The Calculation of the Energy Levels of Acetaldehyde by a Semi-empirical Molecular Orbital Method Including the Hyperconjugation Effect

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It is well-known that the introduction of a methyl group into unsaturated bond system results in a spectral shift from the spectrum of the unsubstituted parent molecule. A molecular-orbital treatment for a molecule containing a methyl group has been developed by many workers[1]. In this paper, we will calculate the lowest (n, π^*) and (π, π^*) electronic state energies for acetaldehyde by a semi-empirical molecular orbital method[2,3] including a group orbital for the methyl group. The molecular structure of acetaldehyde is shown in Fig. 1[4].

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[1] For example, C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, **1952**, 2052; R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941); N. Muller, L. W. Pickett and R. S. Mulliken, ibid., **76**, 4770 (1954).

[2] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

[3] T. Anno, I. Matubara and A. Sadō, This Bulletin, **30**, 168 (1957).

[4] R. W. Kilb, C. C. Lin and E. B. Wilson, Jr., *J. Chem. Phys.*, **26**, 1695 (1957).

TABLE I. TRANSITION ENERGIES AND OSCILLATOR STRENGTHS OF THE LOWEST n-π^* AND π-π^* TRANSITIONS OF AN ACETALDEHYDE MOLECULE

Orbital jump	Electronic transition	Transition energy, eV.		Oscillator strength	
		Calcd.	Obs.	Calcd.	Obs.
$n\rightarrow\pi_3$	$^3A''\leftarrow{}^1A'$	3.40			
$n\rightarrow\pi_3$	$^1A''\leftarrow{}^1A'$	3.83	3.86[a]	1.57×10^{-4}	3.15×10^{-4}
$\pi_2\rightarrow\pi_3$	$^3A'\leftarrow{}^1A'$	4.83			
$\pi_2\rightarrow\pi_3$	$^1A'\leftarrow{}^1A'$	7.35	7.51[b]	6.83×10^{-2}	

a) V. R. Rao and I. A. Rao, *Indian J. Phys.*, **28**, 491 (1954).
b) A. D. Walsh, *Proc. Roy. Soc.*, **A185**, 176 (1945).

A line combining two hydrogen atoms, H_a and H_b, is perpendicular to the molecular plane, and a third atom, H_c, is contained in its plane as Fig. 1 shows. From the point of view of the molecular orbital method, the methyl group conjugates with the $2p\pi$ orbital of the carbonyl group. For the methyl group, Mulliken[1] used the following group orbitals:

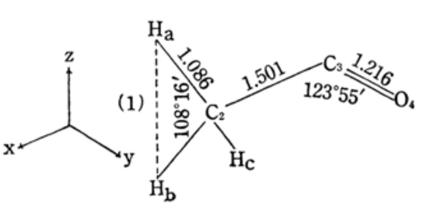

Fig. 1. A model of acetaldehyde molecule; (1) represents a quasi-atom.

$$\psi_1=(h_a+h_b+h_c)/(3+6S)^{1/2} \qquad [\sigma]$$
$$\psi_2=(2h_c-h_a-h_b)/(6-6S)^{1/2} \qquad [\pi]$$
$$\psi_3=(h_a-h_b)/(2-2S)^{1/2} \qquad [\overline{\pi}]$$

Among these orbitals, the ψ_3 orbital conjugates with the $2p\pi$ orbitals of the carbonyl group. We assume the ψ_3 orbital to be a quasi-$2p\pi$ orbital; the node is on the midpoint of a line connecting H_a with H_b, and it is separated by 1.086 Å from the neighboring carbon atom. The orbital energy of ψ_3 is calculated by the following equation:

$$W(\psi_3)=\int\psi_3{}^*H\psi_3\,d\tau$$

in which H is a Hartree-Fock type Hamiltonian[5]:

$$H=T+U_{H_3}$$
$$U_{H_3}=-1/r_a-1/r_b-1/r_c+(h_\sigma h_\sigma|+(h_\pi h_\pi|$$
$$-1/2(h_\sigma|h_\sigma-1/2(h_\pi|h_\pi$$

in which $-1/r_i$ is a potential force from a hydrogen nucleus i, and $(h_ih_i|$ and $(h_i|h_i$ are Coulomb and repulsion forces of the h_i electron respectively. For the 1s orbital energy of a hxdrogen atom, we use -13.595 eV., and the three center integrals are calculated by means of Sklar's approximation[6] and Kotani's table[7]. Paoloni proposed a relation between the effective nuclear charge, Z_μ, and one center Coulomb integral, $(\mu\mu|\mu\mu)=3.29_4\,Z_\mu$[8]. We use the above relation for calculating the effective nuclear charge of the quasi-$2p\pi$ orbital.

$$(\psi_3\psi_3|\psi_3\psi_3)=8.430\text{ eV.}$$

Therefore, we obtain $Z_\mu=2.56$.

The nonbonding orbital for lone pair electrons on the oxygen atom can be approximately represented as follows:

$$\varphi_n=\chi_n$$

χ_n being the $2p\pi$ AO of the oxygen atom, the nodal plane of which is perpendicular to the molecular plane and contains the CO axis. At any rate, we assume that the orbital of the H_3 group participates in hyperconjugation with the residual part of the molecule; the $2p\pi$ group orbital has the effective nuclear charge of 2.56 and the valence state ionization potential of 8.804 eV. The interelectronic Coulomb integrals which appear in this calculation are evaluated according to Roothaan's table[9] for the case of $r>2.80$ Å and according to Pariser-Parr's method[2] for $r\leq2.80$ Å. Particularly, the empirical formula of the interelectronic Coulomb integrals $(H_3H_3|CC)$ is obtained as follows:

$$(H_3H_3|CC)=9.755-2.1680\,r+0.1551\,r^2$$

We use Kon's[10] formula for the calculation of the core integral, β_{co}, between carbon and oxygen atoms. The core integral, β_{H_3-C}, between H_3 and the neighboring carbon atom, C, is substituted by $\beta_{H_2-C}\cdot\beta_{H_2-C}$ can be obtained by assumption of the proportionality relation, $\beta_{H_2-C}/\beta=S_{H_2-C}/S$, where β and S are core and overlap integrals respectively in a benzene molecule. The MO's of acetaldehyde have been obtained by the simple LCAO MO method

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[5] S. Aono, *Busseiron Kenkyu*, No. 94, 24 (1959).

[6] A. L. Sklar, *J. Chem. Phys.*, **7**, 984 (1939).

[7] M. Kotani, A. Amemiya, E. Ishiguro and T. Kimura, "Table of Molecular Integrals", Maruzen Co., Ltd., Tokyo (1955).

[8] L. Paoloni, *Nuovo Cimento*, **4**, 410 (1956).

[9] C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951).

[10] H. Kon, This Bulletin, **28**, 275 (1955).

disregarding overlap integrals. As a methyl group has electron-donating property, it is known that its electronegativity is larger than that of a carbon atom. Accordingly, we adopt the following parameters[1]: $\alpha_{\mathrm{H}_3}=\alpha-0.5\beta$, $\alpha_2=\alpha-0.1\beta$, $\alpha_3=\alpha$, $\alpha_4=\alpha+1.5\beta$, $\beta_{12}=2.92\beta$, $\beta_{23}=0.834\beta$, $\beta_{34}=2^{1/2}\beta$, in which α and β are Coulomb and resonance integrals for a benzene molecule. We obtained the following orbitals:

$e_1=-2.8919$

$\varphi_1=0.5547\chi_1+0.6443\chi_2+0.3693\chi_3+0.3753\chi_4$

$e_2=-2.1786$

$\varphi_2=0.3744\chi_1+0.3435\chi_2-0.3726\chi_3-0.7765\chi_4$

$e_3=0.8305$

$\varphi_3=0.2436\chi_1-0.0276\chi_2-0.8288\chi_3+0.5029\chi_4$

$e_4=3.3990$

$\varphi_4=0.7019\chi_1-0.6827\chi_2+0.1496\chi_3-0.0568\chi_4$

in which χ_i represents the 2pπ AO of the ith atom shown in Fig. 1. The results of the calculation are summarized in Table I, together with observed data.

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