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Non Empirical LCAO SCF MO Investigations of Electronic Reorganizations Accompanying Core Ionizations

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Calculations have been carried out on an extensive series of molecules for both the neutral species and core ionized states. Substituent effects on C_{1s}, N_{1s}, O_{1s}, and F_{1s} levels have been investigated and where available comparison has been drawn with experiment. Comparison with Koopmans' theorem has allowed a relatively detailed study of change in relaxation energies as a function of substituent effect on a given core level. Whilst for C_{1s} levels the computed shifts in core binding energies are approximately linearly related to differences in relaxation energies for the N_{1s}, O_{1s}, and F_{1s} levels, the relative electronegativity of the substituent can invert this correlation. The empirical correction of Koopmans' theorem for differences in relaxation energies at different sites has been investigated for large molecules. The results compare well with direct hole state calculations.

Key words: Core ionization – Ionization, core ~

1. Introduction

Theoretical interpretations of molecular core binding energies, measured by ESCA, within the Hartree Fock formalism have centred around five models, namely: core hole state calculations [1], Koopmans' theorem [2], equivalent core model [3], potential at an atom model and the charge potential model [4].

The extensive discussions of experimental data utilizing these models have assumed that nuclear relaxation is slow compared with the typical lifetimes of core hole states. On the other hand the importance of electronic reorganizations accompanying photoionizations of core electrons has clearly been established. However, theoretical studies in which electronic reorganization has been specifically incorporated have been confined to relatively simple molecules and few systematic studies are available in which the importance of differences in electronic relaxation energies for different core holes has been investigated. The data currently available does suggest however, that for atoms of similar bonding environment, relaxation energies are closely similar.

Our objectives in this paper are four-fold:

(a) To investigate the importance of nuclear relaxation accompanying core ionization on both absolute and relative binding energies;

(b) to investigate, with a common basis set, substituent effects on shifts in core binding energies for a large range of compounds and bonding types;

(c) to investigate systematically the relative importance of relaxation energy contributions to shifts in core binding energies;

(d) consequent on (b) and (c), to investigate the possibility of making systematic corrections to Koopmans' theorem thus enabling shifts for relatively large systems to be obtained from ground state calculations.

2. Computational Details

The calculations discussed in this work were performed with STO 4-31 G basis sets [5]. Clementi's best atom exponents [6] were used for C, N, O, and H. The deficiencies of an STO basis set for fluorine dictated the use of a comparable Gaussian expansion of Hartree Fock orbitals (HF 4, 31 G) [7]. For the more detailed studies in (a) an STO 6-1, 1, 1, 1 G basis gave added flexibility to the valence basis. The calculations were performed using the ATMOL system of programs [8] implemented on an IBM 370/195. Experimental geometries have been used where these were known, in other cases geometries were estimated from standard tables.

3. Results and Discussion

3.1. *An Investigation of Nuclear Relaxation in the Core Hole State of Methane*

In the Hartree Fock formalism the binding energy corresponding to photoionization of a core electron is given by:

$$\mathrm{BE} = (\Delta E)_{\mathrm{HF}} + (\Delta E)_{\mathrm{rel}} + (\Delta E)_{\mathrm{corr}}$$

where

$$\Delta E = E_{(\mathrm{ion})} - E_{(\mathrm{ground\ state})} \,.$$

Recent theoretical and experimental studies have indicated that at least for first and second row atoms the absolute magnitudes of the relativistic and correlation energy differences are very small [9]. Our previous studies have indicated the relative importance of basis set dependence of computed binding energies (as a difference between the neutral molecule and the ion) and this is of some importance since most calculations have by necessity employed basis sets a long way from the HF limit. Good agreement in general is obtained between calculated and observed binding energies on the assumption that nuclear relaxation is unimportant. The success of the equivalent cores model (employing either experimental or theoretically generated thermodynamic data) also suggests that nuclear relaxation during photoionization is unimportant. Experimental evidence to date suggests that the lifetimes of core hole states are typically in the range 10^{-13}–10^{-17} sec. Of particular interest as far as this work is concerned is the observation that some Auger transitions involving carbon have a halfwidth of the order of 0.1 eV. This suggests therefore that under appropriate conditions the natural linewidth of a carbon 1*s* core level might be of the same order of magnitude. If this is so then from the uncertainty principle one might expect the lifetime for a carbon 1*s* hole state to be of the same order of magnitude as a vibrational frequency (i.e. $\sim 10^{-13}$ sec). Indeed it has been demonstrated recently by Siegbahn and co-workers [10] (employing a high resolution spectrometer based on a fine focus X-ray monochromatization scheme), that the

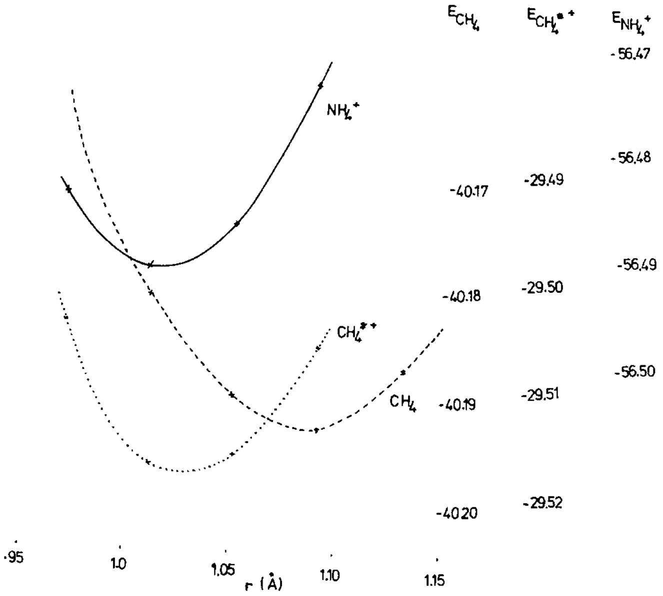

Fig. 1. Variation of total energy with bond length for methane and its core hole and equivalent core states

carbon 1*s* spectra for CH_4 (in the gas phase), exhibits a marked degree of asymmetry. This has been attributed to a Frank Condon envelope and clearly provides the first evidence for a change in geometry in going to the hole state.

It is of some interest therefore to investigate the energy minimised geometries for CH_4 and for its C_{1s} hole state and for comparison (since it is of some important w.r.t. the equivalent cores approximation) the equivalent cores species NH_4^+. For such small systems, extended basis set calculations become feasible. Geometry minimizations have therefore been carried out for the three species using an STO 6, 1, 1, 1, 1 G basis set, with exponents optimized for a molecular environment, being taken from the extensive studies of Pople and co-workers. The resultant potential energy curves are shown in Fig. 1. For the optimum ground state geometry the binding energy is calculated to be 290.8 eV in excellent agreement with the experimental (290.8 eV).

There are several interesting features which emerge from this. Firstly, it can be seen qualitatively (and demonstrated quantitatively by fitting to a quadratic), that the three curves are very similar, with the hole state and equivalent cores species being displaced by ~.06 Å to shorter bond length. The minimised geometries are in excellent agreement with experiment [11]; C–H 1.09 (1.09 Å) for CH_4 and N–H 1.03 (1.03 Å) for NH_4^+, the experimental values being given in parentheses. Taking a typical vibrational frequency (~3000 cm^{-1}) the observed band envelope for the C_{1s} level of methane may readily be accounted for. The calculated binding energy corresponding to the minima for neutral molecule and hole state differs by only ~0.3 eV from that computed from the geometry appropriate to the neutral molecule. It is clear therefore that the assumption o an unchanged nuclear framework on core ionization is a good approximation This possibility has also been discussed recently in a different context b Meyer [12]. In the remainder of this work therefore, nuclear relaxation has bee ignored.

3.2. Substituent Effects

As we have previously indicated there have been numerous theoretical an experimental studies of substituent effects on core binding energies. There ha been no previous systematic theoretical study however of a large range o substituent effects on different core levels studied with a comparable basis set In an attempt to rectify this deficiency we have investigated substituent effect on C_{1s}, N_{1s}, O_{1s}, and F_{1s} core levels in a range of both saturated and unsaturated systems. Calculations have been carried out within the RHF formalis with a 4.31 G basis set. Since a variety of experimental and theoretical studie have shown that on the ESCA timescale core holes are localised [13], th calculations reported refer only to the localised core hole states. Experimenta geometries were employed where available but preliminary studies indicate that the binding energies were virtually unchanged for subtle variations in th geometry.

The emphasis in these particular calculations has been on shifts in bindin energies rather than absolute values and therefore the limitations of such a basi set are to some extent relatively minor as has been previously shown i calculations on the fluoromethanes [14]. As a preliminary check the absolut binding energy for the C_{1s} levels of CH_4 is calculated to be 294.3 eV. In the nex section a detailed discussion of relaxation energies will be given but at this stag it should be emphasized that by comparison with the results from Koopmans theorem the basis underestimates the magnitude of the relaxation energy Considerable evidence is available that this relaxation energy is associated almos solely with the valence electrons and the underestimation of this quantity wit the 4-31 G basis is readily understandable since the exponents are optimised wit respect to the neutral species. That this is the case may be readily demonstrate by re-computing the total energy for the hole state with exponents appropriat for the valence atomic orbitals of the equivalent core (viz. N for CH_4). Th excellent agreement (Table 1) for the absolute binding energies for the molecule studied by this approach is most encouraging and indicates a computationall

Table 1. Effect of optimised core valence atomic orbital exponents on core binding energies

X	Unoptimised	Optimised[a]	Experimental[b]
CH_4	294.18	290.71	290.8
H_2O	545.49	539.12	539.4
CO	548.47	541.89	542.3
CO	300.78	296.71	296.2

[a] In this context optimised is taken to mean that the valence atomic orbital exponents correspon to the equivalent core species for the hole state.

[b] Thomas, T. D.: J. Chem. Phys. 53, 1744 (1970).

less expensive means of calculating absolute binding energies, as compared to large basis computation.

It is convenient in discussing these results to consider the effect of substituents on a given core level in different bonding environments and then proceed to a comparison as outlined in (b). Where results are available comparison has been made with experimental data.

3.2.1. Binding Energies in Saturated Systems

The range of substituents which have been studied are indicated in Tables 2 and 3 with the primary substituent effect with respect to the methyl substituent taken as standard. This is more reasonable than employing hydrogen substituent as reference since it is not clear in cases where strong hydrogen bonding is possible that the experimental results refer to the free molecule. Where direct experimental data is available or where it may be inferred the agreement between theory and experiment is good. The shifts in the binding energies are in accord with chemists intuitive ideas concerning the nature of substituent effects viz. at the two extremes replacing H by Me or F results in a shift to lower and higher binding energies respectively for all core levels. Of some interest is the fact that substituent effects are such that in progressing across the series from C_{1s} to F_{1s} core levels

Table 2. Substituent effects on carbon core binding energies

Carbon	X	Calc.	Exptl.[a]	Carbon	X	Calc.	Exptl.[a]
$C\mathrm{H_3}$–X	$\mathrm{CH_3}$	(0)	(0)	XCHO	$\mathrm{CH_3}$	3.40	3.4
	H	0.23	0.2		H	3.87	3.4
	$\mathrm{CH_2F}$	0.61			$\mathrm{NH_2}$	4.30	
	$\mathrm{CHF_2}$	1.26			OH	5.32	5.2
	$\mathrm{CF_3}$	1.96	2.2[b]		F	7.28	
	CHO	0.57	0.8				
	$\mathrm{NH_2}$	0.89	0.9[c]		Miscellaneous		
	OH	1.55	1.8		$\mathrm{CH_3}C\mathrm{H_2F}$	2.96	
	F	3.46	3.0		$\mathrm{CH_3}C\mathrm{HF_2}$	6.04	
$C\mathrm{H_2}$=X	$\mathrm{CH_2}$	0.22	0.3		$\mathrm{CH_2}C\mathrm{F_3}$	9.13	
	CHF	0.80			$\mathrm{F_2}CO$	10.73	
	$\mathrm{CF_2}$	1.54			$\mathrm{H}C\mathrm{CF}^*$	2.03	
	NH	1.97			$\mathrm{FC}C\mathrm{F}$	5.29	
	O	3.87	3.4		$\mathrm{CH_2}C\mathrm{HF}$	3.17	
$\mathrm{HC}{\equiv}C$–X	H	1.18	0.6		$\mathrm{CH_2}C\mathrm{F_2}$	6.29	
	F	4.46					

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[a] Schwartz and Switalski: J. Am. Chem. Soc. **94**, 6298 (1972). Collection of experimental data from references: Davis, D. W., Shirley, D. A., Thomas, T. D.: J. Chem. Phys. **92**, 4184 (1970); Thomas, T. D.: J. Am. Chem. Soc. **92**, 4184 (1970); Davis, D. W., Hollander, J. M., Shirley, D. A., Thomas, T. D.: J. Chem. Phys. **52**, 3295 (1970); Siegbahn, K., *et al.*: ESCA applied to free molecules. Amsterdam: North Holland 1969.

[b] Estimated from thin film measurements on benzotrifluoride and benzene, cf. Clark, D. T., Kilcast, D., Musgrave, W. K. R.: J. Chem. Soc. (D) 516 (1971).

[c] Estimated from thin film measurements on pyrrole, cf. Clark, D. T., Lilley, D. M. J.: Chem. Phys. Letters **9**, 234 (1971).

Table 3. Substituent effects on N, O, F core binding energies

	X	Calc.	Exptl.^{a}	BE(1*s*)	Calc.	Exptl.
Nitrogen						
$\mathit{N}\mathrm{H}_2$–X	CH_3	(0)	(0)	$\mathrm{CH_2}\mathit{N}\mathrm{H}$	0.40	
	H	0.78	0.5			
	CHO	1.17	1.0			
	NH_2	0.88				
	OH	1.44				
	F	3.75				
Oxygen						
$\mathrm{H}\mathit{O}$–X	CH_3	(0)	(0)	$\mathrm{CH_2}\mathit{O}$	0.60	−1.3
	H	1.0	0.8	$\mathrm{CF_2}\mathit{O}$	3.12	
	CHO	1.77	1.5	$\mathrm{CH_3CH}\mathit{O}$	−0.30	−1.3
	NH_2	0.49		$\mathrm{NH_2CH}\mathit{O}$	−1.37	
	OH	1.30		$\mathrm{OHCH}\mathit{O}$	−0.17	−0.1
	F	4.52		$\mathit{O}\mathrm{HCHO}$	1.78	1.5
				$\mathrm{FCH}\mathit{O}$	1.84	
Fluorine						
F–X	CH_3	(0)		$\mathit{F}_2\mathrm{CO}$	3.16	
	H	2.24	1.6^{b}	$\mathrm{CH_2CH}\mathit{F}$	0.40	
	CH_2CH_3	−0.28		$\mathrm{CH_2C}\mathit{F}_2$	1.78	
	$CHFCH_2$	0.77	0.9^{c}	$\mathrm{HCC}\mathit{F}$	2.84	
	CF_3CH_3	1.84	1.4^{c}	$\mathrm{FCC}\mathit{F}$	3.29	
	CHO	1.41				
	NH_2	0.58				
	OH	0.89				
	F	4.0	4.3^{b}			

[a] Values as Table 2 (a).

[b] Shaw, R. W., Thomas, T. D.: Chem. Phys. Letters **22**, 127 (1973).

[c] Extrapolated from experimental data on fluoromethanes (see text).

there is generally relatively little variation due to Me, NH_2, OH, and F substituents. The net effect is that the difference in shifts arising from these substituents remains relatively constant for the different core levels.

There is sufficient data available to consider both primary and secondary substituent effects on core binding energies and these results are shown in the case of fluorine substitution in Table 4. The marked consistency of primary and secondary shifts at carbon of ~3.0 eV and ~0.7 eV respectively are in excellent agreement with available experimental data obtained from studies of simple homopolymers [15]. It is clear that for fluorine, the primary and secondary substituent effects, in not only saturated but also unsaturated systems are essentially constant in accord with the observed shifts in the fluorobenzenes [16]. By employing appropriate primary and secondary shift data it is possible to estimate shifts in core binding energies for other systems. In difluoroacetylene for example, a shift of 4.06 eV is anticipated with respect to acetylene in accord with a calculated value of 4.12 eV. The experimentally observed gas phase shifts in the fluoromethanes by comparison with the fluoroethanes are also well reproduced by this data [17] for both the C_{1s} and F_{1s} core binding energies.

Table 4. Effect of fluorine substitution on α and β core binding energies

	Primary (α)	Secondary (β)
CH_3–CH_3	(0)	(0)
CH_2F–CH_3	2.96 (2.96)	0.61 (0.61)
CHF_2–CH_3	6.04 (3.08)	1.26 (0.65)
CF_3–CH_3	9.13 (3.09)	1.96 (0.70)
CH_2=CH_2	(0)	(0)
CHF=CH_2	2.95 (2.95)	0.58 (0.58)
CF_2=CH_2	6.07 (3.12)	1.32 (0.74)
H–C≡C–H	(0)	(0)
F–C≡C–H	3.20	0.86
H_2C=O	(0)	(0)
HFC=O	3.41 (3.41)	1.24 (1.24)
F_2C=O	6.86 (3.45)	2.40 (1.16)
H–C≡N	(0)	(0)
F–C≡N	3.3	1.09

For the F_{1s} levels the computed primary and secondary shifts for a methyl substituent are 2.2 eV and 0.3 eV respectively. It is interesting to note that by contrast, the primary effect of methyl for C_{1s} levels is only 0.4 eV and this large difference in substituent effects at different core levels is also reproduced by the experimental data. The two sets of results for the effect of fluorine on C_{1s} levels and of methyl on fluorine 1*s* levels emphasizes once again the short range nature of substituent effects in saturated systems.

3.2.2. Binding Energies in Unsaturated Systems

A similar analysis has been undertaken for some unsaturated species. Reasonable agreement is again evident between the calculated and experimental results where available. Introduction of a double or triple bond to the core ionised centre is seen to have little effect on the primary and secondary shifts with the notable exception of the O_{1s} shifts in the carbonyl compounds where the shift is approximately twice as large. The primary shifts at the carbonyl carbon correlate quite well with those observed at a saturated carbon, the shifts (w.r.t. CH_3) being slightly larger.

3.3. Relaxation Energies

The computational expense etc. of performing calculations on core hole states for each core level has meant that considerable emphasis in the literature has been placed on the interpretation of shifts using Koopmans' theorem. As we have already indicated the energy lowering due to the relaxation of the valence electrons in going from the neutral molecule to the core ionised species is quite appreciable in absolute terms (of the order of 10–20 eV for first row atoms). Previous investigation in which comparisons have been made between Koopmans' theorem and hole state calculations have shown that the relaxation energies are closely similar for a given core level in a closely related series of molecules [14]. Experimental data is available however which suggests that for different bonding environments there may be significant contributions to shifts in core binding energies arising from differences in relaxation energies. A particular example is the shift in carbon 1*s* levels for the methyl and carbonyl carbons in acetaldehyde. Experimental measurements both in the gas and solid phase give a shift of between 2.7 and 2.9 eV [18]. The shift however computed from Koopmans' theorem is always smaller by approximately 0.4 eV, independent of the basis set, provided a suitably balanced basis is employed. By contrast the hole state calculations reported here are in excellent agreement with the measured shift in C_{1s} levels for acetaldehyde thus suggesting a small but significant difference in relaxation energy at the two carbon atoms. In studying an extensive series of molecules covering a number of core levels and a variety of bonding situations we may investigate the importance of differences in relaxation energy in contributing to these shifts.

Firstly considering the data for core ionisation at carbon, Fig. 2 shows a plot of calculated shifts in binding energies versus differences in relaxation energies

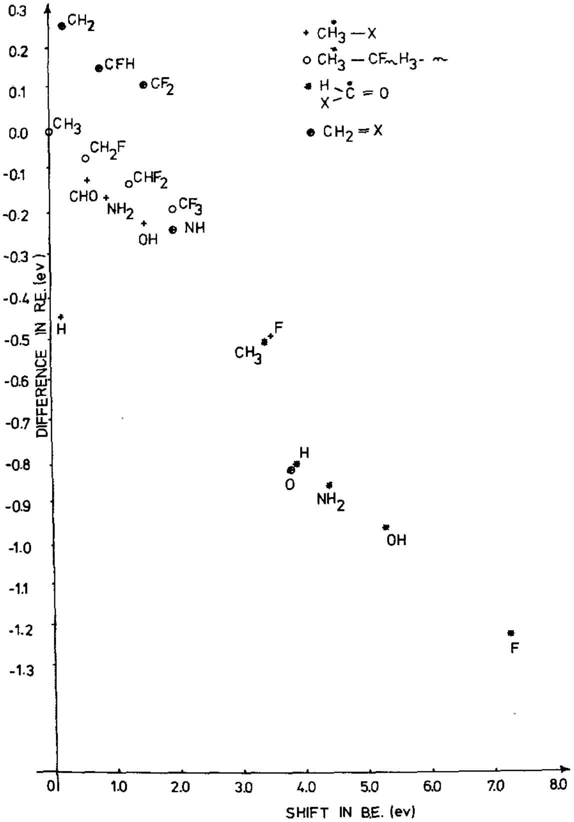

Fig. 2. Plot of computed differences in relaxation energy versus shifts in binding energy (both w.r.t. ethane as standard) for some C_{1s} levels

covering C_{1s} levels in both saturated and unsaturated systems. It is interesting to note that the relaxation energies span a range of ~1.5 eV whilst the corresponding range for the shifts is ~7 eV. There is a clear trend established between shift and relaxation energy and this has also been noted recently for a very limited series of molecules by Hillier and co-workers [19]. Good linear correlations are observed for the four individual series of molecules studied. The relaxation energies are obviously lowest for those core levels corresponding to the largest shift in binding energy. This is not unreasonable since the valence electron clouds will already be somewhat contracted in the neutral molecule. The good overall correlation between shift and relaxation energy goes some way to rationalizing why in general the charge potential model works so well. Indeed this is not so unexpected in the light of a recent analysis [20] of the contributions to relaxation energies in terms of local and neighbouring atom contributions with both the former and latter containing charge dependent terms.

$$\mathrm{RE} = kq_a + E_{\mathrm{flow}} + l_a \qquad (1)$$

where l_a is the relaxation energy due to orbital contraction around a neutral atom in the molecule.

In a previous investigation we have discussed in detail the constancy of the relaxation energy in the case of the fluoromethanes [14]. In this case the constancy was attributed to the cancellation of charge dependent terms arising from local and nearest neighbour charge distributions. For the particular case of the simple fluoro-substituted ethanes we have pursued a similar analysis. The data are collected in Table 5. Considering firstly the effect of substituents on the CH_3 core levels in proceeding from CH_3 to CF_3 as substituent the binding energy increases by 1.96 eV and the relaxation energy decreases by 0.19 eV. From Mulliken population analyses the changes in valence electron population in going from neutral molecule to the hole state have been computed for both the atom on which the core hole is located and the nearest neighbour atoms. There is little change across the series in population of this carbon atom in the neutral

Table 5

Core	ΔBE	ΔRE	q	$\Delta(\Delta_{\mathrm{pop}})^a$	$\Delta(\Delta n_i)^b$
CH_3–CH_3	(0)	(0)	−0.061	(0)	(0)
CH_3–CFH_2	0.6	−0.07	−0.116	−0.026	−0.004
CH_3–CF_2H	1.26	−0.13	−0.164	−0.048	+0.005
CH_3–CF_3	1.96	−0.19	−0.209	−0.060	+0.021
CFH_2–CH_3	2.96	−0.14	0.439	+0.033	−0.029
CF_2H–CH_3	6.04	−0.21	0.905	+0.088	−0.089
CF_3–CH_3	9.13	−0.19	1.344	+0.169	−0.183

Δ BE – shift in binding energies
Δ RE – difference in relaxation energy
q – charge on C in neutral molecule

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[a] Δ_{pop} = el. pop C^* – el. pop C (-ve indicates decreased flow of electronic charge).
[b] Δn_i = sum over bonded atoms (pop X* – pop X).

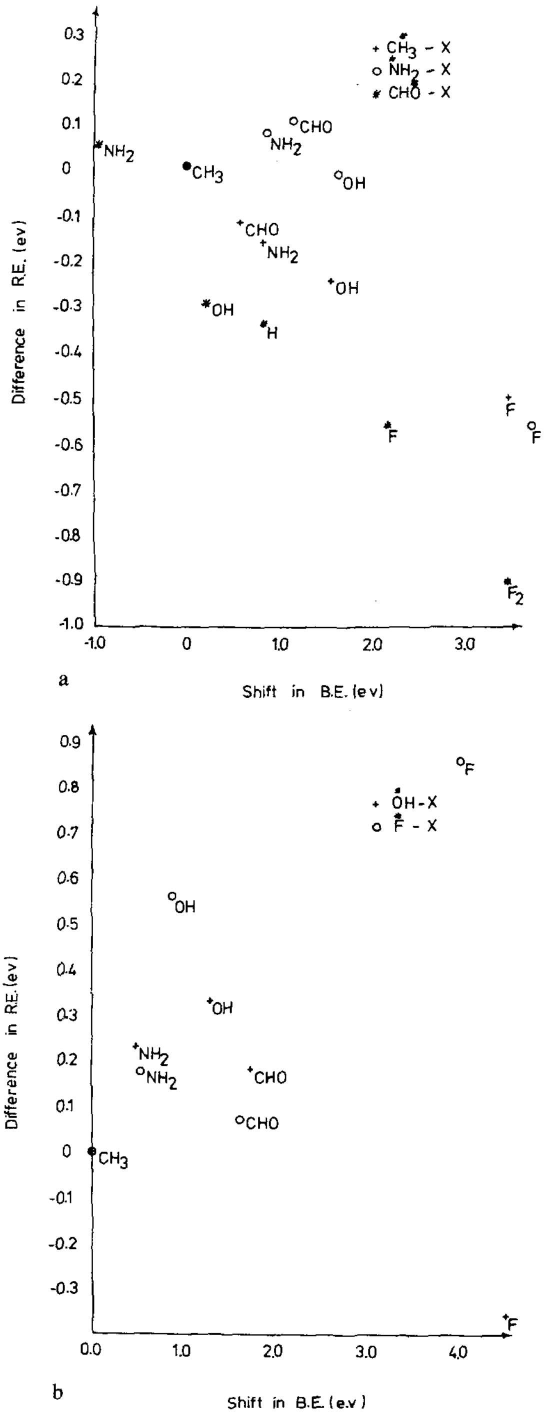


Fig. 3a and b. Plot of computed differences in relaxation energy versus shifts in binding ener (both w.r.t. CH_3 substituent as standard) for some N_{1s}, O_{1s}, F_{1s} levels molecule. In going to the hole state, whilst the change in nearest neighbour populations are effectively constant, there is considerably less electron flow in the case of CF_3 as substituent than for CH_3 and the relaxation energy decreases. By contrast the effect of a methyl substituent in the series CF_nH_{3-n}–CH_3 is such that the change in population at the atom concerned and on the nearest neighbours are similar in magnitude and opposite in sign. The large decrease in population in the neutral molecule however results in the smaller calculated relaxation energies in accord with Eq. (1).

In Fig. 3a and b are shown similar plots of differences in relaxation and shifts in binding energies for some N, O, and F core hole states with the data for carbon included for comparison. Although for the C_{1s} levels there is a clear correlation between the two (as we have previously discussed) for the N_{1s}, O_{1s}, and F_{1s} core levels the relationship is less clear cut. Of some interest however is the change in slope for the core hole states of O and F. This can be most simply rationalized by consideration of prototype species MX*–Y where the core hole on X is being investigated as a function of change in substituent Y (with M remaining unchanged). Thus when the effective electronegativity of Y is greater than X there is a decrease in RE with an increase in BE and vice versa with the effective electronegativity of Y less than X. This has been investigated for the C, N, O, and F holes with a similar range of substituents by means of a population analysis, the results of which are shown in Table 6. For the neutral

Table 6. Substituent effects on reorganization energies and electronic charge

Core	Δ RE	q	$\Delta(\Delta_{pop})$
CH_3–H	−0.46	−0.146	−0.015
CH_3–CH_3	(0)	−0.061	(0)
CH_3–CHO	−0.12	−0.093	−0.052
CH_3–NH_2	−0.16	−0.027	0.066
CH_3–OH	−0.25	0.029	0.099
CH_3–F	−0.50	0.331	0.043
NH_2–H	−0.63	−0.409	−0.024
NH_2–CH_3	(0)	−0.287	(0)
NH_2–CHO	0.10	−0.206	−0.063
NH_2–NH_2	0.07	−0.288	0.050
NH_2–OH	−0.01	−0.278	0.085
NH_2–F	−0.56	0.039	0.055
*O*H–H	−1.06	−0.419	−0.078
*O*H–CH_3	(0)	−0.276	(0)
*O*H–CHO	0.14	−0.177	−0.021
*O*H–NH_2	0.24	−0.261	0.056
*O*H–OH	0.33	−0.233	0.100
*O*H–F	−0.36	0.033	0.105
F–H	−1.42	−0.489	−0.085
F–CH_3	(0)	−0.483	(0)
F–CHO	0.07	−0.405	0.001
F–NH_2	0.18	−0.395	0.087
F–OH	0.56	−0.307	0.166
F–F	0.86	0.0	0.311

molecules the effect of the very electronegative fluorine is to polarize the valence electrons. In going to the F_{1s} hole state then there is a less effective increase in polarising power from the core ionised fluorine atom and a similar decrease in electronic flow to this centre is observed. The flow will be smallest when the effective electronegativity of the substituent is lowest, and from the form of Fig. 3a and b will be in the opposite sense to the trend exhibited by the C_{1s} levels and hence contribute more to the relaxation energy. This is apparent for the O_{1s} levels where with $Y < X$ a positive slope is observed which is reversed for the very electronegative F. It is of interest to note that whilst the carbonyl oxygen exhibits considerably larger differences in relaxation energies (than for the comparable H*O*X series) the correlation with shift in binding energy is closely linear and the slope negative. This is understandable on the basis that the combined effective electronegativity of the =CHX group is consistently less than that of oxygen.

In an interesting approach to relaxation effects Perry and Jolly [21] have estimated the relative relaxation energies attributable to substituents (F, Cl, Br, Me) for a series of germanium hydrides (GeH_3Y). Their findings are in good qualitative agreement with ours if the analogous CH_3–Y series is taken for comparison. It is of some importance that for the series HX and X_2 ($X = CH_3$, NH_2, OH, F) the relaxation energy differences [RE(X_2)–RE(HX) 0.46, 0.70, 1.39, 2.28 eV] are comparable to the calculated differences in binding energy [BE(X_2)–BE(HX) −0.23, 0.10, 0.30, 1.8 eV]. This supports the suggestion by Jolly and Perry that the former energies may account for the small observed shifts in the analogous species with X = Cl, Br though further study is required to establish the relative magnitudes of these relaxation energies.

3.4. Estimation of Shifts in Binding Energies from Koopmans' Theorem and Relaxation Energy Corrections

We have stressed above the importance of electronic relaxation concomitant upon core ionisation and that between certain core holes there is an appreciable calculated error in their shift if this is not taken into consideration. There appears however in these small molecules to be fairly systematic variations in the reorganisation energies of a particular atom in similar environments which may be quite general for the nearest neighbour environment. The possibility then arises of making systematic corrections to core level ionisation energies as calculated from Koopmans' theorem to estimate the core binding energies. This is of considerable importance for comparison with ESCA studies of larger molecules since computations with a basis set of comparable size would require considerable c.p.u. expenditure if the individual core hole states were to be studied. As a suitably complex test case we have studied the biologically important 5-azauracil. Experimental studies [22] of the core binding energies for an extensive range of pyrimidine bases has allowed, by direct correlation, an assignment of core binding energies in the order:

$$C_{1s} \quad C2 > C4 > C6$$

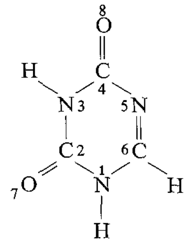
$$N_{1s} \quad N1 > N3 > N5 .$$

The charge potential model (CNDO/2 charges) and Koopmans' theorem correctly predict the ordering of N_{1s} levels, however the shift between C4 and C6 is calculated to be small and in both cases in the opposite sense to that inferred from the experimental correlations. It should be emphasized of course that the measurements refer to the solid phase and that extensive hydrogen bonding may modify the pattern of binding energies that might be expected from the free molecule. This will be discussed in detail elsewhere [22].

In studying relaxation energies as a function of structural type however, it is clear that significant differences in relaxation energies might be expected at different sites within the molecule. Direct hole state calculations have therefore been carried out and, from the series of small molecules exhibiting the appropriate structural features, estimates have been made of differences in relaxation energies, which may be used as corrections to Koopmans' theorem. The results are presented in Table 7. The corrected Koopmans' theorem results are in excellent agreement with the direct hole state calculations and in complete agreement with the experimentally determined ordering of C_{1s} and N_{1s} levels.

The agreement between the estimated and calculated binding energies is most encouraging and we are currently engaged in further investigations of a more extensive series encompassing C_{1s}, N_{1s}, O_{1s}, and F_{1s} core hole states in comparable chemical environments.

Table 7. Shifts in core binding energies (eV) in 5-azauracil



Core	Koopmanns' theorem	Hole state	Estimated RE	Estimated BE[a]
N 1	2.08	2.52	-0.43^{b}	2.51
N 3	1.15	1.82	-0.43^{b}	1.58
N 5	(0)	(0)	$(0)^{c}$	(0)
C 2	0.83	1.70	-0.60^{d}	1.43
C 4	−0.19	0.54	-0.60^{d}	0.41
C 6	(0)	(0)	$(0)^{e}$	(0)
O 7	0.54	0.92		
O 8	(0)	(0)		

[a] BE = Koopmans-RE.
[b] Estimated from $\mathit{N}\mathrm{H_2CHO}$ (14.29).
[c] Estimated from $\mathit{N}\mathrm{H{=}CH_2}$ (14.72).
[d] Estimated from $\mathrm{NH_2CHO}$ (10.56).
[e] Estimated from $\mathrm{HN{=}CH_2}$ (11.16).

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