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COMPARISON OF CORE-LEVEL BINDING ENERGY SHIFTS IN MOLECULES
WITH PREDICTIONS BASED ON KOOPMANS' THEOREM*

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X-ray photoelectron spectroscopy allows the determination of core-electron binding energies, which exhibit environment-sensitive "chemical shifts".¹ The fact that core-electron binding energies increase with oxidation is well known,¹⁻⁵ but there have been few rigorous theoretical calculations with which to compare the experimental shifts. Recently, however, SCF-MO calculations on several small molecules have become available.^{6,7,8} In this letter we compare experimental values of shifts of carbon, nitrogen, and oxygen 1s binding energies in some of these molecules with theoretical estimates from these calculations.

Core-electron binding energies obtained by photoemission experiments in atoms are much closer to those computed for an "adiabatic" process than for a "sudden" process.⁹ The adiabatic process can be thought of as taking place in two (fictitious) steps: (1) The photoelectron is ejected suddenly, leaving a hole in the K shell and leaving the other (passive) electrons "frozen" in their initial ground-state orbitals, and (2) the passive orbitals quickly relax toward the positive hole, accelerating the outgoing electron.

By Koopmans' Theorem,¹⁰ "sudden" values of binding energies may be obtained from Hartree-Fock calculations: they are just the one-electron

orbital energies. Adiabatic binding energies are harder to calculate, because for these the energies of both the initial state and the (unstable) final "hole-state" must be evaluated. It is of interest to learn if the one-electron energies are adequate for predicting chemical shifts. This would be the case if electronic relaxation in the chemical environment either is negligible or constant. In contrast, if electronic relaxation in the molecule is significant, a differential, structure-dependent violation of Koopmans' Theorem would be noted.

The measurements were made on gases at room temperature in the Berkeley iron-free spectrometer, using $MgK\alpha_{1,2}$ x-rays. Pressures in the sample chamber were maintained at about 0.02 Torr; the observed kinetic energy values were however relatively insensitive to pressure. Every compound was compared directly with a standard compound. The observed shifts are summarized in Table 1.

In Fig. 1 the experimental 1s-electron binding-energy shifts, $\Delta E = E(C, N, \text{ or } O) - E(CH_4, NH_3, \text{ or } H_2O)$, are plotted against "sudden" values based on SCF calculations.^{6,7,8} Two conclusions may be drawn from this comparison. First, the SCF calculations of Basch and Snyder give quite good predictions of the shifts. The agreement is encouraging; it suggests that a rigorous theoretical understanding of core-level chemical shifts may not be far in the future.

Second, however, the agreement between ΔE_{expt} and ΔE_{sudden} for these molecules is not perfect. An average deviation of about 1 eV is noted for the elements studied (with ΔE_{sudden} being larger in each case), and the rms spread about this deviation is also about 1 eV. The cause of this

almost constant deviation is not presently known. In all three elements, the hydride was chosen as the standard molecule.

The data do show that there are no significant structure-dependent deviations from the SCF "frozen orbital" values. It is concluded that these calculations can be used to give estimates of the binding energy shifts in these molecules to within about 1 eV.

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- † Permanent address: Department of Chemistry, Princeton University, Princeton, New Jersey.
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 9. P. S. Bagus, *Phys. Rev.* 139, A619 (1965).
 10. T. Koopmans, *Physica* 1, 104 (1933).
 11. It is noted that the Basch and Snyder calculations⁷ made use of a "double zeta" set of gaussian functions while Ha and Allen⁶ used a minimal basis set.
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Table 1. Binding energy shifts (in eV) of 1s electrons from C, O, and N compounds, relative to CH₄, H₂O, and NH₃.

Compound	$\Delta E(\text{expt})^a$	$\Delta E(\text{sudden})^f$	Compound	$\Delta E(\text{expt})^a$	$\Delta E(\text{sudden})^f$
<u>C 1s shifts:</u>			<u>O 1s shifts:</u>		
C ₂ H ₆	-0.2 ^b	0.2	C ₂ H ₄ O	-1.05(5)	0.2
C ₂ H ₄	-0.1 ^b	0.9	CH ₃ OH	-0.80(10)	-0.2
C ₂ H ₂	0.4 ^b	1.4	CO ₂	1.44(5)	3.2
C ₂ H ₄ O	2.01(5)	2.4	HCO ₂ H ^h	0.67(5)	2.0
CH ₃ OH	1.9(2)	2.0	N ₂ O	-0.95(5)	0.8
HCO ₂ H	4.99(10)	6.0		1.54(10)	2.9
CO ₂	6.84(5)	8.3	CO	2.94(10) ^c	3.3
CO	5.4 ^c	5.5	O ₂ , ⁴ Σ	3.47(5)	
CH ₃ F	2.8 ^d	3.0 ⁱ	O ₂ , ² Σ	4.59(5)	
		4.9 ^g	O ₂ , wtd. ave.	3.84(6)	4.3
cyclo- propane	-0.23(5)	0.5			
CHF ₃	8.3 ^d	9.4 ⁱ	<u>N 1s shifts:</u>		
		15 ^g	N ₂ h	4.35(20)	5.4
CF ₄	11.0 ^d	12.7 ⁱ	N ₂ O ^h	3.17(10),	6.1
HCN	2.6(2) ^e	2.8		7.04(5)	9.3
			HCN	0.55(20) ^e	3.0

^aError in last place given parenthetically. From this work unless otherwise noted. Shifts positive if no sign given.

^bT. D. Thomas, J. Chem. Phys., to be published.

^cT. D. Thomas, to be published elsewhere.

^dT. D. Thomas, submitted to J. Am. Chem. Soc.

^eP. Finn, J. M. Hollander, and W. L. Jolly, unpublished data.

^fFrom Ref. 7, unless otherwise indicated.

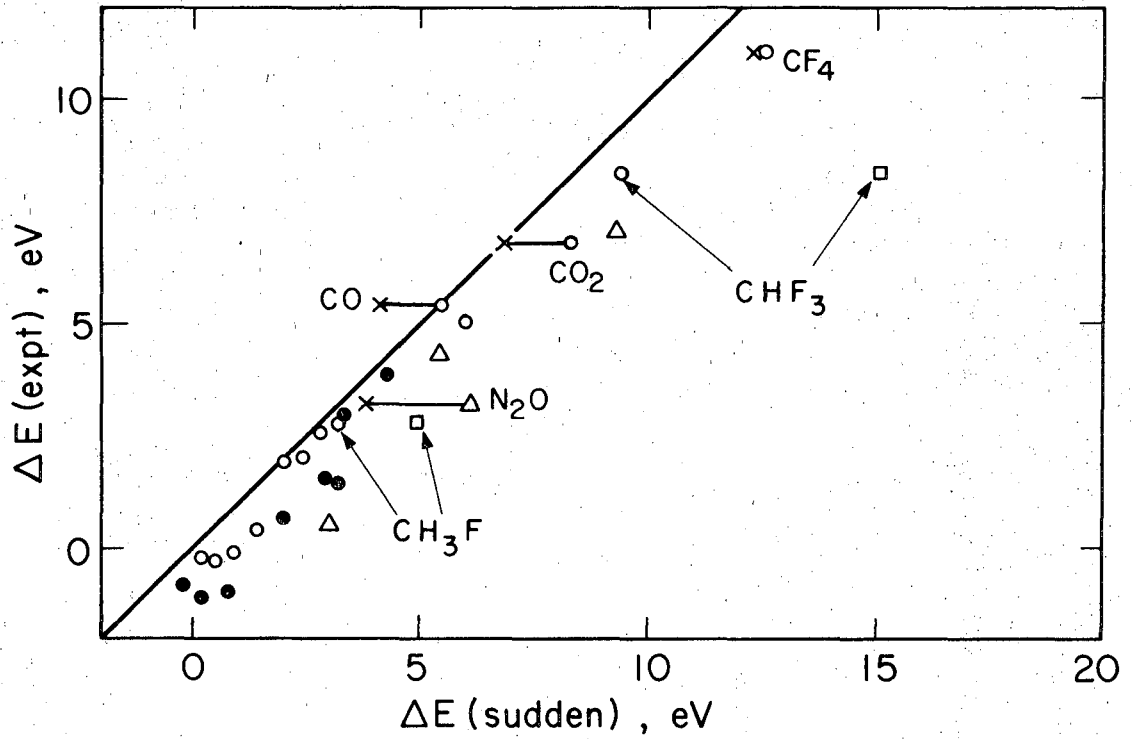
^gRef. 6.

^hTwo lines of equal intensity. Hence two possible ways to assign lines.

ⁱRef. 8.

FIGURE CAPTION

Experimental binding-energy shifts vs. "sudden" estimates for carbon 1s (open circles), oxygen 1s (filled circles), and nitrogen 1s (triangles) electrons in compounds listed in Table 1. For $\Delta E(\text{expt}) = \Delta E(\text{sudden})$, points would lie on the solid line. Carbon values from Ref. 6 are indicated by open squares.¹¹ W. L. Jolly has made thermochemical estimates¹² for several compounds: these are indicated by X's.



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Fig. 1.

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