Calculation on the Electronic States of the Acrolein Molecule by the Semi-Empirical Molecular Orbital Method

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It is known that the semi-empirical molecular orbital method proposed by Pariser and Parr[1] gives good agreement with observation for the $\pi-\pi^*$ transitions of conjugated hydrocarbons and heteromolecules. Anno et al.[2-4] used the Pariser-Parr method to calculate the electronic state energies of some molecules containing C=O and N atoms, obtaining reasonably good agreement between calculated and observed values. Eastwood and Snow[5] have carried out a detailed vibrational analysis for the $n-\pi^*$ absorption spectrum of acrolein, while the experiment in vacuum ultraviolet region was done by Walsh[6]. In a previous paper[7] we were not certain whether or not the very weak band at 24647 cm^{-1} in acrolein spectrum was due to a singlet-triplet transition. In order to get some information about the electronic state energies of the acrolein molecule, we calculated the electronic states of acrolein by the Pariser-Parr method which is expected also to yield successful results for the electronic state energies of some molecules exhibiting $n-\pi^*$ transitions.

Calculation and Results

The calculation of the electronic state energies of acrolein was done with the semi-empirical method proposed by the previous authors[1-3]. The π-MO's take in this paper are

$$\phi_1=1/2(\chi_1^{\mathrm{O}}+\chi_2^{\mathrm{C}}+\chi_3^{\mathrm{C}}+\chi_4^{\mathrm{C}})$$
$$\phi_2=1/2(\chi_1^{\mathrm{O}}+\chi_2^{\mathrm{C}}-\chi_3^{\mathrm{C}}-\chi_4^{\mathrm{C}})$$
$$\phi_3=1/2(\chi_1^{\mathrm{O}}-\chi_2^{\mathrm{C}}-\chi_3^{\mathrm{C}}+\chi_4^{\mathrm{C}})$$
$$\phi_4=1/2(\chi_1^{\mathrm{O}}-\chi_2^{\mathrm{C}}+\chi_3^{\mathrm{C}}-\chi_4^{\mathrm{C}})$$

where χ_1^{O}, χ_2^{C}, χ_3^{C} and χ_4^{C} are $2p\pi$AO's of the oxygen and carbon atoms.

In addition to the above orbitals the acrolein molecule has a nonbonding orbital which can approximately be represented as follows:

$$\phi_n=\chi_n^{\mathrm{O}}$$

χ_n^{O} being the $2p\pi$AO of the oxygen atom, the nodal plane of which is perpendicular to the

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

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

[3] T. Anno, I. Matubara and A. Sadō, *J. Chem. Phys.*, **26**, 967 (1957).

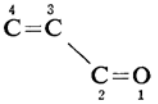
[4] T. Anno and A. Sadō, ibid., **26**, 1759 (1957).

[5] E. Eastwood and C. P. Snow, *Proc. Roy. Soc.*, **149A**, 446 (1935).

[6] A. D. Walsh, *Trans. Faraday Soc.*, **41**, 498 (1945).

[7] K. Inuzuka, This Bulletin, **33**, 678 (1960).

molecular plane and contains the CO axis. The electron diffraction study of the acrolein molecule in the ground electronic state[8] shows that it is planar, having the following bond lengths and bond angles



$$r_{12}=1.21\pm0.02\,\text{Å}$$
$$r_{23}=1.46\pm0.03\,\text{Å}$$
$$r_{34}=1.36\pm0.02\,\text{Å}$$
$$\angle\gamma_{123}=\angle\gamma_{234}=120\pm3^\circ$$

Since the molecule belongs to the point group Cs, all the transition are symmetry-allowed. The energy integrals which appear in this calculation were evaluated according to the equation derived by Roothaan[9] and by Anno et al.[2] for the case of $r>2.80\,\text{Å}$ and of $r<2.80\,\text{Å}$, respectively. We used Kon's formula[10] for the conculation of core integral β_{CO} between carbon and oxygen atoms, and the Pariser-Parr formula for β_{CC} between carbon and carbon atoms. For the evaluation of core integrals the Coulomb penetration integrals between next-neighboring neutral atoms were taken into consideration, and since we restricted the calculation of energy state up to 10 eV., singly and doubly excited electronic configurations[11] were taken in the calculation of energies for the excited electronic state. Since it is known that the calculation of energy state in $\pi-\pi^*$ transition usually results in a good agreement with the observed value without configuration interaction[12], we did not include the configuration interaction. On the other hand, as for $n-\pi^*$ transition the configuration interaction was taken into account but all the configurations more than 10 eV. higher than the ground configuration were neglected. Even for the configurations considered, we imposed the condition to reduce the order of the C. I. matrix: $(H_{ij}/H_{ii}-H_{jj})^2>1/10$, where H_{ij} is the interaction matrix element between the configurations i and j. Neglected configurations within the 10 eV. energy range were taken into account by the second order perturbation theory. Calculated energy values are shown in Table I. From this result it is seen that in acrolein the (n, π^*) triplet state is the lowest excited electronic state.

TABLE I. TRANSITION ENERGIES OF $n-\pi^*$ AND $\pi-\pi^*$ TRANSITIONS OF ACROLEIN MOLECULE

Orbital jump	Electronic transition	Transition energy no C.I. eV.	including C.I. eV.	experimental eV.
$n-\pi_3$	${}^3A'\leftarrow{}^1A''$	5.55	2.85	
$n-\pi_3$	${}^1A'\leftarrow{}^1A''$	5.98	3.85	3.71
$n-\pi_4$	${}^3A'\leftarrow{}^1A''$	7.23	6.00	
$n-\pi_4$	${}^1A'\leftarrow{}^1A''$	7.66	6.53	
$\pi_2, n-\pi_3, \pi_3$	${}^3A'\leftarrow{}^1A''$	10.68	7.86	
$\pi_2, n-\pi_3, \pi_3$	${}^1A'\leftarrow{}^1A''$	11.11	8.36	
$\pi_2-\pi_3$	${}^3A'\leftarrow{}^1A'$	4.17		
$\pi_2-\pi_3$	${}^1A'\leftarrow{}^1A'$	6.08		5.96
$\pi_2-\pi_4$, $\pi_1-\pi_3$	${}^3A'\leftarrow{}^1A'$	5.85		
$\pi_2-\pi_4$, $\pi_2-\pi_3$	${}^1A'\leftarrow{}^1A'$	7.76		
$\pi_1-\pi_4$	${}^3A'\leftarrow{}^1A'$	7.53		
$\pi_1-\pi_4$	${}^1A'\leftarrow{}^1A'$	9.44		

Discussion

Acrolein in *n*-hexane solution has three absorption maxima in the 1800~4000 Å region, λ's$_{\max}$ 2078 Å (5.96 eV., $\log\varepsilon_{\max}=3.89$), 3345 Å (3.71 eV., $\log\varepsilon_{\max}=1.13$) and 4020 Å (3.08 eV., $\log\varepsilon_{\max}=\bar{1}.13$). The last two absorption bands are assigned to the $n-\pi^*$ transition from the solvent effect. The first absorption band has the extinction coefficient of 7700, showing that this transition may be regarded as an allowed one. It is assigned to a $\pi-\pi^*$ transition from the red-shift in the solvent effect.

From these observations the absorption bands at 5.96 and 3.71 eV., may be assigned to the ${}^1A'\leftarrow{}^1A'$ and ${}^1A'\leftarrow{}^1A''$ transitions, respectively. In Table I they correspond to the calculated 6.07 eV. (π, π^*) and 3.85 eV. (n, π^*) transitions. The third absorption band may correspond to the lowest calculated singlet-triplet transition 2.85 eV. To account for this small discrepancy we tried to obtain the phosphorescence spectrum of acrolein in cyclohexane and ethyl alcohol solutions at liquid air temperature, but failed. The *n*-hexane solution of acrolein

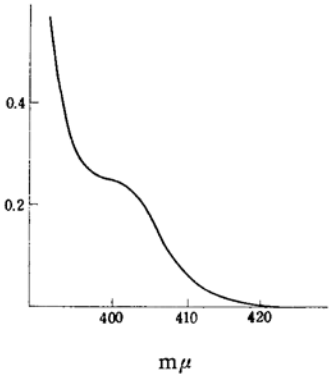


Fig. 1. Absorption band of acrolein in *n*-hexane solution (1.71 mol./l.) at 10°C.

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[8] H. Mackle and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 691 (1951).

[9] C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 116 (1951).

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

[11] J. N. Murrell and K. L. McEwen, *J. Chem. Phys.*, **25**, 1143 (1956).

[12] J. W. Sidman, ibid., **27**, 429 (1957).

has an absorption maximum at 4020 Å ($\varepsilon=0.136, f=1.16\times10^{-7}$) as shown in Fig. 1. These values of ε and f are somewhat greater than those usually given for a singlet-triplet absorption. According to Kasha[13] it may be expected to have increased intensity in ethyl iodide solution because of the spin-orbit coupling. However, we could not observe any increase of the absorption, due to the overlapping of an intense absorption of the iodine molecule which exists in the solution. On the other hand, this band in ethyl alcohol solution showed a remarkable decrease of intensity at dry ice temperature compared with that at 10°C. Hence, we assigned this 4000 Å band as a hot band. Fig. 2 shows the temperature dependence of this band in ethyl alcohol solution. This weak band lies at 1226 cm^{-1} on the red side of the $0-0$ band in vapor state.

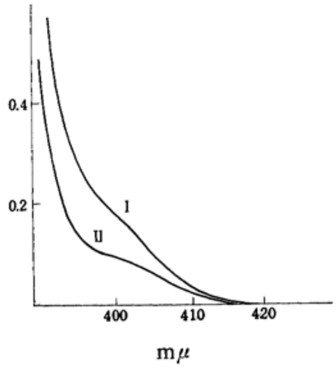

Fig. 2. The effect of temperature on the absorption band of acrolein in ethyl alcohol solution (0.956 mol./l.), curve I at 10°C, curve II at dry ice temperature.

The corresponding frequency could not be found in the infrared and Raman spectra[14], and we could not decide the vibrational mode of this band.

Summary

It was found that the semi-empirical method proposed by Pariser and Parr can be applied to the $n-\pi^*$ transition as well as the $\pi-\pi^*$ transition in acrolein. In acrolein the (n, π^*) triplet state is the lowest state. A weak band in the red side of the $0-0$ band is a hot band and it is not the $n-\pi^*$ singlet-triplet transition band. The $n-\pi^*$ triplet band anticipated from calculation could not be found.

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