On the Electronic Structures of Butadiene

By Yuji MORI

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Introduction

The interpretation of the ultraviolet absorption spectra of molecules is approached by two methods in principle. The first is the molecular orbital[1] method, and the second is the valence bond method[2]. The hybridized method between these two, which was developed by London and was used in the calculation of the ultraviolet absorption spectra of diphenyl[3], has been employed in the present study. The outline of this method is as follows*. The molecule under consideration is divided into some parts in such a way that they have simple forms of molecular orbitals. Then the wave function of the entire molecule is approximated by the products of antisymmetrized molecular orbitals of these parts. For instance, styrene is divided into two parts, i. e., the phenyl radical and the vinyl radical. Then the wave functions of the π-electron system of styrene are expressed by the antisymmetrized products of molecular orbitals of the benzene ring and of the vinyl radical.

The important character of this treatment is that the electronic states of the entire molecule are expressed by those of the simple parts included in it. So this method may be thought of as the valence bond method which has the local molecular orbitals taking the place of the atomic orbitals.

In this treatment, polar structure which means charge transfer from one part to another is important for the excited state. Previously the absorption spectra[4] of styrene was studied by this treatment including polar structures, and it was shown that polar structures are important for excited states.

In the present paper, polar and bonding structures between π-electron systems of the two vinyl radicals of butadiene are introduced, and for convenience the semi-empirical treatment investigated by Parizer and Parr[5] is applied in the later section.

Wave Functions and Computations

The "*trans*-form" model is chosen for butadiene in the present calculation, and the bond distances and the bond angle of skeleton are equal to those of the model in the calculation of Parr and Mulliken[6] (Fig. 1).

Fig. 1.

The wave functions of the π-electron system of butadiene are expressed by the π-electron wave functions of two vinyl radicals having the molecular orbitals as

$$\varphi_1=\frac{1}{\sqrt{2\sigma_1}}(\chi_1+\chi_2),\quad \varphi_3=\frac{1}{\sqrt{2\sigma_3}}(\chi_3+\chi_4),$$

$$\varphi_2=\frac{-1}{\sqrt{2\sigma_2}}(\chi_1-\chi_2),\quad \varphi_4=\frac{1}{\sqrt{2\sigma^4}}(\chi_3-\chi_4),$$

where χ_i is the atomic orbital, and σ_i is the normalization factor.

Thus the unperturbed wave functions of butadiene are

$$({}^1A_g),\ \psi_1=\frac{1}{\sqrt{4!}\sqrt{N_1}}\sum_P(-1)^P P\varphi_1(1)\bar{\varphi}_1(2)\varphi_3(3)\bar{\varphi}_3(4),$$

$$({}^1A_g),\ \psi_2=\frac{1}{\sqrt{4!}\sqrt{N_2}}\sum_P(-1)^P P\frac{1}{2}\Big\{\varphi_1(1)\bar{\varphi}_2(2)\varphi_3(3)\bar{\varphi}_3(4)$$
$$-\bar{\varphi}_1(1)\varphi_2(2)\varphi_3(3)\bar{\varphi}_3(4)+\varphi_1(1)\bar{\varphi}_1(2)\varphi_3(3)\bar{\varphi}_4(4)$$
$$-\varphi_1(1)\bar{\varphi}_1(2)\bar{\varphi}_3(3)\varphi_4(4)\Big\},$$

$$({}^1B_u),\ \psi_3=\frac{1}{\sqrt{4!}\sqrt{N_3}}\sum_P(-1)^P P\frac{1}{2}\Big\{\varphi_1(1)\bar{\varphi}_2(2)\varphi_3(3)\bar{\varphi}_3(4)$$
$$-\bar{\varphi}_1(1)\varphi_2(2)\varphi_3(3)\bar{\varphi}_3(4)-\varphi_1(1)\bar{\varphi}_1(2)\varphi_3(3)\bar{\varphi}_4(4)$$
$$+\varphi_1(1)\bar{\varphi}_1(2)\bar{\varphi}_3(3)\varphi_4(4)\Big\},$$

$$({}^1A_g),\ \psi_4=\frac{1}{\sqrt{4!}\sqrt{N_4}}\sum_P(-1)^P P\frac{1}{2}\Big\{\varphi_1(1)\bar{\varphi}_4(2)\varphi_3(3)\bar{\varphi}_3(4)$$
$$-\bar{\varphi}_1(1)\varphi_4(2)\varphi_3(3)\bar{\varphi}_3(4)+\varphi_1(1)\bar{\varphi}_1(2)\varphi_3(3)\bar{\varphi}_2(4)$$
$$-\varphi_1(1)\bar{\varphi}_1(2)\bar{\varphi}_3(3)\varphi_2(4)\Big\},$$

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[1] Concerning the simple MO method, Eyring, "Quantum Chemistry", (1949), p. 192, 254. Concerning the ASMO method, M. Goeppert-Mayer and A. L. Sklar, *J. Chem. Phys.*, 6, 645 (1938); D. P. Craig, *Proc. Roy. Soc.*, A200, 474 (1950). Concerning the LCAOSCF method, C. C. J. Roothaan, *Rev. Mod. Phys.*, 23, 69 (1951).

[2] L. Pauling, *J. Chem. Phys.*, 1, 280 (1933); Eyring "Quantum Chemistry," (1949) p 243.

[3] A. London, *J. Chem. Phys.*, 13, 364 (1945).

* Reference 3).

[4] Unpublished, presented at the Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1951.

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

[6] R. G. Parr and R. S. Mulliken, *J. Chem. Phys.*, 18, 1338 (1950).

$$({}^1B_u),\quad \psi_5=\frac{1}{\sqrt{4!}\sqrt{N_5}}\sum_P(-1)^P P\frac{1}{2}\Big\{\varphi_1(1)\bar{\varphi}_4(2)\varphi_3(3)\bar{\varphi}_3(4)$$
$$-\bar{\varphi}_1(1)\varphi_4(2)\varphi_3(3)\bar{\varphi}_3(4)-\varphi_1(1)\bar{\varphi}_1(2)\varphi_3(3)\bar{\varphi}_2(4)$$
$$+\varphi_1(1)\bar{\varphi}_1(2)\bar{\varphi}_3(3)\varphi_2(4)\Big\},$$

$$({}^1A_g),\quad \psi_6=\frac{1}{\sqrt{4!}\sqrt{N_6}}\sum_P(-1)^P P\frac{1}{2}\Big\{\varphi_1(1)\bar{\varphi}_2(2)\varphi_3(3)\bar{\varphi}_4(4)$$
$$-\bar{\varphi}_1(1)\varphi_2(2)\varphi_3(3)\bar{\varphi}_4(4)-\varphi_1(1)\bar{\varphi}_2(2)\bar{\varphi}_3(3)\varphi_4(4)$$
$$+\bar{\varphi}_1(1)\varphi_2(2)\bar{\varphi}_3(3)\varphi_4(4)\Big\},$$

$$({}^1A_g),\quad \psi_7=\frac{1}{\sqrt{4!}\sqrt{N_7}}\sum_P(-1)^P P\frac{1}{2}\Big\{\varphi_1(1)\bar{\varphi}_2(2)\varphi_3(3)\bar{\varphi}_4(4)$$
$$-\bar{\varphi}_1(1)\bar{\varphi}_2(2)\varphi_3(3)\varphi_4(4)-\varphi_1(1)\varphi_2(2)\bar{\varphi}_3(3)\bar{\varphi}_4(4)$$
$$+\bar{\varphi}_1(1)\varphi_2(2)\bar{\varphi}_3(3)\varphi_4(4)\Big\},$$

where P means the permutation of electrons, and $(-1)^P$ takes $+1$ or -1 according to even or odd permutation respectively, and N_i is the normalization factor. The wave functions ψ_1, ψ_2, ψ_3 are non-polar, and ψ_4, ψ_5 are polar. ψ_6, ψ_7 represent bonding structures.

The perturbed wave function of butadiene Φ_i is

$$\Phi_i=\sum_l a_{ij}\psi_j.$$

The secular determinant is thus

$$\det|H_{ij}-N_{ij}W|=0,$$

where

$$H_{ij}=\int\psi_i H\psi_j d\tau,\quad N_{ij}=\int\psi_i\psi_j d\tau.$$

The matrix elements are expanded into the integrals over the molecular orbitals φ_i of vinyl radicals. Further these integrals are expanded with the integrals over atomic orbitals χ_i which have already been given by Parr and Mulliken⁶⁾. The numerical values of integrals necessary for the present calculation are listed in Tables I and II.

TABLE I

$s_{12}=0.27854$
$s_{13}=0.03371$
$s_{14}=0.00218$
$s_{23}=0.23281$

$(1:12)=2.27950$ e.v.
$(2:23)=1.63069$
$(1:22)=0.98620$
$(2:33)=0.67476$
$(1:13)=0.30278$
$(1:23)=0.03460$
$(2:34)=0.03027$
$(2:14)=0.01730$
$(1:33)=0.00865$
$(1:14)=0.00000$
$(1:24)=0.00000$
$(1:34)=0.00000$
$(1:44)=0.00000$

$(11:11)=16.92975$
$(11:22)=9.23913$
$(22:33)=8.69412$
$(11:33)=5.52358$
$(11:44)=3.82801$

$(11:12)=3.60741$
$(22:23)=2.93264$
$(22:34)=1.93346$
$(11:23)=1.66096$
$(11:34)=1.25870$
$(11:13)=0.29845$
$(11:24)=0.18599$
$(22:13)=0.46282$
$(11:14)=0.01730$
$(22:14)=0.03027$
$(12:12)=1.09000$
$(23:23)=0.73099$
$(12:23)=0.63583$
$(12:34)=0.46282$
$(12:13)=0.12543$
$(12:24)=0.06920$
$(13:23)=0.10813$
$(12:14)=0.00432$
$(14:23)=0.00865$
$(13:13)=0.01730$
$(13:24)=0.00865$
$(13:14)=0.00000$
$(14:14)=0.00000$

TABLE II

$\sigma_1=1.27854$	$E_1=2W_{2p}-12.11931$
$\sigma_2=0.72146$	$E_2=2W_{2p}-1.44338$
$S_{13}=0.11826$	
$S_{14}=0.12007$	$[11:13]=1.15565$
$S_{24}=0.11613$	$[11:14]=1.26194$
$\varepsilon_1=W_{2p}-12.60205$ e.v.	$[11:23]=1.10343$
$\varepsilon_2=W_{2p}-6.01337$	$[11:24]=1.16176$
$\lambda_1=-12.00831$	$[11:34]=1.26546$
$\lambda_2=-12.34752$	$[22:13]=1.14301$
$\lambda_{12}=-2.88461$	$[22:14]=1.24381$
$\omega_{13}=-5.50703$	$[22:23]=1.12520$
$\omega_{14}=-5.43695$	$[22:24]=1.20289$
$\omega_{24}=-5.09605$	$[22:34]=1.26878$
$K_{11}=13.08479$	$[12:13]=0.31791$
$K_{12}=13.00330$	$[12:14]=0.35521$
$K_{22}=13.37096$	$[12:23]=0.32708$
$K_{13}=5.84053$	$[12:24]=0.36362$
$K_{14}=5.88618$	$[12:34]=0.39976$
$K_{24}=6.07678$	$[13:14]=0.19285$
$J_{12}=4.16874$	$[13:24]=0.18874$
$J_{13}=0.18853$	$[14:23]=0.18874$
$J_{14}=0.19812$	$[14:24]=0.18571$
$J_{24}=0.17659$	
$H_{11}=-93.69588$	$N_1=0.97210$
$H_{22}=-82.05927$	$N_2=0.95815$
$H_{33}=-84.14202$	$N_3=0.98605$
$H_{44}=-85.31311$	$N_4=1.01395$
$H_{55}=-84.44434$	$N_5=0.98605$
$H_{66}=-72.54143$	$N_6=0.97210$
$H_{77}=-85.96205$	$N_7=1.01395$
$H_{12}=+2.24563$	$N_{12}=-0.02890$
$H_{14}=-24.01682$	$N_{14}=+0.24188$
$H_{16}=+2.24209$	$N_{16}=-0.01435$
$H_{17}=+3.48230$	$N_{17}=-0.02810$
$H_{24}=+0.00508$	$N_{24}=-0.00216$
$H_{26}=+2.00350$	$N_{26}=-0.02890$
$H_{27}=+1.04476$	$N_{27}=-0.01415$
$H_{46}=+10.77883$	$N_{46}=-0.12094$
$H_{47}=+22.75446$	$N_{47}=-0.23684$
$H_{67}=-35.53348$	$N_{67}=+0.48956$
$H_{35}=-22.08459$	$N_{35}=+0.23770$

In these tables E_1 and E_2 are the energy levels of the vinyl radical whose wave functions are

$$E_1;\ \sum_P(-1)^P P\varphi_1(1)\bar{\varphi}_1(2),$$

$$E_2;\ \sum_P(-1)^P P\frac{1}{\sqrt{2}}\Big\{\varphi_1(1)\bar{\varphi}_2(2)-\bar{\varphi}_1(1)\varphi_2(2)\Big\},$$

The integral I_i is the core energy of the molecular orbital of vinyl radical and λ_i is the energy of perturbation from another vinyl radical core. Then the next relation is

$$\int\varphi_i(\nu)H_{\mathrm{core}}(\nu)\varphi_i(\nu)d\tau_\nu=I_i+\lambda_i.$$

The other integrals in these tables are

$$\lambda_{12}=\int\varphi_1(\nu)H_{\mathrm{core}}(\nu)\varphi_2(\nu)d\tau_\nu,$$
$$\omega_{ij}=\int\varphi_i(\nu)H_{\mathrm{core}}(\nu)\varphi_j(\nu)d\tau_\nu(i=1\text{ or }2,\ j=3\text{ or }4),$$
$$S_{ij}=\int\varphi_i(\nu)\varphi_j(\nu)d\tau_\nu,$$

$$K_{ij}=\iint|\varphi_i(\nu)|^2\frac{e^2}{r_{\nu\mu}}|\varphi_j(\mu)|^2d\tau_\nu d\tau_\mu\,,$$

$$J_{ij}=\iint\varphi_i(\nu)\varphi_j(\nu)\frac{e^2}{r_{\nu\mu}}\varphi_j(\mu)\varphi_i(\mu)d\tau_\nu d\tau_\mu\,,$$

$$[jk:lm]=\iint\varphi_j(\nu)\varphi_k(\nu)\frac{e^2}{r_{\nu\mu}}\varphi_l(\mu)\varphi_m(\mu)d\tau_\nu d\tau_\mu\,,$$

$$(r:st)=\int\chi_s(\nu)\boldsymbol{H}_r(\nu)\chi_t(\nu)d\tau_\nu,\quad s_{rs}=\int\chi_r(\nu)\chi_s(\nu)d\tau_\nu\,,$$

$$(rs:tu)=\iint\chi_r(\nu)\chi_s(\nu)\frac{e^2}{r_{\nu\mu}}\chi_t(\mu)\chi_u(\mu)d\tau_\nu d\tau_\mu\,,$$

where

$$H_{\text{core}}(\nu)=\sum_{r=1}^{4}H_r(\nu)\,,$$

$$H_r(\nu)=\boldsymbol{H}_r(\nu)-\int\left(\frac{e^2}{r_{\nu\mu}}\right)|\chi_r(\mu)|^2d\tau_\mu\,,$$

and $\boldsymbol{H}_r(\nu)$ is the potential due to the neutral carbon atom.

The energy levels of butadiene obtained by the present calculation are shown in Fig. 2 (left column), and those of ASMO SCF CI calculation using the SCF wave functions by Parr and Mulliken[6], and including the same configurations as in Coulson's calculation[7] are also shown in Fig. 2 (second column).

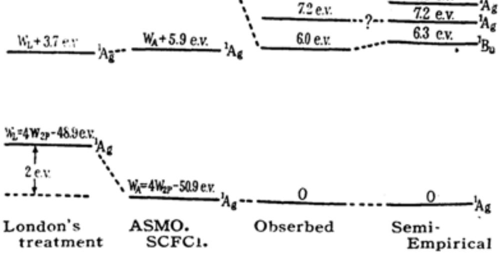

Fig. 2.

The wave functions of the ground state and the lowest ^1B_u state are

$({}^1A_g)$(ground state);

$$\psi_1=0.9326\phi_1+0.0381\phi_2+0.1500\phi_4+0.0491\phi_6-0.1688\phi_7,$$

$({}^1B_u)$; $\psi_3=0.6062\phi_3+0.6641\phi_5,$

Discussion

The absorption spectra of butadiene[8] show the strong absorption bands about 2000 Å and 1700 Å. No absorption band has been observed in the wave length region longer than 2000 Å.

The selection rule shows that the ^1A_g—^1B_u transition is allowed and the ^1A_g—^1A_g transition is forbidden. Then, the strong bands of 2000 Å and 1700 Å may correspond to the ^1A_g—^1B_u transitions*.

By this calculation the lowest ^1B_u state exceeds 8.1 e.v. over the ground state and the lowest ^1A_g—^1A_g transition is about 3.7 e.v. The ASMO SCF CI calculation predicts that the lowest ^1A_g—^1B_u excitation energy is about 9.6 e.v. and the lowest ^1A_g—^1A_g excitation energy is about 5.6 e.v. These two calculations agree qualitatively in the next point. The lowest excited ^1A_g state is lower than the lowest ^1B_u state. If this is true there may be a weak absorption band in the wave length longer than 2000 Å, while this weak band has not been observed. The cause of discrepancy may be interpreted as follows. In general the detailed ASMO calculation gives the high excitation energy for the excited singlet state and low excitation energy for the triplet state. This is mainly due to the overestimation of one center repulsion energy as Moffitt[9] mentioned it. This energy integral is important to determine the energies of polar structures. The ASMO wave functions of excited singlet states include more polar structures than that of ground state in most cases, and the contributions of polar structures for the triplet states are less than for the singlet ground state. In the case of ethylene the triplet state includes no polar structure, and the singlet excited $^1B_{1u}$ state is given by the linear combination of the polar structures only in usual estimation. Thus the overestimation of one centre repulsion energy results in the high excitation energy for singlet—singlet transition and results in the low energy for the triplet state. In the case of the lowest excited ^1A_g state of butadiene, however, the contributions of polar structures are slight, as the important configuration of this state is ψ_l, which is the product of the two triplet states of vinyl radicals. So the excitation energy for this ^1A_g state may be low in the non-empirical calculation. Therefore the excitation energy (5.9 e. v.) by ASMO SCF CI calculation may coincide with the experimental value better than that (3.7 e. v.) by this hybridized treatment, because the contributions of polar structures to the ground state are greater in this hybridized calculation than in ASMO SCF CI calculation owing to the neglect of the high energy structures as.

$$\sqrt{\frac{1}{4\,!}}\sum_{P}(-1)^PP\frac{1}{\sqrt{2}}\{\varphi_2(1)\bar{\varphi}_2(1)\varphi_3(3)\varphi_3(4)+\varphi_1(1)\bar{\varphi}_1(1)\varphi_4(3)\bar{\varphi}_4(3)\},\cdots\cdots\cdots.$$

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7) C. A. Coulson and J. Jacobs, *Proc. Roy. Soc.*, A206, 287 (1951).

8) E. P. Carr, L. W. Pickett and H. Stücklen, *Rev. Mod. Phys.*, 14, 260 (1942).

* For *cis*-butadiene, the $^1A_1$—$^1A_1$ transition (A_g—A_g transition in *trans*-butadiene) is allowed but the intensity of the lowest $^1A_1$—$^1A_1$ transition may not be so strong.

9) W. Moffitt, *Proc. Roy. Soc.*, A210, 224, 245 (1951).

Then the weak forbidden band may not be observed, owing to the superposition with the strong allowed transition band.

The electron affinity of carbon atom is negative when the $2p$ and $2s$ orbitals with the usual screening constant for the neutral carbon atom are also used in the calculation of the energy of the negative carbon ion. Further, the electron affinity of vinyl radical which is calculated by the ASMO method is negative. This is an example of the error by the overestimation of the one center repulsion energy. In the negative carbon ion the electron cloud becomes larger on account of the increased electrostatic repulsion. So the consideration for the expansion of the electron cloud will be needed in the calculation of the energy of the negative carbon ion. Then in the valence bond method the variation of the screening constant of the negative carbon ion in polar structures will be the one approach to the energy levels of molecules avoiding this error. More directly the use of semi-empirical value of the one center repulsion integral which is determined by the consideration of the energy of the negative carbon ion was proposed by Moffitt[9)] and by Parizer and Parr[5)].

In the molecular orbital method the perfect non-empirical treatment may be given by the inclusion of the higher excited Rydberg orbitals and the effect of the σ-electrons. But this treatment will be too complicated to be useful or calculating the energy levels of the complex molecule. For London's treatment in this paper the use of semi-empirical values from the energy levels of the vinyl radical (or ethylene molecule) is interesting.

The energy of the ground state by this calculation exceeds 2 e. v. over the result of ASMO SCF CI calculation. This discrepancy is due to the neglect of the higher energy configurations, for instance the inclusion of the structure mentioned before,

$$\frac{1}{\sqrt{4\,!}}\cdot\sum_{P}(-1)^{P}P\frac{1}{\sqrt{2}}\{\varphi_2(1)\bar{\varphi}_2(2)\varphi_3(3)\bar{\varphi}_3(4)$$

$$+\varphi_1(1)\bar{\varphi}_1(1)\varphi_4(3)\bar{\varphi}_4(4)\},$$

depresses the ground state by about 2 e. v.. If the energy depression of the ground state by the interaction with the neglected high energy structures is assumed to be 2 e. v. and the depressions of the other states are assumed to be zero, the energy levels by this treatment of London's will be close to those by the ASMO SCF CI calculation. But in order to obtain the same result as that by the ASMO SCF CI calculation one needs more complicated computations by this treatment for the large molecule.

The energy depression of the ground state by the interaction between the two vinyl radicals is about 0.3 e.v. and is mainly contributed by polar structure and by bonding structures. By this result one can expect the small resonance energy of butadiene.

From the wave function of the lowest ${}_1B_u$ state, it can be seen that the weight of polar structure is great, and that in London's treatment polar structures can not be ignored.

Semi-Empirical Calculation

Parizer and Parr[5)] presented the semi-empirical method and obtained good results for the lower excited states of conjugated molecules by a simple procedure. They omitted many integrals except the Coulomb repulsion and resonance integrals, and simplified the procedure of calculation. Using their method the energy levels of butadiene are calculated in order to compare them with the results of the last section. The procedure of calculation is the same as that in the second section. The penetration integrals (11 : 3), (11 : 4) and (22 : 3)are assumed to be −(11 : 33), −(11 :44) and −(22 :33) respectively. The values of the integrals used in this calculation are shown in Table III, and the other integrals are omitted. Then the matrix elements are easily computed. The result is shown in Fig. 2 (right column).

TABLE III

$(11:\ 11)=10.53$	$H_{11}=W_1$
$(11:\ 22)=7.38$	$H_{22}=W_1+7.46$
$(11:\ 33)=5.35$	$H_{33}=W_1+7.36$
$(11:\ 44)=3.75$	$H_{44}=W_1+7.82$
$(22:\ 33)=7.16$	$H_{55}=W_1+7.82$
	$H_{66}=W_1+14.82$
$\beta_{12}=-2.92$	$H_{77}=W_1+10.11$
$\beta_{23}=-1.68$	$H_{12}=-0.68$
	$H_{14}=-1.68$
$\varepsilon_1=W_{2p}+\alpha-2.92$	$H_{16}=+0.10$
$\varepsilon_2=W_{2p}+\alpha+2.92$	$H_{17}=+0.05$
	$H_{24}=0$
$\lambda_{12}=-2.04$	$H_{26}=-0.68$
$\lambda_i=\alpha'$	$H_{27}=-0.34$
	$H_{46}=+0.84$
$K_{11}=K_{12}=8.95$	$H_{47}=+1.68$
$K_{13}=K_{14}=K_{24}=5.40$	$H_{67}=\frac{1}{2}W_1+7.41$
$J_{12}=1.57$	$H_{35}=-1.68$
$[11:\ 34]=0.85$	
$[12:\ 34]=0.05$	
	$N_i=1$
$\omega_{ij}=-0.84$	$N_{ij}=0$ (except N_{67})
$E_1=2W_{2p}+2\alpha+3.11$ $E_2=E_1+7.41$	$N_{67}=\frac{1}{2}$

The calculation by this treatment predicts the absorption bands at 1950 Å, 1700 Å and 1500 Å. The 1950 Å band is an allowed transition $^1A_g—^1B_u$ and corresponds to the 2000 Å strong absorption band observed experimentally. The 1700 Å and 1500 Å bands by this calculation are forbidden transitions and may have weak intensities. The important result of this calculation is that the lowest $^1A_g—^1A_g$ transition is higher than the lowest $^1A_g—^1B_u$ transition. Then this result supports the possibility that the lowest $^1A_g—^1A_g$ transition band might overlap with the strong absorption band and be impossible to observe.

The energy depression of the ground state by the interaction between the vinyl radicals is about 0.4 e. v., and is mainly contributed by the polar structures.

Conclusion

The energy levels of butadiene were calculated by London's treatment and by the semi-empirical treatment including polar structurs, and compared to the results by the ASMO SCF CI calculation and to the experimental data. According to this comparison, the non-empirical treatment which is described in this paper shows the same results as those by the ASMO SCF CI method. But for the experimental results, the non-empirical treatment does not show agreement. Most of the error in the excitation energy of the non-empirical treatment is due to the overestimation of the one centre repulsion energy, and this will be clear by the comparison to the result of the semi-empirical treatment. The result of the semi-empirical treatment is fairly good approximation to the experimental data. The effect of polar structures for the excited states is important and can not be ignored.

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Laboratory of Physical Chemistry,
Tokyo Institute of Technology,
Tokyo