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ELECTRON DISTRIBUTION IN THE XENON FLUORIDES AND XENON OXIDE TETRAFLUORIDE BY ESGA AND EVIDENCE FOR ""ORBITAL INDEPENDENCE"" IN THE XENON-FLUORINE BONDING

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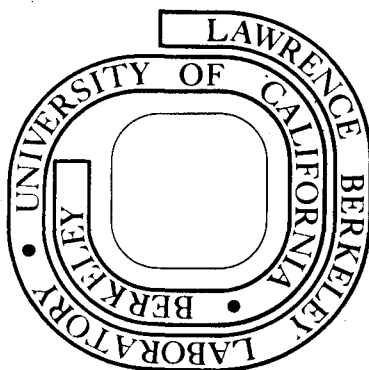
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## Electron Distribution in the Xenon Fluorides and Xenon Oxide Tetrafluoride by ESCA and Evidence for "Orbital Independence" in the Xenon-Fluorine Bonding

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**Abstract:** We have measured fluorine 1s, oxygen 1s, and xenon 3d electron binding energies in the compounds Xe, XeF<sub>2</sub>, XeF<sub>4</sub>, XeF<sub>6</sub>, XeOF<sub>4</sub>, and F<sub>2</sub>. The absolute binding energy for 3d<sub>5/2</sub> in Xe is 676.44 (5) eV and for 1s in F<sub>2</sub> is 696.71 (5) eV. Shifts of xenon 3d<sub>5/2</sub> binding energies (in electron volts) relative to that in xenon are XeF<sub>2</sub>, 2.87 (2); XeF<sub>4</sub>, 5.41 (2); XeF<sub>6</sub>, 7.64 (3); XeOF<sub>4</sub>, 7.07 (2), in good agreement with those measured elsewhere. The fluorine 1s binding energies relative to F<sub>2</sub> are XeF<sub>2</sub>, -5.48 (4); XeF<sub>4</sub>, -4.60 (5); XeF<sub>6</sub>, -3.38 (5); XeOF<sub>4</sub>, -3.62 (4). The oxygen 1s binding energy in XeOF<sub>4</sub> is -3.29 (4) eV less than the centroid of the 1s binding energies in O<sub>2</sub>. The measured shifts are less than half those predicted by *ab initio* calculations. We have used a point charge model with these data to assign charges to the atoms in the molecules. For all of the molecules the charge on the fluorine is about -0.24 e. For oxygen in XeOF<sub>4</sub>, the charge is -0.43 e. The charges assigned by this method are significantly smaller than those determined from other methods (Mössbauer spectroscopy and nmr). There is not a ready explanation for either the smallness of the charge we have derived or for its independence of the number of fluorines. It is possible that these are evidence for extensive back donation of charge from the fluorines to the xenons *via*  $\pi$  bonds and for orbital independence in the xenon-fluorine bonding. The ratio of oxygen charge to fluorine charge in XeOF<sub>4</sub> can be easily understood in terms of simple Lewis structures.

Since their discovery a decade ago, the noble gas halides and oxides have attracted the attention of both experimental and theoretical chemists.<sup>2</sup> This interest has arisen not only because these compounds had not been expected to exist but also because of the additional insights they provide concerning such topics as molecular geometry and multicenter bonding. There are, for example, many parallels between the structure and bonding of the noble gas halides and those of interhalogen compounds and polyhalide ions. In spite of considerable research, however, there is not yet an unambiguous description of the charge distribution in these compounds.

In the conceptually simplest model, the xenon atom in the xenon fluorides shares one electron with each of the fluorine atoms, completing the octet of the fluorine

while maintaining the octet on the xenon. The charge on each fluorine is  $-e/2$  and on the xenon is  $+ne/2$ , where  $n$  is the number of fluorine atoms. Analyses of Mössbauer spectra,<sup>3</sup> nmr spectra,<sup>4a</sup> and heats of sublimation,<sup>4b</sup> as well as SCF calculations,<sup>5</sup> yield charges for the fluorine atoms in these compounds between -0.4 and -0.75 e, in accord with this simple picture. As will be discussed below, however, there is reason to believe that most of these methods overestimate the charge.

The molecular orbital approach also predicts high electron migration from xenon to fluorine on bond formation. The F-Xe-F system of XeF<sub>2</sub> can be under-

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(5) H. Basch, J. W. Moskowitz, C. Hollister, and D. Hankin, *J. Chem. Phys.*, **55**, 1922 (1971).

(1) (a) Oregon State University; (b) University of California.

(2) (a) "Gmelins Handbuch der Anorganischen Chemie, Edelgasverbindungen," Band 1, Weinheim, 1970; (b) N. Bartlett and F. O. Slatky, "Comprehensive Inorganic Chemistry," Vol. 1, A. F. Trotman-Dickenson, Ed., Pergamon Press, Oxford, 1973.

stood as forming three-center, four-electron bonds. One filled orbital is bonding and one filled orbital is nonbonding, for a bond order of one. The electrons in the nonbonding orbital are located entirely on the fluorines; those in the bonding orbital are partly on the xenon and partly on the fluorine. This bonding scheme gives rise to large negative charges on the fluorines. A similar description applies to  $\text{XeF}_4$ , which has two sets of three-center bonds perpendicular to one another. Xenon hexafluoride can also be considered to have three such mutually perpendicular bonds. We note that  $\text{XeF}_6$  is not perfectly octahedral, as such a description would require, but is sufficiently close that this picture has some value. (For detailed descriptions of this structure see work by Bartell and coworkers<sup>6-8</sup> and Klemperer and coworkers.<sup>9,10</sup>)

Either of these descriptions provides a framework in which to view some of the properties of the xenon fluorides. In the xenon fluorides the xenon-fluorine bonds become shorter as the oxidation state increases. This suggests either an increasing electrostatic attraction between the positively charged xenon and the negatively charged fluorine atoms or a marked contraction in the xenon atom size. However, the average Xe-F bond energy is nearly the same for all three binary fluorides. This indicates that bond formation for  $\text{XeF}_x + 2\text{F} \rightarrow \text{XeF}_{x+2}$  is, energetically, much the same as for  $\text{Xe} + 2\text{F} \rightarrow \text{XeF}_2$ .

Over the same time that has seen extensive investigation of the noble gas compounds, X-ray photoelectron spectroscopy (ESCA) has developed into a valuable technique for the study of molecular properties. The shifts in core-electron binding energies provide a direct test of molecular orbital calculations. Less directly, these shifts give information on the molecular charge distribution; correlations between core-electron binding energies and atomic charges are well known.<sup>11</sup> More quantitatively, a simple point charge model can be used to determine the charges on atoms in molecules from core-electron binding energies.<sup>12-16</sup> In many cases, charges so inferred have been found to be in good agreement with those calculated theoretically and with those expected from other evidence.

The xenon fluorides ( $\text{XeF}_2$ ,  $\text{XeF}_4$ ,  $\text{XeF}_6$ , and  $\text{XeOF}_4$ ) are a particularly suitable series of compounds for investigation by this technique. Not only are they

interesting in their own right, but they also provide some special advantages for increasing our understanding of the relation between core-electron binding energies and charge distribution; it is possible to measure a core-electron binding energy for each atom in the molecule; most other studies have dealt with molecules containing hydrogen, which has no core electrons. Elemental xenon, fluorine, and oxygen provide convenient reference materials in which the atomic charge can be assumed to be zero. Finally, when we consider that the sum of the atomic charges in a neutral molecule is zero, we find that there are more constraints than unknowns in the point charge analysis. Data on the xenon fluorides then provide a check on the consistency of the point charge model.

There exists a growing body of data representing other experimental information concerning charge distributions such as nmr, Mössbauer spectroscopy, ultraviolet photoelectron spectroscopy, and far ultraviolet absorption spectroscopy. X-Ray photoelectron measurements of binding energies have been reported<sup>17</sup> for xenon  $3d_{5/2}$  electrons in  $\text{Xe}$ ,  $\text{XeF}_2$ ,  $\text{XeF}_4$ ,  $\text{XeF}_6$ , and  $\text{XeOF}_4$ . Since the  $3d_{5/2}$  binding energies by themselves are insufficient to provide a good description of the charge distributions in these molecules, we have re-measured them and measured the  $\text{Xe } 3d_{5/2}$ ,  $\text{F } 1s$ , and  $\text{O } 1s$  binding energies. We present here the results of these measurements and an account of the subsequent analysis with comparison to other experimental results.

## Experimental Section

**Procedures.** Measurements were made in the Oregon State University cylindrical-mirror electrostatic spectrometer, using aluminum  $K\alpha$  X-rays.<sup>18</sup> All samples were run in the gas phase at pressures of about 0.1 Torr in the gas cell. In each case the line of interest was run simultaneously with a reference standard, in order that any variations in line position with time would be compensated. For each xenon compound, we made such a direct comparison between the xenon  $3d_{5/2}$  line of the compound of interest and that of xenon itself. In separate experiments we determined the splitting between the  $3d_{5/2}$  and  $3d_{3/2}$  lines and the spacing between the xenon  $3d_{5/2}$  and fluorine  $1s$  binding energies in the elements themselves. For the oxygen  $1s$  binding energy in  $\text{XeOF}_4$ , we ran a mixture of this compound with  $\text{O}_2$ . These measurements were sufficient to give the relative xenon binding energies, the relative fluorine binding energies, and the spin-orbit splittings for the entire series of compounds. Further checks were provided by measuring  $\text{XeF}_2$  and  $\text{XeF}_4$  together. Absolute kinetic energies were obtained by comparison of the kinetic energies of ejected  $\text{Xe } 3d$  and  $\text{F}_2 1s$  electrons with those of neon  $^{10}\text{B}$  Auger electrons, whose kinetic energy was taken to be 804.56 eV.<sup>19</sup> To help protect the inside of the spectrometer and the electron multiplier from possible damage by the strongly oxidizing gases, we placed a number of dishes of sodium iodide at various locations within the spectrometer. That this precaution was at least partially effective was demonstrated by the strong color of iodine on the surface of the material after the experiments and by a heavy deposit of iodine on a cold finger cooled to liquid nitrogen temperature. In spite of these precautions, there was a significant loss of gain in the electron detector.

The various spectra were fit with Gaussian shapes and linear backgrounds by least-squares techniques. Spectra showing typical data and fitted curves are illustrated in Figure 1. The peak to background ratio was about 5 to 1.

A particular problem arose in the analysis of the  $\text{XeF}_2$  data,

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- (8) L. S. Bartell and R. M. Gavin, Jr., *J. Chem. Phys.*, **48**, 2466 (1968).
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- (11) K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.-E. Karlsson, I. Lindgren, and B. Lindberg, "ESCA, Atomic, Molecular, and Solid State Structure Studied by Means of Electron Spectroscopy," Almqvist and Wiksell, Uppsala, 1967, pp 98-139.
- (12) Reference 11, p 79.
- (13) K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Hedén, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, "ESCA Applied to Free Molecules," North-Holland Publishing Co., Amsterdam, 1969, pp 104-136.
- (14) D. W. Davis, D. A. Shirley, and T. D. Thomas, *J. Amer. Chem. Soc.*, **94**, 6565 (1972).
- (15) G. D. Stucky, D. A. Matthews, J. Hedman, M. Klasson, and C. Nordling, *J. Amer. Chem. Soc.*, **94**, 8009 (1972).
- (16) W. L. Jolly and W. B. Perry, *J. Amer. Chem. Soc.*, **95**, 5442 (1973).

(17) S.-E. Karlsson, K. Siegbahn, and N. Bartlett, unpublished data quoted in ref 13.

(18) P. H. Citrin, R. W. Shaw, Jr., and T. D. Thomas in "Electron Spectroscopy," D. A. Shirley, Ed., North-Holland Publishing Co., Amsterdam, 1972, p 105.

(19) R. W. Shaw, Jr., and T. D. Thomas, submitted for publication to *Phys. Rev.*

since the xenon  $3d_{5/2}$  line and the fluorine  $1s$  line are almost exactly superimposed. In order to extract a binding energy for fluorine electrons, we have assumed that the intensity and width of the  $3d_{5/2}$  line could be determined from the intensity of the  $3d_{3/2}$  line in  $\text{XeF}_2$  and from the relative intensities and widths of the  $d_{5/2}$  and  $d_{3/2}$  lines in the other compounds studied. Some additional uncertainty in the fluorine  $1s$  binding energy and the spin-orbit splitting in  $\text{XeF}_2$  arises from these assumptions.

## Results

The results of our measurements are summarized in Table I, where we have given the value of the spin-orbit

Table I. Experimental Binding Energy Shifts and Splittings

| Spin-Orbit Splittings of Xenon 3d Electrons (eV)                               |                    |
|--|--------------------|
| Xe   | $12.79 \pm 0.02^a$ |
| $\text{XeF}_2$   | $12.78 \pm 0.04$   |
| $\text{XeF}_4$   | $12.66 \pm 0.04$   |
| $\text{XeF}_6$   | $12.75 \pm 0.04$   |
| $\text{XeOF}_4$  | $12.69 \pm 0.04$   |
| Shifts of Xenon $3d_{5/2}$ Binding Energies Relative to That of Xe (eV)        |                    |
| $\text{XeF}_2$   | $2.87 \pm 0.02$    |
| $\text{XeF}_4$   | $5.41 \pm 0.02$    |
| $\text{XeF}_6$   | $7.64 \pm 0.03$    |
| $\text{XeOF}_4$  | $7.07 \pm 0.02$    |
| Shifts of Fluorine $1s$ Binding Energies Relative to That of $\text{F}_2$ (eV) |                    |
| $\text{XeF}_2$   | $-5.48 \pm 0.04$   |
| $\text{XeF}_4$   | $-4.60 \pm 0.05$   |
| $\text{XeF}_6$   | $-3.38 \pm 0.05$   |
| $\text{XeOF}_4$  | $-3.62 \pm 0.04$   |
| Shift of Oxygen $1s$ Binding Relative to Centroid of That of $\text{O}_2$ (eV) |                    |
| $\text{XeOF}_4$  | $-3.29 \pm 0.04$   |

<sup>a</sup> Average of three measurements. Error quoted for this value is the root mean square deviation of the three measurements. Other errors are based on the results of the least-squares fits.

splitting of the xenon  $3d$  electrons in the various compounds, the shift of xenon  $3d_{5/2}$  binding energy relative to that of elemental xenon, the shift of fluorine  $1s$  binding energy relative to that of  $\text{F}_2$ , and the shift of the oxygen  $1s$  binding energy in  $\text{XeOF}_4$  relative to that in  $\text{O}_2$ .

For fluorine  $1s$  in  $\text{F}_2$ , our experimentally determined absolute binding energy of  $696.71 \pm 0.05$  eV is in excellent agreement with a value of 696.8 eV we have inferred for neutral fluorine from the analysis done by Davis, Shirley, and Thomas on fluorobenzenes.<sup>14</sup> This close agreement lends support to the validity of the method they have used to extract atomic charges from chemical shifts. We find  $676.44 \pm 0.05$  eV for the binding energy of a  $3d_{5/2}$  electron in xenon, in excellent agreement with a value of  $676.4 \pm 0.1$  eV reported by Siegbahn and coworkers.<sup>20</sup> The uncertainty in our absolute numbers arises from uncertainties in the neon Auger energies (about 0.03 eV), in the aluminum K X-ray energy ( $1486.58 \pm 0.03$  eV),<sup>21,22</sup> and in our determination of the xenon-neon and xenon-fluorine differences (0.03 eV).

The spin-orbit splitting for xenon given in Table I is within experimental error of the value  $12.6 \pm 0.2$  eV from the work of Siegbahn and coworkers.<sup>20</sup> This splitting is nearly constant for all of the compounds. The range of variation is 0.13 eV. Our measurements are, however, accurate to about 0.04 eV; we may, therefore, conclude that there is a small but significant

(20) Reference 13, p 47.

(21) K. Luger, *J. Phys. Chem. Solids*, **32**, 609 (1971).

(22) J. A. Bearden, *Rev. Mod. Phys.*, **39**, 78 (1967).

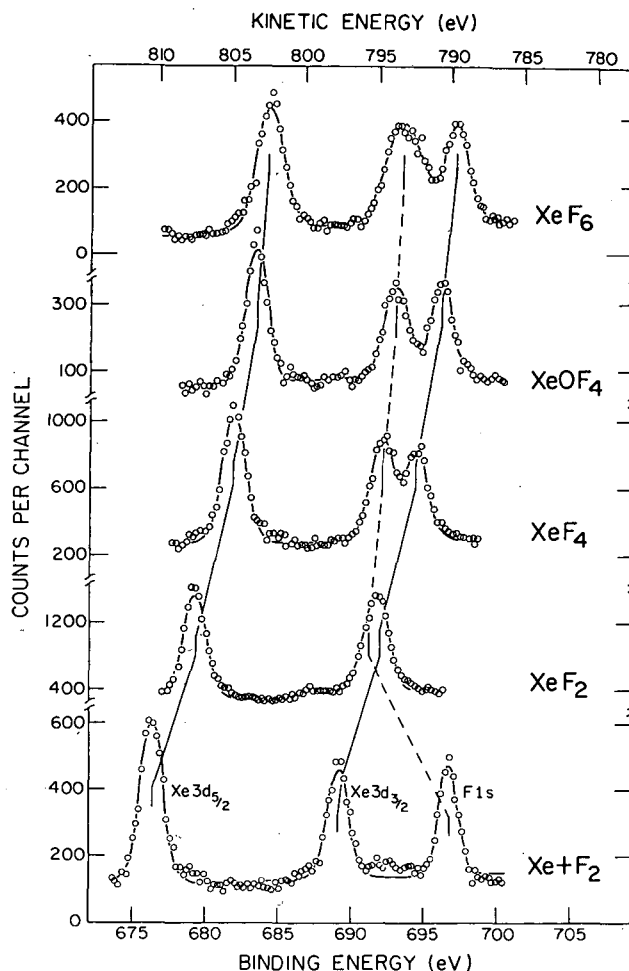


Figure 1. Photoelectron spectra of fluorine  $1s$  electrons and xenon  $3d$  electrons in the indicated compounds. Exciting radiation is  $\text{Al K}\alpha_{12}$ . The solid curves are least-squares fits to the data.

variation in the spin-orbit splitting among these compounds.

The shifts of the xenon  $3d_{5/2}$  binding energies are, with one exception, well within experimental error of the values determined by Karlsson, Siegbahn, and Bartlett.<sup>17</sup> For  $\text{XeF}_6$  we have found a value of  $7.64 \pm 0.04$  eV compared with their value of  $7.88 \pm 0.18$ , the difference being only slightly more than the combined uncertainties.

The uncertainties in the shifts and splittings given in Table I arise from several sources. The ratio of focusing voltage to electron kinetic energy (spectrometer constant) is known with an accuracy of somewhat better than one part per thousand. The corresponding uncertainty in the measured shifts is less than 0.01 eV. The major uncertainty arises from the statistical fluctuations in the raw data. We can obtain an estimate of this from the fact that about 1000 counts were taken for each peak and the full widths at half maximum of the peaks were 1 to 2 eV. Converting the widths to standard deviations and dividing by the square root of 1000 gives a standard deviation from this source of about 0.03 eV. We have obtained similar but more meaningful values from our least-squares analysis. Additional uncertainty arises because we have analyzed the data as if the peaks were Gaussian, which they are not. Analyses of synthetic spectra show that the error from this source is smaller than that from other sources.

## Discussion

**Point Charge Analysis.** The measured energy shifts have been analyzed by the method described by Davis, Shirley, and Thomas<sup>14</sup> and by others<sup>15,23</sup> to give a charge for each atom in the molecule. According to this procedure, the shift in binding energy,  $\Delta E_i$  of a core electron in atom  $i$  relative to the binding energy of the same electron in a neutral atom is

$$\Delta E_i = k_i q_i + \sum_{j \neq i} q_j (e^2/R_{ij})$$

Here  $k_i$  is the shift in core-electron binding energy when a valence electron is removed. The  $q$ 's are charges on the various atoms in the molecule, and  $R_{ij}$  is the distance between the  $i$ th and  $j$ th nuclei. In addition to the equations relating the binding energy shifts to the atomic charges, we have the requirement that the sum of the charges in a neutral molecule is zero; the appropriate equation is  $\sum q_i = 0$ . For the four molecules of interest there are, altogether, 13 equations for the four xenon shifts, four fluorine shifts, one oxygen shift, and four constraints of charge neutrality. There are nine unknown charges and three values of  $k$ , one each for xenon, fluorine, and oxygen. The values of  $k$  can be estimated from atomic Hartree-Fock calculations,<sup>24,25</sup> from other approximate calculations for atoms,<sup>26</sup> from the use of the equivalent cores assumption,<sup>27</sup> together with thermochemical data, or from other analyses of binding energy shifts.<sup>13-16</sup> (In some treatments,  $k$  is set equal to  $e^2\langle 1/r \rangle$ , where  $\langle 1/r \rangle$  is the expectation value of  $1/r$  for the valence electrons on the atom of interest. This approximation is valid only if there is no expansion or contraction of the valence shell when electrons are added or removed; see Appendix.) Alternatively, the values of  $k$  may be treated as unknown and the 12 unknown quantities derived from 12 of the equations; the 13th equation then provides a check on the overall consistency. The derived values of  $k$  may then be compared with those determined from other methods.

In our analysis we assume that none of the values of  $k$  are known. From the data for XeF<sub>4</sub> and XeF<sub>6</sub> and the requirements of charge neutrality we have six equations in six unknowns: two fluorine charges, two xenon charges,  $k_{Xe}$ , and  $k_F$ . When these equations have been solved, we can derive charges in XeOF<sub>4</sub> and the value of  $k_O$ . Finally, there remain two sets of data to determine the charges in XeF<sub>2</sub>: charge neutrality plus the fluorine shift, and charge neutrality plus the xenon shift. The agreement of the two sets of charges derived for XeF<sub>2</sub> and the agreement between the derived values of  $k$  and those determined from other methods provide the tests of our model. The results of the analysis are given in Table II as derived charges and in Table III as derived  $k$ 's together with  $k$  values from other methods. The various theoretical calculations of  $k$  are described briefly in the Appendix. We will defer discussion of the chemical significance of the charges for the moment, noting here only that the charge per fluorine is small (about  $-0.2 e$ ) and is nearly independent of the number of fluorines and that the charge on

Table II. Atomic Charges Derived from Binding Energy Shifts

|                   | $q_F/e$            | $q_{Xe}/e$      | $q_O/e$ |
|-------------------|--------------------|-----------------|---------|
| XeF <sub>2</sub>  | $-0.24^a$          | $0.48^a$        |         |
|                   | $-0.23^b$          | $0.47^b$        |         |
| XeF <sub>4</sub>  | $-0.24 \pm 0.01^c$ | $0.97 \pm 0.06$ |         |
| XeF <sub>6</sub>  | $-0.24 \pm 0.01$   | $1.43 \pm 0.08$ |         |
| XeOF <sub>4</sub> | $-0.24$            | $1.37$          | $-0.43$ |

<sup>a</sup> Derived from the assumption of charge neutrality and the xenon binding energy shift. <sup>b</sup> Derived from the assumption of charge neutrality and the fluorine binding energy shift. <sup>c</sup> Uncertainties, where quoted, reflect only uncertainties in the measurements and not those due to the assumptions made in the analysis.

Table III. Values of  $k$  from Experiment and Theory (eV/e)

| Element | This work        | Free atom values |        |        |        |        | Other ESCA values                 |
|---------|------------------|------------------|--------|--------|--------|--------|-----------------------------------|
|         |                  | $b$              | $c$    | $d$    | $e$    | $f$    |                                   |
| Xe      | $13.0 \pm 0.4^a$ |                  |        |        | $13.0$ | $14.9$ |                                   |
| F       | $34.4 \pm 1.2$   | $19.3$           | $18.6$ | $17.9$ | $20.9$ | $34.5$ | $27.6,^g 32.5,^h 30.0,^i 34.5,^j$ |
| O       | $22.5$           | $17.5$           | $16.8$ |        | $18.7$ | $30.6$ | $26.0,^k 25.8,^g 30.4,^l$         |

<sup>a</sup> See footnote c, Table II, for discussion of errors. <sup>b</sup> Reference 24. <sup>c</sup> Reference 26. <sup>d</sup> See Appendix for a discussion of how this number was calculated from the results given in ref 25. <sup>e</sup> Calculated from first and second ionization potentials of the appropriate species. See Appendix and ref 27. <sup>f</sup>  $e^2\langle 1/r \rangle$  from ref 28. <sup>g</sup> Reference 13, p 136. <sup>h</sup> Reference 14. <sup>i</sup> Reference 29. <sup>j</sup> Reference 16. <sup>k</sup> Reference 15.

oxygen in XeOF<sub>4</sub> is nearly twice that of fluorines. In addition, we see that the charges on fluorine in XeF<sub>2</sub> derived from two different sets of data (xenon shift, fluorine shift) are in agreement with one another. The point charge model meets this test in a satisfactory way.

For xenon there is excellent agreement between our derived value of  $k$ , 13 eV, and the thermochemical value, also 13 eV. Agreement of both of these with the theoretical value of  $\langle 1/r \rangle e^2$  (14.9 eV for the atomic 5p shell<sup>28</sup>) is fair. For fluorine, on the other hand, the agreement between our value (34.4) and all of the theoretical free atom values (18 to 21) is quite poor, whereas that with Mann's<sup>28</sup> value of  $\langle 1/r \rangle e^2$  (34.5 for the 2p shell) is excellent. For oxygen our value of 22.5 is intermediate between the various free atom values (17 to 19) and the value of  $\langle 1/r \rangle e^2$  (31 for the 2p shell).

The last column of Table III shows values of  $k_O$  and  $k_F$  derived from other ESCA experiments;<sup>13-16,29</sup> we see that these are all higher than the free atom values and less than or equal to the values of  $\langle 1/r \rangle e^2$ .

From these results we can conclude that the point charge model is self-consistent with respect to the derived charges. We will see below, however, that these charges are much smaller than those obtained by other experimental techniques. In addition, there are some discrepancies between the derived values of  $k$  and those obtained from other methods. In particular, the  $k$ 's derived by us and by others from ESCA measurements are consistently higher than those calculated for free atoms either using the equivalent cores approximation or by other theoretical methods.<sup>30</sup> The use of

(23) R. W. Shaw, Jr., T. X. Carroll, and T. D. Thomas, *J. Amer. Chem. Soc.*, **95**, 5870 (1973).

(24) Reference 11, pp 84-85.

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(26) L. C. Snyder, *J. Chem. Phys.*, **55**, 95 (1971).

(27) W. L. Jolly in "Electron Spectroscopy," D. A. Shirley, Ed., North-Holland Publishing Co., Amsterdam, 1972, p 629.

(28) J. B. Mann, "Atomic Structure Calculations. II. Hartree-Fock Wavefunctions and Radial Expectation Values: Hydrogen to Lawrencium," Los Alamos Scientific Laboratory, 1968.

(29) D. T. Clark, D. B. Adams, and D. Kilcast, *Chem. Phys. Lett.*, **13**, 439 (1972).

(30) Disagreements in the same direction have previously been noted by Snyder, ref 26.

lower  $k$  values in our calculations would lead to larger values of the derived charges in better agreement with other experimental results but at the expense of self-consistency. In particular, the use of  $k_F$  as small as is suggested by the free atom values (18 to 21) leads to charges that are physically unreasonable in most cases. It is entirely possible that a value of  $k$  appropriate to a free atom is not appropriate for that atom in a molecule.

A number of assumptions are made in the use of the point charge model, any one of which might lead to error. These are that relaxation energies are the same for all of the molecules studied, that the core-electron binding energy varies linearly with the atomic charge (that is,  $k$  is a constant), that all charges are spherically distributed about their atomic centers, that each atom lies outside the sphere of charge around the other atoms, and that effects of overlap populations can be ignored. We are not yet in a position to assess the importance of these and must, therefore, be somewhat cautious about the atomic charges determined by this method.

With these reservations in mind, we can summarize the results of the point charge analysis: (1) the charge per fluorine is  $-0.24 e$  regardless of compound; (2) the charge on oxygen in  $\text{XeOF}_4$  is nearly twice the charge on the fluorine. The positive charge at the xenon nucleus does indeed increase with the number of fluorine atoms in the molecule, as the structural findings had already implied. Surprisingly, however, our analysis shows that the positive charge build-up at the xenon nucleus is simply proportional to the number of fluorine atoms bound to the xenon. This result implies that regardless of the number of fluorine atoms previously attached to the xenon atom, each additional fluorine atom removes the same charge as did the previous ones. One might expect the withdrawal of negative charge by the fluorine to become more difficult as the positive charge on the xenon increases. Although the effect observed may be an artifact of the point charge analysis, we believe, on the basis of the following supportive evidence, that this surprising finding is real.

The average Xe-F bond energy is essentially the same in all xenon fluorides ( $30 \text{ kcal mol}^{-1}$  per bond).<sup>2</sup> This constancy has not previously been interpreted; it is likely, however, that it is related to the effect we have observed. If each fluorine atom attachment to xenon involves a constant electron transfer, as our results and model imply, it is perhaps not surprising that the thermochemical bond energy is constant.

If the constant electron transfer feature is real, we would expect to find similar effects in electronically related nonnoble gas compounds. Consider, for example, the formation of the halogen fluorides. The central atom of the monofluorides can be thought of as a pseudo-rare-gas atom and the subsequent formation of the trifluorides and pentafluorides *via* a three-center bonding scheme is analogous to the formation of rare gas difluorides and tetrafluorides. If the constant electron transfer is due to "independence" of the perpendicular, three-center bonds, we could expect the two equivalent fluorines in  $\text{BrF}_3$  each to have the same charge as each of the four equivalent fluorines in  $\text{BrF}_5$ . The X-ray photoelectron spectra of these molecules have been measured in this laboratory and are currently being analyzed. Finally, it is known that the thermo-

chemical relationships of the halogen fluorides resemble those of the xenon fluoride sequence, in that the bond energy per halogen-fluorine bond (after the first one) is almost constant for each series:<sup>2b</sup>  $\text{ClF} \rightarrow \text{ClF}_3 \rightarrow \text{ClF}_5$ ;  $\text{BrF} \rightarrow \text{BrF}_3 \rightarrow \text{BrF}_5$ ;  $\text{IF} \rightarrow \text{IF}_3 \rightarrow \text{IF}_5$ .

As the Cl atom in ClF might be thought of as pseudo-argon, so might S in  $\text{SF}_2$  and P in  $\text{PF}_3$ , as has been noted elsewhere.<sup>23</sup> Since the relationships of  $\text{SF}_4$  and  $\text{SF}_6$  to  $\text{SF}_2$  are like those of  $\text{XeF}_2$  and  $\text{XeF}_4$  to Xe, we would expect to find some features of the xenon fluoride behavior appearing in the sulfur fluorides. In an analysis of the  $\text{SF}_4$  and  $\text{SF}_6$  photoelectron spectra,<sup>23</sup> it is pointed out that  $\text{SF}_4$  may be represented as possessing two electron-pair S-F bonds (equatorially) and two three-center, four-electron S-F bonds (axially). The point charge analysis gives a charge of  $-0.15 e$  for each equatorial (electron-pair bound) fluorine atom and  $-0.24 e$  for each axial (single-electron bound) fluorine atom. In  $\text{SF}_6$ , which may be represented as a resonance hybrid of two electron-pair and four single-electron S-F bonds, the point charge for the fluorines, calculated on the basis of the  $\text{SF}_4$  results, assuming constancy of electron transfer as in the xenon fluoride case, is  $-0.21 e$ . This compares well with the charge of  $-0.22 e$  derived in the point charge analysis of the data for  $\text{SF}_6$ .

In short, we see that the bonding of fluorine ligands to noble gas or pseudo-noble-gas species by single-electron bonding involves an electron transfer to a fluorine atom which does not vary with the number of F atoms attached.

It may be that this independence of the charge transfer from the noble gas or pseudonoble gas atoms is a result of canceling effects. On the one hand, removal of  $p$  electrons from the central atom by a given pair of fluorine atoms will make the remaining  $p$  electrons more tightly bound. On the other, charge back donated from the fluorine *via*  $\pi$  bonding will make the remaining  $p$  electrons less bound. If these effects balance one another, the charge removed per fluorine could be independent of the number of fluorine ligands.

**The Equivalent 'Cores Model.** According to the "equivalent cores" or "thermochemical" model proposed by Jolly and Hendrickson<sup>31</sup> for estimating core-electron binding energy shifts, one may replace the core of an atom that has an inner-shell electron vacancy with the core of the atom of one higher atomic number. Core level binding energy shifts can then be calculated from known thermochemical values for the species involved. Using some reasonable assumptions, Jolly<sup>27</sup> has shown that the shift in xenon core binding energy per fluorine (about 1.3 eV, or 31 kcal/mol) should be, and is, equal to the average xenon-fluorine bond energy (30 kcal/mol).

For fluorine binding energies the predictions of the simple equivalent cores approximation disagree with the measured core-electron binding energy shifts by several electron volts in some cases.<sup>27</sup> Shaw and Thomas<sup>32</sup> have suggested that these discrepancies arise because of Jolly's assumption that the heats of formation of all neon-cation adducts (relative to free neon plus the

(31) W. L. Jolly and D. N. Hendrickson, *J. Amer. Chem. Soc.*, **92**, 1863 (1970).

(32) R. W. Shaw, Jr., and T. D. Thomas, *Chem. Phys. Lett.*, **22**, 127 (1973).



cation) are the same. Abandoning this assumption Shaw and Thomas have used the fluorine core-electron binding energies reported here to calculate heats of formation for the adducts of neon with  $\text{XeF}^+$  (1.7 eV),  $\text{XeF}_3^+$  (2.4 eV), and  $\text{XeF}_5^+$  (4.0 eV). All of the adducts are unstable and the stability decreases as the number of fluorine atoms in the cation increases.

### Other Experimental and Theoretical Results

**Comparison with SCF Calculations.** A limited basis set SCF calculation for the xenon fluorides has been made by Basch, Moskowitz, Hollister, and Hankin.<sup>5</sup> According to the authors, this calculation is not expected to reproduce absolute values but, rather, trends in properties. Further, as the authors show by comparison of results of some of their calculations with those using more complete basis sets, the absolute accuracy is better for valence than for core electrons.

The experimentally measured shifts in binding energy for the Xe 3d electrons for Xe,  $\text{XeF}_2$ ,  $\text{XeF}_4$ , and  $\text{XeF}_6$  are about half as large as the calculated values for the orbital energies. The calculated shift per fluorine increases slightly while the experimental values decrease with increasing number of fluorines. Similarly, the calculated shifts for the F 1s binding energies are much larger than the experimental values and constant while the experimental numbers decrease with increasing numbers of fluorine ligands. We are, of course, assuming in this comparison that differences in relaxation energy associated with core ionization in these molecules are insignificant, and hence we may compare experimental binding energy shifts with calculated orbital energy shifts.

Basch, *et al.*, have reported the results of a Mulliken population analysis of their calculation; these are compared with our experimentally derived atomic charges in Table IV. The SCF fluorine charges are two to

**Table IV.** Comparison of Atomic Charges ( $q_F$ ) in Xenon Fluorides by Different Methods

|                 | Mössbauer <sup>a</sup> | Nmr <sup>b</sup> | SCF <sup>c</sup> | Photoelectron spectroscopy <sup>d</sup> |
|-----------------|------------------------|------------------|------------------|---|
| $\text{XeF}_2$  | -0.72                  | -0.70            | -0.652           | -0.24                                   |
| $\text{XeF}_4$  | -0.75                  | -0.55            | -0.614           | -0.24                                   |
| $\text{XeF}_6$  |                        | -0.40            | -0.576           | -0.24                                   |
| $\text{XeOF}_4$ |                        | -0.40            |                  | -0.24                                   |

<sup>a</sup> Charge is derived from measurements on xenon. Reference 3.  
<sup>b</sup> Reference 4a. <sup>c</sup> Reference 5. <sup>d</sup> This work.

three times as large as those derived from our work and decrease with increasing xenon coordination while ours remain constant. This sort of discrepancy has been noted by Basch, *et al.*, and attributed in part to the tendency of single-configuration MO calculations to overestimate charge transfer.

It is also likely that the limited basis set used by Basch, *et al.*, is responsible for some of the disagreement between the experimental and theoretical results. The highest occupied orbitals on  $\text{XeF}_2$ ,  $\text{XeF}_4$ , and  $\text{XeF}_6$  are, respectively, the  $10\sigma_g$ ,  $10a_{1g}$ , and  $8a_{1g}$ ; according to the calculation these are nearly all fluorine 2p with little

xenon participation. With a more flexible basis set, there would be the possibility for back donation of these fluorine electrons to the central xenon with a lowering of both the calculated orbital energy shifts and the calculated charge transfer and better agreement with observations.

**Far Ultraviolet Absorption Spectroscopy Comes, *et al.***<sup>33</sup> have recently reported the results of their far ultraviolet absorption measurements on Xe,  $\text{XeF}_2$ , and  $\text{XeF}_4$ . Two of their observations are of interest relating to our work. First, they observe shifts in the series Xe,  $\text{XeF}_2$ , and  $\text{XeF}_4$  of the energies of the transitions from the 4d to Rydberg type states. The positions of those latter states are relatively insensitive to atomic charges, whereas the 4d states are essentially core levels and shift with the atomic charge. Thus, the shifts of these transitions should correspond closely to the observed xenon photoelectron shifts. They observe for  $\text{XeF}_2$  and  $\text{XeF}_4$ , relative to Xe, 2.5 and 5.0 eV (4d-6p) and 2.9 and 5.8 eV (4p-6s), respectively, close to the results of our measurements. One cannot make a direct comparison because the 6s and 6p states do shift slightly, possibly because of interaction with the negative fluorine ligands.

Second, fine structure in the 4d transitions is observed and attributed to ligand field splitting of the 4d levels. The observed splittings are only  $1/3$  the values calculated by Basch, *et al.*, again pointing out that the SCF calculations probably overestimate the charges.

We note that the ligand field splittings of the 4d states are of the order of 0.25-0.5 eV. Since the axial and tetragonal interactions involve terms in a crystal field potential proportional to the expectation values  $\langle r^2 \rangle_{4d}$  and  $\langle r^4 \rangle_{4d}$ , we can estimate that the splittings of the 3d levels will be smaller by at least an order of magnitude. In other words, the observed 3d spin-orbit splittings and line widths will not show noticeable ligand field effects.

**Comparison with Mössbauer and Nmr Results.** Summarized in Table IV are the results of three experimental methods used to determine the apparent charge distributions in xenon fluorides: nuclear magnetic resonance ( $^{19}\text{F}$ ), Mössbauer spectroscopy ( $^{129}\text{Xe}$  and  $^{131}\text{Xe}$ ), and X-ray photoelectron spectroscopy. The analyses of the experimental results in turn involve three models: Karplus and Das' method of correlation of gross orbital populations with nmr chemical shifts,<sup>34</sup> Townes and Dailey's correlation of nuclear quadrupole coupling constants with hybridization and electron transfer,<sup>35</sup> and the point charge model used to analyze core-electron binding energy shifts observed in photoelectron spectroscopy. In essence all three depend on the same basic assumption that the charges can be represented as fractional transfer of electrons between the xenon 5p and fluorine 2p bonding orbitals, and hence one would hope for at least a fair agreement between the results of the three methods.

The  $^{19}\text{F}$  nmr results have been summarized by Hindman and Svirmickas<sup>4a</sup> and the  $^{129}\text{Xe}$  Mössbauer spectroscopic results by Perlow.<sup>3</sup> The main assumption underlying the analysis of nmr shifts is that the

(33) F. J. Comes, R. Haensel, U. Nielsen, and W. H. E. Schwarz, *J. Chem. Phys.*, **58**, 516 (1973).

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

(35) C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).

predominant contribution to the observed chemical shift results from the paramagnetic shielding,  $\sigma^{(p)}$

$$\sigma^{(p)} = \sigma^{(o)}[(P_{xx} + P_{yy} + P_{zz}) - \frac{1}{2}(P_{xx}P_{yy} + P_{yy}P_{zz} + P_{zz}P_{xx})] \quad (1)$$

$$\sigma^{(o)} = -\frac{2e^2\hbar^2}{3\Delta E m^2 c^2} \langle 1/r^3 \rangle_{2p} \quad (2)$$

$\sigma$  is the shift, the  $P_{ii}$  are p orbital populations, and  $\Delta E$  is an "average excitation energy." There is also a diamagnetic shielding constant, given by

$$\sigma^{(d)} = \frac{e^2}{3mc^2} \sum_k \langle 1/r \rangle_k \quad (3)$$

in which the sum is over all electrons in the molecule. This latter term has led to the anticipation that successful correlations between nmr and core-electron binding energy shifts might occur. The uncertainty of the paramagnetic contribution to the chemical shift has made it difficult to establish these correlations.

The assumption that double bonding and s hybridization can be neglected leads to the simple result

$$\sigma^{(p)} = \sigma^{(o)}(1 - I) \quad (4)$$

where  $I$  is the ionic character of the bond orbital. For fluorine,  $\sigma^{(o)} = -863$  ppm (the observed shift of  $F_2$  relative to  $F^-$ ). From the observed shifts of the  $^{19}F$  resonances, then, approximate charges may be calculated. The results, given in Table IV, are much higher than the charges we have obtained. One major reason for the disagreement is the neglect of  $\sigma^{(d)}$  in the original nmr analysis. An estimate of the importance of  $\sigma^{(d)}$  can be made by replacing eq 3 with

$$\sigma^{(d)} \approx \frac{e^2}{3mc^2} \sum_i \frac{Z_i}{r_i} \quad (5)$$

a sum over the other atoms  $i$  in the molecule, each with  $Z_i$  electrons and at a distance  $r_i$  from the  $^{19}F$  nucleus. The results of such an estimate show that  $XeF_2$ ,  $XeF_4$ , and  $XeF_6$  should have diamagnetic shifts of the order of +260, +310, and +380 ppm, respectively, relative to  $F^-$ . The net result of including this factor in the analysis is to increase the magnitude of  $\sigma^{(p)}$  and reduce substantially the derived charges. In addition, the use of  $\sigma^{(o)}$  equal to  $-863$  ppm is questionable since  $\sigma^{(o)}$  is known to increase as fluorine bonds to heavier atoms.<sup>36</sup> This is supported by the observation that the  $\sigma$  of  $XeF_6$ , corrected for  $\sigma^{(d)}$ , is actually more negative with respect to  $F^-$  than is  $F_2$ , the shift of the latter being taken to indicate pure covalency and a charge of zero. (The calculation gives, if  $\sigma^{(d)}(XeF_6) = 380$  ppm relative to  $F^-$ ,  $\sigma^{(p)} = -933$  ppm, as compared with  $\sigma^{(p)}(F_2) = -863$  ppm.) Clearly, this must be accounted for before one is to analyze the shifts and derive charges. Because of the difficulty of evaluating  $\sigma^{(d)}$  precisely and because of the uncertain assumptions involved in the use of eq 4, the prospects of deriving realistic charge distributions from the nmr data are poor. It is not valid to ignore  $\sigma^{(d)}$  relative to  $\sigma^{(p)}$  for these molecules.

The  $^{129}Xe$  Mössbauer spectrum has been reported by Perlow<sup>3</sup> for  $XeF_2$  and  $XeF_4$ . In his analysis, he as-

sumed that a quadrupole coupling constant of 1740 MHz corresponds to a  $5p_z$  hole and  $-870$  MHz to a  $5p_x$  or  $5p_y$ . On the basis of these assumptions, he derived apparent charges ("p holes") from the observed quadrupole splittings. The results, given in Table IV, are, again, much higher than ours.

As Perlow has mentioned, at least two corrections were neglected in his calculation of charges. One is the dependence of  $\langle r^{-3} \rangle_{5p}$  on charge state<sup>36</sup> (which may be as large as 15% increase per charge removed); the other is the lattice contribution to the electric field gradient. The field gradient  $q$  is written as

$$q = (1 - R)q_{val} + (1 - \gamma_{\infty})q_{lat}$$

where  $R$  and  $\gamma_{\infty}$  are the internal and external (Sternheimer) antishielding factors and  $q_{val}$  and  $q_{lat}$  are respectively the contributions of the valence electrons and the lattice to the field gradient.

For  $XeF_2$ , the major contribution to  $q_{lat}$  comes from negative charge on the two fluorines bonded to the xenon. For a xenon-fluorine distance of 2 Å,  $q_{lat}$  is roughly 0.1% of  $q_{val}$ . Calculations<sup>37</sup> for  $Cs^+$  and  $I^-$  indicate that  $\gamma_{\infty}$  is of the order of  $-100$ , making the quantity  $(1 - \gamma_{\infty})q_{lat}$  nonnegligible compared to  $q_{val}$ . Since  $q_{lat}$  opposes  $q_{val}$ , ignoring it leads to an underestimate of  $q_{val}$ , and hence to a calculated charge on the xenon atom that is too small. Perlow argued, however, that since the effect of  $q_{lat}$  and that of the change in  $\langle r^{-3} \rangle$  with charge are of comparable magnitude and of opposite sign it was better to neglect both.

The effect of  $q_{lat}$  is, however, probably not so great as has been indicated above and we cannot, therefore, assume that this correction cancels that due to changes in  $\langle r^{-3} \rangle$  with charge. The nearest neighbor nonbonded fluorines reduce  $q_{lat}$  by about  $1/3$ . The value of  $\gamma_{\infty}$  is sensitive to effects caused by the extension of the p orbitals beyond the perturbing charges and may be significantly overestimated. Correction for these effects will cause the derived charges to be lower than Perlow has calculated. It is unlikely, however, that these corrections will bring the results of Mössbauer spectroscopy in accord with our results.

We note that the correspondence between the quadrupole coupling constant and the number of p holes is based on a measurement of the quadrupole coupling constant for xenon with a 5p electron excited to the 6s state. It is assumed in the analysis of the data for the compounds that the antishielding factor  $R$  for the compounds is the same as that for the atom. If this is not so, the derived charges will be in error. We do not, however, see any reason why the antishielding factor should be independent of valence electron distribution.

The possible sources of error in the point charge analysis have been discussed above. We have attempted to estimate some of these but have not found any that can account for the factor of 3 discrepancy between our results and the Mössbauer results.

That the quadrupole splitting measured by Mössbauer spectroscopy is sensitive to  $\langle 1/r^3 \rangle$  and the core binding energy shifts are sensitive to  $\langle 1/r \rangle$  provides a possible explanation for the discrepancies between the charges derived by the two methods. The quadrupole splitting will be very sensitive to electrons withdrawn from the 5p

(36) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill, New York, N. Y., 1955, p 239.

(37) R. E. Watson and A. J. Freeman, *Phys. Rev.*, **135**, A1209 (1964).

orbitals of xenon but relatively insensitive to charge that is back donated into outer orbitals of greater radial extent. The core bonding energy shifts, on the other hand, will be relatively sensitive to both of these effects. Charges derived on the basis of the number of p holes may, therefore, be too large.

### Conclusion

The point charge analysis of the core-electron binding energy shifts indicates that the charge removed per fluorine is about 0.24 e and is independent of the number of fluorines. This constancy of charge transfer is surprising but, in our interpretation, is consistent with some of the thermochemical properties of these compounds. The charges derived are substantially smaller than those predicted from Hartree-Fock calculations with a limited basis set or with those determined from Mössbauer spectroscopy. It seems likely that part of this discrepancy would be removed if one allowed for substantial back donation of charge from the fluorines to the xenons *via*  $\pi$  bonds. Such a mechanism might also help account for the constancy of charge withdrawal per fluorine atom.

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### Appendix

There are a variety of methods for calculating  $k$ , the change in core-electron binding energy upon removal of one valence electron. To illustrate this we take a fluorine ion as an example. We use the following notation: F = a neutral fluorine atom,  $F^-$  = a fluorine atom with an added valence electron,  $F^{*+}$  = a fluorine atom with a core hole,  $F^*$  = a fluorine atom with a core hole and an added valence electron.

**Hartree-Fock Methods** If Hartree-Fock calculations are available for all of the four species shown above, it is easy to show that

$$k = E(F^{*+}) - E(F) + E(F^-) - E(F^*)$$

where  $E(F^{*+})$ , etc., refer to the Hartree-Fock energy for the indicated species. This method has been used by Siegbahn, *et al.*, to give a value of 19.3 eV<sup>24</sup> for the 1s binding energy difference between the F atom and the  $F^-$  ion. If calculations are available for the species F and  $F^-$  only, we may use Koopmans' theorem to estimate  $k$

$$k \simeq \epsilon(F^-) - \epsilon(F)$$

where  $\epsilon$ 's are the orbital energies (negative quantities) of the Hartree-Fock calculations. Bagus' results give 15.0 eV for this difference.<sup>25</sup> This calculation assumes that the relaxation energy for the two species is the same; it is, however, greater for  $F^-$ , which has one more valence electron. Comparing Bagus' calculated orbital energies with experimental ionization potentials, we find a relaxation energy of 2.85 eV per valence electron. The corrected value of  $k$  is then 17.9 eV.

In some treatments it is assumed that  $k$  is equal to  $e^2\langle 1/r \rangle$ , where  $\langle 1/r \rangle$  is the expectation value of  $\langle 1/r \rangle$  for the valence electrons on the atom of interest. This quantity is easily taken from tables of atomic Hartree-Fock calculations<sup>28</sup> and in some cases is in agreement with values derived from ESCA measurements. In general, however, this method is not justified, as the following argument will demonstrate. The potential energy arising from the interaction of a 1s electron with the 2p electrons on  $F^-$  is  $6e^2\langle 1/r \rangle_-$ ; that for a 1s electron of F is  $5e^2\langle 1/r \rangle_0$ . The negative of the difference between these two quantities is the change in 1s binding energy, or  $k$ . Thus

$$\begin{aligned} k &= 6e^2\langle 1/r \rangle_- - 5e^2\langle 1/r \rangle_0 \\ &= e^2\langle 1/r \rangle_- + 5e^2(\langle 1/r \rangle_- - \langle 1/r \rangle_0) \end{aligned}$$

From Bagus' wave functions<sup>25</sup> we find that  $e^2\langle 1/r \rangle_-$  is 31.6 eV and from Mann's table<sup>28</sup> that  $e^2\langle 1/r \rangle_0$  is 34.6 eV. We then have that  $k$  is 16.7, quite different from the value of  $e^2\langle 1/r \rangle_0$ , but in reasonable agreement with the values mentioned above. The importance of the dependence of valence radius on valence population has been noted by Snyder.<sup>26</sup>

**Equivalent-Cores Approximation.** Jolly<sup>27</sup> has shown that the change in core binding energy  $\epsilon$  of a species with ionic charge  $n$  and atomic number  $Z$  can be written as

$$\epsilon(n, Z) - \epsilon(n + 1, Z) = IP(n, Z) - IP(n + 1, Z + 1)$$

The symbol IP refers to the ionization potential of the least bound electrons on the indicated species. From the electron affinity of fluorine (3.4 eV) and the first ionization potential for neon (21.6 eV), we have  $k = 18.2$  eV, in agreement with the Hartree-Fock values.

**Other Methods.** Snyder<sup>26</sup> has generalized the Slater-Zener expression for the total energy of an atom to obtain values of  $k$ . For fluorine, he finds  $k = 18.6$ , also in agreement with that obtained by the other methods.

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