Binding Energies and Structures of NaI−$(CH_3CN)_{n=1-9}$ Clusters: Theoretical Study of the Contact Ion Pair versus the Solvent-Separated Ion Pair Structures in a Molecular Cluster

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We present a theoretical study of the charge separation of NaI clustered with acetonitrile molecules. A model potential specially devised for the NaI−$(CH_3CN)_n$ system has been built up according to the exchange perturbation theory as developed by Claverie. The potential energy surface (PES) exploration has been carried out using the Monte Carlo growth method (MCGM) at different fixed internuclear NaI distances, to obtain a minimum energy profile for the NaI bond breaking. From four to nine solvent molecules, the NaI−$(CH_3CN)_n$ PES exhibits two local minima along the NaI internuclear distance. The first one is related to the contact ion pair (CIP) structure and the second where the two ions are separated by two or three acetonitrile molecules in a solvent-separated ion pair (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 structures with the cluster size. This can be related to a recent gas phase photoionization experiment on NaI−$(CH_3CN)_n$ and leads to the same conclusion: the charge separation of NaI should be achieved within a cluster containing fewer than 10 acetonitrile molecules.

1. Introduction

The dissociation reaction of a salt in a polar environment has been the topic of both experimental and theoretical approaches.[1−6] It is well-known that an ion pair molecule, which is mainly stabilized in the gas phase by strong electrostatic forces, can be dissociated in two separated ions in a polar liquid, water for instance, at room temperature. Small molecular clusters allow us to investigate the fundamental solvation process, which is essential to understand this simple chemical reaction observed in the condensed phase. Clusters are used to determine the critical number of solvent molecules necessary to converge to one of the condensed phase properties, in our case, the charge separation induced by the solvent. Many studies have been already devoted to the solvation of single ions, either experimentally or theoretically but the (alkali halide)−(polar solvent)$_n$ case, which is the simplest system for the dissociation process, still remains of interest since only very few gas phase experiments have been successfully undertaken.

Indeed, recently, the charge separation of the NaI ion pair embedded in clusters of polar molecules, namely water, ammonia, or acetonitrile, has been studied by one-color pump/probe nanosecond photoionization.[7] In this experiment, a first photon excites the NaI molecule from its ground ionic state, Na^+...I^-, to the first excited covalent state, Na(3s)...I(5p), which is dissociative along the Na...I coordinate. A second photon from the same nanosecond laser pulse ionizes the Na−(solvent)$_n$ complexes issued from the Na...I bond breaking in the clusters. The analysis of the corresponding mass spectra has revealed a solvent selective behavior in the distribution of the detected Na^+-S_n ions. With ammonia and acetonitrile, only product ions up to respectively 10 and 7 solvent molecules can be observed whereas $Na^+-(H_2O)_n$ clusters have been detected up to $n = 60$. The absence of large ions in the mass spectra for ammonia and acetonitrile has been related to the formation of a solvent-separated ion pair within the clusters before any laser excitation, the accurate number of solvent molecules being difficult to determine due to solvent evaporation events in either the excited or ionic states. Conversely, the detection of large $Na^+-(H_2O)_n$ ions indicates that the charge separation of NaI within a water cluster is not achieved even with 60 water molecules.

Experimentally, the dissociation reaction in the cluster can be related to an important decrease of the A ← X dipole moment transition. This transition corresponds in a crude approximation to an electron transfer from I^- to Na^+. Peslherbe et al.[8] have calculated its oscillator strength, which is exponentially decreasing with the internuclear distance between the two ions. For the bare molecule, it decreases from 0.16 at $r = 2.7$ Å to 0.07 at $r = 6$ Å. By inserting a water molecule between the two ions, in a solvent-shared ion pair structure, the oscillator strength drops again by a factor of 2 and so becomes nearly 5 times lower than the one related to the contact ion pair structure. This important change in the oscillator strength is experimentally underlined by the absence of large product ions in the mass spectrum.

The aim of this paper is to investigate theoretically the relative binding energy of a solvent-separated ion pair structure (SSIP) versus a contact ion pair structure (CIP) in the case of NaI−$(CH_3CN)_n$ clusters in relation with recent experimental results. We focus on the arrangement of the solvent molecules around the ion pair, and the determination of the lowest energy equilibrium structures has been performed at several fixed internuclear distances between the two ions Na^+ and I^-. In this way, we obtain a minimum energy profile for the Na^+I^- charge separation. The PES exploration of the NaI−$(CH_3CN)_{n=1-9}$ clusters has been carried out using the Monte Carlo growth

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method (MCGM),[9] and the configurations obtained for each cluster size are then locally optimized to yield the minima.

A reliable description of the interaction energies in a cluster requires an elaborate potential energy function. An extensive exploration of large systems cannot be easily done with high-level ab initio techniques, and we have thus used a model potential as accurate as possible. Consequently, we have developed a semiempirical potential specially devised for this cluster, which involves three different types of interactions, ion−ion, ion−solvent, and solvent−solvent. This semiempirical potential is based on the model initially proposed by Claverie,[10,11] which has already been successfully applied to molecular clusters.[12] This accurate potential requires expensive calculation times, mainly for the local optimization step, and we have then restricted the maximum size of our system to nine acetonitrile molecules. Contrary to the water molecule where many studies have been devoted to reproduce bulk liquid[13−15] or gas phase properties[16−19] with accurate but simple potentials, our NaI−CH_3CN semiempirical potential, and especially the electrostatic and polarization terms, lead to calculation times that are too expensive to perform by molecular dynamics (MD) computations. The Monte Carlo growth method allows us to treat such large systems described by an elaborate potential and has already proven its efficiency.[9]

The outline of the paper is as follow. In the first part, we present our PES exploration method and the intermolecular potential used in the calculation. In the second section, the lowest energy minima and the structures of NaI−$(CH_3CN)_{n=1-9}$ clusters for five fixed Na...I internuclear distances are analyzed. In the last part of this manuscript, the entropy contribution and the temperature influence will be estimated in order to compare our calculations with experimental results.

2. Methodology

2.1. PES Exploration Method. The Monte Carlo growth method (MCGM) was first developed by Garel et al.[20,21] for the study of macromolecules and successfully applied, for instance, to homogeneous molecular clusters of acetonitrile by Bertolus et al.[9] The MCGM consists of growing the cluster molecule per molecule to generate a Boltzmann sample at a "fictive temperature" ***T***. The geometry of a molecular subunit is kept frozen, and each molecule is defined by three translation coordinates, i.e., the position of the mass center and three orientation coordinates, i.e., the Euler angles. The MCGM has been extensively explained,[9] and we only give here an overview of its application.

The procedure is recursive, the configurations generated at size $n + 1$ are determined from the ones found at size n. A topological criterion is introduced to exclude from the exploration of the surface the areas with a strong repulsive interaction energy. The three translation coordinates of the newly added molecule are randomly drawn in the space between two spheres of radii r_{min} and r_{max} centered at the mass center of a randomly chosen species of the cluster (2.6 and 7 Å for Na^+, 3.5 and 8 Å for I^-, 3.5 and 7 Å for CH_3CN). Then, we check the distances between the mass center of the newly added molecule and the previous ones to exclude those that lead to a strongly repulsive interaction energy. Nevertheless, this criterion is not efficient to avoid an unfavorable orientation of the new molecule since the intermolecular distance and the size of an acetonitrile molecule are nearly identical. We then minimize the repulsion interaction by randomly drawing the three Euler angles. This procedure ensures an attractive interaction of the new molecule with at least another species of the cluster and then should lead to the main low-energy areas of the surface.

The growth has been performed at several fictive temperatures, 200, 500, 1000, and 1500 K to test the optimal temperature conditions. At low temperature, significant minima may be excluded from the exploration, and at too high temperature, a lot of configurations will lead after local optimization to a large enhancement of the high-energy minima. Computations at temperatures higher than 500 K do not yield significant new low-energy minima, and the exploration has been done at this latter temperature. It should be kept in mind that the temperature of the growth does not correspond to a real temperature of the cluster but is introduced to generate a Botlzmann sample of configurations before the local optimization calculation step. These configurations are then locally optimized by the pseudo Newton method (BFGS).[22] The first and second derivatives of the interaction energy are numerically calculated, the Hessian eigenvalues being probed to ensure that each stationary point obtained corresponds to a real minimum.

We have performed the MCGM at fixed Na...I internuclear distances in order to analyze the interaction energies in the clusters as a function of the Na...I coordinate. Several growths have been carried out starting from the isolated Na^+I^- ion pair molecule to a cluster with nine acetonitrile molecules. We have chosen five distances that should be representative of the two structures CIP and SSIP:

−two short distances of 2.72 Å, which corresponds to the equilibrium distance of the bare molecule and 2.85 Å, because we expect a small increase of the distance upon the solvation even if the two ions remain in contact in the cluster[4]

−two longer distances of 5 and 7 Å, which should be large enough to allow a or a few acetonitrile molecules to be shared between the ions

−an intermediate value of 3.75 Å, meant to probe an eventual potential energy barrier between the two structures

Furthermore, calculations were also performed for a distance of 10 Å to probe the interaction energy corresponding to a more complete dissociation of NaI in the case of NaI−$(CH_3CN)_8$ clusters.

2.2. Model Potential. In the semiempirical model developed for neutral systems,[10−11] all the contributions to the interaction energy are expressed by simplified analytical formulas that derive from their expression obtained at the second order of the exchange perturbation treatment. The electrostatic term is calculated as a sum of multipole−multipole interactions. The polarization term is an n-body term based on the same multipole expansion as above, plus experimental atom- and bond-polarizability increments and corresponds to the sum of all the polarization energies of the molecules. The set of multipoles on each molecule (a charge, a dipole, and a quadrupole on each atom and chemical bond) are generated through a systematic procedure of reduction of the number of centers[23] from the multipolar multicentric development of its electronic distribution. It has been proved that in order to accurately describe the electrostatic and corresponding electric fields involved in the polarization contribution, the multipolar multicentric development must be derived from a correlated wave function within at least a double-ζ plus polarization basis set.[24] Both dispersion terms calculated as a sum of three terms ($C_6/r_6 + C_8/r_8 + C_{10}/r_{10}$) and the repulsion term are expressed as sums of atom−atom contributions.

In our system, the basic idea is to model the NaI interaction energy from experimental data using an ion pair model and to consider, for the other interactions, the ion pair as a molecule containing a sodium cation and an iodide anion with a distance dependent multipolar distribution. In this way, at least for the

TABLE 1: Repulsion Parameters for Each Atom/Atom Interaction Pair

	$A(i,j)$ (kcal/mol) $C(i,j)$ (Å^{-1}) $R_0(i,j)$ (Å)				
	Na^+	I^-	N	C	H
Na^+		11.71 2.83 3	10 4.4 2.2	15 2.4 2.25	2.45 7.65 2
I^-			8.6 2.46 3.05	10.5 2.67 3.05	1.96 2.46 3.05
N			12 3.9 2.4	11.06 3.9 2.5	2.6 3.52 2.2
C				12 3.9 2.4	2 3.5 2.2
H					2.05 4.91 2

TABLE 2: Atomic Dispersion Parameters

dispersion param	$\sigma(i)$ (Å)	$\epsilon(i)$ (kcal/mol)
Na^+	2.24	0.034
I^-	4.68	0.032
N	3.3	0.05
C	3.4	0.05
H	2.35	0.035

pairwise interactions that are the electrostatic, repulsion, and dispersion terms, the total energy of the system can be expressed as the sum of three contributions: a contribution depending on the Na−I distance and resulting from the ion pair interaction, a contribution resulting from the interactions between the NaI subunit and the acetonitrile molecules, and a contribution resulting from the interactions among the acetonitrile molecules themselves. Concerning the polarization contribution that is an *n*-body term, it has been taken into account in an approximate way discussed below.

2.2.1. NaI Model Potential. The NaI interaction energy has been fitted to the RKR potential of Schaefer et al.[25] using an ion pair model that contains electrostatic, polarization, repulsion, and dispersion terms:

$$E_{NaI}(R) = E_{elec}(R) + E_{pol}(R) + E_{rep}(R) + E_{disp}(R)$$

$$E_{elec} + E_{pol} = -e^2\left(\frac{1}{R} + \frac{(\alpha_{Na^+} + \alpha_{I^-})}{2R^4} + 2\frac{\alpha_{Na^+}\alpha_{I^-}}{R^7}\right)$$

$$E_{rep} = A(Na^+,I^-)\exp[-C(Na^+,I^-)(R - R_0(Na^+,I^-))]$$

$$E_{disp} = -C_6/R_{ij}^{\ 6} \quad \text{with} \quad C_6 = 4\epsilon(Na^+,I^-)\sigma^6(Na^+,I^-)$$

where

$$\epsilon(Na^+,I^-) = (\epsilon(Na^+)\epsilon(I^-))^{1/2} \quad \text{and}$$

$$\sigma(Na^+,I^-) = \frac{\sigma(Na^+) + \sigma(I^-)}{2}$$

R is the Na^+−I^- distance, α_{Na^+} is the experimental polarizability of the sodium cation (0.15 Å^3), and α_{I^-} is the polarizability of the iodide anion (7 Å^3).[26] The repulsion/dispersion terms are expressed using the classical Buckingham potential, and the parameters are listed in Tables 1 and 2.

2.2.2. NaI−Acetonitrile and Acetonitrile−Acetonitrile Model Potentials. Electrostatic Contribution. The electrostatic contributions are evaluated as explained above, i.e., as sums of multipole−multipole interactions.

For the acetonitrile molecule, the multipolar multicentric development used is issued from the correlated wave function obtained by performing a multiconfigurational self-consistent field calculation using a homemade MCSCF program. The atomic basis sets[27] used are (11s6p2d/5s3p2d) for C and N and (6s2p/3s2p) for H, and the geometry is the experimental one. The resulting calculated dipole moment of the molecule (3.83 D) is very close to the experimental one, 3.92 D.

In the case of the NaI subunit, the multipolar distribution contains a charge +1 au on the Na atom, a charge −1 au on the I atom and a distance dependent induced dipolar moment on each atom resulting from the electric field created by the charge of the other atom. At the equilibrium distance of the NaI molecule (2.72 Å), the total dipole moment of the NaI subunit (8.85 D) calculated is close to the experimental value obtained for the bare NaI molecule, 9.2 D.

Repulsion Contribution. The repulsion contribution is described with a model potential identical to that used for the ion pair model. According to the NaI−acetonitrile and the acetonitrile−acetonitrile contributions, two different approaches have been carried out to determine the parameters.

For the description of the acetonitrile−acetonitrile interactions, the parameters are issued from the fit of the repulsion energy obtained with the more sophisticated formulas issued from the exchange perturbation theory and considering only one set of parameters for the pairwise interactions with the two carbon atoms of the acetonitrile molecule (Table 1).

Concerning the NaI−acetonitrile interactions, the pairwise ion−atom parameters are obtained from the fit of the repulsion energy deduced from ab initio calculations performed on [Na−acetonitrile]$^+$ and [I−acetonitrile]$^-$ systems using the supermolecule approach. In this approach, the interaction energy of the system is computed as the difference between the energy of the entire system and the sum of those of the isolated species, namely the ion and the acetonitrile molecule, and the basis set superposition error (BSSE) has been taken into account. At the Hartree−Fock level (HF), the binding energy contains the electrostatic, polarization, and repulsion contributions. Consequently, using the semiempirical approach described above for modeling the electrostatic−polarization contributions, the repulsion energy can be directly obtained by subtracting from the HF binding energy the electrostatic−polarization contributions.

In the ab initio calculations, we have used for the acetonitrile molecule the basis set already described, and averaged relativistic effective core potentials (ARECP) including the two 1s electrons for the sodium[28] and 46 electrons for the iodide atom.[29] The original associated basis sets, (6s4p) for Na and (3s3p) for I, were contracted and increased by additional functions in order to obtain a (4s4p3d) basis set for the two atoms. The BSSE was calculated in the counterpoise approximation and we used the GAUSSIAN 94 package for all the calculations.[30]

To obtain a description of the electrostatic−polarization contributions at the same level in the ab initio and model calculations, we used in the model for the acetonitrile molecule a multipolar distribution obtained from the HF wave function. For the ions, the multipolar distribution contains only a charge, +1 au for the sodium cation and −1 au for the iodide anion. Furthermore, we have checked that the polarizabilities of the acetonitrile molecule and the ions obtained in the ab initio and used in the model calculation are in good agreement.

The optimized parameters for the repulsion contribution have been reported in Table 1. For the two ion−acetonitrile systems,

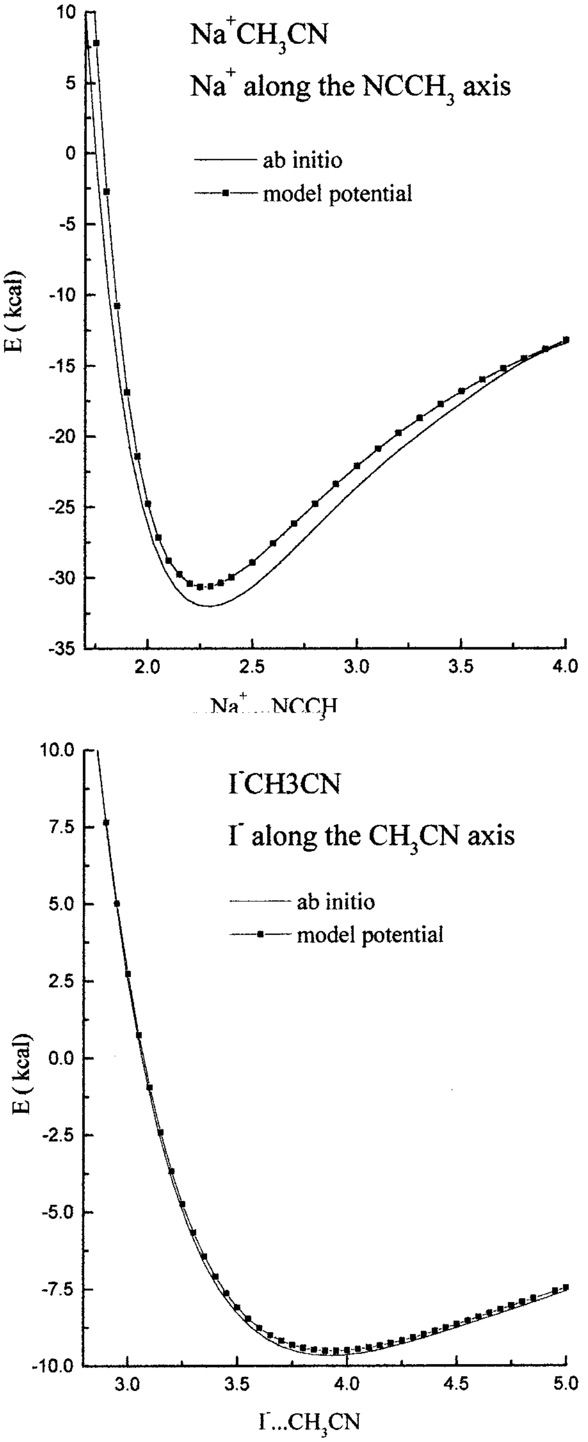

Figure 1. Comparison between the SCF HF level calculations and our semiempirical potential for the ion$-$acetonitrile complexes. Top: Na$^+$...CH$_3$CN. The sodium lies on the axis of the solvent molecule on the nitrogen side. Bottom: I$^-$...CH$_3$CN. The iodide lies on the axis of the solvent molecule on the methyl group side.

four different geometries have been considered to parametrize the repulsion terms. The first two correspond to the ion along the acetonitrile axis, on either the nitrogen or methyl group side. For the two others, the ion lies either above the nitrogen or along one of the C$-$H bond axis of the methyl group.

In Figure 1, we have reported the binding energy issue from both ab initio and model calculations for two configurations of the considered system: the Na$^+-$CH$_3$CN interaction energy as a function of the distance between the sodium (along the molecular axis) and the nitrogen and the I$^-$CH$_3$CN energy as a function of the distance between the iodide (along the molecular axis) and the carbon of the methyl group. The geometries of these two complexes are the most stable ones, the optimum binding energy of the Na$^+-$CH$_3$CN being 3 times higher than for I$^-$CH$_3$CN (-32.1 kcal/mol at 2.28 Å versus -9.5 kcal/mol at 3.8 Å). In a recent density functional study performed at the B3LYP level,[31] the calculated binding energy of Na$^+-$CH$_3$CN is very close to the one reported here, 33.7 kcal/mol for an Na$-$N intermolecular distance of 2.264 Å. The small discrepancy (less than 1 kcal/mol) between our semiempirical method and the ab initio results on the Na$^+-$CH$_3$CN potential energy curve is related to the difficulty of adjusting the repulsion term with a single-exponential decay function for the short intermolecular distances.

Dispersion Contribution. As in the case of the repulsion contribution, for the sake of intrinsic consistency and simplicity of the model, the dispersion contribution is described as a sum of atom$-$atom terms like the ion pair potential. The different parameters reported in Table 2 are determined from the fit of the dispersion energy obtained with the exchange perturbation theory. We have considered only one set of parameters for the two carbon atoms of the acetonitrile molecule and used the standard combination rules to determine the pairwise ion$-$atom coefficients. It can be noted that the NaI$-$acetonitrile contribution of this term to the total binding energy should be rather small since the electrostatic forces, relevant in the ion$-$molecule interaction, are at least 1 order of magnitude higher than the dispersion ones.

2.2.3. Polarization Contribution. The polarization contribution can be expressed as the sum of the polarization energies of all the molecules. Each molecule is decomposed into polarizable sites and the polarization energy of a molecule could be calculated both self-consistently or approximately (one-step calculation) by using the electric field generated at a site by the permanent multipoles of the other molecules. We have decided to use the approximate approach to calculate the electric field and to take into account only the dipolar polarizability of the sites. In this way, we neglected the correction to the electric fields resulting from the induced multipoles as well as terms due to higher orders polarizabilities such as quadrupolar polarizability or hyperpolarizability. Furthermore, we have considered the NaI subunit as a molecule whatever the intermolecular Na...I distance since a polarization term has been already introduced in the NaI model potential. The polarizable sites of the NaI subunit are then the two ions, and the distance dependent multipolar distribution corresponds to its permanent multipoles. For the acetonitrile molecule, the polarizable sites are atoms plus one point per chemical bond and its multipolar distribution corresponds to its permanent multipoles.

3. Lowest Energy Minima and Structural Properties of NaI$-$(CH$_3$CN)$_{n=1-9}$ Clusters

3.1. General Remarks. For the five Na...I internuclear distances, the lowest energy minima of NaI$-$(CH$_3$CN)$_{n=1-9}$, the number of configurations obtained by the growth and the number of minima found after local optimization are listed in Table 3. Except for the small clusters with less than three solvent molecules, the number of configurations issued from the nonlocal exploration of the PES using the Monte Carlo growth method at the temperature of 500 K is quite large, around 150$-$200. We can hope that these numbers are large enough to obtain a reasonable statistic and so to be confident about the validity of our PES exploration technique.

Except for the complex with one acetonitrile molecule, the configurations where the ions are separated from 2.85 Å have

TABLE 3: Lowest Energy Minima and the Ratio of the Total Number of Optimized Geometries over the Total Number of Configurations Obtained by the MCGM of NaI−(CH$_3$CN)$_{n=1-9}$ for the Five Internuclear Distances Na$^+$...I$^-$ [a]

	d(Na...I) = 2.72 Å $E_{\mathrm{NaI}} = -119.04$		d(Na...I) = 2.85 Å $E_{\mathrm{NaI}} = -117.43$		d(Na...I) = 3.75 Å $E_{\mathrm{NaI}} = -93.26$		d(Na...I) = 5 Å $E_{\mathrm{NaI}} = -68.26$		d(Na...I) = 7 Å $E_{\mathrm{NaI}} = -47.91$	
	$E_{\min}$ (kcal/mol)	nb min/ initial nb	$E_{\min}$ (kcal/mol)	nb min/ initial nb	$E_{\min}$ (kcal/mol)	nb min/ initial nb	$E_{\min}$ (kcal/mol)	nb min/ initial nb	$E_{\min}$ (kcal/mol)	nb min/ initial nb
NaI−(CH$_3$CN)$_1$	−134.1	1/63	−133.44	1/54	−115.06	2/57	−99.81	1/18	−88.96	1/10
NaI−(CH$_3$CN)$_2$	−143.04	4/71	−143.67	3/50	−134.03	1/30	−126.39	1/33	−118.86	1/35
NaI−(CH$_3$CN)$_3$	−150.79	5/154	−151.61	6/104	−148.45	1/18	−145.98	1/25	−138.43	2/47
NaI−(CH$_3$CN)$_4$	−158.01	7/191	−159.16	12/148	−156.53	5/121	−157.64	3/35	−153.36	2/39
NaI−(CH$_3$CN)$_5$	−164.23	25/188	−166.09	24/143	−163.47	6/143	−165.17	7/140	−161.44	4/68
NaI−(CH$_3$CN)$_6$	−171.12	49/233	−173.22	52/145	−170.20	22/185	−171.53	22/108	−170.85	6/166
NaI−(CH$_3$CN)$_7$	−177.34	111/230	−179.54	43/142	−177.31	66/177	−178.31	30/125	−177.94	25/136
NaI−(CH$_3$CN)$_8$	−183.37	104/208	−185.61	49/131	−182.86	112/166	−184.7	30/157	−185.46	39/167
NaI−(CH$_3$CN)$_9$	−189.65	40/197	−191.97	71/161	−189.32	123/151	−191.23	54/162	−192.24	88/202

[a] E_{NaI} is the binding energy (kcal/mol) of the bare molecule for the different internuclear distances.

their binding energies higher than those at 2.72 Å. Furthermore, from four acetonitrile molecules, the configurations obtained for a Na...I internuclear distance of 3.75 Å always have their interaction energies lower than those at 2.85 Å and (5, 7 Å). This result underlines the existence of two minima areas on the NaI−(CH$_3$CN)$_{n\geq 4}$ PES along the Na...I coordinate, one corresponding to the contact ion pair CIP structure (2.85 Å) and the second related to the solvent-separated ion pair SSIP structure (5 and 7 Å) with a potential energy barrier (3.75 Å) between the two forms CIP and SSIP. The height of the barrier cannot be deduced from this calculation since the internuclear Na...I distance is not optimized. The estimated barrier, for instance 3 kcal/mol found for the NaI−(CH$_3$CN)$_9$ clusters, is then a lower limit, which is already quite large.

The configurations at 2.85 Å have their binding energy at least 2 kcal/mol higher than those at 2.72 and 3.75 Å. The large interaction energy difference between these close internuclear distances exhibits a well-defined potential well for the CIP structure along the Na...I coordinate, with a global minimum for this structure located between 2.72 and 3.75 Å. On the other hand, the most stable internuclear distance of the SSIP structure evolves from 5 Å, for six and seven acetonitrile molecules, to 7 Å from eight solvent molecules. This second PES minimum area, which becomes deeper as the size increases, exhibits a shallow profile along the Na...I coordinate, and the potential well is rather large as compared to the CIP one. Furthermore, we have calculated the interaction energy of the NaI−(CH$_3$CN)$_8$ cluster for an internuclear distance of 10 Å in order to investigate the relative binding energy of the SSIP versus a more complete dissociation of the ion pair within the cluster. The first lowest energy minima found for this configuration are at least 8 kcal/mol higher in energy and so, the global minimum of the SSIP structure corresponds effectively to a Na...I internuclear distance spacing between 5 and 10 Å.

3.2. Binding Energy of the CIP and the SSIP Structures as a Function of the Cluster Size. From the results reported in Table 3, it is clear that the lowest energy minima of the small cluster sizes, typically with less than six or seven acetonitrile molecules, are obtained when the two ions are in contact (2.85 Å). However, for eight acetonitrile molecules, the binding energy difference between the two structures is now very tiny, and finally, for nine acetonitrile molecules, the lowest energy minima found for an internuclear distance of 7 Å have a higher binding energy than the ones obtained when the two ions stay in contact (2.85 Å).

When the two structures have almost the same interaction energy, as in the case of NaI−(CH$_3$CN)$_{8,9}$, we have analyzed the number of significant minima in a range of 2 kcal/mol above the global minimum for each cluster size. The results (histograms) are reported in Figure 2. The column bars depict the relative proportion of different isomers grouped together in an energy scale of 0.1 kcal/mol. For small cluster sizes, this number does not have a great significance, since only a few isomers are found, but becomes relevant as the size increases. For eight molecules, the two structures are almost isoenergetic but the CIP structure exhibits a higher density of low minima. However, this tendency evolves for nine acetonitrile molecules with the highest binding energy and a higher number of low-energy minima for the SSIP structure. As can be seen in Figure 2, there is a gap of 0.9 kcal/mol between the lowest and the second minima found for the NaI−(CH$_3$CN)$_8$ cluster when the two ions are separated by 7 Å. This gap could be correlated to an insufficient exploration of the PES due to a low temperature of the growth (500 K) and so excluding some areas leading to new minima. We have then run another exploration of the PES by increasing the temperature of the growth from 500 to 1000 K and locally optimized the new 200 configurations. No new minimum has been found, and this gap should be intrinsic to this cluster.[32]

3.3. Structural Properties of the Clusters. We have analyzed the structural properties of the NaI−(CH$_3$CN)$_n$ clusters. Since the NaI distance has not been optimized, we will focus on the acetonitrile arrangement around the ion pair.

3.3.1. Small Clusters. NaI−(CH$_3$CN)$_{1-3}$. The lowest energy minima of these clusters are depicted in Figure 3 and have revealed some important features.

First, the NaI−CH$_3$CN complex, for which an antiparallel configuration was expected in order to maximize the dipole−dipole interaction, exhibits an unexpected geometry. The acetonitrile molecule is strictly along the Na...I axis, on the sodium side. An analysis of the different component of the binding energy shows that this linear geometry results from the strong electrostatic interaction between Na$^+$ and the partially negatively charged nitrogen of the acetonitrile molecule. This strongly fixed geometry allows us to investigate experimentally some reactive collision processes where the impact parameter between the two bodies is equal to zero. In fact, we can expect that all the (alkali halide)−CH $_3$CN clusters will have this linear geometry. As a matter of fact, a recent femtosecond pump/probe ionization experiment on this system seems to agree with this calculation.[33]

The NaI−(CH$_3$CN)$_2$ cluster displays two lowest minima (143.67 and 143.47 kcal/mol) with two distinct geometries, as can be seen in Figure 3. For these two isomers, we have divided the total binding energy over the interaction pairs Na$^+$−(CH$_3$CN)$_{1,2}$, I$^-$−(CH$_3$CN)$_{1,2}$, CH$_3$CN−CH$_3$CN, and the CH$_3$CN

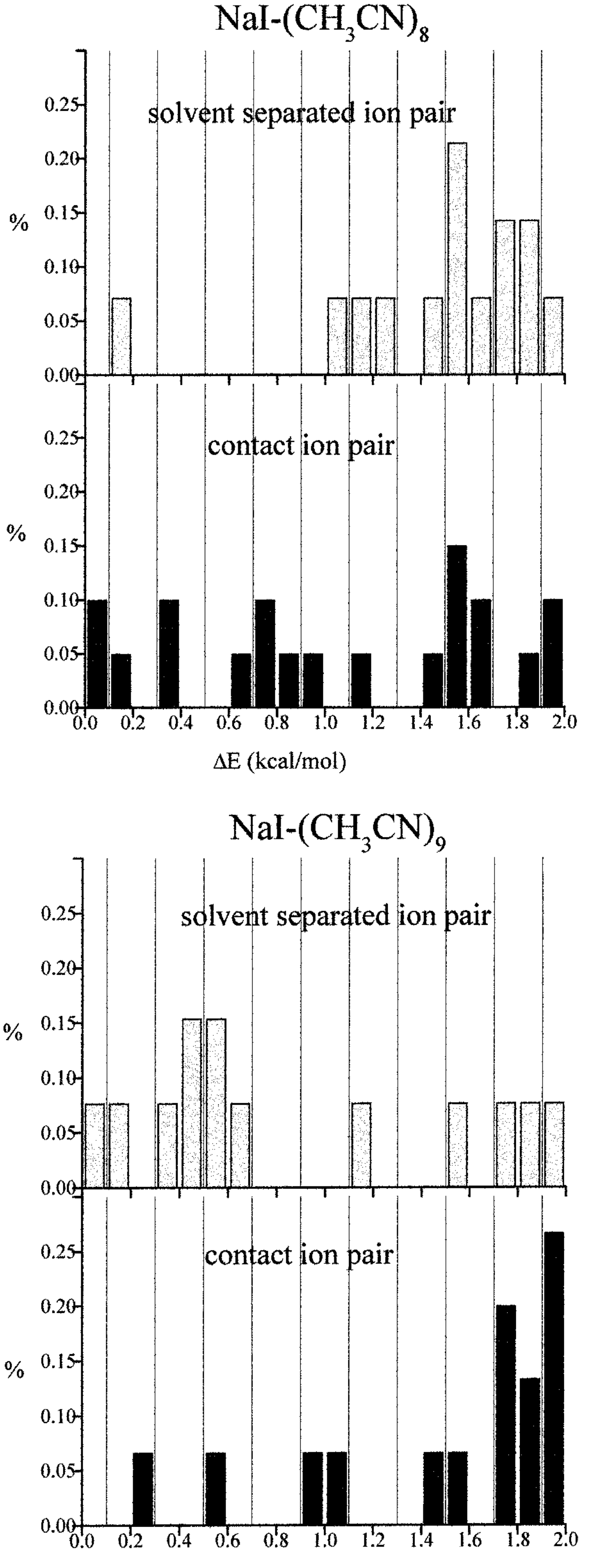

Figure 2. Density of low energy minima for NaI$-$(CH$_3$CN)$_{n=8,9}$ in contact ion pair and in solvent-separated ion pair structures. The column bars depict the number of isomers grouped together in 0.1 kcal/mol.

TABLE 4: Interaction Energy Decomposition (kcal/mol) of the Two Lowest Energy Minima of NaI$-$(CH$_3$CN)$_2$

NaI$-$(CH$_3$CN)$_2$	Na$^+$...0.1	Na$^+$...0.2	I$^-$...0.1	I$^-$...0.2	1...2	polarization
Min1: $E = -143.67$	-21.77	-14.56	9.57	3.95	1.76	-5.18
Min2: $E = -143.47$	-21.27	-21.27	9.44	9.44	2.28	-4.7

polarization energy. The results are listed in Table 4 and the acetonitrile subscripts, 1 or 2, referred to the ones plotted in Figure 3. For the isomer at 143.47 kcal/mol, the two acetonitrile molecules interact symmetrically with NaI, in a C_{2v} geometry. As in the NaI$-$CH$_3$CN complex, the Na$^+$...CH$_3$CN attractive contribution ($-$21.3 kcal/mol) is maximized while I$^-$...CH$_3$CN is strongly repulsive (9.4 kcal/mol) and the solvent$-$solvent contribution is also repulsive (2.3 kcal/mol). However, for the lowest minimum energy ($-$143.67 kcal/mol), one of the acetonitrile molecules forms a dipole-like interaction with NaI in a head-to-tail geometry. The binding energy of Na$^+$...CH$_3$CN is lower ($-$14.6 kcal/mol), and the I$^-$...CH$_3$CN interaction is less repulsive than in the C_{2v} structure. One can notice that the NaI$-$CH$_3$CN contribution in a head-to-tail geometry is lower than the one where the acetonitrile molecule lies rather on the sodium cation ($-$10.6 versus $-$12.2 kcal/mol), the latter being very close to the one found for the linear dimer NaI$-$CH$_3$CN ($-$12.5 kcal/mol at 2.85 Å). While the solvation energy of the two ions is less important in this geometry, the enhancement of the solvent polarization energy and the decrease of the CH$_3$CN$-$CH$_3$CN repulsion lead to a higher interaction energy. This competition is also found for the NaI$-$(CH$_3$CN)$_3$ complex, the two lowest energy minima exhibiting these two kinds of geometry, as pictured in Figure 3. However, the total binding energies of each different geometry are still very close.

We can deduce from this decomposition the relative strength of the binding energy over the three specific interactions, which rules the arrangement of the solvent molecules around the two ions when they are in contact: Na$^+$...CH$_3$CN, CH$_3$CN$-$CH$_3$CN, and I$^-$...CH$_3$CN. As we will see below, a different order will be found when the two ions are separated by 7 Å, which will lead to a different geometry of the clusters.

3.3.2. Large Clusters. NaI$-$(CH$_3$CN)$_9$. Since the internuclear distance between the two ions is not optimized, it is clearly impossible to assert that the distances of 2.85 and 7 Å lead effectively to the lowest energy minima of, respectively, the CIP and SSIP structures. However, the arrangement of the acetonitrile molecules in the cluster for the two corresponding configurations that have been reported in Figure 4 are very different and should not dramatically change for the two local minima of the CIP and SSIP structures.

As the cluster size increases, a classical way to analyze the arrangement of the solvent around a solute is to divide the total binding energy into solute$-$solvent and solvent$-$solvent contributions. The results are pictured in Figure 5 for the Na$^+-$CH$_3$CN, I$^-$CH$_3$CN, and CH$_3$CN$-$CH$_3$CN interaction energies as a function of the cluster size for the CIP and SSIP structures. We have also added the polarization energy of the solvent molecules. Since the binding energy of the NaI ion pair evolves with the internuclear distance, we have also reported on the right side of Figure 5 the binding energy difference of NaI at 7 and 2.85 Å, which is very large, 71.13 kcal/mol. All the interaction energies reported here are normalized to the number of solvent molecules.

The Na$^+-$CH$_3$CN interaction does not dramatically change for the two structures CIP and SSIP, although the binding energies are higher in the SSIP than in the CIP as the clusters size increases. On the other hand, the I$^-$CH$_3$CN and CH$_3$CN$-$CH$_3$CN binding energies are of opposite sign according to the CIP and SSIP structures. For instance, the attractive and repulsive interactions of I$^-$CH$_3$CN contributions found respectively for the SSIP and the CIP structures reveal that the iodide is better solvated in the separated ion pair configuration. Furthermore, the negative values of the solvent$-$solvent interaction energies in the CIP case emphasize that the NaI molecule

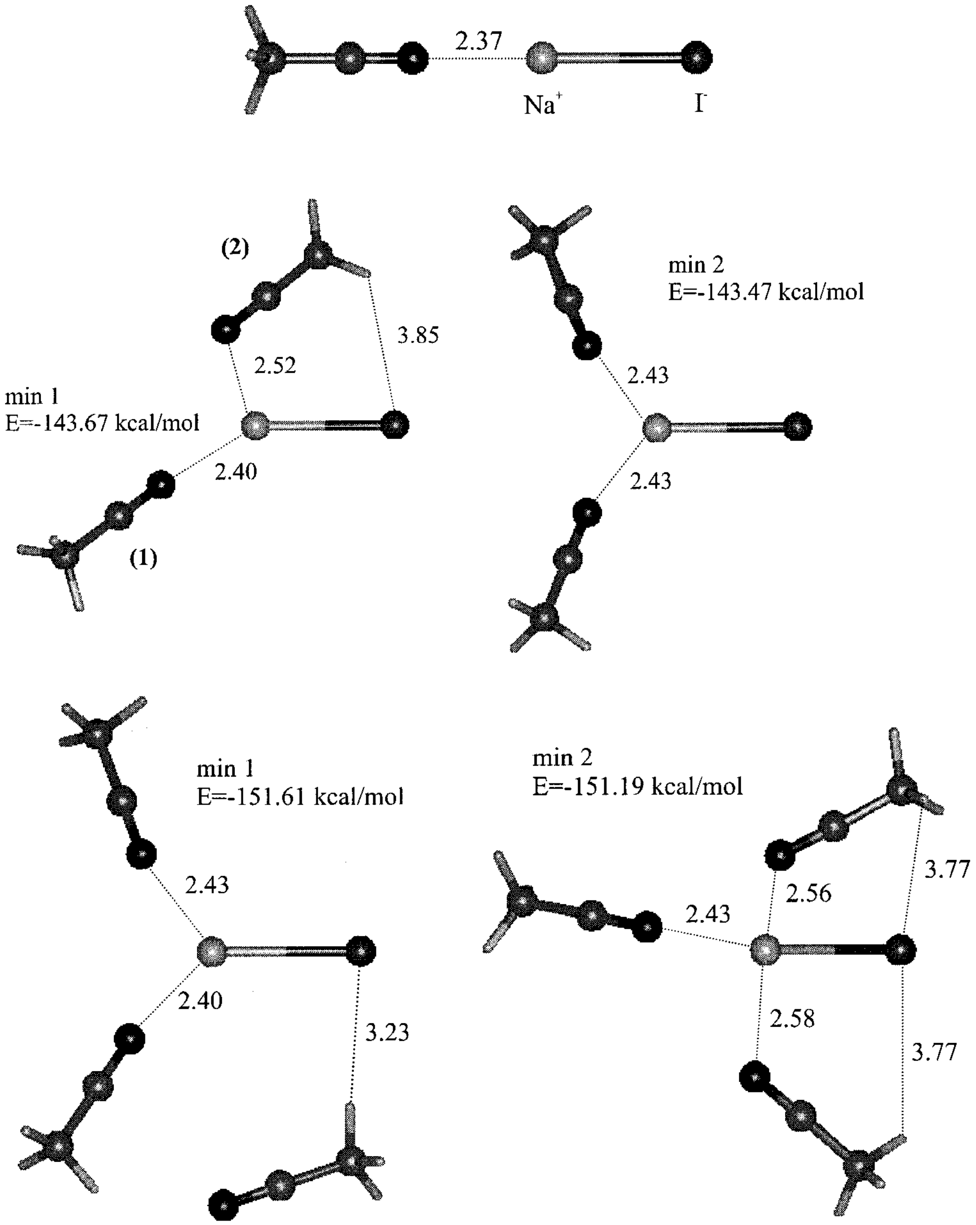

Figure 3. Optimized structures of NaI$-$(CH$_3$CN)$_{1-3}$ complexes. The NaI internuclear NaI distance is 2.72 Å for $n = 1$ and 2.85 Å after. With one acetonitrile, the solvent molecule lies along the NaI axis, on the sodium side. For the larger clusters, the acetonitrile molecules balance between a linear and a head-to-tail geometry.

does not totally disturb the solvent network, the iodide anion dragging the sodium cation to the surface of the cluster. The polarization energy of the acetonitrile molecules is also very different according to the two structures. The high values of the polarization energy in the solvent-separated ion pair structure emphasize the presence of solvent molecules shared between the ions. Nevertheless, we have neglected in the polarization the higher order of the development, for instance, the induced–induced contribution. In this case where the polarization energy is high, this term could be more or less important and tends to diminish the polarization energy, specially for the shared solvent molecules.

The mechanism of charge separation based on the interaction energy decomposition is fairly difficult to understand. Since all the ion–solvent, solvent–solvent, and polarization contributions are not independent from the others, no general rule can be deduced to predict the most stable geometry of the cluster. The binding energy difference between the lowest energy minima of the CIP and SSIP structures is very weak. Nevertheless, evidence of a lower degree of ion solvation in the CIP structure is underlined by the attractive solvent–solvent contribution, like, for example, in the Na$-$(H$_2$O)$_n$ clusters[34] where the sodium atom lies rather on the surface of the water cluster, the water–water interaction being stronger than the atom–solvent contribution.

4. Comparison with Experimental Results: Estimation of the Entropy Contribution

The presence of solvent molecules between the two ions induces a vanishing of the dipole moment transition A $\leftarrow$ X of NaI within the cluster.[8] First of all, the lowest energy minima of the SSIP configuration exhibit this structural property. According to the experimental results,[5] it was concluded that this structure is expected for more than seven acetonitrile molecules. Nevertheless, solvent evaporation from the detected Na$^+$$-$(CH$_3$CN)$_n$ ions should occur as was shown in the case of NaI$-$(NH$_3$)$_n$ clusters.[35] Furthermore, during the Na...I excited

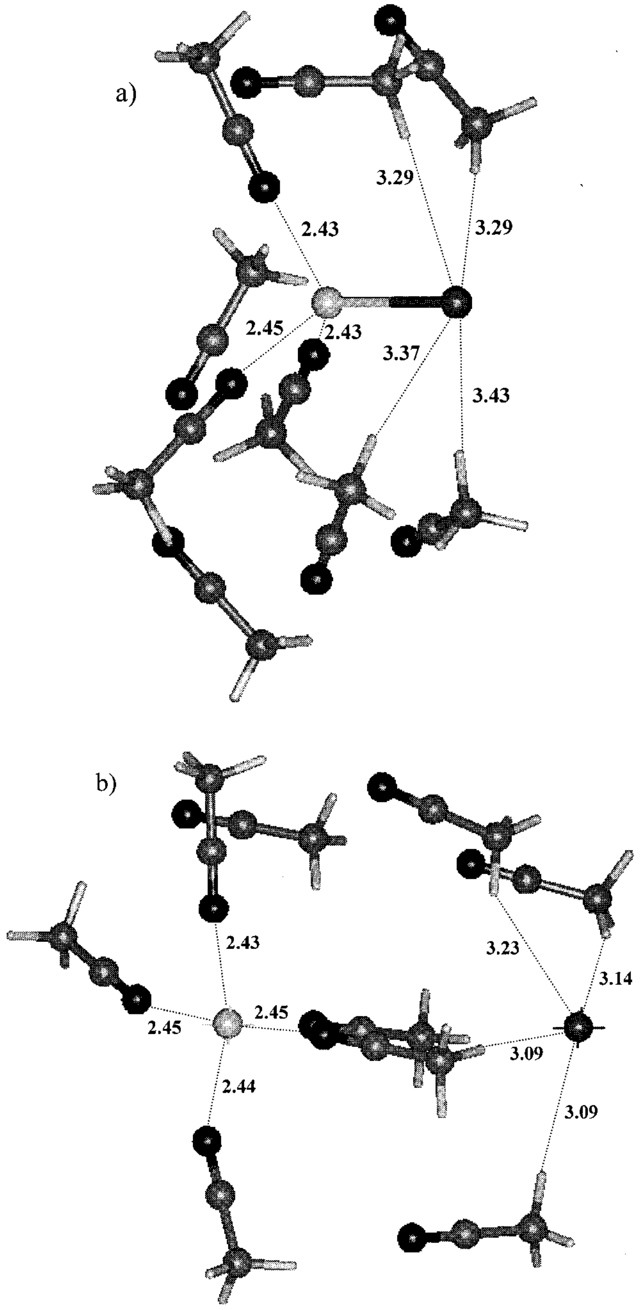

Figure 4. Optimized geometries of NaI−$(CH_3CN)_9$ according to two Na...I internuclear distances of 2.85 and 7 Å: (a) the CIP structure, where the iodide remains outside of the solvent network; (b) the SSIP structure, where two acetonitrile molecules are shared between the ions.

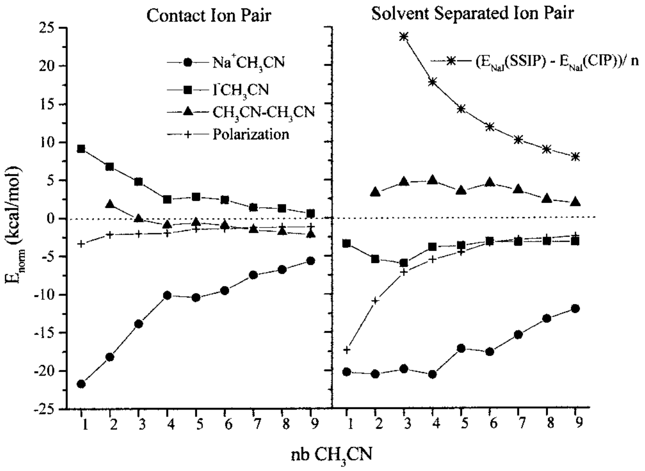

Figure 5. Interaction energy decomposition of the NaI−$(CH_3CN)_n$ as a function of the cluster size. On the right side of the figure, we have reported the binding energy difference of the NaI ion pair at 7 and 2.85 Å. Because of the large interaction energy change of the NaI ion pair according to the two internuclear distances, we have plotted this contribution only from three solvent molecules. All these contributions are normalized to the number of acetonitrile molecules. The negative values of the solvent−solvent contribution in the CIP structure show that the solvent network is not strongly disturbed by the NaI molecule. Conversely, the attractive interaction of I^-CH_3CN reveals a better solvation of the iodide in the SSIP structure than in the CIP configuration.

state bond breaking, some acetonitrile molecules could leave with the iodine. These two points imply that the critical size for the charge separation is somewhat higher, of one or two acetonitrile molecules, than the one deduced from the largest ion mass detected.

In our calculation, we treat interaction energies, i.e., at 0 K, and the temperature influence, i.e., the free energy, has to be questioned in order to compare with experimental results. From the results of Figure 2 for the NaI−$(CH_3CN)_9$ cluster, the density of local minima near the global one is higher for the SSIP than for the CIP configurations. This number, which can be related to a statistical entropy contribution, tends to estimate the probability of observing such isomers in a gas phase experiment where the clusters have a nonzero temperature. As a matter of fact, the SSIP configurations should be favored as compared to the CIP ones and we can thus expect that clusters containing about 10 solvent molecules are more probably in the SSIP structure.

The temperature of a molecular cluster in a gas phase experiment, i.e., its internal energy, still remains difficult to measure but can be estimated either from previous experiments specially devoted to that or from theoretical models. Experimentally, temperatures of small acetonitrile clusters have been estimated below 120 K[36] or between 150 and 200 K.[37] Theoretically, the evaporative model developed by Klots[38] allows us to calculated the upper limit T_{max} of cluster temperatures as a function of the cluster size. Using this approach, Desfrançois et al.[12] have evaluated the T_{max} values between 80 and 120 K for dimers and hexamers acetonitrile clusters. Since their experimental conditions are comparable to those of ref 7, we can estimated an upper limit of 150 K for NaI−$(CH_3CN)_n$ clusters experimentally studied.

Molecular dynamics studies on similar systems, as NaI−$(H_2O)_n$[8] and KCl−$(H_2O)_n$[4−5] clusters, using potential of mean force (PMF) calculations at 200 and 300 K have been already achieved. From eight solvent molecules, two local minima along the NaI internuclear distance coordinate are clearly outlined, related to the CIP and SSIP structures. For the CIP structure, a slight enhancement of the NaI internuclear distance is observed with the cluster size,[4] but this local minimum still remains well localized around the equilibrium NaI distance. Conversely, for the SSIP configurations, the PMF exhibits a very shallow profile,[5,8] which extends to a wide range of interionic distances. The calculations reported in our manuscript are in total agreement with these previous results, which seems to indicate that the temperature influence on the potential energy profile is weak.

Finally, it has been already shown that a rise of the temperature, and then a more pronounced contribution of the entropy term in the free energy, favors a more complete solvation of an anion for instance,[13,39] leading to an interior geometry of the ion−solvent cluster. We can expect a similar behavior for the NaI−(CH$_3$CN)$_n$ clusters, which should imply that the Na...I charge separation reaction should be favored by an increase of the temperature.

In conclusion, the critical number of nine acetonitrile molecules needed to obtain lower energy minima at 0 K for an internuclear distance of 7 Å rather than 2.85 Å are in good agreement with experimental results.

5. Conclusions

Binding energies and structures of the contact ion pair and the solvent-separated ion pair configurations in NaI−(CH$_3$CN)$_{n=1-9}$ clusters have been reported. An elaborate intermolecular potential has been parametrized to correctly reproduce both solvent−solvent and ion−solvent interaction energies. First, the NaI−CH$_3$CN cluster displays an unexpected geometry, the acetonitrile molecule being along the NaI axis on the sodium ion side. This particular geometry should be relevant for photodissociation study of NaI−CH$_3$CN, where the impact parameter should be equal to zero. For clusters with less than eight solvent molecules, the two ions stay in contact, the iodide being poorly solvated by the acetonitrile molecules. From nine acetonitrile molecules, the highest binding energies are found for a Na...I internuclear distance of 7 Å rather than 2.85 Å, emphasizing a change from the CIP to the SSIP structures with the cluster size. Furthermore, in the solvent-separated ion pair structure, few acetonitrile molecules are shared between the ions, as was presumed from the experimental results.[7] In conclusion, we find a nice agreement between our calculations and what has been observed in the experimental study on NaI−(CH$_3$CN)$_n$ clusters.

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References and Notes

(1) Peslherbe, G. H.; Bianco, R.; Hynes, J. T.; Ladanyi, B. M. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 977.

(2) Guardia, E.; Rey, R.; Padro, J. A. *Chem. Phys.* **1991**, *155*, 187.

(3) Canales, M.; Sesé, G. *J. Chem. Phys.* **1998**, *109*, 6004.

(4) Laria, D.; Fernandez-Prini, R. *Chem. Phys. Lett.* **1993**, *2058*, 260.

(5) Laria, D.; Fernandez-Prini, R. *J. Chem. Phys.* **1995**, *102*, 7664.

(6) Asada, T.; Nishimoto, K. *Chem. Phys. Lett.* **1995**, *232*, 518 and references therein.

(7) Gregoire, G.; Mons, M.; Dedonder-Lardeux, C.; Jouvet, C. *Eur. Phys. J. D* **1998**, *1*, 5.

(8) Hynes, J. T.; Peslherbe, G. H. Submitted to *J. Phys Chem. A*.

(9) Bertolus, M.; Brenner, V.; Millié, P.; Maillet, J. B. *Z. Phys. D* **1997**, *39*, 239.

(10) Claverie, P. In *Intermolecular Interaction*: *From diatomics to biopolymers*; Pulmann, B., Ed.; J. Wiley: New York, 1978; Chapter 2.

(11) Hess, O.; Caffarel, M.; Langlet, J.; Caillet, J.; Huiszoon, C.; Claverie, P. In *Procedings of the 44th International Meeting of Physical Chemistry on Modelling of Molecular Structure and Properties in Physical Chemistry and Biophysics*, Nancy, France, 11−15 September 1989; Rivail, J. L., Ed.; Elsevier: Amsterdam, 1990.

(12) Desfrançois, C.; Abdoul-Carime, H.; Khelifa, N.; Schermann, J. P.; Brenner, V.; Millié. P. *J. Chem. Phys.* **1995**, *102*, 4952.

(13) Peslherbe, G. H.; Ladanyi, B. M.; Hynes, J. T. *J. Phys. Chem. A* **1999**, *103*, 2561 and references therein.

(14) Chandrasekhar, J.; Spellmeyer, D. C.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1984**, *106*, 903.

(15) Jorgensen, W. L.; Chandrasekhar, J.; Madura, J. D.; Imprey, R. W.; Klein, M. L. *J. Chem. Phys.* **1981**, *79*, 926.

(16) Wales, D. J.; Ohmine, I. *J. Chem. Phys.* **1993**, *98*, 7245.

(17) Caldwell, J.; Dang, L. X.; Kollman, P. A. *J. Am. Chem. Soc.* **1990**, *112*, 9144.

(18) Dang, L. X.; Garrett, B. C. *J. Chem. Phys.* **1993**, *99*, 2972.

(19) Gai, H.; Dang, L. X.; Schenter, G. K.; Garrett, B. C. *J. Phys. Chem.* **1995**, *99*, 13303.

(20) Garel, T.; Orland, H. *J. Phys. A* **1990**, *23*, L621.

(21) Garel, T.; Niel, J. C.; Orland, H.; Velikon, B. *J. Chem. Phys.* **1991**, *88*, 2473.

(22) Fletcher, R. *Comput. J.* **1970**, *13*, 317. Goldfarb, D. *Math. Comput.* **1970**, *24*, 23. Shanno, D. F. *Math. Comput.* **1970**, *24*, 647.

(23) Vigné-Maeder, F.; Claverie, P. *J. Chem. Phys.* **1988**, *88*, 4934.

(24) Brenner, V.; Millié, P. *Z. Phys. D* **1994**, *30*, 327.

(25) Schaefer, S. H.; Bender, D.; Tiemann, E. *Chem. Phys.* **1984**, *89*, 65.

(26) Lefevre, R. J. W. *Advances in Physical Organics Chemistry*; Academic Press: New York, 1965; Vol 13, p 1.

(27) van Duigneveldt, F. B. *IBM Res. Rep.* 1971, RJ945.

(28) Fernandez Pacios, L.; Christiansen, P. A. *J. Chem. Phys.* **1985**, *82*, 2664.

(29) Lajohn, L. A.; Christiansen, P. A.; Ross, R. B.; Atashroo, T.; Ermler, W. C. *J. Chem. Phys.* **1987**, *87*, 2812.

(30) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P: M.W.; Johnson, B. J.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanow, B. B.; Nanayaklara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A.; *Gaussian 94*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(31) Ohshimo, K.; Tsunoyama, H.; Yamakita, Y.; Misaizu, F.; Ohno, K. *Chem. Phys. Lett.* **1999**, *301*, 356.

(32) A detailed analysis of the isomers found for the solvent-separated ion pair case has revealed two kinds of structure according to the number of solvent molecules, either two or three, located between the two ions.

(33) Gregoire, G.; Mons, M.; Dimicoli, I.; Dedonder-Lardeux, C.; Jouvet, C.; Martrenchard, S.; Solgadi, D. *Eur. Phys. J. D*, in press.

(34) Hashimoto, K.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 11436.

(35) Grégoire, G.; Mons, M.; Dimicoli, I.; Dedonder-Lardeux, C.; Jouvet, C.; Martrenchard, S.; Solgadi, D. *J. Chem. Phys.* **1999**, *110*, 1521.

(36) Al-Mubarak, M. S.; Del Mistro, G.; Lethbrigde, P. G.; Abdul-Sattar, N. Y.; Stace, A. J. *Faraday Discuss. Chem. Soc.* **1988**, *88*, 209.

(37) Mengel, M. H.; Scoles, G. *The Chemical Physics of Atomic and Molecular Clusters*; CVII Enrico Fermi Scholl: Varenna, 1988.

(38) Klots, C. E. *J. Chem. Phys.* **1985**, *83*, 5854. *Z. Phys. D* **1991**, *20*, 105.

(39) Combariza, J. E.; Kestner, N. R.; Jortner, J. *J. Chem. Phys.* **1994**, *100*, 2851.