Figure 2. Wavelength-resolved spectrum obtained upon pumping the ν_{18}' band of the $C_6F_6^+$ excitation spectrum at 21 874 cm^{-1}. The assignments for the strongest bands are indicated, ν_{18}'' ($^3/_2$), for example, refers to the $j = ^3/_2$ component[12] of the ν_{18}'' ($v = 1$) level (see text).

as our calculations become inaccurate higher up the ground-state vibronic level stack due to basis-set truncation effects.

The analysis of the spectrum obtained on excitation of ν_{17}' at 22 031 cm^{-1} follows in similar fashion. In this case we can distinguish emission bands corresponding to transitions to both ν_{18}'' ($v = 1, j = ^3/_2$) and ν_{17}'' ($v = 1, j = ^3/_2$). The latter is predicted to be weaker and partially overlapped by the strong ν_{18}'' ($j = ^1/_2$) band in the ν_{18}' excitation experiment. Features further from the laser are all assignable to relaxed emission from either ν_{18}' or ν_0' levels.

4. Conclusions

The vibronic structure of a Jahn–Teller distorted state such as the $^2E_{1g}$ state of $C_6F_6^+$ is clearly quite complicated. It is therefore very desirable to have complete and redundant determinations of level positions. Because of the operative selection

rules, the lines observed in the wavelength-resolved spectrum obtained by laser pumping the electronic origin and transitions from excited levels of the $j = ^1/_2$ manifold appearing as hot bands in the excitation spectrum independently determine the positions of the ν_i'' ($j = ^1/_2$) levels. Comparison of Tables I and II indicates very good agreement between the positions determined in these two experiments. These same level positions are also determined by the emission spectrum obtained in solid Ne as described in ref 9. Comparison of the present results with those in this reference again indicates very good agreement for the levels mutually observed.

The $j = ^3/_2$ stack is likewise redundantly determined. In this case the direct determination comes from the wavelength-resolved emission spectra obtained via pumping ν_{17}' or ν_{18}'. From these levels emission is allowed into both the $j = ^1/_2$ and $^3/_2$ stacks, although the latter is usually stronger. No discrepancies are observed with the previous $j = ^1/_2$ positions, and new values are obtained for the $j = ^3/_2$ levels. These $j = ^3/_2$ level positions can now be used to interpret the hot-band structure to the high frequency side of the origin in the excitation spectrum. As seen from Table I, these hot-band transitions confirm the $j = ^3/_2$ assignments. The $j = ^3/_2$ lines observed are, where overlap exists, also in good agreement with the unrelaxed matrix spectra. Finally one or two lines in the $j = ^5/_2$ stack have been observed, both in the gas phase and in the matrix, due to mixing of the $j = \pm^1/_2$ and $j = \pm^5/_2$ stacks by quadratic effects.

Taken together the experimental data fairly extensively and redundantly establish the positions of a number of the Jahn–Teller perturbed vibronic levels of the ground state. This information along with the observed line intensities forms a good data base for understanding the Jahn–Teller effect in $C_6F_6^+$. In a future manuscript[12] we will describe extensive calculations which have been carried out to determine Jahn–Teller parameters for the active modes. The agreement of these calculations with experiment and the resulting information on the Jahn–Teller stabilization energies and distorted geometries will also be reported.[12]

Charge Distribution and Bonding in the Series $(CF_3)_2O_n$ ($n = 0-3$) and in CF_3SCF_3 Deduced from Gas-Phase X-ray Photoelectron Spectroscopy. Evidence for Double Bonding in Saturated Compounds

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Abstract: Core-level binding energies for the gases hexafluoroethane, bis(trifluoromethyl) oxide, bis(trifluoromethyl) peroxide, bis(trifluoromethyl) trioxide, and bis(trifluoromethyl) sulfide have been measured. Unusual binding energy shifts were observed in the series $(CF_3)_2O_n$ ($n = 0-3$). Semiempirical minimum neglect of differential overlap (MNDO) molecular orbital calculations were performed on all of the molecules examined. Excellent correlations between the observed core-level binding energies (corrected for the site potentials) and calculated atomic charges are found. The X-ray photoelectron spectra and MNDO calculations reveal the π-type oxygen lone-pair interactions with σ^* orbitals of the $-CF_3$ groups are important in the $(CF_3)_2O_n$ ($n = 1-3$) compounds. A similar interaction is also present in $(CF_3)_2S$ but is only half as strong due to the poorer sulfur lone-pair $-CF_3$ σ^* overlap.

Introduction

Catenation is not a common phenomenon in oxygen chemistry and chains are generally limited to two oxygen atoms. The only well-documented, stable, three oxygen atom species are ozone and

the bis(perfluoroalkyl) trioxides.[2] With the tetrad of stable compounds CF_3CF_3, CF_3OCF_3, CF_3OOCF_3, and CF_3OOOCF_3, we are afforded the opportunity to examine the effects arising from successive oxygen atom insertions on core-level binding energies

(1) (a) Naval Research Laboratory. (b) Georgetown University.

(2) (a) Anderson, L. R.; Fox, W. B. *J. Am. Chem. Soc.* **1967**, *89*, 4313. (b) Thompson, D. G. *Ibid.* **1967**, *89*, 4316.

330   *J. Am. Chem. Soc., Vol. 103, No. 2, 1981*

Brant et al.

Table I.   Core-Level Binding Energies for Bis(trifluoromethyl)
Oxides and Bis(trifluoromethyl) Sulfide

molecule	binding energies,[a] eV		
	C 1s	F 1s	O 1s
C_2F_6	299.72 (1.11)	694.80 (1.70)	
$(CF_3)_2O$	301.09 (1.15)[b]	694.88 (1.76)	541.78 (1.40)
$(CF_3)_2O_2$	300.78 (1.04)	694.74 (1.76)	541.93 (1.25)
$(CF_3)_2O_3$	300.69 (1.02)	694.71 (1.82)	542.67 (1.13), 541.52 (1.32)
$(CF_3)_2S$	299.41 (1.15)	694.39 (1.68)	172.51[c] (1.25)

[a] All binding energies are referenced to an Ar $2p_{3/2}$ binding
energy of 248.62 eV.   [b] Values in parentheses are peak full
widths at half maxima, in eV.   [c] Sulfur $2p_{3/2}$.

of the constituent atoms. Including CF_3SCF_3 in the above series, the effects of sulfur and oxygen atom insertion can also be compared in these molecules. The core-level binding energies measured by X-ray photoelectron spectroscopy (XPS) are examined in detail with the aid of the point-charge potential model in conjunction with semiempirical, MNDO MO[3] calculations. Of particular interest in these molecules is the extent of oxygen and sulfur lone-pair interaction with the C–F antibonding orbitals.[4-6]

Experimental Section

Hexafluoroethane (>99%, PCR, Inc.) was a gift from the Chemistry Department of George Mason University, while bis(trifluoromethyl) oxide, CF_3OCF_3, was a gift from Allied Chemical Corp.[7] The stated purity of the C_2F_6 was corroborated by mass spectrometry. The CF_3O–CF_3 was purified by trap-to-trap distillation. After distillation the mass spectrum of the CF_3OCF_3 indicated the sample purity was ≳95%. Bis(trifluoromethyl) peroxide, CF_3OOCF_3, was purchased from PCR, Inc. The stated purity of the CF_3OOCF_3 was >99%, and it was used without further purification. Bis(trifluoromethyl) trioxide, CF_3OOOCF_3, was prepared and purified following the procedure in the literature.[2] Its purity was established by infrared spectroscopy. The sample was vacuum distilled prior to use. Bis(trifluoromethyl) sulfide was prepared according to the literature method[8] and purified by trap to trap distillation. The material was identified from its boiling point and mass spectrum.

All spectra were recorded with a McPherson ESCA-36 photoelectron spectrometer equipped with an Al Kα X-ray source, gas sample cell, and automated data collection and display system. All samples were mixed with argon gas (purity 99.99%) prior to introduction into the gas cell. The mixture pressure was approximately 0.1–0.2 torr before admission into the spectrometer. The $2p_{3/2}$ line (E_B = 248.62 eV)[9] of the argon gas was used as a calibrant for the core-level binding energies of all four $(CF_3)_2O_n$ (n = 0–3) compounds as well as for CF_3SCF_3.

The C 1s, F 1s, O 1s (or S 2p) and Ar $2p_{3/2}$ binding-energy regions were scanned sequentially and the sequence traversed additively two to four times. Under these conditions the full width at half maximum of the Ar $2p_{3/2}$ line (1.09–1.14 eV) remained the same as was obtained for pure argon gas. Replicate core level binding energy measurements for all compounds except CF_3OOCF_3 and CF_3SCF_3 demonstrated that the binding energies were reproducible on this instrument to within ±0.05 eV. MNDO semiempirical molecular orbital calculations were carried out on the IBM 370/148 computer at Georgetown University by using a slightly modified version of QCPE program No. 353. Details of the calculational procedures are published elsewhere.[3]

Results and Discussion

The gas-phase core-level binding energies for C_2F_6, CF_3OCF_3, CF_3OOCF_3, and CF_3OOOCF_3, as well as CF_3SCF_3, are listed in Table I and the oxygen 1s spectrum of CF_3OOOCF_3 is displayed in Figure 1. Core-level binding-energy shifts for hexafluoroethane relative to CH_4 and F_2 have been reported earilier.[10]
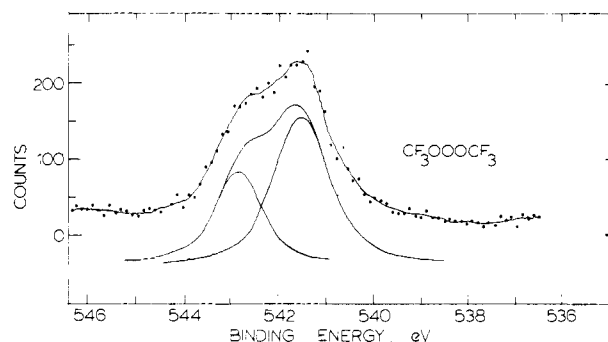
Figure 1. Oxygen 1s spectrum of CF_3OOOCF_3 and a "best fit" deconvolution of the curve envelope into two components with relative intensities of 1.00:2.02 and peak to peak separation of 1.15 eV.

However, since the absolute core-level binding energies have not been published and since there have been discrepancies in binding energies measured with different instruments,[11] we measured the core-level binding energies on our own instrument in order to compare small shifts in absolute binding energies with confidence. Approximate core-level intensity ratios (O 1s:F 1s:C 1s) obtained from the spectra were determined to be 1.00:1.58:0.52. Errors in the measured ratios are estimated to be less than ±20% on the basis of standard deviations obtained from seven different core-level intensity comparisons—see Experimental Section. These ratios are in reasonable agreement with those obtained from theoretical photoionization cross-section calculations (1.00:1.51:0.34).[12]

In all but one case, single Gaussian–Lorentzian peaks were found in the C 1s, F 1s, and O 1s regions. The sole exception is the O 1s spectrum of CF_3OOOCF_3 which exhibited a distinct shoulder on the high binding-energy side of the peak. Since there are two structurally distinct forms of oxygen in bis(trifluoromethyl) trioxide, the spectrum was deconvoluted by an iterative procedure using two Gaussian–Lorentzian functions with an approximate intensity ratio of 1:2. The results for the best fit simulated spectrum are compared with that obtained experimentally in Figure 1. The area ratio of the two generated peaks, separated by 1.15 eV, was found to be 1.00:2.02 and their full widths at half maxima were 1.13 and 1.32 eV (higher E_B peak, lower E_B peak). It was also observed during the several simulations that the contour of the simulated curve envelope was very sensitive to small incremental changes (≲5%) in the constituent curve parameters, so the fit obtained is considered a nearly unique representation of the data and it is believed that the errors in the parameters are no more than twice the magnitude of the errors on single, undeconvoluted peaks. The greater breadth of the lower binding-energy peak is consistent with previously observed line width–binding energy correlations.[13]

Comparison of the O 1s spectrum of CF_3OOOCF_3 with that reported for ozone[14] shows that the splitting of the central oxygen peak from the end oxygens decreases 3.5–3.6 eV on attachment of the CF_3 groups to the end oxygens. Such a result is in keeping with the valence bond descriptions for these molecules
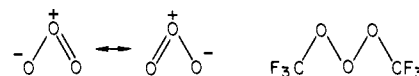
which indicate that the charge separation between the central and terminal oxygen atoms in ozone is greater than that in the trioxygen unit of CF_3OOOCF_3.

Core-level binding-energy shifts arising from successive oxygen atom insertions into the C–C bond of hexafluoroethane are il-

(3) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. (b) *Ibid.* **1977**, *99*, 4907.
(4) Williams, F. J. A. *Trans. Faraday Soc.* **1961**, *57*, 2089.
(5) Williams, F. J. A. *Tetrahedron* **1962**, *18*, 1477.
(6) Lucken, E. A. C. *J. Chem. Soc.* **1959**, 2954.
(7) $(CF_3)_2O$ was obtained by Dr. W. B. Fox as a minor side product in the reaction of CF_3OF with COF_2 to produce $(CF_3)_2O_2$.
(8) Haas, A.; Oh, D. Y. *Chem. Ber.* **1969**, *102*, 77.
(9) Johansson, G.; Hedman, J.; Berndtsson, A.; Klassen, M.; Nilsson, R. *J. Electron Spectrosc.* **1973**, *2*, 295.

(10) (a) Jolly, W. L.; Perry W. B. *J. Am. Chem. Soc.* **1973**, *95*, 5442. (b) *Inorg. Chem.* **1974**, *13*, 2686.
(11) (a) Carroll, T. X.; Smith, S. R.; Thomas, T. D. *J. Am. Chem. Soc.* **1975**, *97*, 659. (b) Powell, C. J.; Erickson, N. E.; Madey, T. E. *J. Electron Spectrosc.* **1979**, *17*, 361.
(12) Scofield, J. H. *J. Electron Spectrosc.* **1976**, *8*, 129.
(13) Thomas, T. D. *J. Chem. Phys.* **1970**, *52*, 1373.
(14) Banna, M. S.; Frost, D. C.; McDowell, C. A.; Noodleman, L.; Wallbank, B. *Chem. Phys. Lett.* **1977**, *49*, 213.

Bonding in the Series $(CF_3)_2O_n$ $(n = 0-3)$

J. Am. Chem. Soc., Vol. 103, No. 2, 1981 331
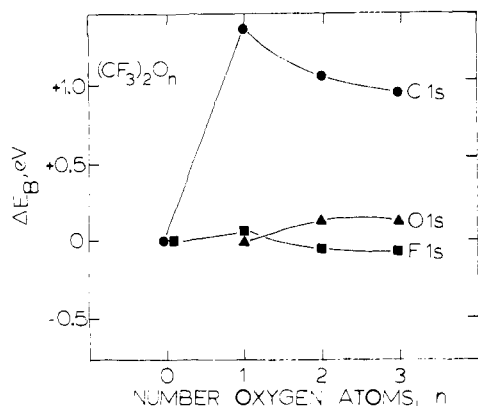
Figure 2. Binding-energy shifts as a function of the number of oxygen atoms in the chain $CF_3O_nCF_3$ where $n = 0-3$. The oxygen 1s shift for CF_3OOOCF_3 was determined from the weighted average of the O 1s binding energies for the two types of oxygen present in the compound (see Figure 1).

Table II. Values of k and l Determined from Least-Squares Fits of $(E_b - V)$ vs. Q (MNDO)

core level	k	l
C 1s	23.54 (83)[a]	291.12 (53)
O 1s	21.16 (1.06)	542.30 (34)
F 1s	23.58 (1.24)	695.78 (45)
S $2p_{3/2}$	13.88 (34)	170.14 (34)

[a] Values in parentheses are estimated standard deviations.

lustrated in Figure 2. The shifts observed in the oxygen 1s and fluorine 1s binding energies are small (between –0.2 and +0.2 eV), whereas the shifts in the carbon 1s binding energies extend from +1.37 eV (first oxygen atom insertion) to –0.11 eV (third oxygen atom insertion). The large, positive C 1s BE shift encountered as a result of the first oxygen atom insertion is in marked contrast to the modest, negative carbon and fluorine 1s BE shifts (–0.31 and –0.41 eV, respectively) experienced due to sulfur atom insertion. In addition, the reversals in both the carbon and fluorine 1s BE shifts arising from subsequent oxygen atom insertions into CF_3OCF_3 appear to be unusual. Given the electronegativities of oxygen and the $-CF_3$ group, which are nearly equal ($\chi_O = 5.21$ and $\chi_{CF_3} \approx 5.18$; Sanderson's electronegativity scale),[15] and employing the simplest BE model[16,17] ($\Delta BE \propto \Delta Q$) as a qualitative guide, one would not expect the large C 1s BE shift and the reversals in the C 1s and F 1s BE shifts. Therefore, in addition to the site-potential contribution to each binding energy, it appears that there are contributions to the observed binding energies from one or both of the following phenomena: (1) bonding interactions between the oxygen "lone pairs" and the carbon–fluorine σ-antibonding orbitals; (2) differential, or nonconstant, core-hole relaxation effects.[18] To simplify the analysis of the data, one can assume that one of the two contributions is negligible and attempt to fit the results accordingly. Using this approach, we assume differential core-hole relaxation effects to be equal to zero. The binding-energy data can then be examined by using the point-charge coulomb potential model[17] in which the binding energy (E_b) is expressed as eq 1 where Q is the ground-state charge of

$$E_b = kQ + V + l \qquad (1)$$

the ionized atom, V is the potential at the ionized site, and k and l are empirically determined constants. We have used the

(15) Sanderson, R. T. "Chemical Bonds and Bond Energy"; Academic Press: New York, 1971.

(16) Siegbahn, K.; Nordling, C.; Johansson, G.; Hedman, J.; Heden, P. F.; Hamrin, K.; Gelius, U.; Bergmark, T.; Werme, L. O.; Manne, R.; Baer, Y. "ESCA Applied to Free Molecules"; North-Holland Publishing Co.: Amsterdam, 1969.

(17) Finn, P.; Pearson, R. K.; Hollander, J. M.; Jolly, W. L. *Inorg. Chem.* **1971**, *10*, 378.

(18) Shirley, D. A. *J. Electron Spectrosc.* **1974**, *5*, 135.

Table III. Atomic Charges from Semiempirical MNDO Molecular Orbital Calculations for $(CF_3)_2O_n$ $(n = 0-3)$ and $(CF_3)_2S$

|	q_C	q_F	q_O
C_2F_6	0.59	–0.20	
CF_3OCF_3	0.81	–0.20	–0.45
CF_3OOCF_3	0.74	–0.19	–0.17
CF_3OOOCF_3	0.73	–0.19	–0.19,[a] +0.08[b]
CF_3SCF_3	0.63	–0.20	–0.02[c]

[a] Charge for end oxygens. [b] Charge for central oxygen. [c] q_S.

Table IV. Calculated (MNDO) Bond Order Per C–O Bond

compd	σ	π
C_2F_6	0.866[a]	0.043[a]
$(CF_3)_2O$	0.799	0.185
$(CF_3)_2O_2$	0.785	0.151
$(CF_3)_2O_3$	0.781	0.153
$(CF_3)_2S$	0.756[b]	0.092[b]

[a] Calculated bond order for C–C bond. [b] Calculated bond order per C–S bond.

semiempirical MNDO molecular orbital method to calculate Q, V, and orbital populations for optimized geometries. The values of k and l were empirically determined from a least-squares fit of C 1s, O 1s, F 1s, and S $2p_{3/2}$ site-potential-corrected binding energies ($E_b - V$) vs. Q (MNDO) for a variety of well-characterized molecules (excluding those examined in the present study) and are given in Table II. Atomic charges for $(CF_3)_2O_n$ ($n = 0-3$) and CF_3SCF_3 are assembled in Table III. Pertinent bond orders are summarized in Table IV. The π type interaction from which the π bond orders in Table IV are derived arises from oxygen or sulfur "lone-pair" overlap with the σ^* orbital sets of the $-CF_3$ groups. Such an interaction is depicted schematically for bis(trifluoromethyl) oxide in I.
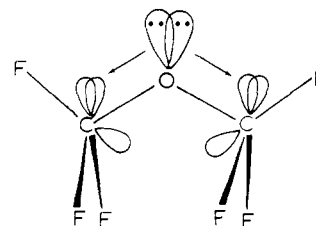

It is clear from examination of Tables III and IV that the MNDO MO calculations indicate a strong back-bonding effect among the bis(trifluoromethyl) oxides, an effect which decreases with increasing number of oxygen atoms and which is markedly less in bis(trifluoromethyl) sulfide. The calculations also clearly suggest that these interactions are the source of an unusual trend in charge distribution among the atoms in each compound through the series.

If the MNDO picture is correct, then one should be able to satisfactorily explain the XPS data for these compounds by correlating the two using the point-charge potential model (eq 1). Comparisons of the fits for the (site-potential-corrected) core-level binding energies with calculated charges for these compounds vs. the fits obtained for other compounds provide a useful method to evaluate our interpretation of the XPS data.

The results of the correlations of atomic charge with the O 1s, C 1s, F 1s, and S $2p_{3/2}$ core-level binding energies are shown in Figures 3 through 6. In Figures 3 and 4 two least-squares lines are drawn, one for the $(E_b - V)$ vs. Q correlation of all points plotted excluding those representing the data for the compounds examined in the present study and the other for a correlation of only the points representing the compounds examined in this study. Analysis of the two least-squares fits for the O 1s data shows that the two lines are indistinguishable. However, in the case of the C 1s data the slope of the line (k) determined from the correlation of $(E_b - V)$ vs. Q for the compounds examined here (25.24 ± 0.97) is significantly greater than that obtained from a fit of the correlation for all other compounds (23.54 ± 0.83). We ascribe the

332 *J. Am. Chem. Soc., Vol. 103, No. 2, 1981*

Brant et al.
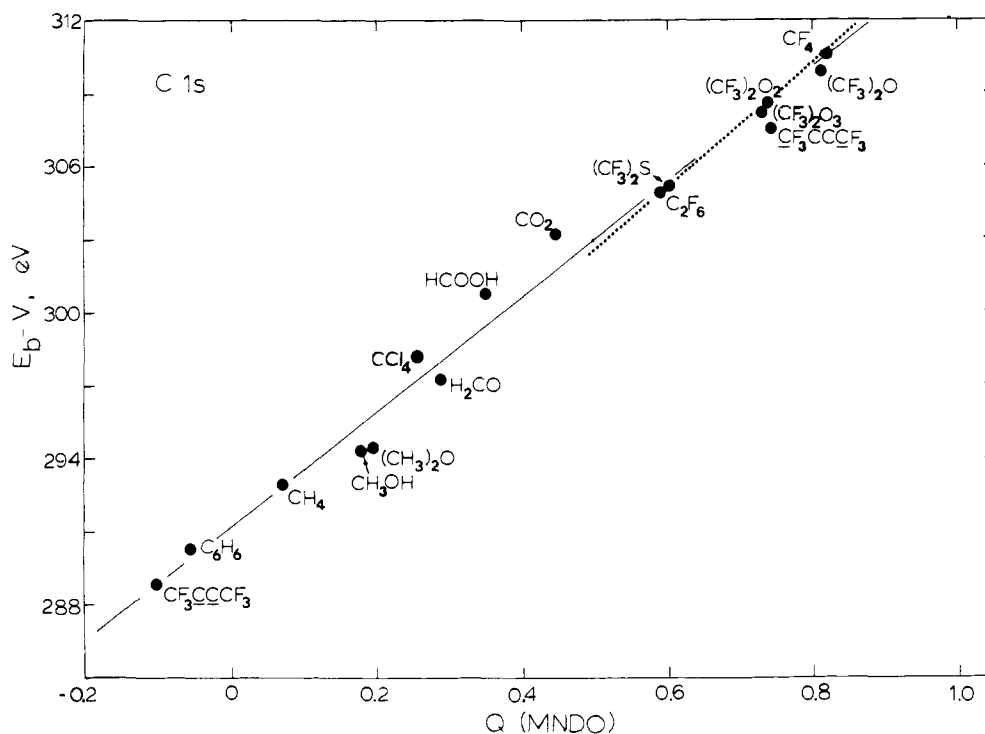
Figure 3. Correlation of site-potential-corrected C 1s binding energies with MNDO MO-calculated atomic charges. The solid line is a least-squares fit of C 1s data for all compounds except those examined in the present study. The equation for this line is $(E_b - V) = 23.54\ (83)Q_c + 291.12\ (83)$. The dashed line is a least-squares fit of the C 1s data for $CF_3O_nCF_3$ ($n = 0–3$) compounds and CF_3SCF_3. For these five data the equation for the least-squares fit is $(E_b - V) = 25.24\ (97)\ Q_c + 289.88\ (68)$. Carbon 1s binding-energy data used for this plot were taken from ref 10a, 11a, and 20–26.
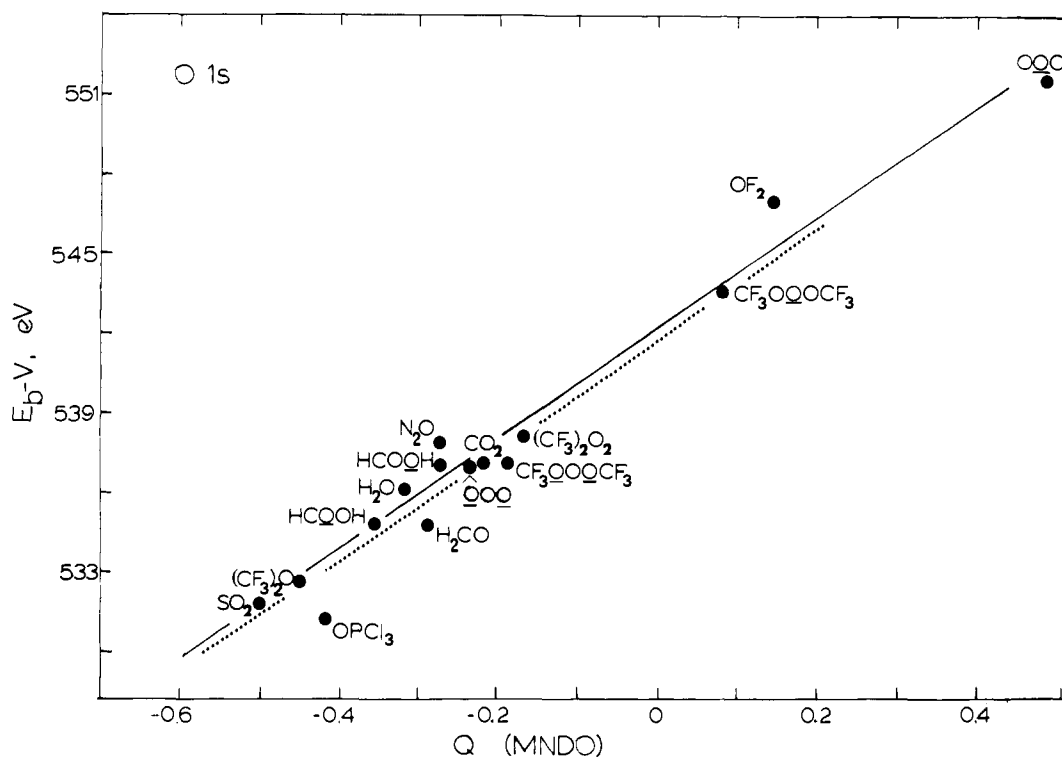
Figure 4. Correlation of site-potential-corrected O 1s binding energies with effective atomic charges calculated by the semiempirical MNDO MO method. The solid line is a least-squares fit of O 1s data for all compounds excluding those examined in the present study, while the dashed line is a fit for the compounds examined in this work. The least-squares fit for these four data points is $(E_b - V) = 20.53\ (1.26)Q_o + 541.68\ (33)$ while the fit for all other data is $(E_b - V) = 21.16\ (1.06)Q_o + 542.30\ (34)$. Oxygen 1s binding-energy data used in this plot were taken from ref 10, 11a, 14, 20, 22, 24, and 27–30.

greater value of k for the fit of the bis(trifluoromethyl) oxides, hexafluoroethane, and bis(trifluoromethyl) sulfide to the fact that all of these compounds contain very positively charged carbon atoms. The value of k is larger for this set of data because k is roughly proportional to the expectation value[19] $\langle 1/r \rangle$ and with

more positively charged atoms, r decreases so of course k increases. The corelation for the F 1s data is presented in Figure 5. Here

(19) Lu, C. C.; Carlson, T. A.; Malik, F. B.; Tucker, T. C.; Nestor, C. W. *At. Data* **1971**, *3*, 1.
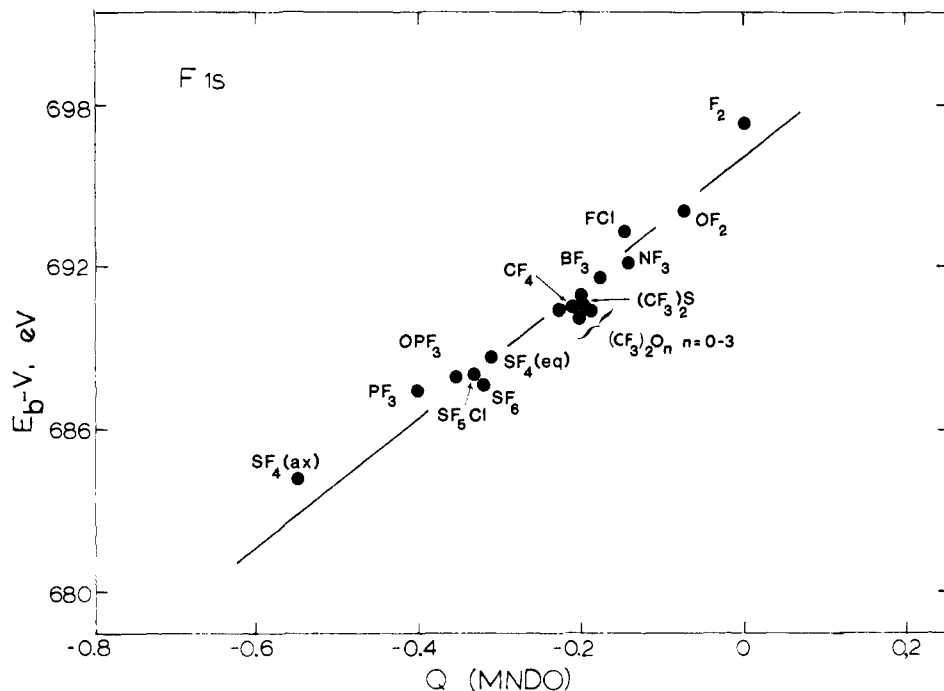
Figure 5. Least-squares fit of $(E_b - V)$ vs. Q_F for all fluorine compounds listed excluding those for which data were obtained in the present study—$(CF_3)_2O_n$ ($n = 0$–3) and $(CF_3)_2S$. The equation for the linear least-squares fit is $(E_b - V) = 23.58 \ (1.24)Q_F + 695.78 \ (45)$. Fluorine 1s data are taken from references 10, 16, 27, and 30–35.
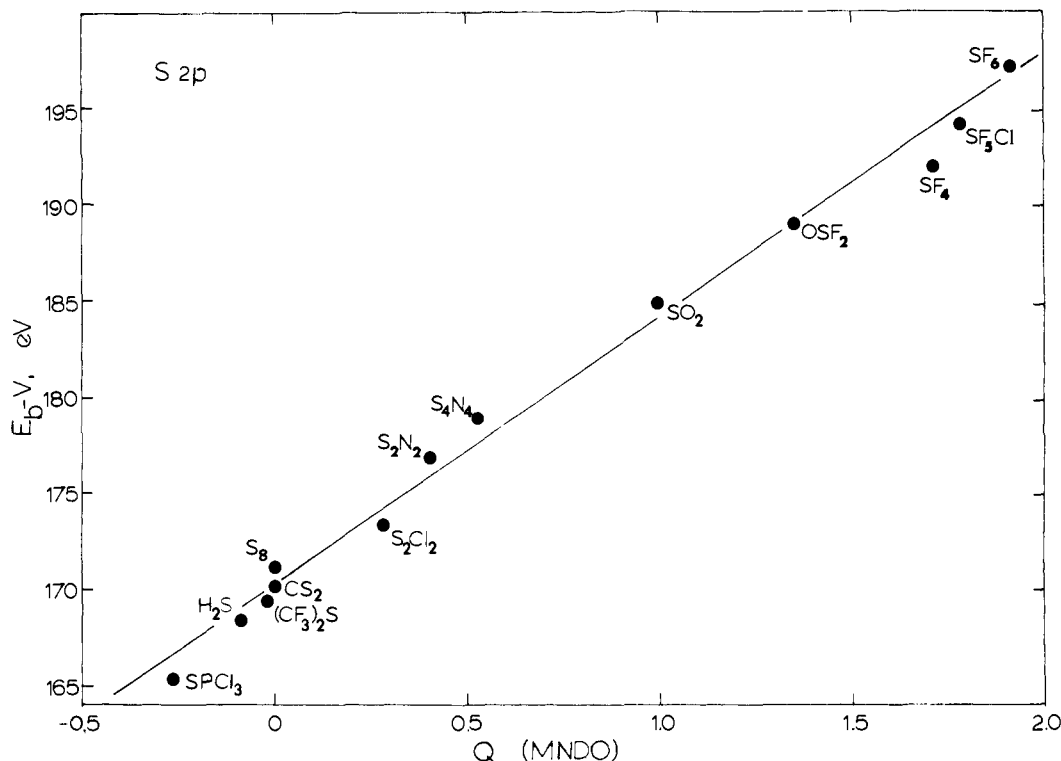

Figure 6. Least-squares fit of $(E_b - V)$ vs. Q_S for all sulfur compounds excluding $(CF_3)_2S$. The equation for the fit is $(E_b - V) = 13.88 \ (34)Q_S + 170.14 \ (34)$. Sources for the S $2p_{3/2}$ binding-energy data are references 16, 29, and 35–39.

we find the data for $(CF_3)_2O_n$ ($n = 0$–3) and $(CF_3)_2S$ clustered together on or near the linear least-squares fit for the other fluorine compounds. The excellent proximity of these data to the least-squares line is further indication of the accurate interpretation

(20) Jen, J. S.; Thomas, T. D. *J. Electron Spectrosc.* **1974**, *4*, 43.

(21) Perry, W. B.; Jolly, W. L. *Inorg. Chem.* **1974**, *13*, 1211.

(22) Jolly, W. L.; Schaaf, T. F. *J. Am. Chem. Soc.* **1976**, *98*, 3178.

(23) Brant, P.; Berry, A. D.; De Marco, R. A.; Hashmall, J. A.; Carter, F. L.; Fox, W. B. *J. Electron Spectrosc.*, in press.

(24) Thomas, T. D.; Shaw, R. W. *J. Electron Spectrosc.*, **1976**, *5*, 1081.

(25) Barber, M.; Baybutt, P.; Connor, J. A.; Hillier, I. H.; Meredith, W. N. E.; Saunders, V. R. "Electron Spectroscopy"; D. A. Shirley, Ed.; American Elsevier: New York, 1972; p 753.

(26) Gelius U.; Allan, C. J.; Allison, D. A.; Siegbahn, H.; Siegbahn, K. *Chem. Phys. Lett.* **1971**, *11*, 224.

(27) Avanzino, S. C.; Jolly, W. L.; Lazarus, M. S.; Perry, W. B.; Rietz, R. R.; Schaaf, T. F. *Inorg. Chem.* **1975**, *14*, 1595.

(28) Davis, D. W.; Hollander, J. M.; Shirley, D. A.; Thomas, T. D. *J. Chem. Phys.* **1970**, *52*, 3295.

(29) Perry, W. B.; Schaaf, T. F.; Jolly, W. L. *J. Am. Chem. Soc.* **1975**, *97*, 4899.

(30) Koepke, J. W.; Jolly, W. L. *J. Electron Spectrosc.* **1976**, *9*, 413.

Table V. Structural Data for the Series $(CF_3)_2O_n$ ($n = 0$-3) and for $(CF_3)_2S^d$

		bond distances, Å			bond angles, deg			
		C–F	C–O	O–O	∠FCO	∠(COC or COO)	∠OOO	ref
CF_3CF_3	MNDO	1.346	1.676^a		110.7^b			
	EDS^c	1.330 (5)			110^b			41
CF_3OCF_3	MNDO	1.344	1.410		109.4	132.0		
	EDS	1.320 (2)	1.360 (5)		110.1 (3)	124.0 (6)		42, 43
CF_3OOCF_3	MNDO	1.343	1.440	1.290	109.2	113.7		
	EDS	1.32 (1)	1.40 (1)	1.42 (2)	109.0 (5)	107.2 (1.2)		44
		1.317 (2)	1.398 (6)	1.52 (2)	110.3 (2)	130 (2)		42, 43
CF_3OOOCF_3	MNDO	1.343	1.440	1.290	109.3	116.7	111.1	
	EDS	1.321 (2)	1.407 (6)	1.51 (2)	110.5 (2)	125 (2)	120 (1)	42, 43

		bond distances, Å		bond angles, deg		
		C–F	C–S	∠FCS	∠CSC	
CF_3SCF_3	MNDO	1.347	1.819	110.9	109.8	
	EDS	1.32 (1)	1.82 (1)	109.5 (1.0)	105.6 (3.0)	45

^{a} r_{C-C}. ^{b} ∠CCF. ^{c} Electron diffraction study. ^{d} Optimized ground-state geometries from MNDO molecular orbital calculations vs. geometries obtained from gas-phase electron diffraction studies.

of the data. We also evaluated the correlation of the shift in binding energy for the S $2p_{3/2}$ level of bis(trifluoromethyl) sulfide with calculated sulfur charge (Q_s(MNDO) = +0.60). The deviation of the datum point for the sulfide from the least-squares fit for a variety of other sulfur compounds is quite small, as can be seen in Figure 6; in fact it is smaller than the average deviation obtained for the other compounds.

We find then in all cases that the correlations of the MNDO-calculated ground-state effective atomic charges with the observed core-level binding energies for CF_3CF_3, $(CF_3)_2O_n$ and CF_3SCF_3 are excellent. These results indicate that the unusual binding-energy shifts recorded for this series indeed reflect an unusual pattern of charge variation due to the oxygen lone-pair-CF_3 σ^* orbital set interactions.

Based on our successful treatment of the binding-energy shifts for these compounds according to effective ground-state atomic charge differences, we have no reason to believe that the differences arise from differential core-hole relaxation effects and so have not pursued the calculation of such effects further.

While the excellent correlations of the MNDO-calculated atomic charges with site-potential-corrected BE's are gratifying, the strong π-type interaction between the oxygen atom(s) and $-CF_3$ groups at first appeared to be in conflict with NMR results for the bis(trifluoromethyl) oxides.[40] Based on the MNDO results, one might expect the π-type interaction to result in a significant rotation barrier about the O–C bonds and a preferred conformer for each compound, yet no such rotational barrier was observed in the ^{13}C or ^{19}F spectra. We therefore undertook additional MNDO calculations to evaluate the energy of the rotational barrier

about the C–O bonds in CF_3OCF_3, the member of the series with the strongest π-type interaction. In fact, these calculations showed that the free rotational energy barrier is less than 0.01 kcal/mol, considerably less than kT and consistent with the NMR data.

Finally, we have compared in Table V the optimized ground-state geometries derived for these compounds from the MNDO MO calculations with the structures determined from gas-phase electron diffraction studies (EDS).[44,45] We find good agreement between the calculated and observed geometries except in the comparisons of the O–O distances and COO (or COC) and OOO bond angles for $CF_3O_nCF_3$ ($n = 1$-3) where the values do not coincide. There are discrepancies as well between EDS studies on the same molecule—CF_3OOCF_3— where, for example, the derived COO angles are at variance by 23°.

In spite of the above discrepancies, there is, on the whole, agreement in general trends between the MNDO-calculated and EDS-derived geometries. For example, both MNDO calculations and EDS results indicated that the π-type interaction is structurally manifested in a larger COC angle (132°, MNDO; 124°, EDS) relative to the same angle in dimethyl ether (111°)[46] where no such π-type interaction exists.

Similar COO angle increase trends are noted for CF_3OCF_3 and CF_3OOOCF_3. We find, furthermore, that MNDO calculations and EDS results are in reasonable agreement as to the structure of CF_3SCF_3 where no particular increase in CSC angle is noted (109.8, MNDO; 105.6 (3.0), EDS) relative to that for CH_3SCH_3 (105°, EDS)[47] and a substantially smaller π type interaction is found.

Summary

Through the allied use of X-ray photoelectron spectroscopy and semiempirical MNDO calculations, an important π-type bonding interaction has been identified in the bis(trifluoromethyl) oxides, $(CF_3)_2O_n$ ($n = 1$-3). The π-type interaction appears to be a significant source of lone-pair stabilization in these compounds and to be relevant to the oxygen atom catenation. These results offer specific reinforcement for the broad arguments first put forth by Lucken[6] and Williams[4,5] concerning π-type interactions between $-CF_3$ groups and heteroatom lone pairs.

Excellent correlations between measured core-level binding energies and calculated effective atomic charges have been obtained by using the point-charge potential model.

(31) Allison, D. A.; Johansson, G.; Allan, C. J.; Gelius, U.; Siegbahn, H.; Allison, J.; Siegbahn, K. *J. Electron Spectosc.* **1972/1973**, *1*, 269.

(32) Shaw, R. W.; Carroll, T. X.; Thomas, T. D. *J. Am. Chem. Soc.* **1973**, *95*, 5870.

(33) Carroll, T. X.; Thomas, T. D. *J. Chem. Phys.* **1974**, *60*, 2186.

(34) Thomas, T. D. *J. Am. Chem. Soc.* **1970**, *92*, 4184.

(35) Jolly, W. L.; Lazarus, M. S.; Glemser, O. *Z. Anorg. Allg. Chem.* **1974**, *406*, 209.

(36) Brant, P.; Weber, D. C.; Ewing, C. T.; Carter, F. L.; Hashmall, J. A. *Inorg. Chem.* **1980**, *19*, 2829.

(37) Salaneck, W. R.; Lin, J. W.-p.; Paton, A.; Duke, C. B.; Ceasar, G. P. *Phys. Rev.* B **1976**, *13*, 4517.

(38) Banna, M. S.; Frost, D. C.; McDowell, C. A.; Wallbank, B. *Chem. Phys. Lett.* **1976**, *43*, 426.

(39) Banna, M. S.; Frost, D. C.; McDowell, C. A.; Wallbank, B. *J. Chem. Phys.* **1977**, *66*, 3509.

(40) De Marco, R. A.; Fox, W. B.; Moniz, W. B.; Sojka, S. A. *J. Magn. Reson.* **1975**, *18*, 522.

(41) Swick, D. A.; Karle, I. L. *J. Chem. Phys.* **1955**, *23*, 1499.

(42) Yokozeki, A.; Bauer, S. H. *Top. Curr. Chem.* **1974** *53*, 71.

(43) Hilderbrandt, R. L.; Bauer, S. H. "Third Austin Symposium on Gas Phase Molecular Structure", Austin, Texas, 1970.

(44) Marsden, C. J.; Bartell, L. S.; Diodati, F. P. *J. Mol. Struct.* **1977**, *39*, 253.

(45) Bowen, H. J. *Trans, Faraday Soc.* **1954**, *50*, 452.

(46) Kimura, K.; Kubo, M. *J. Chem. Phys.* **1959**, *30*, 151.

(47) Brockway, J. O.; Jenkins, H. O. *J. Am. Chem. Soc.* **1936**, *58*, 2036.