Reinterpretation of the Lengths of Bonds to Fluorine in Terms of an Almost Ionic Model

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We have calculated the electron density distributions, electron densities at the bond critical point, and atomic charges in the period 2 and 3 fluorides and a number of their cations and anions. On the basis of this information and an analysis of X−F bond lengths, we have examined the factors that determine the lengths of these bonds. We have shown that all the molecules except NF_3, OF_2, and F_2 have considerable ionic character. The bond lengths of the fluorides reach a minimum value at BF_3 in period 2 and at SiF_4 in period 3 when the product of the charges on the central atom and a fluorine reaches a maximum, consistent with a predominately ionic model for these fluorides. The length of a given A−F bond decreases with decreasing coordination number, and we show that it is determined primarily by packing considerations. This provides an alternative to the previously proposed back-bonding model explanation, for which our work provides no convincing evidence. There is also no evidence to support the Schomaker−Stevenson equation which has been widely used to correct A−F bond lengths calculated from the sum of the covalent radii of A and F for the difference in the electronegativities of A and F. We propose a new value for the covalent radius of fluorine and point out the limitations of its use.

Introduction

On the basis of a detailed analysis of A−F bond lengths and an analysis of calculated electron density distributions in a variety of AF_n molecules and ions, we have investigated the factors that determine the lengths of X−F bonds.

It is common practice to deduce information about the nature of bonds, particularly their multiple bond character, from their lengths by comparing an observed bond length with that calculated from the sum of the appropriate covalent radii. However, for bonds to fluorine and oxygen, this is an unreliable procedure for two reasons. First, almost all bonds to oxygen and fluorine are highly polar because of their large electronegativities, so the validity of using covalent radii to predict the lengths of such bonds is doubtful. Second, there has been considerable uncertainty and disagreement concerning the values to be adopted for the covalent radii of these elements. For most elements, the covalent radius is taken as one-half of the distance between two atoms of the element joined by a single bond, such as the Cl−Cl bond in Cl_2 or the C−C bond in diamond. Covalent radii for doubly bonded and triply bonded atoms can be obtained in a similar way. Bond lengths predicted from these radii agree well with experimental values for many molecules, although there are also many exceptions, for which a variety of explanations have been proposed. In particular, the values given by Schomaker and Stevenson[1] for the covalent radii of nitrogen, oxygen, and fluorine of 74, 74, and 72 ppm, respectively, give predicted bond lengths in almost all other molecules that are much too large. These values were obtained from the experimental data available at that time on the lengths of the N−N bond in N_2H_4, the O−O bond in H_2O_2, and the F−F bond in F_2. The most recent data on these bond lengths[2] lead to the only very slightly different values of 72 pm for nitrogen, 73 pm for oxygen, and 71 pm for fluorine. However, it is widely recognized that the F−F bond in F_2, the O−O bond in H_2O_2, and the N−N bond in N_2H_4 are abnormally weak, as is shown by the following bond energies: F−F, 155; Cl−Cl, 240; O−O, 142; S−S, 260; N−N, 167; and P−P, 201 kJ mol^{-1}.[3] Pitzer suggested some time ago[4] that the abnormal weakness of these bonds can be attributed to lone pair−lone pair and lone pair−bond pair repulsions in the small and crowded valence shells of these elements, and although this explanation has been widely accepted, other explanations have also been proposed. So it is reasonable to conclude that these bonds are also abnormally long and that, therefore, the "normal" covalent radii of oxygen and fluorine cannot be obtained from these bond lengths. Before these bond lengths had been measured experimentally, Pauling[5] had deduced the smaller values of 70, 66, and 64 pm for nitrogen, oxygen, and fluorine, respectively. He appears to have obtained the value for fluorine from the spectroscopically determined interatomic distance in what later turned out to be an excited state of F_2 and the values for nitrogen and oxygen by interpolating between this value and the value of 77 ppm for carbon.[1] When the experimental values for the O−O and F−F bond lengths became available, however, the higher values for the covalent radii obtained from these bond lengths were generally adopted. Some explanation then had to be found for the fact that bond lengths calculated from these radii are almost invariably longer than the experimental values for most X−F and X−O bonds.

Because Pauling had shown that an X−Y bond has a bond energy that is generally larger than the average of the X−X and Y−Y bond energies,[6] it was generally supposed that such polar X−Y bonds would be shorter than predicted by the sum of the covalent radii, which presumably would give the length of a "pure" covalent bond between the two elements. Schomaker and Stevenson,[1] therefore, proposed an empirical equation based on the difference in electronegativitives of the two bonded atoms which they claimed could be used to correct a bond length calculated from covalent radii using the new longer values for

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(1) Schomaker, V.; Stevenson, D. P. *J. Am. Chem. Soc.* **1941**, *63*, 37.

(2) (a) Morino, Y.; Iijima, T.; Murata, Y. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 46. (b) Andrychuk, D. *Can. J. Phys.* **1951**, *29*, 151. (c) Khachkuruzov, G. A.; Przhevalskii, I. N. *Opt. Spectrosc. (USSR)* **1979**, *46*, 1034.

(3) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed.; Harper Collins: New York, 1993.

(4) Pitzer, K. S. *J. Am. Chem. Soc.* **1947**, *70*, 2140.

(5) Pauling, L. *The Nature of the Chemical Bond,* 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 224.

(6) Reference 5, p 80.

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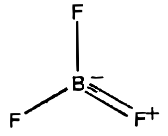
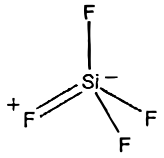
nitrogen, oxygen, and fluorine. Their equation has the form

$$d_{\mathrm{AB}} = r_{\mathrm{A}} + r_{\mathrm{B}} - C|x\mathrm{A} - x\mathrm{B}|$$

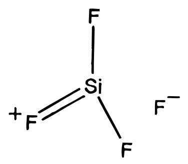
where d_{AB} is the predicted bond length, r_{A} and r_{B} are the covalent radii in picometers, and $|x\mathrm{A} - x\mathrm{B}|$ is the absolute difference in the (Pauling) electronegativities of A and B. Schomaker and Stevenson gave the constant C the value of 9 pm. Subsequently, to achieve a better fit with experimental data, Pauling[7] modified this value to 8 pm for bonds involving one or two period 2 elements and to 6, 4, and 2 pm for bonds formed by an element from periods 3, 4, and 5, respectively, with a more electronegative element. However, most authors still use the equation in its original form. During the following years, a large number of new bond lengths were accurately determined, and many, particularly the lengths of bonds to fluorine and oxygen, were found to be in poor agreement with the values predicted by the Schomaker−Stevenson equation, as has been pointed out previously by Wells[8] and many others.[9] For example, the Si−O bond length is predicted to be 171 pm, whereas the observed length is 163.5 pm in disiloxane[10] and 163 pm in SiO_2.[11] Similarly, the Si−F bond length is predicted to be 169 pm, compared with the observed bond length of 155 pm in SiF_4.[12] Apart from the fact that the Schomaker−Stevenson equation is a purely empirical equation with no quantum mechanical basis, its major weakness is that it is based on covalent radii obtained from the lengths of the bonds in N_2H_4, H_2O_2, and F_2, which have long been recognized as being abnormally long and weak. Thus, an important reason for having to apply significant corrections to predict heteronuclear bond lengths from the sum of covalent radii could simply be that the covalent radii used are too large to be generally applicable. Moreover, the validity of using covalent radii to estimate the lengths of polar bonds between such electronegative elements and other substantially less electronegative elements is clearly doubtful.

Pauling was aware of the inadequacy of the Schomaker−Stevenson equation, but rather than question its validity, he proposed an additional effect, "back-bonding",[13] to account for that part of observed shortening of the lengths of bonds, such as the B−F and Si−F bonds, that was not accounted for by the Schomaker−Stevenson equation. In this model, it is supposed that fluorine donates electrons into a vacant boron or silicon orbital, giving the bonds a certain amount of double bond character that is described as (p−p)π bonding in the case of BF_3 and related molecules and as (p−d)π bonding in the case of SiF_4 and related molecules. Back-bonding can be approximately represented by resonance structures such as the following:





Despite its very shaky foundation—the inadequacy of the empirical Schomaker−Stevenson equation—this model became widely accepted and is still used today not only to explain the bond lengths but also to explain the otherwise unexpected order of stability of the complexes $BF_3{\cdot}NH_3 < BCl_3{\cdot}NH_3 < BCl_3{\cdot}NH_3 < BBr_3{\cdot}NH_3$.[14] The (p−d)$\pi$ back-bonding model and the nature of the bonding in SiF_4 and related molecules has, however, been the subject of extensive and lengthy discussion and controversy when the results of ab initio calculations were interpreted to show that there is no significant contribution to the bonding from d orbitals on the central atom. This work been reviewed and discussed in some detail by Reed and Schleyer,[15] with particular reference to hypervalent molecules. On the basis of their own ab initio calculations, they conclude that X−O and X−F bonds where X is a period 3 element are partially ionic and that d orbitals are not involved in the σ bonds and play only a secondary role in the π bonding; in other words, there is no significant (p−d)π back-bonding. They proposed, however, that there is π bonding arising from donation of ligand lone pairs into X−F and X−O antibonding orbitals, i.e., from $n \rightarrow \sigma^*$ negative hyperconjugation. The bonding in SiF_4 can then be approximately described in terms of resonance structures, such as



Several other authors have commented on the strongly polar nature of the Si−F bond and have suggested that this might contribute significantly to the apparent bond shortening. For example, in an experimental study of the series of molecules $SiMe_4$, $SiMe_3F$, $SiMe_2F_2$, $SiMeF_3$, and SiF_4, Rempfer et al.[9] found that both Si−C and Si−F bonds decreased in length in this series. They proposed that this decrease in bond length is due to the contraction of the silicon valence shell with increasing charge on Si and that it could not be attributed to (p−d)π bonding, which cannot cause a shortening of the Si−C bonds. In another study, Gronert et al.[16] have shown from ab initio calculations on a series of substituted silanes and the calculation of atomic charges that Si−X bonds are extensively polarized to give significant charge transfers. They conclude that bonds between silicon and highly electronegative elements such as O and F are dominated by ionic interactions.

The foregoing discussion shows that there is clearly a need to re-examine the factors that influence A−F bond lengths. We have, therefore, calculated and analyzed the electron density distribution in a variety of AF_n molecules and ions to obtain more insight into the nature of the bonding and its effect on bond length. In particular, we were interested in determining if there is any evidence for back-bonding or negative hyperconjugation, to what extent polarity affects bond length, and if there are any other factors that influence the bond lengths of fluorides.

In a previous paper, in which we discussed the covalent radius of fluorine,[17] we noted that the lengths of the bonds in AF_n

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(7) Reference 5, p 229.

(8) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, UK, 1984; p 289.

(9) See, for example: Rempfer, B.; Oberhammer, H.; Auner, N. *J. Am. Chem. Soc.* **1986**, *108*, 3893.

(10) Allmenningen, A.; Bastienen, O.; Ewing, V.; Hedberg, K.; Traetteberg, M. *Acta Chem. Scand.* **1963**, *17*, 2455.

(11) Reference 8, p 1006.

(12) Hagen, K.; Hedberg, K. *J. Chem. Phys.* **1973**, *59*, 1549. Beagely, B.; Brown, D. P.; Freeman, J. H. *J. Mol. Struct.* **1973**, *18*, 337.

(13) Reference 5, p 311.

(14) See, for example: Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1984; p 221. Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 173. Shriver, D. E.; Atkins, P. W.; Langford, C. H. *Inorganic Chemistry*; Freeman: New York, 1990; p 335.

(15) Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 1434.

(16) Gronert, S.; Glaser, R.; Streitweiser, A. *J. Am. Chem. Soc.* **1989**, *111*, 3111.

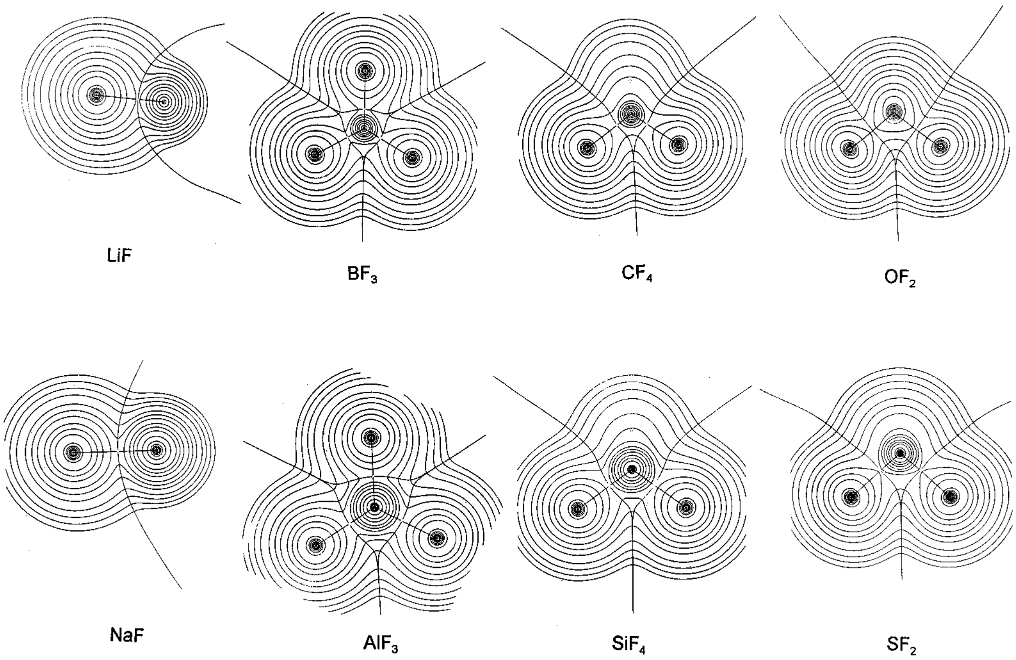

Figure 1. Contour plots of the electron density ρ for some period 2 and 3 fluorides. The contours are in atomic units, with the outermost contour having the value 0.001 and the other contours increasing in value inward, with the values 2×10^n, 4×10^n, 8×10^n, with n having the increasing integral values -3, -2, -1, ... The bond paths connecting the nuclei and the atomic boundaries (intersection of the zero flux surfaces with the molecular plane) are also shown.

molecules in which A has its maximum coordination number of 4 for B, C, and N and 6 for Si, P, S, Cl, Ge, As, and Br are longer than those in period 2 fluorides in which A is only three-coordinated and those in period 3 and 4 fluorides in which A is only four-coordinated. We attributed the shorter bonds in molecules in which the coordination number was less than the maximum value to back-bonding. In this paper, we re-examine this explanation. We also noted in the same paper that A$-$F bonds are longer than expected when the central atom has one or more lone pairs in its valence shell. We attributed this bond lengthening to repulsions between the lone pairs on A and those on F, just as has been proposed to account for the abnormally long bond in F$_2$.

Calculations

We have calculated the wave function and the electron density distribution for each of the following molecules and ions: LiF, BeF$_2$, BF$_3$, CF$_4$, NH$_3$, OF$_2$, F$_2$; NaF, MgF$_2$, AlF$_3$, SiF$_4$, PF$_3$, SF$_2$, ClF; BeF$_3^-$, BeF$_4^{2-}$, BF$_4^-$, CF$_3^+$, NF$_4^+$, AlF$_4^-$, AlF$_6^{3-}$, SiF$_6^{2-}$, PF$_4^+$, PF$_6^-$. The calculations were done using the Gaussian 94 package[18] at the HF/6-311++G(2d,2p) with 6d functions level and at the B3LYP/6-311++G-(2d,2p) level.[19] For CF$_3^+$, calculations were also carried out at the MP2/6-311++G(2d,2p) level. The analysis of the electron density distributions[20] was carried out using the AIMPAC suite of programs.[21]

Results

Contour plots of the electron density distribution obtained from the HF calculations for a selection of the molecules and ions are given in Figure 1. In each case, there is a local maximum at each nucleus. At such a maximum, all three curvatures in the electron density, $\partial^2\rho/\mathrm{d}x^2$, $\partial^2\rho/\mathrm{d}y^2$, and $\partial^2\rho/\mathrm{d}z^2$, are negative. Nuclei that are bonded together are joined by a line called a *bond path*, along which the electron density is larger than that in any direction perpendicular to this line. The point of minimum electron density along a bond path is called the *bond critical point*. This point is a saddle point at which two of the curvatures in the electron density are negative and one is positive. There is a *zero-flux surface* separating each atom from its neighbors.[20] These zero-flux surfaces serve to define the atom in the molecule, and by integrating the electron density over the regions defined by these interatomic surfaces, the *charge* on each atom can be found. In contour maps of the electron density in a plane, such as those in Figure 1, we see lines along which a zero-flux surface cuts the plane.

Calculated and experimental bond lengths and bond angles, atomic charges, electron densities at the bond critical point, and energies for the fluorides are given in Tables 1 and 2 and for the fluorocations and anions in Table 3.

The calculated bond lengths and bond angles agree well with the experimental values, particularly in the case of the B3LYP calculated values. That the agreement with experiment is better for the B3LYP values than for the HF values, particularly for the strongly covalent NF$_3$, OF$_2$, and F$_2$ molecules, is expected as, unlike the HF calculations, the B3LYP calculations take account of electron correlation, which is particularly important in these molecules. In general, the HF calculated bond lengths are slightly smaller than the experimental values, while the B3LYP values are slightly larger. In the case of CF$_3^+$, there is good agreement between the MP2 and the B3LYP values and with the bond lengths calculated by Olah et al.,[22] confirming that the latter are, in general, more reliable than the HF values. The atomic and molecular parameters quoted in the text are the B3LYP values unless otherwise stated.

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(17) Gillespie, R. J.; Robinson, E. A. *Inorg. Chem.* **1992**, *31*, 1960.

(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Oritz, J. V.; Forsman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Gaussian, Inc.: Pittsburgh, PA, 1994.

(19) Becke, A. *J. Phys. Chem.* **1993**, *98*, 5648.

(20) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Clarendon Press: Oxford, UK, 1991.

(21) Biegler-König, F. W.; Bader, R. F. W.; Tang, T.-H. *J. Comput. Chem.* **1982**, *3*, 317.

(22) Olah, G. A.; Rasul, G.; Yudin, A. K.; Burrichter, A.; Surya Prakash, G. K.; Chistyakov, A. L.; Stankevich, I. V.; Akhrem, I. S.; Gambaryan, N. P.; Vol'pin, M. E. *J. Am. Chem. Soc.* **1996**, *118*, 1446.

Table 1. Results of HF Calculations for the Period 2 and 3 Fluorides[a]

molecule	bond length (pm)	bond angle (deg)	ρ_b (au)	$-q$(F)	q(X)	$-E$ (au)
LiF	156.5 (156.4)		0.076	0.941	0.941	106.978 94
BeF_2	136.2 (140)	180	0.150	0.904	1.807	213.760 38
BF_3	129.3 (130.7)	120	0.292	0.859	2.576	323.308
CF_4	129.5 (131.9)	109.5	0.319	0.741	2.964	435.787 77
NF_3	132.0 (136.5)	102.9 (102.3)	0.377	0.362	1.086	352.661 26
OF_2	132.9 (141.8)	103.5 (103.1)	0.371	0.116	0.232	273.550 44
F_2	132.9 (140.5)		0.367	0	0	198.747 55
NaF	192.9 (192.6)		0.052	0.941	0.941	261.356 86
MgF_2	173.5 (177)	180	0.083	0.913	1.826	398.691 03
AlF_3	161.4 (163)	120	0.122	0.882	2.647	540.580 79
SiF_4	154.1 (155.5)	109.5	0.163	0.857	3.418	687.264 51
PF_3	154.6 (157.0)	97.3 (97.7)	0.179	0.837	2.511	639.264 51
SF_2	157.1 (158.8)	97.2 (98.0)	0.195	0.714	1.427	596.412 71
ClF	160.6 (162.8)		0.210	0.496	0.496	558.884 32

[a] Experimental data are given in parentheses. References: LiF, NaF, ref 8, p 444; BeF_2, MgF_2, AlF_3, Volkov, L. V.; Rambidi, N. G.; Spiridonov, V. P. *Zh. Strukt. Khim.* **1967**, *8*, 715; BF_3, Yamamoto, S.; Kuwabara, R.; Takami, N.; Kuchitsu, K. *J. Mol. Spectrosc.* **1986**, *115*, 333; CF_4, Fink, M.; Schhmeidekamp, C. W.; Gregory, D. *J. Chem. Phys.* **1976**, *71*, 5238; NF_3, OF_2, Morino, Y.; Saito, S. *J. Mol. Spectrosc.* **1966**, *19*, 435; F_2, ref 2b; SiF_4, ref 11; PF_3, Morimo, Y.; Kuchitsu, K.; Moritani, T. *Inorg. Chem.* **1969**, *8*, 867; SF_2, Kirchhoff, W. H.; Johnson, D. R.; Powell, F. X. *J. Mol. Spectrosc.* **1973**, *48*, 157; ClF, Edwards, A. J.; Christe, K. O. *J. Chem. Soc., Dalton Trans.* **1976**, 175.

Table 2. Results of DFT Calculations for the Period 2 and 3 Fluorides[a]

molecule	bond length (pm)	bond angle (deg)	ρ_b (au)	$-q$(F)	q(X)	$-E$ (au)
LiF	157.3 (156.4)		0.0750	0.922	0.922	107.471 94
BeF_2	137.8 (140)	180	0.1452	0.876	1.752	214.688 73
BF_3	131.4 (130.7)	120	0.2165	0.808	2.433	324.682 98
CF_4	132.6 (131.9)	109.5	0.3086	0.612	2.453	437.641 19
NF_3	138.2 (138.5)	101.9 (102.3)	0.3142	0.277	0.834	274.759 98
OF_2	140.4 (140.5)	104.0 (103.1)	0.2950	0.133	0.266	399.580 67
F_2	139.9 (141.8)		0.2879	0	0	542.326 02
NaF	194.3 (192.6)		0.0512	0.906	0.906	262.226 98
MgF_2	175.2 (177)	180	0.0795	0.878	1.756	399.998 97
AlF_3	163.9 (163)	120	0.1153	0.845	2.538	542.326 02
SiF_4	157.0 (155.5)	109.5	0.1541	0.813	3.255	689.305 71
PF_3	159.1 (157.0)	97.4 (97.7)	0.1678	0.758	2.277	641.116 29
SF_2	162.5 (158.8)	98.8 (98.0)	0.1824	0.579	1.159	597.918 92
ClF	166.5 (162.8)		0.1868	0.379	0.379	560.021 06

[a] Experimental data are given in parentheses. For references, see Table 1.

Discussion

Effect of Ionic Character (Atomic Charges) on Bond Length. We see from Tables 1 and 2 that the charge on F decreases steadily from LiF to F_2O and from NaF to ClF, indicating an increasing covalent character of the bonds in both series. The charges on fluorine correlate well with the electronegativities of the atom X, as shown in Figure 2. The charge on X reaches a maximum at carbon in the period 2 series and at silicon in the period 3 series, while the product of the charges on X and F reaches a maximum value of 1.97 at boron in the period 2 series and 2.65 at silicon in the period 3 series. In the second period, the electron density at the bond critical point, ρ_b, increases steadily from a small value of 0.075 au for LiF, which is characteristic of predominately ionic bonding, to a value of 0.314 au for NF_3, characteristic of predominately covalent bonding, and then decreases very slightly, reflecting the relative weakness of the bonds in OF_2 and F_2. The electron density at the bond critical point increases in a similar manner from NaF to ClF, but the values are smaller in the period 3 molecules than for the coresponding period 2 molecules.

In both series, the bond length initially decreases, passing through a minimum at boron for the period 2 fluorides and at silicon for the period 3 fluorides and then increasing again. It is striking that the minimum bond length occurs for the same molecules for which the product of the charges on X and F reaches a maximum (Figure 3), strongly suggesting that electrostatic attraction between the oppositely charged atoms is an important factor in determining the bond length. Figure 3 also shows predicted covalent bond lengths calculated from our covalent radii of 60 pm for F and 65 pm for O (see later discussion) and standard values for the other elements. For all the period 2 elements up to carbon and all the period 3 elements up to sulfur, the observed bond lengths are considerably shorter than those calculated from covalent radii. However, they are in better agreement with bond lengths calculated from the ionic radii of Shannon,[23] at least for the elements up to boron in period 2 and up to silicon in period 3. In most cases, the Shannon radii are for coordination numbers that are higher than the values appropriate in these molecules, and so they give values for the bond lengths that are somewhat higher than the observed values. The difference between the sum of the ionic radii and the experimental bond length decreases across the period, becoming negligible for BF_3 and SiF_4, for which the ionic radii for the correct coordination numbers of III and IV are given by Shannon.

We conclude that, for the period 2 fluorides up to boron and for the period 3 fluorides up to Si, and probably for P as well (for which no reliable ionic radius is available), the bond lengths are more consistent with an ionic model than with a covalent model and the apparent shortening of the bonds in these molecules is largely due to their considerable ionic character. Because the charge on fluorine in BF_3 and SiF_4 is so large (-0.8), it is unlikely that there is any appreciable amount of back donation, because this involves the transfer of charge from fluorine to the central atom. It is noteworthy that the B−F and Si−F bonds for which the product of the atomic charges reaches a maximum are among the strongest known single bonds, as

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(23) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

Table 3. Results of Calculations for Some Fluoro Anions and Cations

	bond length (pm)					
ion	exptl[a]	calc	ρ_b (au)	$-q$(F)	q(X)	$-E$ (au)
			HF Calculations			
BeF_3^-	149	145.8	0.107	0.933	1.80	313.352 02
BeF_4^{2-}	155.4	158.2	0.07	0.952	1.81	412.696 48
BF_4^-	138.6	138.7	0.166	0.895	2.58	422.885 19
CF_3^+		120.8	0.398	0.675	3.03	335.920 03
NF_4^+	130	127.3	0.455	0.146	1.09	451.671 59
AlF_4^-	165.8	167.4	0.100	0.913	2.65	640.218 71
AlF_6^{3-}	181	186.9	0.056	0.947	2.69	838.754 08
SiF_6^{2-}	169.4	169.5	0.103	0.907	2.65	886.048 32
PF_4^+		145.7	0.236	0.776	4.12	738.447 68
PF_6^-	164	159.5	0.162	0.846	4.08	937.843 90
			DFT Calculations			
BeF_3^-	149	147.6	0.104	0.914	1.75	341.717 05
BeF_4^{2-}	155.4	160.0	0.070	0.939	1.76	414.505 14
BF_4^-	138.6	141.1	0.164	0.856	2.43	424.698 01
CF_3^+		123.5[b]	0.373	0.527	2.59	337.343 13
NF_4^+	130	131.8	0.387	0.078	1.32	453.606 50
AlF_4^-	165.8	169.9	0.096	0.888	2.56	642.392 64
AlF_6^{3-}	181	189.7	0.056	0.930	2.58	841.822 07
SiF_6^{2-}	169.4	172.9	0.101	0.875	3.26	889.118 12
PF_4^+		149.2	0.219	0.693	3.78	740.663 97
PF_6^-	164	163.6	0.154	0.782	3.70	940.939 14
			MP2 Calculations			
CF_3^+		123.4	0.370	0.564	2.70	336.809 39

[a] References: BeF_3^-, Spiridonov, E. V.; Erohkin, E. V.; Brezgin, Y. A. *Zh. Strukt. Khim.* **1972**, *13*, 321; BeF_4^{2-}, Collins, D. M.; Mahar, M. C.; Whitehurst, F. W. *Acta Crystallogr.* **1983**, *39B*, 303; BF_4^-, Burton, B. *Acta Crystallogr.* **1969**, *B25*, 2161; NF_4^+, Christe, K. O.; Lund, M. D.; Thorup, N.; Russell, D. R.; Fawcett, J.; Bau, R. *Inorg. Chem.* **1988**, *27*, 2450; AlF_4^-, Herron, N.; Harlow, R. L.; Thorn, D. L. *Inorg. Chem.* **1993**, *32*, 2985; AlF_6^{3-}, Naray Szabo, S.; Susvari, K. *Z. Crystallogr.* **1938**, *92*, 155; SiF_6^{2-}, Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1; PF_6^-, Bode, H.; Teufer, G. *Acta Crystallogr.* **1956**, *9*, 825. [b] Olah et al. (*J. Am. Chem. Soc.* **1996**, *118*, 1446) obtained CF bond lengths of 124.6 pm in an MP2 calculation and 124.4 pm in a DFT calculation.

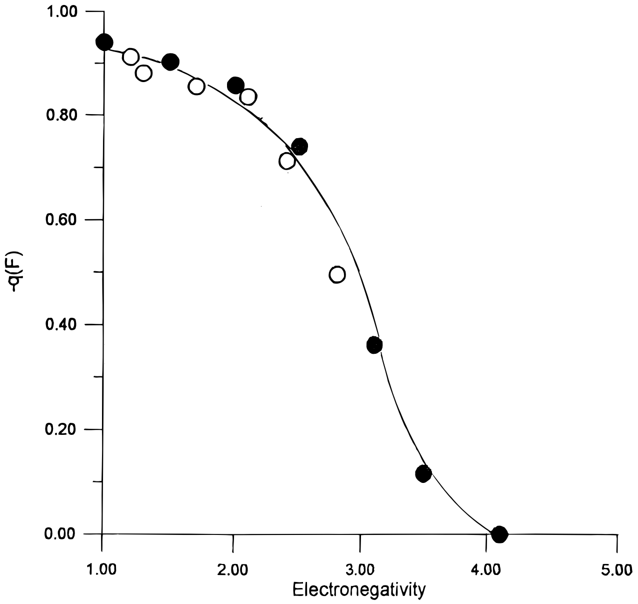

Figure 2. Plot of the charge on fluorine against the Allred−Rochow electronegativity of the central atom in the fluorides of periods 2 (●) and 3 (○).

shown by their bond energies, which have been estimated to be 613 and 565 kJ mol^{-1} for BF and SiF, respectively.[3]

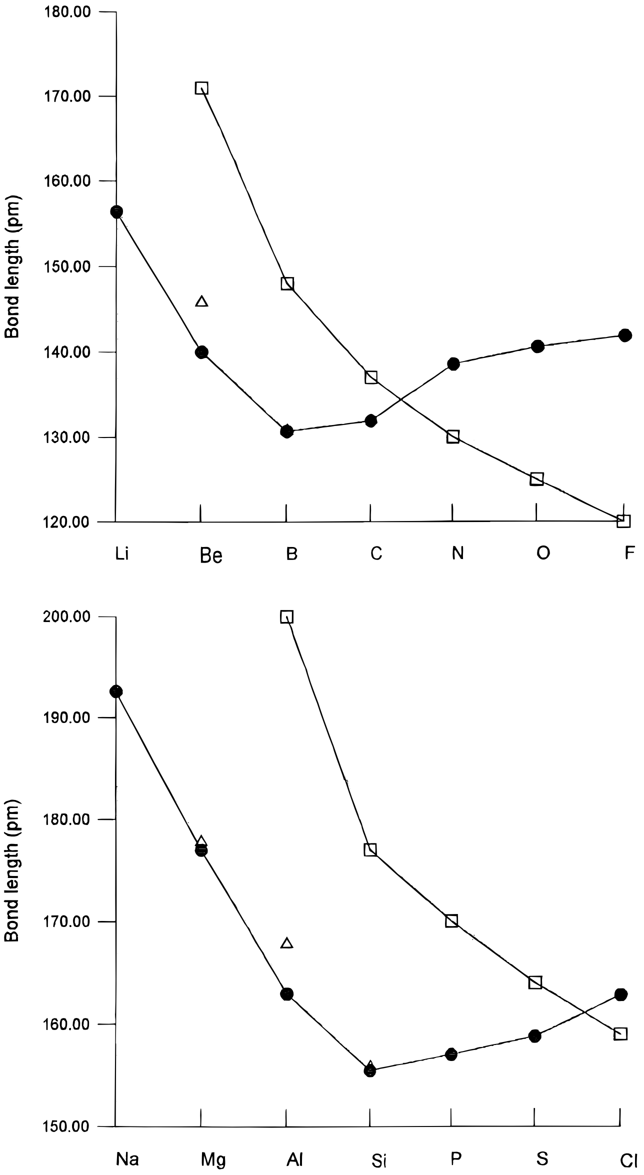

Figure 3. Bond lengths of the period 2 and 3 fluorides. ●, Experimental bond lengths; □, sum of the covalent radii (r_F = 60 pm); △, sum of the ionic radii (the following values of Shannon's effective ionic radii[23] were used: F^- (II) = 128 pm; Li^+ (IV) = 59 pm; Be^{2+} (III) = 16 pm; B^{3+} (III) = 1 pm, Na^+ (IV) = 99 pm; Mg^{2+} (IV) = 57 pm; Al^{3+} (IV) = 39 pm; Si^{4+} (IV) = 26 pm).

Bonding and Coordination Numbers in Fluorides. In the series of molecules LiF, BeF_2, BF_3, CF_4, NF_3, OF_2, F_2 and NaF, MgF_2, AlF_3, SiF_4, PF_3, SF_2, ClF, it is often assumed that the abrupt change in melting points between BeF_2 (1287 °C) and BF_3 (−127 °C) and between AlF_3 (1290 °C) and SiF_4 (−90 °C), due to the change from a three-dimensional solid lattice structure to a molecular structure, represents a change from ionic bonding to covalent bonding. Thus, substances such as BF_3 and SiF_4 are often described as consisting of covalent molecules, while BeF_2 and AlF_3 are described as ionic solids. However, our results show that there is a continuous change from nearly 100% ionic to 100% covalent bonding in period 2 and from nearly 100% ionic to rather less than 100% covalent bonding in period 3. It is clear from the preceding discussion that BF_3 and SiF_4 are not correctly described as covalent molecules; they could with just as much accuracy be described as ionic molecules like LiF and NaF. The reason for the abrupt change in properties from BeF_2 to BF_3 and from AlF_3 to SiF_4 is not a sudden change in the nature of the bonding. Rather, it arises from the necessity for the central atom of an AF_n molecule to achieve a certain coordination number if it is to condense into a three-dimensional solid. Whereas BeF_2 molecules condense at high temperature to a solid in which Be is four-coordinated and fluorine two-coordinated, in order for BF_3 to form a three-dimensional lattice structure, each boron atom would have to be six-coordinated and fluorine two-coordinated, but boron is too small to support six-coordination by fluorine. In contrast, the larger Al atom can be six-coordinated by F, and so AlF_3 forms an ionic solid. However, for SiF_4 to form an ionic solid, the silicon would have to be eight-coordinated, and silicon is too small for this to be possible. In contrast, ZrF_4 is a high melting point solid in which the larger Zr atom is eight-coordinated.[24]

Our conclusion that the bonding in BF_3 and SiF_4 has a considerable ionic character which is responsible for the short lengths of their bonds adds further doubt to the back-bonding explanation of these bond lengths. The back-bonding model has also been justified for BF_3 on the grounds that, if BF_3 is formulated with three single bonds, it does not obey the octet rule. However, the octet rule has little relevance for such an ionic molecule, just as it clearly has little relevance for the LiF molecule.

Bond Lengths and Coordination Number. In our previous paper on the covalent radius of fluorine,[17] we pointed out that bond lengths in AF_n molecules appear to be related to the coordination number of the central atom A. For example, the bonds in BF_3 are shorter than those in BF_4^-, and those in SiF_4 are shorter than those in SiF_6^{2-}. Such differences have previously been used as support for the back-bonding model. We consider two alternative explanations for the effect of coordination number on bond lengths.

One possibility is that atomic charges might be smaller in the higher coordination number molecules. However, reference to Tables 1, 2, and 3 shows that the charges in AF_4 molecules are very similar to, and slightly larger than, those in the corresponding AF_3 molecule, and those in AF_6 molecules are slightly larger than those in the corresponding AF_4 molecule.[25] Thus, the decrease in bond length with decreasing coordination number cannot be due to a difference in the atomic charges.

A second possibility is that bond lengths might decrease with decreasing coordination number for steric reasons. In a pure ionic model, interatomic (interionic) distances are determined by the number of anions that are packed around a central cation. It seems reasonable to suppose that, in those molecules in which the atoms have relatively large charges, the number of fluorine atoms packed around the central atom would be an important factor influencing the bond length. That this is the case is strongly supported by the data in Tables 4−7. In Table 4, we see that the intramolecular F- - -F distance in a variety of F_2BX and F_3BX molecules has a nearly constant value of 226 ± 1 pm, despite changes in the ligand X and large changes in the bond lengths and bond angles. There is a clear correlation between bond angle and bond length: the smaller the FBF bond angle, the longer the BF bond. The largest bond angle (120°) and the shortest bond (130.7 pm) are observed in BF_3, and the longest bond (142.4 pm) and the smallest bond angle (105.4°) are observed in $F_3BCH_3^-$. These observations strongly suggest that the F ligand has an almost constant size in these molecules and that the bond distances are determined by the ligands packing as closely as possible around the central boron. When the ligand X is more strongly bonded than F, and hence approaches more closely to the boron, the FBF bond angle decreases and the BF bonds increase in length correspondingly. Consistent with the notion that the bond lengths are determined primarily by packing considerations, the average B−F bond length for the three-coordinated molecules is 131.6 pm, while for the four-coordinated molecules it is 137.0 pm. Moreover, the ratio of the bond lengths in BF_4^- and BF_3 is 1.06, in excellent agreement with the geometrically predicted value of 1.061 for F atoms of constant size packed as closely as possible around the boron.

Table 4. Bond Lengths and F- - -F Distances in Some BF_n Groups

species	B−F (pm)	∠FBF (deg)	F--F (pm)	ref
F_2B-F	130.7	120	226	*a*
F_2B-OH	132.3(10)	118.0(10)	227(3)	*b*
F_2B-NH_2	132.5(12)	117.9(7)	227(3)	*c*
F_2B-CH_3	131.5(5)	116.9(5)	224(1)	*d*
$F_2B-C{\equiv}CH$	132.3(5)	116.5(10)	225(2)	*e*
F_2B-Cl	131.5(5)	118.1(5)	226(2)	*f*
F_2B-H	131.1(5)	118.3(10)	225(2)	*g*
F_2B-BF_2	131.7(2)	117.2(2)	225(1)	*h*
F_2B-SiF_3	131.2(5)	118.5(5)	226(1)	*i*
F_3B-F^-	139.6(4)	109.4(4)	226(1)	*j*
F_3B-OH_2	138.8	111.5	229	*k*
$F_3B-OH_2{\cdot\cdot}H_2O$	138.3(3)	109.8(2)	226(1)	*l*
F_3B-OMe_2	132.5(3)	117(1)	226(2)	*m*
$F_3B-O(H)Me$	137.0	112.0	227	*k*
$F_3B-OPPh_3$	134.8(4)	111.2(2)	223(1)	*n*
$F_3B-OAsPh_3$	135.6(5)	110.8(4)	223(1)	*n*
F_3B-NH_3	136.7	114.4	230	*o*
$F_3B\text{-}NMe_3$	135.4(6)	113.1(9)	226(2)	*p*
	137.2(2)	112.9(3)	229(1)	*q*
$F_3B-N{\equiv}CH$	135.6	113.0	226(1)	*r*
$F_3B-NC_2H_3$	134.7(6)	113.0(5)	225(1)	*s*
$F_3B-CH_3^-$	142.4(5)	105.4(4)	226(1)	*t*
$F_3B-CF_3^-$	139.1(5)	109.9(5)	228(1)	*u*
F_3B-PH_3	137.2(2)	112.1(4)	228(1)	*v*
		average	226 ± 1	

[a] Yamamoto, S.; Kuwabara, R.; Takami, M.; Kuchitsu, K. *J. Mol. Spectrosc.* **1986**, *155*, 333. [b] Takeo, H.; Curl, R. F. *Microwave Spectrosc.* **1972**, *56*, 4314; *Chem. Abstr.* **1972**, 146917v. [c] Lappert, M. F.; Power, D. P.; Sawyer, A. R.; Srivasava, R. C. *Metal and Metalloid Amines*; Ellis Horwood: Chichester, 1980. [d] Bauer, S. H.; Hastings, J. M. *J. Am. Chem. Soc.* **1942**, *64*, 2686. [e] Lafferty, W. J.; Ritter, R. J. *J. Mol. Spectrosc.* **1971**, *30*, 181. [f] Kroto, H.; Maier, M. *J. Mol. Spectrosc.* **1977**, *65*, 280. [g] Gerry, M. C. L.; Lewis-Bevan, W.; Maclennan, D. J.; Merer, A. J.; Westwood, N. P. C. *J. Mol. Spectrosc.* **1986**, *98*, 143. [h] Danielson, D. D.; Patton, J. V.; Hedberg, K. *J. Am. Chem. Soc.* **1977**, *99*, 6484. [i] Landridge-Smith, P. R. R.; Cox, A. P. *J. Chem. Soc., Faraday Trans. 2* **1983**, *79*, 1089. [j] Burton, G. *Acta Crystallogr.* **1969**, *B25*, 2161. [k] Mootz, D.; Steffen, M. *Z. Anorg. Allg. Chem.* **1981**, *483*, 171. [l] Mootz, D.; Steffen, M. *Acta Crystallogr.* **1981**, *37B*, 1110. [m] Iijima, K.; Yamada, T.; Shibata, S. *J. Mol. Struct.* **1981**, *77*, 271. [n] Burford, N.; Spence, R. E. V.; Linden, A.; Cameron, T. S. *Acta Crystallogr.* **1990**, *46C*, 92. [o] Fujiang, D.; Fowler, P. W.; Legon, A. C. *J. Chem. Soc., Chem. Commun.* **1995**, 113. [p] Hargittai, M.; Hargittai, I. *J. Mol. Struct.* **1977**, *39*, 79. [q] Shibata, S.; Iijima, K. *Chem. Lett.* **1977**, 29. [r] Burns, W. A.; Leopold, K. R. *J. Am. Chem. Soc.* **1993**, *115*, 11622. [s] Swanson, B.; Shriver, D. F.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 2182. [t] Braüer, D. J.; Bürger, H.; Pawelke, G. *J. Organomet. Chem.* **1982**, *238*, 267. [u] Braüer, D. J.; Bürger, H.; Pawelke, G. *Inorg. Chem.* **1977**, *16*, 2305. [v] Reetz, M. T.; Hüllmann, M.; Massa, W.; Berger, S.; Rademacher, P.; Heymanns, P. *J. Am. Chem. Soc.* **1986**, *108*, 3937.

Table 5 gives corresponding data for CF_3X and CF_2X molecules. Again, we see that the intramolecular F- - -F distance is remarkably constant, with a value of 216 ± 1 pm, and that the CF bond length increases with decreasing bond angle. The longest CF bond (139.2 pm) is observed in CF_3O^-, in which the FCF bond angle has the smallest value of 101.3°, and the shortest bond is observed in CF_3^+ (124 pm), in which the bond angle is 120°. Moreover, the ratio of the CF_4 and

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(24) Reference 8, p 436.

(25) We use the term molecule to refer to both neutral molecules and charged molecules (polyatomic ions).

Table 5. Bond Lengths and F- - -F Distances in Some CF_n Groups

species	C−F (pm)	∠FCF (deg)	F- - -F (pm)	ref
CF_3^+	123.5[a]	120	214	this paper
	124.6[a]	120	216	*b*
CF_4	131.9	109.5	215	*c*
F_3C-CF_3	132.6(2)	109.8(1)	217(1)	*d*
$F_3C-BF_3^-$	134.3(5)	104.9(3)	213(1)	*e*
$(F_2C)_3$	131.6(1)	112.2(1)	219	*f*
$(F_2C)_4$	132.1(4)	109.2	215	*g*
$(F_2C)_6$	133.8(2)	109.1(3)	218(1)	*h*
F_3C-OF	131.9(3)	109.4(10)	215(2)	*i*
F_3CO^-	139.2	101.3	215	*j*
$(F_3C)_2NN(CF_3)_2$	132.5(5)	108.2(5)	215(1)	*k*
F_3C-CN	133.5	107.5	215	*l*
$F_3C-C\ CH$	133.5(10)	107.5(10)	215(2)	*m*
F_3C-H	133.2(8)	108.8(8)	217(1)	*n*
F_3C-Cl	132.5(2)	108.6(2)	215(1)	*o*
F_3C-Br	132.6(2)	108.8(4)	216(1)	*o*
F_3C-I	133.0(3)	108.1(2)	215(1)	*o*
F_2CH_2	135.7(1)	108.3(1)	220	*p*
$(F_3C)_3CH$	133.6(2)	108.0(2)	216(1)	*q*
$F_3C-CH(O)$	133.2(7)	108.7(1)	216(2)	*n*
$F_3C{=}CF_2$	131.9(1)	112.4(4)	219(1)	*r*
$F_2C{=}CCl_2$	131.5(15)	112.1(25)	218(6)	*s*
$F_2C{=}CH_2$	132.4(1)	109.4(6)	216(1)	*r*
$F_2C{=}CHF$	133.6(1)	109.2(6)	218(1)	*r*

[a] Calculated value. [b] Olah, G. A.; Rasul, G.; Yudin, A. K.; Burrichter, A.; Surya Prakash, G. K.; Chistyakov, A. L.; Stankevich, I. V.; Akhrem, I. S.; Gambaryan, N. P.; Vol'pin, M. E. *J. Am. Chem. Soc.* **1996**, *118*, 1446. [c] Fink, M.; Schmeidekamp, C. W.; Gregory, D. *J. Chem. Phys.* **1976**, *71*, 258. [d] Gallaher, K. L.; Yokozeki, A.; Bauer, S. H. *J. Phys. Chem.* **1974**, *78*, 2389. [e] Brauer, D. J.; Bürger, H.; Pawelke, G. *Inorg. Chem.* **1977**, *16*, 2305. [f] Chiang, J. F.; Bernett, W. A. *Tetrahedron* **1971**, *27*, 975. [g] Chang, C. H.; Porter, R. F.; Bauer, S. H. *J. Mol. Struct.* **1971**, *7*, 89. [h] Hjortaas, K. E.; Strømme, K. O. *Acta Chem. Scand.* **1968**, *22*, 2965. [i] Diodati, F.; Bartell, L. S. *J. Mol. Struct.* **1971**, *8*, 395. [j] Farnham, W. B.; Smart, B. E.; Middleton, W. J.; Calebrese, J. C.; Dixon, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 4565. [k] Bartell, L. S.; Higginbotham, H. K. *Inorg. Chem.* **1965**, *4*, 1346. [l] Thomas, L. F.; Heeks, J. S.; Sheridan, J. Z. *Z. Electrochem.* **1957**, *61*, 935. [m] Shoolery, J. N.; Shulman, R. G.; Sheehan, J. F.; Schomaker, V.; Yost, D. M. *J. Chem. Phys.* **1951**, *19*, 1364. [n] *Tables of Interatomic Distances*; Sutton, L. E., Ed.; Chemical Society Special Publ. Nos. 11 and 18; Chemical Society: London, 1958 and 1965. [o] Typke, V.; Dakkouri, M.; Oberhammer, H. *J. Mol. Struct.* **1978**, *44*, 85. [p] Hirota, E.; Tanaka, T.; Sakakhira, A.; Ohashi, Y.; Morino, Y. *J. Mol. Struct.* **1970**, *34*, 222. [q] Stølevik, R.; Thom, E. *Acta Chem. Scand.* **1971**, *25*, 3205. [r] Carlos, J. L.; Karl, R. R.; Bauer, S. H. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 177. [s] Lowrey, A. H.; D'Antonio, P.; George, C. *J. Chem. Phys.* **1976**, *64*, 2884.

Table 6. Bond Lengths and F- - -F Distances in Some SiF_n Groups

species	Si−F (pm)	∠FSiF (deg)	F- - -F (pm)	ref
SiF_6^{2-}	169.4(39)	90	240(5)	*a*
SiF_4	155.5(2)	109.5	254	*b*
	155.2(2)	109.5	254	*c*
$F_3Si-BF_3^-$	156.7(5)	108.0(2)	254(1)	*d*
F_3Si-CH_3	156.7(6)	107.7(6)	253(2)	*e*
$F_3Si-C_6H_5$	157.2(6)	105.0(21)	249(4)	*f*
$F_3Si-NMe_2$	156.7(6)	105.0(9)	249(2)	*g*
$F_3Si-OCH_3$	155.9(6)	108.2(16)	253(3)	*h*
$(F_3Si)_2O$	155.4(10)	108.8(5)	253(2)	*i*
F_3Si-Cl	156.0(5)	108.5(10)	253(2)	*j*
F_3Si-Br	156.0(2)	108.6(1)	253(1)	*d*
F_3Si-H	156.5(5)	108.3(5)	254(2)	*k*
$F_3Si-SiF_3$	156.9(2)	110.6(3)	258(1)	*l*
F_2SiH_2	157.7(1)	107.9(1)	255	*m*
$F_2Si(H)Me$	158.3(2)	106.7(5)	254(1)	*n*

[a] Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1. [b] Beagley, B.; Brown, D. P.; Freeman, J. M. *J. Mol. Struct.* **1973**, *18*, 337. [c] Hagen, K.; Hedberg, K. *J. Chem. Phys.* **1977**, *59*, 1549. [d] Landridge-Smith, P. R. R.; Cox, A. P. *J. Chem. Soc., Faraday Trans. 2* **1983**, *79*, 1089. [e] Durig, J.; Li, Y. S.; Tong, C. C. *J. Mol. Struct.* **1972**, *14*, 255. [f] Souza, G. G. B.; Wieser, J. D. *J. Mol. Struct.* **1975**, *25*, 442. [g] Airey, W.; Glidewell, C.; Robiette, A. G.; Sheldrick, G. M.; Freeman, J. M. *J. Mol. Struct.* **1971**, *6*, 42. [h] Airey, W.; Glidewell, C.; Robiette, A. G.; Sheldrick, G. M. *J. Mol. Struct.* **1971**, *8*, 4. [i] Airey, W.; Glidewell, C.; Rankin, D. W. H.; Robiette, A. G.; Sheldrick, G. M.; Cruickshank, D. W. *J. Trans. Faraday Soc.* **1970**, *66*, 551. [j] Sheridan, J.; Gordy, W. *J. Chem. Phys.* **1951**, *19*, 965. [k] Heath, G. A.; Thomas, L. F.; Sheridan, J. *Trans. Faraday Soc.* **1954**, *50*, 779. [l] Rankin, D. W. H.; Robertson, A. *J. Mol. Struct.* **1975**, *27*, 438. [m] Laurie, V. W. *J. Chem. Phys.* **1957**, *26*, 135. [n] Swalen, J. D.; Stoicheff, B. P. *J. Chem. Phys.* **1958**, *28*, 671.

Table 7. Bond Lengths and F- - -F Distances in Some PF_n Groups

species	P−F (pm)	∠FPF (deg)	F- - -F (pm)	ref
PF_6^-	164	90	232	*b*
PF_4^+	145.7[a]	109.5	238	*a*
F_3P	157.0(1)	97.8(2)	237(1)	*c*
F_3P-BH_3	153.8(8)	99.8(10)	235(3)	*d*
$F_3P{=}O$	152.4(3)	101.3(2)	236(1)	*e*
$F_3P{=}S$	153.8(3)	99.6(3)	235(1)	*f*
$F_2(H)P-BH_3$	155.2(6)	100.0(5)	238(2)	*g*
$F_2(HP)P{=}S$	155.1(5)	98.6(2)	235(1)	*h*
	154.6(2)	99.1(1)	235	
$F_2(H)P{=}O$	153.9(5)	99.8(2)	235(1)	*i*
$F_2PO_2^-$	156.2	96	232	*j*

[a] Calculated value (this paper). [b] Bode, H.; Teufer, G. *Acta Crystallogr.* **1956**, *9*, 825. [c] Moritani, T.; Kuchitsu, K.; Morino, Y. *Inorg. Chem.* **1969**, *8*, 867. [d] Kuczkowski, R. L.; Lide, D. R. *J. Chem. Phys.* **1967**, *46*, 357. [e] Moritani, T.; Kuchitsu, K.; Morino, Y. *Inorg. Chem.* **1971**, *10*, 344. [f] Karakida, K.; Kuchitsu, K. *Inorg. Chim. Acta* **1976**, *16*, 29. [g] Pasinski, J. P.; Kuczkowski, R. L. *J. Chem. Phys.* **1971**, *54*, 1903. [h] Nave, C. R.; Sheridan, J. *J. Mol. Struct.* **1973**, *15*, 391. Blair, P. D.; Cradock, S.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1985**, 755. [i] Centofanti, L. F.; Kuczkowski, R. L. *Inorg. Chem.* **1968**, *7*, 2582. [j] Granier, W.; Durand, J.; Cot, L.; Galigné, J. L. *Acta Crystallogr.* **1975**, *B31*, 2506.

CF_3^+ bond lengths of 1.06 is in excellent agreement with the geometrically determined ratio of 1.061.

Table 6 gives bond angles and bond lengths for a variety of four-coordinated molecules of silicon, together with the value for SiF_6^{2-}. Again, we see that the F- - -F intramolecular distance is remarkably constant, with an average value of 253 pm for all the four-coordinated molecules. The slightly smaller value of 240 pm for SiF_6^{2-} suggests that the fluorine ligands in the four-coordinated molecules are not quite closely packed. The ratio of the bond lengths in SiF_4 and SiF_6^{2-} is 1.09, which does not agree well with the geometrically predicted value of 1.155, suggesting again that the fluorine ligands in the four-coordinated molecules are not quite closely packed around the relatively large silicon, but the difference in the bond lengths is, nevertheless, consistent with the view that it is largely due to packing effects.

Table 7 gives bond angles and bond lengths for a variety of F_3PX and F_2PX_2 molecules and for PF_3 and PF_6^-. The intermolecular F- - -F distance is reasonably constant, with an average value of 235 pm, despite the considerable differences in the bond lengths and bond angles. The ratio of the bond lengths in PF_6^- and PF_4^+ is 1.125, which is in quite good agreement with the geometrically predicted value of 1.155. Even in PF_3, in which the presence of the lone pair decreases the FPF bond angle to 97.8° while correspondingly increasing the PF distance to 157.0 pm, the F- - -F distance has the same constant value.

The model that we are proposing is not a truly ionic model, because the F- - -F distance decreases from B to C and from Si to P, with decreasing charge on fluorine and the corresponding expected decrease in the size of the fluorine ligand, which although not a true ion is, nevertheless, much larger than a neutral F atom.

On the basis of our model, we would expect that a two-coordinated molecule would have an even shorter A−F bond than the corresponding three-coordinated molecule. In agreement with this expectation, the B−F bond has a length of 128.3 pm in F−B═O[26] and 126.5 pm in the BF molecule,[27] compared to 130.7 pm in BF_3. Similarly, the N−F bond in the two-coordinated FNN^+ ion[28] has a length of 124 pm, which is shorter than its length of 130 pm in four-coordinated NF_4^+. It is noteworthy that the bond length in NF_4^+ is equal to the sum of the covalent radii of 70 pm for nitrogen and 60 pm for fluorine (see following section), which is consistent with the small value of −0.15 for the product $q(\mathrm{N})q(\mathrm{F})$. In NF_3, the bond is longer (136.5 pm) because of the repulsive effect of the lone pair, but the F- - -F distance is 212 pm in both NF_4^+ and NF_3.

Our conclusions are very similar to those of Bartell,[29] who showed that bond angles and bond lengths in ethylene derivatives and related molecules appear to be determined by the packing of spherical atoms of constant radius around a carbon atom. Bartell gave a radius of 108 pm for fluorine bonded to carbon, which gives the same F- - -F distance as in Table 5.

Other authors have commented on the constancy of inter-ligand distances in a variety of molecules. For example, Landridge-Smith and Cox[30] have previously noted the constancy of F- - -F distances in a variety of SiF_3X molecules but did not conclude that such ligand−ligand interactions might be important in determining bond lengths. Hargittai,[31] however, has commented on the constancy of O- - -O, O- - -F, and O- - -C distances in a large variety of $XYSO_2$ molecules and has suggested that the constancy of these distances must be taken into account in discussing the variation of bond lengths and angles in these molecules.

While it would be premature to conclude that, for a given A−F bond, the only factor determining its length is the coordination number of A, it is clear that this is an important factor that must be taken into account before conclusions can be reached about the importance of other postulated effects, such as back-bonding, hyperconjugation, and changes in hybridization.

Lewis Acid Strength of BF_3. It has been well-known for a long time that the Lewis acid strength of the boron trihalides increases in the order $BF_3 < BCl_3 < BBr_3$, as is shown by the increasing stability of complexes with ammonia and other bases. The charge on boron is expected to decrease from BF_3 to BCl_3 to BBr_3 with decreasing electronegativity of the ligand, and this is confirmed for BF_3 and BCl_3 by the calculated charges, which are +2.43 for BF_3 (Table 1) and +1.50 for BCl_3.[33] Since a decreasing charge on boron would be expected to lead to a decreasing stability of complexes with bases, not the increase observed, it has been commonly accepted that back-bonding from the halogen to boron decreases from F to Cl to Br, which increases the availability of the 2p orbital on boron to accept an electron pair from the base and thus increases the strength of complexes with bases.

This explanation has been questioned, for example by Brinke et al.,[34] who proposed that the acid strength is determined by a parameter that they call the "charge capacity" of the atom, which for boron increases from BF_3 to BCl_3 to BBr_3. However, the results reported in this paper suggest a simple alternative explanation. The coordination number of boron increases from three to four as the geometry changes from planar to tetrahedral when it forms an acid−base complex, and the bond length increases correspondingly. For example, the BF bond length increases from 131 to 136 pm in $BF_3{\cdot}NH_3$, and the BCl bond length increases from 174 to 184 pm (calculated[33]) in $BCl_3{\cdot}NH_3$. In other words, the formation of a complex involves the stretching of the B−X bonds as the molecule distorts from a planar toward a tetrahedral geometry. Thus, it follows that the more easily the B−X bond can be stretched, the stronger will be the complex formed. Since the charges in BF_3 (B, +2.43; F, −0.81) are larger than those in BCl_3 (B, +1.50; Cl, −0.50) and the B−F bond is much shorter (131 pm) than the B−Cl bond (174 pm), the BF bond is considerably stronger than the BCl bond, and so it will take more energy to distort the planar BF_3 molecule to the tetrahedral geometry in forming a complex than to similarly distort the BCl_3 molecule, so it is not surprising that BF_3 is a weaker Lewis acid than BCl_3.

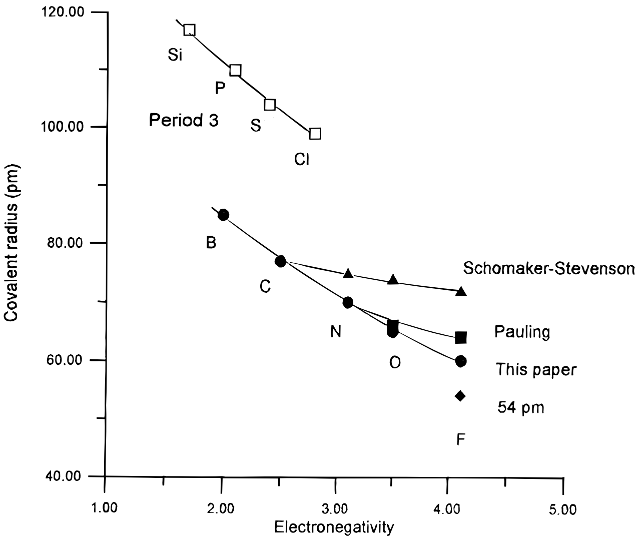

Figure 4. Plots of the covalent radii of the nonmetallic elements of periods 2 and 3 against the Allred−Rochow electronegativity.

Covalent Radius of Fluorine. Because all A−F bonds are polar, and because the F_2 molecule has an abnormally long and weak bond, it is not possible to deduce a true covalent radius of fluorine from measured bond lengths. In our previous paper,[17] we suggested the new value of 54 pm based on the bond lengths of AF_4 molecules of period 2 elements and AF_6 molecules of period 3 and 4 elements. However, as we have shown in this paper, the atomic charges in most of these molecules are large so that the bonds have a considerable ionic character. Moreover, as those molecules that are much less ionic, such as NF_3, OF_2, and F_2, have abnormally long bonds, there are no molecules from which the covalent radius of fluorine could, in principle, be determined. Nevertheless, we can estimate a value for the covalent radius of fluorine from plots of covalent radii against electronegativity.

The values of covalent radii decrease steadily in each period across the periodic table as the increasing effective nuclear charge contracts the valence shell. It seems reasonable, then, to suppose that the covalent radius should vary in a regular manner with electronegativity. Figure 4 shows the covalent radii for the elements in periods 2 and 3 plotted against their Allred−Rochow electronegativities.[32] The covalent radii decrease smoothly across period 3. However, for period 2, the Schomaker−Stevenson radii for N, O, and F of 74, 74, and 72 pm,

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(26) Kawashima, Y.; Kawaguchi, K.; Endo, Y.; Hirota, E. *J. Chem. Phys.* **1987**, *87*, 2006.

(27) Onaka, R. *J. Chem. Phys.* **1957**, *27*, 374.

(28) Christe, K. O.; Wilson, R. D.; Wilson, W. W.; Bau, R.; Sukamar, V.; Dixon, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 3795.

(29) Bartell, L. S. *J. Chem. Phys.* **1960**, *32*, 827.

(30) Landridge-Smith, P. R. R.; Cox, A. P. *J. Chem. Soc., Faraday Trans. 2* **1983**, *79*, 1089.

(31) Hargittai, I. *The Structure of Volatile Sulfur Compounds*; D. Reidel Publishing Co.: 1985 (see also references therein).

(32) Allred, A. L.; Rochow, E. G. *J. Inorg. Nucl. Chem.* **1958**, *5*, 264.

(33) Unpublished calculation.

(34) Brinck, T.; Murray, J. S.; Pollitzer, P. *Inorg. Chem.* **1993**, *32*, 2622.

Table 8. Values for the Covalent Radii of Oxygen, Nitrogen, and Fluorine (pm)

atom	Pauling value[a]	S−S[b]	S−S (revised)[c]	this paper
N	70	74	72	70
O	66	74	73	65
F	64	72	71	60

[a] Reference 5, p 224. [b] Reference 1. [c] Reference 2.

respectively, give a curve of quite different form. The original Pauling values of 70, 66, and 64 pm for these elements also give a curve that does not decrease as rapidly with increasing electronegativity as for the elements in period 3. On the other hand, our previously proposed value of 54 pm for fluorine appears to be too small, while a value of 60 pm, together with a value of 65 pm for oxygen and Pauling's original value of 70 pm for nitrogen, fit a smooth curve, consistent with the curves for period 3. We propose, therefore, that the best value for the covalent radius of fluorine is 60 pm, while for oxygen it is 65 pm, which is scarcely different from Pauling's value of 66 pm, and for nitrogen it is 70 pm, which is identical with Pauling's value. These values are summarized and compared with previous values in Table 8. It is interesting that Pauling, with his usual insight originally proposed values for F, O, and N that are either identical with or very close to our "best" values and that differ considerably from the larger values that have subsequently been widely adopted and which Pauling himself later accepted. His acceptance of these larger values led to his proposal of the back-bonding model. It is a reflection of his great and lasting influence that it is only in recent years that this model has been seriously questioned. However, it must be admitted that the value of 60 pm that we propose for the covalent radius of fluorine is of little practical value. In principle, it should apply to any X−F bond with little ionic character, and as we have seen, it can be used to predict the length of the bond in NF_4^+, but in any other predominately covalent molecule, such as NF_3, F_2O, and F_2, the lone pairs on the central atom lead to the bonds being unusually long and weak.

Describing the Bonding in Molecular Fluorides. The bonds in the period 2 fluorides LiF to CF_4 and in the period 3 fluorides NaF to SF_2 have more than 50% ionic character. It seems that it would be preferable, therefore, to formulate them as ionic molecules, i.e., as Li^+F^-, $Be^{2+}(F^-)_2$, $B^{3+}(F^-)_3$, and even $C^{4+}(F^-)_4$, and similarly for the period 3 fluorides up to SF_2. However, this suggestion is so unconventional, at least for BF_3 and CF_4 in period 2 and for SiF_4, PF_3 and SF_2 in period 3, that it seems unlikely that it will be widely adopted. Yet formulating a molecule such as BF_3 with covalent bonds gives an incorrect picture of the bonding and leads to a continuation of the misconception that the bonding is predominately covalent. Of course, it is generally recognized that all bonds between different atoms have some polar character, and it is common to indicate this in the following way: $B^{\delta+}-F^{\delta-}$. This is probably satisfactory if δ is taken to mean any fractional charge and not just a small charge ($\ll 1$), as is often the case. In cases where the atomic charges are known, it would be preferable to indicate these charges. A bond line is usually taken to indicate a covalent bond, but an alternative solution would be to use a bond line simply to indicate that two atoms are bonded together. This would be consistent with Bader's definition of a bond path.[20] We are not proposing a definite solution to what appears to be a not unimportant problem concerning the representation of molecules with considerable ionic character but are simply raising it for discussion.

Conclusions and Summary

In this paper, we have shown the following:

(1) All bonds to fluorine, with the exception N−F, O−F, and F−F, have considerable ionic character, so the vast majority of AF_n molecules are more appropriately described in terms of an ionic model rather than a covalent model.

(2) The length of A−F bonds in the period 2 fluorides reaches a minimum at boron and in period 3 fluorides at silicon when the product of the charges on A and F reaches a maximum value, consistent with the ionic model and with the observation that the B−F and Si−F bond energies are the largest of all A−F bond energies.

(3) The length of a given A−F bond in a series of AF_n molecules and ions decreases with decreasing coordination number n and is determined primarily by the value of n. In other words, the length of a given A−F bond is determined to a large extent by the number of F atoms (almost ions) closely packed around the central atom A.

(4) Our work gives no evidence for the back-bonding model that has previously been used to account for the apparently short bond lengths in BF_3 and SiF_4.

(5) As almost all AF_n molecules are predominately ionic, very few A−F bond lengths can be predicted from the sum of the covalent radii. Moreover, it does not seem possible to correct such lengths for the difference in electronegativities of A and F. There is no justification for the use of the Schomaker−Stevenson equation for this purpose, as it has no theoretical foundation and is based on an inappropriate value for the covalent radius of fluorine.

(6) The increasing Lewis acid strength in the series $BF_3 < BCl_3 < BBr_3$ can be accounted for in terms of the decreasing energy needed to stretch the BX bonds to accommodate the change from planar three-coordination to tetrahedral four-coordination.

(7) A "best" value for the covalent radius of fluorine has been obtained from a plot of covalent radii against electronegativity, but there are very few molecules for which this value can be used to predict bond lengths.

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