Properties and Reactivity in Groups of the Periodic System: Ion−Molecule Reactions $HX + HX^{\bullet +}$ (X = F, Cl, Br, I, At)

J. V. Burda,* P. Hobza, and R. Zahradník

J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic,
Dolejškova 3, 182 23 Prague 8, Czech Republic

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The radical cations of hydrogen halogenide dimers $(HX)_2^{\bullet +}$ (X = F−At) and products of their decomposition have been investigated, using beyond-Hartree−Fock methods (MP2, QCISD, and CCSD(T)). Both all-electron and pseudopotentials techniques were considered. The $(HF)_2^{\bullet +}$ system differs significantly from the remaining $(HX)_2^{\bullet +}$ systems. The energy barrier height for transfering the H-bonded system to the hemibond structure is very low, causing the spontaneous conversion of the H-bonded structures to the hemibond ones, with the exception of the $(HF)_2^{\bullet +}$ dimer where the inverse situation exists. The characteristics for the overall process $HX + HX^{\bullet +} \rightleftharpoons H_2X^+ + X^\bullet$ were obtained from the experimental heats of formation and from calculated characteristics. The ΔH_{298} values based on the pseudopotentials are satisfactory for the F- and Cl-containing systems; however, the agreement is less satisfactory for heavier systems.

I. Introduction

About two centuries of effort in the realm of chemistry are connected with more than 10 million well-defined species, mostly molecular. Most of them are related to the elements of the first two rows of the periodic system. Although the number of systems connected with elements of higher periods is impressive, they nevertheless represent only a small fraction of the total ensemble. Clearly, most of them belong to the field of organic chemistry.

If we consider the impressive fact that in recent years it has been possible to coherently develop chemistry along experimental and computational (mainly quantum chemical) lines, we cannot be satisfied with the situation with theoretical studies of species containing atoms of heavier elements. The difficulties are due to a significant increase of the role of relativistic effects when passing from light to heavier elements. With heavy elements these effects become critical for a correct theoretical description.[1−5] The other complication is connected with the fact that frequently the spin component of the total wave function is complicated. This concerns mainly transition metals, rare earths, and actinides but rarely the main group elements.

The chemistry and physics of species including elements of the lower part of the periodic systems seem to be the Promised Land. This is true especially because it is gradually becoming possible to carry out, besides experiments, reliable quantum chemical calculations. The subject is topical for several reasons. First, we believe that with contemporary preparative tools, new structural prototypes might be discovered. Second, an idea widespread among chemists is not quite correct. Namely, it is said that chemistry of the first-row elements frequently differs significantly from the chemistry of higher periods, where the changes are not very important and rather monotonous. In fact, irregularities exist which are due to relativistic effects and to the appearance of f-electrons. Third, one of the most topical and fascinating subjects in chemistry, catalysis, is mostly connected with systems containing heavier and heavy elements. Sophisticated and extensive treatment of general features of catalysis and of numerous specific catalytic processes still await realization.

Because it is our wish to theoretically investigate chemical reactivity along groups of the periodic system, we need beyond-Hartree−Fock, relativistic calculations carried out from the very beginning; i.e., electron correlation and relativistic corrections should not be included as a posteriori corrections to Hartree−Fock (or Dirac−Fock) calculations. This is, for the moment, too demanding. In spite of this we feel that it is expedient to begin with scheduled calculations. We hope that sophisticated relativistic calculations, including a large enough portion of electron correlation as well as deeper physical analysis of the significance of the individual terms of a quasi-relativistic many-electron Hamiltonian or the Breit−Pauli Hamiltonian and terms of perturbation, will be settled in the near future.

In order to be able to study representative sets of reactions, we have adopted the following strategy. We carried out all-electron beyond-Hartree−Fock calculations for species containing elements ranging from the first to the third row and for species containing halogens from F to At with relativistic effective potential. This means that the two sets of calculations do partially overlap, which offers information on the reliability of calculations. We have not been able to find papers closely related to this approach. It is expedient, however, to cite a few representative theoretical studies on properties in groups. These works are connected with, e.g., relativistic contributions to binding energy in alkali halide species,[6] with properties of interhalogens,[7] with physical properties and atomization energies of sixth group hydrides,[8] with the series CH_4 to PbH_4[9] and $(114)H_4$ related to PbH_4,[10] and with hydrides of Cr, Mo, W, and related systems.[11] These phenomena play a distinguished role in connection with electronic and magnetic properties of alloys, surfaces, and interfaces.[12]

The other strategic decision has been connected with proper selection of reaction series for investigating the regularities in the groups. We decided to begin with ion−molecule reactions[13] for several reasons. First, these processes can be relatively easily

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* Author to whom correspondence is to be addressed. E-mail: burda@jh-inst.cas.cz.

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TABLE 1: Total Energies (au) of the System[a] under Study

X	system / method	I	II	III	IV	V	VI	VII
F	AE1	−100.184 16	−99.620 43	−199.895 45	−199.884 60	−199.852 50	−100.383 31	−99.490 00
	AE2	−100.190 11	−99.632 44	−199.912 42	−199.894 33	−199.876 44	−100.390 08	−99.500 49
	AE3	−100.265 72	−99.681 75	−200.026 66	−200.010 78	−199.993 76	−100.455 40	−99.551 94
	PS2	−24.652 29	−24.085 37	−48.819 79	−48.803 41	−48.784 96	−24.843 78	−23.959 66
Cl	AE1	−460.202 15	−459.753 58	−919.989 28	−920.003 90	−919.974 51	−460.412 58	−459.563 16
	AE2	−460.211 59	−459.764 64	−920.004 61	−920.022 12	−919.996 92	−460.425 65	−459.570 48
	AE3	−460.272 30	−459.813 14	−920.123 62	−920.136 54	−920.112 23	−460.491 31	−459.612 22
	PS2	−15.459 99	−15.013 27	−30.510 27	−30.520 83	−30.494 97	−15.676 04	−14.819 45
Br	AE1	−2572.945 14	−2572.526 40	−5145.503 93	−5145.524 60	−5145.492 87	−2573.162 97	−2572.32 336
	PS2	−13.859 17	−13.443 39	−27.332 77	−27.348 32	−27.321 81	−14.082 56	−13.235 28
I	PS2	−11.890 31	−11.513 19	−23.427 60	−23.446 25	−23.420 20	−12.125 22	−11.287 58
At	PS2	−11.562 43	−11.206 54	−22.792 42	−22.805 95	−22.784 78	−11.798 26	−10.977 34

[a] Cf. section III.

investigated under well-defined conditions in molecular beams. Second, some of these processes are also topical from a practical point of view, e.g., in the realm of catalysis. Finally, our colleagues have extensive experimental experience with this type of process, and we have been interested in these processes in terms of quantum chemistry for some years.

The processes under study involve hydrides of the main group elements (4b, 5b, 6b, 7b, and 0) possessing four, three, two, one, and zero hydrogen atoms. We are going to deal with reactions between these hydrides and radical−ions thereof. In general, processes of the following type are considered (cf. ref 14):

$$AH_n + AH_n^{\bullet+} \leftrightarrow [AH_n]_2^{\bullet+} \leftrightarrow AH_{n+1}^{+} + AH_{n-1}^{\bullet} \qquad (1)$$

The intermediate dimer radical cation, $(AH_n)_2^{\bullet+}$, can occur in the form of several isomers: Two of them assume special importance. The first one (**1**) is a hydrogen-bonded form, and the other one (**2**) involves a two center-three electron (2c-3e)

$$\underset{\mathbf{1}}{[H_nA\cdots HAH_{n-1}]^{\bullet+}} \quad \underset{\mathbf{2}}{[H_nA{-}AH_n]^{\bullet+}}$$

bond, also called a hemibond. This is the case for intermediates derived from NH_3, H_2O, and HF, but it does not apply to the extreme hydrides in the sets under study, i.e., CH_4 (a hydride the central atom of which does not possess a lone pair) and Ne (a hydride with zero hydrogen atoms). In the former case only an unusual hydrogen bond[15] occurs (**3**), while in the neon radical cation dimer the only $[Ne{-}Ne]^{\bullet+}$ (**4**) structure involves a 2c-3e bond.

$$\underset{\mathbf{3}}{[H_3C{-}H{-}H{-}CH_3]^{\bullet+}} \quad \underset{\mathbf{4}}{[Ne{-}Ne]^{\bullet+}}$$

The subject of this first part is a reaction set (eq 2)

$$HX + HX^{\bullet+} \leftrightarrow [HX]_2^{\bullet+} \leftrightarrow H_2X^{+} + X^{\bullet} \qquad (2)$$

where X is F, Cl, Br, I, and At, respectively.

II. Calculations

The radical cations of hydrogen halide dimers $(HF)_2^{\bullet+}$, $(HCl)_2^{\bullet+}$, $(HBr)_2^{\bullet+}$, $(HI)_2^{\bullet+}$, $(HAt)_2^{\bullet+}$, and products of their decomposition have been investigated. These systems have been treated at the *ab initio* level with inclusion of correlation energy (the MP2, QCISD, and CCSD(T) methods). The contribution of electron correlation is significant for the systems under study. First, the optimization of geometries were performed for both hemibonded structures (point group of symmetry C_2 for all halogen elements except fluorine, where C_{2h} symmetry was determined for $(HF)_2^{\bullet+}$) and hydrogen-bonded arrangements (C_s point group). Then transition states (C_1) between them were found by locating critical points on the potential surface with one negative eigenvalue of the respective Hessian. The beyond-SCF methods, MP2 and QCISD, were chosen since the optimization routines with analytical gradients are available for open shell systems in Gaussian 92.

Standard 6-31G* and Dunning aug-cc-pVDZ[16a−c] basis sets were used for the H, F, and Cl atoms. For Br the SV+P basis set,[16d] related to 6-31G*, was used. Despite the great progress in development of pseudopotentials (PS) the selection of suitable pseudopotentials for the whole halogen group (F−At) was not easy. Our first choice was the energy-adjusted scalar relativistic pseudopotentials from the Stuttgart group as published by Dolg et al.[17,18] The advantage of these potentials is their use of extended valence basis sets which are better suited for more sophisticated electron correlation calculations. On the other hand, the composition of a basis set for At prevents us from performing the respective calculations. The At pseudopotentials are constructed with an h-projector;[19] this azimuthal number is not available in the Gaussian code. It is available in MOLPRO code, but this code does not include open shell MP2 calculations. Hence, we used Christiansen's average relativistic effective pseudopotential (AREP[20]). Our calculations on Cl-containing species demonstrated that AREPs give total energies at the MP2 level in close agreement with those evaluated by all-electron (AE) 6-31G*, and MWB and SDF pseudopotentials when augmented by the d-polarization functions from Stuttgart's MWB basis sets (MWB means M for a fit of neutral atom energies and WB for the Wood−Boring quasi-relativistic method of evaluation of atoms energies; *S* for a fit of single-valence-electron ion energies and *DF* for the Dirac−Fock method). Also, comparison was made with Hay−Wadt PS for chlorine-containing species.

Relativistic effects, which are very important for heavier elements, are effectively included in the pseudopotentials used. It has been shown in several papers[20c,26] that this way of covering of relativity effects is sufficiently correct. Nevertheless, we are aware of the fact that attention should be paid to spin−orbit coupling, which is not covered in pseudopotential treatment; spin−orbit coupling was not considered in the present work.

The energy, geometry, and vibrational calculations for all the systems studied were performed at the MP2 level. For the F- and Cl-containing species geometry optimization was also

TABLE 2: Bond Length (Å) and Bond Angles (deg) of the Systems[a] under Study

system X	method	I H−X	II $H{-}X^{\bullet+}$	III H−X	III X−H	III H⋯X	III HXH	III XHX	VI H−X	VI HXH
F	AE3	0.923	1.009	0.957	1.020	1.440	114.3	173.6	0.966	112.1
	PS2	0.934	1.021	0.974	1.021	1.507	114.1	173.1	0.982	112.4
	exptl[b]	0.918	1.024							
Cl	AE3	1.291	1.330	1.312	1.415	1.851	95.9	176.9	1.319	94.8
	PS2	1.277	1.307	1.295	1.335	2.109	97.0	177.6	1.298	96.5
	exptl[b]	1.274	1.315							
Br	AE1	1.423	1.455	1.442	1.537	2.109	93.4	177.7	1.448	93.0
	PS2	1.429	1.455	1.443	1.508	2.166	93.2	177.8	1.447	92.7
	exptl[b]	1.408	1.459							
I	PS2	1.628	1.647	1.635	1.731	2.348	90.6	179.4	1.639	90.6
	exptl[b]	1.608								
At	PS2	1.762	1.774	1.764	1.959	2.209	90.5	179.1	1.767	90.1

system X	method	IV H−X	IV X−X	IV HXX	IV HXXH	V H−X	V X−X	V X−H	V HXX	V XXH	V HXXH
F	AE3	0.961	1.861	96.8	180.0	0.949	2.096	1.006	115.3	44.0	116.2
	PS2	0.976	1.861	97.5	180.0	0.963	2.118	1.023	117.9	44.3	116.8
Cl	AE3	1.310	2.614	92.9	100.5	1.305	3.066	1.358	99.9	29.4	90.5
	PS2	1.292	2.633	95.4	112.0	1.286	3.181	1.320	109.4	31.2	84.5
Br	AE1	1.440	2.865	92.0	100.6	1.433	3.370	1.489	100.1	30.7	85.6
	PS2	1.442	2.865	92.9	98.2	1.437	3.471	1.476	99.9	27.9	85.2
I	PS2	1.635	3.267	89.4	94.8	1.633	3.924	1.681	93.5	23.7	85.2
At	PS2	1.767	3.474	90.9	91.7	1.761	4.061	1.792	92.9	31.1	87.3

[a] Cf. section III. [b] Reference 24.

performed at the AE-QCISD level; for the stationary points found, the energy calculations were carried out at the CCSD(T) level, (CCSD(T)//QCISD). The same strategy was also applied in the case of the pseudopotential treatment, where all the halogen-containing species were investigated.

Interaction energies for the hemibonded and H-bonded dimers as well as for the transition structure connecting them were corrected for basis set superposition error by utilizing the Boys−Bernardi function counterpoise method [21] (all the MO's of the "ghost" atoms were considered).

Zero-point vibrational energies (ZPVE) for all the species were evaluated with standard MP2 harmonic vibrational frequencies. When determining the ZPVE of transition species, the respective imaginary frequency was not taken into account.

III. Results

In this part numerical results necessary for analysis of reactivity and structural features are presented.

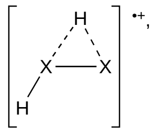
First of all, total energies of reactants (I, II), intermediates (III, IV), transition state (V) separating the intermediates, and products (VI, VII) are presented in Table 1.

XH **I**

$XH^{\bullet+}$ **II**

$(HX\bullet\bullet HX)^{\bullet+}$ **III**

$(HX{-}XH)^{\bullet+}$ **IV**



V

H_2X^+ **VI**

$X^{\bullet}$ **VII**

More specific features of the AE and PS methods are given by a number associated with the symbols AE, PS, respectively; in the same line are specified elements for which the respective level was applied. The symbols used have the following meanings:

AE1, MP2/6-31G*	F, Cl, Br
AE2, CCSD(T)/6-31G*//QCISD/6-31G*	F, Cl
AE3, CCSD(T)/aug-cc-pVDZ//QCISD/aug-cc-pVDZ	F, Cl
PS1, MP2/AREP	F, Cl, Br, I, At
PS2, CCSD(T)/AREP//QCISD/AREP	F, Cl, Br, I, At

Furthermore, geometry characteristics and charges are presented in Tables 2 and 3, respectively. Results for other pseudopotentials mentioned above (Stuttgart MWB and SDF and Hay−Wadt) calculated at the MP2 level do not differ significantly from the PS1 values and are therefore not presented in the tables. They are available upon request from the authors.

IV. Discussion

Reaction Profiles. In Table 4 energy differences, ΔE, obtained from energy values of Table 1 are presented. The ΔE values are specified by two indices, x and y, [$\Delta E(x,y)$]. For the sake of comparison the energy of hemibonded radical cation dimer, $HXXH^{\bullet+}$, was set to equal zero. The first index, x, specifies the process:

$$HXXH^{\bullet+} \rightleftharpoons HX + HX^{\bullet+} \qquad x = 1$$

$$HXXH^{\bullet+} \quad \text{transition state} \qquad x = 2$$

$$HXXH^{\bullet+} \rightleftharpoons (HX\cdots HX)^{\bullet+} \qquad x = 3$$

$$HXXH^{\bullet+} \rightleftharpoons HXH^{+} + X^{\bullet} \qquad x = 4$$

The second index, y, specifies the type of energy change: $y = 1$ is an *ab initio* energy difference, $y = 2$ is the energy difference

TABLE 3: Charges Obtained by Mulliken Population Analysis (in electron)

system		$H_1X_1H_2X_2$ (**III**)				HXXH (**IV**)		$H_1X_1H_2X_2$ (**V**)			
X	method	H_1	X_1	H_2	X_2	H	X	H_1	X_1	X_2	H_2
F	AE3	0.53	−0.23	0.71	−0.01	0.53	−0.03	0.45	−0.39	0.27	0.66
	PS2	0.67	−0.42	0.68	0.07	0.66	−0.16	0.62	−0.55	0.22	0.71
Cl	AE3	0.30	0.12	0.54	0.05	0.31	0.19	0.24	−0.17	0.47	0.46
	PS2	0.41	0.11	0.34	0.15	0.38	0.12	0.35	−0.25	0.48	0.41
Br	AE1	0.40	0.20	0.39	0.01	0.35	0.15	0.32	−0.19	0.50	0.37
	PS2	0.36	0.15	0.30	0.18	0.35	0.15	0.31	−0.18	0.50	0.37
I	PS2	0.27	0.30	0.18	0.25	0.25	0.25	0.21	−0.06	0.51	0.26
At	PS2	0.19	0.32	0.11	0.38	0.19	0.31	0.16	0.01	0.63	0.20

TABLE 4: Energy Differences Required for Energy Profile Construction (in kcal/mol)

system	F				Cl				Br		I	At
method	AE1	AE2	AE3	PS2	AE1	AE2	AE3	PS2	AE1	PS2	PS2	PS2
$\Delta E(1,1)^a$	50.2	45.1	39.7	41.3	30.2	28.8	32.1	29.9	33.3	28.7	26.8	23.2
$\Delta E(1,2)$	51.3	46.0	41.2	43.0	28.5	27.2	30.8	27.6	30.6	27.0	25.5	22.1
$\Delta E(1,3)$	47.5	42.2	37.4	39.3	26.5	25.1	28.8	25.6	28.9	25.2	22.9	20.9
$\Delta E(2,1)$	20.1	11.2	10.7	11.6	18.5	15.8	13.0	16.2	19.9	16.6	16.3	13.3
$\Delta E(2,3)$	18.0	9.1	8.6	9.4	17.3	14.7	12.0	15.1	18.8	15.5	15.3	12.4
$\Delta E(3,1)$	−6.8	−11.4	−10.0	−10.3	9.2	11.0	8.1	6.6	13.0	9.8	11.7	8.5
$\Delta E(3,3)$	−8.0	−12.5	−11.1	−11.0	9.5	11.3	8.4	6.9	12.7	9.6	11.2	7.8
$\Delta E(4,1)$	7.1	2.4	2.2	0.0	17.7	16.3	20.7	15.9	24.0	19.1	21.0	19.0
$\Delta E(4,2)$	7.3	2.2	3.3	0.3	17.7	15.6	23.9	14.7	23.4	19.2	22.0	26.3
$\Delta E(4,3)$	5.4	0.2	1.3	−1.6	17.3	15.2	23.6	14.4	23.3	18.9	21.9	26.3

[a] $\Delta E(x,y)$: $x = 1$, $HXXH^{\bullet+} \rightleftharpoons HX + HX^{\bullet+}$; $y = 1$, total energy differences; $x = 2$, $HXXH^{\bullet+} \rightleftharpoons HHXX^{\bullet+}$; $y = 2$, BSSE + def. corrections; $x = 3$, $HXXH^{\bullet+} \rightleftharpoons HXHX^{\bullet+}$; $y = 3$, ZPVE corrections; $x = 4$, $HXXH^{\bullet+} \rightleftharpoons HXH^{+} + X^{\bullet}$.

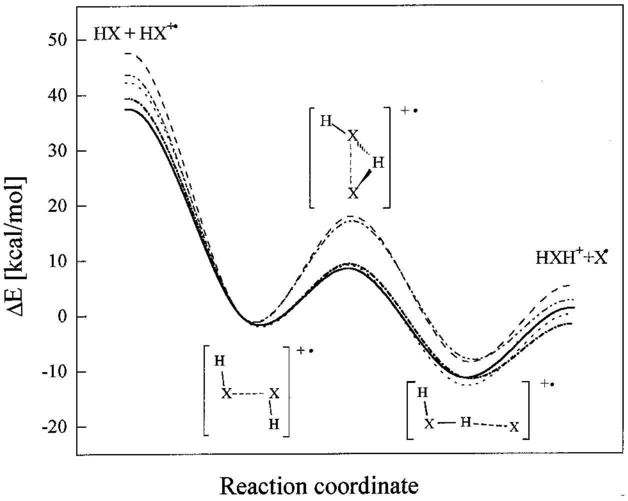


Figure 1. Reaction profile of the HF + HF$^{\bullet+}$ process: dashed line, MP2/6-31G* (AE1); dotted line, CCSD(T)/6-31G*//QCISD/6-31G* (AE2); solid line, CCSD(T)/ang-cc-pvdz//QCISD/ang-cc-pvdz (AE3); dash−dot−dot line, MP2/AREPs (PS1); short dash−dot line, CCSD(T)/AREPs/QCISD/AREPs (PS2).

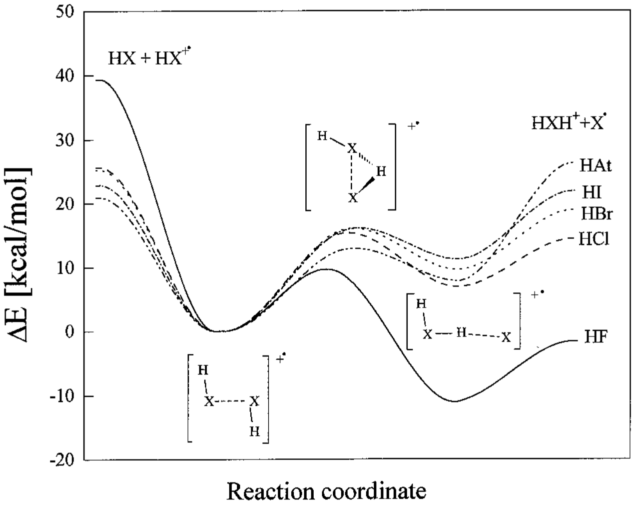


Figure 2. Reaction profile of the HX + HX$^-$ process. Calculations with Christiansen pseudopotentials. X = F (—), Cl (- - -), Br (•••), I (—•—), At (—••—).

corrected for BSSE and deformation energy, and $y = 3$ includes moreover the ZPVE.

Figures 1 and 2 were constructed on the basis of energy differences of Table 4. With the $(HF)_2^{\bullet+}$ and $(HCl)_2^{\bullet+}$ it is seen that it is not easy to reach a level of computation where ΔE is not sensitive any more to augmentation of the basis set and the description of electron correlation. From the point of view of quantitative computational attempts, this is a rather disappointing result. From Figure 1 it is further evident that AREPs augmented by polarization functions yield reliable results. Figure 2 shows that energy profiles strongly depend on the type of halogen atoms. The $(HF)_2^{\bullet+}$ system differs significantly from all the other systems. The global minimum of $(HF)_2^{\bullet+}$ corresponds to the H-bonded structure. This structure is separated from the hemibonded one by the transition barrier which is higher than the energy corresponding to the asymmetric decomposition channel ($H_2F^+ + F^{\bullet}$). For all the other halogens, the hemibonded structure is more stable than the H-bonded one, which was already shown earlier.[14,22] The energies of hemibonded complexes were therefore taken as a reference zero energy level (cf. Figure 2). The activated complex, separating the two $(HX)_2^{\bullet+}$ isomers, assumes the same type of structure. The barrier height for passing from the H-bonded system to the hemibonded structure is in all the systems, except for the $(HF)_2^{\bullet+}$ dimer, so low that H-bonded systems will be spontaneously converted to the hemibonded structures. The energy barrier in the opposite direction, from hemibonded to H-bonded complexes, is the lowest for fluorine ($\Delta E(2,3)$ in Table 4), and it is about twice as large for chlorine. For the remaining halogen atoms (Cl, Br, and I) it is nearly constant and for astatine it decreases. Also in the case of the stability of H-bonded complexes, astatine shows irregularity, being more stable than iodine and bromine complexes. Moreover, energies of asymmetric decomposition monotonically increase with halogen atomic number, which makes the H-bonded astatine complex even more stable in comparison with iodine and/or bromine

TABLE 5: Observed and Calculated (MP2 with Christiansen Pseudopotentials and the CCSD(T)) Adiabatic Ionization Potentials (in eV) of Hydrogen Halogenides, HX; Values in Parentheses Correspond to the All-Electron Results (AE3 Values)

method	F	Cl	Br	I	At
MP2	15.59	12.20	11.37	10.31	9.71
CCSD(T)	15.42 (15.90)	12.16 (12.49)	11.31	10.26	9.68
exptl	16.04	12.75	11.66	10.39	

TABLE 6: Calculated Reaction Heats, ΔH_0 (kcal/mol), for Reaction 3 in the Case of Chlorine. Observed Value Amounts to −11.0 kcal/mol[23]

method	AE1	AE2	AE3	PS1	PS2
ΔH_0	−10.88	−10.82	−9.69	−12.51	−12.22

complexes. Comparing the beginning and the end of reaction coordinates in Figure 2 (symmetric and asymmetric decomposition channels), we conclude that energies of asymmetric decomposition ($\Delta E(4,3)$) increase with atomic number, while energies of symmetric decomposition ($\Delta E(1,3)$) behave in the opposite way. So that with increasing atomic number of halogen, the overall reaction 2 becomes energetically less advantageous. For the fluorine system, this reaction passes over two barriers which are relatively small with respect to the energy obtained from association of $HX + HX^{\bullet +}$. In case of the other halogens, the transition state barrier is comparable to the corresponding association step. For the three heaviest systems, the products ($H_2X^+ + X^\bullet$) are slightly less stable than the reactants ($HX + HX^{\bullet +}$), which means that the H_2X^+ acid is stronger than $HX^{\bullet +}$.

Ionization Potentials. Adiabatic ionization potentials of the HX (X = F, Cl, Br, I) molecules were obtained by inspection of photoelectron spectra.[23] Theoretical values were obtained as the difference between energies of HX and $HX^{\bullet +}$ species; ZPVE were included (Table 5).

The agreement between experimental and CCSD(T)/AE values is satisfactory in the case of HF. For HCl the obtained results are slightly worse. CCSD(T)/PS values for all the hydrogen halides differ from experimental results which may be due to the relatively small valence basis sets used.

Enthalpy Changes. These characteristics for the overall process (eq 1) were obtained on the basis of experimental heats of formation[23] of reactants and products. The set of the ΔH_0 values calculated for the process 3 agree reasonably with the experimental ΔH_{298} value, which for

$$HCl + HCl^{\bullet +} \leftrightarrow H_2Cl^+ + Cl^\bullet \qquad (3)$$

amounts to −11.0 kcal/mol (Table 6). It should be mentioned here that theoretical ΔH values cannot be obtained directly from the respective energies (Table 4) because these values also contain the BSSE. ΔH values based on pseudopotentials are satisfactory for the F- and Cl-containing systems but are getting poorer when passing to heavier systems. For example, experimental ΔH_{298} value for the I-containing system amounts to −2.2 kcal/mol; the PS2 calculated value amounts to −4.5 kcal/mol. Selected calculated values (ΔH_0) and experimental ΔH_{298} values are presented in Table 7. We feel that the accuracy of available experimental heats of formation for species containing heavier elements is not high enough for discussing agreement between experimental and observed values at a higher level of sophistication. From a semiquantitative point of view the results (Table 7) are satisfactory.

To improve the agreement with experiment, we carried out an additional calculation with a larger basis sets on iodine (from original [2s2p] to [3s3p2d1f]) and hydrogen (from original [2s] to [3s]). The resulting ΔH at MP2 and CCSD(T) levels (−1.7 and −2.0 kcal/mol, respectively) agree better with the mentioned experimental heat of reaction. Performing, however, the same strategy for all the other systems, the rather good agreement with experiment (Table 7) deteriorated. The respective ΔH values increased by about 2.0 kcal/mol which is comparable to the ΔH increase in the case of the I-containing reaction. Further, another attempt was made to utilize the Stuttgart MWB PS with more extended basis sets recommended for Br and I.[18] In this case the ΔH values increased as well.

TABLE 7: Calculated (ΔH_0) and Observed (ΔH_{298}) Reaction Heats (in kcal/mol) for Reaction 1

X	AE1	PS1	PS2	exptl
F	−41.3	−39.8	−39.5	−36.8
Cl	−10.9	−12.5	−12.2	−11.0
Br	−7.8	−8.1	−8.1	−8.8
I		−4.4	−4.5	−2.2
At		−2.9	−3.0	

TABLE 8: Stretching Frequencies Observed and Calculated (cm^{-1}) in Halogen Acids (HX) and Radical Cations Thereof

		X				
frequenceie		F	Cl	Br	I	At
neutral	obsd	3915	2886	2560	2230	
	calcd	4070	3078	2706	2190	2119
radical-cation	obsd[a]		2660	2420	2100	
	calcd	3042	2814	2535	2236	2084

[a] Values corresponding to $^2P_{1/2}$ state.

Bond Lengths. Calculated geometry characteristics obtained with several methods (Table 2) offer a rather homogeneous picture. For four hydrogen halides and for two radical cations thereof, experimental bond lengths are available;[24] agreement between calculated and observed values is fair. The calculated bond length in HX increases gradually from about 0.93 Å (HF) to 1.75 Å (HAt). Increase of the bond length and weakening of bond strength (cf. also the respective vibrational frequencies) when passing from HX to $HX^{\bullet +}$ is due to the bonding character of the highest molecular orbital in the parent HX systems. Changes in geometrical characteristics when passing from F- to At-containing remaining systems are gradual and offer a consistent picture.

The calculated (AREP) bond lengths of hydrogen halides and their cation radicals differ from respective experimental values by less than 0.02 Å. A similar error could therefore be expected also in case of HAt and $HAt^{\bullet +}$.

Vibrational Frequencies and Charge Distribution. While vibrational spectra of hydrogen halides are accessible by straightforward measurements, the best source of the stretching frequencies of the hydrogen halides radical cations is represented by photoelectron spectra. The separation in energy of the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states (which are due to spin−orbit coupling) is observable and increases significantly when passing from HCl to HI.[25] Due to overlap of bands, the stretch of $H{-}Br^{\bullet +}$ for the $^2\Pi_{3/2}$ state cannot be obtained. As the differences in stretching vibrations associated with the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states are rather small, values corresponding to the $^2\Pi_{1/2}$ state are presented in Table 8. There is a reasonable agreement between calculated and observed values.

As to the charge distribution (Table 3), there is a significant change when passing from the F-containing systems to systems containing heavier halogens. With increasing coordination number of the halogen atom, electron density increases. In complexes **III**, it is only fluorine with coordination number two which is negatively charged. Such a charge is associated with all the halogen atoms with coordination number three.

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References and Notes

(1) Jørgensen, C. K. *J. Chem. Phys.* **1979**, *76*, 630.

(2) Pitzer, K. S. *Acc. Chem. Res.* **1979**, *12*, 271.

(3) Pitzer, K. S. *Int. J. Quantum Chem.* **1984**, *25*, 131.

(4) Christiansen, P. A.; Ermler, W. C.; Pitzer, K. S. *Annu. Rev. Phys. Chem.* **1985**, *36*, 407.

(5) Ermler, W. C.; Ross, R. B.; Christiansen, P. A. *Adv. Quant. Chem.* **1988**, *19*, 139.

(6) Matcha, R. L. *J. Chem. Phys.* **1976**, *65*, 1962.

(7) Perera, S. A.; Bartlett, R. J. *Chem. Phys. Lett.* **1993**, *216*, 606.

(8) Pisani, L.; Clementi, E. *J. Chem. Phys.* **1994**, *101*, 3079.

(9) Desclaux, J. P.; Pyykkö, P. *Chem. Phys. Lett.* **1974**, *29*, 534.

(10) Pyykkö, P.; Desclaux, J. P. *Nature* **1977**, *266*, 336.

(11) Pyykkö, P.; Desclaux, J. P. *J. Phys., Colloq. C4,* **1979**, Suppl. No. 4, 222; *Chem. Phys.* **1978**, *34*, 261.

(12) Weinberger, P. In 4th Central European Workshop on Electronic and Magnetic Properties of Alloys, Surfaces and Interfaces, Brno, 1995.

(13) Zahradník, R. *Acc. Chem. Res.* **1995**, *28*, 306.

(14) Zahradník, R. *Collect. Czech. Chem. Commun.* **1993**, *58*, 1.

(15) Havlas, Z.; Bauwe, E.; Zahradník, R. *Chem. Phys. Lett.* **1986**, *123*, 331.

(16) (a) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007. (b) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796. (c) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358. (d) Binning, R. C., Jr.; Curtiss, L. A. *J. Comput. Chem.* **1990**, *11*, 1206.

(17) Bergner, A.; Dolg, M.; Kuechle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431.

(18) Schwerdtfeger, P.; Dolg, M.; Schwarz, W. H. E., Bowmaker, G. A.; Boyd, P. D. W. J. *Chem. Phys.* **1989**, *91*, 1762.

(19) Kuechle, W.; Dolg, M.; Stoll, H.; Preuss, H. *Mol. Phys.* **1991**, *74*, 1245.

(20) (a) Pacios, L. F.; Christiansen, P. A. *J. Chem. Phys.* **1985**, *82*, 2664. (b) Hurley, M. M.; Pacios, L. F.; Christiansen, P. A.; Roos, R. B.; Ermler, W. C. *J. Chem. Phys.* **1986**, *84*, 6840. (c) LaJohn, L. A.; Christiansen, P. A.; Roos, R. B.; Atashroo, T.; Ermler, W. C. *J. Chem. Phys.* **1987**, *87*, 2812. (d) Roos, R. B.; Powers, J. M.; Atashroo, T.; Ermler, W. C.; La John, L. A.; Christiansen, P. A. *J. Chem. Phys.* **1990**, *93*, 6654.

(21) Boys, F. S.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(22) Gill, P. M. V.; Radom, L. *J. Am. Chem. Soc.* **1988**, *110*, 4931.

(23) Lias, G. S.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. A.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17* (Suppl. 1).

(24) *Tables of Interatomic Distances and Configuration in Molecules and Ions*; Special Publ. No. 11; The Chemical Society: London, 1958.

(25) Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. R. Molecular Photoelectron Spectroscopy; Wiley-Interscience: London, 1979.

(26) (a) Lee, Y. S.; Ermler, W. C.; Pitzer, K. S. *J. Chem. Phys.* **1977**, *67*, 5861. (b) Kahn, L. R.; Hay, P. J.; Cowan, R. D. *J. Chem. Phys.* **1978**, *68*, 2386. (c) Kaldor, U.; Hess, B. A. *Chem. Phys. Lett.* **1994**, *230*, 1.