Table III. Dimer Properties

$(LiF)_2$	LiF	$(NaH)_2$	NaH
	Orbital Energies		
−26.1535	−26.1004	−40.4645	−40.4923
−26.1535	−2.4384	−40.4645	−2.7732
−2.3993	−1.3621	−2.7455	−1.5215
−2.3960	−0.4844	−2.7453	−1.5215
−1.4231	−0.4617	−1.4968	−1.5208
−1.4189	−0.4617	−1.4951	−0.2715
−0.5581		−1.4947	
−0.5368		−1.4940	
−0.5286		−1.4936	
−0.5271		−1.4934	
−0.5128		−0.3216	
−0.5100		−0.2742	
	Atomic Populations		
Li 2.220		Na 10.355	
F 9.780		H 1.645	
	Quadrupole Moments[a] (Buckinghams)		
$\theta_{xx} = 13.39$		$\theta_{xx} = 21.28$	
$\theta_{zz} = 0.76$		$\theta_{zz} = -0.19$	

[a] Molecule in xy plane, metal along x axis.

clude three calculations[9,15,16] of varying degrees of sophistication. The simplest calculation,[9] which includes only ionic and repulsion terms, appears to come closest to our calculations and experiment, with a $\Delta E = -57.6$ kcal/mol, $r(\text{Li}\cdots\text{Li}) = 2.26$ Å, and $r(\text{F}\cdots\text{F}) = 2.50$ Å. When one includes polarizability and dispersion terms,[15,16] the agreement is somewhat less satisfactory, although the "second approximation" of ref 16 gives reasonable values for ΔE (-57.0 kcal/mol), $r(\text{Li}\cdots\text{Li}) = 1.83$ Å, and $r(\text{F}\cdots\text{F}) = 2.74$ Å.

The calculated orbital energies, atomic populations, and quadrupole moment components for the cyclic dimers of LiF and NaH are presented in Table III. The properties of $(NaH)_2$ are similar to those of $(LiH)_2$:[3] all of its orbital energies are raised relative to those of the monomer NaH; the metal loses 0.17 electron on dimerization (0.07 lost by Li in $(LiH)_2$); and it has a very large quadrupole moment ($\theta_{xx} = 21.3$ *vs.* 18.6 for $(LiH)_2$). In $(LiF)_2$, the orbital energies (with the exception of the one at −2.4 au) are lowered relative to the monomer, the atomic populations are almost the same as in the monomer, and the quadrupole moment is somewhat smaller than the hydrides. The LiF monomer is much more ionic than the hydrides to begin with, so one can understand the lack of atomic population change upon dimerization by noting that Li has very little further electron charge to dispense. The smaller quadrupole moment for $(LiF)_2$ is partially due to the fact that it is a more compact structure and also to the fact that the fluoride probably holds its charge more tightly than the hydride.

Conclusions

The calculated and experimental energies for the LiF dimer are in good agreement; thus, the predicted structure of $(LiF)_2$ and the predicted structure and relative energetics of LiH and NaH dimerization are "targets" for further experimental work, perhaps employing supersonic nozzle beams.[17]

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(15) T. Berkowitz, *J. Chem. Phys.*, **29**, 1386 (1958).

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X-Ray Photoelectron Spectroscopy of Chlorine Trifluoride, Sulfur Tetrafluoride, and Phosphorus Pentafluoride

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Abstract: The fluorine 1s binding energies for ClF_3, SF_4, and PF_5 have been measured. For equatorial fluorines the values found are 694.76 (4), 695.26 (2), and 695.3 (1) eV, respectively, and for axial fluorines they are 692.22 (3), 692.88 (2), and 694.1 (1) eV, respectively. The inequivalence of the equatorial and axial fluorines is clearly seen and is more pronounced for ClF_3 and SF_4 than for PF_5. The consistently lower binding energies of the axial fluorines are consistent with the idea that these fluorines are bonded to the central atom with partially ionic, three-center bonds. The data are analyzed with a point-charge model to assign charges to the individual fluorine atoms. The results of this analysis are also in accord with the idea of three-center bonding. Comparison is made with results of molecular orbital calculations. The equivalent cores approximation is used to develop a further understanding of the binding-energy shifts, and the relationship between the point-charge analysis and the equivalent cores analysis is discussed.

The central atoms of the molecules PF_5, SF_4, and ClF_3 display higher coordination numbers than do their congeners N, O, and F and each has higher coordination than is required to supply a complete octet of electrons. Structural analyses have shown that each has a trigonal bipyramid structure if the lone pairs of the central atom are included in the structure.[1] The trigonal bipyramid structure is unusual in that the ligand positions are not all equivalent; PF_5, for ex-

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(1) PF_5: K. W. Hausen and L. S. Bartell, *Inorg. Chem.*, **4**, 1775 (1965); SF_4: V. C. Ewing and L. E. Sutton, *Trans. Faraday Soc.*, **59**, 1241 (1963); ClF_3: D. F. Smith, *J. Chem. Phys.*, 21, 609 (1953).

ample, has two "axial" fluorines lying on either side of, and along a line normal to, the plane defined by the central atom and the three equatorial fluorines. A great deal of experimental evidence shows that the axial bonds in PF$_3$ are longer and weaker than are the equatorial bonds.[2] Similarly, in SF$_4$ and ClF$_3$, considerations of ligand arrangement, bond strength, and bond length allow us to assign the various ligands as axial or equatorial. Distortions in the SF$_4$ and ClF$_3$ structures may be ascribed to electron pair repulsions.

A proper model for the chemical bonding in these molecules must account for the appearance of hypercoordinated compounds with second row but not with first row central atoms and for the ligand inequivalence. Most descriptions of chemical bonding in these molecules have followed either the three-center bond model[3] or the sp^3 d hybridization model. Both models account for the greater stabilizing effect of fluorine relative to other ligands and the fact that the axial bonds are longer than the equatorial bonds. Both predict that the axial ligands should be more negatively charged than equatorial ones.

A great deal of experimental evidence indicates that pentacoordinated structures are unstable with respect to large amplitude vibrations.[4,5] In particular, nmr spectra of PF$_5$ indicate that, above −197°, all fluorines appear equivalent and hence are rapidly exchanging on an nmr time scale.[5] This ease of exchange may be explained by calculations showing that the trigonal bipyramid and square pyramid configurations lie very close to each other in energy,[6] and Berry has proposed an intramolecular exchange mechanism in which the trigonal bipyramid passes through a square pyramid intermediate.[7]

The interpretation of nmr experiments on SF$_4$ and ClF$_3$ is not so clear. Early measurements[8] indicated that exchange of inequivalent fluorines takes place but at much higher temperatures than for PF$_5$. Recent work by Janzen, *et al.*,[9] indicates that fluorine exchange observed in earlier experiments may have been due to reactions with impurities and sets a higher temperature for onset of rapid exchange in SF$_4$. It is not clear, however, that fluorine exchange proceeds by an intramolecular mechanism in SF$_4$ and ClF$_3$. Both are associated in the liquid phase and evidence for dimer formation in rare gas matrices has been found.[10] One can, at least, assert with confidence that the barrier to intramolecular fluorine exchange in SF$_4$ and ClF$_3$ is significantly higher than that in PF$_5$.

X-Ray photoionization takes place on a time scale that is very fast relative to the processes discussed above. Hence we expect that a measurement of the binding energies of fluorine core electrons will yield information about the degree of inequivalence of the ligands in PF$_5$, SF$_4$, and ClF$_3$ and about the chemical bonding. In the following sections, measurements of the fluorine 1s binding energies in these molecules are reported and discussed in terms of recent molecular orbital calculations and two models that have been developed for the interpretation of molecular core electron binding energies: the equivalent cores thermochemical model[11] and the point-charge model.[12–14]

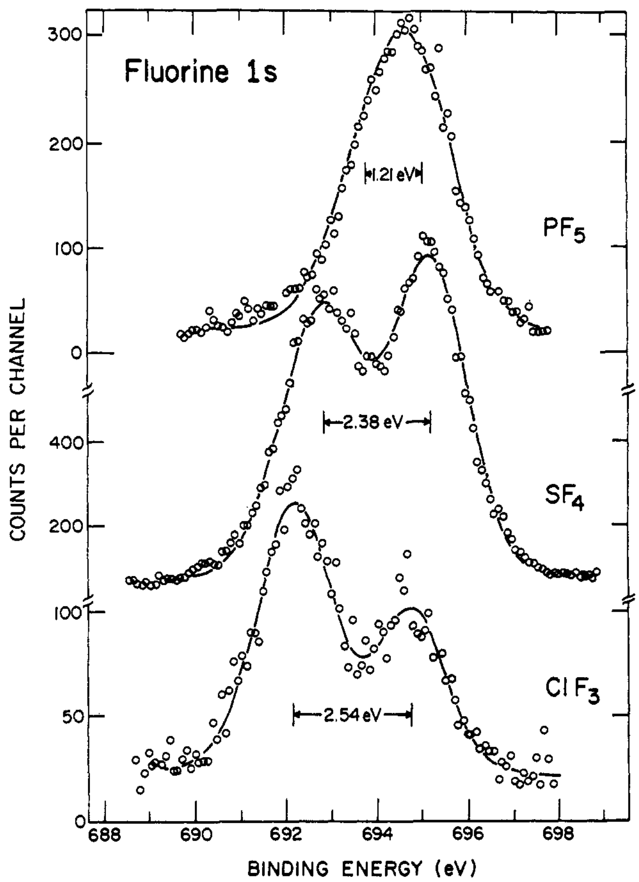

Figure 1. Photoelectron spectra of fluorine 1s electrons in PF$_5$, SF$_4$, and ClF$_3$. Exciting radiation is Al Kα_{12}. The solid curves are least-squares fits to the data.

Results

A previous publication[15] has described the experimental procedure. Several spectra were taken for each molecule. In all cases, background spectra were monitored in the area where contaminants, if any, would appear. No evidence for contamination was found.

The photoelectron spectra for the fluorine 1s electrons in PF$_5$, SF$_4$, and ClF$_3$ are shown in Figure 1. Unconstrained two-Gaussian least-squares fits were

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(2) K. Ramaswamy and B. Rao, *Z. Phys. Chem.* (*Leipzig*), 242, 18 (1969); P. C. Van der Voorn and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 3255 (1966).

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(15) R. W. Shaw, T. X. Carroll, and T. D. Thomas, *J. Amer. Chem. Soc.*, **95**, 2033 (1973).

Table I. Fluorine 1s Binding Energies in ClF_3, SF_4, and PF_5

	Binding energy, eV		Line width, eV			Area ratio,
	F_{eq}	F_{ax}	F_{eq}	F_{ax}	Splitting, eV	F_{eq}/F_{ax}
ClF_3	694.76 (4)	692.22 (3)	1.74 (8)	2.00 (5)	2.54 (5)	1.98 (15)
SF_4	695.26 (2)	692.88 (2)	1.87 (3)	2.15 (4)	2.38 (3)	0.99 (3)
PF_5	695.3 (1)	694.1 (1)			1.2 (1)	

possible for SF_4 and ClF_3; for the PF_5 spectrum we constrained the widths to be equal to 2.0 eV and the area ratio to be 2:3, corresponding to the numbers of axial and equatorial fluorines. Although the inequivalence of the fluorines in PF_5 is not readily apparent, careful inspection of the spectrum reveals that the peak is skewed to the left and significantly broader than related compounds. The full width at half maximum of the PF_5 photoelectron peak is 2.53 eV, whereas that of SF_6, in which all fluorines are equivalent, is 2.01 eV. For the individual peaks of SF_4 and ClF_3 the average width is 1.93 eV.

The absolute binding energies were determined with respect to the KLL $^1D_2$ auger energy of neon, which was measured simultaneously with each fluorine compound. A self-consistent analysis[16] of neon auger and photoelectron energies yields the values 804.57 (4) eV and 1486.58 (3) eV for the neon auger calibration line and the Al $K\alpha_{1,2}$ exciting X-ray, respectively. The resulting values for the binding energies, line widths, splittings, and area ratios of the inequivalent fluorines in ClF_3, SF_4, and PF_5 are given in Table I. The indicated uncertainties are those associated with the fitting procedure; the remaining uncertainties in the absolute values are due to errors in the calibration energies given above. It is not possible to assign the fluorine peaks in SF_4 unambiguously. We choose, on an empirical basis, to follow the behavior in PF_5 and ClF_3 where the lower binding energy peak is due to the axial fluorine ligands.

Absolute binding energies of the central atom core and the core levels in SF_6 were also measured. For the sake of completeness we report all these numbers here, but restrict the discussion to the fluorine 1s shifts. The binding energies are: Cl(2s) in ClF_3, 284.04 (9); S(2p) in SF_4, 178.2 (1); P(2s) in PF_5, 145.94 (9); S(2p) in SF_6, 181.0 (1); and F(1s) in SF_6, 695.04 (2) eV. The spin-orbit splittings of the sulfur 2p lines were not resolved but the value for SF_6 does nearly agree with a weighted average (180.8 eV) of the 2p doublet binding energies reported by Siegbahn, *et al.*[14] Our value for the F(1s) binding energy in SF_6 differs more substantially from that reported by Siegbahn, *et al.* (694.6 eV).

According to Table I, the equatorial fluorine 1s binding energies are all within 0.5 eV of each other, the axial fluorine 1s binding energies range over 1.9 eV, and the axial–equatorial splittings in SF_4 and ClF_3 are twice as large as that in PF_5. The spectral lines associated with 1s ionization of axial fluorines are systematically broader than those associated with equatorial fluorines. The correlation between line position and line width is consistent with previously reported chemical effects on core level widths.[17]

Discussion

A. The Point-Charge Model. We may interpret the inequivalence of the 1s binding energies of the inequivalent fluorines in ClF_3, SF_4, and PF_5 in terms of the different valence electron densities in the neighborhood of the fluorine atomic centers. The core electrons of a given atom become less bound as the local valence electron density increases; hence the measurement of chemical shifts in binding energies provides an experimental valence electron population analysis.

In developing a quantitative relationship between the core electron binding energies and valence electron densities it is important to distinguish between the ionization potential of the core electron (the measured quantity) and the orbital energy of that electron. It is the orbital energy that reflects the distribution of valence electrons. Were Koopmans' theorem valid, the orbital energy and the ionization potential would be identical; in fact, the former is greater than the latter by an amount known as a relaxation energy. In order to infer orbital-energy shifts (and hence charge distributions) from measured ionization potentials, it is necessary to assume that relaxation energies for the atom of interest are the same in different chemical environments or, at least, that changes in relaxation energy are small compared with changes in the ionization potential. There is evidence that this assumption is a good one, provided that we make comparisons between similar compounds.[18]

The point-charge model is conceptually and computationally simple and has been successful in interpreting core-electron ionization energy shifts in structurally related families of molecules. One uses a model of the molecule in which the charge associated with each atomic center in the molecule is taken to be spherically distributed about the centers. Thus the effect on a core-electron binding energy due to the presence of a valence electron on the the same atom is equal to $e^2\langle 1/r\rangle$, where $\langle 1/r\rangle$ is the expectation value of $1/r$ for the valence electron. The effect due to an electron on a different atom is e^2/R, where R is the internuclear separation. The expression for the core-electron binding energy for atom A in a given molecule relative to the binding energy of A in a purely covalently bonded molecule (all atomic charges zero) is

$$\Delta BE_A = q_A e^2\langle 1/r\rangle + \sum_{B\neq A}\frac{q_B e^2}{R_{AB}} \qquad (1)$$

where ΔBE_A is the binding-energy shift, the q's are the atomic charges in the molecule, and the R_{AB}'s are the distances between nuclei.[19] The radial expecta-

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(16) R. W. Shaw and T. D. Thomas, unpublished results.

(17) R. W. Shaw and T. D. Thomas, *Phys. Rev. Lett.*, **29**, 689 (1972); R. M. Friedman, J. Hudis, and M. L. Perlman, *ibid.*, **29**, 692 (1972).

(18) D. W. Davis, J. M. Hollander, D. A. Shirley, and T. D. Thomas, *J. Chem. Phys.*, **52**, 3295 (1970); T. D. Thomas, *J. Amer. Chem. Soc.*, **92**, 4184 (1970).

(19) The expression as written does not take into account that the valence radius may be different in the molecule of interest from what it is in the reference species. Important corrections may result from this neglect.

tion values may be taken from atomic structure calculations.[20] Alternatively, one may write eq 1 as

$$\Delta \mathrm{BE_A} = k_\mathrm{A} q_\mathrm{A} + \sum_{\mathrm{B} \neq \mathrm{A}} \frac{q_\mathrm{B} e^2}{R_\mathrm{AB}} \qquad (2)$$

and treat k_A as an empirically derived parameter equal to the change in core-electron binding energy upon removal of a valence electron ($\mathrm{d}E/\mathrm{d}q$). For a given molecule there is a binding-energy shift equation for each distinguishable atomic center and the equation expressing charge conservation which is $\Sigma_\mathrm{B} q_\mathrm{B} = 0$.

Neither eq 1 nor eq 2 explicitly includes a correction for relaxation energy. It has been shown,[13] however, that if one follows the model by Snyder[21] for electronic relaxation, in which the energy of relaxation depends linearly on valence population density, then the correction for relaxation appears implicitly in the k_A parameter in eq 2.

With this model we have calculated the atomic charges for ClF_3, SF_4, and PF_5 using the values of the fluorine 1s binding energies relative to that for fluorine in F_2. The k parameter for fluorine was taken to be 32.5 eV/e; this value is the same as that used by Davis, *et al.*, in an analysis of fluorine binding-energy shifts in the fluorobenzenes[12] and is very nearly equal to a value derived from a self-consistent analysis of the xenon fluorides.[22] It is also approximately equal to the expectation value for $\langle 1/r \rangle$ calculated for valence electrons on fluorine, but is substantially larger than $\mathrm{d}E/\mathrm{d}q$ for free fluorine atoms (15 to 20 eV/e). The atomic charges are given in Table II, along with the results of a similar analysis for the related molecules SF_6 and ClF, and are compared in this table with values derived from theoretical calculations and other kinds of measurements.

Table II. Fluorine Atomic Charges

	This work	MO calculations		Nmr[b]	Molecular Zeeman effect[c]
		a	*b*		
ClF_3	−0.236	−0.42	−0.45	−0.40	
	−0.135	−0.13	−0.37	−0.58	
SF_4	−0.230	−0.430	−0.43	−0.51	−0.33
	−0.141	−0.216	−0.36	−0.45	+0.1
PF_5	−0.21		−0.36	−0.71	
	−0.17		−0.30		
ClF	−0.090	−0.24		−1.22	
SF_6	−0.201		−0.39	−0.53	

[a] References 23 and 24. [b] Reference 25. [c] Reference 26.

In Table II we see that the axial fluorine charges in ClF_3, SF_4, and PF_5 are significantly greater than equatorial fluorine charges. This result agrees with molecular orbital calculations,[23–25] with interpretations of nmr chemical shifts[25] (with an exception noted below) and molecular Zeeman effect information.[26] The magnitudes of the charges we have derived are, however, significantly smaller than those obtained by the other methods.

The detailed behavior of the fluorine charges from the point-charge analysis follows the model suggested by Rundle for highly coordinated molecules.[3] According to this model the equatorial ligands in these pentacoordinated species are bound by two-center, two-electron bonds and the axial ligands by three-center, four-electron bonds. In Table II we see that equatorial fluorine charges increase with decreasing electronegativity of the central atom, as would be expected for two-electron, two-center bonds. The change in axial fluorine charge in the sequence PF_5, SF_4, ClF_3 is not so great as that of the equatorial fluorine charges. This suggests that the PF_3, SF_2, and ClF fragments, in which the bonds are all two-center, two-electron bonds, appear to the axial fluorines as pseudo-argon centers; hence the axial fluorines bond to these centers with nearly the same redistribution of charge. The situation here is apparently similar to that in the xenon fluorides, where the fluorines are believed to be bonded to the octet center by three-center, four-electron bonds.[22] Molecular orbital calculations by Collins[23] indicate that SF_4 resembles a rare gas difluoride.

The fluorine charge on SF_6 is intermediate between the fluorine charges on SF_4; this result agrees with the idea that the equivalent bonds in SF_6 are resonance superpositions of three-center and two-center bonds. Similarly the electron-pair bond in ClF is closely related to the electron-pair equatorial bond in ClF_3; and the charge on the equatorial F in ClF_3 lies much closer to that in ClF than to the axial fluorine charges.

According to the point-charge analysis, the axial–equatorial charge difference in PF_5 is significantly less than that in SF_4 and ClF_3. We may, therefore, infer that the axial and equatorial fluorines in PF_5 are more nearly equivalent to each other than are those in SF_4 and ClF_3 and that conditions for intramolecular fluorine exchange are most favorable in PF_5.

Comparison in Table II of the charges derived by various methods shows that the point-charge model yields charges of rather small absolute value. The results from nmr chemical shifts were calculated using the approximate method of Karplus and Das;[27] according to this method the equatorial fluorines in ClF_3 are found to be more negative than the axial fluorines; this is a serious disagreement with all other entries in the table.

Although the point-charge model yields charges that are qualitatively consistent with those obtained by other quantitative methods and with expectations from other kinds of chemical evidence, there remains some question about the absolute value of the charges. We see here that the derived charges are distinctly smaller than those obtained by other methods; a similar effect is seen in the point-charge analysis of the xenon–fluoride binding-energy shifts.[22] Neglected in the point-charge analysis are contributions from asymmetric distribution of charge around the various atoms and from overlap population in the bonds. It remains to be seen how important these effects are.

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(27) M. Karplus and T. P. Das, *J. Chem. Phys.*, **34**, 1683 (1961).

B. Molecular Orbital Calculations. Recent calculations on the molecules of interest here were carried out by Brown and Peel,[25] Collins,[23] and Breeze, Cruickshank, and Armstrong.[24] Atomic charges from these calculations are given in Table II. The molecular orbital calculations by Brown and Peel were self-consistent for the valence electrons and used the approximation of neglect of diatomic differential overlap (NDDO). Collins and Breeze, *et al.*, carried out *ab initio* SCF–MO calculations with augmented basis sets using best atom exponents of Clementi and Raimondi. It is interesting that the considerably more complete *ab initio* calculations lead to a greater charge difference between the inequivalent fluorines in a molecule than do the NDDO calculations; the greater charge difference occurs, in part, because of a greater concentration of central atom 3s orbital in the equatorial bonds. The behavior of the *ab initio* calculations follows, in general, that of the simple model by Rundle,[3] in which the central atom contributes a 2p orbital to the three-center axial bonds and sp^2 hybrid orbitals to the two-center equatorial bonds.

The calculated orbital energy differences for the 1s electrons of the inequivalent fluorines are (in Koopmans' approximation) 3.67 and 2.45 eV for ClF_3 and SF_4, respectively. We may compare these to our experimental binding-energy differences of 2.51 and 2.39 eV. Collins and Breeze, *et al.*, conclude that the role of 3d orbitals is to provide polarizing character to the electron distribution in SF_4 and ClF_3, but that the essential bonding character of these molecules may be understood in terms of s and p orbitals alone. This agrees with the analysis by Coulson,[28] who calculated that sulfur requires the coordination of six fluorines around it to sufficiently stabilize the 3d orbitals to contribute to bonding structure in a major way. Collins and Breeze, *et al.*, have constructed electron density maps for the molecular orbitals of SF_4 and ClF_3, respectively. In both cases molecular orbitals can be identified with the strongly bonding two-electron equatorial bonds and the somewhat weaker bonding and nonbonding orbitals of the four-electron, three-center axial bonds.

C. The Equivalent Cores Model. Jolly has proposed a model for the interpretation of the relative binding energies of core electrons for a given atom in different molecular environments.[11] According to the model one can replace the core (nucleus and inner shells) of an atom with an inner shell electron vacancy by the core of the atom of next higher atomic number. The approximations and areas of expected validity for this model will be discussed elsewhere.[29] We believe that the model should work very well for the cases of interest here (molecules with inequivalent fluorines attached to the same central atom), and we believe that this is the first such application of this model.

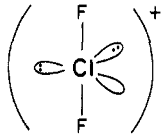
To apply the equivalent cores model to the relative core-electron binding energies of the inequivalent fluorines in ClF_3, we write

$$\Delta E(\mathrm{ClF_{3ax}} - \mathrm{ClF_{3eq}}) = \mathrm{ClF_3} + \mathrm{ClF_{3(eq)}}^{*+} \longrightarrow \mathrm{ClF_{3(ax)}}^{*+} + \mathrm{ClF_3} \qquad (3)$$

where ΔE is the 1s binding energy of the axial fluorine minus that of the equatorial fluorine, and $ClF_{3(eq)}{}^{*+}$ represents a ClF_3 with a 1s vacancy at the equatorial fluorine atomic center. (The chemical reaction to the right of the equals sign is to represent the energy change for that reaction.) Cancellation and the equivalent cores approximation yields

$$\Delta E = (\mathrm{F_2ClNe_{eq}})^+ \longrightarrow (\mathrm{F_2ClNe_{ax}})^+ \qquad (4)$$

where in $F_2ClNe_{eq}{}^+$ a neon core has replaced the core-ionized fluorine at the equatorial position. We now assume, following Jolly, that the heats of formation of neon cationic adducts are equal. We believe this to be a good approximation in this case—binding of neon to various sites on the same molecular ion. Departure of the neon from an equatorial site and an axial site on the ClF_2Ne^+ molecular ion leaves the remaining ion fragment in the configurations **1** and **2**, respectively.



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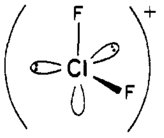

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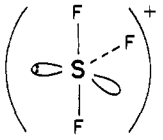
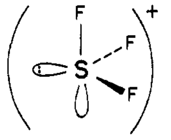
From Table I we find that the difference in energy between **1** and **2** is 2.5 eV with **2** more stable than **1**. The greater stability of the $ClF_2{}^+$ species with a F–Cl–F angle of 90° agrees with measurements of the isoelectronic molecule SF_2, which has a ground state F–S–F angle of 98.2°[30] and measurements of $ClF_2{}^+$ cations in crystals for which the F–Cl–F angle has been determined to be 95.9 and 103.2°.[31] This striking result indicates that information about the energetics of gross molecular structure may be inferred from core-electron binding energies.

A similar analysis for SF_4 leads to an energy difference between configurations **3** and **4** of 2.4 eV with **4** the



3



4

more stable. Again, the greater stability of configuration **4** follows the observed ground state structure of the isoelectronic molecule PF_3 which has F–P–F angles of 97.8°[32] and measurements of the $SF_3{}^+$ cation which has a F–S–F angle of 97.5°.[33] Using measured force constants for PF_3 we have estimated the energy difference between the two configurations **3** and **4** to be greater than 1 eV, in order of magnitude agreement with our calculated value of 2.4 eV.

For PF_5 we find that configuration **6** is more stable than **5** by 1.2 eV. It is well known that phosphorus tetrahalide cations are tetrahedral, and we may infer from our results that configuration **6** is more closely related to tetrahedral symmetry than is **5**.

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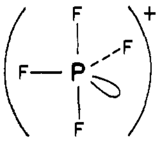

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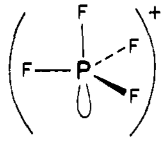

6

On the surface the two analyses, atomic charge and equivalent cores, appear to be quite different. Using the former, we conclude that the difference in core-electron binding energies for the inequivalent fluorines arises from different charge distributions in the vicinity of the fluorines. From the latter, we conclude that the different binding energies reflect different molecular configurations. On the one hand, it appears that we are concerned with electronic distribution, on the other, with the positions of the nuclei.

This apparent difference of the two approaches is, however, only superficial. The energies of the different molecular configurations are closely tied to the electron distributions; this idea has been developed extensively in Walsh's rules[34] and by later theoretical discussions of Walsh's rules.[35] For instance, if we consider the two configurations of ClF_2^+ shown above, we recognize that the linear structure must have a three-center, four-electron bond, for a bond order of 1. The bent structure, however, can have two electron-pair bonds, for a bond order of 2, and is thus the more stable structure. A similar situation exists for the other two molecules. In each case, the residual structure with both axial fluorines can rearrange to a different structure with conversion of three-center bonds to lower energy two-center bonds. We see, then, that there is a very direct connection between the shape of the molecule and the electron distribution and hence between thermochemical quantities and the charge distribution.

Summary

The inequivalence of the fluorines in the compounds ClF_3, SF_4, and PF_5 is demonstrated by the fluorine 1s photoelectron spectra. This inequivalence is not seen in room temperature nmr experiments. The difference between the results of the two different techniques is presumably attributable to the characteristic time scale of the measurements, relatively slow for nmr and relatively fast for photoelectron spectroscopy. The splitting between the peaks due to the inequivalent fluorines correlates with the ease of exchange of fluorines as determined by nmr. The splitting is larger for ClF_3 and SF_4 and smaller for PF_5, just as the slower fluorine exchange is for ClF_3 and SF_4 and the faster for PF_5.

The lower binding-energy electrons for ClF_3 and PF_5 (and presumably SF_4, for which the assignment is ambiguous) are associated with the axial fluorines. This result is in agreement with the idea that the equatorial bonds are two-center, electron-pair bonds and that the axial bonds are more ionic, three-center bonds. A more detailed analysis of the charges on the fluorines bears out this conclusion.

With the equivalent cores approximation, we have seen that the binding-energy shifts can be understood in terms of the energy of the different configurations of cations of the type ClF_2^+, SF_3^+, and PF_4^+ that are left after the departure of the core-ionized atom. The energies derived from the analysis are qualitatively consistent with expectations for the shapes of these fragments. In particular, we note that fragments with approximately 180° bond angles for the F–A–F angle are at a higher energy than those with approximately 90° angles, the difference being due to the more favorable bonding possible in the bent configuration.

The two models used to analyze the data, point charge and equivalent cores, are closely connected with one another even though one depends on the distribution of valence electrons in the molecule and the other on the energies of different configurations of the nuclei. The relationship is that the energies of the different molecular shapes are determined to a large extent by the distribution of electrons in the molecule.

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