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K-ELECTRON BINDING ENERGY SHIFTS IN FLUORINATED METHANES AND BENZENES: COMPARISON OF A CNDO POTENTIAL MODEL WITH EXPERIMENT*

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Shifts in 1s electron binding energies can yield valuable information about electronic charge distributions in molecules. The origins of core-level binding-energy shifts are well understood, and the shifts have been interpreted with various degrees of sophistication,[1,2] from valence-bond models to *ab initio* calculations on hole states.[3] Good correlations between measured shifts and other parameters have been obtained in nearly every case. Until now, however, a hiatus has existed between experiment and theory that has, in most cases, rendered a completely satisfactory interpretation impractical. Only *ab initio* calculations have yielded quantitative predicted shifts that were both in agreement with experiment and free of empirical parameters. Although it is adequate to use ground-state orbital energies from *ab initio* results together with Koopmans' theorem to predict shifts, the expense of these calculations hampers their use in investigations involving large numbers of sizable molecules. It would be desirable to be able to predict core-level binding-energy shifts from one of the simpler "intermediate-level" molecular orbital approaches, such as the CNDO model.[4]

In this letter we report a possible solution to the above problem. For four fluorinated methanes and six fluorinated benzenes good agreement was obtained within each group between observed shifts in the carbon and fluorine 1s binding-energies and shifts in the electrostatic potentials at the carbon and fluorine nuclei, as calculated from CNDO wave functions. To a good approximation, shifts in the Coulomb potentials experienced by the nuclei and by the 1s electrons are equivalent. Since both CNDO calculations and the integrations required for evaluating the potentials require very little computer time, it appears feasible to predict core-level binding-energy shifts by this method for essentially any case of interest.

The measurements were made as described previously.[5] The calculations were done as follows: (1) For each molecule a CNDO calculation was carried out, yielding molecular orbitals ψ_i expressed in terms of atomic orbitals ϕ_i, $\psi_j = \sum_i C_{ji}\ \phi_i$. (2) The contribution of the occupied valence orbitals of the molecule to the electrostatic potential energy, V, at each carbon and fluorine nucleus was evaluated. The portion of this energy arising from occupied valence orbitals on the parent atom was, in each case, evaluated directly by calculating matrix elements of r^{-1}. The portion arising from the other atoms in each molecule was evaluated in two different ways, each based on CNDO populations: a point charge calculation, and evaluation of r^{-1} integrals by retaining only the diagonal matrix elements between atomic orbitals and off-diagonal matrix elements between inequivalent p orbitals at the same center. The reason for choosing these approaches will be discussed in a later publication. The numerical results of the two calculations are quite close. (3) The difference between the binding energies of electrons in 1s orbitals of a given element in two different sites was taken as (minus) the difference between the potential energies V calculated for the two sites, $\Delta E = -\Delta V$. Basch[6] has discussed the validity of this approach.

Theory and experiment are compared in Table I. Agreement within each group (methane derivatives and benzene derivatives) seems to be comparable to that obtained from ground-state _ab initio_ calculations.[1,5,7] This is not too surprising, as we have calculated the quantity of interest (ΔE_B) directly, rather than as a small difference between two large energies. There has been other evidence that the CNDO approximation give orbital populations consistent with observed binding-energy shifts. For example, a plot of binding energies _vs_. CNDO "atomic charges" shows about the right slope.[2] A point-charge analysis based on CNDO populations also shows a good correlation with experiment after suitable empirical parameters were determined by least-squares fitting.[1] The CNDO-potential model described here has not been used previously to predict shifts. Schwartz[8] used the same approach with extended-Hückel wave functions, obtaining shifts that were much larger than experiment, in agreement with the well-known fact that the Hückel model exaggerates polarization effects.

A detailed study of the application of the CNDO potential model to a wider range of molecules will be reported later.

FOOTNOTES AND REFERENCES

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

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Table I. Carbon and fluorine 1s electron binding-energy shifts.

Compound	ΔE(carbon 1s), in eV[a]			ΔE(fluorine 1s), in eV[b]		
	Calculated, (point charge)	Calculated, diagonal plus p-p' elements	Experimental[c]	Calculated (point charge)	Calculated, diagonal plus p-p' elements	Experimental[c]
fluorobenzene, C_F[d]	2.30	2.84	2.43(4)	0.07	0.16	-0.04(10)
C_H	0.33*[e]	0.36*	0.39(3)			
o-difluorobenzene, C_F	2.49	2.93	2.87(6)	0.08	0.15	0.33(15)
C_H	0.72*	0.64*	0.72(4)			
m-difluorobenzene, C_F	2.68	3.26	2.92(6)	0.48	0.55	0.26(11)
C_H	0.29*	0.47*	0.70(5)			
p-difluorobenzene, C_F	2.38	2.88	2.74(6)	0.29	0.35	0.26(15)
C_H	0.63	0.65	0.76(4)			
1,3,5-trifluorobenzene, C_F	3.21	3.85	3.02(9)	0.70	0.91	0.47(13)
C_H	0.50	0.48	0.56(13)			
hexafluorobenzene	3.75	4.45	3.57(9)	1.75	1.82	1.34(10)
methyl fluoride	2.58	2.97	2.8 (2)	--	--	--
difluoromethane	4.99	5.58	5.55(5)	1.07	0.82	0.73(5)
fluoroform	7.32	8.54	8.3 (2)	2.09	1.60	1.7 (2)
carbon tetrafluoride	9.52	11.14	11.0 (2)	3.11	2.37	2.6 (2)

(continued)

Table I. (continued)

[a] Carbon shifts in fluorinated methanes and benzenes are referred to methane and benzene, respectively. The two scales disagree by 0.9 eV.

[b] All fluorine shifts are referred to methyl fluoride.

[c] Error in last place given parenthetically.

[d] Here C_F and C_H are carbons directly bonded to fluorine and hydrogen, respectively.

[e] Asterisk denotes weighted average over inequivalent carbons. Experimentally only one C_F and one C_H peak was seen in each case.

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