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Core Electron Binding Energies of Thiazyl Fluoride and Other Sulfur Compounds

By W. L. Jolly, M. S. Lazarus, and O. Glemser1)

With 1 Figure

Abstract. Core electron binding energies were measured for the atoms in NSF_3, SF_5Cl, and S_2Cl_2. These data and similar data from the literature for other sulfur compounds were correlated by the point charge potential method using CHELEQ atomic charges. The results indicate that the bonding in a wide variety of sulfur compounds can be explained using only s and p valence orbitals. The low fluorine 1s binding energies observed for NSF_3 and OSF_2 are attributed to "no-bond" resonance structures.

Introduction

It has often been asserted that the 3d orbitals of the second row elements, Si, P, S, and Cl, can be significantly involved in pπ→dπ bonding, especially when these atoms are bonded to electronegative atoms such as nitrogen, oxygen, and fluorine 2). However, a recent study of volatile compounds of silicon and germanium by x-ray photoelectron spectroscopy showed that the electron distribution in these compounds is not affected strongly, if at all, by pπ→dπ bonding 3). It was therefore of interest to apply this same technique to volatile compounds of sulfur. Of particular interest is thiazyl trifluoride, for which an N≡S triple bond has been proposed 4). In this investigation, we determined core binding energies for each of the atoms in the following compounds: NSF_3, SF_5Cl, and S_2Cl_2.

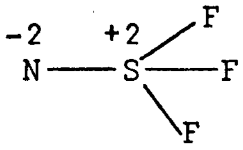
Experimental

The NSF_3 was prepared in Göttingen in the laboratory of Prof. O. Glemser 5). After receipt in Berkeley, a simple distillation in vacuo yielded a material having the correct infrared spectrum 5) and a vapor pressure of 85 torr at -65° (literature, 85 torr) 7). The other compounds were obtained from commercial sources and were distilled before use.

Spectra were obtained with the Berkeley iron-free, double-focuing magnetic spectrometer$^{8)}$. Magnesium K_α x-rays (1253.6 eV) were used, and the argon $2p_{3/2}$ photoline (E_B = 248.45 eV) was used as a reference standard. The measured sulfur $2p_{3/2}$ binding energies, as well as literature$^{9-12)}$ values for all the other volatile sulfur compounds for which data are available, are given in Table 1. The nitrogen 1s binding energy of NSF_3 is 406.23 eV; the fluorine 1s binding energies of NSF_3 and SF_5Cl are 695.68 and 695.13 eV, respectively, and the chlorine $2p_{3/2}$ binding energies of SF_5Cl and S_2Cl_2 are 207.27 and 206.64 eV, respectively.

Results and Discussion

For each of the compounds in Table 1 we have calculated the atomic charges using the CHELEQ electronegativity equalization procedure$^{13)}$. For most of the compounds, these calculations were straightforward. However, in the case of NSF_3, the nature of the bonding is disputable, and we calculated atomic charges for three different electronic structures, I, II, and III. In structure I, each



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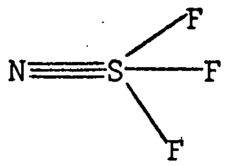

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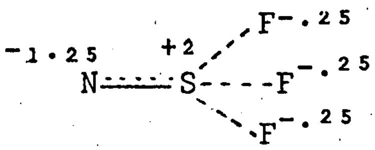
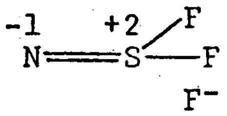
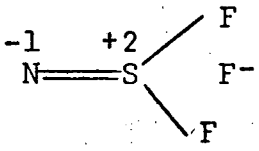
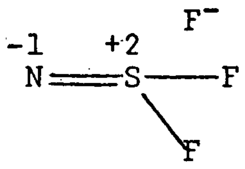


III

atom has exactly an octet of valence electrons, corresponding to formal charges of +2 and -2 on the sulfur and nitrogen atoms, respectively. Structure II is the same as structure I, except that two $p\pi \rightarrow d\pi$ bonds have been formed between the nitrogen and sulfur atoms, yielding zero formal charges on these atoms. Structure III is an equal-weighted hybrid of structure I and the following three "no-bond" resonance structures. In structure III,







the N-S bond order is 1.75, the S-F bond order is 0.75, and all the atoms have finite formal charges.

Table 1

Sulfur $2p_{3/2}$ Binding Energies and Calculated Sulfur Atom Charges for Gaseous Sulfur Compounds

Compound	$E_B(S\ 2p_{3/2})$, eV	Q_S	Ref
SF_6	180.4	1.14	9)
SF_5Cl	179.1	1.07	This work
SF_4	177.6	0.79	10)
NSF_3	176.8	0.82	This work
OSF_2	176.2	0.68	9)
SO_2	174.8	0.57	9)
S_2Cl_2	171.4	0.03	This work
OCS	170.6	-0.03	11)
H_2S	170.2	-0.12	9)
C_4H_4S	169.9	-0.06	12)
CS_2	169.8	-0.04	9)

The point charge potential equation has been shown to be very useful for correlating and calculating core binding energies[9].

$$E_B = kQ_A + \sum_{i \neq A} (Q_i/R_i) + \ell$$

In this equation, E_B is the core binding energy, Q_A is the atomic charge on the core-ionizing atom, Q_i is the atomic charge on an atom situated a distance R_i from the core-ionizing atom, and k and ℓ are empirical constants. By using this equation in conjunction with the atomic charges calculated for structures I, II and III, we have calculated[15] the corresponding binding energies for the sulfur $2p_{3/2}$, nitrogen 1s and fluorine 1s electrons in NSF_3. The deviations of these calculated binding energies from the experimental values are given in Table 2. The data clearly

Table 2

Deviations of Calculated and Experimental Core Binding Energies for NSF_3

Structure	E_B(calc) - E_B(expt), eV		
	S	N	F
I	0.84	-24.74	5.32
II	-4.21	3.86	-1.28
III	0.15	-4.27	-0.15

indicate that structure III is a much better representation of NSF_3 than either structure I or structure II. We conclude that "no-bond" resonance is of considerable importance in NSF_3 and that it is unnecessary to involve the use of sulfur 3d orbitals in the bonding.

It remains to explain the fact that the stretching force constant of the N-S bond in NSF_3 corresponds to an effective bond order of 2.7 according to the empirical relation of Siebert[6,16]), whereas structure III has an N-S bond order of only 1.75. The apparent discrepancy disappears when one recognizes that the strength of a bond increases not only with increase in bond order, but also with increase in the separation of charge between the bonded atoms. The charges of the S, N, and F atoms as calculated for structure III are 0.82, -0.44, and -0.13, respectively. The high polarity of the N-S bond apparently contributes about 1 unit to the effective bond order. It is interesting to note that the results of a recent u.v. photoelectron spectroscopic study[17]) of NSF_3 are also consistent with high electron density on the nitrogen atom.

Figure 1 shows a plot of experimental E_B values for sulfur $2p_{3/2}$ electrons against the corresponding calculated values. The atomic charges for OSF_2 were calculated using a structure analogous to structure III. The low standard deviation of ±0.43 eV gives us confidence in the CHELEQ charge calculation method and shows that the bonding in a wide variety of sulfur compounds can be explained using only s and p valence orbitals.

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References

(1). Anorganish-Chemisches Institut der Universität, 34 Göttingen.

(2). T. B. Brill, J. Chem. Education 50, 392 (1973).

(3). W. B. Perry and W. L. Jolly, to be published.

(4). O. Glemser, Angew. Chem. Intl. Ed. 2, 530 (1963).

(5). We thank Mr. Keller for the preparation of NSF_3.

(6). H. Richert and O. Glemser, Z. anorg. allg. Chem. 307, 328 (1961).

(7). O. Glemser and H. Richert, Z. anorg. allg. Chem. 307, 313 (1961).

(8). J. M. Hollander, M. D. Holtz, T. Novakov and R. L. Graham, Arkiv Fysik 28, 375 (1965).

(9). 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, Amsterdam, 1969.

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

(11). C. J. Allan, U. Gelius, D. A. Allison, G. Johansson, H. Siegbahn, and K. Siegbahn, J. Electron Spectr. 1, 131 (1972).

(12). U. Gelius, C. J. Allan, G. Johansson, H. Siegbahn, D. A. Allison, and K. Siegbahn, Phys. Scripta 3, 237 (1971).

13). W. L. Jolly and W. B. Perry, J. Amer. Chem. Soc. 95, 5442 (1973). For sulfur, we used the Hinze and Jaffé14) values of x(s) and x(p), 5.12 and 2.63, respectively, and values for h and c of 9.82 and 2.5, respectively.

14). J. Hinze and H. Jaffé, J. Amer. Chem. Soc. 84, 540 (1962).

15). For calculating the sulfur $2p_{3/2}$ binding energies, we used the values k = 17.43 and ℓ = 170.61, obtained by least-squares fitting of the E_B data in Table 1 to the appropriate sets of calculated atomic charges. For calculating the nitrogen 1s binding energies, we used the values of k and ℓ previously determined in the correlation of many other N1s binding energy data13). For calculating the fluorine 1s binding energies, we used k = 25.28 and ℓ = 695.09, corresponding to a least-squares fitting of all known E_B data for fluorine compounds.

16). H. Siebert, Z. anorg. allg. Chemie 273, 170 (1953).

17). D. O. Cowan, R. Gleiter, O. Glemser and E. Heilbronner, Helv. Chim. Acta 55, 2418 (1972).

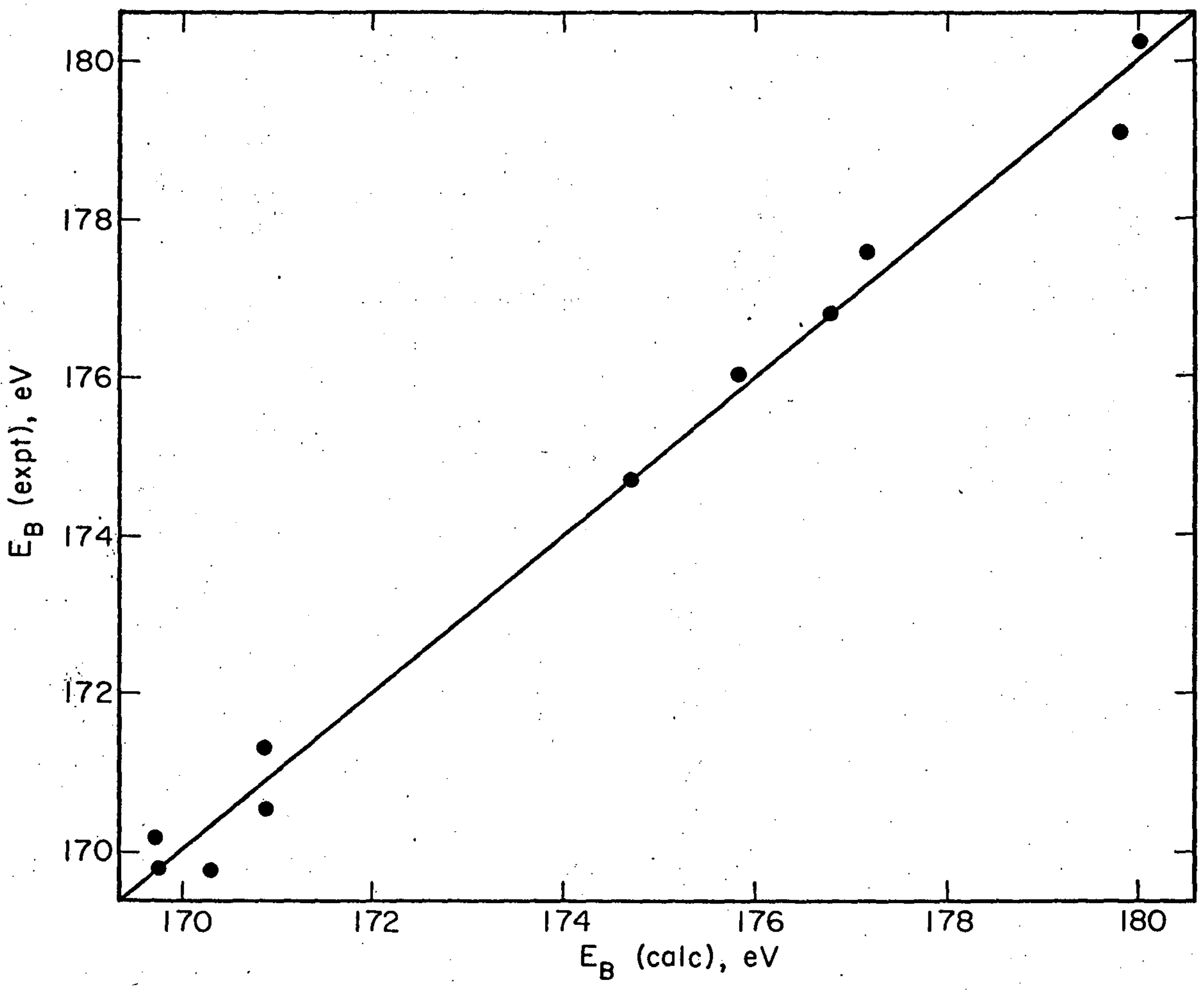

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Figure 1. A plot of E_B(expt) vs. E_B(calc) for the sulfur $2p_{3/2}$ electrons of the compounds in Table 1.

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