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Modified CNDO 2 Calculations of Ionization Potentials for Some Unsaturated Hydrocarbons

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The orbital energies of several unsaturated hydrocarbon molecules have been calculated using a modified CNDO/2 method, with the electron repulsion integrals evaluated from Klopman's formula and the σ–π separation factor proposed by Tinland and Jaffé. The empirical parameters are determined to reproduce the observed ionization potentials for ethylene and benzene *via* Koopmans' theorem. The results are shown to agree well with the available experimental ionization potentials and with the assignments of the photoelectron spectra.

Photoelectron spectroscopy provides much information on the ionized states of molecules; not only are the adiabatic first ionization potentials and the higher ionization potentials determined by the measurement of the excess kinetic energies of photoelectrons,[1-7] but also information on the symmetry of ionized states can be obtained from the observed angular distribution of photoelectrons.[8] On the other hand, based upon Koopmans' theorem,[9] the development of molecular orbital methods made it possible to compare the observed vertical ionization potentials with the calculated orbital energies not only for π-electrons but for σ-electrons. They also enable us to compare the assignments of the electron energy levels expected from the observed angular distribution of photoelectrons with those derived from the symmetry of molecular orbitals. However, the methods have not been sufficient to give reasonable interpretation of the observed photoelectron spectra.

Although the all-electron *ab initio* methods have also been advanced, the calculations are time consuming and not always more reliable than the semi-empirical calculations.

In the present paper, we modified the CNDO method introduced by Pople *et al.*[10,11] and established a simpler and more reliable method for the assignment and prediction of photoelectron spectra of unsaturated hydrocarbon molecules.

Method and Parametrizations

The method used here is almost the same as the CNDO/2 method proposed by Pople and Segal;[11] the following semi-empirical parametrizations are taken.

(1) The electron repulsion integrals, γ_{AB}, are evaluated from Klopman's formula:[12]

$$\gamma_{AB} = e^2/\sqrt{R_{AB}^2 + G_{AB}^2}$$

and:

$$G_{AB} = \frac{e^2}{2}(\gamma_{AA}^{-1} + \gamma_{BB}^{-1})$$

where R_{AB} is the interatomic distance between A and B. For one-center repulsion integrals, the semi-empirical values are used:

for carbon atoms, $\gamma_{AA}(C) = 11.144$ eV,

and

for hydrogen atoms, $\gamma_{AA}(H) = 12.845$ eV.

(2) The resonance integrals, β_{AB}, are determined by the use of the following formula;

$$\beta_{AB} = \frac{\beta_A^\circ + \beta_B^\circ}{2} S_{AB},$$

where S_{AB} is the overlap integral between the two atomic orbitals. β_A° is an empirical parameter depending upon the kind of atom. For carbon atoms, we introduced another parameter, k, which is a σ–π separation factor proposed by Tinland[13] and Jaffé[14];

$$\beta^\circ(C\pi) = k\beta^\circ(C),$$

$$\beta^\circ(C\sigma) = \beta^\circ(C).$$

Now, we have three unknown empirical parameters, $\beta^\circ(H)$, $\beta^\circ(C)$, and k, for unsaturated hydrocarbon molecules. These parameters must be determined in order to reproduce the observed spectra. As the simplest parametrization, we chose the first three levels of ethylene, (πb_{1u}), (σb_{1g}), and (σa_g), and the first two levels of benzene, (πe_{1g}) and σe_{2g}), as the standards; they should be fitted to the first three observed ionization potentials of ethylene and the first two of benzene respectively.

The orbital energies of ethylene and benzene were calculated as a function of the unknown parameters, the ranges of the parameters, $-10.0\ \text{eV} \geqq \beta^\circ(C) \geqq -14.0\ \text{eV}$, $-6.0\ \text{eV} \geqq \beta^\circ(H) \geqq -10.0\ \text{eV}$, and $0.2 \leqq$

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$k \leqq 0.6$, the calculated orbital energies were arranged as (πb_{1u}), (σb_{1g}), (σa_g), (σb_{2u}), ⋯ for ethylene, and as (πe_{1g}), (σe_{2g}), (πa_{2u}), ⋯ for benzene, and no interchanges of the orders were found. Although the optimization was not completely carried out, a set of the following values for the parameters leads to satisfactory results with regard to the standard levels;

$$\beta°(\mathrm{C}) = -12.0\,\mathrm{eV},\quad \beta°(\mathrm{H}) = -7.0\,\mathrm{eV},$$

and $k = 0.40$.

With these parameters, the orbital energies of other unsaturated hydrocarbon molecules were calculated by means of a FACOM-270-20/30 Computer.

Results and Discussion

The parameter values determined in the previous section were used in the calculations of the orbital energies of ethylene, *trans* 1,3-butadiene, benzene, naphthalene, and azulene. Based upon Koopmans' theorem, the absolute values of the calculated orbital energies were compared with the (vertical) ionization potentials obtained from the available data of the photoelectron spectra, and also with the calculated values by Dewar[15] and others.[16–21] The results are shown in Tables 1—5. As can be seen in the tables, the calculated ionization potentials smaller than 16 eV agree, in general, with the observed values. Especially for ethylene and butadiene, our results seem much better than the MINDO calculations by Dewar. From the present results, it may be concluded that both of the first two levels for *trans* 1,3-butadiene are to be attributed to π-electrons, as has been previously reported.[22,23] Furthermore, we are encouraged by the fact that the assignment of the photoelectron spectra for benzene from the calculated orbital energies and their symmetries completely coincides with the recent assignment from the angular distribution data of the photoelectrons reported by Carlson and Anderson.[8] These assignments are not only consistent with the analysis of the vibrational structure by Turner;[3] they also agree with the order of the orbital energies predicted by Jonsson and Lindholm.[5] In addition, since the three lowest IP bands of naphthalene are sharp,[3,6,7] it seems reasonable to assign these bands to the three highest occupied π-orbitals, as assigned in Table 4. In the case of azulene, our calculation also explains the first three bands as π-excitations.

Table 1. Ionization potentials of ethylene (in eV)

Obsd 4)	Calcd		
	This calcn	MINDO[15]	*ab initio*[16]
10.51	10.62 $\pi 1b_{1u}$	10.37 π	10.17 $\pi 1b_{1u}$
12.38	12.96 $1b_{1g}$	11.47	14.00 $1b_{1g}$
14.47	14.51 $3a_g$	11.65	15.81 $3a_g$
15.68	18.61 $1b_{2u}$	14.37	17.82 $1b_{2u}$
18.87	21.61 $2b_{3u}$	19.21	21.66 $2b_{3u}$
	29.54 $2a_g$	28.01	28.29 $2a_g$

The general conclusion of our results is that the calculated π-electron ionization potentials are in comparatively good agreement with those obtained by the MINDO calculations, but that the calculated ionization potentials for σ-electrons are quite different from these obtained by MINDO. It seems that the introduction of the fairly small σ–π separation factor has led to appropriate separations between the σ-

Table 2. Ionization potentials of benzene (in eV)

Obsd				Calcd			
a)	b)	c)	d)	This calcn	MINDO[15]	CNDO[17]	*ab initio*[18]
9.25	9.3	9.2, 9.5	πe_{1g}	9.77 πe_{1g}	9.54 π	9.4 πe_{1g}	10.31 πe_{1g}
11.49	11.4	11.6	e_{2g}	11.48 e_{2g}	10.07	9.8 e_{2g}	14.30 e_{2g}
11.7, 12.2	12.1	12.3	πa_{2u}	12.55 πa_{2u}	11.30	13.0 e_{1u}	14.64 πa_{2u}
13.8	13.8	14.0	e_{1u}	14.68 e_{1u}	12.29	13.8 b_{2u}	17.04 e_{1u}
14.7	14.7	14.8	b_{2u}	15.30 b_{2u}	12.49 π	14.3 b_{1u}	17.96 b_{2u}
15.4	15.4	15.4	b_{1u}	16.34 b_{1u}	14.80	15.2 πa_{2u}	18.33 b_{1u}
16.8	16.9	16.8	a_{1g}	20.93 a_{1g}	15.22	19.6 a_{1g}	20.16 a_{1g}
18.3, 19.9	19.2	19.0	e_{2g}	22.50 e_{2g}	19.24	20.1 e_{2g}	23.09 e_{2g}
				28.18 e_{1u}	26.05	24.8 e_{1u}	28.38 e_{1u}
				35.74 a_{1g}	32.75	31.2 a_{1g}	31.94 a_{1g}

a) Turner *et al.*[3] b) Jonsson and Lindholm.[5] c) Carlson and Anderson.[8] d) Assignment from Refs. 5 and 8.

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Table 3. Ionization potentials of *trans* 1,3-butadiene (in eV)

Obsd 3)	Calcd			
	This calcn	MINDO[15]	CNDO[19]	*ab initio*[20]
9.08	9.78 πb_g	9.51 π	9.40 πb_g	9.78 πb_g
11.34	11.47 πa_u	10.30	10.00 a_g	13.01 πa_u
12.3	11.97 a_g	11.27	11.47 a_g	14.04 a_g
13.1	13.03 a_g	11.38 π	12.20 b_u	15.54 b_u
(14.0)	13.99 b_u	11.68	12.69 πa_u	15.68 a_g
15.2	16.85 b_u	13.47	14.90 b_u	18.03 b_u
18.0	17.63 a_g	13.72	16.33 a_g	18.14 a_g
19.4	21.42 b_u	18.00	19.30 a_g	21.17 b_u
20.2	22.18 a_g	19.58	19.71 b_u	22.89 a_g
	27.93 b_u	25.81	24.45 b_u	27.89 b_u
	31.92 a_g	30.36	27.62 a_g	30.30 a_g

Table 4. Ionization potentials of naphthalene (in eV)

Obsd 6, 7, 3)	Calcd		
	This calcn	MINDO[15]	*ab initio*[21]
8.12	9.21 $\pi 1a_u$	8.62 π	9.30 $\pi 1a_u$
8.91	9.48 $\pi 2b_{1u}$	9.30 π	10.20 $\pi 2b_{1u}$
10.08	10.49 $\pi 1b_{3g}$	9.37	11.84 $\pi 1b_{3g}$
10.85	10.62 $6b_{1g}$	9.86	13.51 $\pi 1b_{2g}$
11.05	10.83 $9a_g$	10.24	14.20 $9a_g$
11.35	11.56 $\pi 1b_{2g}$	10.32 π	14.41 $6b_{1g}$
11.90	12.43 $7b_{3u}$	11.21	15.43 $7b_{3u}$
12.5	13.13 $\pi 1b_{1u}$	11.31 π	15.66 $\pi 1b_{1u}$
13.5	13.52 $6b_{3u}$	11.62	16.57 $7b_{2u}$
13.7	13.62 $7b_{2u}$	11.63	17.15 $6b_{3u}$
14.45	14.56 $5b_{1g}$	12.00	17.26 $5b_{1g}$
15.9	15.25 $8a_g$	13.17 π	17.99 $8a_g$
16.25	15.77 $6b_{2u}$	13.19	18.19 $6b_{2u}$
	17.81 $4b_{1g}$	14.04	19.52 $7a_g$
	17.86 $7a_g$	14.65	20.25 $5b_{3u}$
	20.03 $5b_{3u}$	15.97	20.36 $4b_{1g}$
	22.90 $5b_{2u}$	18.93	23.15 $6a_g$
	23.37 $6a_g$	19.16	23.71 $5b_{2u}$
	23.39 $4b_{3u}$	19.99	24.11 $4b_{3u}$
	26.89 $3b_{1g}$	24.10	27.88 $3b_{1g}$
	27.76 $5a_g$	25.48	28.47 $5a_g$
	29.97 $4b_{2u}$	27.60	29.64 $4b_{2u}$
	33.89 $3b_{3u}$	30.21	31.16 $3b_{3u}$
	37.18 $4a_g$	34.23	33.00 $4a_g$

Table 5. Ionization potentials of azulene (in eV)

Obsd 6)	Calcd		
	This calcn	MINDO[15]	*ab initio*[21]
7.42	8.59 $\pi 2a_2$	8.22 π	8.26 $\pi 2a_2$
8.52	9.04 $\pi 3b_1$	8.73 π	9.44 $\pi 3b_1$
10.0	10.71 $\pi 1a_2$	9.74	12.37 $\pi 1a_2$
11.0	11.18 $17a_1$	9.91	13.49 $\pi 2b_1$
11.35	11.38 $12b_2$	10.15	14.08 $17a_1$
12.5	11.55 $\pi 2b_1$	10.51	15.08 $12b_2$
13.2	11.94 $16a_1$	10.59 π	15.44 $\pi 1b_1$
14.5	12.46 $11b_2$	11.02	15.44 $11b_2$
15.7	13.03 $10b_2$	11.37 π	15.72 $16a_1$
	13.05 $\pi 1b_1$	11.46	16.28 $15a_1$
	13.56 $15a_1$	12.90 π	16.87 $10b_2$
	16.16 $14a_1$	12.93	18.24 $9b_2$
	16.32 $9b_2$	13.23	18.36 $14a_1$
	18.14 $13a_1$	14.65	19.56 $13a_1$
	18.20 $8b_2$	15.13	20.31 $8b_2$
	20.28 $12a_1$	16.07	21.20 $12a_1$
	21.86 $11a_1$	17.12	21.43 $11a_1$
	22.28 $7b_2$	19.60	24.06 $7b_2$
	24.29 $10a_1$	20.78	24.99 $10a_1$
	26.49 $6b_2$	23.68	27.05 $6b_2$
	27.98 $9a_1$	25.08	28.21 $9a_1$
	30.34 $5b_2$	27.97	30.02 $5b_2$
	33.49 $8a_1$	30.32	31.13 $8a_1$
	37.31 $7a_1$	33.72	32.84 $7a_1$

electron levels and the π-electron levels. Moreover, the parameters, $\beta^\circ(C)$ and $\beta^\circ(H)$, were adjusted to reproduce the shallow levels for ethylene and benzene; thus, it is natural that the present results are plausible for the ionization potentials smaller than about 16 eV. Although the physical meaning of the choice of the empirical parameters is not very clear, the present method may provide, as in the sense of the Pariser-Parr-Pople calculations for the electronic spectra of π-electron system, a complementary means for interpreting or predicting the photoelectron spectra of unsaturated hydrocarbon molecules.