3CN)_n$ system built up according to the exchange perturbation theory.[200] In the case of water, many studies have been devoted to reproduce bulk-liquid- or gas-phase properties with accurate but simple potentials, but for the $NaI-(CH_3CN)_n$ system, the semiempirical potential, and especially the electrostatic and polarization terms, leads to calculation times which are too expensive to perform molecular dynamics (MD) computations. The potential energy surface exploration has been carried out using the Monte Carlo growth method at different fixed internuclear NaI distances, to obtain a minimum energy profile for the NaI bond breaking.[200]

For $NaI-CH_3CN$, this method finds a collinear structure for the minimum energy, which simpler potentials do not find. This result is corroborated by the experimental femtosecond dissociation study of the related complex, $CsI-CH_3CN$, where the appearance of recurrences is assigned to vibrations of the nascent $Cs\cdots NCCH_3$ bond. The $Cs\cdots N$ bond is stabilized only if the initial geometry is linear.[241]

From four to nine solvent molecules, the $NaI-(CH_3CN)_n$ potential energy surface exhibits two different minima along the NaI internuclear distance. The first one is related to the CIP structure, and the second has the two ions separated by two or three acetonitrile molecules in a SSIP structure. With less than eight solvent molecules, the CIP configurations have the highest binding energies, but for nine acetonitrile molecules, the configurations where the two ions are separated by 7 Å have a higher binding energy than those where the two ions stay in contact (2.85 Å), reflecting an evolution from the CIP to the SSIP structure with the cluster size. This can be related to the gas-phase photoionization experiment on $NaI-(CH_3CN)_n$[178,206] and leads to the same conclusion: the charge separation of NaI should be achieved within a cluster containing less than 10 acetonitrile molecules.

G. Conclusions

Calculations as well as experiments agree that, in small clusters, salts such as NaCl or NaI remain as a contact ion pair. In larger clusters, calculations indicate a tendency to form a stable solvent-separated ion pair, in water as well as in acetonitrile. However, the experimental results for NaI in water clusters do not show any sign of charge separation for sizes as large as 60. This could be due to a temperature effect, the water cluster being too cold to allow NaI inside. For other solvents, ammonia, and acetonitrile, it seems that charge separation occurs for clusters containing around 10 solvent molecules.

The comparison with the charge separation induced in acids is quite interesting. It appears from theoretical[170−174] as well as experimental[162−169] works that the cluster size necessary to obtain the charge separation is a lot smaller than what is seen in salt (four water molecules for HBr). Although not clearly proven, it seems that one key point is the ability of the acid or the salt to penetrate into the cluster. For acids, the very small proton allows an easy penetration of the acid into the cluster. Moreover, in protic solvents, H^+ is integrated into the hydrogen bond network of the solvent. At the opposite, for salts such as NaI, the size of the anion is so large that a surface location may be a better place for the salt. This is like an Archimed effect, for similar binding energies (weight for a boat), the larger the system, the better the floating. This seems to have been well demonstrated for atoms or simple ions in molecular clusters, but a more systematic study of salt$-$(solvent)$_n$ clusters would be necessary to clarify this issue. Recent molecular dynamics simulations have indeed shown that in a cluster containing 96 NaCl molecules for 864 water molecules, the density of chlorine anions on the surface exceeds that of sodium cations.[242] This excess chlorine concentration may enhance the interfacial reactivity on aqueous NaCl aerosols.

H. Glossary

CIP	When a molecule with an ionic state, M^+X^-, is in solution or in a solvent cluster, the structure where the positive and negative ions stay in contact [$M^+X^- -$(solvent)$_n$] with a common solvation sphere is called a *contact ion pair* (see Figures 2, 7, and 8).
SSIP	When a molecule with an ionic state, M^+X^-, is in solution or in a solvent cluster, the structure where the two ions are separately solvated [$M^+ -$ (solvent)$_m$$\cdots$$X^- -$(solvent)$_p$] is called a *solvent-separated ion pair* (see Figures 2, 7, and 8).
CTTS bands	The visible and UV region absorption spectra of molecules and ions in solution present transition bands called *charge-transfer to solvent bands* corresponding to the redistribution of an electron initially localized on the molecule (or ion) over the nearby solvent molecules according to: $M_{sol} \rightarrow {}^*M^+_{sol} + {}^*e^-_{sol}$ or $M^-_{sol} \rightarrow {}^*M^0_{sol} + {}^*e^-_{sol}$, where the asterisk indicates that the geometrical structure is the same as before photoexcitation, which means that ${}^*e^-_{sol}$ represents an excited state of the conventional solvated electron bound to the still organized solvation sphere of M (or M^-).
AID/ADI	When the excited-state photodissociation of clusters is studied with pump probe techniques, two excitation ionization schemes are often in competition. (1) *Absorption* of the pump photon by the parent cluster, *ionization* of the parent cluster by the probe photon and *dissociation* in the ion state. (2) *Absorption* of the pump photon, *dissociation* in the excited state and *ionization* of the photodissociation product by the probe photon. A well-known example is the photodissociation of ammonia clusters studied by resonance-enhanced two-photon ionization, where the *absorption−ionization−dissociation* process, $(NH_3)_n + h\nu_1 \rightarrow (NH_3)_n{}^*$, $(NH_3)_n{}^* + h\nu_2 \rightarrow (NH_3)_n{}^+ + e^- \rightarrow (NH_3)_{n-2}NH_4{}^+ + NH_2 + e^-$ is in competition with the *absorption−dissociation−ionization* process, $(NH_3)_n + h\nu_1 \rightarrow (NH_3)_n{}^* \rightarrow (NH_3)_{n-2}NH_4 + NH_2$, $(NH_3)_{n-2}NH_4 + NH_2 + h\nu_2 \rightarrow (NH_3)_{n-2}NH_4{}^+ + NH_2 + e^-$, leading to the same final product, $(NH_3)_{n-2}$-$NH_4{}^+$.

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CR990059S