# Computational Study of the Interaction in $X^-(CH_3NH_2)_n$ Clusters ($X = F, Cl$; $n = 1-4$). The Balance between Ion−Molecule and Molecule−Molecule Interactions

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A computational study of clusters consisting of a fluoride or chloride ion and up to four methylamine molecules was conducted using ab initio and density functional theory (DFT) methods. A large number of structures corresponding to minima on the potential surfaces for the different clusters were obtained that included interior structures (where the methylamine molecules lie around the halide ion) and surface structures (where a cluster of methylamine molecules interacts as a unit with the ion). On the basis of the results, fluoride ion tends to form no surface structures; the most stable structure for each cluster is of the interior type. On the other hand, chloride ion forms surface structures where methylamine molecules interact with one another via N−H···N bonds. Whether or not a surface structure can be formed depends on the balance between ion−molecule and molecule−molecule interactions. In interior structures, the stabilizing effect arises from strong ion−molecule attractions; in surface structures, ion−molecule interactions weaken at the expense of interactions between methylamine molecules. In the fluoride clusters, ion−molecule interactions are so strong that the potential formation of hydrogen bonds between methylamine molecules cannot overcome the tendency of the molecules to interact with the ion and form interior structures. On the other hand, ion−molecule interactions are weaker for chloride, so the hydrogen bonding between molecules is strong enough for surface structures to be formed. At some minima, the N−H···X interaction was replaced with less stable C−H···X bonds; in the chloride clusters, however, such a stability loss was offset by the interaction between methylamine molecules, and the resulting structures were as stable as those of the interior forms. The N−H symmetric stretching frequencies are red-shifted by the effect of the interaction; also, they differ between interior and surface structures. Thus, the interior structures give signals that span only a narrow frequency range. The structures forming N−H···N hydrogen bonds exhibit the most markedly red-shifted signals, which, in addition, span a broader frequency range.

## 1. Introduction

The solvation of ions by various types of solvents is a process of interest for a wide range of applications. One can derive useful information about the solvation mechanism from studies in the gas phase, which help pinpoint the different factors involved.[1−5] This type of study allows one to determine the nature of the transition between the molecular cluster in the gas phase and the solvated ion in the liquid phase. The use of theoretical methods for studying clusters formed by ions and several solvent molecules provides even wealthier information about the mechanism governing the transition.

One especially interesting aspect of the microsolvation of ions by different types of solvents to form clusters consisting of a few molecules is the competition between ion−solvent and solvent−solvent interactions.[1,6−8] In simple ions such as those of alkaline elements, solvent molecules in the gas phase can be expected to surround the ion in order to maximize the ion−solvent interaction and to depart from one another as far as possible in order to minimize steric repulsion. This behavior is observed in the solvation of ions with a high charge/radius ratio and in solvents with little tendency to aggregate. The situation can be different if the solvent concerned tends to associate (e.g. through intermolecular hydrogen bonding). Under these conditions, interactions between solvent molecules may be able to overcome the ion−solvent interaction and form so-called “surface structures”,[1,6−8] where a cluster of solvent molecules interacts as a single unit with the solvent, but without completing its coordination sphere. The effect of this competition between ion−solvent and solvent−solvent interactions was first observed in mixed clusters of $Cs^+$ with acetone and methanol;[9] although

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acetone possesses a higher dipole moment than methanol and interacts more strongly with the ion as a result, the alcohol invariably occupies the first coordination sphere by virtue of its ability to form intermolecular hydrogen bonds.

Most studies on this topic have focused on clusters consisting of alkaline[1−8,10−18] or halide[19−29] ions and a variable number of water molecules. On the other hand, studies on the solvation of ions with solvents other than water are much scantier,[19,30−35] and most of them have considered methanol as solvent. The results obtained for the solvation of chloride ion by methanol—which are very similar to those obtained in water—suggest that the occurrence of surface structures depends more strongly on the nature of the anion than on that of the solvent.[30,31] However, both water and methanol clusters can clearly form relatively strong intermolecular hydrogen bonds, which facilitate the formation of surface structures. Methylamine is similar to methanol. In fact, it is a moderately polar molecule, which, however, forms weaker hydrogen bonds than methanol.[36] Therefore, the clusters of methylamine with ions can be expected to exhibit a lower tendency to form surface structures. The use of a solvent with a less marked tendency to associate, but still capable of forming hydrogen bonds, should allow one to determine whether the occurrence of surface structures is mainly governed by the nature of the anion or that of the solvent. Also, the methylamine molecule can interact with anions via the amino group and simultaneously with another molecule via the second hydrogen atom in the amino group or a hydrogen atom in the methyl group. To elucidate the characteristics of the interaction in clusters consisting of fluoride or chloride and methylamine, in this work we performed ab initio and density functional theory (DFT) calculations on clusters formed by either ion and up to four methylamine molecules.

## 2. Computational Details

The structures of the $X^-(CH_3NH_2)_n$ clusters (X = F, Cl; $n = 1-4$) were optimized by using the DFT and MP2 methods in conjunction with the 6-31+G* basis set with a view to locating the more relevant stationary points on the corresponding potential energy surfaces. The functional employed in DFT calculations was B3LYP.[37,38] Once stationary points were located, a vibrational study was performed on all clusters—those with four methylamine molecules and the MP2 method excepted owing to the high computational cost of the calculations—in order to ascertain whether all frequencies were real and the corresponding stationary point corresponded to actual minima as a result. The starting structures were chosen from among those used in previous studies on similar systems and also on the basis of chemical intuition.

Once the stationary points on the potential surface energy were located, their respective interaction energies were calculated. Cluster energies are known to be subject to the basis set superposition error (BSSE);[39,40] consequently, all energies were calculated using the Boys−Bernardi counterpoise method (i.e. employing the basis set for the whole cluster):[41]

$$\Delta E_n^{\mathrm{CP}} = E_n(1,2,...,n) - \sum_i E_i(1,2,...,n) \tag{1}$$

Only the interaction energies for the fragments in the geometric arrangement of the minimum were considered when calculating this quantity. Obtaining the complexation energy for a specific cluster entails incorporating that required to distort the molecules from their geometry in isolation to that in the cluster.[42,43] Such a contribution (the deformation energy) is obtained by using the basis set for each molecule and calculated from the following expression:

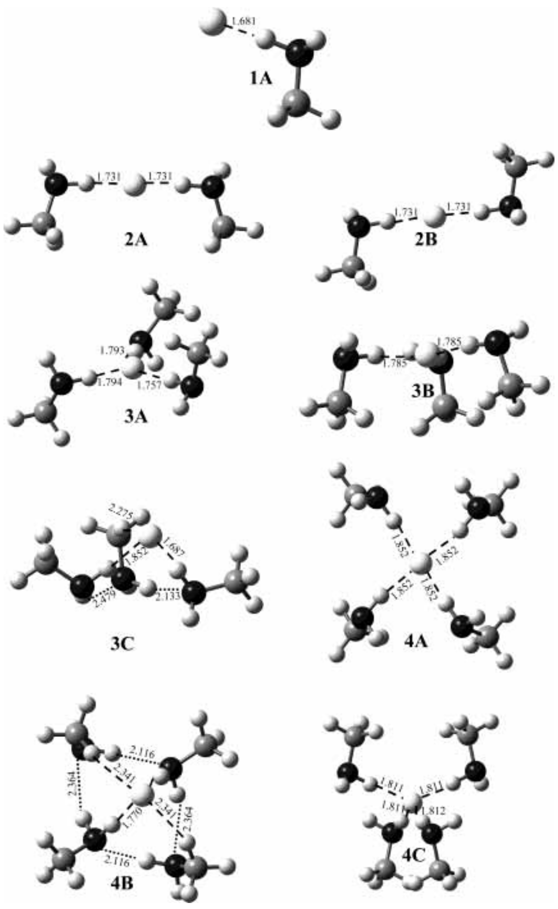

**Figure 1.** Structures identified on the potential energy surfaces for the fluoride clusters. Distances in Å obtained with the MP2 method.

$$E_{\mathrm{def}} = \sum_i (E_i^{\mathrm{cluster}} - E_i^{\mathrm{isolated}}) \tag{2}$$

where superscripts denote the geometry to be used in each case.

It should be noted that the structure obtained in the optimization process was subject to BSSE, as the potential energy surface on which the optimization was performed was uncorrected. However, we believe the effect was negligible and must thus have had little effect on the results.[44]

To more carefully examine the characteristics of the interaction, the interaction energy was split into the contributions of the ion−solvent and solvent−solvent interactions.[6−8,34,35] The energy of interaction between solvent molecules was obtained by calculating the interaction energy for the cluster formed by the methylamine molecules in the cluster structure.

$$\Delta E_{\mathrm{S}} = E_{(\mathrm{CH_3NH_2})_n}(1,2,...,n) - \sum_i^n E_i(1,2,...,n) \tag{3}$$

The difference between this quantity and the interaction energy yielded the ion−solvent interaction energy.[6−8,34,35] We also obtained the interaction energy for each pair of fragments in each cluster, which enabled a more detailed study of the interaction. All calculations were done with Gaussian 98.[45]

## 3. Results

**3.1. Fluoride Clusters.** Figure 1 shows the structures of the stationary points located for the fluoride-containing clusters, and

**TABLE 1: Interaction Energies (kcal/mol) for the Clusters with Deformation Energies in Parentheses**

| | F | | | | Cl | | | |
|---|---|---|---|---|---|---|---|---|
| | B3LYP | | MP2 | | B3LYP | | MP2 | |
| | $\Delta E^{CP}$ | $E_{def}$ | $\Delta E^{CP}$ | $E_{def}$ | $\Delta E^{CP}$ | $E_{def}$ | $\Delta E^{CP}$ | $E_{def}$ |
| **1** | −18.06 | (1.30) | −15.74 | (0.98) | −8.61 | (0.38) | −7.94 | (0.39) |
| **2A** | −31.73 | (1.47) | −28.60 | (1.29) | −16.38 | (0.67) | −15.27 | (0.67) |
| **2B** | −31.71 | (1.48) | −28.58 | (1.29) | −16.35 | (0.67) | −15.36 | (0.67) |
| **2C** | | | | | −16.69 | (0.63) | −15.99 | (0.71) |
| **3A** | −42.44 | (1.49) | −39.56 | (1.49) | −23.39 | (0.85) | −22.80 | (0.87) |
| **3B** | −42.55 | (1.49) | −39.81 | (1.54) | −23.02 | (0.90) | −22.30 | (0.85) |
| **3C** | −38.63 | (1.81) | −36.35 | (1.61) | −22.88 | (0.65) | −22.47 | (0.75) |
| **4A** | −51.17 | (1.42) | −49.57 | (1.66) | −31.00 | (0.98) | −30.23 | (1.25) |
| **4B** | −46.01 | (1.93) | −44.59 | (1.80) | −29.93 | (0.84) | −29.83 | (1.10) |
| **4C** | −51.69 | (1.42) | −49.50 | (1.56) | | | | |

Table 1 gives the corresponding interaction energies. The two computational methods used provided similar structures, with a few slight discrepancies. Thus, structure **2B** was not a minimum with MP2. Also, the B3LYP method provided interaction energies that were more negative than the MP2 values—the differences, however, were minimal, and the values obtained with both methods exhibited identical trends.

The cluster consisting of fluoride ion and a single methylamine molecule forms an F···HN hydrogen bond with a length of 1.62 Å with B3LYP and 1.68 Å with MP2. The interaction energy for this structure is −18.1 kcal/mol with B3LYP and −15.7 kcal/mol with MP2. As expected, this is an especially strong interaction, on account of the relatively high charge/radius ratio of fluoride ion. The incorporation of a second methylamine molecule increases the number of possible structures. Of the two minima found, structure **2B** is clearly of the interior type, with the molecules on opposite sides of the anion and the methyl groups also facing each other. It should be noted that this structure is not an actual minimum with MP2, as it exhibits an imaginary frequency. The other structure, **2A**, has the methyl groups on the same side and the molecules on opposite sides of the anion. This structure is also of the interior type, as the H···F···H angle is 179°. Both structures have energies in the region of −32 kcal/mol (−29 kcal/mol with MP2) that differ by less than 0.1 kcal/mol; this suggests that whether the methyl groups lie on the same or opposite sides is irrelevant in energetic terms, owing to the large distance between the molecules. The incorporation of the second molecule, however distant from the first, weakens the interaction with the anion and results in a departure of the molecules from the fluoride ion.

The three structures identified for the fluoride cluster with three methylamine molecules are rather different. One, **3A**, corresponds to a minimum of the interior type, with the three molecules surrounding the ion and the methyl groups occupying alternate positions. Both the nitrogen atoms and the central anion lie virtually in the same plane, as shown by the fact that the sum of H···F···H angles is 360°—there is thus no pyramidalization around the central ion. The second structure, **3B**, exhibits some differences depending on the particular computational method. Thus, with B3LYP, it is an interior structure with the three methyl groups on the same side and H···F···H angles summing 360°. With MP2, however, the fluoride ion appears to be in a different plane than that defined by the three hydrogen atoms interacting with it; in this case, the combined H···F···H angles are 324°, so there is substantial pyramidalization around the central ion. The third structure, **3C**, is completely different from the previous two: one of the methylamine molecules interacts with the fluoride ion with the methyl group instead of doing it with the $NH_2$ unit. The $NH_2$ group in such a molecule can form hydrogen bonds with the other two methylamine molecules. The contact via the methyl group exhibits F···HC distances in the region of 2.28 Å, which implies a weaker interaction with the anion; this effect, however, is partly offset by the formation of two N−H···N bonds; that is one methylamine molecule acts simultaneously as donor and acceptor in two different hydrogen bonds with a respective NH···N distance of 2.13 and 2.48 Å.

Of the three structures considered for the cluster with $n = 3$, **3B** is the most stable; however, **3A** is only 0.1−0.3 kcal/mol less stable. Structure **3C** is considerably less stable, with a 3−4 kcal/mol difference from the previous two. Therefore, the loss of the interaction associated with the methyl group−fluoride contact is not offset by the formation of hydrogen bonds between the methylamine molecules.

We obtained up to three different structures for the fluoride clusters with four methylamine molecules—with some discrepancies between the two computational methods, however. Thus, **4A** exhibits an imaginary frequency with B3LYP. In this structure, the methylamine molecules lie around the anion, with the methyl groups on the same side; the protons and the anion lie in the same plane (the combined angles are 360°). In structure **4C**, the nitrogen atoms lie roughly at the vertexes of a tetrahedron. None of the previous structures appears to form hydrogen bonds between the methylamine molecules. On the other hand, structure **4B**, which is similar to **3C** (with two molecules interacting with the anion via the methyl groups), forms such bonds. This is clearly a surface structure where the four nitrogen atoms lie in a different plane than the anion. The interaction energies for these structures are in the region of −50 to −52 kcal/mol for **4A** and **4C**, whereas that for **4B** is 5 kcal/mol less negative. Therefore, at least up to $n = 4$ and as with water, fluoride ion forms no surface structures with methylamine.

Despite the strong interaction established between fluoride and methylamine, the deformation energy supposes a small contribution that does not surpass 5% of the interaction energy in most structures.

One of the effects of the hydrogen bonding interaction is lengthening of the N−H distances in the groups involved in the hydrogen bonds. The clusters studied in this work exhibit three different phenomena, namely, major bond lengthening due to X···HN contacts, minor lengthening associated with N···HN contacts, and virtually zero lengthening in N−H distances in those groups not directly involved in a hydrogen bond.

The formation of the fluoride cluster with a single methylamine molecule lengthens the N−H distance by 0.046 Å; the other N−H unit undergoes marginal lengthening (only 0.003 Å), as it does not interact directly with the anion. The incorporation of the second molecule precludes such a strong interaction with the ion, so the bond lengthening is smaller (ca. 0.032 Å). Because no NH···N bonds are formed, the N−H distances in the groups not interacting with the anion remain virtually unchanged.

The clusters with $n = 3$ exhibit similar trends as those with two methylamine molecules, with even less marked bond lengthening and no changes in the other groups. However, one of the NH···F contacts in structure **3C** undergoes more marked lengthening than even with $n = 2$; also, one of the NH groups that does not interact with the anion contacts the adjacent molecule and causes a lengthening by 0.01 Å, which is much greater than those observed in the interior structures for N−H groups not directly interacting with the anion. The clusters with $n = 4$ exhibit similar trends to those of the smaller ones.

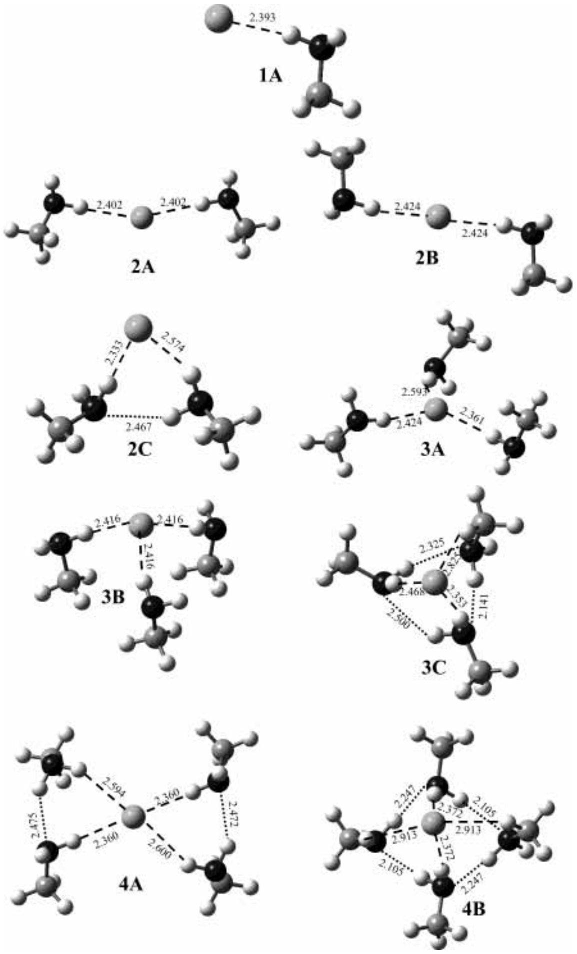

**Figure 2.** Structures identified on the potential energy surfaces for the chloride clusters. Distances in Å obtained with the MP2 method.

From the foregoing it follows that the interior structures exhibit increasingly lower deformation in the NH units with growing cluster size; this trend is reversed in the surface clusters, which, owing to the formation of N−H···N hydrogen bonds, have at least one molecule with an N−H distance longer than that expected for interior structures.

**3.2. Chloride Clusters.** Figure 2 shows the structures examined for the chloride clusters, and Table 1 gives their respective interaction energies.

The cluster with $n = 1$ is similar to the fluoride cluster with a single methylamine molecule; however, because of the larger size of the $Cl^-$ ion, the Cl···H distance is 2.39 Å and the interaction energy only −8.6 kcal/mol (−7.9 kcal/mol with MP2). The addition of a new methylamine molecule gives rise to up to three different structures. Structure **2A** has the methylamine molecules on opposite sides and the methyl groups on the same side of the anion. This structure is no minimum with MP2. Also, unlike the fluoride clusters, structure **2B** is no minimum with either computational method; this reflects the higher tendency of chloride ion to form surface structures. Finally, the third structure, **2C**, has no parallel in the fluoride clusters. This minimum is of the surface type, with the two methylamine molecules on the same side of the ion and an H···Cl···H angle of only 64° compared to 174° for the other structures; this structure forms an NH···N hydrogen bond between the two methylamine molecules. The Cl···HN distance reflects major changes with respect to **2A** and **2B**. Thus, the molecule acting as donor is at ∼2.57 Å, whereas that acting as acceptor lies at ∼2.33 Å—which is even shorter than that in the cluster with a single methylamine molecule. Therefore, one molecule can be expected to interact strongly with the anion, whereas the other will interact more weakly as a result of its simultaneous contact with the previous methylamine molecule. The N−H···N contact distance is 2.47 Å, and the hydrogen bond is distorted (the angle is 140°, which is rather different from that for the ideal linear contact). The interaction energies for the clusters are in the region of −16 kcal/mol, and the most stable structure is **2C**; this reflects the tendency of chloride ion to establish contacts of the surface type.

The three structures obtained with $n = 3$ are similar to those exhibited by the fluoride clusters. However, structure **3A** is not a minimum with either computational method. In structure **3B** the nitrogen and chloride atoms are in different planes. The combined H···Cl···H angles are 318° with B3LYP and 250° with MP2; this reflects pyramidalization of the structure around the central atom. The interaction energy for these structures is about −23 kcal/mol. The other minimum observed, **3C**, is similar to that obtained for fluoride. However, the interaction energy for the chloride cluster is only 0.5 kcal/mol lower than that for the more stable structure—such a difference is 3 kcal/mol for the fluoride cluster. These results suggest that NH···N contacts in the chloride clusters are of similar intensity to Cl···HN contacts, so surface structures can be formed with ease.

The clusters with $n = 4$ shown in Figure 2 exhibit similar trends to those of the smaller clusters. The geometric optimization yields none of the tetrahedral structures observed in the fluoride clusters. Thus, minimum **4A** is an interior structure with the four atoms in a plane that also contains the chloride. However, this structure forms two hydrogen bonds between as many pairs of methylamine molecules and resembles two coupled **2C** minima. The presence of hydrogen bonds in interior structures hinders the formation of surface structures, as the establishment of such bonds at surface minima implies a smaller energetic advantage relative to that of interior structures already possessing hydrogen bonds. Finally, structure **4B** is similar to that for the fluoride cluster. The interaction energies are all in the region of −30 kcal/mol. The **4B** minimum is only slightly less stable than **4A**, so it is probable that the most stable structures for clusters consisting of larger anions and more methylamine molecules present contacts of the C−H···X type.

In the chloride cluster with $n = 1$, N−H bond elongation amounts to 0.012 Å and is thus smaller than that in the corresponding fluoride cluster, which is consistent with the lower charge/radius ratio of chloride ion. The distance decrease with increase in the number of molecules in the interior structures is less abrupt than that in the fluoride cluster, as chloride can more readily accommodate the molecules within its coordination sphere without the interaction being significantly weakened through intermolecular repulsion. The surface structure **2C** possesses an NH bond that is more strained than that in the cluster with $n = 1$. Also, the N−H group that interacts with another methylamine molecule is lengthened by 0.004 Å (i.e. roughly twice as much as in the other clusters with $n = 2$). The clusters with $n = 3$ behave similarly to their fluoride counterparts, and additional elongations are only observed in **3C**. Finally, the clusters with $n = 4$ depart from the previous trends, since even **4A** exhibits hydrogen bonds between methylamine molecules and lengthened N−H distances as a result. The most marked lengthening is that in **4B**, which is the structure most readily forming the hydrogen bonds.

**3.3. Energies.** Additional information about the interaction can be obtained by examining the energy involved in incorporating a new molecule into an existing cluster (Table 2). As

**TABLE 2: Variation of the Interaction Energy ($\Delta E_n - \Delta E_{n-1}$ in kcal/mol) as New Methylamine Molecules Are Incorporated into the Cluster**

| | F | | Cl | |
|---|---|---|---|---|
| | B3LYP | MP2 | B3LYP | MP2 |
| **1** | −18.06 | −15.74 | −8.61 | −7.94 |
| **2A** | −13.67 | −12.86 | −7.77 | −7.33 |
| **2B** | −13.65 | −12.84 | −7.74 | −7.42 |
| **2C** | | | −8.08 | −8.05 |
| **3A** | −10.71 | −10.96 | −7.01 | −7.53 |
| **3B** | −10.82 | −11.21 | −6.64 | −7.03 |
| **3C** | −6.90 | −7.75 | −6.50 | −7.20 |
| **4A** | −8.62 | −9.76 | −7.98 | −7.93 |
| **4B** | −3.46 | −4.78 | −6.91 | −7.53 |
| **4C** | −9.14 | −9.69 | | |

noted earlier, the formation of the fluoride cluster with a single methylamine molecule introduces a stabilization of −18.1 kcal/mol (−15.7 with MP2). The energy change decreases as further methylamine molecules are incorporated. Accordingly, the incorporation of a new molecule stabilizes the preceding structure by formation of a new NH···F contact but increases steric hindrance, so the net result is a gradual decrease in interaction intensity. Thus, the stabilization observed in the formation of the cluster with $n = 4$ is one-half that obtained with $n = 1$. Surface structures introduce even lower stabilization, as their formation is markedly hindered in fluoride clusters. The situation is rather different for the chloride clusters. Thus, the formation of the cluster with $n = 1$ introduces a stabilization of −8.6 kcal/mol (−7.98 with MP2) that remains virtually constant as new methylamine molecules are incorporated. These results reveal that the incorporation of a new molecule is hardly affected by the presence of other molecules in the cluster, as chloride ion is fairly bulky and can accommodate them quite readily. In any case, the interior structures exhibit a gradually decreased stabilization, a trend that is only broken by the clusters forming N−H···N bonds. Thus, the incorporation of the second molecule with MP2 (structure **2C**) introduces greater stabilization than that of the first by the effect of the hydrogen bond formed between the methylamine molecules.

One can conduct an even more detailed study of the interaction by resolving it into ion−solvent and solvent−solvent interactions, and calculating the energies for fragment pairs in each cluster. The results for fluoride and chloride are summarized in Tables 3 and 4, respectively. The values thus shown were obtained with the MP2 method, which provides a more accurate representation of the interaction between methylamine molecules than does B3LYP.[36] The interaction between the anion and a single molecule is −15.7 kcal/mol for $F^-$ and −7.9 kcal/mol for $Cl^-$. In the fluoride cluster with $n = 2$, the energy of interaction of the ion with each methylamine molecule is slightly lower (−15.2 kcal/mol); in addition, the two molecules interact slightly repulsively with each other and tend to destabilize the complex. With $n = 3$, the interaction with each methylamine molecule is even weaker in **3A** and **3B**. However, the three molecules as a whole interact in an attractive manner—with energies less than −0.8 kcal/mol, however. The situation is different in **3C**: two molecules contribute to the interaction energy about −15 kcal/mol each via an NH···F contact; by contrast, the molecule that interacts via the methyl group contributes only −6.9 kcal/mol. This results in a loss of ∼ −9 kcal/mol in the interaction that is only partly offset by the contribution of the interaction between methylamine molecules (an overall −4.6 kcal/mol). The situation is identical with $n = 4$. Each CH···F contact involves a loss of −8.5 kcal/mol that is not offset by the NH···N hydrogen bonds, which contribute −10 kcal/mol as a whole. Therefore, the fluoride clusters exhibit a weakening in the H···F interaction that is not compensated by the contacts between solvent molecules. As a result of this balance, the fluoride clusters exhibit no surface structures.

The situation is different in the chloride clusters. With $n = 2$, the interaction between the ion and methylamine molecules in minimum **2C** is slightly weakened on average; however, that between the molecules is of the attractive type and contributes −1.1 kcal/mol to the interaction, thus offsetting the previous effect. The clusters with $n = 3$ echo the behavior of their fluoride counterparts. Thus, the ion−molecule interaction is slightly weaker, but now the three solvent molecules interact in an attractive manner, the effect increasing with increasing likelihood of hydrogen bonds being formed. Minimum **3C** loses −4.0 kcal/mol in stability through the CH···Cl contact; however, the hydrogen bonds formed between the methylamine molecules offset such a loss by contributing −6.3 kcal/mol. The clusters with $n = 4$ exhibit an identical behavior. Despite being an interior structure, **4A** presents two hydrogen bonds between methylamine molecules, combining two stabilization effects: ion−solvent interaction of similar magnitude to that observed for interior structures with one or two methylamine molecules, and also an extra stabilization associated with hydrogen bonds.

Therefore, the formation of a stable surface structure relies on the hydrogen bonds between molecules offsetting the weakening effect of the interaction with the ion. In those structures that exhibit C−H···X contacts, each contact causes a stability loss roughly half that introduced by an N−H···X interaction (viz. ∼ −8.0 kcal/mol for $F^-$ and −4.0 kcal/mol for $Cl^-$). Although the loss is much greater for fluoride, the contribution of the hydrogen bonds between methylamine molecules is similar in both cases, so it compensates for the loss in the chloride clusters but not in the fluoride ones. For this reason, chloride clusters can form surface structures but

**TABLE 3: Resolution of the Interaction Energy (kcal/mol) for the Fluoride Clusters (MP2) into Several Contributions with $\Delta E_S$ Denoting the Energy of Interaction between Solvent Molecules, $E_{F-met}$ that between the Ion and Each Methylamine Molecule, and $E_{met-met}$ that between Each Pair of Methylamine Molecules**

| | 1 | 2A | 2B | 3A | 3B | 3C | 4A | 4B | 4C |
|---|---|---|---|---|---|---|---|---|---|
| $\Delta E^{CP}$ | −15.74 | −28.60 | −28.58 | −39.56 | −39.82 | −36.35 | −49.57 | −44.59 | −49.50 |
| $\Delta E_S$ | | 0.09 | 0.09 | −0.55 | −0.73 | −4.62 | −1.55 | −10.46 | −0.82 |
| $E_{F-met}$ | | −15.26 | −15.24 | −14.90 | −15.02 | −14.89 | −14.66 | −14.64 | −14.70 |
| | | −15.26 | −15.24 | −14.93 | −15.02 | −14.64 | −14.66 | −14.62 | −14.70 |
| | | | | −14.93 | −15.02 | −6.87 | −14.66 | −6.14 | −14.70 |
| | | | | | | | −14.66 | −6.16 | −14.70 |
| $E_{met-met}$ | | 0.09 | 0.09 | −0.34 | −0.22 | −0.41 | −0.32 | −0.53 | −0.05 |
| | | | | 0.08 | −0.22 | −2.23 | −0.32 | −2.16 | −0.13 |
| | | | | −0.21 | −0.22 | −1.61 | 0.05 | −1.63 | −0.12 |
| | | | | | | | 0.05 | −1.64 | −0.12 |
| | | | | | | | −0.32 | −2.16 | −0.12 |
| | | | | | | | −0.32 | −0.57 | −0.05 |

**TABLE 4: Resolution of the Interaction Energy (kcal/mol) for the Chloride Clusters (MP2) into Several Contributions with $\Delta E_S$ Denoting the Energy of Interaction between Solvent Molecules, $E_{Cl-met}$ that between the Ion and Each Methylamine Molecule, and $E_{met-met}$ that between Each Pair of Methylamine Molecules**

| | 1 | 2A | 2B | 2C | 3A | 3B | 3C | 4A | 4B |
|---|---|---|---|---|---|---|---|---|---|
| $\Delta E^{CP}$ | −7.94 | −15.27 | −15.36 | −15.99 | −22.80 | −22.30 | −22.47 | −30.23 | −29.83 |
| $\Delta E_S$ | | 0.03 | 0.06 | −1.11 | −1.08 | −0.14 | −6.42 | −2.27 | −11.82 |
| $E_{Cl-met}$ | | −7.94 | −7.96 | −7.46 | −7.56 | −7.94 | −7.28 | −8.11 | −7.64 |
| | | −7.94 | −7.96 | −8.13 | −8.05 | −7.94 | −7.52 | −7.42 | −7.64 |
| | | | | | −7.99 | −7.94 | −3.39 | −7.42 | −3.14 |
| | | | | | | | | −8.11 | −3.14 |
| $E_{met-met}$ | | 0.03 | 0.06 | −1.11 | −1.06 | −0.04 | −1.20 | 0.06 | −0.86 |
| | | | | | 0.01 | −0.04 | −2.50 | −1.23 | −2.31 |
| | | | | | 0.04 | −0.04 | −2.04 | 0.08 | −1.83 |
| | | | | | | | | 0.06 | −1.83 |
| | | | | | | | | −1.23 | −2.31 |
| | | | | | | | | 0.07 | −0.63 |

**TABLE 5: Shifts ($cm^{-1}$) in the N−H Symmetric Stretching Vibration for the Clusters as Calculated with the B3LYP Method[a]**

| | 1 | 2A | 2B | 2C | 3A | 3B | 3C | 4A | 4B | 4C |
|---|---|---|---|---|---|---|---|---|---|---|
| F | −427.3 | −417.5 | −417.3 | - | −357.5 | −354.6 | −392.5 | −278.5 | −388.4 | −263.5 |
| | | −412.4 | −411.9 | - | −352.3 | −354.6 | −296.8 | −259.1 | −347.7 | −263.2 |
| | | | | | −287.0 | −287.4 | −133.6 | −220.4 | −170.0 | −263.0 |
| | | | | | | | | −172.6 | −165.1 | −195.0 |
| Cl | −162.1 | −134.4 | −135.2 | −187.9 | −114.9 | −122.6 | −152.8 | −141.5 | −186.1 | |
| | | −125.9 | −126.3 | −75.5 | −114.5 | −122.6 | −132.8 | −130.1 | −180.8 | |
| | | | | | −105.3 | −112.4 | −108.3 | −58.3 | −141.8 | |
| | | | | | | | | −57.1 | −132.9 | |

[a] The B3LYP frequency for the isolated methylamine molecule is 3488.5 $cm^{-1}$.

fluoride clusters cannot. Also, on the basis of these results, structures of the C−H···X type with larger ions such as $Br^-$ could be even more favorable. Also worth noting here is that the contribution of hydrogen bonds increases with increasing cluster size, as the molecules lie at more favorable positions. Thus, an N−H···N bond in **2C** contributes only −1.1 kcal/mol, whereas **4B** contributes −2.3 kcal/mol.

**3.4. Frequencies.** Interactions between molecules are known to be able to cause appreciable changes in the vibrational frequencies for some normal modes directly involved in them. Specifically, the formation of hydrogen bonds between molecules causes red-shifts of up to a few hundred reciprocal centimeters in the N−H stretching frequency. In this work, we examined the vibrational frequencies for the clusters in order to identify their most salient spectral features. For this purpose, we monitored the N−H stretching and $NH_2$ wagging frequencies. The methylamine molecule exhibits two N−H stretching frequencies that behave very similarly in the clusters, and so does the $NH_2$ wagging frequency—which, however, is blue-shifted. For brevity, only the N−H symmetric stretching frequencies are shown in Table 5.

The formation of the fluoride cluster with a single methylamine molecule causes a marked shift in the N−H stretching frequency (~ −430 $cm^{-1}$). The shift for the chloride cluster is smaller (−160 $cm^{-1}$), as a result of the weaker interaction involved.

The fluoride clusters with $n = 2$ exhibit a similar behavior. Thus, the signals for the N−H stretch are red-shifted to a smaller extent, owing to a weaker X···HN interaction. The chloride clusters exhibit an identical behavior in structures **2A** and **2B**, but not in **2C**. Because the two methylamine molecules in this last structure are not equivalent, they cannot give a pair of signals at virtually the same frequency; rather, the molecule that acts as the donor in the N−H···N hydrogen bond exhibits a shift of only −75 $cm^{-1}$ (nearly half those observed in the other structures), whereas the other molecule exhibits a shift of almost −190 $cm^{-1}$. Therefore, the presence of a surface structure results in the appearance of two well-defined signals more than 100 $cm^{-1}$ apart—in interior structures, such a separation hardly reaches 10 $cm^{-1}$.

Structures **3A** and **3B** in the clusters with $n = 3$ behave similarly to the previous ones; that is, they exhibit red-shifted signals, which, however, span a narrow frequency range. On the other hand, the presence of hydrogen bonds between the molecules in the **3C** minima results in the signals spanning a broader range (260 $cm^{-1}$ for $F^-$ and 50 $cm^{-1}$ for $Cl^-$).

The fluoride clusters with four methylamine molecules exhibit no hydrogen bonds between molecules, so their N−H stretching frequencies are worth no special comment. Only **4B** can form such bonds and behaves similarly to the clusters with $n = 3$ as a result. Thus, it exhibits two pairs of signals 180 $cm^{-1}$ apart. On the other hand, all the chloride clusters with $n = 4$ form hydrogen bonds between their methylamine molecules, so they exhibit a differential spectral behavior. Thus, both **4A** and **4B** give two pairs of signals that are 80 and 45 $cm^{-1}$ apart in the former and latter, respectively.

The interior structures adopt highly symmetric arrangements that give $n$ signals for a cluster with $n$ methylamine molecules; such signals appear at very close frequencies but are strongly red-shifted with respect to the isolated molecule. The presence of hydrogen bonds between the methylamine molecules gives rise to $n$ signals that span a broader frequency range. The structures that form N−H···N bonds exhibit more markedly red-shifted signals for the clusters with the same $n$ value; also, such signals are usually the strongest in the spectra. The above-described behavior echoes that of other vibrational modes involved in the interaction (e.g. N−H asymmetric stretching or $NH_2$ wagging, the latter of which is blue- rather than red-shifted).

## 4. Conclusions

We performed theoretical calculations on fluoride and chloride clusters with up to four methylamine molecules, using the B3LYP and MP2 methods in conjunction with the 6-31+G* basis set. The structures thus identified were of either of two types, namely, interior or surface structures. In the former, the methylamine molecules surround the central anion and form no N−H···N hydrogen bonds; by contrast, the latter form such bonds and the methylamine molecules lie all on the same side of the anion.

On the basis of our calculations, fluoride ion tends to form no surface structures, so the most stable structures for the minima are always of the interior type. On the other hand, chloride clusters clearly tend to form structures of the surface type.

Whether an interior or surface cluster is formed depends on the energy balance between ion−molecule and molecule−molecule interactions. Ion−molecule interactions weaken as cluster size increases, since the presence of further molecules forces them to further depart from the central anion and the resulting destabilization cannot be offset by any other effect. The structures that form N−H···N bonds behave differently, and the interaction of the anion with each methylamine molecule decreases more abruptly than is the case in the other structures. However, the decrease is partly offset by the additional stability provided by the N−H···N hydrogen bond. In the fluoride clusters, the anion−methylamine interaction is very strong—so much so that the formation of hydrogen bonds between the solvent molecules cannot by itself overcome the previous interaction and no surface structures can be formed. The anion−molecule interaction in the chloride clusters is weaker and N−H···N hydrogen bonds are more readily formed. This is especially so in those structures where an N−H···X contact is replaced with a C−H···X contact, which results in a marked loss of stability. With chloride ion, however, such a loss is offset by the formation of N−H···N hydrogen bonds, which results in structures similarly stable to those that exhibit N−H···X contacts alone.

The N−H symmetric stretching frequencies are markedly red-shifted by the effect of the interaction. In structures that form no hydrogen bonds between molecules, the shift is similar for all those frequencies in a cluster and decreases with increasing cluster size. In the presence of N−H···N bonds, the signals span a broader frequency range and exhibit even greater red-shifts.

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## References and Notes

(1) Stace, A. J. *Phys. Chem. Chem. Phys.* **2001**, *3*, 1935.
(2) Dzidic, I.; Kebarle, P. *J. Phys. Chem.* **1970**, *74*, 1466.
(3) Keesee, R. G.; Castleman, A. W. J. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1011.
(4) Searles, S. K.; Kebarle, P. *Can. J. Chem.* **1969**, *47*, 2619.
(5) Steel, E. A.; Merz, K. M. J.; Selinger, A.; Castleman, A. W. J. *J. Phys. Chem.* **1995**, *99*, 7829.
(6) Hashimoto, K.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 11436−43.
(7) Hashimoto, K.; Morokuma, K. *Chem. Phys. Lett.* **1994**, *223*, 423−30.
(8) Hashimoto, K.; He, S.; Morokuma, K. *Chem. Phys. Lett.* **1993**, *206*, 297.
(9) Selegue, T. J.; Cabarcos, O. M.; Lisy, J. M. *J. Chem. Phys.* **1994**, *100*, 4790−6.
(10) Merrill, G. N.; Webb, S. P.; Bivin, D. B. *J. Phys. Chem. A* **2003**, *107*, 386−396.
(11) Glendening, E. D.; Feller, D. *J. Phys. Chem.* **1995**, *99*, 3060.
(12) Sobolewski, A. L.; Domcke, W. *J. Phys. Chem. A* **2002**, *106*, 4158−4167.
(13) Vicens, M. C.; Lopez, G. E. *J. Comput. Chem.* **2000**, *21*, 63−68.
(14) Feller, D.; Glendening, E. D.; Woon, D. E.; Feyereisen, M. W. *J. Chem. Phys.* **1995**, *103*, 3526−42.
(15) Feller, D.; Glendening, E. D.; Kendall, R. A.; Peterson, K. A. *J. Chem. Phys.* **1994**, *100*, 4981−97.
(16) Hashimoto, K.; Kamimoto, T. *J. Am. Chem. Soc.* **1998**, *120*, 3560−3570.
(17) Guo, B. C.; Conklin, B. J.; Castleman, A. W. J. *J. Am. Chem. Soc.* **1989**, *111*, 6506.
(18) Watanabe, H.; Iwata, S. *J. Phys. Chem. A* **1997**, *101*, 487−496.
(19) Ayala, R.; Martínez, J. M.; Pappalardo, R. R.; Sánchez-Marcos, E. *J. Phys. Chem. A* **2000**, *104*, 2799.
(20) Ayotte, P.; Weddle, G. H.; Johnson, M. A. *J. Chem. Phys.* **1999**, *110*, 7129−7132.
(21) Ayotte, P.; Weddle, G. H.; Kim, J.; Kelley, J.; Johnson, M. A. *J. Phys. Chem. A* **1999**, *103*, 443−447.
(22) Baik, J.; Kim, J.; Majumdar, D.; Kim, K. S. *J. Chem. Phys.* **1999**, *110*, 9116−9127.
(23) Combariza, J. E.; Kestner, N. R. *J. Phys. Chem.* **1994**, *98*, 3513−17.
(24) Tobias, D. J.; Jungwirth, P.; Parrinello, M. *J. Chem. Phys.* **2001**, *114*, 7036−7044.
(25) Weis, P.; Kemper, P. R.; Bowers, M. T.; Xantheas, S. S. *J. Am. Chem. Soc.* **1999**, *121*, 3531−3532.
(26) Kim, J.; Lee, H. M.; Suh, S. B.; Majumdar, D.; Kim, K. S. *J. Chem. Phys.* **2000**, *113*, 5259−5272.
(27) Majumdar, D.; Kim, J.; Kim, K. S. *J. Chem. Phys.* **2000**, *112*, 101−105.
(28) Thompson, W. H.; Hynes, J. T. *J. Am. Chem. Soc.* **2000**, *122*, 6278−6286.
(29) Lee, H. M.; Kim, D.; Kim, K. S. *J. Chem. Phys.* **2002**, *116*, 5509−5520.
(30) Cabarcos, O. M.; Weinheimer, C. J.; Martinez, T. J.; Lisy, J. M. *J. Chem. Phys.* **1999**, *110*, 9516−9526.
(31) Cabarcos, O. M.; Weinheimer, C. J.; Lisy, J. M.; Xantheas, S. S. *J. Chem. Phys.* **1999**, *110*, 5.
(32) Cabaleiro-Lago, E. M.; Ríos, M. A. *Chem. Phys.* **2000**, *254*, 11.
(33) Cabaleiro-Lago, E. M.; Rodríguez-Otero, J. *J. Phys. Chem. A* **2002**, *106*, 7195.
(34) García-Muruais, A.; Cabaleiro-Lago, E. M.; Hermida-Ramón, J. M.; Rios, M. A. *Chem. Phys.* **2000**, *254*, 109.
(35) Islam, M. S.; Pethrick, R. A.; Pugh, D. *J. Phys. Chem. A* **1998**, *102*, 1089.
(36) Cabaleiro-Lago, E. M.; Ríos, M. A. *J. Chem. Phys.* **2000**, *112*, 2155.
(37) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(38) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(39) Van Lenthe, J. H.; Van Duijneveldt-Van De Rijdt, J. G. C. M.; Van Duijneveldt, F. B. *Adv. Chem. Phys.* **1987**, *124*, 521.
(40) Van Duijneveldt-Van De Rijdt, J. G. C. M.; Van Duijneveldt, F. B.; Van Lenthe, J. H. *Chem. Rev.* **1994**, *94*, 1873.
(41) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
(42) Chalasinski, G.; Szczesniak, M. M. *Chem. Rev.* **1994**, *94*, 1723.
(43) Szalewicz, K.; Jeziorski, B. *J. Chem. Phys.* **1998**, *109*, 1198−1200.
(44) Simón, S.; Durán, M.; Dannenberg, J. J. *J. Phys. Chem.* **1996**, *100*, 11024.
(45) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J.; Stratmann, R. E.; Burant, J. C.; Pprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.