

An ab Initio Study of Linear XH–HX Hydrogen Halide Anions

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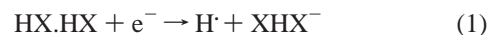
This paper examines the stabilities of singly charged anions with the linear opposed dipole structures: FH–HF, ClH–HCl and BrH–HBr at MP2 and CCSD(T) levels. With 6-311+G(3df,2p) basis sets on Cl and Br and aug-cc-pvdz on H and F, MP2 structures were obtained for all three systems. Since the neutral dimers with opposed dipoles are unstable, the energies for the electron detachment processes were evaluated relative to separated free neutrals, viz.: $\text{XH–HX}\cdot^- \rightarrow e^- + 2\text{HX}$. At the CCSD(T) level these energies were 0.26 and 0.84 V for HCl and HBr, respectively, but the value for HF is negative. The addition of diffuse orbitals at the central point between the two H atoms lowered the energy and caused the H–H distance in the FH–HF species to increase. Also the excess electron moved into the diffuse orbitals and the species assumed a solvated electron structure, a finding which is in agreement with previous work. In contrast, for the HCl and HBr species the addition of diffuse orbitals had no significant effect. The optimized geometries, charge and spin distributions, and the adiabatic electron detachment energies all remained essentially unchanged. This result and other molecular parameters indicated that in the ClH–HCl and BrH–HBr anions the extra electrons were located in valence orbitals made up from the σ^* orbitals of the two HX molecules. The nature of these orbitals was discussed. Since the dipole moment of the HCl.HCl neutral dimer is considered too small for formation of a dipole-bound anion state (as occurs with HF.HF), it is quite probable that HCl dimer anion observed experimentally is of the XH–HX \cdot^- type.

Introduction

The attachment of electrons to small clusters of molecules has been a subject of interest for many years.^{1,2,3} Three types of interaction are possible. First the electron may be in a valence orbital of one of the molecules, thus forming an anion which is solvated by the remaining ones in the cluster. Second, where the molecules have significant polarity, it may be held in the resultant dipole field of the cluster. This “dipole bound” electron is describable by a diffuse orbital an order of magnitude larger than molecular dimensions. The critical dipole moment for this is 2.2 D^{4,5} and the electron is described as being in a “dipole bound state” (DBS). In the third case the electron may interact with the collection of dipoles, either on the surface or from inside of the cluster. The difference from the DBS configuration lies in “the dimensionality of the problem and the symmetry of the electrostatic field” which it encounters.² This type of anion cluster is generally referred to as a “solvated electron structure” (SE), and usually requires a fairly large number of molecules. By contrast DBS can even occur with a single molecule, provided it has a dipole moment in excess of the critical value.² Many dimer anions of highly polar closed shell species, including those of H₂O and HF, have been shown to be DBS states.^{6–9} Also of interest is the fact that some molecular anions are able to exist in either DBS or valence states,^{2,10} and transitions may be observed between them.¹¹

Dipole bound anion states and solvated electron structures of low molecular weight hydrides of first row elements have been studied quite extensively.^{1,2} Rather less attention has been paid to the interactions of electrons with clusters of hydrides and other polar molecules containing atoms of second row elements. For example, while the case for the HF dimer DBS

anion is now well established,^{8,9} the structures and properties of dimer anions of the other hydrogen halides, HCl and HBr, have received much less attention. All three form neutral H–X \cdots H–X dimers with the H–X \cdots H angle near 90° and the X \cdots H–X near 180°. One important trend in the series HF, HCl, HBr is the weakening of the H–X bond. This leads to a lowering of the σ_{HX}^* orbital energy and causes the energy thresholds for dissociative electron capture by the monomers to decrease along the series F, Cl, Br.^{12–14} The solvation energy of the X[–] halide ion by the second HX in the dimer further assists this, causing reaction 1 to have a lower threshold than dissociative capture in the monomers.



Thermochemical data¹⁵ show that reaction 1 is strongly endothermic for HF and also unfavorable for HCl. However, in the case of HBr it is exothermic. Also both chemical experiments¹⁶ and electron swarm studies¹⁷ have shown that at thermal energies dissociative capture by the neutral dimer is fast. Recent ab initio calculations¹⁸ have confirmed that the potential energy barrier for this process is negligible, and the BrHBr[–] carries excess vibrational energy. However, the computed dipole moment of the neutral dimer of HBr¹⁸ is well below the critical value of 2.2 D, and a DBS state is not therefore considered as an intermediate.

The case of HCl.HCl is somewhat more interesting. While reaction 1 would be slow, a DBS would still not be stable, because the dipole moment is again expected to be below the critical value.¹⁹ Yet evidence for (HCl)₂[–] with a 100 μs or longer lifetime has come from both chemical experiments^{16,20} and seeded beam gas discharge studies.⁶ These findings have induced us to carry out an ab initio study of possible structures of this species.

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TABLE 1: Electronic Energies (in hartrees) and MP2 ZPEs (in parentheses in kJ mol⁻¹) of HX and XH–HX⁻ Species

basis sets ^a :	normal		normal + 4 central diffuse functions		
	level:	MP2	CCSD(T) ^b	MP2	CCSD(T) ^b
HF		-100.25581(23.4)	-100.26364	-100.25583	-100.26367
FH–HF ⁻		-200.50495(49.6)	-200.52128	-200.51117 ^c	
HCl		-460.29699(17.4)	-460.32573	-460.29707	-460.32581
ClH–HCl ⁻		-920.60691(33.3)	-920.66224	-920.60703 ^d	-920.66237 ^d
HBr		-2573.31030(15.6)	-2573.32338	-2573.31032	-2573.32339
BrH–HBr ⁻		-5146.65816(34.6)	-5146.68134	-5146.65821	-5146.68131 ^e

^a Normal basis sets were: aug-cc-pvdz for H and F, and 6-311+G(3df,2p) for Cl and Br. ^b Unless stated otherwise, on ROMP2 geometries for anions and MP2 for HX. ^c MP2 energy at H–H distance of 6.4 Å. This structure did not optimize, and its energy fell to that of two neutrals as $r_{\text{H-H}}$ increased. ^d For three diffuse functions. ^e On MP2 geometry.

As pointed out above, the structure of the neutral hydrogen halide dimers is such that the second HX is hydrogen bonded to the first at a right angle to its HX bond. Thus in the absence of a stable DBS the electron should enter the σ^* orbital of the first HX, since this H–X⁻ anion would be stabilized by the second HX through the X \cdots HX hydrogen bond. That is the dimer anion would be of the first type discussed above. The work in ref 18 showed that the stabilization is quite appreciable, lowering the σ^* level by about 35 kJ mol⁻¹ in the case of HBr. However, it did not give rise to a stable clustered anion, and subsequent work showed this also to be the case for the HCl dimer. It was therefore apparent that a different geometry must be obtained for (HCl)₂⁻ to be stable. It occurred to us that the stabilization might be larger, if the two HCl molecules were made equivalent by pointing their dipoles at each other. Preliminary studies showed that that geometry indeed had a profound effect, giving rise to a Cl–H \cdots H–Cl⁻ species of considerable stability. It was then obviously of interest to compare the electron binding in similar structures for HF and HBr. This publication presents and discusses our ab initio results on the structures and energies of dimer anions with opposed dipole geometries, viz.: XH–HX⁻, for these three hydrogen halides. One study on the HF system has already been reported.²¹ Precise details of the FH–HF⁻ geometry were not given, but it was clearly a solvated electron type of structure with minimum perturbation of the HF bonding. It was also reported to be unstable with respect to the neutral HF.HF dimer.

Computational Details

The ab initio calculations were performed with the Gaussian-98 molecular orbital packages.^{22,23} The geometry optimizations and vibrational frequency calculations were carried out at the MP2 and ROMP2 (FC) levels with 6-311+G(3df,2p) basis sets on Cl and Br and aug-cc-pvdz on H and F. These basis sets, which are referred to subsequently as the normal basis sets, are already quite large and should suffice for orbitals of normal negative ion species. However, as a means of testing whether the electron would prefer to escape into DBS or “solvated electron” type structures (or altogether), up to four additional diffuse functions were added at the central point between the two H atoms. The ones used were the sets of s-, p-, and d-type Gaussian functions with exponents 0.005625, 0.001125, 0.000225, and 0.000045. They are similar to those used in refs 9, 18, and 21. Single point CCSD(T) calculations were carried out on the optimized MP2 and ROMP2 structures. In the estimation of energies for detachment of the electron, with simultaneous formation of two free HX molecules, basis set superposition errors (BSSEs) were calculated. The BSSEs were estimated at the MP2 level by calculating the energies of neutral X–H \cdots H’–X’ complexes, where the HX bond distance was the computed equilibrium distance of the HX monomer and the

H–H’ and H’–X’ distances were the optimized values for the dimer anion. The H’ and X’ atoms had the basis sets noted above for H and X, but their nuclear charges were set to zero. The BSSEs were taken as twice the difference in electronic energies of the monomer HX and the X–H \cdots H’–X’ neutral. This procedure properly accounts for the geometry deformation of the complexing monomers in the dimeric complex. The BSSE values were 0.6, 4.8, and 6.5 kJ mol⁻¹ for HF, HCl, and HBr, respectively. The BSSE due to the presence of the diffuse orbitals was also estimated, in this case by putting the diffuse orbitals on the H atom of the neutral HX. It was less than 0.1 kJ mol⁻¹ for all three HXs and was ignored. Vibrational frequencies and zero-point energies (ZPEs) were computed at the MP2 level and scaled by 0.96.²⁴

Results and Discussion

Geometries, Frequencies, and Binding Energies. The results obtained in the absence of the diffuse functions at the MP2 level are discussed first. The electronic energies and ZPEs are summarized in columns two and three of Table 1. Optimized geometries and frequencies are listed in Table 2. It can be seen that with only the normal basis sets all three of the halogens gave XH–HX⁻ structures with no imaginary frequencies, indicating that at this level the structures in Table 2 are all minima. In the case of FH–HF⁻ there was no significant difference between the energies, geometries, and frequencies obtained at the MP2 and ROMP2 levels. However, with the anions of Cl and Br there were a few minor differences in geometries and frequencies, and the electronic energies were \sim 0.1 V lower at the ROMP2 level. For ClH–HCl⁻ and BrH–HBr⁻ only the ROMP2 results are reported in Tables 1 and 2, and the CCSD(T) calculations were done on the ROMP2 geometries, except in the case of BrH–HBr⁻ with diffuse orbitals.

Reference to the geometries and frequencies in Table 2 shows that there is a distinct difference between the structures of ClH–HCl⁻ and BrH–HBr⁻ on one hand and that of FH–HF⁻ on the other. In the former two cases the X–H distances are much larger than in the neutral monomers, while the H₂–H₃ distances (see subscript numbering on structure in Table 2) are quite short, being only slightly larger than in the H₂ molecule ($r_e = 0.74$ Å²⁵). In keeping with these observations, the symmetrical and unsymmetrical stretching frequencies of ClH–HCl⁻ and BrH–HBr⁻ are much lower than those of the neutral monomer. These strong perturbations of the HX monomer structures indicate that for HCl and HBr the excess electron is in a symmetrical valence orbital of the XH–HX⁻ structures, which includes both monomers.

The situation with the FH–HF⁻ system is the opposite. The H₂–H₃ distance is quite large and there is only a small \sim 0.02 Å increase in the H–F distances over the value in the neutral

TABLE 2: Geometries^a (in Å) and Vibrational Frequencies^a (in cm⁻¹) of XH–HX⁻ Species and Neutral Monomers

<u>Anion</u>	X ₁ — H ₂ — H ₃ — X ₄					<u>Neutral</u>
<u>Species:</u>						<u>Monomer^b</u>
	<u>r_{H₂-H₃}</u>		<u>r_{X₁-H₂}</u>		<u>r_{X₁-H₂}</u>	
FH-HF ^c	3.186		0.948		0.925	
ClH-HCl	0.980		1.662		1.281	
BrH-HBr	0.915		1.853		1.419	
	<u>2-3 Str. Stretch</u>	<u>Unsym. Rot. of HXs (x2)</u>	<u>Sym. Rot. of HXs (x2)</u>	<u>Unsym X-H-H-X Stretch</u>	<u>Sym. X-H-H-X Stretch</u>	<u>X-H Stretch^b</u>
FH-HF ^c	53	266	453	3391	3416	3917
ClH-HCl	226	242	1014	1051	1779	2905
BrH-HBr	125	214	996	1033	2210	2607

^a At the ROMP2 level, unless otherwise stated, and without diffuse orbitals. ^b At the MP2 level. ^c In this case the MP2 and ROMP2 levels gave the same results – see text.

HF monomer. Likewise the HF stretching frequencies are closer to those of the monomer. This apparent lack of perturbation of the monomer geometry is in keeping with the view that FH–HF⁻ is tending toward an SE type structure.

The Effect of Adding Diffuse Functions. Since the aug-cc-pvdz basis set used on H and F in the calculations would be too small to allow for a truly optimized SE structure, the FH–HF⁻ structure was reoptimized with various sets of diffuse functions added on a “bq” (ghost) atom at the central point between the two H atoms. Also these optimizations were carried out at the higher CCSD(T) level. Stationary points were found with one or two of the smallest sets of s and p or s, p, and d functions.²⁶ It is worth noting that in these cases the Mulliken population analyses showed that close to 100% of the spin and negative charge were located on the central dummy atom and the charge distribution on the F and H atoms became similar to that of the HF monomer. That clearly demonstrated the preference for a SE structure, and these observations are in accord with the conclusions of ref 21. When corrections were made for the BSSE, the binding energy of the electron relative to two free HF neutrals was negligible. Also on the addition of further diffuse orbitals no energy minimum was found for that species. In attempts to optimize, starting from the FH–HF⁻ structure obtained with one set of diffuse functions, the H–H distance kept on increasing and the electronic energy fell progressively while the H–F distances remained near 0.924 Å. The MP2 energy in column four of Table 1 was obtained with four sets of s and p orbitals.

In direct contrast to the effects described above, the re-optimization of the ClH–HCl⁻ and BrH–HBr⁻ structures with the addition of up to four central diffuse functions had no significant effect on the geometries. Also the Mulliken charge and spin densities on the central dummy atom were negligible (<0.003), and those on the hydrogens and halogens remained largely unchanged. This finding is consistent with the XH–HX⁻ valence orbital structures being more stable than any accessible SE type of structure. Given that the dipole moments of HCl and HBr are even weaker than that of HF, this is to be expected.

The Nature of the SOMO for HCl and HBr. An orbital interaction diagram for the “dipoles opposed” H–X dimer is

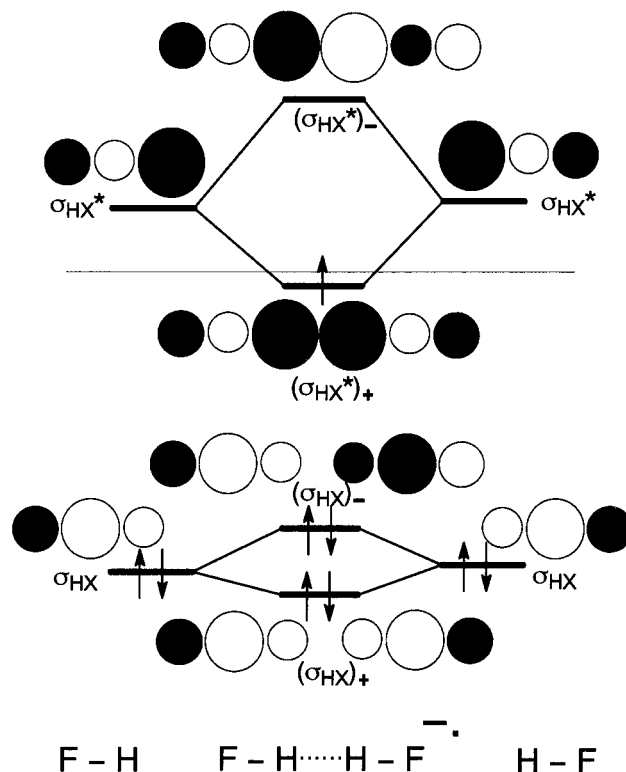


Figure 1. Orbital interaction diagram for XH–HX⁻ in the “dipoles opposed” geometry. The nonbonded electron pairs have been omitted for clarity.

shown in Figure 1. For clarity, the weakly interacting nonbonded electron pairs of the halogen are not shown. The H–X sigma orbitals, σ_{HX} and σ_{HX}^* , are strongly polarized in the directions shown. As a consequence, interaction of the bonding σ_{HX} orbitals is relatively weak and the interaction of the antibonding σ_{HX}^* orbitals is much stronger. In the absence of the extra electron, the four electron–two orbital interaction of the σ_{HX} orbitals is repulsive. The extra electron occupies an in-phase combination of the σ_{HX}^* orbitals. This is bonding between the two H atoms and antibonding between the H and X atoms. Thus, a shortening of the H–H separation and a lengthening of the

TABLE 3: Adiabatic Detachment Energies to Separated Neutrals and Vertical Detachment Energies (in eV) of Linear XH–HX^{•-} Anions^a

	adiabatic electron detachment energies	vertical detachment energy
ClH–HCl ^{•-}	0.26	3.1
BrH–HBr ^{•-}	0.84	3.4

^a At the CCSD(T) with aug-cc-pvdz basis sets for H and 6-311+G(3df,2p) for Cl and Br.

H–X separation is expected. If the σ_{HX} and σ_{HX}^* orbitals are close together, the secondary interaction between the $(\sigma_{\text{HX}})_+$ and $(\sigma_{\text{HX}}^*)_+$ orbitals could lead ultimately to a structure describable as $X^-(\text{H}_2)^+X^-$. Although none of the present halogens represents this situation, Cl and Br appear to be well advanced along this route.²⁷

From an inspection of the ClH–HCl^{•-} and BrH–HBr^{•-} geometries, it would appear that, if it existed, a FH–HF^{•-} valence structure would have an H₂–H₃ distance near 1.0 Å and $r_{\text{H-F}}$ greatly expanded from the r_e value of 0.924 Å. Thus it might be separated from the structure reported in Table 2 by a barrier and could have been missed. To ensure that this was not the case, a scan was made over the PE surface for $0.9 < r_{\text{H-F}} < 1.35$ Å and $1.0 < r_{\text{H-H}} < 2.0$ Å at the CCSD(T) level with one set and four sets of diffuse orbitals. This confirmed that all geometries analogous to those of the ClH–HCl^{•-} and BrH–HBr^{•-} valence structures collapse, without activation, into separated HF monomers and a free electron. Thus it appears that the HF orbitals are too far apart for any significant interaction of the type seen with HCl and HBr.

Stability of the XH–HX^{•-} Dimer Anions of HCl and HBr. Neutral dimers with the opposed dipoles are of course unstable. The stabilities of the present anion structures were therefore determined with reference to the free neutrals, the energies of which are also given in the Table 1. The energy changes for reaction 2 at 0 K were calculated from the CCSD(T) level results, with



corrections for the ZPEs and BSSEs. The values for ClH–HCl^{•-} and BrH–HBr^{•-} have been presented in Table 3.²⁸ These adiabatic electron detachment energies (ADEs) are both positive, and it is evident that the ClH–HCl^{•-} and BrH–HBr^{•-} species should be stable with respect to electron loss. From the point of view of possible comparison with experiment, it was also of interest to obtain estimates of the vertical detachment energies (VDEs) for the latter two systems, especially for HCl where there is already published evidence for its existence. The VDEs were taken as the differences in CCSD(T) electronic energies of the XH–HX^{•-} anion and neutral XH–HX structures of the same geometry. They have been given in the last column of Table 3. The values are much larger than the ADEs. This is because of the strong distortion of the H–X bonds and the short H–H distances in the anion geometries.

Conclusions

Opposed dipole XH–HX geometries give rise to symmetrical valence orbitals capable of binding electrons for HCl and HBr. The ADEs are in the region of several tenths of a volt to 1 V. Binding in the valence orbitals of FH–HF^{•-}, however, does not occur. The addition of diffuse orbitals does not give rise to evidence of stable solvated electron XH e⁻ HX structures for any of these systems.

Since the neutral dimers of opposed dipole geometry are unstable, formation of their XH–HX^{•-} anions may require special conditions. However, there is already experimental evidence for a dimer anion species of HCl, which may well belong to this category. Finally, the obvious difference between first row (F) and higher row elements (Cl and Br) in these electron interactions of the molecules is of general interest.

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- The H–H and H–F distances of the stationary point with the first two spd functions were 1.937 and 0.931 Å, respectively.
- Some information about the separation of the $(\sigma_{\text{HX}})_-$ and $(\sigma_{\text{HX}}^*)_+$ orbitals may be obtained from the CCSD(T) calculation of the neutral dimer. Thus, the coefficient of the doubly excited configuration, $\dots(\sigma_{\text{HX}})_+^2(\sigma_{\text{HX}})_-^0(\sigma_{\text{HX}}^*)_+^2$, i.e., the “maximum amplitude” in the G98 output, is 0.15 and 0.20, in Cl–H...H–Cl and Br–H...H–Br, respectively.
- The value for FH–HF^{•-} was negative for the energies in Table 1 and those obtained with the single sets of diffuse functions (~ -0.2 V).