CNDO/2 Calculations of the Ionization Potentials and Electronic Spectra of Some Unsaturated Hydrocarbons

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A modified CNDO/2 method in which local core matrix elements are taken to be empirical parameters is presented. Using this method, the ionization potentials and electronic spectra of some unsatutated hydrocarbons, ethylene, *trans*-, *cis*-1,3-butadienes, cyclobutene, cyclopentadiene, benzene and naphthalene, were calculated. The results are in general agreement with the previously available experimental information.

SCF MO methods including all valence-shell electrons have already been advanced by many authors.[1] It is, however, known that the traditional SCF calculations in *ab initio* and semiempirical frameworks are not always reliable in reproducing the electronic spectra and the ionization potentials at the same time.

The Complete Neglect of Differential Overlap method (CNDO), which is the simplest one among the SCF methods including all valence-shell electrons, was developed by Pople and his co-workers.[2-4] Although this method is quite successful in predicting ground-state geometries, it is not so useful in calculating electronic spectra and in interpreting ionization potentials through the use of Koopmans' theorem.[5]

In view of these facts, Tinland,[6] Clark,[7-8] and Del-Bene and Jaffé[9-11] have introduced empirical elements into the original CNDO/2 method and have thus obtained results which reproduce well the observed excitation energies. A new parameter set for reproducing ionization potentials has recently been proposed by Ohno *et al.*[13] It should be noted, however, that these modifications do not lead to a good result in predicting both the electronic spectra and the ionization potentials at the same time.

Under these circumstances, we wish now to propose a new parameter set to calculate both the ionization potentials and the electronic spectra within the framework of the CNDO approximation. We will apply this method to some unsaturated hydrocarbons and will compare the predicted electronic spectra with those obtained using the π-electron approximation and the calculated ionization potentials with those of other SCF MO calculations.

Method of Calculation

Tajiri *et al.*[14] and Ohmichi *et al.*[15] have calculated the electronic spectra of a number of saturated and unsaturated compounds using a modified CNDO/2 method which is a compromise between the methods of Bene-Jaffé[9-11] and of Sichel-Whitehead.[12]

Our method differs from the above one in the following points:

1) In the above method, as in the original CNDO/2 scheme, the local core matrix element, $U_{\mu\mu}$, of the atomic orbital, μ, is estimated from the atomic data:

$$U_{\mu\mu} = -\frac{1}{2}(I_\mu + A_\mu) - \left(Z_A - \frac{1}{2}\right)\gamma_{AA}$$

where I_μ and A_μ are the ionization potential and the electron affinity of the appropriate average atomic state respectively and where γ_{AA} is the average interaction energy between two electrons in any valence atomic orbital of the A atom. We consider this matrix element as an additional empirical parameter and adjust its value, together with the selected values of the bonding parameters and the separation constant (*vide infra*), so that a wide range of ionization potentials for ethylene may be reproduced.

2) According to the approximation proposed by Del Bene and Jaffé.[9-11] the core matrix element, $\beta_{\mu\nu}$, between the orbitals, μ and ν, on the A and B atoms respectively is assumed to be proportional to the overlap between them and is given by:[17]

$$\beta_{\mu\nu} = -\frac{1}{2}(\beta_A^\circ + \beta_B^\circ)(S_{\mu\nu}^\sigma + kS_{\mu\nu}^\pi)$$

where β_A° is the bonding parameter, which depends only on the nature of the A atom. $S_{\mu\nu}^\sigma$ is a σ component of the overlap which arises from the projection of the orbitals, μ, and ν, onto the bond axis, and $S_{\mu\nu}^\pi$ is a π component of the overlap which arises from the projections of μ and ν normal to the bond axis. k is the σ-π separation constant. The values of the parameters, $U_{\mu\mu}$, β_A°, and k, adopted in this paper are summarized and compared with those of previous authors in Table 1.

Table 1. Parameter values[a]

Parameter	Method	H	C
U_{ss}	CNDO/2[b]	−17.38	−70.3
	Ohmichi *et al.*[c]	−13.60	−50.69
	This method	−13.60	−42.0
U_{pp}	CNDO/2		−61.8
	Ohmichi *et al.*		−41.53
	This method		−40.0
β_A°	CNDO/2	9	21
	Ohmichi *et al.*	8	15
	This method	9	15
k	Ohmichi *et al.*		0.75
	This method		0.70

a) Values for U_{ss}, U_{pp} and β_A° are in eV units. b) Ref. 2—4. c) Ref. 15.

The molecular geometries used in this calculation were mostly taken from Sutton's tables;[18] the co-ordinates are shown in Fig. 1.

All the calculations were carried out on the NEAC 2200 model 700 computer of TOHOKU University, using the program of our modification of the CNDO/2

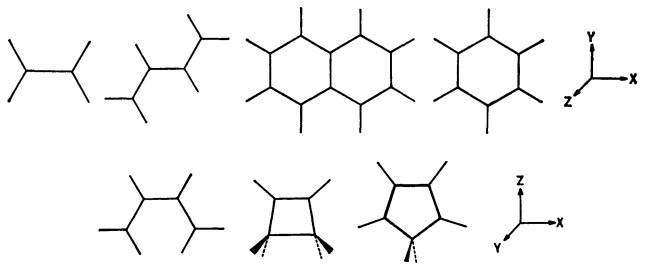


Fig. 1. Co-ordinate systems for calculated molecules.

method, including configuration interactions restricted to the 28 lowest singly excited configurations.

Results and Discussion

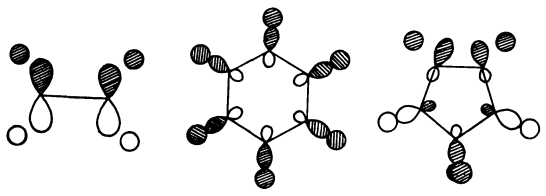
In Tables 2—7, the calculated orbital energies are given in comparison with the observed vertical ionization potentials (I.P.'s) and with the other calculated values.

Table 2. Ionization potentials of ethylene (eV)

Obsd[19]	Orbital	This work	CNDO[13]	MINDO[20]	*ab initio*[21]
10.51π	b_{1u}	10.59π	10.61π	10.39π[b]	10.05π
12.38	b_{1g}	12.95	12.96	11.47	13.91
14.47	a_g	14.41	14.51	11.65	15.88
15.68	b_{2u}	18.52	18.61	14.37	17.48
18.87	b_{3u}	19.74	21.21	19.21	21.70
23, 24.5[a]	a_g	26.63	29.54	28.01	27.97

a) T. Darrah Thomas, *J. Chem. Phys.*, **52**, 1373 (1970).
b) The orbital symmetries are not given in Ref. 20.

For ethylene (Table 2) the calculated energy of the lowest occupied orbital with the a_g symmetry is rather closer to the observed value than other calculations. This may be due to the facts that the main contribution to this orbital is by carbon 2s atomic orbitals and that the value of U_{ss} for the carbon atom chosen here is considerably smaller than that used in other methods (see Table 1). Both the present method and the earlier CNDO method by Ohno *et al.*[13] lead to a predicted energy of the b_{2u} orbital larger by about 3 eV than the observed value. It seems that this is due to the large relaxation energy of the ionized state inherent in this orbital. We have actually calculated the relaxation energies of the various ionized states of ethylene using the second-order perturbation method, and have



(a) (b) (c)

Fig. 2. The atomic-orbital arrangement of; a) the b_2-orbital of ethylene predicted at 18.52 eV, b) the a_1-orbital of benzene predicted at 20.50 eV and c) the a_1 orbital of cyclopentadiene predicted at 18.50 eV.

shown that the relaxation energy of this orbital is considerably larger than those of the other orbitals.[24] This is probably related to the atomic-orbital arrangement characteristic of this orbital, shown in Fig. 2; in this orbital, carbon 2p orbitals which are normal to the bond axis and which lie in the molecular plane are mutually bonding: at the same time, they are also bonding with the nearest hydrogen 1s orbitals.

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

Obsd[20]	Orbital	This work	CNDO[13]	CNDO[8]	*ab initio*[23]
9.07π[a]	b_g	9.07π	9.78π	9.40π	9.74π
11.27	a_g	11.95	11.97	10.00	13.99
12.17π[a]	a_u	12.39π	11.47π	12.69π	12.98π
13.11	a_g	12.82	13.03	11.47	15.62
(13.9)[a]	b_u	13.57	13.99	12.20	15.48
15.16	b_u	16.13	16.85	14.90	17.96
17.78	a_g	17.43	17.63	16.33	18.07
19.02	a_g	20.15	22.18	19.30	22.80
20.56	b_u	20.96	21.42	19.71	21.09
	b_u	25.38	27.93	24.45	27.78
	a_g	29.27	31.92	27.62	30.18

a) Taken from the He I spectrum by Brundle and Robin (Ref. 22)

Table 3 shows that the first three bands of *trans*-1,3-butadiene are attributed to the π, σ, and π electrons, in the order of increasing energy. This interpretation differs from those of the earlier SCF MO calculations, but is consistent with the analysis of Brundle and Robin, who observed that the second ionization potential should be attributed to the σ electron because it suffers a large shift to a higher energy on fluorination (the perfluoro-effect).[22] Indeed, using the present method, we found that the second highest orbital with the symmetry, a_g, of *trans*-1,3-butadiene shifts to a

Table 4. Ionization potentials of *cis*-1,3-butadiene and cyclobutene (eV)

cis-1,3-Butadiene[a]			Cyclobutene[b]			
This work	Orbital	*ab initio*[23]	This work	Orbital	Calcd[28]	Obsd[27]
9.03π	a_2	9.63π	9.56π	b_1	10.33(π)	9.43π
12.25	a_1	14.31	10.72	b_2	12.03	10.9
12.33	b_2	14.61	11.22	a_1		
12.41π	b_1	12.98π	13.73	a_2		
13.84	b_2	16.38	14.51	a_1		
15.57	a_1	17.12	17.04	b_2		
17.53	b_2	20.24	18.25	a_1		
19.55	a_1	19.24	19.07	b_1		
21.97	a_1	23.32	21.99	b_2		
24.38	b_2	27.51	22.36	a_1		
30.23	a_1	30.34	34.29	a_1		

a) The bond lengths and the bond angles except the dihedral angle were assumed to be those of *trans*-1,3-butadiene. b) The geometry was assumed to be (in Å unit); C_1, C_4 ($\pm$0.77, $-$1.5167); C_2, C_3 ($\pm$0.67, 0); H_1, H_2, H_5, H_6 ($\pm$1.2463, $-$1.7917, $\pm$0.9526); H_3, H_4, ($\pm$1.22, 0.9526).

lower energy on fluorination,[25] while the first and third highest orbitals suffer no substantial change.

In Table 4, the results for *cis*-1,3-butadiene and cyclobutene, which are isomers of *trans*-1,3-butadiene, are given. The first I.P. of the *trans*-1,3-butadiene obtained is higher by about 0.04 eV than that of its planar *cis* form. This result is in agreement with that of the *ab initio* calculation by Buenker,[23] while the calculations of the MINDO and the π-electron approximation[26] show that the first I.P. of the *cis* form is higher by 0.03 eV than that of the *trans* form. The first two I.P.'s of cyclobutene obtained are attributed to the π and σ electrons, in good agreement with the experimental results.[27]

TABLE 5. IONIZATION POTENTIALS OF BENZENE (eV)

Obsd[29]	Orbital	This work	CNDO[13]	CNDO[7]	*ab initio*[31]
9.3π	e_{1g}	9.41π	9.77π	9.40π	10.31π
11.4	e_{2g}	11.34	11.48	9.79	14.30
12.1π	a_{2u}	13.93π	12.55π	12.99π	14.64π
13.8	e_{1u}	13.95	14.68	13.81	17.04
14.7	b_{2u}	14.79	15.30	14.26	17.96
15.4	b_{1u}	15.27	16.34	15.15	18.33
16.9	a_{1g}	20.50	20.93	19.64	20.16
19.2	e_{2g}	20.77	22.50	20.10	23.09
	e_{1u}	25.21	28.18	24.81	28.38
	a_{1g}	33.14	35.74	31.18	31.94

In Table 5, the calculated results of benzene are given, together with those of the photoelectron spectra which were studied and discussed by Lindholm and Jonsson;[29] also given are the results obtained from the viewpoint of the angular distribution by Carlson and Anderson.[30] The calculated order of orbitals is in general agreement with the experimental results, but the energies of the two levels are predicted to be rather larger than the observed values. One is the lower nondegenerate π orbital with the symmetry, a_{2u}, predicted at 13.93 eV, while the other is the a_{1g} orbital predicted at 20.50 eV, which is larger by about 3 eV than the experimental value. In case of the a_{1g} orbital, the disagreement may be related to the fact that the atomic-orbital arrangement of this orbital resembles that of the b_{2u} orbital of ethylene, for which the predicted I.P. is larger by 3 eV than the observed one (see Fig. 2).

TABLE 6. IONIZATION POTENTIALS OF CYCLOPENTADIENE (eV)

Obsd[32]	Orbital	This work	SPINDO[33]	EH[32]
8.57	a_2	8.77π	9.20π	12.6π
10.72	b_1	11.32π	10.68π	13.8π
12.2	a_1	11.63	12.24	13.5
12.6	b_2	12.05	12.38	13.8
13.2	b_2	12.81	13.30	14.0
13.8	a_1	13.21	12.87	13.9
14.8	b_1	16.85π	14.54π	15.6π
16.4	a_1	18.50	16.55	16.4
17.5	b_2	18.63	16.98	17.5
18.4	a_1	19.44	17.75	18.1
22.0	b_2	23.29	22.03	22.5
22.3	a_1	24.28	21.51	22.3
	a_1	33.85	26.17	26.5

As is shown in Table 6, the present results for cyclopentadiene are in good agreement with the values of the photoelectron spectra observed by Derrick *et al.*[32] and by Fridh *et al.*,[33] and also with those of the SPINDO calculation by Fridh *et al.*[33] except for the orbital symmetries of the two levels, which are found experimentally at 13.2 and 13.8 eV. The lowest π-orbital (b_1) predicted at 16.85 eV should correspond to the band observed at 14.8 eV, since, in our method, the energy of the lowest π-orbital is usually calculated to be larger by about 2 eV than the observed one. Furthermore, considering that the calculated energies for the b_{2u} orbital of ethylene and the a_{1g} orbital of benzene are higher by about 3 eV than the observed values, the a_1 orbital predicted at 18.50 eV may be assigned to the observed band at 16.4 eV, since this orbital includes the part resembling the b_{2u} orbital of ethylene (see Fig. 2).

The photoelectron spectra of naphthalene are more complicated, and the assignment of the higher I.P.'s is considerably difficult. From the discussion for the lowest π orbitals in benzene and cyclopentadiene, it seems that the lowest π orbital with the symmetry, b_{1u}, of naphthalene corresponds to the band at about 13 eV (Table 7).

TABLE 7. IONIZATION POTENTIALS OF NAPHTHALENE (eV)

Obsd[19,34]	Orbital	This work	CNDO[13]	*ab initio*[36]
8.11	a_{1u}	8.11π	9.21π	9.30π
8.79	b_{1u}	9.05π	9.48π	10.20π
9.96	b_{3g}	10.36π	10.49π	11.84π
10.90	b_{1g}	10.47	10.62	14.41
11.35	a_{1g}	10.69	10.83	14.20
11.90	b_{3u}	12.15	12.43	15.43
12.26	b_{2g}	12.16π	11.56π	13.51π
13.22	b_{2u}	12.79	13.62	16.57
	b_{3u}	13.13	13.52	17.15
	b_{1g}	13.72	14.56	17.26
	b_{2u}	14.42	15.77	18.19
	a_{1g}	14.66	15.25	17.99
	b_{1u}	14.98π	13.13π	15.66π
15.73	b_{1g}	15.69	17.81	20.36
	a_{1g}	17.10	17.86	19.52
18.65	b_{3u}	18.89	20.03	20.25
21.03	b_{2u}	21.09	22.90	23.71
	b_{3u}	21.81	23.39	24.11
	a_{1g}	22.16	23.37	23.15
	b_{1g}	23.76	26.89	27.88
	a_{1g}	24.89	27.76	28.47
	b_{2u}	26.86	29.97	29.64
	b_{3u}	31.41	33.89	31.16
	a_{1g}	34.33	37.18	33.00

The calculated transition energies were compared with the available experimental values and also with those obtained by the π-electron approximation. The lower ten singly excited states and the corresponding oscillator strengths are listed in Table 8. It may be seen that the calculated values are in good agreement

Table 8. The calculated and experimental transition energies (eV)

Compound	Type	Symmetry	Transition energy (f) This work	π-Approxn.[a]	Obsd
Ethylene	σ–π^*	$^1B_{3g}$	7.08		
	σ–π^*	$^1B_{2g}$	7.60		
	π–π^*	$^1B_{3u}$	7.64 (0.72)	7.6	7.64[b] (0.29)[c]
	π–σ^*	$^1B_{3g}$	8.73		
	⋮	⋮	⋮		
	σ–σ^*	$^1B_{3u}$	12.68 (0.2)		
trans-1,3-Butadiene	π–π^*	^1B_u	5.87 (1.07)	6.21	5.93[d] (0.53)[e]
	σ–π^*	^1A_u	5.94		
	σ–π^*	^1A_u	6.74		
	π–π^*	^1A_g	6.93 (0.0)	7.87	7.14
	σ–π^*	^1B_g	7.21		
	⋮	⋮	⋮		
	π–π^*	^1A_g	8.58 (0.0)	8.51	
	⋮	⋮	⋮		
	π–π^*	^1B_u	10.07 (0.42)	9.50	
cis-1,3-Butadiene	π–π^*	$^1B_2$	5.35 (0.404)	5.91	
	σ–π^*	$^1A_2$	6.28		
	σ–π^*	$^1B_1$	6.35		
	π–π^*	$^1A_1$	6.86 (0.114)	8.29	
	σ–π^*	$^1A_2$	7.23		
	⋮	⋮	⋮		
	π–π^*	$^1A_1$	8.89	8.34	
	⋮	⋮	⋮		
	π–π^*	$^1B_2$	9.92	9.25	
Cyclobutene	σ–π^*	$^1B_1$	5.48 (0.001)		
	σ–π^*	$^1A_2$	5.84		
	π–π^*	$^1B_2$	6.48 (0.328)	6.10[f]	6.32 (0.28)[g]
	π–σ^*	$^1A_2$	8.40		
	π–σ^*	$^1B_1$	8.69		
Cyclopentadiene	π–π^*	$^1B_2$	5.11 (0.23)	4.8 (0.105)[h]	4.8 (0.07)[i]
	σ–π^*	$^1B_1$	6.01 (0.002)		
	σ–π^*	$^1A_2$	6.29		
	π–π^*	$^1A_1$	6.36 (0.016)	6.3 (0.049)	6.3(s)
	σ–π^*	$^1A_2$	6.94		
	π–π^*	$^1B_1$	7.27 (0.004)	7.4 (0.002)	7.4(s)
	σ–π^*	$^1A_2$	8.03		
	π–π^*	$^1A_1$	8.12 (1.23)	7.9 (0.468)	7.9(vs)
	π–σ^*	$^1A_2$	8.34		
Benzene	π–π^*	$^1B_{2u}$	4.93 (0.0)	4.9	4.89[j]
	π–π^*	$^1B_{1u}$	6.03 (0.0)	5.3	6.14
	σ–π^*	$^1A_{2u}$	6.46		
	σ–π^*	$^1E_{2u}$	6.49		
	σ–π^*	$^1A_{2u}$	6.52		
	π–π^*	$^1E_{1u}$	6.89 (1.18)	7.0	6.76 (0.88)[e]
	σ–π^*	$^1B_{2g}$	7.80		
	π–π^*	$^1E_{2g}$	8.08 (0.0)		
	π–π^*	$^1E_{2g}$	10.25 (0.0)		
Naphthalene	π–π^*	$^1B_{3u}$	4.21 (0.0)	4.02 (0.0)[k]	3.97 (0.002)[l]
	π–π^*	$^1B_{2u}$	4.46 (0.23)	4.49 (0.256)	4.46 (0.18)
	σ–π^*	$^1B_{3g}$	5.40		
	π–π^*	$^1B_{1g}$	5.63 (0.0)	5.51 (0.0)	
	π–π^*	$^1B_{3u}$	5.70 (2.02)	5.94 (2.115)	5.63 (1.70)
	σ–π^*	$^1B_{2g}$	5.74		
	π–π^*	$^1A_{1g}$	5.75 (0.0)	7.10 (0.0)	
	σ–π^*	$^1B_{2g}$	6.19		
	π–π^*	$^1B_{2u}$	6.23 (0.59)	6.31 (0.966)	6.51 (0.21)
	π–π^*	$^1B_{1g}$	6.34 (0.0)	5.99 (0.0)	

a) Ref. 37, b) Ref. 38, c) Ref. 39, d) Ref. 40, e) Ref. 41, f) Ref. 28, g) Ref. 42, h) Ref. 10, i) Ref. 43, 44, j) Ref. 45, k) Ref. 46, l) Ref. 47.

with the observed ones. It may be noted here that the first two excited states of ethylene calculated are attributed to σ-π^* transitions, whereas the first excited state was observed as the Rydberg state by Willkinson.[36] If an extended basis set is used, then the Rydberg state might be calculated as the first excited state.

In our calculations, the triplet states are generally found to be lower by 0.5—1.0 eV than the experimental values. This point will not be discussed here.

In the following papers we will apply this method to the calculation of the electronic spectra and the ionization potentials of the unsaturated compounds containing O, N, and F atoms.

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