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Short communication

The Core Electron Binding Energies of Oxygen Difluoride

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All of the oxygen 1s binding energies which have been reported for oxygen-containing compounds are lower than that of molecular oxygen.** In all of the oxygen compounds which have been studied, the oxygen atoms are bonded to less electronegative atoms and are probably negatively charged. In this study, we determined the oxygen 1s and fluorine 1s binding energies of gaseous OF_2 , in which the oxygen atom is believed to be positively charged.² These data and the 1s binding energies of O_2 and F_2 ³ can be used with the point charge potential equation¹ to calculate the atomic charges of OF_2 . We can also use the data, with the equivalent cores approximation,^{4,5} to calculate the heat of formation of the gaseous F_3^+ ion.

*For correspondence.

**Siegbahn et al.¹ have reported that the O 1s binding energy of NO is 0.2 eV greater than the more intense line of O_2 ; from their data one calculates that it is 0.2 eV lower than the center of gravity of the O_2 doublet.

EXPERIMENTAL

Oxygen difluoride from the Allied Chemical Corporation was used as received. Its infrared spectrum agreed with the literature.⁶ The XPS spectra were obtained with the Berkeley iron-free, double-focusing magnetic spectrometer.⁷ Magnesium K_{α} X-rays (1253.6 eV) were used as the photo-ionizing radiation. Sample pressures were maintained at approximately 40 μ . The Ne 1s line (870.23 eV) was used as a reference of OF_2 and the Ar $2p_{3/2}$ line (248.45 eV) for O_2 . The sample gas and the reference gas were scanned alternately. The spectrometer constant was determined separately for each spectrum by use of the energy difference between the Ne 1s and Ne 2s lines (821.95 eV). The positions of the peaks were determined by a least-squares fitting of the data to Lorentzian line shapes.

RESULTS AND DISCUSSION

The experimental binding energies are listed in Table 1. The value

TABLE 1

EXPERIMENTAL BINDING ENERGIES

Compound	E_B , eV	
	O 1s	F 1s
OF_2	545.19	694.93
O_2	543.58	
F_2		696.71 ^a

^aFrom Ref 3.

for O_2 is the weighted average of the two peaks of the spin doublet and is in good agreement with the value 543.5 eV calculated from the data of Siegbahn et al.¹ The value for F_2 was reported by Carroll et al.³ The

oxygen 1s binding energy of OF_2 is 1.61 eV more positive than that of O_2 and is the highest oxygen 1s binding energy known. The fluorine 1s binding energy of OF_2 is higher than that of most fluorine compounds; however a few compounds, in which fluorine atoms are bonded to very electro-negative or π -electron-withdrawing groups, have still higher fluorine 1s binding energies. For example, CF_4 , COF_2 , and NOF_3 have fluorine 1s binding energies of 695.36, 695.26, and 695.13 eV, respectively.⁸

The shift in the fluorine 1s binding energy between OF_2 and F_2 may be expressed by the point-charge potential equation,¹

$$\Delta E_B = kQ_F + \frac{Q_F}{R_F} - \frac{2Q_F}{R_O} \quad (1)$$

in which k is a constant to be evaluated theoretically, Q_F is the fluorine atom charge, and R_F and R_O are the distances from one fluorine atom to the center of charge on the other fluorine atom and the oxygen atom, respectively. In writing equation 1, we make the assumption (which we believe to be very reasonable) that the relaxation energy associated with the F 1s ionization of OF_2 is the same as that of F_2 . We use the equivalent cores approximation^{4,5} to calculate $k = 20.83$; i.e., we assume that k is one-half the energy of the following reaction,

As a first approximation, we shall assume that R_F and R_O are equal to the F-F and F-O internuclear distances, respectively. Equation 1 can then be solved by substitution of the calculated value of k , experimental values of the internuclear distances,⁹ and the value of ΔE_B calculated from data in Table 1. We thus calculate $Q_F = -0.26$ and $Q_O = +0.52$. These values are considerably greater in absolute magnitude than the values $Q_F = -0.12$ and $Q_O = +0.23$ obtained by Rothenberg and Schaefer²

from a Mulliken population analysis based on ab initio SCF calculations for OF_2 . We believe our calculated charges are too large because of the use of internuclear distances for R_F and R_O . In OF_2 , the negative charge of each fluorine atom is concentrated on the side of the atom farthest from the oxygen atom, and the positive charge of the oxygen atom is concentrated on the side farthest from the fluorine atoms.* Thus the distances from a given fluorine nucleus to the effective centers of charge of the other two atoms (R_F and R_O) are greater than the corresponding internuclear distances. We find that if we use R_F and R_O values equal to the internuclear distances plus $0.5 \text{ \AA}$, the charges calculated from equation 1 are considerably lower, viz. $Q_F = -0.16$ and $Q_O = +0.32$. Clearly the problem of determining the effective centers of charge of atoms deserves further study.

According to the equivalent cores approximation,^{4,5} the difference between the oxygen 1s binding energies of OF_2 and O_2 is equal to the heat of the reaction:

All the heats of formation are known except that of F_3^+ . Use of the values of $340 \text{ kcal/mole}^{11}$ and $-4.4 \text{ kcal/mole}^{12}$ for the heats of formation of OF^+ and OF_2 yields a value of 373 kcal/mol for the heat of formation of F_3^+ . This heat of formation corresponds to $\Delta H^\circ = 49 \text{ kcal/mol}$ for the dissociation

* This type of distribution of the excess electron density on the fluorine atoms of LiF and HF can be seen in the atomic difference plots of Streitwieser and Owens.¹⁰

of an F^+ ion from F_3^+ .

The corresponding dissociation reactions for ClF_2^+ , BrF_2^+ , and IF_2^+ have much higher ΔH° values (172, 167, and 240 kcal/mol, respectively).¹¹

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