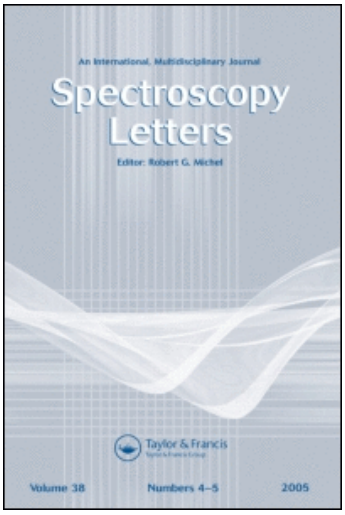

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On the Relation Between Core Electron Binding Energies and Atomic Charge

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ON THE RELATION BETWEEN CORE ELECTRON BINDING ENERGIES AND ATOMIC CHARGE

Key words: XPS, core electron binding energies, molar polarizabilities, atomic charge.

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ABSTRACT

It is suggested that the term, a , describing the difference between gas phase and solid state XPS data is related to the molar polarizability P by the general expression $a = b\ P^{-1/3} + c$ From previously obtained values of the parameters b and c (b= 8.30 eV cm $mol^{-1/3}$ and c= 4.15 eV) we can derive the binding energy of gaseous carbon atoms, E_b = 296.4 eV. The close agreement with the experimentally found E_b = 296.2 eV is regarded as a validification of the above-mentioned formula and also of the concept of atomic charge.

By using literature data of core electron binding energies for a series of alkanes and their corresponding polarizabilities we have derived parameters of the above-mentioned relation , b = 8.1 eV cm $mol^{-1/3}$ and c = 3.34 eV . The fair agreement is regarded as favouring the model used.

In order to perform these latter operations we have made ab initio calculations of the mean atomic charges of the alkanes.

INTRODUCTION

For many years we have advocated the idea [1-3] that it is possible to describe, core electron binding energies as a linear relation of the atomic charge, q , of the atom investigated. This idea developed after we had constructed a good calibration system, relating to the mean binding energy of the carbons of a phenyl group. This method of calibration has been described in detail[4] .

In order to discuss, use and compare data that are not calibrated in this way we have introduced a correction term "a" so that it describes the difference between the investigated system and the standard level of our calibration method. This means that if the investigation under dicussion had given a certain binding energy, E_b', we say that

$$E_b' = E_b + a, \qquad (1)$$

where E_b is the value that we should read from our calibration system (defined for the solid state).
As mentioned above it holds that

$$E_b = k\,q + E_{b0} \qquad (2)$$

Hence it must also hold that

$$E_b' = k\,q + E_{b0} + a \qquad (3)$$

By combining an appropriate number of such relations for a given molecule and using the condition of electroneutrality, we can solve for the q-values of the atoms in the molecule and the term "a".
It is observed, that "a" for solid substances varies within about ± 1 eV, reasonable variations in the techniques of calibration. For gaseous samples, however, the "a"- values are larger ,

ca 6 - 8 eV. This difference between gas phase and solid state binding energies has been discussed ever since the birth of the ESCA technique. The variation seemed to depend on the size of the molecule.

In a recent paper[3] it was suggested that the term "a" is related to the polarizability of the molecule that is under scrutiny.
Actually we obtained - in an empirical way - a simple relation between "a" and P, the molar polarizability of the molecule.

$$a = 8.30\ P^{-1/3} + 4.15 \qquad (4)$$

The purpose of this paper is now to strengthen the validity of this relation by indicating its strength of prognosis and also its power of covering other substances, quite different from those that were used to establish it. It follows that if this relation can be shown to be a good one in the pragmatic sense of the word, the relations between E_b and the atomic charge should also be valid and useful. This in its turn implies that the use of the concept atomic charge is meaningful.

GASEOUS CARBON

The first example relates to the investigation of Bisgaard et al.[5] reporting a binding energy value of 296.2 eV for gaseous carbon.

The molar polarizability P of free carbon is given[6] as 2.591 cm^3/mol. This quantity is derived from carbon containing substances from the assumption of additivity of atomic refractions to build up the molar one. This assumption works very well as is generally accepted [7]. One can also compare the molar

polarizabilities obtained from data for diamond and graphite, respectively[8]. Thus $P_{diamond} = 2.10$ cm^3/mol; $P_{graphite} = 2.90$ or 2.29 cm^3/mol (the latter value along the c axis)
This quantity can be introduced in relation (4) and we obtain

$$a_{(carbon)} = 8.30 * 2.591^{-1/3} + 4.15 = 10.19 \qquad (5)$$

The relation for the binding energy of C1s is[3], however,

$$E_b(C1s) = 4.68\ q_C + 286.2 \qquad (2a)$$

when used for substances calibrated according to our adopted method and

$$E_b(C1s) = 4.68\ q_C + 286.2 + a \qquad (3a)$$

when used otherwise. For the case of gas phase spectra , the "a" term is given by (5). For solid state spectra, "a" may vary between ca -1 and +1 eV.

Hence we arrive at a binding energy for gaseous carbon ($q_C = 0$)

$$E_b(C1s) = 286.2 + 10.19 = 296.39 \text{ eV}. \qquad (6)$$

This value should be compared to the experimentally determined one [5], $E_b(C1s) = 296.2$ eV.
The agreement is good . This is the support alluded to in the introduction.

XPS OF ALKANES

We now want to test the validity of relation (4) for substances of quite another composition than those for which it was empirically derived [3]. The alkanes form a suitable series of

TABLE 1

XPS Data for Alkanes[9,10] and the Carbon Mean Charges from the Present Calculations

Compound	E_b(C1s) / eV	Mean Carbon Charge	a / eV
Methane	290.90	-0.665	7.81
Ethane	290.79	-0.475	6.81
Propane	290.66	-0.426	6.45
n-Butane	290.59	-0.399	6.26
n-Pentane	290.51	-0.385	6.11
n-Hexane	290.45	-0.376	6.01
cyclo-Hexane	290.3	-0.342	5.70
n-Decane	290.33	-0.358	5.80

related molecules. The fact that they contain hydrogen atoms which are not meaningfully investigated by XPS makes us to rely only on the relation (2) for carbon

Pireaux et al [9] have measured C1s binding energies for a series of alkanes. The binding energies are given relative to that of methane.

By accepting E_b(C1s) = 290.9 eV for methane[10] absolute values were obtained for all the compounds investigated by Pireaux et al.[9]. The results are given in Table 1 together with the additional data for cyclohexane taken from the collation of data by Jolly et al.[10].

Introducing the parameter "a" in the sense described above, we can write:

$$E_b(\text{C1s})_{\text{alkane}} = 4.68\, q_C + 286.2 + a \qquad (7)$$

Charge calculations

In order to calculate "a" we need to know q_C for all the hydrocarbons. We have not found any good ab initio calculation, that covers all the seven molecules. A recent paper by Cioslowski[11], however, gives a good survey of Mulliken population data for CH_4 and C_2H_6.

As we needed charge data for all the compounds in Table 1 we have performed an ab initio calculation using the MOLCAS program package[12] The main problem is to choose an adequate AO basis set for the calculation. We have chosen the basis set of Duijneveldt et al.[13] which is based on a primitive set consisting of 12 s-type and 8 p-type gaussian functions for the C atoms and 6 s-type ones for the H atoms. These are contracted to 4 s and 3 p for carbon and 2 s for hydrogen, respectively.
The geometry of each of the alkane molecules was defined from an energy minimizing procedure according to the "Molecular Mechanics 2" program [14,15]. The results of these calculations, to be described in larger detail in a following communication[16], are included in Table 1 . Obviously the actual values obtained for the charges are strongly dependent on the choice of the basis set. Our present data compare well with the extreme ones of Cioslowski[11], e.g. $q_C(CH_4) = -0.61$ and $q_C(C_2H_6) = -0.45$ from STO 4-31G . They show, however, a higher C-H polarity than those derived by Boulanger et al.[17].

As a matter of interest one can mention that the charge of the hydrogen atoms are, e.g., +0.17 charge units for methane, +0.16 for ethane and +0.17 for cyclo-hexane. Theses values are quite close to our previous "experimental" determination for q_H in CH_3 groups[18] i.e. $q_H \approx +0.12$. These latter values were obtained from XPS data for much heavier elements combined with the required electroneutrality of the molecules in question. The present choice of basis sets is therefore well adapted to treating XPS data.

TABLE 2

Polarizability Data for Alkanes using the Mean Values of Data given by Miller[19]

Compound	α /Å^3	P / cm^{3}mol^{-1}	P$^{-1/3}$ / mol$^{1/3}$cm^{-1}
Methane	2.60	6.560	0.534
Ethane	4.47	11.28	0.446
Propane	6.29	15.87	0.398
n-Butane	8.12	20.49	0.366
n-Pentane	9.99	25.21	0.341
n-Hexane	11.81	29.80	0.323
cyclo-Hexane	10.99	27.73	0.330
n-Decane	19.15	48.32	0.275

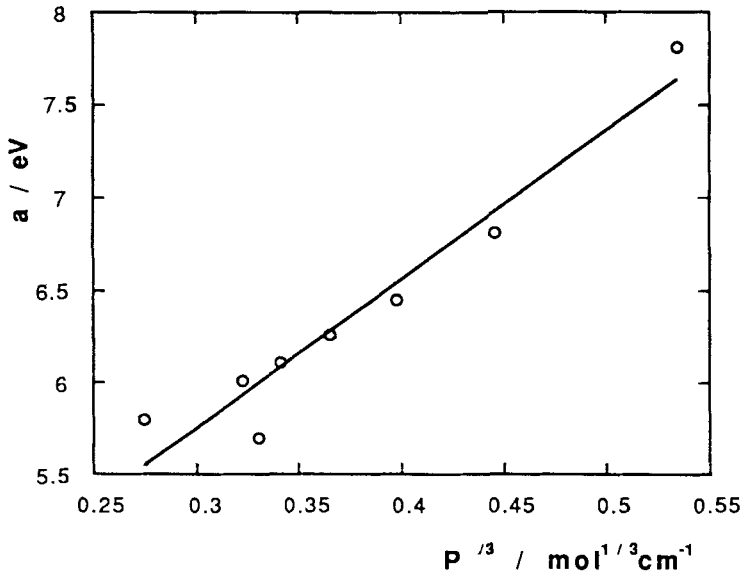

FIG . 1 The "a" data from Table 1 as a function of the polarizabilities of Table 2. The correlation coefficient = 0.967.

The molecular polarizabilities α (Å^3) for the hydrocarbons in question were obtained from the recent collation of Miller[19]. These data were transformed to molar polarizabilities P (cm^3 mol^{-1}) (vide, Table 2) by the relation

$$P = 4/3\ \pi N\ \alpha = 2.523\ \alpha \qquad (8)$$

In Figure 1 we have plotted "a" from Table 1 versus $P^{-1/3}$ from Table 2. .

It is interesting to note that the points fit a line with the slope of 8.06 eV cm mol$^{-1/3}$. (Correlation coefficient = 0.967)

$$a = 8.1\ P^{-1/3} + 3.34 \qquad (4a)$$

Thus the slope is in good agreement with the "experimental" value that we obtained in our previous paper[3], viz., 8.3 eV cm mol$^{-1/3}$. We are , however, troubled by the low value of the intercept of the line, 3.34 eV as compared with 4.15 as found before[3]. Perhaps the term c in the general expression

$$a = b\ P^{-1/3} + c \qquad (4b)$$

is varying with the structure and composition of the molecule . The alkanes are exceptional in the sense that the molecules contain a lot of hydrogen atoms. As hydrogen takes a very extreme position among the elements it may not be unexpected that our present result differs slightly from that[3] for compounds of the heavier elements. All in all there is a striking agreement between the two sets of data, or in another way between the relation (4a) found here and the one (4) found previously[3]. We think that this validifies the concept of linear relations between core electron binding energies and atomic charges.

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