Title

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

Permalink

https://escholarship.org/uc/item/14b0t2f5

Authors

Davis, D.W.
Hollander, J.M.
Shirley, D.A.
et al.

Publication Date

1969-11-01

Submitted to Journal of Chemical Physics

UCRL-19515 Rev.
Preprint

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

D. W. Davis, J. M. Hollander, D. A. Shirley,
and T. D. Thomas

December 1969

AEC Contract No. W-7405-eng-48

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

DISCLAIMER

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

D. W. Davis, J. M. Hollander, D. A. Shirley, and T. D. Thomas†

Department of Chemistry and
Lawrence Radiation Laboratory
University of California
Berkeley, California 94720

December 1969

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 <u>atoms</u> 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.

REFERENCES

*Work performed under the auspices of the U. S. Atomic Energy Commission.

†Permanent address: Department of Chemistry, Princeton University, Princeton, New Jersey.

1. S. B. M. Hagström, C. Nordling, and K. Siegbahn, z. Physik 178, 433 (1964).
2. K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, C. 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) 97-137.
3. J. M. Hollander, D. N. Hendrickson, and W. L. Jolly, J. Chem. Phys. 49, 3315 (1968).
4. R. Nordberg, R. G. Albridge, T. Bergmark, U. Ericson, J. Hedman, C. Nordling, K. Siegbahn, and B. J. Lindberg, Arkiv för Kemi 28, 257 (1967).
5. K. Hamrin, G. Johansson, A. Fahlman, C. Nordling, and K. Siegbahn, Chem. Phys. Letters 1, 557 (1968).
6. Tae-Kyu Ha and L. C. Allen, International Journal of Quantum Chemistry, 1S, 199 (1967).
7. H. Basch and L. C. Snyder, Chem. Phys. Letters 3, 333 (1969).
8. H. Basch, private communication (December 1969).
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 calculations[7] made use of a "double zeta" set of gaussian functions while Ha and Allen[6] used a minimal basis set.
12. W. L. Jolly, University of California, Berkeley, private communication, October, 1969.

Table 1. Binding energy shifts (in eV) of 1s electrons from C, O, and N compounds, relative to CH_4, H_2O, and NH_3.

Compound	ΔE(expt)[a]	ΔE(sudden)[f]	Compound	ΔE(expt)[a]	ΔE(sudden)[f]
C 1s shifts:			O 1s shifts:		
C_2H_6	-0.2[b]	0.2	C_2H_4O	-1.05(5)	0.2
C_2H_4	-0.1[b]	0.9	CH_3OH	-0.80(10)	-0.2
C_2H_2	0.4[b]	1.4	CO_2	1.44(5)	3.2
C_2H_4O	2.01(5)	2.4	HCO_2H[h]	0.67(5) -0.95(5)	2.0 0.8
CH_3OH	1.9(2)	2.0	N_2O	1.54(10)	2.9
HCO_2H	4.99(10)	6.0			
CO_2	6.84(5)	8.3	CO	2.94(10)[c]	3.3
CO	5.4[c]	5.5	O_2, $^4\Sigma$	3.47(5)	
CH_3F	2.8[d]	3.0[i] 4.9[g]	O_2, $^2\Sigma$	4.59(5)	
cyclopropane	-0.23(5)	0.5	O_2,wtd.ave.	3.84(6)	4.3
CHF_3	8.3[d]	9.4[i] 15[g]	N 1s shifts:		
CF_4	11.0[d]	12.7[i]	N_2	4.35(20)	5.4
HCN	2.6(2)[e]	2.8	N_2O[h]	3.17(10), 7.04(5)	6.1 9.3
			HCN	0.55(20)[e]	3.0

[a] Error in last place given parenthetically. From this work unless otherwise noted. Shifts positive if no sign given.

[b] T. D. Thomas, J. Chem. Phys., to be published.

[c] T. D. Thomas, to be published elsewhere.

[d] T. D. Thomas, submitted to J. Am. Chem. Soc.

[e] P. Finn, J. M. Hollander, and W. L. Jolly, unpublished data.

[f] From Ref. 7, unless otherwise indicated.

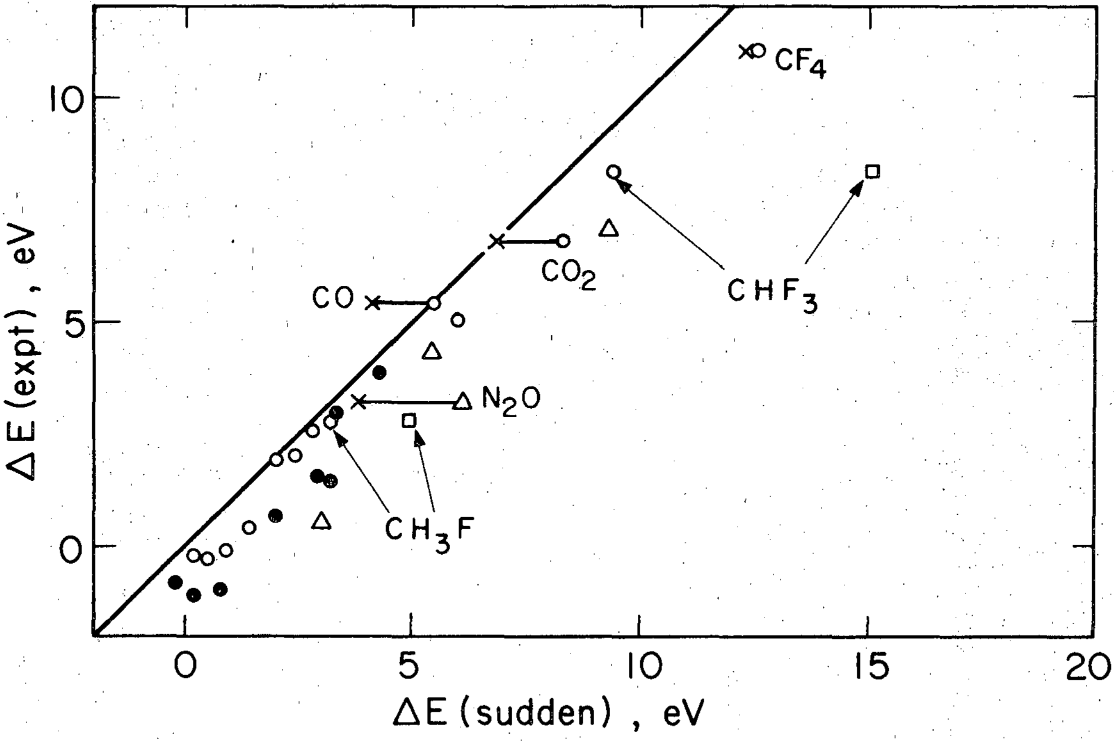
[g] Ref. 6.

[h] Two lines of equal intensity. Hence two possible ways to assign lines.

[i] Ref. 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 $\Delta E(\mathrm{expt}) = \Delta E(\mathrm{sudden})$, points would lie on the solid line. Carbon values from Ref. 6 are indicated by open squares.[11] W. L. Jolly has made thermochemical estimates[12] for several compounds: these are indicated by X's.


10
5
0
ΔE (expt), eV
0
5
10
15
20
ΔE (sudden), eV
CF_4
CO
CO_2
CHF_3
N_2O
CH_3F

XBL6911-6303

Fig. 1.

TECHNICAL INFORMATION DIVISION
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720