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CNDO Calculations on the Electronic Spectra of Several Saturated Compounds

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CNDO calculations of the excited states were performed on the first three members of paraffinic hydrocarbons —methane, ethane, and propane, and on three compounds of saturated three-membered rings—cyclopropane, ethylenimine, and ethylene oxide. The method gives a reasonable interpretation of the electronic spectra of both kinds of compounds.

Most of the molecular orbital calculations on excited electronic states of organic compounds have so far been confined to π-electronic systems. There have been very few systematic and quantitative studies of electronic spectra on saturated compounds either theoretically or experimentally. One reason for this has been that the energy range of the electronic transitions in saturated compounds lies in the vacuum ultraviolet region, so that we had to wait until the spectroscopes of this energy range became avialabe for chemists.

Recently many experimental results on the electronic excitations in this energy region have been reported. Raymonda and Simpson¹⁾ observed the vacuum ultraviolet absorption spectra of alkanes, while Lassettre *et al.*²⁾ and Brongersma *et al.*³⁾ reported the results of their electron-impact experiments on methane, ethane, and cycloalkanes. Particularly, the low-energy electron-impact excitation spectra observed by Brongersma *et al.* provide information about the singlet-triplet transitions in saturated hydrocarbons.³⁾ Moreover, Basch *et al.* reported very important experimental results in which they distinguished Rydberg transitions from valence-shell absorptions by making a condensed-phase vacuum ultraviolet experiment.⁴⁾

As for theoretical treatments, several new molecular orbital methods, in which all valence electrons are treated and which can be applied to saturated molecules, have been proposed, one after another. Particularly, the CNDO method first proposed by Pople, Santry and Segal⁵⁻⁷⁾ has recently been used by many authors for MO calculations, mainly of the ground states of molecules. On the other hand, Del Bene and Jaffé⁸⁻¹⁰⁾ succeeded in reproducing experimental results on the electronic spectra of π-electronic systems including heteroatoms by using a modified version of this method. There have been however, few studies of the electronic spectra of σ-systems within the framework of the CNDO method.¹¹,¹²⁾

In view of these circumstances, we previously proposed¹³⁾ an approximate method with a new parametrization for the bonding parameter, $\beta_A{}^0$, and the two-center electron repulsion integral, γ_{AB}, within the framework of the CNDO/2 method; this method can be applied to the calculation of the electronic spectra of both saturated and unsaturated molecules.

In the present paper, we will apply this method to a series of paraffinic hydrocarbons and to a series of saturated three-membered ring compounds. We will compare the calculated electronic spectra of these molecules with those of Katagiri and Sandorfy,¹⁴⁾ who used the Pariser-Parr-Pople-type method on paraffinic hydrocarbons, and with those of Clark, obtained using the Pople-Segal CNDO/2 method¹¹⁾ on ring compounds.

Method of Calculation

As we mentioned in the previous paper, our method is a compromise between the methods of Bene-Jaffé⁸⁾

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Table 1. Parameter values (eV)

		H	C	N	O
U_{ss}	CNDO/2	-17.38	-70.3	-106.03	-149.07
	Sichel and Whitehead[a)] This work	-13.60	-50.69	-70.09	-101.31
U_{pp}	CNDO/2	—	-61.8	-93.99	-132.80
	Sichel and Whitehead[a)] This work	—	-41.53	-57.85	-84.28
γ_{AA}	CNDO/2	20.40	16.06	19.27	22.49
	Clark[b)]	12.85	11.11	12.02	13.00
	Sichel and Whitehead[a)] This work	12.85	10.21	11.05	13.63
$\gamma_{AA}{}^*$	Sichel and Whitehead[a)] This work	12.85	10.33	11.31	13.91
β_A^0	CNDO/2	9	21	25	31
	Clark[b)]	12	17	26	45
	Sichel and Whitehead[a)]	5.4	8.2	8.8	12.8
	This work	8.0	15.0	23.0	41.0

a) Ref. 15. b) Ref. 11.

and of Sichel-Whitehead.[15)] The F matrix elements are given in this method as:

$$F_{\mu\mu} = U_{\mu\mu} + \left(P_{AA} - \frac{1}{2}P_{\mu\mu}\right)\gamma_{AA} + \sum_{B \neq A}(P_{BB} - Z_B)\gamma_{AB}, \quad (1)$$

$$F_{\mu\nu} = \kappa/2(\beta_A^0 + \beta_B^0)S_{\mu\nu} - \frac{1}{2}P_{\mu\nu}\gamma_{AB}, \quad (2)$$

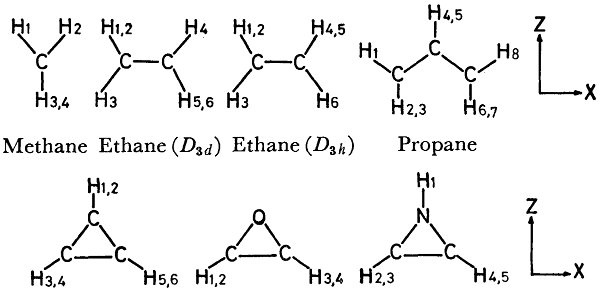
where μ and ν denote atomic orbitals centered on the A atom and the B atom respectively. The empirical parameter, κ, is taken as 0.75 for the π-bonds and as 1.0 otherwise. $U_{\mu\mu}$ is the diagonal matrix element of the atomic orbital, ϕ_μ, for the core Hamiltonian of the A atom. $P_{\mu\nu}$ is the charge density and bond-order matrix. P_{AA} is the total charge on the A atom. γ_{AB} is an average interaction energy between an electron in any valence atomic orbital of the A atom with another in an orbital of the B atom. β_A^0 is the bonding parameter, which depends only on the nature of the A atom.

For $U_{\mu\mu}$ and γ_{AA}, we used the values of Sichel and Whitehead.[15)] In evaluating the interatomic electron repulsion integral, γ_{AB}, we employed Mataga-Nishimoto's formula;

$$\gamma_{AB} = 1/(R_{AB} + a), \qquad a = 2/(\gamma_{AA}{}^* + \gamma_{BB}{}^*), \quad (3)$$

where $\gamma_{AA}{}^*$ is the "extrapolated" one-center electron repulsion integral.[15)] The empirical parameter, κ, and the bonding parameters, β_H^0 and β_C^0 were so reparametrized that they reproduce the experimental spectra of the reference molecules—methane, ethylene, and benzene.[13)] The values of β_N^0 and β_O^0 needed for calculating ethylenimine and ethylene oxide were determined using pyrole and furan as reference molecules. In Table 1, the parameter values used in this work are compared with those used in other methods.

The geometries of methane, cyclopropane, ethylenimine, and ethylene oxide were taken from Sutton's tables.[16)] For ethane and propane, all the angles are assumed to be tetrahedral, and the bond lengths of C-C and C-H are assumed to be 1.54 Å and 1.09 Å respectively; this is done for convenience in calculation and in comparison of the results. For ethane, we adopted two thermally-probable conformers, staggered (D_{3d}) and eclipsed (D_{3h}).



Methane Ethane (D_{3d}) Ethane (D_{3h}) Propane

Cyclopropane Ethylene oxide Ethylenimine

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

The calculations were carried out on the NEAC 2200 Model 500 computer of Tohoku University, using the program of our modified CNDO method including configuration interactions restricted to 30 lowest singly-excited configurations.

Results and Discussion

Electronic Spectra of Paraffinic Hydrocarbons. *Methane:* Table 2 shows the calculated and observed energies of excited states of methane. The calculated $T_2 \leftarrow A_1$ transition at 10.64 eV was used, together with some transitions in ethylene and benzene, for the parametrization of κ, β_H^0 and β_C^0.[13)] The next higher allowed transition is calculated to be 13.42 eV($T_2 \leftarrow A_1$). This value is too high to be associated with the observed second transition at 11.7 eV.[3)] We may, therefore, reasonably assign this observed band to one of the quintuply-degenerate forbidden transitions, $E \leftarrow A_1$ and $T_1 \leftarrow A_1$, at 12.27 eV. These forbidden transitions may be perturbed by vibrations belonging to the T_2 symmetry and may become vibronically-allowed by borrowing intensity from the $T_2 \leftarrow A_1$ transition at 13.42 eV, which is very intense.

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TABLE 2. EXCITATION ENERGIES (in eV) AND INTENSITIES OF METHANE

	Obs. (Ref. 3)	This work		Katagiri and Sandorfy (Ref. 14)	
Singlet	9.7—10.2	T_2	10.64(0.22)	T_2	10.26
	11.7	$E+T_1$	12.27(0)	$A_1+E+T_1+T_2$	10.48
		T_2	13.42(1.77)		
Triplet	8.8	T_2	9.39	T_2	9.31
	11.0	A_1	10.74	$A_1+E+T_1+T_2$	10.11
		T_2	11.57		

TABLE 3. EXCITATION ENERGIES (in eV) AND INTENSITIES OF ETHANE

		Obs.		This work		Katagiri and Sandorfy (Ref. 14)	
		Light absorption (Ref. 2)	Electron impact (Ref. 3)				
C_2H_6 (D_{3d})	Singlet	8.5		E_u	8.81(0.26)	E_u	7.81
						E_g	8.78
		9.4	9.3	A_{2u}	9.55(0.32)	$A_{1u}+A_{2u}+E_u$	8.84
				E_g	9.77(0)		
				A_{1g}	10.22(0)		
				A_{1u}	10.70(0)		
		10.68		E_u	11.02(0.15)	A_{2u}	10.15
				E_u	11.43(0.57)		
	Triplet		7.1 (onset) ≀ 9.3	E_u	7.88	E_u	7.37
				E_g	8.66	$A_{1u}+A_{2u}+E_u$	8.01
				A_{2u}	8.83	E_g	8.05
C_2H_6 (D_{3h})	Singlet			E'	8.80(0.29)	E''	7.84
				A_2''	9.58(0.32)	E'	8.51
				E''	9.64(0)	$A_1''+A_2''+E''$	8.56
				A_1'	10.20(0)	A_2''	10.12
				A_1''	10.63(0)		
				E''	11.02(0)		
				E'	11.24(0.02)		
	Triplet			E'	7.83	E''	7.25
				E''	8.54	E'	7.87
				A_2''	8.83	$A_1''+A_2''+E''$	7.89
				A_1'	9.72	A_2''	9.27

Using the low-energy electron impact as a spectroscopic tool, Brongersma *et al.*[3] observed excitation spectra for saturated hydrocarbons considerably different from the optical ones. The difference arises from the fact that the selection rules for electronic excitation by electron impact differ fundamentally from those encountered in light-absorption spectroscopy. In the case of low-energy electron impact, in particular, as it is thought that the exchange between the incident electron and a molecular electron is possible, the difference between the two types of spectra may mainly be a result of singlet-triplet transitions. For methane, Brongersma *et al.* reported a low-energy electron impact excitation spectrum—a trapped electron (TE) spectrum—showing singlet-triplet transitions at 8.8 and 11.0 eV.[3] Our results on the triplet states of methane are in good agreement with their experimental data.

Ethane: Table 3 shows the calculated and observed excited states of ethane. The difference in predicted spectrum between the conformational isomers of ethane, staggered and eclipsed, turned out to be very small. We assign the observed values to the predicted values for the staggered ethane, thermally-most-probable conformer. According to Lassettre *et al.*, [2] three transitions are observed, at 8.5, 9.4, and 10.68 eV (third column). They may be assigned to the $E_u \leftarrow A_{1g}$ transition predicted at 8.81 eV (0.26), the $A_{2u} \leftarrow A_{1g}$ transition at 9.55 eV (0.32), and the $E_u \leftarrow A_{1g}$ transitions at 11.02 eV (0.15) and 11.43 (0.57) respectively. Thus, a good agreement between theory and experiment is obtained.

For triplet states, the present calculation predicted the first transition at 7.88 eV with a transition type of $E_u \leftarrow A_{1g}$. Brongersma *et al.*[3] observed the first peak at 9.3 eV, one with an onset at 7.1 eV, by using the low-energy electron-impact technique. In the optical[1] and high-energy electron-impact[2] spectra, the onset is at 8.1 eV. According to Brongersma *et al.*, the difference between these two types of spectra suggests that the contribution of singlet-triplet transitions is important. It is likely that the absorption between 7.1 eV and 8.1 eV observed in the TE spectrum is due mainly to the singlet-triplet transition, which is predicted at 7.88 eV by our method.

Propane: The results of the calculation of the elec-

TABLE 4. EXCITATION ENERGIES (in eV) AND INTENSITIES OF PROPANE

	Obs. (Ref. 1 and 2)	This work		Katagiri and Sandorfy (Ref. 14)	
Singlet	8.1 (Shoulder)	B_1	8.40(0.16)	B_1	7.53
	8.9	B_2	8.37(0.35)	A_2	8.22
		A_1	8.63(0.24)	B_1	8.28
		A_1	9.16(0.01)	A_1	8.31
		B_2	9.18(0.04)	A_1	8.49
		A_2	9.24(0)	B_2	8.91
	9.6	B_2	9.65(0.02)	A_1	8.98
		B_1	9.72(0.00)		
		A_1	9.93(0.05)		
		A_2	10.24(0)		
Triplet		B_1	7.55	B_1	7.00
		B_2	7.73	A_1	7.77
		A_1	7.86	B_1	7.79
		A_2	8.51	A_1	7.79

tronic-transition energies of propane are given in Table 4, together with the experimental results. We calculated the excited states of propane, assuming an all-*trans* C_{2v} conformation. Actually, however, the propane molecule is not fully in an all-*trans* conformation; rather, it takes various *gauche*-type forms. Although each conformer will have excitation energies different from those of other conformers, the difference, may be guessed from the results concerning ethane conformers, may be very small. Thus, we may tentatively give the assignments shown in Table 4.

The lowest singlet-singlet transition ($B_2 \leftarrow A_1$) was calculated to be at 8.37 eV, with the very large oscillator strength of 0.35. From the experimental data given by Raymonda *et al.*[1] and by Lassettre *et al.*,[2] however, we can read the weak absorption at 8.1 eV as the first band. According to Salahub *et al.*[12] and Katagiri *et al.*,[14] the symmetry of the predicted first transition for propane is B_1. Our method, on the other hand, predicts the lowest $B_1 \leftarrow A_1$ transition at 8.40 eV (0.16), higher by 0.03 eV than the lowest calculated transition. This energy difference is so small that the order of these two predicted transitions is not essential for this type of calculation. We may thus assign the weak band observed at 8.1 eV as a shoulder to the $B_1 \leftarrow A_1$ transition predicted at 8.40 eV and the next strong absorption band observed at 8.9 eV to the group transitions including the $B_2 \leftarrow A_1$ transition calculated at 8.37 eV.

The transitions predicted by Katagiri and Sandorfy[14] seem, in general, to be too low to be assigned to the observed spectrum.

Electronic Spectra of the Saturated Three-membered Rings. Several discussions of the electronic structures of saturated three-membered rings have been reported; the earlier works focussed on the bonding nature,[17,18] and the more recent works, on their spectral properties.[4,11,19–22] Walsh has discussed the olefin-like structures of cyclopropane and ethylene oxide.[18] The results of our calculations of the electronic spectra of these molecules seem to support the study of Walsh,[18] since all the first singlet-singlet transitions of these molecules are predicted to be in about the 7 eV energy region, considerably lower than in the case of ususal saturated molecules and rather close to those met with in the case of olifins.

Cyclopropane: The calculated excited states of cyclopropane are shown in Table 5, alobg with the experimental values. Our calculations provide results very close to those predicted by Clark.[11] He associated the calculated transitions with the experimental ones obtained by Wagner and Duncan, including Rydberg transitions.[20] Recently Basch *et al.*[4] have reported new spectral data on cyclopropane: they proposed the values of 7.4, 8.6, and 10.3 eV for the N→V transitions. These values were obtained by comparing the gas-phase and condensed-phase spectra·

TABLE 5. EXCITATION ENERGIES (in eV) AND INTENCITIES OF CYCLOPROPANE

	Obs.				This work		Clark (Ref. 11)		Brown and Krishna (Ref. 21)	
	Light absorption			Electron impact						
	Ref. 20	Ref. 1	Ref. 4	Ref. 3						
Singlet					A_2'	6.76(0)	A_2'	6.68(0)		
	6.79						E'	6.93(0.04)		
		7.0(onset)								
			7.4 (N→V)	7.4	E'	7.39(0.06)				
	7.78	7.8	7.67(Ryd.)				A_1'	7.77(0)	A_2'	7.23
					A_1'	8.34(0)				
	8.55	8.6	8.6 (N→V)	9.7	E'	8.87(0.17)	E'	8.46(1.10)	E'	7.72
					E''	9.14(0)	E''	8.48(0)	A_1'	8.71
					E''	9.71(0)	E''	8.79(0)		
	10.32		10.3 (N→V)		A_2''	9.73(0.67)	A_2''	9.72(0.44)	E'	11.66
Triplet				5.9(onset) ~ 7.4	A_2'	6.76	E'	5.95	A_2'	6.79
					E'	7.10	A_2'	6.68	E'	6.95
					A_1'	7.85	E'	7.19	E'	8.07

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Table 6. Excitation energies (in eV) and intensities of ethylene oxide

	Obs. Ref. 22	Obs. Ref. 4	This work			Clark (Ref. 11)		
Singlet						A_2	5.61	(0)
						B_2	6.30	(0.06)
	5.83~7.23 (tail)		A_2	7.26	(0)	B_1	6.34	(0.03)
						A_1	6.53	(0.00)
	7.23	7.24 (Ryd.)				B_2	6.99	(0.05)
						A_2	8.27	(0)
		7.7 (N→V)	B_2	7.74	(0.11)			
	7.89	7.89 (Ryd.)				B_1	8.39	(0.00)
						B_1	8.40	(0.01)
		8.6 (N→V)	B_1	8.15	(0.17)			
			A_1	8.46	(0.00)			
	8.64	8.64 (Ryd.)				B_2	8.49	(0.43)
			A_2	8.75	(0.00)			
	8.96	8.97 (Ryd.)				A_1	8.68	(0.12)
	9.56	10.54 (N→V)	B_1	9.28	(0.24)	A_1	9.39	(0.05)
			A_1	10.06	(0.04)			
Triplet			A_2	6.43		B_2	5.16	
			B_1	6.80		A_2	5.59	
			B_2	7.23		B_1	6.19	

This is based on the fact that Rydberg bands do not appear in condensed phases. We may assign these observed transitions to the predicted 7.39 eV ($E'\leftarrow A_1'$ (0.06), 8.87 ev($E'\leftarrow A_1'$) (0.17), and 9.73 eV ($A_2''\leftarrow A_1'$) (0.67) transitions respectively.

The TE spectrum of cyclopropane reported by Brongersma *et al.*[3] is quite different from the optical spectrum in the region of about 6—7.5 eV, suggesting that there is an important contribution of the singlet-triplet transition in the TE spectrum. In addition, Wagner *et al.*[20] observed a weak absorption centered around 6.79 eV for cyclopropane. The calculation by Brown *et al.*[21] suggests that this absorption is due to a singlet-triplet transition. In accordance with these peices of evidence, our calcualtion gives the $A_2'\leftarrow A_1'$ transition at 6.76 eV as the first singlet-triplet transition. The corresponding value calculated by Clark[11] is 5.95 eV ($E'—A_1'$).

Table 7. Excitation energies (in eV) and intensities of ethylenimine

	Obs. (Ref. 4)	This work		Clark (Ref. 11)	
Singlet	6 (Ryd.)			A''	5.98(0.04)
	6.9 (Ryd.)			A'	6.50(0.01)
	7.4 (N→V)	A''	7.13(0.03)	A'	6.81(0.01)
		A'	7.91(0.02)	A''	7.22(0.03)
	8.4 (Ryd.)			A'	7.87(0.04)
		A''	8.76(0.01)	A'	8.19(0.02)
		A'	9.01(0.09)		
		A'	9.07(0.02)		
		A''	9.07(0.05)		
		A'	9.40(0.37)		
	9.0 (N→V)	A''	9.72(0.09)		
	~	A'	9.77(0.00)		
	10.5 (N→V)	A'	10.20(0.08)		
		A''	10.30(0.03)		
		A''	10.43(0.00)		
		A''	10.94(0.00)		
		A'	11.09(0.04)		
		A'	11.29(0.04)		
		A''	11.33(0.78)		
Triplet		A''	6.83	A''	5.22
		A'	7.37	A'	6.27
		A''	7.80	A''	6.62
		A'	8.00	A'	6.70

Ethylene Oxide: The calculated and observed excited states of ethylene oxide are listed in Table 6. Our method and Clark's method[11] give quite different results. Moreover, his assignments seem to be inadequate, for, according to Bash *et al.*,[4] some experimental values to which Clark assigned his calculated values come from Rydberg transitions. For example, the observed values of 7.23, 7.89, 8.64, and 8.96 eV[22] with which Clark associated his calculated values turned out to be due to Rydberg transitions.[4] The results of our calculation of ethylene oxide agree fairly well with the new experimental results.

Our calculation predicts three low-lying triplet states at 6.43 eV ($A_2\leftarrow A_1$), 6.80 eV ($B_1\leftarrow A_1$), and 7.23 eV ($B_2\leftarrow A_1$); they are higher than Clark's results by ca. 1 eV.

Ethylenimine: In Table 7 we show the calculated and observed excited states of ethylenimine. Here again our method gives results quite different from those obtained usnig Clark's method.[11] This molecule belongs to the point group C_s, so that all singlet-singlet transitions are allowed. According to Basch *et al.*,[4] the lowest N→V transition is observed at 7.4 eV, so Clark's values[11] seem to be too low. The two rather close transitions predicted using our method, the $A''\leftarrow A'$ transition at 7.13 eV (0.03) and the $A'\leftarrow A'$ transition at 7.91 eV (0.02), may be associated with the observed first transition at 7.4 eV. In the energy region above 8 eV, our method predicts a large number of transitions very close to each other. We may associate these predicted transitions with the two bands observed at 9.0 and 10.5 eV, which are very broad, probably because of the overlapping of transitions.

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