DOPA molecule. The appearance of a band at 390 mμ for the CuL$_2^{2-}$ complex of *o*-tyrosine is consistent with interaction of the phenolic oxygen with copper(II). The band at 790 mμ could be associated with copper(II)–nitrogen interactions. These proposals for the copper(II) complexes of tyrosine, *m*-tyrosine, and *o*-tyrosine are consistent with the thermodynamic data. The spectral parameters measured for the complexes are meant to act as further qualitative evidence for the conclusions based on the thermodynamic data.

Acknowledgments. J. E. L. wishes to thank the Monsanto Chemical Company and the University of Missouri Space Sciences Research Center for summer scholarships. J. E. L. particularly expresses his gratitude to the American Chemical Society (Petroleum Research Fund) for a fellowship for 1968–1969.

Dipole Moments, Atomic Charges, and Carbon Inner-Shell Binding Energies of the Fluorinated Methanes

Maurice E. Schwartz, C. A. Coulson, and Leland C. Allen

Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana, the Mathematical Institute, Oxford, England, and Frick Chemical Laboratory, Princeton University, Princeton, New Jersey.

Received July 18, 1969

Abstract: *Ab initio* self-consistent field molecular orbital (SCF–MO) wave functions for the series of molecules CH_4, CH_3F, CH_2F_2, and CHF_3 have been analyzed in terms of the simple concepts of bond dipoles and effective atomic charges. By assuming that the "true" C–H and C–F bond dipoles are proportional to bond dipoles calculated from the Mulliken populations, and by calibrating against the standard bond dipoles (C–H in CH_4 and C–F in CH_3F), we have calculated molecular dipole moments for the series CH_3F to CHF_3 in good agreement with experimental values. The effective atomic charges based on the calibrated bond dipoles, as well as those based on Mulliken population analysis of the SCF–MO wave functions, do not exhibit charge alternation similar to that found by the semiempirical CNDO calculations of Pople and Gordon. The carbon 1s energy level shifts for multiple fluorination seem to be the sum of shifts which arise for a single fluorination. The binding energies of the carbon 1s electrons are essentially linear functions of the charge at carbon calculated by either of the abovementioned ways. A consideration of this binding energy–charge correlation and others from the literature show that such correlations exist for several different definitions of atomic charge, and that they should consequently be regarded primarily as useful relationships allowing statements to be made about relative charges, but not necessarily reflecting the absolute physical situation.

Recent advances in *ab initio* quantum mechanical calculations for molecules of chemical interest have produced many opportunities for fresh insight into, and analysis of, molecular electronic structure. In this paper we use the simple concepts of bond dipoles and atomic charges to analyze the electronic structures of the series CH_4, CH_3F, CH_2F_2, and CHF_3, based on the SCF–MO wave functions determined by Ha and Allen.[1] These wave functions consist of molecular orbitals expanded as linear combinations of groups of Gaussian functions which are themselves accurate representations of the SCF atomic orbitals.

There are several reasons for this analysis. (1) The experimental values[2] of the molecular dipole moments for CH_3F, CH_2F_2, and CHF_3 do not follow a simple additive bond dipole relation.[3] This has been discussed and rationalized in the "bond polarizability" model.[3,4] Since the electronic structures described by the wave functions depend in a self-consistent way on all the electrons and nuclei in the systems, we hoped to extract this dipole moment behavior from the wave functions. (2) The charge distributions are also of interest, particularly in view of the results from the approximate CNDO calculations of Pople and Gordon,[5] which suggested that charge alternation may be characteristic of inductive and mesomeric effects. (3) The accessibility of inner shell binding energies by the ESCA techniques[6] and the apparent linear correlation of measured binding energy with atomic charge for sulfur[7] and nitrogen[8] in molecules suggest that a consideration be made of the carbon 1s binding energies and atomic charges.

Dipole Moments and Atomic Charges

Table I presents the total dipole moments for CH_3F, CH_2F_2, and CHF_3 (i) from experiment,[2] (ii) from direct calculation of the expectation value of the dipole moment operator with the SCF–MO wave functions,[1]

---

(1) T. K. Ha and L. C. Allen, *Int. J. Quantum Chem., Symp.*, **1**, 199 (1967), and unpublished calculations.

(2) R. D. Nelson, Jr., D. R. Lide, Jr., and A. A. Maryott, "Selected Values of Electric Dipole Moments for Molecules in the Gas Phase," National Standard Reference Data Series, National Bureau of Standards Circular, No. 10, U. S. Government Printing Office, Washington, D. C., 1967.

(3) L. Pierce and J. F. Beecher, *J. Amer. Chem. Soc.*, **88**, 5406 (1966).

(4) R. P. Smith, T. Ree, J. L. Magee, and H. Eyring, *ibid.*, **73**, 2263 (1951).

(5) J. A. Pople and M. Gordon, *ibid.*, **89**, 4253 (1967).

(6) K. Siegbahn, *et al.*, "ESCA—Atomic Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Nova Acta Regiae Societatis Scientiarum Upsaliensis, Ser. IV, Vol. 20, Almqvist and Wiksells, Sweden, 1967.

(7) K. Hamrin, *et al.*, *Chem. Phys. Lett.*, **1**, 557 (1968).

(8) J. M. Hollander, D. N. Hendrickson, and W. L. Jolly, *J. Chem. Phys.*, **49**, 3315 (1968).

Table I. Dipole Moments (D)

	Exptl[a]	$\langle\psi|\mu|\psi\rangle$[b]	Std bond moment[c]
CH_3F	1.85	2.43	1.81
CH_2F_2	1.97	2.61	2.12
CHF_3	1.65	2.21	1.81

[a] Reference 2. [b] Reference 1. [c] Reference 3.

and (iii) from the simple additive bond dipole model.[3] The additive bond dipole model, which uses for the entire series the standard bond dipoles[9] of 0.40 D for μ_{C-H} (C^--H^+) and 1.41 D for μ_{C-F} (C^+-F^-), does not predict the proper behavior. Though the *ab initio* wave functions give moments which are too large, they do predict the correct trend of the dipole moments through the series. Thus the description of the relative electron distribution through the series seems correct.

A dipole moment can always be considered to be due to charges appropriately arranged in space, but of course one can make up an infinite number of charge arrangements which have the same net dipole moment. In molecular structure one frequently assumes that atoms carrying appropriate fractional charges give rise to molecular dipole moments, and we shall take that point of view. How shall we get the charges for our present purposes? The population analysis due to Mulliken[10] is a simple and very convenient way to partition the electron distribution for LCAO-SCF-MO wave functions into atomic contributions. Table II summarizes these quantities for the CH_4-CHF_3 series, taken from the calculations of Ha and Allen.[1] It is well known that one cannot in general expect to calculate accurate dipole moments based directly on charges found from a Mulliken population analysis, and that such an analysis may be rather sensitive to the basis functions.[10b] But the Mulliken analysis has been useful for comparisons among related molecules. Since both bond lengths and atomic populations change through the series (Table II), it is clear that the SCF-MO wave functions do indicate some changes in C-H and C-F bonds through the series. If we first use the crudest possible idea that for each molecule we can compute the "bond dipoles" as the products of the atomic charges from the Mulliken analysis and the bond lengths (taking carbon at the origin), we find the results of Table III. The bond moments and total dipole moments are much too large. However, in a relative sense the bond dipole moments do show "polarization" through the series, and the total moments do exhibit the correct qualitative behavior. This suggests that we might calibrate these bond moments based on the Mulliken populations against some standard bond dipole moments and obtain an accurate set of bond and total dipole moments.

Table II. Bond Lengths and Gross Atomic Populations[a]

	Bond lengths, Å		Gross atomic populations[b]	
	C-H	C-F	H	F
CH_4	1.091		0.724	
CH_3F	1.109	1.385	0.704	9.343
CH_2F_2	1.092	1.385	0.683	9.323
CHF_3	1.098	1.332	0.656	9.302

[a] From ref 1. [b] In electron units.

Table III. Crude Bond Dipoles and Total Molecular Dipole Moments Calculated Directly with Distances and Charges Obtained from Table II[a]

	Bond dipoles, D		Total molecular dipole moment, D
	C-H	C-F	
CH_4	1.446		0
CH_3F	1.576	2.281	3.86
CH_2F_2	1.662	2.106	4.32
CHF_3	1.814	1.931	3.75

[a] The electronic charge used is 4.8016×10^{-10} esu.

Let μ^p denote a bond dipole moment from the population analysis (*i.e.*, those of Table III) and μ^e denote the "effective" bond dipole, that is, a bond dipole, which, when combined with other such moments, will hopefully generate the correct total molecular dipole moment. We assumed a proportionality of the two kinds of moments for the C-H and C-F bonds

$$\mu^e{}_{C-H} = K_{C-H}\mu^p{}_{C-H}$$

$$\mu^e{}_{C-F} = K_{C-F}\mu^p{}_{C-F}$$

With 0.40 D for the standard[9] C-H moment (in CH_4) we take $\mu^p{}_{C-H} = 1.446$ D from Table III and find $K_{C-H} = 0.278$. Similarly, the standard C-F moment[9] of 1.41 D combines with the CH_3F value of $\mu^p{}_{C-F} = 2.281$ D from Table III to yield $K_{C-F} = 0.618$. That these proportionality constants deviate from unity is not surprising, and may be due either to a poorly balanced basis set (*cf.* ref 10b) or perhaps a fundamental inability of the Mulliken charges to give correct dipole moments. Since Mulliken did find[10b] close agreement of the directly computed dipole moment and that based on the population analysis for an extended, near-Hartree-Fock wave function for hydrogen fluoride, there is reason to hope that this latter deficiency may not be too bad. It would be nice to have more data on this point from highly accurate LCAO-SCF-MO wave functions for a variety of systems.

The proportionality constants are used with μ^p values of Table III to compute the effective bond dipoles given in Table IV. Note how these effective dipoles change through the series. The increasing C-H bond moments reflect the increasing electron-withdrawing

Table IV. Effective Bond Dipole Moments and Total Molecular Dipole Moments[a]

	Effective bond dipole moments, D		Total molecular dipole moment, D
	C-H	C-F	
CH_4	0.400		0.0
CH_3F	0.436	1.410	1.83
CH_2F_2	0.460	1.302	2.04
CHF_3	0.502	1.194	1.73

[a] As found by the calibrated calculations described in the text.

---

(9) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, pp 239-244.

(10) (a) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955); (b) *ibid.*, **36**, 3428 (1962).

effects on a given C–H bond due to multiple fluorination, and the correspondingly decreasing C–F bond moments reflect the increasing "competition" for electrons between fluorines.

The total molecular dipole moments calculated[11] from the effective bond dipoles are also included in Table IV, and comparison with Table I shows that these calculated values are in remarkable agreement with experiment. This supports our contention that the relative description of the series is given accurately by the SCF–MO wave functions, and justifies the assumption of proportionality between effective bond dipoles and those calculated from Mulliken populations for these systems.

These molecular dipole moments are, incidentally, in rather better agreement with experiment than those found with the bond polarizability model.[3] The CNDO calculations[5] do not give the correct sequence of dipole moments, but, rather, their qualitative behavior is like that of the additive, transferable bond dipoles: CH_3F and CHF_3 have the same calculated dipole moments.

Since the effective bond dipoles of Table IV give good molecular dipole moments, these, in turn, can now be used to find effective atomic charges, by using the bond lengths of Table II. This definition of atomic charge is certainly unambiguous, and it does, of course, produce the correct dipole moments. These effective atomic charges are given in Table V. These charges are much smaller than those from the population analysis. They seem more rational, since in a nonpolar molecule such as methane it is not very sensible to suppose that each hydrogen atom carries a positive charge as large as 0.28 e. The value of about 0.08 e shown in Table V is chemically more reasonable. Notice that the hydrogen atoms are slightly more positive in CH_3F than in CH_4, and that carbon is, of course, somewhat more positive in CH_3F than in CH_4. (Charges based on the Mulliken populations of Table II also show the same behavior.) These reflect the effects of the substitution of a highly electronegative fluorine for a hydrogen, and show that the electron-withdrawing effect of fluorine extends throughout the molecule. This is contrary to the findings of Pople and Gordon[5] from CNDO calculations, which indicated that the hydrogens in CH_3F are slightly more negative than the hydrogens in CH_4, and that charge alternation may be a characteristic of inductive effects. Because their CNDO calculations are based on not-fully-understood approximations applied to the rigorous SCF–MO formulations, one must regard their findings with some skepticism, since the rigorous SCF–MO results considered here give opposite results.

Table V. Effective Atomic Charges Calculated from the Effective Bond Moments of Table IV and the Bond Lengths of Table II[a]

	q_H	q_F	q_C
CH_4	+0.076		−0.305
CH_3F	+0.082	−0.212	−0.034
CH_2F_2	+0.088	−0.200	+0.224
CHF_3	+0.095	−0.208	+0.530

[a] Charges are in electron units.

Carbon 1s Energy Shifts

To the knowledge of the authors the 1s binding energies of carbon in this series of molecules have not yet been measured experimentally. Some discussion of the partitioned energies associated with carbon 1s orbitals for these calculations was given previously.[1] But this paper will consider the orbital energies ϵ associated with these orbitals, since by Koopmans' theorem they correspond to ionization potentials, which can now be measured by ESCA techniques.[6] Though it is known that the *absolute* values of the 1s binding energies found in this way will not be correct, the *trends* (*i.e.*, the shifts in binding energy) are expected to be well represented across the series.[12]

In Table VI are summarized these 1s energies and the carbon atomic charges from the Mulliken analysis, and also from the effective atomic charges. Note that as the "positive nature" of carbon increases, its 1s binding energy ($-\epsilon_{1s}$) becomes greater. In fact, the changes in energies and charges of Table VI show an almost linear binding energy–charge relation for both of the atomic charges defined! Thus, the substitution of F for H produces a net increment in both the charge and 1s binding energy of carbon which is roughly constant through the series. The same behavior was found for boron in recent theoretical studies[13] of BH_3, BH_2F, BHF_2, and BF_3. It will be interesting to see if, in general, multiple substitution at an atom produces an inner shell energy level shift which is a sum of shifts due to single substitutions. If this were general, it would be a very powerful rule of thumb for ESCA applications.

Table VI. Carbon 1s Energies and Carbon Atomic Charges

Quantities	ϵ^a	Mulliken charge[b]	Effective charge[c]
CH_4	−11.211	−1.104	−0.305
CH_3F	−11.389	−0.544	−0.034
CH_2F_2	−11.569	+0.016	+0.224
CHF_3	−11.753	+0.576	+0.530
Changes			
CH_4 CH_3F	−0.178	+0.564	+0.272
CH_3F CH_2F_2	−0.180	+0.560	+0.258
CH_2F_2 CHF_3	−0.184	+0.560	+0.306

[a] From ref 1. In hartrees: 1 hartree = 27.21 eV. [b] Based on Table II. [c] From Table V.

Now it has been seen that there are (at least) two sets of charges which can be associated with carbon in the series CH_4 to CHF_3, and that the carbon 1s binding energies correlate almost linearly with either set. From experiments, it has been found that similar correlations exist between nitrogen 1s binding energies and CNDO calculated charges,[8] and between sulfur 2p binding energies and charges based on electronegativity concepts.[7] Free ion calculations for various sulfur atomic ions also

---

(11) In computing the total dipole molecular moments we have used the experimental nontetrahedral angles (*cf.* ref 1) for the series. The values obtained by assuming tetrahedral angles are essentially the same: 1.85, 2.03, and 1.70 D.

(12) One of us (M. E. S.) is actively pursuing such problems by *direct* SCF–MO calculations on both the ground state molecules and the 1s hole states of their positive ions. For the two series of molecules studied so far (B in BH_3 and BH_2F, and C in CH_4, CH_3F, and H_2CO) the 1s shifts based on Koopmans' theorem and those based on direct calculation are the same to within the accuracy available from ESCA measurements. Further work is underway.

(13) M. E. Schwartz and L. C. Allen, submitted for publication.

give similar results.[14] It is thus apparent that the binding energy–charge relationships are to be regarded primarily as useful correlations and not necessarily as absolute representations of physical reality. It is noteworthy, however, that in some very recent Hartree–Fock calculations[15] on various carbon ions, the Koopmans' theorem 1s binding energy increased by 0.56 hartree from the neutral atom to the unipositive ion. This is similar to the present results (Table VI) that from CH_4 to CHF_3 a 1s binding energy increase of 0.54 hartree occurs for an effective carbon atom charge change of 0.83 e.

Despite the difficulty of defining atomic charges, once a choice is made one can then obtain a "feel" for the relative charges of atoms in different environments, and thus gain useful insight into inner-shell binding energies and their relations to molecular structure.[6] Hopefully, the discussions here will encourage other researchers to consider these matters of dipole moments, atomic charges, and inner-shell energy levels in relation to one another.

Acknowledgments. The work of M. E. S. at Notre Dame is partially supported by a grant from the Petroleum Research Fund administered by the American Chemical Society, and that of L. C. A. at Princeton by the National Science Foundation and the Directorate of Chemical Sciences of the Air Force Office of Scientific Research.[15a]

---

(14) F. A. Gianturco and C. A. Coulson, *Mol. Phys.*, **14**, 223 (1968).

(15) F. A. Gianturco, "Influence of Chemical Substitution on Carbon 1s Electrons," Paper B1, Oxford University, Mathematical Institute, Wave Mechanics and Quantum Theory Progress Report, 1967–1968.

(15a) NOTE ADDED IN PROOF. Thomas[15b] has recently measured the binding energies of carbon 1S in the halomethanes. He finds smaller shifts for the fluoromethanes than those from the present wave functions (*e.g.*, 2.8 eV from CH_4 to CH_3F as compared to 4.85 eV from here) and attributes the discrepancy to the failure of the use of orbital energies to account for reorganization upon ionization. However, M. E. S.[15c] has recently completed calculations with more extended basis sets, and found that orbital energies do reflect energy shifts as well as those from direct calculation on both ground state and ion (*e.g.*, a shift of 3.2 eV from CH_4 to CH_3F is given by both methods with the extended basis). The discrepancy here is due[15c] to the inflexibility of the accurate *atomic* functions as *molecular basis* functions in accounting for inner-shell energies. Experimentally,[15b] the shifts are still linear and additive and the extended basis calculations[15c] do show the same sort of charge-dipole behavior found here; (b) T. D. Thomas, submitted for publication; (c) M. E. Schwartz, submitted for publication.

Translational Energy Dependence of the Bond Energy Effect for Abstraction from *n*-Perdeuteriobutane by Fast Hydrogen Atoms

Richard George Gann, Will Mann Ollison, and J. Dubrin

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received July 17, 1969

Abstract: Hydrogen atoms at various well-known initial kinetic energies, 0.67, 0.92, 1.15, 1.67, and 2.05 eV, were generated by the photodissociation of HI and HBr and reacted with n-C_4D_{10} and n-$CD_3(CH_2)_2CD_3$. Abstraction at the weaker secondary C-D bonds is strongly favored over reaction at the primary positions (the bond energy effect was first observed in recoil systems, where the T is produced at essentially infinite energy on the chemical scale). The integrated yield ratio, HD(prim)/HD(sec), increases from 0.24 at the lowest source energy to 0.59 at the highest source energy. This significant energy dependence is consistent with a higher threshold energy for primary abstraction. At high relative energies (~2 eV), where the individual abstraction cross sections are only weakly energy dependent, the secondary cross section is ~30–50% greater than the primary cross section.

The familiar atomic hydrogen-saturated hydrocarbon abstraction reaction has been extensively investigated at thermal energies under equilibrium conditions,[1] very high kinetic energies in recoil media,[2] and at intermediate energies in photolytic systems.[3] Equilibrium thermal measurements can give little information about the energy-dependent form or size of the reaction cross section at energies much greater than the threshold energy. Indeed, $k(T)$ measurements of extremely high accuracy are necessary to distinguish the commonly used line of centers cross section form from other possible threshold excitation functions.

In the last 10 years two nonequilibrium techniques have been widely used to study H-saturate kinetics. In the recoil method, atomic tritium is produced at essentially infinite energy on the chemical scale and hence its chemistry may be conveniently observed over the whole reactive range (~50–0.5 eV). The fast tritiums undergo two major reaction modes with saturates.[2]

$$\begin{aligned} T + CH_4 &\longrightarrow TH + CH_3 \text{ (abstraction)} \\ &\longrightarrow CH_3T + H \text{ (displacement)} \end{aligned}$$

The abstraction threshold energy is ~0.3–0.5 eV, whereas, the rather unique displacement process has a threshold of 1.5–2.0 eV. A collision model for the displacement or exchange reaction has been discussed in detail by Wolfgang.[2]

---

(1) A. F. Trotman-Dickenson, "Gas Kinetics," Butterworth and Co., Ltd., London, 1955; V. N. Kondratev, "Chemical Kinetics of Gas Reactions," Addison Wesley Co., Reading, Mass., 1964; I. Amdur and G. G. Hammes, "Chemical Kinetics: Principles and Selected Topics," McGraw-Hill Book Co., Inc., New York, N. Y., 1966.

(2) R. Wolfgang, *Ann. Rev. Phys. Chem.*, **16**, 15 (1965); E. K. C. Lee and F. S. Rowland, *J. Amer. Chem. Soc.*, **85**, 897 (1963).

(3) (a) R. J. Carter, W. H. Hamill and R. R. Williams, Jr., *ibid.*, **77**, 6457 (1955); (b) R. M. Martin and J. E. Willard, *J. Chem. Phys.*, **40**, 3007 (1964).