

Substituent effect on ionisation potential in a series of related molecules : A theoretical study in a molecular orbital framework

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Abstract. The effect of replacing the hydrogen atoms in thioformaldehyde by halogen atoms (F, Cl) on the ionisation potential of the non-bonding electron is analysed by using the Hellman-Feynman theorem, regarding the nuclear charge of the substituent as a parameter in the many-electron Hamiltonian. The trends predicted by our theory nicely agree with the relevant ionisation potentials computed either by applying Koopmans' theorem or by the ΔE_{SCF} method. For the carbonyls, available experimental data indicate the reliability of our prediction.

Keywords. Perfluoro effect ; substituent effects ; ionisation potential ; molecular orbital framework ; thioformaldehyde ; halogen atoms.

1. Introduction

With the recent advances made in the field of photo-electron spectroscopy (Carlson 1975; Ghosh 1978; Turner *et al* 1970) the measurement of various quantities, associated with the process of photoionisation (*e.g.*, ionisation potential, ionisation cross-section, angular distribution of photoelectrons, etc.) is fast emerging as an important probe for obtaining information about the details of molecular-electronic structure. As experimental data of this kind continue to accumulate, chemists are confronted with the problem of correlating the discernible trends or patterns (if any) exhibited by the observed quantities with changes in molecular structural parameters. The present paper concerns one specific aspect of the problem. To be a little more specific, we have considered the following series of molecules, viz., H_2CS , $HFCS$, F_2CS , $ClFCS$, Cl_2CS and H_2CO , $HFCO$, F_2CO , Cl_2CO with a view to analysing and interpreting the trend displayed by the ionisation potential of the non-bonding electron (nb_2). It may be noted that a previous theoretical study of the so-called 'perfluoro-effect' (Brundle *et al* 1972) involved

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an analysis of the changes in the composition of the different one-electron orbitals of the substituted molecules individually and as such is rather a *posteriori* in nature. Viewed against this, our theory aims at making an *a priori* estimate of the nature of the effect of fluorine or other halogen substitution. However, the theory in the present form is approximate in nature and involves, as we shall see later, the use of unrelaxed orbitals for the ionic states so that it is expected to work in cases where Koopmans' theorem holds.

2. Theory

Let ψ_0 be the $2n$ electron SCF wavefunction of the H_2CS molecule in the ground state and ψ_+ be the corresponding $(2n - 1)$ electron ionic-state function at the Koopmans' level of approximation (Koopmans' 1933). Let ϕ_i be the orbital from which the electron is removed. If we now consider the replacement of the hydrogen atoms in H_2CS by fluorine atoms simply as an increase in the nuclear charge (Z) of the substituent from $Z = 1$ to $Z = 9$ in an adiabatic manner we can write

$$(dE/dZ)_{Z=Z_H} = \sum_i (\partial E/\partial Q_i) (\partial Q_i/\partial Z) + (\partial E/\partial Z)_{Q_0} \quad (1)$$

where the Q_i 's represent the different nuclear coordinates of the molecule concerned; $Z = Z_H$ implies that the derivatives are evaluated at $Z = 1$.

Assuming the H_2CS molecule (the parent neutral) to be in its equilibrium ground state geometry,

$$(\partial E/\partial Q_i) = 0, \text{ for all the } Q_i\text{'s.}$$

Accordingly, we have from equation (1)

$$(dE/dZ)_{Z=Z_H} = (\partial E/\partial Z)_{Q_0} \quad (2)$$

where Q_0 stands for the collection of equilibrium nuclear coordinates of parent neutral.

Assuming that the ion too has an identical equilibrium geometry we have,

$$(dE^+/dZ)_{Z=Z_H} = (\partial E^+/\partial Z)_{Q_0} \quad (3)$$

where E^+ represents the energy of the ion derived from H_2CS . This however, is not-too-unjustified an assumption for an ion, formed by the removal of an electron from the non-bonding orbital (ϕ_i) of the parent neutral.

From (2) and (3) we can write

$$(d\Delta E/dZ)_{Z=Z_H} = (\partial E^+/\partial Z)_{Q_0} - (\partial E/\partial Z)_{Q_0} \quad (4)$$

where $\Delta E = (E^+ - E)$. Applying the Hellmann-Feynman theorem (Hellmann 1973; Feynman 1939) we have, from (4)

$$\begin{aligned} (d\Delta E/dZ)_{Z=Z_H} = & \left\langle \psi_+ \left| \frac{\partial H(2n-1)}{\partial Z} \right| \psi_+ \right\rangle \\ & - \left\langle \psi_0 \left| \frac{\partial H(2n)}{\partial Z} \right| \psi_0 \right\rangle \end{aligned} \quad (5)$$

where $H(2n-1)$ is the $(2n-1)$ electron Hamiltonian of the ion and $H(2n)$ is the $2n$ electron Hamiltonian of the neutral. ΔE clearly measures ionisation potential estimated by the application of Koopmans' theorem so that the derivative on the left side of (4) or (5) represents the rate of change of ionisation potential (IP) with change in the nuclear charge of the atoms bonded to the carbon atom of the thiocarbonyl group. Evaluation of the expectation values on the right side of (5) is straightforward. Remembering that ψ_0 and ψ_+ are single-determinant wave-functions built up from the same set of variationally determined one-electron spin-orbitals ($\{\phi_i\}$) (Hartree-Fock) of the parent neutral, (5) can be easily simplified. Thus

$$\begin{aligned} & \left\langle \psi_+ \left| \frac{\partial H(2n-1)}{\partial Z} \right| \psi_+ \right\rangle_{Z_H} \\ &= \frac{2Z_C}{R_{CH}} + \frac{2Z_S}{R_{SH}} + \frac{2Z_H}{R_{HH'}} - \sum_{i=1}^{2n-1} \left\langle \phi_i \left| \frac{1}{r_{iH}} \right| \phi_i \right\rangle \\ & \left\langle \psi_0 \left| \frac{\partial H(2n)}{\partial Z} \right| \psi_0 \right\rangle_{Z_H} \\ &= \frac{2Z_C}{R_{CH}} + \frac{2Z_S}{R_{SH}} + \frac{2Z_H}{R_{HH'}} - \sum_{i=1}^{2n} \left\langle \phi_i \left| \frac{1}{r_{iH}} \right| \phi_i \right\rangle, \end{aligned}$$

where R_{AB} , in general, stands for the distance between the nuclei A and B while Z_A represents the nuclear charge of atom A . Using the above two equations we have,

$$(d\Delta E/dZ)_{Z_H} = \left\langle \phi_i \left| \frac{1}{r_{iH}} \right| \phi_i \right\rangle, \quad (6)$$

assuming that ionisation has occurred from the spin-orbital ϕ_i . Since in the LCAO-MO approximation of SCF theory,

$$\phi_i = \sum_p C_p \chi_p$$

where $\{\chi_p\}$ represent basis functions centred on different atomic centres, (6) can be further expanded as follows:

$$(d\Delta E/dZ)_{Z_H} = \sum_p \sum_q C_{pi}^* C_{qi} \left\langle \chi_p \left| \frac{1}{r_{iH}} \right| \chi_q \right\rangle. \quad (7)$$

Since we would be working within the limitations of the CNDO/2 framework, (7) can be further simplified. Thus, finally

$$(d\Delta E/dZ)_{Z_H} = \sum_p |C_{pi}|^2 \left\langle \chi_p^A \left| \frac{1}{r_{iH}} \right| \chi_p^A \right\rangle. \quad (8)$$

where χ_p^A denotes the p th basis function centred on the A atom. Clearly (8) can form the basis of predicting the nature of shift in the ionisation energy of the

i th orbital of H_2CS following the replacement of H atoms by heavier counterparts. There is, however, a limitation in the predictive power of (9) in that its practical success will depend on whether the relaxation energy associated with the ionisation from the orbital ϕ_i remains fairly constant for the series of molecules under study. If the relaxation energy strongly varies from one substituted molecule to the other, *a priori* prediction of the nature of substituent effect becomes impossible unless one has some independent means of correlating the relaxation effect with the nature of the substituent. The other alternative is to use the proper SCF wavefunction $\tilde{\psi}_+$ of the ion to evaluate the right side of (5). In that case, however, the simplicity of (8) is lost and the analysis turns out to be rather *a posteriori* in nature. We shall, therefore base our analysis on (8) to examine how far does it mimic the trends discernible in the IP calculated by Koopmans' theorem and to what extent these predictions are affected by the orbital relaxation effects.

3. Results and Discussion

We would like to discuss our results under two different headings: (i) the predictions based on our model, (ii) the results obtained by applying Koopmans theorem and the ΔE_{SCF} method. For the SCF calculations we have used the CNDO/2 method (Pople *et al* 1965; Pople and Segal 1965, 1966) with the Sp basis set (not spd). For the ΔE_{SCF} calculations, we resorted to the UHF technique for SCF calculations on the doublet ions. However, for the ions, electronic energy was not corrected for the spin contamination effect since the spin polarisation was observed to be very small in all the cases (not unlikely at the CNDO/2 level of approximation).

3.1. Results from our model

Let us first consider (8). The right side of (8) must be a positive quantity (the intrinsic sign of the nuclear-attraction integrals has been taken care of already in forming the difference (6)). Evaluated at $Z = 1$, $(d \Delta E)/dZ$ is thus a positive quantity implying thereby that the replacement of the H atoms in H_2CS by heavier atoms would cause an increase in the ionisation energy of an electron in the orbital ϕ_i . Our model thus suggests a gradual increase in the ionisation energy of the non-bonding electron along the $\text{H}_2\text{CS} \rightarrow \text{HFCS} \rightarrow \text{F}_2\text{CS} \rightarrow \text{ClFCS} \rightarrow \text{Cl}_2\text{CS}$ sequence as a first approximation.

A little reflection, however, suggests that this would represent an oversimplification of the problem; for the replacement of fluorine by a chlorine atom leads not only to an increase in Z , but also to a simultaneous decrease in the electronegativity of the substituent and this fact has to be reckoned with while considering the $\text{F}_2\text{CS} \rightarrow \text{ClFCS} \rightarrow \text{Cl}_2\text{CS}$ sequence.

If we consider the replacement of H by an atom X as causing simultaneous changes in the nuclear charge Z and the electronegativity parameter η we can write

$$(\partial \Delta E / \partial \eta)_{Z_{\text{H}}} = (\partial \Delta E / \partial Z)_{Z_{\text{H}}} / (\partial \eta / \partial Z)_{Z_{\text{H}}}. \quad (9)$$

We have already seen that $(\partial \Delta E / \partial Z)_{Z_H}$ is generally a positive quantity. $(\partial \eta / \partial Z)_{Z_H}$ has recently been estimated (Feller *et al* 1980) in an approximate manner and the value is ≈ 6.88 . Hence the right side of (9) is expected to be a positive quantity. From this, one can make an approximate guess of the pattern of change in the ionisation potential of the non-bonding electron caused by the replacement of H by other atoms. Considering the replacement of H by F and Cl separately, for example, we have

$$(\partial \Delta E)_{H \rightarrow F} \approx \left(\frac{\partial \Delta E}{\partial Z} \right)_{Z_H} (\eta_F - \eta_H)$$

and $(\partial \Delta E)_{H \rightarrow Cl} \approx \left(\frac{\partial \Delta E}{\partial Z} \right)_{Z_H} (\eta_{Cl} - \eta_H)$

Since $\eta_H < \eta_F$ and η_{Cl} , in each of the above cases we expect an increase in the ionisation potential. Using (10) and (11) we can write further,

$$(\partial \Delta E)_{F \rightarrow Cl} = (\partial \Delta E / \partial Z)_{Z_H} (\eta_{Cl} - \eta_F).$$

Since $\eta_{Cl} < \eta_F$ one expects that the replacement F by Cl would cause a lowering of the IP of the non-bonding electron. *We therefore expect that the IP in question should increase in the $H_2CS \rightarrow HFCS \rightarrow F_2CS$ sequence and decrease in $F_2CS \rightarrow ClFCS \rightarrow Cl_2CS$ sequence.* Obviously, we could have assumed ClFCS or Cl₂CS to be derived from the parent F₂CS molecule and a parallel analysis could have been carried out using $(\partial \Delta E / \partial Z)_{Z_F}$ and $(\partial \Delta \eta / \partial Z)_{Z_F}$. The only difficulty is that it would be difficult to make a fairly reliable estimate of $(\partial \eta / \partial Z)_{Z_F}$. However, if we make the not-too-unrealistic assumption that $(\partial \eta / \partial Z)_{Z_F}$ is a positive quantity and carry out a similar analysis based on F₂CS as the parent molecule, we have

$$(\partial \Delta E)_{F \rightarrow Cl} \approx (\partial \Delta E / \partial Z)_{Z_F} (\eta_{Cl} - \eta_F).$$

Arguing just as before $(\partial \Delta E / \partial Z)_{Z_F}$ is expected to be a positive quantity so that replacement of fluorine in F₂CS by Cl would lead to a decrease in the IP of the electron concerned as a result of the effect of decreased electronegativity of the substituent. Let us now compare the qualitative expectations based on our theoretical model against the results of actual numerical calculations.

3.2. Koopmans' theorem and ΔE_{SCF} results

We have summarised the ionisation potential of the non-bonding electron computed by the application of Koopmans' theorem and the ΔE_{SCF} method separately for all the five thiocarbonyl molecules in table 1. Each of the methods predicts a systematic increase of the ionisation energy of the non-bonding electron (localised mainly on the sulphur atom) along the $H_2CS \rightarrow HFCS \rightarrow F_2CS$ sequence in conformity with the expectation of our theory already outlined in § 3.1. Similarly the decrease of IP anticipated in § 3.1 on the basis of our theoretical analysis (*a priori*) in the $F_2CS \rightarrow ClFCS \rightarrow Cl_2CS$ sequence is also found to be nicely conforming to the results of the actual SCF calculations. It should be

Table 1. Comparison of the ionisation potentials of the series of thiocarbonyl molecules calculated by the application of Koopmans' theorem and ΔE_{SCF} method.

| Molecule | Ionisation potential of the <i>n</i> electron | | | |
|--------------------|---|-------------------------------------|-------------------|----------------------------------|
| | Koopmans' theorem (eV) (a) | ΔE_{SCF} method (eV) (b) | Experimental data | Relaxation energy (a) - (b) (eV) |
| H ₂ CS | 11.96 | 11.21 | 9.34* | 0.75 |
| HFCS | 12.64 | 11.54 | .. | 1.10 |
| F ₂ CS | 13.20 | 12.35 | .. | 0.85 |
| ClFCS | 12.69 | 11.67 | .. | 1.02 |
| Cl ₂ CS | 12.14 | 10.99 | .. | 1.15 |

* Kroto and Suffolk (1972).

pointed out here that the ΔE_{SCF} estimate of the IP of the non-bonding electron in Cl₂CS is less than that of H₂CS contradicting the trend predicted either by Koopmans' theorem values (table 1) or that predicted by (8). This can be explained, however, by noting that the relaxation energy associated with the non-bonding ionisation is much larger in Cl₂CS than in H₂C,S off-setting the first-order effect of perturbation caused by an increase of nuclear charge of the substituent (see the discussion following (8) in § 2). In table 2 we have displayed the results of similar calculations on a few carbonyl analogue (viz., H₂CO, HFCS, F₂CO, Cl₂CO) along with the available experimental data. The trend observed in going from H₂CO → HFCS → F₂CO mimics what has already been observed in the H₂CS → HFCS → F₂CS series. The experimentally observed trend in going from H₂CO → F₂CO also is correctly reproduced. The only disturbing feature lies in the computed ionisation potential (lowest) of Cl₂CO (both the Koopmans' and ΔE_{SCF} values) being lower than that of H₂CO and F₂CO. However, an examination of the nature of the orbital (HOMO) involved in the ionisation, we find that it is a non-bonding orbital localised on the chlorine atoms [*n*(Cl)] and not on oxygen, unlike what is observed in H₂CO, HFCS or F₂CO. Thus, the anomaly is only an apparent one and need not be considered further. In table 3 we have included the computed net charges carried by the carbon and the sulphur (or oxygen) atoms in the ground state of the parent neutrals. Reference to table 1 clearly shows that the trends exhibited by the ionisation potential of the non-bonding electron correlate nicely with the net positive charge carried by the carbon atom in different molecules. Such a correlation is expected to an intuitive ground. Thus, higher the σ -withdrawing ability of the atoms (XY) attached to the carbon atom of the >C=S unit, the stronger is the depletion of the σ -electron density from the carbon atom. The increased positive charge

Table 2. Comparison of the ionisation potentials of the series of carbonyl molecules calculated by the application of Koopmans' theorem and ΔE_{SCF} method (available experimental data are also included).

| Molecule | Ionisation potential of the n electron | | | |
|--------------------|--|------------------------------|--------------------------------|------------------------|
| | Koopmans' theorem (eV) (a) | E_{SCF} method (eV) (b) | Relaxation energy (a) - (b) eV | Experimental data (eV) |
| H ₂ CO | 14.51 | 12.93 | 1.58 | 10.88 * |
| HFCS | 15.88 | 13.98 | 1.89 | |
| F ₂ CS | 17.29 | 15.16 | 2.14 | 13.60 * |
| Cl ₂ CS | 13.51 | 12.73 | 0.72 | |

* Baker *et al* (1968).

Table 3. Comparison of the net charges on the carbon and sulphur or oxygen atoms in the ground state of a series of thiocarbonyl or carbonyl molecules computed by the CNDO/2 (sp.) method.

| Molecule | Net charge on the carbon atom (q_c) | Net charge on the sulphur or oxygen atom (q_s^-) or q_o^- |
|--------------------|---|---|
| H ₂ CS | +0.0806 | -0.1124 |
| HFCS | +0.3076 | -0.1568 |
| F ₂ CS | +0.5233 | -0.2122 |
| ClFCS | +0.4017 | -0.1684 |
| Cl ₂ CS | +0.2918 | -0.1395 |
| H ₂ CO | +0.2219 | -0.1835 |
| HFCS | +0.4315 | -0.2266 |
| F ₂ CO | +0.6616 | -0.2735 |
| Cl ₂ CO | +0.4324 | -0.1835 |

on the carbon atom naturally causes a higher degree of stabilisation of the non-bonding electron localised dominantly on the sulphur (or oxygen) atom leading to the observed increase of ionisation potential. It is interesting to note that the net electron density on the sulphur atom increases in the H₂CS(A) → HFCS(B) → F₂CS(C) sequence and decreases along the F₂CS → ClFCS → Cl₂CS series, reflecting the higher π -donor ability of fluorine atom. The more interesting point is that parallel to the increase of negative charge carried by the sulphur atom in the sequence A → B → C, one would have expected the ionisation energy of the non-bonding electron to decrease in the same sequence. However, it seems that

a much larger increase in the net positive charge on the carbon atom in the same direction more than offsets the effect of increased electron density on the sulphur atom. The observed trend thus merely reflects the balance of σ -withdrawing and π -donating abilities of the substituents. We have also summarised in tables 1 and 2 the relaxation or orbital reorganisation energies of all the different molecules studied by us (thiocarbonyls in table 1 and carbonyls in table 2). An essential difference between the carbonyl and the thiocarbonyl analogues is revealed in the behaviour of the relaxation energy (ΔE_R) as a function of the nuclear charge of the substituents. Thus ΔE_R increases systematically along the $\text{H}_2\text{CO} \rightarrow \text{HFCS} \rightarrow \text{F}_2\text{CO}$ series while the $\text{H}_2\text{CS} \rightarrow \text{HFCS} \rightarrow \text{F}_2\text{CS}$ series shows a rather erratic behaviour in that ΔE_R increases first from H_2CS to HFCS and decreases from $\text{HFCS} \rightarrow \text{F}_2\text{CS}$ while from $\text{F}_2\text{CS} \rightarrow \text{Cl}_2\text{CS}$ ΔE_R progressively increases. A rationalisation of this observed pattern from a theoretical point of view would be interesting.

4. Conclusion

A slightly different version of the present model (Banerjee and Bhattacharyya 1980) was earlier successfully applied for studying the effects of halogen substitution on the singlet triplet splitting of the $\pi\pi^*$ bands of these molecules. Our model seems to be quite useful also for an *a priori* prediction of the expected nature of substituent effect on the ionisation energies of the non-bonding electrons in carbonyl and thiocarbonyl molecules. Indeed, a similar model can be developed for the π -electron ionisation which should take into account the delocalised nature of these orbitals and, therefore, require a consideration of the changes in bond-orders arising from the substitution. It also seems to be perfectly possible to develop the theory in a quantitative fashion. In this connection, it would be extremely important to analyse the variation of relaxation energy with the nature of the substituent with a view to partitioning the total relaxation energy into a sum of atomic and extra-atomic components, if possible. We hope to return to these problems in the near future.

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