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An *ab initio* study of the anionic clusters $Cl^-(HF)_n$ (n = 1–5)

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By performing *ab initio* calculations several stationary points on the potential energy surfaces of the anionic clusters $Cl^-(HF)_n$ (n = 1–5) were characterised with a special emphasis on the competition between interior and surface structures.

The microsolvation theory which considers properties of both solvent and solute species at a discrete molecular level requires, at the initial stages of modelling, a detailed knowledge of the structure of solvation shells. The arrangements of the environmental particles of the solvent around trapped solute molecules may have peculiar shapes, which primarily depend on the intermolecular interaction potentials. When modeling solvation sites at a supramolecular level, one can design solvation shells by consequently adding solvent particles one by one to the solute species and determining the molecular arrangements that correspond to minima on the multidimensional potential energy surfaces. This approach to the microsolvation theory is also typical of the cluster science with relevance to experimental studies in the gas phase and to the corresponding modeling of cluster properties.[1] For obvious reasons, the size-selected clusters containing anionic halogens surrounded by solvent molecules attract an increasing attention. Of special interest are, of course, the water clusters $X^-(H_2O)_n$ (X = Cl, Br, I)[2–13] although other solvents like acetonitrile[14] were also considered.

To characterise solvation sites, different approaches ranging from the use of empirical functions describing intermolecular interaction potentials to a complete *ab initio* analysis by modern methods of quantum chemistry can be applied. Apparent difficulties of such an analysis are related to the shapes of flat multidimensional potential energy surfaces of heteroclusters with multiple stationary points which possess similar energies. In particular, the vast majority of approaches to the structure of $Cl^-(H_2O)_n$ clusters predict that surface states, namely the configurations with Cl^- ions outside neutral water shells, are dominating; however, the energies of interior structures with Cl^- ions surrounded by water molecules are slightly higher than that of the surface states, and the effects of temperature and zero-point energy may easily reverse the conclusions.

In this work, we compare the properties of the anionic clusters $Cl^-(HF)_n$ (n = 1–5) as predicted by *ab initio* methods of quantum chemistry. The above systems have not been described before, only *ab initio* calculations of the binary complexes ClF··HF have been reported.[15–17] In addition to a better understanding of the properties of pure and doped molecular clusters, this work is aimed to provide reference data for the semiempirical diatomics-in-ionic-systems (DIIS) scheme in order to apply it to the modeling of solvation phenomena in this system. Previous data on the DIIS approach to pure hydrogen fluoride clusters $(HF)_n$[18,19] offer promise to the construction of inexpensive and reliable intermolecular potential energy surfaces suitable for a detailed analysis of such species.

A conventional strategy was used for the *ab initio* calculations carried out with the PC GAMESS version[20] of the GAMESS package.[21] Namely, the stationary points on the potential energy surfaces of $Cl^-(HF)_n$ (n = 1–5) have been located, and the standard harmonic vibrational analysis has been performed by the MP2/6-311+G** procedure. Next, the MP4(SDTQ)/6-311+G** method was employed to recompute the energies at the MP2/6-311+G** minimum energy points.

We started the geometry optimization from two sets of initial arrangements with no symmetry restrictions imposed. Namely, in the first series every HF molecule was bound to Cl^-, and in the second series one hydrogen-bonded dimer $(HF)_2$ was coupled to Cl^-, while other (n – 2) monomeric HF species were bound directly to Cl^- ($n \geq 2$). In both cases, the equilibrium configurations were located using the MP2/6-311+G** procedure, and we designate the structures of the second series by '**a**'. For instance, configuration **5** refers to the isomer of $Cl^-(HF)_5$ that corresponds to the interior structure with five HF species surrounding Cl^-, and configuration **5a** denotes the isomer corresponding to the surface structure in which three HF monomers and one $(HF)_2$ dimer are bridged to Cl^-. Different isomers for the structures of the same type are additionally designated by symbols **I** and **II**. Figure 1 shows the structures found for all species. Configurations **4** and **5 I**, **5 II** can be called interior states and **4a I**, **4a II** and **5a**, surface states. For $n \geq 2$, all configurations ***n*a** refer to the structures with some evidence for hydrogen-bonded networks.

With respect to geometry, the following trends in the structures are noteworthy. Within the series of structures **1**–**5**, the equilibrium Cl–H distances gradually increase from 1.91 (n = 1)

Table 1 Harmonic vibrational frequencies computed with the MP2/6-311+G** wave functions. Numerical degeneracies (to within 1 cm^{-1}) given in parentheses do not necessarily reflect the true symmetry of species. The shifts of the highest frequencies referred to the H–F vibrations in the cluster are given with respect to the harmonic frequency of pure HF (4162 cm^{-1}).

Species	Harmonic frequencies/cm^{-1}						Shifts of the highest frequencies with respect to HF/cm^{-1}
1	262	879(2)	3109				–1053
2	28	227	251	798	810	812	–85 9
	854	3303	3371				–79 1
3	23	26(2)	194	230(2)	728	744(2)	–67 7
	769	792(2)	3485(2)	3566			–59 6
4	21(2)	28(3)	169	209(3)	666(3)	723(3)	–54 2
	730	732	3620(3)	3707			–45 5
5 I	4	25(2)	33(2)	34	37	136	–43 7
(C_{4v})	156	189	195(2)	539	595(2)	600	–40 9
	635(2)	675	683(2)	724	3725	3753(2)	–40 3
	3759	3840					–32 2
5 II	5(2)	27(2)	32(2)	33	137	156	–42 9
(D_{3h})	192(2)	556(2)	577(2)	613	650	671(2)	–40 7
	704(2)	3733(2)	3755	3765	3841		–39 8
							–32 1
2a	51	228	379	833	835	947	–1766
	1046	2396	3578				–58 4
3a	8	26	48	215	231	343	–1363
	770	773	777	803	879	1003	–73 0
	2799	3432	3685				–47 8
4a I	9	24	26	28	45	193	–1081
	208	220	316	707	719	721	–60 7
	723	739	760	847	932	3081	–55 4
	3555	3608	3764				–39 9
4a II	6	17	24	26	46	179	–1070
	205	223	319	710	714	720	–59 9
	723	725	757	844	919	3092	–54 6
	3563	3616	3778				–38 4
5a	6	18	21	24	27	27	–86 8
	44	163	191	201	202	295	–48 8
	637	654	655	678	680	698	–48 1
	699	703	776	878	3294	3674	–42 1
	3681	3742	3830				–33 3

Table 2 Total and relative energies of $Cl^-(HF)_n$ clusters with zero-point energy corrections. Binding energies are referred to a single HF ligand: $E_b = \{E[Cl^-(HF)_n] - E(Cl^- + nHF)\}/n$, where the total energies of Cl^- are –459.735676 (MP2) and –459.751701 au (MP4) and the total energies of HF are –100.297417 (MP2) and –100.305374 au (MP4).

Species	Total energies/au		Relative energies/kJ mol⁻¹			
			Binding energies/E_b		Energies of ***n*a** with respect to ***n***	
	MP2	MP4	MP2	MP4	MP2	MP4
1	–560.069069	–560.093178	94.45	94.79	—	—
2	–660.395734	–660.427906	85.62	85.93	—	—
3	–760.716961	–760.757191	77.92	78.21	—	—
4	–861.033913	–861.082195	71.26	71.54	—	—
5 I (C_{4v})	–961.344339	–961.400790	63.84	64.18	—	—
5 II (D_{3h})	–961.344580	–961.400975	63.97	64.27	—	—
2a	–660.391134	–660.423293	79.58	79.87	+6.04	+6.06
3a	–760.714303	–760.754522	75.59	75.88	+2.33	+2.34
4a I	–861.032787	–861.081061	70.52	70.80	+0.74	+0.74
4a II	–861.032412	–861.080687	70.28	70.55	+0.99	+0.99
5a	–961.347373	–961.403708	65.43	65.71	–1.47	–1.44

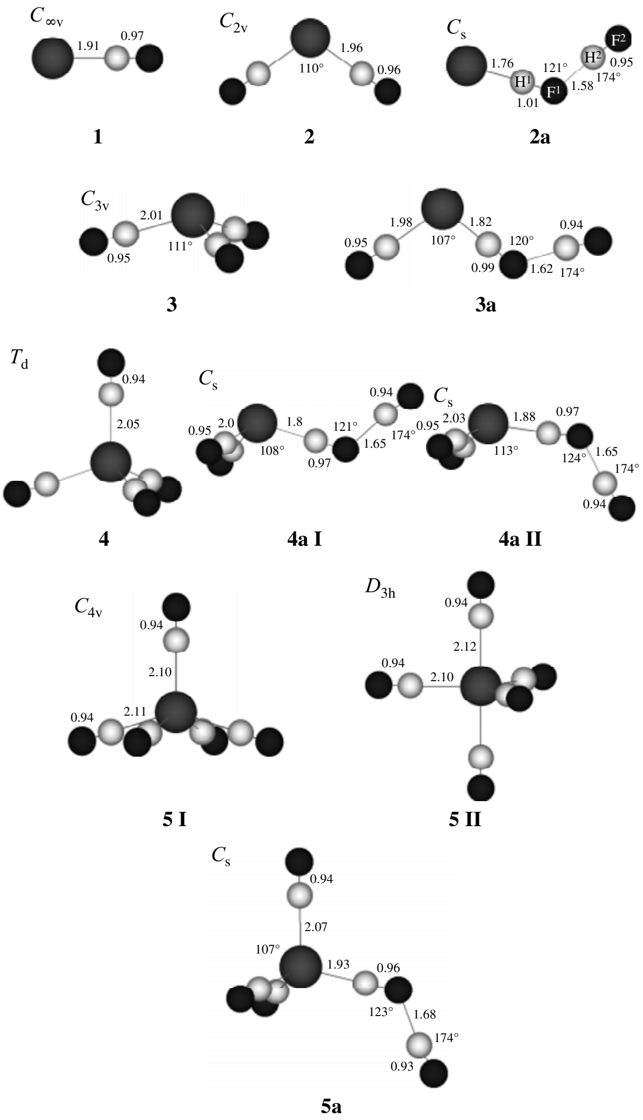

Figure 1 Geometry configurations optimised at the MP2/6-311+G** level. Bond lengths are given in Å

to 2.10–2.12 Å (*n* = 5) while the H–F distances decrease from 0.97 (*n* = 1) to 0.94 Å (*n* = 5). The valence angles HClH do not show large variations: 110° (*n* = 2), 111° (*n* = 3), 109° (*n* = 4), 90°–120° (*n* = 5). A tetrahedral configuration for $Cl^-(HF)_4$ and two structures for $Cl^-(HF)_5$, a bipyramid (D_{3h}) and a tetragonal pyramid (C_{4v}), were obtained in these calculations. For structures **2a**–**5a**, a familiar motive of the hydrogen fluoride dimer (H^1–F^1···H^2–F^2) is easily recognised[22] with the F–F distances 2.52 (*n* = 2), 2.56 (*n* = 3), 2.59 (*n* = 4) and 2.61 Å (*n* = 5); the F^1···H^2 hydrogen bond lengths 1.58 (*n* = 2), 1.62 (*n* = 3), 1.65 (*n* = 4) and 1.68 Å (*n* = 5), and a value of 4° for the hydrogen bond angles $H^2F^2H^1$ practically independent on the cluster size. The distances from Cl^- to the closest hydrogen of the (–H^1–F^1··· ···H^2–F^2) chain H^1 are noticeably shorter than the Cl–H distances in the series of **2**–**5** (1.76, 1.82, 1.88 and 1.93 Å for **2**, **3**, **4** and **5**, respectively), while the tendencies for changes in the remaining geometry parameters are approximately the same as for the series of **2**–**5**.

Table 1 contains unscaled harmonic frequencies computed with the MP2/6-311+G** wave functions at the corresponding equilibrium configurations. The main reason to show these values is to confirm that the found structures correspond to the true minimum energy points. However, it is interesting to trace the shifts in high frequencies obviously originated from vibrations of the H–F fragments with respect to the frequency of a pure HF molecule accompanying its association into $Cl^-(HF)_n$ clusters. The predicted red shifts, which may be important for practical identification of these complexes, are presented in Table 1.

Table 2 summarises the computed energies at the equilibrium points for all species predicted by the MP2/6-311+G** and MP4//MP2/6-311+G** procedures. Corrections due to zero points vibrations are taken into account. The binding energies are referred to one HF molecule: $E_b = \{E[Cl^-(HF)_n] - E(Cl^- + nHF)\}/n$. The clear tendency of gradual reduction of E_b with cluster size is demonstrated. Another tendency is a gradual reduction of the gap between the energies of ***n*** and ***n*a** configurations. For *n* = 5, the energy of surface state **5a** is lower than those of interior states **5 I** and **5 II**.

A conclusion drawn from these calculations is that in the case of hydrogen fluoride complexes $Cl^-(HF)_n$ the structures with hydrogen-bonded networks (denoted as **2a**–**5a**), which may be called surface structures, are unfavourable as compared to interior structures (**2**–**5**), in which Cl^- is surrounded by HF molecules, by energy criteria. The energy differences between configurations ***n*** and ***n*a** decrease with *n*. Note that, in spite of differences between the absolute values of energies computed with the MP2 and MP4 approaches, the energy gaps between structures ***n*** and ***n*a** are reproduced well already at the MP2 level.

Additionally, the energies of structures ***n*a** with respect to the decomposition $Cl^-(HF)_n \rightarrow Cl^-(HF)_{n-2} + (HF)_2$ were estimated at the MP2 level (with corrections for zero point vibrations). We found that all these clusters are stable towards dissociation not only to hydrogen fluoride, but also to a hydrogen fluoride dimer and a smaller size cluster with the binding energies gradually decreasing with *n* from 147 (**2a**) to 81 kJ mol⁻¹ (**5a**).

We cannot exclude the possibility that a refinement of the treatment like a basis set extension, more accurate calculations of correlation contributions, or the inclusion of basis set superposition corrections will force us to change qualitative conclusions on the relative stability of the isomers. The corresponding energy differences are so small, especially for *n* = 4 and 5, that the final choice is hard to formulate unambiguously. We cannot also exclude the chances for another geometry arrangements beyond those reported in this work. Some initial guesses based on the previous experience with $(HF)_n$[19] may be easily suggested, *e.g.*, for the $(HF)_n$ chains ended up with Cl^- or for the $(HF)_m$ rings ($m \geq 3$) bound to $Cl^-(HF)_{n-m}$. However we believe that a more efficient strategy in this respect is to construct a cheap interaction potential for $Cl^-(HF)_n$ in the spirit of the DIIS theory, to scan large areas of the configuration space with its help and to verify predictions for the stationary points by *ab initio* methods. Less expensive potentials will allow us to use more powerful algorithms to locate minimum energy points in the surfaces.[23,24] Studies along this line are in progress, and the configurations found and reported here provide valuable information for checking the semiempirical potential functions.

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