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Rapid Note

Is NaI soluble in water clusters?

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Abstract. NaI$-$(solvent)$_n$ clusters (solvents being NH_3, H_2O or CH_3CN) have been studied by resonance enhanced two photons ionization, leading to the detection of $Na^+$$-$(solvent)$_n$ clusters. When water is the solvent, large clusters up to $n > 50$ can be observed, whereas for NH_3 and CH_3CN no clusters larger than 10 could be evidenced. Because the first step in the ionization process is the excitation from the ground solvated (Na^+-I^-) ion pair state to a covalent excited state, the differences in the cluster size distribution for different solvent may be interpreted as a difference in cluster structures leading to a difference in the charge separation in the ground state.

PACS. 36.40.Mr Spectroscopy and geometrical structure of clusters – 31.70.Dk Environmental and solvents effects

Introduction

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. In the molecular solvation processes, charge separation induced by solvent is one of the most simple and important process in nature. It has been studied in clusters in the case of proton transfer [1–4]. The simplest and the most well known case of charge separation induced solubility in liquid (water) is obviously the dissolution of a salt in water.

In all school textbooks, it is written that NaCl in water separates in Na^+ and Cl^- ions surrounded by water molecules. From simple saturation concentration argument, it can be derived that at 300 K about 9 water molecules per salt molecule are necessary to dissolve NaCl in water and only about 5 for NaI. We have undertaken the study of solubility of salts in solvents at the microscopic level by studying the spectroscopy and dynamics of NaI embedded in solvent clusters of ammonia (NH_3), water (H_2O) or acetonitrile (CH_3CN). NaI was chosen because it can be fairly easily vaporized and because the excited state ionic/covalent mixing has been well studied and characterized [5–8].

We present here results indicating that the charge separation process is not as straightforward to understand as expected. They have been obtained with NaI$-$(solvent)$_n$ clusters prepared in a supersonic expansion, ionized by a one-color resonant two-photon scheme using nanosecond lasers and detected with a time of flight mass spectrometer.

Experimental

The apparatus has been described previously [8]. The most difficult part of the experiment has been the design of a pulsed valve with a tiny oven behind which allows to evaporate NaI (temperature required 500 °C) and to cool down the jet efficiently enough to obtain clusters. It should be mentioned that the conventional way for seeding molecules in a supersonic expansion, the laser ablation source, cannot be used in our case: the detection scheme based on resonant two-photon ionization through an intermediate state will lead mostly, in the case discussed here, to the dissociation of NaI in Na + I, so that the NaI$-$(solvent)$_n$ clusters are going to be detected as $Na^+$$-$(solvent)$_n$ clusters. Therefore Na$-$(solvent)$_n$ clusters must be absent in the expansion before excitation. The laser ablation technique, which is a rather hard evaporation technique, will produce a lot of sodium atoms from NaI and thus cannot be used. We have also tried the pick-up method but unsuccessfully.

Results

The mass spectra obtained for the excitation of NaI$-$(solvent)$_n$ clusters with three different solvent

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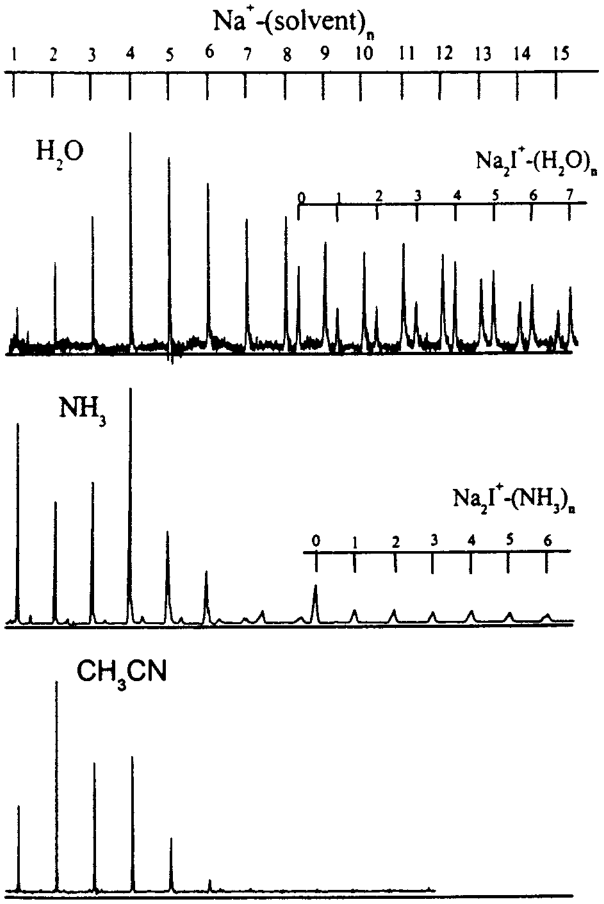

Fig. 1. $Na^+$$-$(solvent)$_n$ mass spectra obtained after the excitation/ionization of NaI$-$(solvent)$_n$ clusters, the solvent being H_2O (upper), NH_3 (middle), CH_3CN (lower). A second series of peaks corresponding to $Na_2I^+$$-$(solvent)$_n$ is also observed. The mass scale is such that clusters having the same number of solvent molecules are one below the other. The three spectra have been recorded under similar experimental conditions: He backing pressure 3.5 bars, solvent partial pressure: $p(H_2O) = 100$ torrs, $p(CH_3CN) = 400$ torrs and $p(NH_3) = 300$ torrs, laser wavelength 250 nm.

molecules (ammonia, acetonitrile and water) are presented in Figure 1. The experimental conditions are nearly the same for all species. In the three spectra, the $NaI^+$$-$(solvent)$_n$ ions are not observed, only $Na^+$$-$(solvent)$_n$ are detected. When the oven temperature is increased, clusters such as $Na_2I^+$$-$(solvent)$_n$ are also observed: these can be assigned to the excitation/ionization of $(NaI)_2$$-$(solvent)$_n$ clusters.

The striking point in the results presented here is that, when water is the solvent, clusters containing up to 50 water molecules are observed (only 15 are presented in Fig. 1) whereas, with CH_3CN or NH_3, all the attempts to detect clusters with more than 6 or 9 solvent molecules respectively have been unsuccessful.

These results are found to be robust. They are not sensitive neither to the laser wavelength used (320$-$230 nm range) nor to the expansion conditions.

Although the maximum absorption of the NaI$-$$(NH_3)_n$ clusters is found at lower energy than that of NaI$-$$(CH_3CN)_n$ and NaI$-$$(H_2O)_n$, no strong changes in the cluster size distribution are observed when the wavelength is varied, as long as the clusters can be excited.

Concerning the effects of the expansion conditions, an increase of the backing pressure is expected to lead to an increase of the mean cluster size. Such a behavior is clearly observed for the NaI$-$$(H_2O)_n$ clusters. For NaI$-$$(CH_3CN)_n$ and NaI$-$$(NH_3)_n$, however, the ion signal intensity reaches a maximum for a pressure of 3 bars and decreases beyond without any shift toward higher masses. This decrease of the total ion current is a strong experimental indication that larger NaI$-$$(NH_3)_n$ and NaI$-$$(CH_3CN)_n$ clusters are formed in the expansion but are nevertheless not detected.

Discussion

In the present experiment the excitation scheme for a NaI molecule is the following: the first photon excites the NaI molecule from the ionic (Na^+I^-) $X(^1\Sigma)$ ground state to the first excited $A(^1\Sigma)$ state which has a strong covalent character. This latter state is repulsive and short-lived bound states are only obtained through the weak coupling of the A state with the ionic Na^+I^- potential which correlates to the X state. The lifetime of these excited states is in the order of a few picoseconds [5–8] so that at the nanosecond time scale the excited NaI molecule dissociates very quickly to $Na + I$. In a NaI$-$(solvent)$_n$ cluster, the same excitation step is expected to occur, eventually shifted to the blue because of a strong stabilization effect on the ionic ground X state. After excitation, dissociation on the A state surface is expected to lead to the formation of Na$-$(solvent)$_x$ and/or I$-$(solvent)$_y$ clusters, where x and y represent the number of molecules which remain stuck on the atomic fragments, while several *(n-x-y)* molecules can evaporate during the process. Then a second photon can ionize the solvated Na and I atoms. The ionization potentials of Na$-$$(NH_3)_n$ and Na$-$$(H_2O)_n$ are known to be in the 2.3$-$4.5 eV energy range [9,10]. On the other hand, the ionization potentials of the I$-$(solvent)$_y$ clusters are unknown but are expected to be higher in energy, *i.e.*, 1 or 2 eV below that of the iodine atom (10.45 eV [12]). Since we use 310 to 230 nm laser wavelengths (4 to 5.4 eV), only the Na$-$(solvent)$_x$ clusters produced in the dissociation of NaI$-$(solvent)$_n$ will be efficiently ionized in a one-photon ionization scheme, which is in agreement with the absence of solvated iodine clusters in the mass spectra.

Let us now discuss the solvent dependence of the cluster size distribution.

This dependence is neither due to a solvation shift of the cluster absorption band (as mentioned above, the absorption intensity varies with the laser wavelength but similarly for all sizes observed) nor to a size dependence of the ionization efficiency (the ionization potential of the clusters are expected to decrease with solvation).

The possibility of a solvent-dependent evaporation process, occurring either in the excited or in the ionic state, can be also considered. However it would imply large energetics differences between $\mathrm{Na-(H_2O)}_n$ *versus* $\mathrm{Na-(NH_3)}_n$ or $\mathrm{Na-(CH_3CN)}_n$ clusters, which have not been seen in calculations, at least for the clusters with water and ammonia [9].

The absence of large $\mathrm{NaI-(NH_3)}_n$ and $\mathrm{NaI-(CH_3CN)}_n$ clusters detection has been tentatively ascribed to a strong decrease of the $A \leftarrow X$ oscillator strength of the large clusters in connection with the increase of the ground state equilibrium distance. In a crude approximation the $A \leftarrow X$ transition is due to the transfer of the electron from the I^- (in the Na^+I^- (X) ionic 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 wavefunctions of I^- and Na ($3s^2\ S_{1/2}$) and is therefore expected to be strongly dependent on the Na...I interatomic distance. This suggests that a vanishing excitation efficiency might be considered as an indicator of a beginning of the charge separation in the cluster, premise of what is observed in solution.

Under this assumption, the absence of large $\mathrm{Na-(NH_3)}_n$ and $\mathrm{Na-(CH_3CN)}_n$ clusters in the mass spectra (Fig. 1) may be indicative of a first step in the charge separation for cluster sizes around 9 and 6 respectively. The exact size cannot be clearly given since evaporation processes can likely occur during the NaI dissociation dynamics and after ionization as well.

The observation of the $A \leftarrow X$ transition for large $\mathrm{NaI-(H_2O)}_n$ clusters indicates that no beginning of charge separation occurs for clusters containing as many as 50 water molecules. This is however somewhat surprising since NaI is very soluble in water.

A possible explanation is that the NaI molecule is not in the volume of the water cluster but on the surface. A similar geometry has indeed been proposed for the $\mathrm{Na-(H_2O)}_n$ clusters from both experimental data [10] and calculations [9]. Recent calculations performed on $\mathrm{NaI-(H_2O)}_n$ clusters by J.T. Hynes *et al.* [11] seem to confirm this trend: the NaI molecule stays on the surface with the iodine atom sticking out of the water cluster.

With the other solvents, the cluster geometry may be different. In particular, the sodium atom is found to be fully solvated in an ammonia cluster [9,10]. This might also be the case for sodium iodide in ammonia (and acetonitrile) clusters. Such a conformation would increase the effects of solvation on the charge separation.

Conclusion

The results presented here illustrate a solvent-selective ionization behavior for sodium iodide clustered with various solvents. On one hand, clusters with as many as 50 water molecules are observed suggesting that charge separation is not happening under the formation conditions of the studied clusters. On the other hand, large clusters with ammonia and acetonitrile are completely missing, whatever the experimental conditions, which may be indicative of a more complete solvation within these clusters with a beginning of charge separation. Femtosecond pump-probe experiments on the dynamics of the $\mathrm{NaI-(solvent)}_n$ clusters in the excited state are currently under progress and will be published in a forthcoming paper.

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