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Correlation of Hückel Molecular Orbital Energies with π-Ionization Potentials*

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It is shown that simple HMO models which take into account first order bond fixation yield orbital energies for π-systems which correlate closely with the π-band positions in the corresponding photoelectron spectra.

Es wird gezeigt, daß die π-Orbitalenergien, die man unter Berücksichtigung der partiellen Bindungslokalisierung nach dem einfachen HMO-Verfahren berechnet, eng mit den Lagen der π-Banden in den entsprechenden Photoelektronen-Spektren korrelieren.

Les énergies d'orbitales π, calculées par le simple procédé de Hückel en tenant compte de la localisation partielle des doubles liaisons, montrent une correlation étroite avec les positions des bandes π dans les spectres photoélectroniques des hydrocarbures correspondants.

It is a well known, if somewhat disturbing phenomenon, that simple Hückel molecular orbital (HMO) models of π-systems yield predictions which are often as good and sometimes much better than those derived from more sophisticated treatments (e.g. [2–4]).

So far, the many examples known fell into two main categories:

1) "*One-electron properties*" which can be correlated with the characteristic values of a *single* orbital, usually the highest occupied (HOMO) or lowest unoccupied (LUMO) orbital, i.e. with the orbital energy $\varepsilon_J = \alpha + x_J \beta$, or with the coefficients $c_{J\mu}$ of the linear combination $\psi_J = \Sigma\, c_{J\mu} \phi_\mu$. Examples are the reduction potentials [2a, 4a, 5] or oxidation potentials [2b, 4b, 6] of unsaturated hydrocarbons, the interpretation of their ESR spectra [2c, 4c, 7] or the prediction of (frontier) orbital controlled reactions [2d, 4d, 8].

2) "*All-electron properties*" which can be correlated with characteristic values depending on *all* occupied π-orbitals, i.e. with total π-electron energies $E_\pi = \Sigma\, b_J \varepsilon_J$, localization energies A_μ, charge densities q_μ, bond orders $p_{\mu\nu}$ or with the various polarizabilities $\pi_{\mu\nu}$, $\pi_{\mu\nu,\varrho}$, $\pi_{\mu\nu,\varrho\sigma}$. Examples are the thermodynamic properties of unsaturated hydrocarbons [2e, 4e, 9], the rates of reactions which are charge or localization energy controlled [2f, 4f, 10], interatomic distances [2g, 4g, 11] or dipole moments [2h, 4h, 12].

For a review of the early history of applications of simple HMO models the reader is referred to [13].

Photoelectron(PE.-)spectroscopy [14] provides for the first time experimental information that can be rationalized in terms of a *whole set* of orbital energies ε_J,

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* Part 35 of "Applications of Photoelectron Spectroscopy"; Part 34: [1].

if Koopmans' theorem [15]

$$\varepsilon_J^{\mathrm{SCF}} = -I_{v,J} \tag{1}$$

is accepted ($I_{v,J}$ = vertical ionization energy corresponding to ejection of an electron from orbital ψ_J^{SCF}). Even though this theorem refers to SCF orbital energies $\varepsilon_J^{\mathrm{SCF}}$, it seemed of interest to investigate whether its application to simple Hückel orbital energies ε_J will yield a usefull method for the systematization and prediction of PE.-spectra of unsaturated hydrocarbons. That this may indeed be the case, has already been shown by Streitwieser and Nair for the first ionization potential [16, 2i] and by Eland and Danby in a PE.-spectroscopic investigation of aromatic compounds [17].

Table 1 (column 9) contains those vertical ionization potentials $I_{v,J}$ of a series of unsaturated π-systems M, which can be assigned with some confidence to ionization prozesses

$$M + h\nu \rightarrow M^+(\psi_J^{-1}) + e^- \,, \tag{2}$$

where the ejected electron e^- vacates a π-orbital ψ_J. HMO calculations assign an orbital energy $\varepsilon_J = \alpha + x_J\beta$ to ψ_J, so that according to (1) we obtain

$$I_{v,J}^0 = -\varepsilon_J = -(\alpha + x_J\beta)\,. \tag{3}$$

The observed ionization potential $I_{v,J}$ differs from $I_{v,J}^0$ by a stochastic quantity Δ which encompasses all effects due to simplifying assumptions and/or neglected factors of our model. Thus (3) leads to a regressional problem which is solved by standard least squares techniques [18]. The sample consists of all ionization potentials $I_{v,J}$ of Table 1 (except those in brackets) and of the corresponding, independent variables x_J.

$H_2C{=}CH_2$

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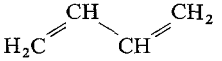
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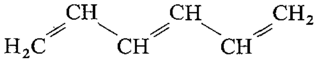
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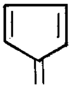

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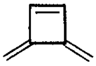

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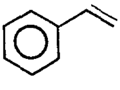

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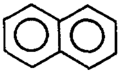

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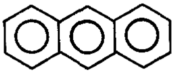

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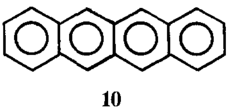

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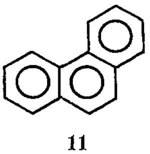

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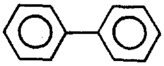

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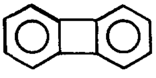

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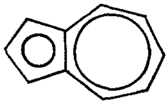

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Table 1. Comparison of calculated and experimental vertical ionization potentials. All values in eV. Values in brackets can not be assigned with confidence to a π-level and have not been used in the regression calculations

Compound	J	x_J [a]	y_J [b]	$I^0_{v,J}$ [c]; HMO	ΔI^0_J [d]	$I'_{v,J}$ [e]; Pert	$\Delta I'_J$ [f]	$I_{v,J}$ [g] (exp.)	Ref.
Ethylene (**1**)	1	1.000	0.167	9.29	−1.22	10.46	−0.05	10.51	[14]
Butadiene (**2**)	2	0.618	0.132	8.42	−0.84	8.92	−0.16	9.08	[14]
	3	1.618	0.022	10.98	−0.50	11.40	−0.07	11.47	[14, 22]
Hexatriene (**3**)	4	0.445	0.106	7.77	−0.43	8.15	−0.05	8.2	[29]
Fulvene (**4**)	5	0.618	0.070	8.24	−0.31	8.44	−0.11	8.55	[22]
	6	1.000	−0.014	9.29	−0.25	9.06	−0.48	9.54	[22]
	7	2.115	−0.071	(12.34)	(−0.46)	(12.33)	(−0.47)	(12.8)	[22]
Bismethylene-cyclo butene (**5**)	8	0.555	0.120	8.07	−0.73	8.62	−0.18	8.80	[22]
	9	0.802	0.092	8.75	−0.69	9.23	−0.21	9.44	[22]
	10	2.247	−0.151	(12.70)	(−0.60)	(12.15)	(−1.15)	(13.3)	[22]
Styrene (**6**)	11	0.662	0.078	8.36	−0.13	8.65	0.16	8.49	[25]
	12	1.000	0.006	9.29	0.02	9.22	−0.05	9.27	[25]
	13	1.414	0.006	10.42	−0.11	10.60	0.07	10.53	[25]
Benzene (**7**)	14	1.000	0.000	9.29	0.05	9.17	−0.07	9.24	[14, 26]
	15	1.000	0.000	9.29	0.05	9.17	−0.07	9.24	[14, 26]
	16	2.000	0.000	12.02	−0.23	12.50	+0.25	12.25	[14, 26]
Naphtalene (**8**)	17	0.618	0.035	8.24	0.12	8.17	0.05	8.12	[17, 27]
	18	1.000	−0.046	9.29	0.39	8.82	−0.08	8.90	[17, 27]
	19	1.303	−0.024	10.12	0.12	10.00	0.00	10.00	[17, 27]
Anthracene (**9**)	20	0.414	0.026	7.69	0.27	7.43	0.02	7.41	[28]
	21	1.000	−0.066	9.29	0.74	8.66	0.11	8.55	[28]
	22	1.000	0.001	9.29	0.13	9.18	0.02	9.16	[28]
	23	1.414	−0.029	10.42	0.26	10.33	0.17	10.16	[28]
	24	1.414	−0.013	(10.42)		(10.45)		[h]	[28]
Naphtacene (**10**)	25	0.295	0.030	7.36	0.41	7.06	0.11	6.95	[30]
Phenanthrene (**11**)	26	0.605	0.031	8.21	0.29	8.10	0.18	7.92	[28]
	27	0.769	−0.003	(8.66)		(8.38)		[i]	[28]
	28	1.142	−0.045	9.68	0.40	9.30	0.02	9.28	[28]
	29	1.306	−0.037	10.12	0.24	9.91	0.03	9.88	[28]
	30	1.516	−0.013	(10.70)	(0.06)	(10.79)	(0.15)	(10.64)	[28]
Biphenyl (**12**)	31	0.705	0.023	8.48	0.28	8.37	0.17	8.20	[17]
Biphenylene (**13**)	32	0.445	0.095	7.77	0.15	8.06	0.44	7.62	[28]
	33	0.879	0.006	8.96	0.07	8.82	−0.07	8.89	[28]
	34	1.247	−0.058	9.96	0.28	9.55	−0.13	9.68	[28]
	35	1.347	−0.056	10.24	0.14	9.89	−0.21	10.10	[28]
Azulene (**14**)	36	0.477	0.004	7.86	0.42	7.46	0.02	7.44	[23, 24]
	37	0.887	−0.040	8.98	0.47	8.49	−0.02	8.51	[23, 24]
	38	1.356	−0.010	10.26	0.18	10.28	0.20	10.08	[23, 24]

[a] See formula (3).

[b] See formula (16).

[c] See formula (4).

[d] $\Delta I^0_J = I^0_{v,J} - I_{v,J}$.

[e] See formula (18).

[f] $\Delta I'_J = I'_{v,J} - I_{v,J}$.

[g] All values from photoelectron-spectra, with exception of 4 (spectroscopic) and 25 (electron-impact).

[h] Unresolved double band: 10.16 eV (23) and ~10.2 to 10.4 eV (24).

[i] Unresolved double band: 7.92 eV (26) and 8.12 eV or 8.35 eV (27).

Regression Line (90% Confidence Limits)

$$I^0_{v,J} = [(6.553 \pm 0.340) + (2.734 \pm 0.333)\, x_J]\,\mathrm{eV}\,. \tag{4}$$

Variance analysis (values in eV^2)

Source	Sum of squares	Degree of freedom	Mean squares	*F*-ratio	
Due to regr.	36.822	1	36.822		(5)
About regr.	5.859	31	0.189	194.8	
Total variance	42.681	32			

Standard Error: $SE(I_{v,J}) = 0.435$ eV.

The correlation of $I_{v,J}$ with $I^0_{v,J}$ (from (4)) is shown in Fig. 1. The confidence limits CL (90% security) have been calculated according to

$$CL(I_{v,J}) = I^0_{v,J} + t_{0.9;\phi} SE(I_{v,J}) \sqrt{1 + \frac{1}{N} + \frac{(x-\bar{x})^2}{S_{xx}}} \tag{6}$$

with $t_{0.9;31} = 1.70$, $N = 33$ and $SE(I_{v,J}) = 0.435$ eV.

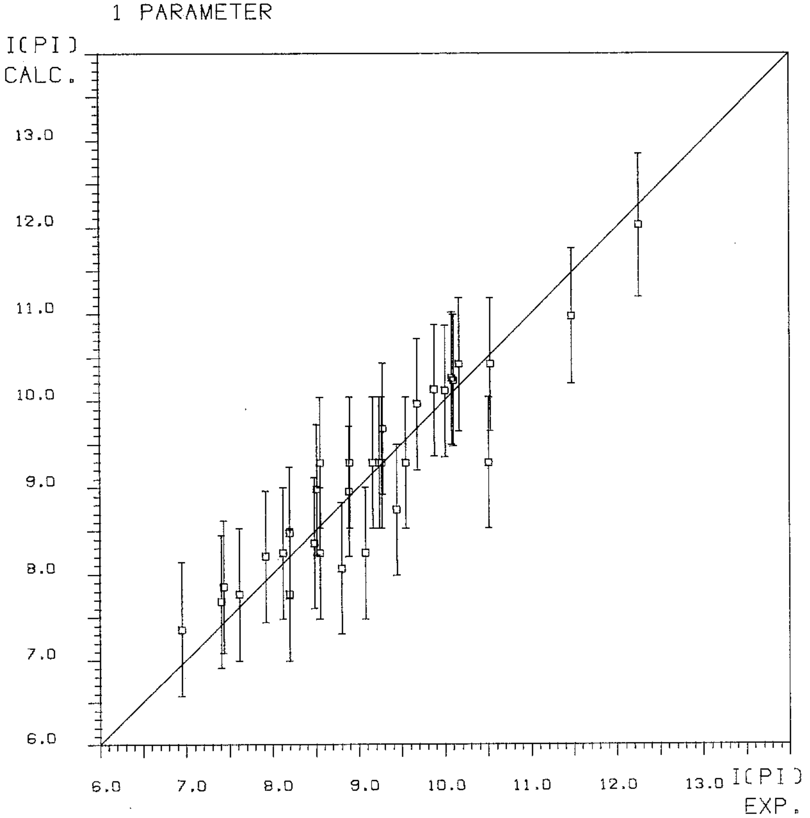

Fig. 1. Correlation of HMO orbital energies $-\varepsilon_J = I^0_{v,J} \equiv I(PI)$CALC. (formula (3)) with observed vertical ionization potentials $I_{v,J} \equiv I(PI)$EXP. The confidence limits attached to each point refer to 90% security

The reason for the poor agreement, i.e. the wide confidence limits is obvious: The eigenvalues x_J have been obtained under the usual assumption of equal resonance integrals $\beta_{\mu\nu} = \beta$ for all π-bonds between centers μ, ν. This is of course unacceptable for compounds with strong first order bond localization [19] such as the hydrocarbons **1** to **6**. However this effect can be taken care of by a simple first order perturbation treatment [20].

As has been discussed previously [19] the total energy $E_T(M)$ of a π-electron system M can be written as the interaction-free sum of the energy of the σ-core and of the π-electron system proper if we postulate complete $\sigma-\pi$ separation:

$$E_T(M) = E_\sigma(M) + E_\pi(M)\,. \tag{7}$$

Assuming that the σ-energy can be written as

$$E_\sigma(M) = \sum_{\mu\nu} \frac{k^0}{2} (r_{\mu\nu} - r_0)^2\,, \tag{8}$$

where k^0 is the force constant and r_0 the equilibrium bond length of a pure $sp^2 - sp^2$ σ-bond, and the π-energy as

$$E_\pi(M) = n\alpha + 2 \sum_{\mu\nu} p_{\mu\nu} \beta_{\mu\nu} \tag{9}$$

(n = number of π centres), then $E_T(M)$ becomes the sum of independent contributions $E_{\mu\nu}(M)$ from each bond,

$$E_T(M) = \sum_{\mu\nu} E_{\mu\nu}(M)\,, \tag{10}$$

as long as only first order bond fixation is taken into account [19]. Consequently the minimum of $E_T(M)$ is reached for the set of interatomic distances $R_{\mu\nu}$ which satisfy the relations

$$\frac{\partial E_T(M)}{\partial r_{\mu\nu}} = \frac{dE_{\mu\nu}(M)}{dr_{\mu\nu}} = 0\,, \tag{11}$$

i.e. (with $\beta'_{\mu\nu} = (d\beta_{\mu\nu}/dr_{\mu\nu})_{R_{\mu\nu}}$):

$$R_{\mu\nu} = r_0 - \left(\frac{2\beta'_{\mu\nu}}{k^0}\right) p_{\mu\nu}\,. \tag{12}$$

The same arguments applied to the total energy $E_T(M^+(\psi_J^{-1}))$ of the radical cation $M^+(\psi_J^{-1})$ (obtained from M by removing an electron from orbital ψ_J) will lead to

$$R^+_{\mu\nu,J} = r_0 - \left(\frac{2\beta'_{\mu\nu}}{k^0}\right) p^+_{\mu\nu,J}\,, \tag{13}$$

where $p^+_{\mu\nu,J}$ is the bond order of the bond μ, ν in $M^+(\psi_J^{-1})$. The derivative $\beta'_{\mu\nu}$ should now be taken at $r_{\mu\nu} = R^+_{\mu\nu,J}$.

Fig. 2 shows the dependence of $E_T(M)$ and $E_T(M^+(\psi_J^{-1}))$ on $r_{\mu\nu}$. In terms of our model, the vertical ionization potential $I'_{v,J}$ corresponds to the transition indicated by the arrow at $r_{\mu\nu} = R_{\mu\nu}$ if we disregard vibrational energy contributions. The assumption of standard HMO theory, namely that all $\beta_{\mu\nu} = \beta$, consists in assigning to $R_{\mu\nu}$ and $R^+_{\mu\nu,J}$ the fixed value R_0, e.g. $R_0 = 1.40$ Å, if benzene with bond order $p_{\mu\nu} = p_0 = 2/3$ is used as a reference. The ionization potential $I^0_{v,J}$ calculated under these conditions is indicated in Fig. 2 by the arrow at $r_{\mu\nu} = R_0$. For each bond $\mu\nu$ of the π-system the vertical ionization potential $I_{v,J}$ differs from

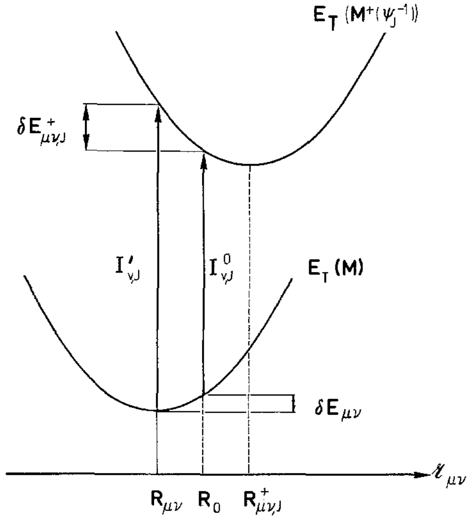

Fig. 2. Dependence of $E_T(M)$ and $E_T(M^+(\psi_J^{-1}))$ on $r_{\mu\nu}$

$I^0_{v,J}$ by the sum of the positive increments $\delta E_{\mu\nu}$ and $\delta E^+_{\mu\nu,J}$, which has been shown to be [20]

$$\delta E_{\mu\nu} + \delta E^+_{\mu\nu,J} = \mathscr{k}\left(\frac{2\beta'}{k^0}\right)^2 (p^+_{\mu\nu,J} - p_{\mu\nu})(p_0 - p_{\mu\nu}) \;, \tag{14}$$

where $\mathscr{k}$ is the force constant of a π-bond (e.g. of a C$\overset{...}{-}$C bond in benzene). Summing over all bonds we obtain with $\Delta p_{\mu\nu,J} = p^+_{\mu\nu,J} - p_{\mu\nu}$

$$I'_{v,J} = I^0_{v,J} + \mathscr{k}\left(\frac{2\beta'}{k^0}\right)^2 \sum_{\mu\nu} \Delta p_{\mu\nu,J}(p_0 - p_{\mu\nu}) \,. \tag{15}$$

Substitution in (15) of $I^0_{v,J}$ by expression (3) and making use of the abbreviations

$$a = -\alpha\,; \quad b_1 = -\beta\,; \quad b_2 = \mathscr{k}\left(\frac{2\beta'}{k^0}\right)^2 \tag{16}$$

$$y_J = \sum_{\mu\nu} \Delta p_{\mu\nu,J}(p_0 - p_{\mu\nu})$$

yields the regression plane

$$I'_{v,J} = a + b_1 x_J + b_2 y_J \,, \tag{17}$$

the parameters of which are again calculated in the usual manner [18]:

Regression Plane (90% Confidence Limits)

$$I'_{v,J} = [(5.847 \pm 0.163) + (3.326 \pm 0.152)\,x_J + (7.733 \pm 1.009)\,Y_J]\ \text{eV}\,. \tag{18}$$

Variance analysis (values in eV^2*)*

Source	Sum of squares	Degree of freedom	Mean squares	F-ratio
Due to regr.	41.801	2	20.900	
About regr.	0.880	30	0.0293	712.5
Total variance	42.681	32		

(19)

Standard Error: $SE(I_{v,J}) = 0.171$ eV.

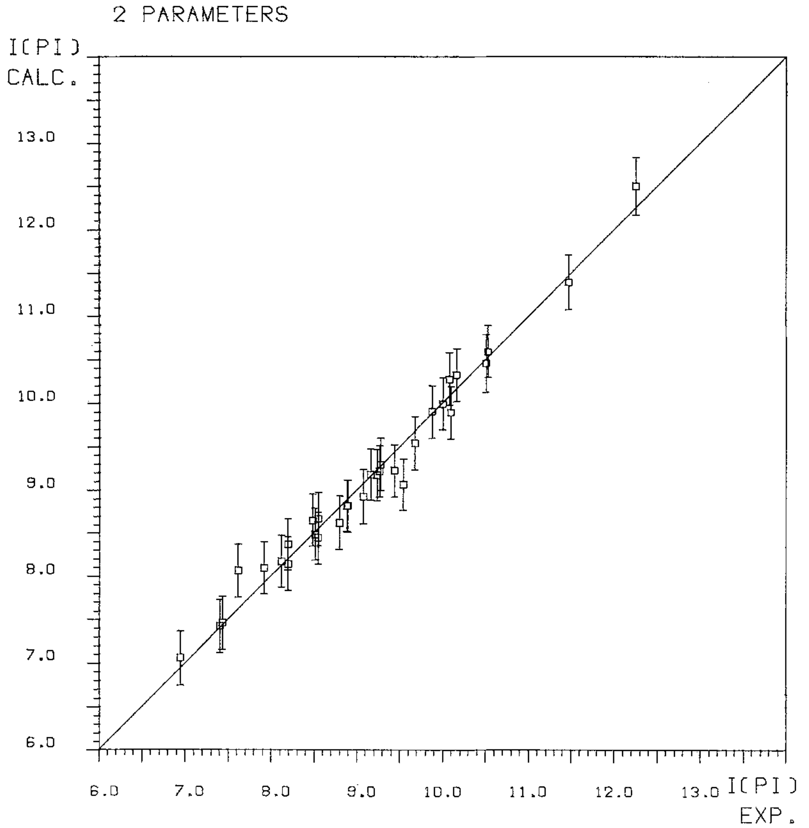

Fig. 3. Correlation of ionization potentials $I'_{v,J} \equiv I(PI)$CALC. obtained by the perturbation treatment leading to formula (18) with observed vertical ionization potentials $I_{v,J} \equiv I(PI)$EXP. The confidence limits attached to each point refer to 90% security

Comparison of the variance analysis (5) and (19) shows that the inclusion of a correction for first order bond fixation has lead to a considerable improvement of the correlation. Indeed, the mean square about the regression has dropped from 0.189 eV^2 to 0.0293 eV^2, corresponding to a F-ratio of 6.45. This should be compared to $F = 3.5$ (for 99.9% security and the appropriate degrees of freedom, i.e. 31 and 30). Thus the improvement is highly significant, as is also evident from a comparison of Figs. 1 and 3. The 90% confidence limits given in Fig. 3 have been calculated according to the rules given in [18], taking into account the contributions from the covariance between the independent variables x_J and y_J ($t_{0.9;30} = 1.70$).

Since photoejection (2) is necessarily accompanied by changes in charge density at the individual π-centres μ, one would expect that inclusion of a perturbation term depending on the charge order increments

$$\Delta q_{\mu,J} = \overset{+}{q}_{\mu,J} - q_\mu \tag{20}$$

will yield an additional improvement of the predictions derived from our simple HMO model. A first-order perturbation treatment based on $\Delta q_{\mu,J}$ as independent variable has been derived previously [20]. It yields the following increments $\delta I''_{v,J}$ for the ionization potentials, which have to be added to $I^0_{v,J}$

or $I'_{v,J}$:

$$\delta I''_{v,J} = -\omega\beta \sum_{\mu} \Delta q_{\mu,J}(q^{+}_{\mu,J} + q_{\mu})\,. \tag{21}$$

The parameter ω is defined as $\omega = (1/\beta)\,(\partial\alpha_{\mu}/\partial q_{\mu})$ [2j, 21]. Adding the perturbation (21) to the regression (17) yields

$$I''_{v,J} = a + b_1 x_J + b_2 y_J + b_3 z_J\ , \tag{22}$$

where $b_3 = -\omega\beta$ and $z_J = \sum_{\mu} \Delta q_{\mu,J}(q^{+}_{\mu,J} + q_{\mu})$.

However, in contrast to expectation, a least squares treatment of (22) does *not* lead to a significant improvement of the correlation between experimental and calculated ionization potentials over that shown in Fig. 3. This is evident from the following results:

Regression Plane (90 % Confidence Limits)

$$\begin{aligned} I''_{v,J} = {} & [(8.403 \pm 1.289) + (3.159 \pm 0.155)\,x_J \\ & + (6.219 \pm 1.153)\,y_J - (1.301 \pm 0.652)\,z_J]\ \mathrm{eV} \end{aligned} \tag{23}$$

Variance analysis (values in eV^2*)*

Source	Sum of squares	Degree of freedom	Mean squares	F-ratio
Due to regr.	42.051	3	14.017	
About regr.	0.630	29	0.0217	645.1
Total variance	42.681	32		

(24)

Standard Error: $SE(I_{v,J}) = 0.147$ eV.

The variance ratio F of the mean squares about the regression taken from (19) and (24) is only $F = 0.0293/0.0217 = 1.35$ and therefore not significant. It should be noted that the covariance between y_J and z_J, i.e. between the corrections due to bond fixation and charge changes, is also not significant. This indicates, that the improvement is entirely due to the correction for bond fixation, in agreement with previous experience [20].

To conclude we wish to add the following comments:

A) From Table 1 it is obvious that the largest discrepancies $\Delta I'_{v,J}$ between observed and calculated ionization potentials (the latter from (18)) occur for fulvene (**4**), bismethylene-cyclobutene (**5**) and biphenylene (**13**) i.e. for hydrocarbons containing a five- or four-membered ring. This strongly suggest that 1,3-interactions, which have been neglected are presumably of importance in such compounds. Indeed, in **5** and **13**, the largest deviation observed i.e. $\Delta I_{v,10} = -1.15$ eV in **5**, $\Delta I_{v,32} = +0.44$ eV in **13**, is associated in each case with the orbital for which inclusion of 1,3-interactions across the diagonals of the four-membered ring would result in the largest shift in orbital energy. Note that these corrections are of the proper sign required to improve the agreement. However on closer examination e.g. in the case of fulvene **4**, one notes that the general situation is presumably too complex to be discussed in a meaningfull way in terms of a simple HMO-model.

B) We now compare the values $I'_{v,J}$ derived from our regression function (18) with the corresponding results obtained by many-electron treatments. In Table 2 we have collected as typical examples vertical ionization potentials calculated by Baird and Dewar [31] using (a) a valence shell SCF-MO model or (b) an SCF-π-model and the *ab-initio* calculations (c) of Christoffersen [32] and (d) of Berthier *et al.* [33]. The orbital energies ε_J (in eV or in a.u.) so obtained are correlated

Table 2. Vertical ionization potentials calculated by many electron treatments. For the meaning of (a), (b), (c), (d) see text

Cpd.	J	(a) [31] $-$eV	(b) [31] $-$eV	(c) [32] $-$a.u.	(d) [33] $-$a.u.
1	1	10.956	10.855		0.4622
2	2	10.139	10.070		0.4078
	3	11.994	12.060		0.5281
4	5	10.076	10.008	0.1594	0.3947
	6	10.321	10.428	0.2156	0.4348
	7	12.968	12.899	0.4030	0.5993
5	8	10.005	10.053	0.1803	0.4285
	9	10.377	10.366	0.2050	0.4050
	10	13.096	13.148	0.3837	0.6032
6	11	9.788	9.804		
	12	10.217	10.293		
	13	11.428	11.506		
7	14, 15	10.184	10.287	0.2169	0.4272
	16	13.100	13.037	0.3915	0.5893
8	17	9.309	9.274	0.1545	
	18	9.965	10.068	0.2002	
	19	11.011	11.110	0.2658	
14	36	8.851	8.666	0.1298	
	37	9.476	9.432	0.1808	
	38	11.256	11.489	0.2982	

with the observed ionization potentials $I_{v,J}$ according to

$$I_{v,J} = A + B\varepsilon_J\,, \tag{25}$$

i.e. including an additive constant A and a scaling factor B. As shown in Table 3 the correlation (25) is significantly worse in all cases than that given in (18), even though two additional parameters A and B have been included in order to scale the theoretical results and thus to minimize the variance about the regression. This illustrates the argument given at the beginning of this paper.

C) On the other hand, vertical ionization potentials can also be calculated by computing separately the total energies $E_T(M)$ of the neutral molecule M and $E_T(M^+(\psi_J^{-1}))$ of the radical cation $M^+(\psi_J^{-1})$ assuming the same structure for both. This has been carried out by Dewar, Hashmall and Venier [34] for a series of unsaturated hydrocarbons, including **1**, **2**, **3**, **6**, **7**, **8**, **9**, and **12**, with M^+ in its electronic ground state, i.e. with $\psi_J \equiv$ HOMO. Correlation of these first ionization potentials with our experimental results, using again a linear regression function of type (25) [with $I_{v,\text{calc}} = E_T(M^+(\text{HOMO}^{-1})) - E_T(M)$ instead of ε_J] yields a variance about the regression of 0.0178 eV^2 as compared to 0.0298 eV^2 for (18). Thus the agreement of the computed values $I_{v,\text{calc}}$ with the experimental ionization potentials is not significantly better than that derived from (18), notwithstanding the restriction to first ionization potentials only. Note that we have scaled the theoretical results [34] by introducing two adjustable parameters A and B, which again tends to reduce the residual variance.

Table 3. Comparison of the results derived from many electron models (cf. Table 2) with those obtained from the regression function (18). N = sample size; $SE(I_{v,J})$ = standard deviation; ϕ = degree of freedom; F = variance ratio relative to the mean square about the regression (= 0.0293 eV) of (19); F (95%) = limit for 95% significance[a]

Model[a]	N	$SE(I_{v,J})$	Mean square about regression (25)	ϕ	F	F (95%)
(a)	21	0.282 eV	0.07924 eV^2	19	2.70	1.92
(b)	21	0.293	0.08567	19	2.92	1.92
(c)	16	0.403	0.16220	14	5.54	2.04
(d)	10	0.349	0.12198	8	4.16	2.27

[a] See text.

D) Those compounds which can occur in non-planar conformations, i.e. **2**, **3**, **6**, and **12** do not yield differences $\Delta I'_J$ (see Table 1) which are significantly different from those observed in other cases. Presumably these molecules are (almost) planar (e.g. **2**, **3**) or small twist angles around the non-essential single bonds lead only to minor changes in the orbital energies if compared to the standard deviation $SE(I_{v,J}) = 0.17$ eV.

E) From the parameters $b_1 = 3.33$ eV and $b_2 = 7.73$ eV of (18) we obtain according to (16) $\beta = -3.33$ eV and $\mathscr{k} = 3.1 \cdot 10^6$ dyn cm^{-1}. These values compare favourably to $\beta = -2.94$ eV and $\mathscr{k} = 3.9 \cdot 10^6$ dyn cm^{-1} derived from a similar analysis of the $^1L_a \leftarrow {}^1A$ transition of π-systems [20]. In both cases $\mathscr{k}$ is too large by a factor of 3 to 4 ($\mathscr{k}(\text{C} \overset{\cdots}{-} \text{C}) \approx 10^6$ dyn cm^{-1}).

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