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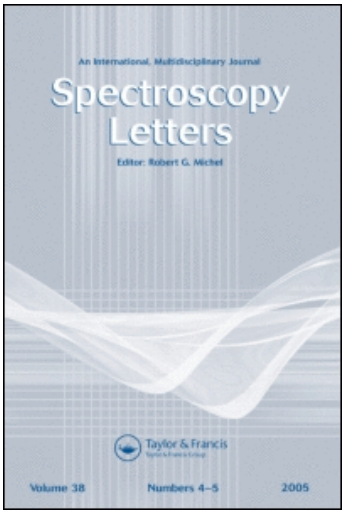

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Ab Initio SCF Calculations Relating to the Cls Chemical Shifts for Some Alkanes

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AB INITIO SCF CALCULATIONS RELATING TO THE C1s CHEMICAL SHIFTS FOR SOME ALKANES

Key words: Alkanes, atom charges, SCF calculations, XPS

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ABSTRACT

Ab initio calculations have been made for a series of simple alkanes and the atomic charges have been estimated in two ways, using the Mulliken population analysis and also using an analysis due to Karlström where the charges are fitted to describe the electrical moments derived from the SCF wave function. Also the orbital energies were calculated. The results were used to interpret experimental data of the carbon core electron binding energies. It is found that the Karlström technique is best suited to describe the XPS data.

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INTRODUCTION

Many attempts have been made to correlate core electron binding energies [1] with estimates of atomic charges. In the simplest approach one has suggested linear relationships between shifts and charges for many classes of compounds[1,2]. E.g., good correlations have been obtained for sulfur[3] and nitrogen[4] in this way, whereas for other elements, especially carbon [5-7], one has met with dfficulties. More complex relations have therefore been proposed including the electrostatic potential from all other atoms in the molecule[2] and the relaxation energies[8]. The latter term desribes the final-state rearrangement. It concerns the physical fact that the energy measured is the difference between the final-state (after ionization) and the ground-state. The charge concept, however, relates to the ground-state only.

In the model of the linear relation between binding energy and charge (1), one assumes that these two effects (electrostatic potential and relaxation) are included in the parameters of the straight line.

$$E_b = k_A q_A + E_b^0 \qquad (1)$$

Other models have also been suggested and tested to include final-state effects. One of these is the transition -potential model [9,10]. In this model the binding energy is related to an orbital energy for a transition state e^T in which half an electron has been removed from the orbital i . Using arguments similar to those for the ground-state model, the transition orbital energy is expressed in the framework of a charge model, and the difference of the orbital energy for the transition state e^T and that of the ground state model e^G is the relaxation energy.

In both models, the ground-state and the transistion-potential model the concept of atomic charge remains the central idea. It is well recognized that atomic charges in a molecule are difficult to calculate, since the concept of an atom within a molecule cannot be precisely defined. Some convention with regard to the partition of the total density among individual atoms is required[11,12]. One such convention for the partition of the electron density into atomic contributions is given by the Mulliken population analysis[13] . Several other methods have also been used[14,15].

The method that we attempt to use in the present investigation is the one proposed by Karlström[17]. In this method, charges are fitted to reproduce the

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electrical moments derived from the SCF wave function . The quantities derived, therefore, retain the physical meaning of charges. The method has been used with advantage when describing intermolecular interactions[17,18].

XPS DATA OF ALKANES

In a previous letter[19] we have discussed a modification[5] of the simple linear ground-state relation for the element carbon, applied to gas phase XPS data of some alkanes[9]. There we describe the results of ab initio SCF calculations for these alkanes and especially the estimation of the Mulliken charges of the carbon atoms. The experimental binding energies have been found[9] to decrease monotonically with increasing number of carbon atoms; from 290.90 eV for CH_4 to 290.33 eV for $C_{10}H_{22}$ (The values from[9] are calibrated against the value of C1s for CH_4 reported by Bakke et al.[20]). This experimental shift is very small (0.57 eV) and thus constitutes a delicate test of any theory or model that wants to treat the chemical shifts of core electron binding energies. Pireaux et al.[9] , e.g., find that their transition-potential model produces about twice as large a shift (1.09 eV) as is actually observed.

The small but accurately determined experimental differences are used in the present paper to test some of the consequences of using Mulliken or Karlström charges for the same basic SCF data on the interpretation of the C1s shift of the alkanes. We will use the ground-state model, both as the simple eqn (1) and in the form (2) developed by Gelius and coworkers[2], where a potential term originating from all the other atoms in the molecule but the atom under analysis is added to the linear relation of (1) .

$$E_b = k_A q_A + \Sigma q_B/R_{AB} + Eb^0 = k_A q_A + V_A + E_b^0 \qquad (2)$$

Writing $k_A q_A + V_A = V_C$ for short

we have $E_b = V_C + E_b^0$ (3)

Obviously the values of k are quite different in equations (1) and (2). Then turning to the ground state model in the form of eqn (2) one notes that the constant k is approximately equal to the electrostatic interaction integral between

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the considered core orbital and valence orbital in the same atom. This interaction is close to the expectation value < 1/r > for the valence electron cloud of the neutral atom. It is usually taken as independent of the charge of the atom of interest although there is no real justification for this.

COMPUTATIONAL PROCEDURE

Calculations have been carried out using the MOLCAS -1 program package[21]. The geometry of each of the alkane molecules was defined from the energy minimizing procedure according to the "Molecular Mechanics 2" program[22,23]. We have choosen the basis set of Duijneveldt et al.[24] : (12, 8/4, 3) for C and (6,12) for the H atom respectively. The atomic charges were calculated according to the Mulliken population analysis[13] and according to the procedure of Karlström[17], respectively.

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RESULTS OF COMPUTATIONS

First we present the results of the SCF calculations in Table 1 with the total energies, and their components Vnn (the nuclear - nuclear repulsion) . In the same Table we also present the sum of the orbital energies, $\sum e_i$, and the sum of the core orbital energies, $\sum e_{i\,,\,core}$. Our data are very similar to the results published by Honegger[25]. The analysis of these data as a function of n (the number of carbon atoms) leads to the following observations:

i) the total SCF energy , E_{tot} is a linear function of the number of C atoms, but its components - V_{nn} and $V_{ee} = E_{tot} - V_{nn}$ (electronic energy) show non-linear dependence on n. These relations for the 4-31 G basis set are reported by Honegger[25] in a graphical form.

ii) the sum of the occupied orbital energies $\sum e_{i\,,}$ where *i* are all occupied orbitals, is a linear function on n. Also the sum of the core orbital energies, $\sum e_{i\,,\,core}$, is a linear function on n (Figure 1). It means that the ratio of the total energies and the sum of the orbital energies or the sum of the core orbital energies

TABLE 1.

The total SCF energies, the nuclear-nuclear repulsion V_{nn} and the orbital energies for the normal alkanes.

	E_{tot} SCF(a.u.)	V_{nn} (a.u.)	Σe_i	$\Sigma e_{i,core}$	$E_{tot}/2\Sigma e_i$	$E_{tot}/2\Sigma e_{i,core}$
CH_4	-40.18955	13.38635	-13.786	-11.207	1.458	1.793
C_2H_6	-79.20989	47.72444	-26.959	-22.442	1.469	1.765
C_3H_8	-118.23407	81.76782	-40.146	-33.665	1.472	1.756
C_4H_{10}	-157.25828	129.58932	-53.328	-44.886	1.474	1.752
C_5H_{12}	-196.28236	183.64077	-66.509	-56.107	1.475	1.749
C_6H_{14}	-235.30629	242.65096	-79.688	-67.328	1.476	1.747
$C_{10}H_{22}$	-391.39464	518.98441	-132.343	-112.187	1.478	1.744

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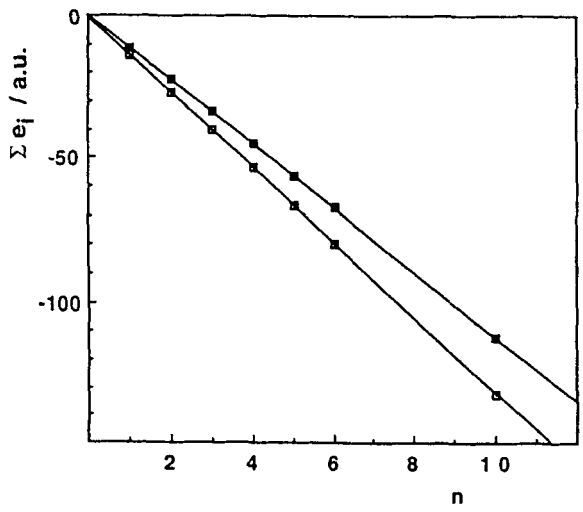

FIG. 1. The sum of all occupied orbital energies (□) and the sum of the core orbital energies (■) as function of the number of carbon atoms in the alkanes.

are approximately constant (Table 1). One can therefore approximate E_{tot} by the sum of the orbital energies as was discussed in [25-27].

The atomic charges, together with the mean value of the charge on the carbon atoms, and the calculated quadrupole moments, Θ, are given in Table 2. Charges from Mulliken population analysis , q, as well as charges calculated according to Karlström [17], Q, are presented. The dependence of the mean values of the charge on the number of carbon atoms, n, are given in Figure 2.

DISCUSSION OF THE RELATION BETWEEN XPS-DATA AND CALCULATED CHARGE

As said above, Pireaux et al.[9] have measured C1s binding energies for the series of alkanes. The experimental core binding energies decrease with increasing number of carbon atoms. The whole shift ranges over 0.59 eV (Fig. 3). According to the authors these small shifts are ruled by the relaxation energy. They claim that the transition potential model for the CNDO/2 wave functions describes the variation of the core-level binding energies, although the calculated shifts are overestimated by a factor of 2. The ground-state potential model with the CNDO/2 wave functions predicts[9] the opposite to the experimental trend.

We now wish to use these experimental XPS data to discuss if it is possible to describe core electron binding energies as a simple function of the atomic charge. We approach this problem in terms of existing theoretical models.

Koopman's Model

In the first approximation, core electron binding energies were obtained by applying Koopman's theorem; $E_i = \Delta \varepsilon_i^{HF}$.

The draw-back of this approach is that the relaxation of the electron cloud is neglected. Sometimes the discrepancy can be about 10%. Nevertheless the trends within a series of compounds might be satisfactorily described[28-30]. Table 3 shows, however, that the calculated mean values of E(C1s) are almost constant.

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TABLE 2.

The calculated values of the charges on the carbon atoms and the quadrupole moments Θ_{zz} resulting from the SCF treatment. q denotes the result of Mulliken population analysis and Q denotes the charges obtained from the method developed by Karlström et al.[17]. All data are given in atomic units and the atoms are counted "from left to right" of the molecule.

	q // q(mean)	Q // Q(mean)	Θ_{zz}
CH_4	-0.665	-0.515	0
C_2H_6	-0.474	-0.375	-0.63076
C_3H_8	-0.491, -0.296,-0.491 // -0.426	-0.368, -0.278, -0.368 //- 0.338	-0.71306
C_4H_{10}	-0.492, -0.306, -0.306, -0.492 // -0.399	-0.385, -0.267, -0.267, -0.385 // -0.326	-1.30849
C_5H_{12}	-0.493, -0.305, -0.328, -0.305,-0.493 // -0.385	-0.382, -0.276, -0.294, -0.276, -0.382 // -0.322	-1.23240
C_6H_{14}	-0.502, -0.268,-0.356, -0.355, -0.263, -0.504 //-0.376	-0.393, -0.248, -0.320, -0.319, -0.248, -0.394 // -0.320	-2.05015
$C_{10}H_{22}$	-0.491, -0.283, -0.348, -0.348, -0.317, -0.317, -0.348, -0.348, -0.283, -0.491 // -0.358		-5.09057

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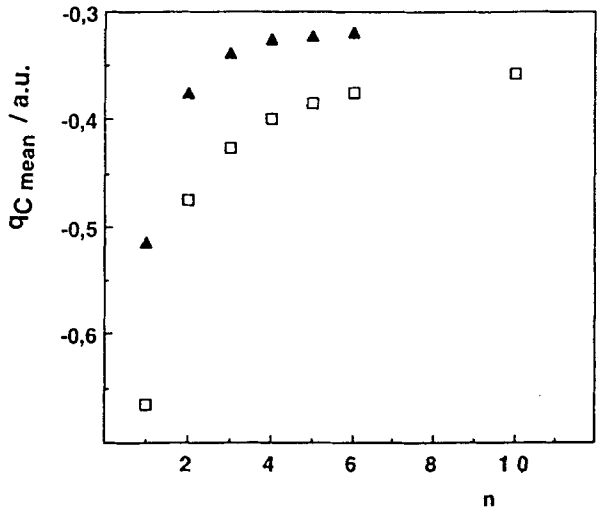

FIG. 2.The calculated mean charges as function of the number of carbon atoms in the alkanes. Mulliken charges are denoted by (□) and Karlström charges by (▲).

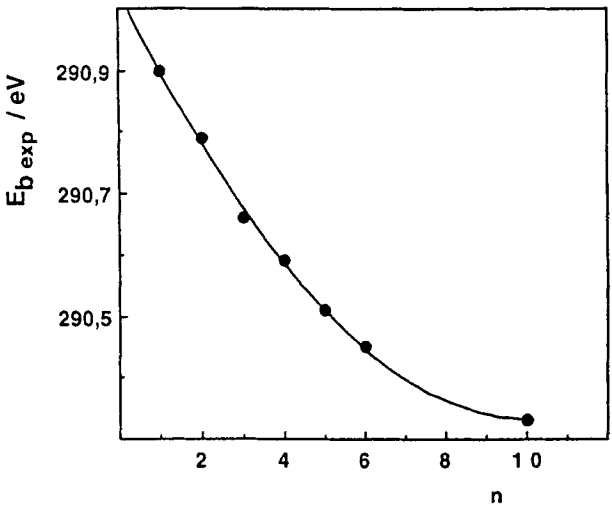

FIG. 3. The experimental C1s binding energies[9] in relation to the number of carbon atoms in the alkanes.

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TABLE 3.

The experimental binding energies and the ground state potential model quantities V_A, V_C (in eV) calculated using the two different sets of mean charges derived in Table 2.

	$E_b(C1s)_{exp}$	$E_b(C1s)_{calc}$	$V_A(q_C)$	$V_A(Q_C)$	$V_C(q_C)^a$	$V_C(Q_C)^a$
CH_4	290.90	304.940	8.809	6.758	-5.290	-4.160
C_2H_6	290.79	305.320	4.775	3.589	-5.274	-4.340
C_3H_8	290.66	305.252	3.640	2.466	-5.391	-4.699
C_4H_{10}	290.59	305.230	2.564	2.213	-5.895	-4.698
C_5H_{12}	290.51	305.220	2.386	2.039	-5.776	-4.787
C_6H_{14}	290.45	305.210	2.020	1.941	-5.951	-4.843
$C_{10}H_{22}$	290.33	305.170	1.732		-5.858	

a) calculated from (2) with k_C = 21.2 eV/ unit charge

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Thus, in this case, they do not describe the decrease of the experimental binding energies as given in the second column of Table 3.

We might anyway test if there is any strong relation between thus calculated binding energies and charges calculated, either via the Mulliken or the Karlström approach. The result of this test is given in Fig 4a. Seemingly, it is rather dissappointing. However, as said above, there is a serious neglect of relaxation effects in this method. It might therefore be tempting to try to apply the polarizability correction - corresponding to relaxation [31] - introduced in an earlier paper[5], viz,

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

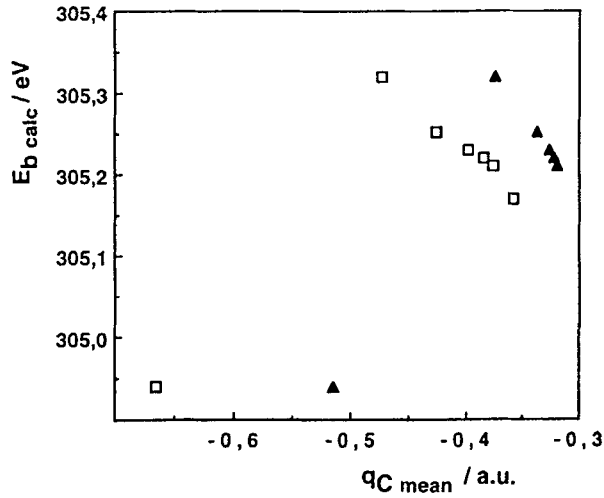

FIG. 4a. The C1s binding energies calculated from the Koopman theorem as a function of the calculated charges. Mulliken charges are (□) and Karlström charges are (▲).

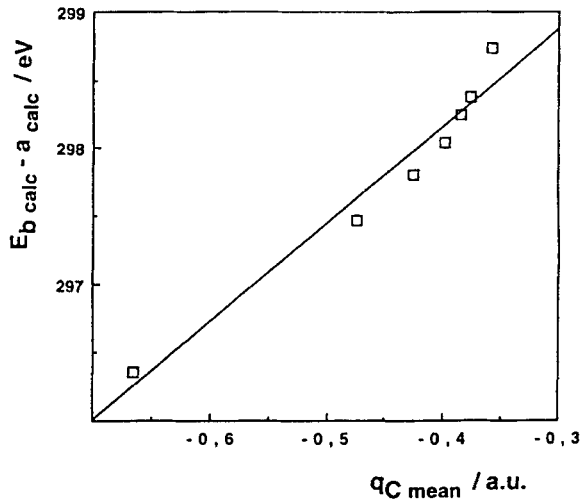

FIG. 4b. The same calculated binding energies as in FIG. 4a but corrected for the polarizability effect, calculated from (4), plotted versus the calculated Mulliken charge. It is for this charge concept that (4) was derived, hence we cannot use (4) with the Karlström charge concept.

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where "a" is a correction term added to the solid state relations[5] to make them correspond to gas phase data and P is the polarizability of the molecule in question. Doing this we find that the corrected data (Fig.4b) correlate very well (actually best as a parabolic function) with the charges (calculated charges) in the sense that if the charge is increasing the binding energy also increases. The slope of the linear fit, 7.2 eV/charge unit , is somewhat larger than that given by our empiric formula[5],

$$E_b\,(C1s) = 4.68\ qC + 296.2\ eV \qquad (5)$$

but much more in agreement with the slope of this empirical description than with the slope of the formula (2) including neighbouring atoms potential contributions, i.e. about 21.2 eV/charge unit.

However, even if the charge correlation is as expected, the values of the binding energies are still too high.

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Ground State Models

Having thus found that the relaxation term in the Koopman related formulae can be empirically corrected, we have set out to test the ground state models, presently in the form of eqn (2) that stresses the importance of the potential term .The formula (1) was tested in a previous paper[19] and was found to work quite well, provided that one corrects for the polarization effect as dicussed above for the Koopman case.

To test eqn (2) we have calculated (Table 3) the ground-state potential term V_A and formed the difference ($E_{i,\,exp} - V_{A,calc}$). The results are given in Fig 5 and Fig 6 for the two sets of charges q_C(mean) and Q_C(mean).The slopes of the straight line give the value of k in eqn (2).

They are 21.5 eV/unit charge and 22.5 eV / unit charge , respectively, in quite good agreement with the value 21.2 eV / unit charge calculated from HF orbitals for the C atom [1].

Above all, the trend is the one expected, an increase in the (potential-corrected) binding energy with increasing charge on the carbon atoms. Introducing the term V_C (eqn (3)) one notes that the first term ($k_A q_A$) of V_C is the dominating one

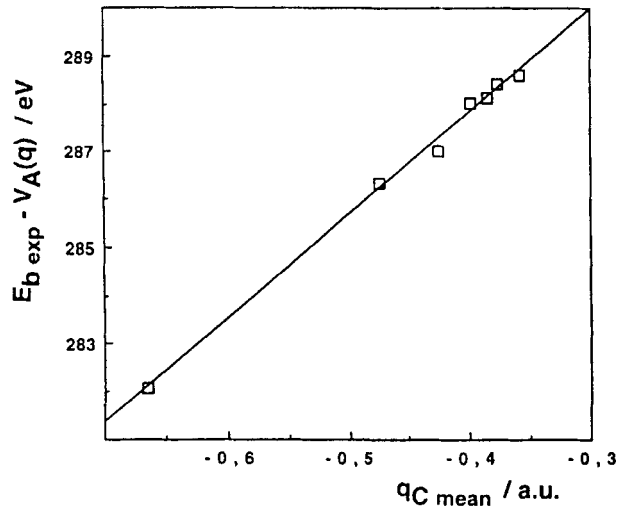

FIG. 5. The experimental binding energies corrected for the potential influence V_A, eqn (2), calculated from the Mulliken charges and plotted against the same.

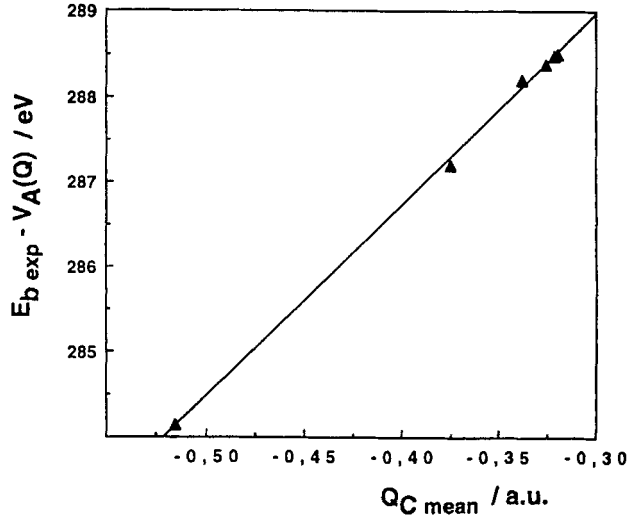

FIG. 6. The experimental binding energies corrected for the potential influence V_A, eqn (2), calculated from the Karlström charges and plotted against the same.

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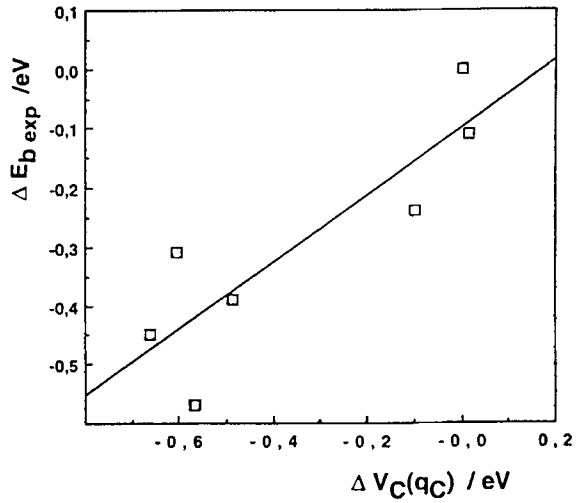

FIG. 7a. The experimental binding energies relative to that of CH_4 plotted against the V_C term, using Mulliken charges, from Table 3 (also relative to CH_4). This type of plotting corresponds to that of Fig 3 of Pireaux et al.[9].

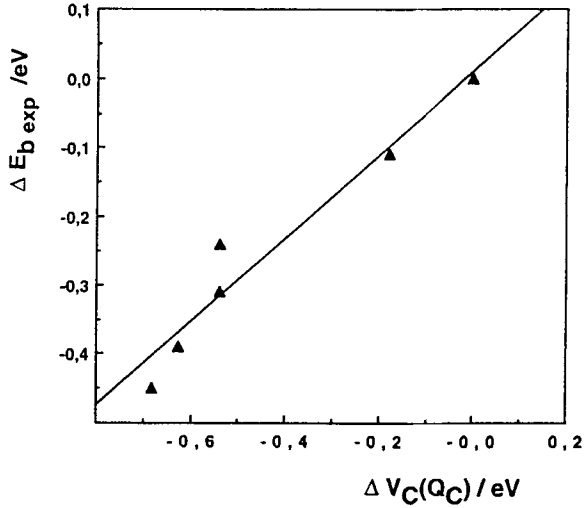

FIG. 7b. The experimental binding energies relative to that of CH_4 plotted against the V_C term, using Karlström charges, from Table 3 (also relative to CH_4).

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and the sign of V_C is governed by the sign of $q_{C(mean)}$ - or $Q_{C(mean)}$. However, only $V_C(Q_{Cmean})$ - not $V_C(q_{C\ mean})$ - was found to be monotonically decreasing with an increasing number of carbon atoms, parallell to the changes of the experimental binding energies E_b(C1s). This observation indicates that the Karlström charges work better than the Mulliken ones in this special case. Now, plotting the values relative to those for CH_4, i.e. the experimental ΔE_b(C1s) against ΔV_C, we obtain the figures 7a and 7b. One notes that the slopes, 0.57 and 0.60, respectively, are still not = 1 but somewhat closer to 1 than that (0.50) given by Pireaux[9] using the transition potential model. The data from Karlström charges show the best correlation coefficient, thus confirming the advantage for this type of charge estimation, at least in the present case.

The main reason why the ground-state potential model does not work in the investigation by Pireaux et al.[9] seems to be the CNDO/2 net atomic charges for the ground state ($P_A{}^G$ in Table II[9]). They are quite different (too small) from the values calculated here. On the other hand, the net atomic charges calculated for the transition state ($P_A{}^T$ in Table II[9]) are more close to the values presented in this work.

Our finding is thus that the shifts observed for the core binding energies in the series of alkanes are better described by electrostatic charges, Q_C(mean), the calculation of which takes into account the multipole moments. This result is in agreement with the results of Thomas et al.[31]. These authors find that for the haloethanes one needs to include higher multipoles for an accurate description of the binding energies.

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