Charge Distribution in Diatomic Halides from Electron Spectroscopy

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Abstract: Core-ionization and Auger kinetic energies for hydrogen halides, atomic iodine, elemental halogen molecules, and chlorine fluoride have been analyzed to give the relative electrostatic potential at the halogen atom in each species and the relative relaxation energy that arises from valence rearrangement upon core ionization. The initial-state potentials together with a point-charge model give the charge on the halogen atom in the hydrogen halides and in chlorine fluoride. These are not only consistent with chemical experience but illustrate the importance of not relying solely on ionization-energy shifts to determine the charge distribution. Ionization energies, initial-state potentials, and relaxation energies have been calculated with ab initio theory. The agreement between theory and experiment is excellent except for the relative initial-state potentials and relaxation energies for fluorine.

The transfer of charge between atoms upon bond formation is a fundamental chemical concept, and a detailed knowledge of molecular charge distribution is of considerable interest in order to understand and predict chemical properties. A number of experimental techniques[2] have been used to provide information on charge distribution in molecules, among them the measurement of dipole moments, nuclear quadrupole resonance spectroscopy, nuclear Zeeman effect, Mossbauer spectroscopy, and measurement of core-ionization energies by X-ray photoelectron spectroscopy (XPS).

Core-ionization energies are, however, affected not only by the initial, ground-state, charge distribution but also by the rearrangement, or relaxation, of valence electrons when a core electron is removed. Because of this complication, analysis of XPS measurements to yield charge distributions has been successful only in a few cases where differential relaxation effects can be ignored.[3-6] Where this simplification does not exist, corrections must be made for relaxation before the charge distribution can be derived from the experimental data.

Combined measurements of core-ionization energies and Auger kinetic energies can be used to determine relative relaxation energies[7-10] and, consequently, the initial-state charge distributions

of the molecules of interest. We let V/e represent the potential at the core of an atom of interest and R the relaxation energy associated with valence rearrangement when a core electron is removed from that atom. Then, letting I represent a core-ionization energy and K an Auger kinetic energy, we can show that

$$\Delta I = \Delta V - \Delta R \tag{1}$$

$$\Delta K = -\Delta V + 3\Delta R \tag{2}$$

$$\Delta \alpha = \Delta I + \Delta K = 2\Delta R \tag{3}$$

where Δ refers to a shift relative to some suitable reference compound. The shift in the Auger parameter, $\Delta\alpha$, is a direct measure of the relative relaxation energy. Derivations of eq 1 and 2 and a discussion of their limitations is given elsewhere.[7,10,11]

Once ΔV has been determined from eq 1 and 2 it can be related to the charge distribution of the molecule by the familiar point charge model[12]

$$\Delta V = k_i q_i + \sum_{j \neq i} q_j e^2 / r_{ij} + l \tag{4}$$

In this equation, q_i is the atomic charge for the ith atom, k_i is

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Table I. Experimental Core-Ionization Energies, I(exptl), and Auger Kinetic Energies, K(exptl), for Diatomic Halides (All Values Are Given in eV with Estimated Errors in Parentheses)

molecule	I(exptl)	ΔI(exptl)	K(exptl)	ΔK(exptl)
	F 1s		KL_1L_1	
F_2	696.63 (5)[a]	0.0	599.10 (5)[a]	0.0
HF	694.23 (8)[b]	−2.40 (9)	595.6 (1)[b]	−3.50 (11)
ClF	694.52 (5)[c]	−2.11 (7)	d	d
	Cl $2p_{3/2}$		$KL_{2,3}L_{2,3}$	
Cl_2	207.81 (4)[e]	0.0	2373.77 (5)[e]	0.0
HCl	207.37 (4)[e]	−0.44 (6)	2372.03 (5)[e]	−1.74 (7)
ClF	209.17 (4)[e]	1.36 (6)	2370.78 (5)[e]	−2.99 (7)
	Br $3d_{5/2}$		$L_3M_{4,5}M_{4,5}$	
Br_2	(77.24 (5))[f]	0.0	1377.0 (2)[g]	0.0
HBr	77.20 (4)[h]	−0.04 (7)[j]	1375.24 (5)[h]	−1.76 (20)
	I $3d_{5/2}$		$M_4N_{4,5}N_{4,5}$	
I_2	627.32 (4)[j]	0.0	506.76 (5)[j]	0.0
HI	627.59 (4)[j]	0.27 (6)	504.44 (5)[j]	−2.32 (7)
I	(628.4 (2))[k]	1.0 (2)[l]	(503.51 (11))[m]	−3.25 (10)[n]

[a] Reference 15. [b] Reference 16. [c] Reference 17. [d] Not measured. [e] Reference 9. [f] Estimated from the corresponding (Br_2–HBr) shift in ref 18. [g] Reference 21. [h] This work. [i] Reference 18. [j] Reference 19. [k] Estimated from the corresponding (I_2–I) shift in ref 20. [l] Reference 20. [m] Estimated from the shift in ref 22. [n] Reference 22.

the change in potential at the core per valence electron removed and is often equated to the expectation value, $\langle 1/r_i \rangle$, for the reciprocal valence radius, r_{ij} is the distance between the ith and jth atoms, and l is a constant. If the reference species is the elemental material, then l is assumed to be zero.

Most attempts to determine charge distributions from XPS measurements have been based on relative core-ionization energies, ΔI, rather than on initial-state potentials, ΔV. We report here the use of ΔV's derived as outlined above together with the point charge model to determine atomic charges in the hydrogen halides and chlorine fluoride. The results are quite reasonable and, in addition, show the danger of trying to infer charge distributions from core-ionization energies alone.

The calculation of charge from electron spectroscopic data depends on the validity of the relaxation model outlined above. Although the model has been the subject of both experimental[9,13,14] and theoretical evaluation,[10,11] there have been few comparisons of the quantities derived from the experimental measurements and corresponding quantities based on ab initio theoretical calculations.[9] The molecules we have studied experimentally are sufficiently small to be treated theoretically by good-quality ab initio calculations. We have performed such calculations for both the neutral ground state and the ionized core-hole state, thus providing theoretical calculations of ΔI, ΔV, and ΔR. Agreement between experimental and theoretical results supports the validity of the relaxation model and gives confidence that it can be applied to other molecules.

Experimental Section and Results

Much of the data on core-ionization and Auger kinetic energies are already available.[9,15-22] The required new measurements on HBr were made by standard procedures with the Oregon State University cylin-

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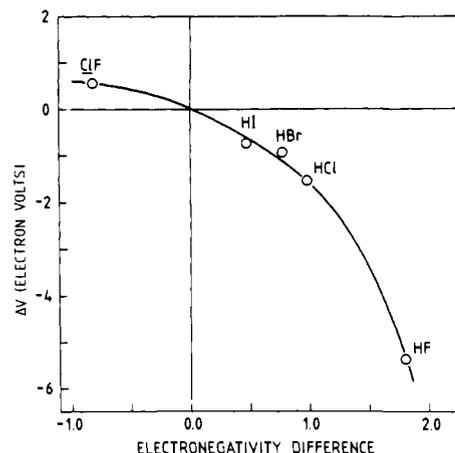
Figure 1. Relative experimental ground-state potential energy for diatomic halides as a function of the difference in atomic electronegativities.

drical mirror analyzer[23] and aluminum Kα X-rays for excitation. The gas sample was mixed with neon, and the neon 1s and 2s photoelectrons were used for calibration.[24,25] Table I shows the experimental results. The Ne 1s and Ne KLL calibration energies have recently been re-examined in this laboratory,[24] and the energies in Table I have been corrected according to the new calibration standards. The corrections are small and in all cases within the uncertainties. Because of inconsistency in calibration schemes in different laboratories, absolute values of observed energies often disagree. Energy differences, however, are much more reproducible. In order to present the data in Table I on a consistent absolute scale, the Br_2 $3d_{5/2}$ and atomic I $3d_{5/2}$ ionization energies have been estimated from reported shifts and given in parentheses. The estimated errors for the shifts are small in most cases and will not obscure the derived quantities, ΔV and ΔR.

The most striking features of Table I are the monotonic change in ionization-energy shifts for HX–X_2 from a value of −2.40 for fluorine to 0.27 eV for iodine and the near equality of the ionization-energy shifts for fluorine in ClF and HF. Interpretation of these shifts as being entirely due to the charge distribution in the neutral molecule would lead to the conclusion that hydrogen withdraws electrons from iodine in HI and that chlorine and hydrogen have comparable electronegativities. These conclusions are contrary to chemical experience and arise because of neglect of relaxation effects, as will be seen in the following paragraphs.

Table II shows the separation of ΔI into ΔV and ΔR on the basis of the measured values of ΔI and ΔK and eq 1 and 2. Also shown is a comparison of these experimentally derived quantities with those obtained from ab initio calculations. The agreement between theory and experiment is generally excellent and will be discussed in a subsequent section.

Considering now the experimental values of ΔV, which reflect the initial-state charge distribution, we see a monotonic decrease for the hydrogen halides from −5.36 eV for HF to −0.75 eV for HI. In contrast to the behavior of the values of ΔI, the values of ΔV are always negative, in keeping with the relative electronegativities of the halogens and hydrogen. Although no experimental value is available for fluorine in ClF, the theoretical results show that there is a striking difference between ΔV for ClF and HF and that the near equality of the ΔI's results from values of ΔR that are also quite different for the two molecules. These results illustrate the danger of using values of ΔI alone to infer charge distributions.

The experimental relative relaxation energies, ΔR, show a sharp drop from −2.96 eV for HF to values of approximately −1 eV for the other molecules. ΔR depends directly on the polarizability of the surrounding molecules and inversely on the distance between the core-ionized atom and its surroundings. Both increase as we move down the periodic table. These compensating effects lead to a variation of ΔR that is not easily predicted.

Atomic iodine is the only halogen atom for which both core-ionization and Auger kinetic energies are known.[20,22] We note that HI and I have

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Table II. Comparison of Experimental and Theoretical Core-Ionization Energies, Relaxation Energies, and Ground-State Potential Energies for HX and ClF Relative to X_2 (All Values in eV)

molecule	ΔI(exptl)	ΔI(calcd)	ΔV(exptl)	ΔV(calcd)	ΔR(exptl)	ΔR(calcd)
F_2	0.0	0.0	0.0	0.0	0.0	0.0
HF	−2.40 (9)	−2.11	−5.36 (15)	−4.48	−2.96 (7)	−2.37
Cl*F*	−2.11 (7)	−2.04		−1.79		0.27
Cl_2	0.0	0.0	0.0	0.0	0.0	0.0
HCl	−0.44 (6)	−0.56	−1.53 (10)	−1.54	−1.09 (5)	−0.98
*Cl*F	1.36 (6)	1.43	0.54 (10)	0.62	−0.82 (5)	−0.81
Br_2	0.0	0.0	0.0	0.0	0.0	0.0
HBr	−0.04 (7)	−0.07	−0.94 (15)	−1.13	−0.90 (11)	−1.06
I_2	0.0	0.0	0.0	0.0	0.0	0.0
HI	0.27 (6)	0.18	−0.75 (10)	−0.68	−1.02 (5)	−0.85
I	1.0 (2)		−0.1 (3)		−1.1 (1)	

Table III. List of Expectation Values k_i (V) for the Italicized Elements, Bond Lengths, r_{ij}(Å), and Halogen Charge Obtained from Different Methods

molecule	k_i	r_{ij}	q_i(es)[a]	q_i(dipole)[b]	q_i(ab initio)[c]
H*F*	36.2	0.917	−0.26 (1)	−0.43	−0.31
H*Cl*	21.3	1.274	−0.15 (1)	−0.18	−0.22
H*Br*	18.0	1.414	−0.12 (2)	−0.12	−0.13
H*I*	15.0	1.609	−0.12 (2)	−0.05	−0.06
*Cl*F	21.3	1.628	0.04 (1)	0.11	0.30

[a] From electron spectroscopy, this work. [b] Estimated from experimental dipole moments. [c] From Mulliken population analysis, this work.

about the same relaxation energy and ΔV for I relative to I_2 is small, as expected, since both are neutral species.

It is interesting to investigate how the change in ground-state potential energy, ΔV, correlates with atomic electronegativities.[26] In Figure 1, we have plotted ΔV against the electronegativity difference $X_X - X_L$, where X_X is the electronegativity of the halogen and X_L is the electronegativity of the ligand (H for HX, and F for ClF). A smooth curve through the points passes through the origin. Thus for homonuclear diatomics $\Delta V = 0$ as should be the case. Once this relationship is established, Figure 1 may be used to estimate the ΔV for other compounds not yet measured. It is, for example, possible to estimate ΔV for F in ClF relative to F_2. Interpolation gives $\Delta V = 1.3$ eV which is not far from the theoretical value 1.8 eV in Table II. The charge on F derived from the potential model (see below) using $\Delta V = 1.3$ agrees with the result for Cl.

Charge Distribution in Diatomic Halides

For diatomic molecules, the point charge model in (4) takes a particularly simple form when the shifts are taken relative to the elemental halogens. In this case $l = 0$ and since $q_j = -q_i$ we get

$$q_i = \Delta V/(k_i - e^2/r_{ij}) \qquad (5)$$

Equation 5 shows that the charge is directly connected to ΔV. The bond lengths r_{ij} are known for all the compounds studied. A logical choice for k is the change in core-ionization energy of the free atom when a valence electron is removed, which can be estimated by a variety of techniques.[4] We have instead used $k = e^2\langle 1/r \rangle$, where $\langle 1/r \rangle$ is the expectation value of $1/r$ for the valence electrons on the atom of interest. This approximation is, in principle, valid only if $\langle 1/r \rangle$ is independent of the occupancy of the valence shell, which is probably not the case. However, values of k based on free atoms are very small and lead to unrealistically large values for the derived charges q. Moreover, Carroll et al.[4] have derived k values from a self-consistent analysis of core-ionization energy shifts in xenon fluorides and have found that these are much closer to $\langle 1/r \rangle$ than to values that allow for the change in valence radius with valence occupancy. The k values used in this study are taken from Carlson's compilation[27] and shown in Table III. The derived halogen charges for the different
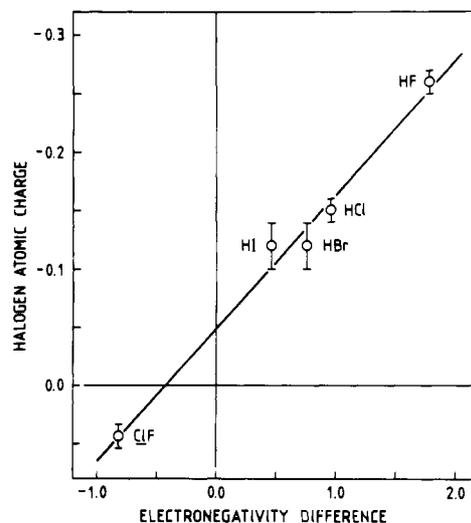
Figure 2. Atomic charge for halogen derived from the potential model as a function of the difference in atomic electronegativities.

compounds are shown in the fourth column of the table. The results are quite reasonable and as expected from chemical experience. It should be mentioned that slightly different sets of values for $\langle 1/r \rangle$ may be found in the literature, but these will give the same overall results. For example, the $\langle 1/r \rangle$ values from Desclaux's tables[28] will raise all charges about 0.02 e.

Atomic charges have traditionally been estimated from experimental dipole moments,[2] as is done in the fifth column of Table III. However, the ionic bond moment is only one of several contributions to the total molecular dipole, and the charges so derived may be greatly in error. Except for fluorine, however, the results compare quite well. Mulliken populations derived from the ab initio results also agree with the electron spectroscopic results, except for HF. It is well-known that the population analysis strongly depends on the basis and polarization functions employed. For example, a recent ab initio calculation for HF, HCl, and HBr with a slightly larger basis set than ours gives −0.38, −0.20, and −0.05, respectively, for the halogen charge.[29] The large value of 0.30 calculated for Cl in ClF might be an artifact of the population analysis. Huheey[2] has discussed existing methods of estimating atomic charges in molecules both from electronegativity values and from experimental measurements of properties related to charge distribution. There seems at the present time to be no other unique way of obtaining atomic charges, and unlike most other methods electron spectroscopy is the only method which relates directly to partial charge.

Since atomic charge and electronegativity are so interconnected, we have plotted the charges derived from ΔV as a function of electronegativity in Figure 2 and obtained a linear relationship (correlation coefficient 0.992). The line does not pass through

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Table IV. Results from ab Initio Calculations of Core-Ionization Energies, I(calcd), Ground-State Potential Energy, V(calcd), and Molecular Relaxation, R(calcd), for X_2, HX, and ClF (All Values in eV)

molecule	orbital	I(calcd)	V(calcd)	R(calcd)
F_2	1s	697.36	719.54	22.18
HF	1s	695.35	715.06	19.81
ClF	1s	695.32	717.75	22.43
Cl_2	2p	208.38	219.80	11.42
HCl	2p	207.82	218.26	10.44
ClF	2p	209.81	220.42	10.61
Br_2	3d	77.79	87.39	9.62
HBr	3d	77.72	86.26	8.54
I_2	3d	643.05	661.81	18.76
HI	3d	643.23	661.13	17.91

origin as in Figure 1. Because of this the point for fluorine in ClF ($q_F = -q_{Cl}$) will not be on the line. It seems that the simplification introduced by the point charge model is not entirely consistent. The difficulties may lie in the choice of k_i parameters in eq 5. It is possible that these need to be determined from experimental data, rather than from theoretical atomic calculations. This could be done if data for interhalogens (presently unavailable) were included with the results given here and analyzed in a self-consistent way, following the procedure given by Carroll et al.[4]

Theoretical Calculations

Ab initio LCAO–SCF calculations of core-electron-ionization energies were carried out for the diatomic halides with the standard Hartree–Fock method with the MOLECULE-ALCHEMY package.[30] The atomic orbital basis set for H is 3 s (ref 31), for F and Cl 7s 3p and 10s 6p (ref 32), for Br 12s 8p 5d (ref 33), and for I 25s 11p 7d (ref 34). These sets are contracted to double-ζ quality and augmented with a p function on the H atoms and with a d function on the halogens for polarization. The exponent for the hydrogen p function was chosen to be 0.90, whereas the d exponents were optimized for the X_2 molecules to be 0.92, 0.53, 0.41, and 0.30 for F, Cl, Br, and I, respectively. All calculations are performed at the experimental bond distances.

Core-ionization energies are obtained as the differences between the total energies of the final state with a localized core hole and the initial closed-shell ground state

$$I(\text{calcd}) = E(M^{*+}) - E(M)$$

These so-called ΔSCF ionization energies take into account the reorganization of electrons after ionization, while Koopmans' theorem (ionization energies equal to $-\epsilon$, where ϵ is the orbital energy) assumes no electronic relaxation. The difference between these two calculated values is the relaxation energy

$$R(\text{calcd}) = -\epsilon - I(\text{calcd}) \qquad (6)$$

and for shifts

$$\Delta R(\text{calcd}) = \Delta(-\epsilon) - \Delta I(\text{calcd})$$

Comparison with eq 1 shows that

$$\Delta V(\text{calcd}) = \Delta(-\epsilon)$$

As shown by Bagus and Schaefer,[35] a large improvement in the ionization energy is obtained when the symmetry restriction

(30) The MOLECULE-ALCHEMY program package incorporates the MOLECULE integrals program written by J. Almlöf and the ALCHEMY programs written by P. Bagus, B. Lin, M. Yoshimine, and D. MacLean and modified by P. Bagus and U. Wahlgren.
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Figure 3. Calculated ionization energy and ground-state potential energy shifts, ΔI and ΔV, plotted against the corresponding experimental values. The line represents a 1:1 relationship.

for the homonuclear X_2 molecules is relaxed and the core holes are localized. This localization introduces some formal difficulties since the solution to the hamiltonian should be symmetry adapted, but it can be shown that using only a hole-left or hole-right wave function is usually a good approximation for core-hole states (for further discussion see ref 36).

Table IV shows the calculated core-ionization energies that correspond to the measured values in Table I. The calculated *absolute* values are only in fair agreement with the experimental results. The discrepancies may arise from inadequate treatment of correlation energies, an insufficiently flexible basis set, and, for the heavy elements, neglect of relativistic effects. We believe, however, that despite the numerical disagreement with absolute experimental values, the calculated energy shifts should be well described because of partial cancellation of the various effects just mentioned. The total relaxation energy in Table IV is seen to increase with the magnitude of the core-ionization energy and shows that the dominant term is atomic relaxation.

The calculated and experimental shifts are compared in Table II and in Figure 3, where the calculated values of ΔV and ΔI are plotted against the corresponding experimental values. (We have omitted the points for ΔR, since these are simply related to those for ΔI and ΔV.) The data fall along the line representing a 1:1 relationship, except for the points for $(HF-F_2)$. This generally excellent agreement supports the model used for deriving values of ΔV and ΔR from experimental energies. Although similar comparisons[9] have been made between experimental and theoretical values of ΔV and ΔR, the latter have been based on semiempirical theory. This is the first systematic comparison with ab initio calculations.

The largest deviations between theory and experiment are for the $(HF-F_2)$ difference. The discrepancy is particularly noticeable for the value of ΔV. This problem may arise either from the theoretical calculations or from deficiencies in the relaxation model. It is well-known that the molecular properties of F_2 are difficult to calculate, and both a large basis set and extensive CI calculations are necessary to describe the molecule.[37] It is possible that the exclusion of correlation energy together with a limited basis set is inadequate for a satisfactory description of the fluorine-containing molecules. The value of ΔI for $(ClF-F_2)$ is better described by the theory than the corresponding values for either $(ClF-HF)$ or $(HF-F_2)$, suggesting that the effect is different for

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Table V. Transfer of Electrons from the Surroundings to the Valence Shell upon Core Ionization (dq/dN) and an Estimate of the Second Order Correction to the Relaxation Energy ($\Delta R(corr)$)

molecule	dq/dN	$\Delta dq/dN$	$\Delta R(corr)^a$ (eV)
F_2	0.62	0.0	0.0
HF	0.26	−0.36	1.39
Cl*F*	0.50	−0.12	0.46
Cl_2	0.45	0.0	0.0
HCl	0.25	−0.20	0.34
C*l*F	0.34	−0.11	0.19
Br_2	0.49	0.0	0.0
HBr	0.27	−0.22	0.23
I_2	0.45	0.0	0.0
HI	0.23	−0.22	0.17

$^a \Delta R(corr) = (2/3)\Delta[(dk/dN)(dq/dN)]$.

HF than for the other two species.

Turning to possible problems with the relaxation model, we note that the fluorine Auger energies are those for population of the $2s^{2-}$ hole state in fluorine. This state is not strictly a core state as required by the model. However, results obtained by Weightman, Thomas, and Jennison[15] indicate that this double-hole state is well localized in F_2 and, therefore, that the model is applicable.

The large value of ΔR for (HF–F_2) suggests that there is a larger transfer of charge toward the ionized atom in F_2 than in HF. In this case, we must consider higher order corrections to the model. Thomas[10] has derived a second-order correction to eq 3. A more correct ΔR value is given by

$$\Delta R = \Delta\alpha/2 + (2/3)\Delta[(dk/dN)(dq/dN)] \qquad (7)$$

where k is the change in core-ionization energy per unit charge removed from the valence shell, N the number of core electrons in the atom to be ionized, and dq/dN the transfer of electrons from the surroundings to the valence shell upon core ionization. The derivative dk/dN is negative, and if more electrons are transferred toward the ionized atom for F_2 than for HF, $\Delta dq/dN$ is also negative and a positive correction term should be added to the negative value for $\Delta R(exptl)$ in Table II. This will make $\Delta R(exptl)$ closer to the theoretical value.

A quantitative analysis of eq 7 is prevented by the uncertainty of estimating dk/dN and dq/dN. However, if we use dk/dN

values derived from Slater orbitals and $\Delta dq/dN$ from the population analysis, an estimate of the correction terms in eq 7 may be obtained. Table V shows that relative to X_2 $\Delta dq/dN$ is negative for all molecules. However, the larger value for HF combined with a large fluorine value for dk/dN make the correction 4 to 8 times larger for this molecule than for the other HX molecules. The calculated corrections are probably overestimated in this analysis, but the results suggest that the second-order correction term is more important for HF than for the other molecules. A reduction of $\Delta R(exptl)$ to the ab initio value for HF would lower $\Delta V(exptl)$ and the fluorine charge by about 10%. The trend and correlation in Figures 1 and 2, however, will not be changed significantly. The corrections for Cl and higher elements are less important since both dk/dN and $\Delta dq/dN$ are smaller for these elements.

Conclusion

The charge distribution in hydrogen halides and chlorine fluoride has been determined experimentally from the relative electrostatic potential at the halogen atom by use of a point-charge model. The potentials are obtained from combined measurements of core-ionization energies and Auger kinetic energies. The derived atomic charges are consistent with chemical experience and are linearly related to the electronegativity of the atoms.

The experimental results are verified by ab initio calculations with the standard Hartree–Fock method. The excellent agreement between experimental and theoretical results supports the validity of the model and gives confidence that it can be applied to other molecules.

The largest deviations between theory and experiment are found for the (HF–F_2) shifts in initial-state potential and relaxation energy. This discrepancy is probably due to a second-order relaxation effect, which is related to large differences in electron transfer upon ionization.

The Intrinsic Reaction Coordinate and the Rotational Barrier in Silaethylene

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Abstract: The intrinsic reaction coordinate (IRC) is a minimum-energy pathway connecting reactants to products via the transition state. An improved algorithm for the determination of an IRC is presented. The method is illustrated for the rotation of the silicon–carbon double bond in silaethylene. This IRC shows all coordinates vary smoothly during the rotation from the planar to twisted structures, except for a slight pyramidalization at carbon. The rotational barrier is found to be about 37 kcal/mol, in good agreement with experimental estimates.

The most promising approach for the extension of chemical dynamics past triatomic systems appears to be a reaction path methodology.[2] Such an approach transforms the large number of nuclear coordinates needed to specify the geometry of a

polyatomic system to a unique coordinate, the distance along a reaction path connecting reactants to products via one or more transition states and possibly stable intermediates. The remaining coordinates are chosen to be orthogonal to the reaction coordinate