The Theoretical Interpretation of Molecular Core Binding Energies as Measured by *X*-Ray Photoelectron Spectroscopy

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Summary A theoretical interpretation of molecular core binding energies as measured by *X*-ray photoelectron spectroscopy is given, and it is shown that simple relationships between "shifts" in binding energies and "charge distributions" can be misleading.

X-RAY photoelectron spectroscopy provides an extremely powerful tool for investigating the electronic structure of molecules. In recent papers[1,2] correlations have been drawn between shifts in binding energies (*e.g.* C_{1s}, N_{1s} *etc.*) and so called "charge densities" calculated empirically employing Pauling electronegativities and Extended Hückel Treatment, or semi-empirically by the all-valence-electron CNDO–SCF–MO method. Intuitively, of course, a relationship between shift and charge density is appealing but "*a priori*" there is no reason why this should be linear, more particularly since the methods so far employed can be criticized on either or both of the grounds of quantum-mechanical validity and definition of atomic populations. It is therefore an opportune moment to introduce a note of caution into the interpretation of such spectra and in particular the "shifts" in energy levels for a given element (*e.g.* C_{1s}) in various electronic environments.

We present here a particularly striking example, where such a correlation breaks down even qualitatively, and indicate briefly how "shifts" may be calculated using Koopmans' theorem.

At whatever level of theoretical sophistication one studies the electronic structure of acetonitrile, the same gross feature emerges that the electron population is much higher on the methyl carbon than on the carbon attached to nitrogen. A nonempirical all-electron SCF–LCAO–MO treatment with a gaussian basis set,† for example, gives gross atomic populations of 6·77 and 5·79 electrons, respectively. Even allowing for the fact that a Mulliken population analysis is a relatively inaccurate way of describing the electron distribution about an atom as a result of the arbitrary division of overlap density there is still *ca.* one electron difference in population for the two atoms (the *net* atomic populations are 5·40 and 4·69 electrons, respectively).

On the basis of correlations between shift and charge density, one might reasonably predict therefore that there would be a substantial shift between the carbon 1*s* levels for acetonitrile and that the carbon bonded to nitrogen should have the highest binding energy. We have now measured the carbon 1*s* *X*-ray photoelectron spectrum of acetonitrile and find a shift of $<0{\cdot}5$ ev.‡ The spectrum which was excited using characteristic Al-K_α radiation, was measured with the prototype of the A.E.I. Scientific Apparatus Ltd. ES 100 Spectrometer, the sample being studied as a thin film on a cooled probe. Full experimental details of our extensive investigations on this and other molecules will be published in due course. The magnitude of the shift alone is sufficient to throw doubt on the correlations which have previously been made.

We now show that it is possible to obtain good estimates of shifts from "*ab initio*" calculations using Koopmans' theorem. The approximations inherent in such an approach have been outlined recently by Richards;[6] however, to some extent this gives an unduly pessimistic viewpoint as far as *core* electrons are concerned. Consider the two ionization processes for the carbon 1*s* levels of acetonitrile. The binding energies may be expressed in terms of six contributions:

$$E_{1s\,\mathrm{binding}} = (E^{\mathrm{HF}} + E^{\mathrm{rel}} + E^{\mathrm{C}})_{\mathrm{molecule}} - (E^{\mathrm{HF}} + E^{\mathrm{rel}} + E^{\mathrm{C}})_{\mathrm{ion}} \qquad (1)$$

where E^{HF}, $E,^{\mathrm{rel}}$ E^{C} are the Hartree–Fock, relativistic, and correlation energies, respectively.

The energy differences between the molecule and the ion refer to perfect Hartree–Fock calculations. With molecules of any size, the basis set used in the expansion method must of necessity be limited and hence give energies somewhat higher than the Hartree–Fock energies. However, only energy differences are required and with a reasonable basis set these can be calculated quite accurately, e.g. *with the limited basis set used here one obtains* ca. 99% *of the HF energy and it has been employed successfully in discussing*[7] *heats of reaction,* etc.

In calculating absolute binding energies, therefore, one requires nonempirical calculations on both the molecule and ions, and estimates of the relativistic and correlation energy corrections. This is an extremely difficult task and for ionizations involving valence electrons the relativistic and correlation energy corrections are usually neglected. Although the neglect of relativistic corrections is reasonable for ionizations involving valence electrons, for core electrons this is not the case, and for both types of ionization, correlation energy corrections must be included. In the case of core ionizations, however, the feature of real interest is the "shift" in various levels, which involves differences in binding energy. The "shift" or difference in binding energy for the carbon 1*s* levels in acetonitrile may be expressed in terms of energy differences:

$$\Delta E_{\mathrm{shift}} = (E^{\mathrm{HF}} - \grave{E}^{\mathrm{HF}})_{\mathrm{ions}} + (E^{\mathrm{rel}} - \grave{E}^{\mathrm{rel}})_{\mathrm{ions}} + (E^{\mathrm{C}} - \grave{E}^{\mathrm{C}})_{\mathrm{ions}} \qquad (2)$$

where E and $\grave{E}$ refer to the ions produced from the carbon 1*s* levels. The first term can, of course, be calculated by

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† The basis set consists of an uncontracted set of 5*s* and 6*p* type functions on carbon and nitrogen and 2*s* on hydrogen. Orbital exponents for carbon and nitrogen were taken from ref. (3) and for hydrogen from ref. (4). The calculations were carried out using the Polyatom System (5).

‡ The spectrum (C_{1s}) shows a single line which is slightly broadened due to the overlap of the two components. The shift is estimated from a computer analysis of the line shape.

carrying out separate calculations on the two ions. Consider now the application of Koopmans' theorem, the energy difference in the first term is then given directly as the difference in 1*s* orbital energies calculated for the neutral molecule. The calculation shows that the orbitals are essentially localized on the two carbon atoms.§ In applying Koopman's theorem to equation (1) to calculate absolute binding energies, we assume that the orbitals are unaltered when going from molecule to ion, *i.e.* there is no re-orientation. This of course is an oversimplification; however, in applying the theorem to energy differences between the *ions* we are making the same approximation for both, and these tend to cancel, particularly with a good basis set. So that to a good level of approximation as we show in this and succeeding communications ΔE orbital energies $\propto$ $(E^{\mathrm{HF}} - \grave{E}^{\mathrm{HF}})$*ions*. This still leaves two terms to be calculated, the relativistic and correlation energy corrections. Since the inner orbitals are essentially localised, these terms can be estimated from atomic data. In going from the neutral atom C(^3P) to the ion (ionized 1*s* state), the relativistic corrections is *ca.* 0·16 ev.[8] The *difference* in relativistic corrections [equation (2)] between the two ions is certainly an order of magnitude less than this. Similarly, since the orbitals are essentially localized, the *difference* in correlation energy correction will be small so that the shift is dominated by the first term in equation (2). This analysis also applies to ionizations involving outer electrons, with one important difference. This concerns the correlation energy correction. Since the higher occupied molecular orbitals may be extensively delocalized, the correlation correction may differ quite substantially between ionized states, and this introduces an extra element of uncertainty in assigning energy levels. For acetonitrile we may therefore calculate the shift in carbon 1*s* levels directly from the orbital energies of the neutral molecule. The calculated value 0·12 ev agrees well with the observed value $<$ 0·5 ev, considering the number of approximations inherent in this approach. In the following communications we apply this theoretical treatment to more complicated molecules. Although the magnitude of the calculated shift is too small for us to make a definite assignment of energy levels in acetonitrile, the calculation assigns the *highest* binding energy to the carbon atom of the methyl group and this emphasizes that one is ill advised to assign energy levels on the basis of charge density.

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§ By essentially localized we mean that the 1*s* orbital coefficient is $>$0·99 on a particular atom.

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