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# Vacuum Ultraviolet Spectra of
# Styrene, Benzaldehyde, Acetophenone, and Benzonitrile

By

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The vacuum ultraviolet absorption spectra of styrene, benzaldehyde, acetophenone and benzonitrile have been measured in the wavelength region of 1500 to 2200 Å. The absorption bands in the vacuum ultraviolet region appear at 200, 196, 189, 180 and 163 mμ for styrene; at 195, 186, 178 and 165 mμ for benzaldehyde; at 196, 191, 179 and 167 mμ for acetophenone; at 187.5, 180 and 167 mμ for benzonitrile.

Theoretical studies of π-electron structures have been carried out with styrene, benzaldehyde and acetophenone by considering configurational interactions among the ground, locally excited, and charge-transfer configurations. The calculated transition energies and oscillator strengths are in good agreement with the observed values. The theoretical results show that the contribution of the charge-transfer configuration amounts to 58 and 68% in the excited states of the 238 mμ band of styrene and of the 232 mμ band of benzaldehyde respectively. This means that these two bands may be regarded as the intramolecular charge-transfer band.

The electron affinity of the C = C and C = O groups were determined to be respectively −0.84 and −1.20 eV from the present analysis of the ultraviolet spectra.

Die Vakuum-Ultraviolettspektren von Styrol, Benzaldehyd, Acetophenon und Benzonitril im Bereich von 1500 bis 2200 Å wurden gemessen: 200, 196, 189, 180 und 163 mμ für Styrol, 195, 186, 178 und 165 mμ für Benzaldehyd, 196, 191, 179 und 167 mμ für Acetophenon und 187,5, 180 und 167 mμ für Benzonitril im Vakuum-UV-Bereich.

Berechnungen der π-Elektronensysteme der drei erstgenannten Verbindungen wurden unter Einschluß von Konfigurationen mit und ohne Charge Transfer durchgeführt und ergaben Übergangsenergien und Oszillatorstärken, die mit den Meßwerten befriedigend übereinstimmen. Zum oberen Zustand der 238 mμ-Bande von Styrol trägt die Charge Transfer Konfiguration 58% bei, und zu dem der 232 mμ-Bande von Benzaldehyd sogar 68%, woraus hervorgeht, daß es sich bei diesen beiden Banden um intramolekulare Charge Transfer Banden handelt.

Die Elektronenaffinität der C = C- und der C = O-Gruppe beträgt nach diesen Berechnungen −0,84, bzw. −1,20 eV.

Nous avons mesuré les spectres d'absorption du styrène, du benzaldéhyde, de l'acétophénone et du benzonitrile entre 1500 et 2200 Å. Les bandes se situent à 200, 196, 189, 180 et 163 mμ pour le styrène; à 195, 186, 178 et 165 mμ pour le benzaldéhyde; à 196, 191, 179 et 167 mμ pour l'acétophénone et à 187,5, 180 et 167 mμ pour le bentonitrile.

Les structures π-électroniques des trois premières molécules ont été étudiées, en considérant l'interaction entre les configurations forndamentales, localement excitées et excitées avec transfert de charge. Les énergies et forces oscillatrices calculées s'accordent bien aux valeurs observées. Le calcul montre que la configuration à transfert de charge entre avec 58% dans la bande à 238 mμ du styrène, et avec 68% dans celle à 232 mμ du benzaldéhyde. Par conséquent ces deux bandes peuvent être attribuées au transfert de charge intramoléculaire. Notre analyse des spectres donne les affinités électroniques des groupes C = C et C = O à −0,84 et −1,20 eV, respectivement.

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# 1. Introduction

Recently, we have experimentally and theoretically studied the vacuum ultraviolet spectra of nitrobenzene [8], aniline and its N-derivatives [2], and phenol, anisole, phenetole, thiophenol, halogeno-benzenes, and toluene [3]. It has been shown that the ultraviolet spectra can well be interpreted in terms of the intramolecular electron transfer between the substituent groups and the benzene ring. In the present study, we have measured the vacuum ultraviolet absorption with styrene, benzaldehyde, acetophenone, and benzonitrile. Furthermore, in order to clarify the nature of the new absorption bands obtained by the present work and to deepen the knowledge on the $\pi$-electronic structures of these molecules, we have carried out theoretical studies on styrene and benzaldehyde, using the same method as employed in our previous studies.

# 2. Experimental

*Materials and Measurements.* – The commercial materials of styrene, benzaldehyde, acetophenone, and benzonitrile were fractionally distilled and the vapors of their purified samples were transferred through a vacuum glass line into the gas cell attached to the apparatus. Absorption measurements from 160 to 220 m$\mu$ for these compounds were carried out in the vapor phase at room temperature by a recording vacuum ultraviolet spectrophotometer, gas cells of 7, 10, and 30 mm path length and with lithium fluoride windows being used. The details of the apparatus and experimental procedure have recently been
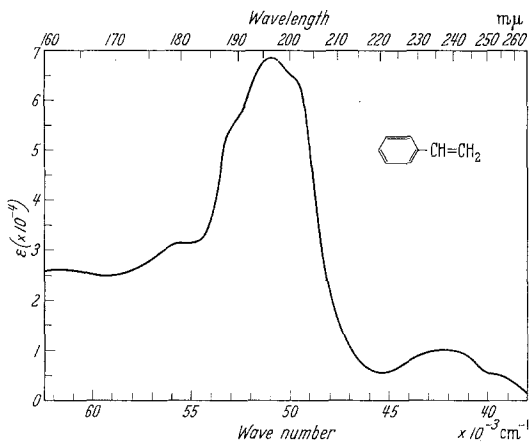


Fig. 1. The ultraviolet absorption spectrum of styrene in the wavelength region 160 ∼ 260 m$\mu$



Fig. 3. The ultraviolet absorption spectrum of acetophenone in the wavelength region 160 ∼ 240 m$\mu$
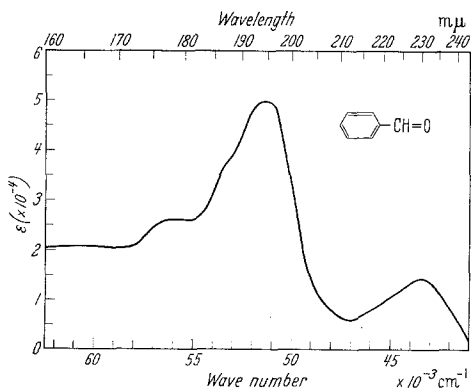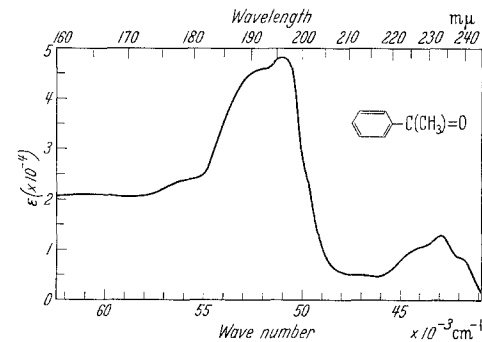


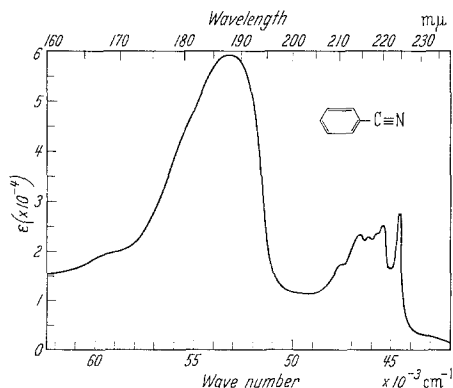Fig. 2. The ultraviolet absorption spectrum of benzaldehyde in the wavelength region 160 ∼ 240 m$\mu$



Fig. 4. The ultraviolet absorption spectrum of benzonitrile in the wavelength region 160 ∼ 240 m$\mu$

published elsewhere [13]. The vacuum ultraviolet spectra for individual compounds were carefully measured several times for different vapor pressures. The ultraviolet absorption spectra in the wavelength region longer than 200 m$\mu$ were measured with a Cary recording spectrophotometer model 14 M.

*Experimental Results.* – The ultraviolet absorption spectra of styrene, benzaldehyde, acetophenone, and benzonitrile measured in the present work are shown in Fig. 1, 2, 3 and 4 respectively.

Tab. 1 summarizes experimental results on the absorption bands of these compounds. The experimental $f$ values were obtained from the integral areas under the absorption curves by the use of the following equation

$$f = 4.32 \times 10^{-9} \int \varepsilon \, dv,$$

where $\varepsilon$ is the molar extinction coefficient and $v$ is the frequency in cm$^{-1}$. Since several bands overlap with each other in the vacuum ultraviolet region, the sum of the oscillator strength values for overlapped bands is shown in Tab. 1.

Table 1. *Experimental results on the electronic spectra of styrene, benzaldehyde, acetophenone, and benzonitrile in the vapor phase*

| Styrene | | | Benzaldehyde | | |
|---|---|---|---|---|---|
| $\lambda$ (m$\mu$) | $\varepsilon$ | $f$ | $\lambda$ (m$\mu$) | $\varepsilon$ | $f$ |
| 280 | 800 | 0.02 | 275 | 1000 | 0.02 |
| 238 | 10000 | 0.24 | 232 | 14000 | 0.26 |
| (200) | 65000 | ⎫ | 195 | 50000 | ⎫ |
| 196 | 68000 | ⎬ | (186) | 36000 | ⎬ 1.7 |
| (189) | 54000 | ⎬ 2.4 | 178 | 26000 | ⎬ |
| 180 | 30000 | ⎭ | 165 | 21000 | ⎭ |
| 163 | 25000 | ⎭ | | | |

| Acetophenone | | | Benzonitrile | | |
|---|---|---|---|---|---|
| $\lambda$ (m$\mu$) | $\varepsilon$ | $f$ | $\lambda$ (m$\mu$) | $\varepsilon$ | $f$ |
| 275 | 950 | 0.02 | 274 | 650 | 0.01 |
| 231 | 13000 | 0.28 | 224 | 23000 | 0.46 |
| 196 | 48000 | ⎫ | 187.5 | 59000 | ⎫ |
| 191 | 46000 | ⎬ 1.7 | (180) | 40000 | ⎬ 1.6 |
| 179 | 24000 | ⎬ | 167 | 18000 | ⎭ |
| 167 | 21000 | ⎭ | | | |

Values in parentheses show the positions of shoulder of the absorption spectra.

The vacuum ultraviolet spectra of styrene, benzaldehyde, and benzonitrile have been measured by Walsh [14] and by Klevens and Platt [4] many years ago. According to Klevens and Platt [4], the absorption peaks of styrene, benzaldehyde and benzonitrile in the vacuum ultraviolet region locate at around 205, 200 and 185 m$\mu$, respectively. Our measurements are extended to shorter wavelength region.

## 3. Theoretical

The $\pi$-electron structures of styrene, benzaldehyde and acetophenone have been studied theoretically by using the method originally presented by Longuet-Higgins and Murrell [5]. In the present calculation, the substituted benzenes under consideration were divided into two components; one is the benzene ring, and the other is the substituent with a double bond. The molecular orbital of

each component have been determined. Thereafter, the interaction between the components has been considered by the configurational interaction among several electron configurations including the ground, locally excited, and charge-transfer configurations.

Tab. 2 shows the wave functions and transition energies for the locally excited configurations of the benzene ring and the substituents. The energy values of the

Table 2. *Wave functions and energy values of the locally excited configurations used in the present calculation of styrene and benzaldehyde*

| Wave Function | Energy (eV)[a] | $f$[a] |
|---|---|---|
| **Benzene Ring** | | |
| $\psi_{B_{2u}} = 2^{-1/2}\left[(\varphi_3^{-1}\,\varphi_5) - (\varphi_2^{-1}\,\varphi_4)\right]$ | $E_{B_{2u}} = 4.89$ | 0.001 |
| $\psi_{B_{1u}} = 2^{-1/2}\left[(\varphi_3^{-1}\,\varphi_4) + (\varphi_2^{-1}\,\varphi_5)\right]$ | $E_{B_{1u}} = 6.17$ | 0.126 |
| $\psi_{E_{1u}} = 2^{-1/2}\left[(\varphi_3^{-1}\,\varphi_5) + (\varphi_2^{-1}\,\varphi_4)\right]$ | $E_{E_{1u}} = 6.98$ | |
| $\psi'_{E_{1u}} = 2^{-1/2}\left[(\varphi_3^{-1}\,\varphi_4) - (\varphi_2^{-1}\,\varphi_5)\right]$ | $E'_{E_{1u}} = 6.98$ $\Big\}$ | 1.035 |

**Substituted Group**

$\psi_L = (\theta_1^{-1}\,\theta_2)$ $\qquad$ $E_{L\,(C=C)} = 7.60$[b] $\qquad$ (styrene)

$\qquad\qquad\qquad\qquad\qquad\quad$ $E_{L\,(C=O)} = 7.92$[c] $\qquad$ (benzaldehyde and acetophenone)

$\qquad\qquad$ Molecular Orbitals*

$\qquad\qquad$ $\varphi_2 = 12^{-1/2}\,(2\,\chi_1 + \chi_2 - \chi_3 - 2\,\chi_4 - \chi_5 + \chi_6)$

$\qquad\qquad$ $\varphi_3 = 2^{-1}\,(\chi_2 + \chi_3 - \chi_5 - \chi_6)$

$\qquad\qquad$ $\varphi_4 = 2^{-1}\,(\chi_2 - \chi_3 + \chi_5 - \chi_6)$

$\qquad\qquad$ $\varphi_5 = 12^{-1/2}\,(-2\,\chi_1 + \chi_2 + \chi_3 - 2\,\chi_4 + \chi_5 + \chi_6)$

$\qquad\qquad$ $\theta_1 = a\chi_7 + b\chi_8$

$\qquad\qquad$ $\theta_2 = b\chi_7 - a\chi_8$

$\qquad\qquad$ where $a = b = 2^{-1/2}$ for styrene, and

$\qquad\qquad$ $a = 0.5472$[d] $\quad$ and $b = 0.8370$[d] $\quad$ both for benzaldehyde and

$\qquad\qquad$ acetophenone

a Refs. 2 and 3. $\qquad$ b Ref. 11. $\qquad$ c Ref. 15. $\qquad$ d Ref. 7.

* $\chi_i$'s are atomic orbitals shown in Fig. 5.

locally excited configurations shown in Tab. 2 were taken from the positions of the $\pi \to \pi^*$ transition bands of benzene [2, 3] ethylene [11] and formaldehyde [15] respectively. The molecular orbitals of the $C = O$ group used in the present calculation are taken from those given already by one of the present authors [7].

The wave functions and energies of the charge-transfer configurations are given by the following formulas:

$\psi_{CT_a} = (\varphi_2^{-1}\,\theta_2),$ $\qquad$ $E_{CT_a} = I_B - A_{C=O} - Q_2$ $\qquad\Big\}$ for benzaldehyde and

$\psi_{CT_b} = (\varphi_3^{-1}\,\theta_2),$ $\qquad$ $E_{CT_b} = I_B - A_{C=O} - Q_3$ $\qquad$ acetophenone

$\psi_{CT_1} = 2^{-1/2}\left\{(\varphi_3^{-1}\,\theta_2) - (\theta_1^{-1}\,\varphi_4)\right\},\ E_{CT_1} = \frac{1}{2}\,(I_B - A_{C=C} + I_{C=C} - A_B - Q_3 - Q_4)$

$\psi_{CT_2} = 2^{-1/2}\left\{(\varphi_2^{-1}\,\theta_2) - (\theta_1^{-1}\,\varphi_5)\right\},\ E_{CT_2} = \frac{1}{2}\,(I_B - A_{C=C} + I_{C=C} - A_B - Q_2 - Q_5)$

$\psi_{CT_3} = 2^{-1/2}\left\{(\varphi_3^{-1}\,\theta_2) + (\theta_1^{-1}\,\varphi_4)\right\},\ E_{CT_3} = \frac{1}{2}\,(I_B - A_{C=C} + I_{C=C} - A_B - Q_3 - Q_4)$

$\psi_{CT_4} = 2^{-1/2}\left\{(\varphi_2^{-1}\,\theta_2) + (\theta_1^{-1}\,\varphi_5)\right\},\ E_{CT_4} = \frac{1}{2}\,(I_B - A_{C=C} + I_{C=C} - A_B - Q_2 - Q_5)$

for styrene

The configurations of $(\varphi_2^{-1}\,\theta_2)$ and $(\varphi_3^{-1}\,\theta_2)$ are due to electron transfers from the benzene ring to the substituent, while those of $(\theta_1^{-1}\,\varphi_4)$ and $(\theta_1^{-1}\,\varphi_5)$ are due to electron transfers in the reverse direction. Here, $I_B$ and $I_{C=C}$ are the ionization potentials of benzene and the $C = C$ group respectively, and $A_B$, $A_{C=O}$ and $A_{C=C}$ are the electron affinities of the phenyl, $C = O$ and $C = C$ groups respectively. $Q_2$, $Q_3$, $Q_4$ and $Q_5$ are the electrostatic energies given by the following equation⋆:

$$Q_2 = [\varphi_2\,\varphi_2 \mid \theta_2\,\theta_2] = \frac{b^2}{12}\,(4\,q_1 + q_2 + q_3 + 4\,q_4 + q_5 + q_6)$$

$$+ \frac{a^2}{12}\,(4\,q_1' + q_2' + q_3' + 4\,q_4' + q_5' + q_6')$$

$$Q_3 = [\varphi_3\,\varphi_3 \mid \theta_2\,\theta_2] = \frac{b^2}{4}\,(q_2 + q_3 + q_5 + q_6)$$

$$+ \frac{a^2}{4}\,(q_2' + q_3' + q_5' + q_6')$$

$$Q_4 = [\varphi_4\,\varphi_4 \mid \theta_1\,\theta_1] = \frac{a^2}{4}\,(q_2 + q_3 + q_5 + q_6)$$

$$+ \frac{b^2}{4}\,(q_2' + q_3' + q_5' + q_6')$$

$$Q_5 = [\varphi_5\,\varphi_5 \mid \theta_1\,\theta_1] = \frac{a^2}{12}\,(4\,q_1 + q_2 + q_3 + 4\,q_4 + q_5 + q_6)$$

$$+ \frac{b^2}{12}\,(4\,q_1' + q_2' + q_3' + 4\,q_4' + q_5' + q_6').$$

Here, $q_i$ and $q_i'$ are two-center repulsion integrals expressed by $(\chi_i\,\chi_i \mid \chi_7\,\chi_7)$ and $(\chi_i\,\chi_i \mid \chi_8\,\chi_8)$, respectively, $i$ being 1, 2, $\cdots$ 6, and $a$ and $b$ are given in Tab. 2. These values were calculated by the use of a quadratic equation of atomic distan-

Table 3. *The off-diagonal matrix elements used in the calculation of styrene, benzaldehyde, and acetophenone (The configurations, $(\theta_1^{-1}\,\varphi_4)$ and $(\theta_1^{-1}\,\varphi_5)$, were not taken into account for benzaldehyde and acetophenone)*

$$H\,(G,\ \theta_1^{-1}\,\varphi_5) = (2/\sqrt{6})\,(-a\beta + a\beta' - b\beta'')$$
$$H\,(G,\ \varphi_2^{-1}\,\theta_2) = (2/\sqrt{6})\,(b\beta + b\beta' - a\beta'')$$
$$H\,(B_{2u},\ \theta_1^{-1}\,\varphi_4) = (1/\sqrt{6})\,(a\beta + a\beta' + b\beta'')$$
$$H\,(B_{2u},\ \varphi_3^{-1}\,\theta_2) = (1/\sqrt{6})\,(-b\beta + b\beta' + a\beta'')$$
$$H\,(B_{1u},\ \theta_1^{-1}\,\varphi_5) = (-1/\sqrt{6})\,(a\beta + a\beta' + b\beta'')$$
$$H\,(B_{1u},\ \varphi_2^{-1}\,\theta_2) = (1/\sqrt{6})\,(-b\beta + b\beta' + a\beta'')$$
$$H\,(E_{1u},\ \theta_1^{-1}\,\varphi_4) = (-1/\sqrt{6})\,(a\beta + a\beta' + b\beta'')$$
$$H\,(E_{1u},\ \varphi_3^{-1}\,\theta_2) = (1/\sqrt{6})\,(-b\beta + b\beta' + a\beta'')$$
$$H\,(E_{1u}',\ \theta_1^{-1}\,\varphi_5) = (1/\sqrt{6})\,(a\beta + a\beta' + b\beta'')$$
$$H\,(E_{1u}',\ \varphi_2^{-1}\,\theta_2) = (-1/\sqrt{6})\,(-b\beta + b\beta' + a\beta'')$$
$$H\,(L,\ \theta_1^{-1}\,\varphi_5) = (1/\sqrt{3})\,(-b\beta + b\beta' + a\beta'')$$
$$H\,(L,\ \varphi_2^{-1}\,\theta_2) = (-1/\sqrt{3})\,(ab + a\beta' + b\beta'')$$
$$H\,(L,\ E_{1u}) = \sqrt{2}\,[(\theta_1\,\theta_2 \mid \varphi_3\,\varphi_5) + (\theta_1\,\theta_2 \mid \varphi_2\,\varphi_4)]$$
$$H\,(L,\ E_{1u}') = \sqrt{2}\,[(\theta_1\,\theta_2 \mid \varphi_3\,\varphi_4) - (\theta_1\,\theta_2 \mid \varphi_2\,\varphi_5)]$$
$$H\,(L,\ B_{1u}) = \sqrt{2}\,[(\theta_1\,\theta_2 \mid \varphi_3\,\varphi_4) + (\theta_1\,\theta_2 \mid \varphi_2\,\varphi_5)]$$
$$H\,(\theta_1^{-1}\,\varphi_4,\ \theta_1^{-1}\,\varphi_5) = -\,(\theta_1\,\theta_1 \mid \varphi_4\,\varphi_5)$$
$$H\,(\varphi_2^{-1}\,\theta_2,\ \varphi_3^{-1}\,\theta_2) = -\,(\varphi_1\,\varphi_3 \mid \theta_2\,\theta_2)$$

⋆ $[\varphi_2\,\varphi_2 \mid \theta_2\,\theta_2]$ is the abbreviation of $\int \varphi_2\,(i)\,\varphi_2\,(i)\left(\dfrac{1}{r_{ij}}\right)\theta_2(j)\,\theta_2(j)\,d\tau_{ij}$, for instance.

Table 4. *Overlap integrals and resonance integrals used in the present calculation of styrene, benzaldehyde, and acetophenone*

| Atom Pair | Atomic Distance | Overlap Integral | Resonance Integral |
|---|---|---|---|
| $C_1 - C_7$ | $r = 1.47$ Å | $S = 0.218$ | |
| $C_2 \cdots C_7$ | $r' = 2.48$ Å | $S' = 0.030$ | $\beta' = 0.138\,\beta$ |
| $C_1 \cdots C_8$ | $r'' = 2.44$ Å | $S'' = 0.032$ | $\beta'' = 0.148\,\beta$ |
| $C_1 \cdots O$ | $r'' = 2.35$ Å | $S'' = 0.012$ | $\beta'' = 0.055\,\beta$ |

Table 6. *Calculated wave functions and energy levels of benzaldehyde and acetophenone*

| | $\psi_G$ | $\psi_{B2u}$ | $\psi_{CT_a}$ | $\psi_{CT_b}$ | $\psi_{B1u}$ | $\psi_{E1u}$ | $\psi'_{E1u}$ | $\psi_L$ |
|---|---|---|---|---|---|---|---|---|
| $\psi_7$ | 0.039 | -0.004 | -0.286 | -0.034 | -0.147 | -0.157 | 0.337 | 0.869 |
| $\psi_6$ | 0.018 | 0.068 | -0.111 | 0.367 | -0.050 | 0.871 | 0.295 | 0.012 |
| $\psi_5$ | 0.018 | -0.032 | 0.106 | -0.150 | 0.072 | -0.231 | 0.862 | -0.405 |
| $\psi_4$ | -0.075 | 0.039 | 0.421 | 0.132 | 0.851 | 0.000 | 0.122 | 0.244 |
| $\psi_3$ | 0.000 | 0.309 | -0.000 | 0.850 | -0.130 | -0.399 | 0.029 | -0.071 |
| $\psi_2$ | -0.169 | -0.030 | 0.825 | -0.044 | -0.480 | 0.032 | 0.203 | 0.123 |
| $\psi_1$ | -0.003 | 0.947 | 0.012 | -0.316 | -0.003 | 0.060 | 0.001 | 0.006 |
| $\psi_0$ | 0.982 | 0.000 | 0.190 | -0.001 | -0.012 | 0.000 | 0.010 | 0.013 |

$E_7 = 8.342 \quad E_6 = 7.154 \quad E_5 = 6.848 \quad E_4 = 6.312$
$E_3 = 6.045 \quad E_2 = 5.507 \quad E_1 = 4.750 \quad E_0 = -0.219$

Table 5. *Calculated wave functions and energy levels of styrene*

| | $\psi_G$ | $\psi_{B2u}$ | $\psi_{CT_1}$ | $\psi_{CT_2}$ | $\psi_{CT_3}$ | $\psi_{CT_4}$ | $\psi_{B1u}$ | $\psi_{E1u}$ | $\psi'_{E1u}$ | $\psi_L$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $\psi_9$ | -0.018 | 0.015 | 0.040 | 0.125 | -0.120 | 0.314 | 0.028 | -0.326 | 0.151 | 0.860 |
| $\psi_8$ | -0.034 | -0.012 | -0.028 | 0.194 | 0.061 | -0.455 | -0.265 | 0.072 | 0.820 | 0.039 |
| $\psi_7$ | -0.009 | -0.099 | -0.228 | 0.058 | 0.506 | 0.205 | 0.067 | 0.744 | -0.004 | 0.280 |
| $\psi_6$ | 0.014 | 0.304 | 0.906 | -0.072 | 0.203 | 0.040 | 0.089 | 0.159 | 0.073 | 0.022 |
| $\psi_5$ | -0.078 | 0.032 | 0.114 | 0.408 | 0.098 | -0.180 | -0.745 | 0.009 | -0.450 | 0.119 |
| $\psi_4$ | -0.154 | 0.090 | 0.048 | 0.767 | -0.408 | 0.188 | 0.303 | 0.229 | 0.035 | -0.173 |
| $\psi_3$ | -0.077 | -0.134 | -0.016 | 0.378 | 0.700 | 0.018 | 0.263 | -0.498 | -0.001 | -0.159 |
| $\psi_2$ | 0.015 | -0.039 | 0.006 | -0.048 | 0.042 | 0.763 | -0.448 | -0.072 | 0.309 | -0.332 |
| $\psi_1$ | 0.002 | 0.932 | -0.331 | -0.006 | 0.129 | 0.021 | -0.010 | -0.064 | 0.008 | -0.015 |
| $\psi_0$ | 0.981 | -0.000 | 0.000 | 0.194 | 0.000 | -0.003 | 0.006 | -0.000 | -0.005 | -0.006 |

$E_9 = 8.154 \quad E_8 = 7.385 \quad E_7 = 7.324 \quad E_6 = 6.572 \quad E_5 = 6.448$
$E_4 = 6.116 \quad E_3 = 6.004 \quad E_2 = 5.014 \quad E_1 = 4.645 \quad E_0 = -0.243$

ces which was obtained in the way suggested by PARISER and PARR [9]

$$(\chi_i \chi_i \mid \chi_C \chi_C) = 0.222 \; r^2 - 2.67 \; r + 10.60$$
$$(\chi_i \chi_i \mid \chi_O \chi_O) = 0.378 \; r^2 - 3.68 \; r + 12.30 \; .$$

Assuming the molecular geometry of planar configuration*, we have: $Q_2 = 4.74$ and $Q_3 = 4.36$ eV for benzaldehyde and acetophenone, and $(Q_3 + Q_4) = 4.06$ and $(Q_2 + Q_5) = 4.46$ eV for styrene.

Off-diagonal matrix elements of the total electron Hamiltonian are shown in Tab. 3. In Tab. 3, $\beta$ is the resonance integral between two atomic orbitals, $\chi_1$ and $\chi_7$, $\beta'$ is that between $\chi_2$ and $\chi_7$, and $\beta''$ is that between $\chi_1$ and $\chi_8$ (see Fig. 5). The values for $\beta'$ and $\beta''$ were calculated on the assumption that the resonance integrals are proportional to the corresponding overlap integrals $S$; that is to say

$$\beta' = \beta \; (S'/S) \text{ and } \beta'' = \beta \; (S''/S).$$

In Tab. 4 are shown the values of $S$, $S'$, and $S''$ taken from the table of MULLIKEN et al. [6]. The inclusion of $\beta'$ and $\beta''$ in the present calculation is one of the characteristics of a series of our calculations for various substituted benzenes [2, 3].

In the calculation of styrene, $(I_B - A_{C=C} + I_{C=C} - A_B)$ and $\beta$ were taken as parameters to be determined from a comparaison between the experimental and theoretical transition energies, and $(I_B - A_{C=O})$ and $\beta$ were taken as parameters


Fig. 5. The atomic orbitals of the substituted benzene

in the case of benzaldehyde and acetophenone. In order to select a best set of these parameter values the energy levels and wave functions were evaluated by a Facom 202 electronic computer, in considerably wide ranges of the parameter values with intervals of 0.2 eV for $(I_B - A_{C=C} + I_{C=C} - A_B)$ and $(I_B - A_{C=O})$ and for $\beta$ values of $-1.30$, $-1.50$, and $-1.70$ eV. The best values of charge transfer energy

were found to be: $I_B - A_{C=C} + I_{C=C} - AB = 20.92$ eV for styrene and $I_B - A_{C=O} = 10.45$ eV both for benzaldehyde and acetophenone, and the best value of $\beta$ is $-1.50$ eV for all the molecules. Tab. 5 and 6 show the best sets of the calculated transition energies and the corresponding wave functions.

The theoretical oscillator strengths were obtained by the use of $f_{ij} = 1.085 \times 10^{11} \nu_{ij} D_{ij}^2$, where $\nu_{ij}$ and $D_{ij}$ are respectively the frequency (in cm$^{-1}$) and moment (in cm) of the $i \to j$ transition. The observed $f$ values corresponding to the $^1A_{1g} \to {}^1E_{1u}$ and $^1A_{1g} \to {}^1B_{1u}$ transitions of benzene were used instead of the theoretical values for the evalution of $f_{ij}$ values from the wave functions and energy levels given in Tab. 5 and 6.

## 4. Discussion

Since the spectrum of acetophenone is very similar to that of benzaldehyde and the difference in the positions of their absorption peaks is too small to be explained in the present theoretical calculation, the same theoretical treatment was commonly applied to the spectra of these two compounds.

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* An angle of 120° was assumed between the double and single bonds of the side chain. $r$ (C – C)$_{Benz.}$ = 1.40 Å, $r$ (C$_1$ – C$_7$) = 1.47 Å, $r$ (C = O) = 1.24 Å, and $r$ (C = C) = 1.35 Å.

Table 7. *Comparison between the experimental and theoretical results of transition energy, given in eV units, and oscillator strength for styrene, benzaldehyde, acetophenone and benzonitrile*

### Styrene

| Present Work Experimental Theoretical | | | | LONGUET-HIGGINS and MURRELL [5] Theoretical |
|---|---|---|---|---|
| $(E - E_0)$ | $f$ | $(E - E_0)$ | $f$ | $(E - E_0)$ |
| 4.42 | 0.02 | 4.89 | 0.01 | 4.72 |
| 5.21 | 0.24 | 5.26 | 0.29 | 5.77 |
| (6.20) | | 6.25 | 0.20 | 6.15 |
| 6.32 | | 6.36 | 0.27 | 6.61 |
| (6.57) | 2.4 | 6.69 | 0.01 | 6.77 |
| 6.88 | | 6.82 | 0.38 | 7.67 |
| | | 7.57 | 0.48 | 8.33 |
| 7.60 | | 7.63 | 0.91 | 8.49 |
| | | 8.40 | 0.98 | 9.18 |

### Acetophenone

| Present Work | | | |
|---|---|---|---|
| Experimental | | Theoretical | |
| $(E - E_0)$ | $f$ | $(E - E_0)$ | $f$ |
| 4.52 | 0.02 | 4.96 | 0.01 |
| 5.37 | 0.28 | 5.72 | 0.30 |
| 6.33 | | 6.26 | 0.23 |
| 6.50 | | 6.53 | 0.04 |
| 6.92 | 1.7 | 7.06 | 1.12 |
| 7.43 | | 7.37 | 1.01 |
| | | 8.56 | 0.51 |

### Benzonitrile

| Present Work Experimental | PEACOCK and WILKINSON [10] Theoretical (SCF) |
|---|---|
| 4.53 | 5.00 |
| 5.54 | 5.55 |
| 6.61 | 6.68 |
| (6.88) | 6.83 |
| 7.44 | |

### Benzaldehyde

| Present Work | | | | TANAKA [12] | | BLOOR and PERADEJORDI [1] |
|---|---|---|---|---|---|---|
| Experimental | | Theoretical | | Theoretical | | Theoretical (SCF) |
| $(E - E_0)$ | $f$ | $(E - E_0)$ | $f$ | $(E - E_0)$ | $f$ | $(E - E_0)$ |
| 4.52 | 0.02 | 4.96 | 0.01 | 4.65 | 0.005 | 4.69 |
| 5.35 | 0.26 | 5.72 | 0.30 | 5.39 | 0.25 | 5.39 |
| 6.35 | | 6.26 | 0.23 | 6.06 | 0.41 | 6.48 |
| (6.68) | | 6.53 | 0.04 | 6.63 | – | 6.88 |
| 6.97 | 1.7 | 7.06 | 1.12 | 7.49 | – | |
| 7.50 | | 7.37 | 1.01 | 7.57 | – | |
| | | 8.56 | 0.51 | | | |

Values in parentheses show the positions of shoulder.

All the bands of styrene, benzaldehyde and acetophenone observed in the present experiment could successfully be assigned by the present theoretical consideration. Tab. 7 shows a comparison between the experimental and theoretical results of transition energy and oscillator strength for styrene, benzaldehyde and acetophenone. As is seen from the comparison shown in Tab. 7, a considerably

good agreement was obtained between the experimental and theoretical results for both the transition energies and the oscillator strengths, except for the longest wavelength bands. A comparatively large discrepancy between the observed and theoretical values was commonly seen for the longest wavelength bands of many monosubstituted benzenes studied by the present authors.

It is no doubt that the excited levels of longest wavelength ($274 \sim 280$ m$\mu$) bands are predominantly of the $B_{2u}$ character of benzene. The present calculation indicates that the charge-transfer configuration, $\psi_{CT_4}$, contributes to the 238 m$\mu$ band of styrene by 58%, and $\psi_{CT_a}$ contributes both to the 232 m$\mu$ band of benzaldehyde and to the 231 m$\mu$ band of acetophenone by 68%. This means that these bands may be regarded as the intramolecular charge-transfer band.

As seen from Tab. 5 and 6, the charge-transfer configurations contribute to the ground states of the molecules by several per cent and the resulting stabilization energies are 5.60 Kcal/mol for styrene, and 5.05 Kcal/mol for benzaldehyde and acetophenone. These values of stabilization energy are intermediate between those of phenol (4.6 Kcal/mol) [3] and aniline (7.4 Kcal/mol) [2].

Next let us try to evaluate of the electron affinities of the $C = C$ and $C = O$ groups from our best values of $I_B - A_{C=C} + I_{C=C} - A_B$ ($= 20.92$ eV) and $I_B - A_{C=O}$ ($= 10.45$ eV). For styrene, assuming that $I_B$ is equal to the ionization potential of benzene (9.25 eV) [16], $A_B$ to the electron affinity of benzene ($- 1.10$ eV) [3] and $I_{C=C}$ to the ionization potential of propylene* (9.73 eV) [16], we have a value of $-0.84$ eV for $A_{C=C}$ which is the electron affinity of the $C = C$ group. In the case of benzaldehyde and acetophenone, again assuming that $I_B$ and $A_B$ are equal to the above corresponding value, we have a value of $-1.20$ eV for $A_{C=O}$ which is the electron affinity of the $C = O$ group. It is interesting to note that this value completely coincides with that successfully used in the interpretation of electronic spectra of formamide and acrolein by one of the present authors [7].

In Tab. 7 are given the results obtained by other authors [1, 5, 10, 12] in comparison with ours. Our calculated transition energies of styrene are considerably different from those by LONGUET-HIGGINS and MURRELL [5]. This is mainly due to the difference between the energy values of the charge-transfer configurations taken by them and those used by us.

The calculated result of transition energy of benzonitrile by PEACOCK and WILKINSON [4] is in good agreement with the present experimental result except for the longest wavelength band. As is clearly seen from Tab. 7, the absorption bands of benzonitrile (Fig. 4) locate in shorter wavelengths than the corresponding bands of benzaldehyde (Fig. 3). This indicates that the energies of the charge-transfer configurations of the former may be much higher than those of the latter.

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* The ionization potential of propylene instead of ethylene was taken for $I_{C=C}$. This procedure has also been applied in the previous works [2, 3] and good results have been obtained: we used the ionization potential of $CH_3R$ instead of HR molecule for that of the substituted group, R.

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