Molecular Orbital Treatment of the Ultraviolet Spectra of Cycloöctatetraene(1)

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1. Introduction

The energy levels of cycloöctatetraene have been calculated in our laboratory by the HLSP method(2) assuming two different structures D_{2d}(3) and D_{4d},(4) and this calculation has been

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(1) Presented at the Annual Meeting of the Chemical Society of Japan, Kyoto, April 2, 1950.

(2) I. Tanaka and S. Shida, *Bull. Chem. Soc. Japan*, **23**, 54 (1950).

(3) H. S. Kaufman, I. Fanckuchen and H. Mark, *J. Chem. Phys.*, **15**, 414–15 (1947); H. S. Kaufman, I. Fanckuchen and H. Mark, *Nature*, **161**, 165 (1948); K. Hedberg and V. Schomaker, *Annual Meeting of Amer. Chem. Soc.*, (1949).

(4) O. Bastiaisen, O. Hassel and A. Langseth, *Nature*, **160**, 128 (1947); O. Bastiaisen and O. Hassel, *Acta chemica scandinavica*, **3**, 209(1949); E. P. Lippincott, R. C. Lord and R. S. MacDonald, *J. Chem. Phys.*, **16**, 548 (1948).

compared with the experimental results on cycloöctatetraene, namely absorption spectra, magnetic susceptibility and thermochemical data.

The purpose of the present paper is to calculate the energy levels of the molecule from the standpoint of the Goeppert Mayer and Sklar's method,(5) assuming the symmetry of cycloöctatetraene as D_{2d}, and to show how this calculation is in agreement with the experimental results.

2. The Orbitals

Table 1

	E	C_2	$2iC_4=S_4$	$2C'_2$	$2\sigma d$
A_1	1	1	1	1	1
A_2	1	1	1	−1	−1
B_1	1	1	−1	1	−1
B_2	1	1	−1	−1	1
E	2	−2	0	0	0
Γ	8	0	0	0	0

Fig. 1.

First, the wave functions of the π-electrons for cycloöctatetraene assuming the symmetry of D_{2d}(3) are determined by the LCAO approximation. The symmetry of the eight levels of cycloöctatetraene can be found from the group theory. The character of the symmetry group D_{2d} is shown in Table 1. The reducible representation Γ is

$$\Gamma = A_1 + A_2 + B_1 + B_2 + 2E.$$

The energy levels and their wave functions are obtained using the variation method. Since there are two kinds of distances between two neighboring carbon atoms, the two different resonance integrals (and similarly the two overlap integrals) must be distinguished from each other.

$$\left.\begin{aligned}\int\tilde{\psi}_2\mathbf{V}_2\psi_1 d\tau=\beta_d,\quad \int\tilde{\psi}_2\psi_1 d\tau=d_d,\\ \int\tilde{\psi}_3\mathbf{V}_3\psi_2 d\tau=\beta_s,\quad \int\tilde{\psi}_3\psi_2 d\tau=d_s,\end{aligned}\right\}\qquad(1)$$

where ψ_f: the $2p\pi$ wave function for the f-th carbon atom,

$\mathbf{V}_f$: the potential from the f-th carbon atom,

and

$$\int\tilde{\psi}_f\left(\sum_{i=1}^{8}V_i - V_f\right)\psi_f d\tau = \alpha. \qquad (2)$$

Putting

$$x=(E_{2p}-E+\alpha)\Big/\{(E_{2p}-E)d_d+\beta_d\}, \qquad (3)$$

$$k=(E_{2p}-E)d_s+\beta_s\Big/\{(E_{2p}-E)d_d+\beta_d\}, \qquad (4)$$

where, E_{2p} is the energy of a 2p electron in a carbon atom in the valence state. Then solving the secular determinant for x we obtain

$$x=\pm(1+k),\quad \pm\sqrt{1+k^2},\quad \pm(1-k). \qquad (5)$$

Thus the wave functions are

$$\left.\begin{aligned}
\varphi_1&=\frac{1}{\sqrt{8\sigma_1}}(\psi_1+\psi_2+\psi_3+\psi_4+\psi_5\\
&\qquad+\psi_6+\psi_7+\psi_8),\\
\varphi_{+2}&=\frac{1}{\sqrt{8\sigma_2}}(\psi_1+\psi_2e^{i\theta_1}+\psi_3e^{i(\theta_1+\theta_2)}\\
&\qquad+\psi_4e^{i(2\theta_1+\theta_2)}+\psi_5e^{i2(\theta_1+\theta_2)}\\
&\qquad+\psi_6e^{i(3\theta_1+2\theta_2)}+\psi_7e^{i3(\theta_1+\theta_2)}\\
&\qquad+\psi_8e^{i(4\theta_1+3\theta_2)}),\\
\varphi_{-2}&=\tilde{\varphi}_{+2},\\
\varphi_3&=\frac{1}{\sqrt{8\sigma_3}}(\psi_1+\psi_2-\psi_3-\psi_4+\psi_5\\
&\qquad+\psi_6-\psi_7-\psi_8),\\
\varphi_4&=\frac{1}{\sqrt{8\sigma_4}}(\psi_1-\psi_2-\psi_3+\psi_4+\psi_5\\
&\qquad-\psi_6-\psi_7+\psi_8),\\
\varphi_{+5}&=\frac{1}{\sqrt{8\sigma_5}}(\psi_1+\psi_2e^{i\theta_3}+\psi_3e^{i(\theta_3+\theta_4)}\\
&\qquad+\psi_4e^{i(2\theta_3+\theta_4)}+\psi_5e^{i2\,\theta_3+\theta_4)}\\
&\qquad+\psi_6e^{i(3\theta_3+2\theta_4)}+\psi_7e^{i3(\theta_3+\theta_4}\\
&\qquad+\psi_8e^{i(4\theta_3+3\theta_4)}),\\
\varphi_{-5}&=\tilde{\varphi}_{+5},\\
\varphi_6&=\frac{1}{\sqrt{8\sigma_6}}(\psi_1-\psi_2+\psi_3-\psi_4+\psi_5\\
&\qquad-\psi_6+\psi_7-\psi_8),
\end{aligned}\right\}\qquad(6)$$

where σ_i is a normalizing factor, and

$$\left.\begin{aligned}
e^{i\theta_1}=\frac{1+ik}{\sqrt{1+k^2}},\ e^{i\theta_3}=\frac{-1+ik}{\sqrt{1+k^2}},\ \theta_1+\theta_2=\frac{\pi}{2},\\
e^{i\theta_2}=\frac{k+i}{\sqrt{1+k^2}},\ e^{\theta_4}=\frac{-k+i}{\sqrt{1+k^2}},\ \theta_3+\theta_4=\frac{3\pi}{2}.
\end{aligned}\right\}\qquad(7)$$

These wave functions are

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(5) G. Mayer and A. L. Sklar, *J. Chem. Phys.*, **6**, 645 (1938).

$$\varphi_1 \subset \mathrm{A}_1, \quad \varphi_{\pm 2} \subset \mathrm{E}, \quad \varphi_3 \subset \mathrm{B}_2,$$
$$\varphi_4 \subset \mathrm{B}_1, \quad \varphi_{\pm 5} \subset \mathrm{E}, \quad \varphi_6 \subset \mathrm{A}_2.$$

When $k = 1$, the wave functions become

$$\varphi_l = \frac{1}{\sqrt{8\sigma_l}} \sum_{f=1}^{8} \psi_f \exp[2\pi i f l/8], \quad l = 0,\ \pm 1,\ \pm 2,\ \pm 3,\ 4, \tag{8}$$

which are the same as those of Hückel.(6) These wave functions appear when the symmetry of cycloöctatetraene is assumed as D_{4d} or D_{8h}.

The antisymmetrized molecular orbitals of 8-electron system for the ground state and the lower excited states are

$$\Phi_l = \frac{1}{\sqrt{8!}} \sum_P (-1)^P P \Psi_l \chi_k, \tag{9}$$

where for the ground state

$$\Psi_0 = \varphi_1(1)\varphi_1(2)\varphi_2(3)\varphi_2(4) \times \varphi_{-2}(5)\varphi_{-2}(6)\varphi_3(7)\varphi_3(8), \tag{10}$$

for the excited states

$$\Psi_1 = \varphi_1(1)\varphi_1(2)\varphi_2(3)\varphi_2(4) \times \varphi_{-2}(5)\varphi_{-2}(6)\varphi_3(7)\varphi_4(8), \tag{11}$$

$$\Psi_2 = \varphi_1(1)\varphi_1(2)\varphi_2(3)\varphi_2(4) \times \varphi_{-2}(5)\varphi_{-2}(6)\varphi_4(7)\varphi_4(8), \tag{12}$$

$$\left.\begin{aligned} \Psi_3 &= \varphi_1(1)\varphi_1(2)\varphi_2(3)\varphi_2(4) \\ &\quad \times \varphi_{-2}(5)\varphi_{-2}(6)\varphi_3(7)\varphi_{+5}(8), \\ \text{or} \quad &= \varphi_1(1)\varphi_1(2)\varphi_2(3)\varphi_2(4) \\ &\quad \times \varphi_{-2}(5)\varphi_{-2}(6)\varphi_3(7)\varphi_{-5}(8), \end{aligned}\right\} \tag{13}$$

$$\left.\begin{aligned} \Psi_4 &= \varphi_1(1)\varphi_1(2)\varphi_2(3)\varphi_2(4) \\ &\quad \times \varphi_3(5)\varphi_3(6)\varphi_{-2}(7)\varphi_4(8), \\ \text{or} \quad &= \varphi_1(1)\varphi_1(2)\varphi_{-2}(3)\varphi_{-2}(4) \\ &\quad \times \varphi_3(5)\varphi_3(6)\varphi_2(7)\varphi_4(8), \end{aligned}\right\} \tag{14}$$

and from the group theory

$$\Psi_0 \subset \mathrm{A}_1,\ \Psi_1 \subset \mathrm{A}_2,\ \Psi_2 \subset \mathrm{A}_1,\ \Psi_3 \subset \mathrm{E},\ \Psi_4 \subset \mathrm{E}.$$

χ_k, spin function, is for the singlet states

$$\left.\begin{aligned} \chi_s &= \alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5) \\ &\quad \times \beta(6)\alpha(7)\beta(8), \\ \text{or} \quad &= \alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5)\beta(6) \\ &\quad \times \frac{1}{\sqrt{2}}\left\{\alpha(7)\beta(8) - \beta(7)\alpha(8)\right\}, \end{aligned}\right\} \tag{15}$$

and for the triplet states.

$$\left.\begin{aligned} \chi_t &= \alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5) \\ &\quad \times \beta(6)\alpha(7)\alpha(8), \\ \text{or} \quad &= \alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5) \\ &\quad \times \beta(6)\beta(7)\beta(8), \\ \text{or} \quad &= \alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5)\beta(6) \\ &\quad \times \frac{1}{\sqrt{2}}\left\{\alpha(7)\beta(8) + \beta(7)\alpha(8)\right\}. \end{aligned}\right\} \tag{16}$$

Thus the energy values for these states will be calculated in Section 3 including electronic interaction.

3. Calculations

The average values of Hamiltonian are given by

$$\mathbf{E}_l = \int \tilde{\Phi}_l \mathrm{H} \Phi_l \, dV. \tag{17}$$

The Hamiltonian H is

$$\mathrm{H} = \sum_{\nu=1}^{8}\left(-\frac{h^2}{8\pi^2 m}\triangle_\nu + \sum_{f=1}^{8} \mathbf{V}_{f\nu}\right) + \sum_{\substack{\nu=1 \\ \nu<\mu}}^{8} \frac{e^2}{r_{\nu\mu}}, \tag{18}$$

where ν and μ show the number of a π-electron, f denotes the number of a carbon atom, and $\mathbf{V}_{f\nu}$ is the potential of a neutral carbon atom(5) minus the potential of a 2pπ electron.

The energies, including electronic interaction, are for the ground state

$$\begin{aligned} (^1\mathrm{A}_1) \quad {}^1\mathbf{E}_0 &= 2\varepsilon_1 + 4\varepsilon_2 + 2\varepsilon_3 + \gamma_{11} + 8\gamma_{12} \\ &\quad + 4\gamma_{13} + 6\gamma_{22} + 8\gamma_{23} + \gamma_{33} \\ &\quad - 4\delta_{12} - 2\delta_{-22} - 2\delta_{13} - 4\delta_{23}, \end{aligned} \tag{19}$$

for the excited singlet states

$$\left.\begin{aligned} (^1\mathrm{A}_2) \quad {}^1\mathbf{E}_1 &= 2\varepsilon_1 + 4\varepsilon_2 + \varepsilon_3 + \varepsilon_4 + \gamma_{11} + 8\gamma_{12} \\ &\quad + 2\gamma_{13} + 2\gamma_{14} + 6\gamma_{22} + 4\gamma_{23} \\ &\quad + 4\gamma_{24} + \gamma_{34} - 4\delta_{12} - 2\delta_{-22} \\ &\quad - \delta_{13} - \delta_{14} - 2\delta_{23} - 2\delta_{24} + \delta_{34}, \\ (^1\mathrm{A}_1) \quad {}^1\mathbf{E}_2 &= 2\varepsilon_1 + 4\varepsilon_2 + 2\varepsilon_4 + \gamma_{11} + 8\gamma_{12} \\ &\quad + 4\gamma_{14} + 6\gamma_{22} + 8\gamma_{24} + \gamma_{44} \\ &\quad - 4\delta_{12} - 2\delta_{-22} - 2\delta_{14} - 4\delta_{24}, \\ (^1\mathrm{E}) \quad {}^1\mathbf{E}_3 &= 2\varepsilon_1 + 4\varepsilon_2 + \varepsilon_3 + \varepsilon_5 + \gamma_{11} + 8\gamma_{12} \\ &\quad + 2\gamma_{13} + 2\gamma_{15} + 6\gamma_{22} + 4\gamma_{23} \\ &\quad + 4\gamma_{25} + \gamma_{35} - 4\delta_{12} - \delta_{13} - \delta_{15} \\ &\quad - 2\delta_{-22} - 2\delta_{23} - \delta_{-25} - \delta_{25} + \delta_{35}, \\ (^1\mathrm{E}) \quad {}^1\mathbf{E}_4 &= 2\varepsilon_1 + 3\varepsilon_2 + 2\varepsilon_3 + \varepsilon_4 + \gamma_{11} + 6\gamma_{12} \\ &\quad + 4\gamma_{13} + 2\gamma_{14} + 3\gamma_{22} + 6\gamma_{23} \\ &\quad + 3\gamma_{24} + \gamma_{33} + 2\gamma_{34} - 3\delta_{12} - 2\delta_{13} \\ &\quad - \delta_{14} - \delta_{-22} - 3\delta_{23} - \delta_{34}, \end{aligned}\right\} \tag{20}$$

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(6) E. Hückel, *Zeits. Physik*, **70**, 204 (1931).

and for the triplet states

$$\begin{aligned} {}^3\mathbf{E}_1 &= {}^1\mathbf{E}_1 - 2\delta_{34}, \quad {}^3\mathbf{E}_3 = {}^1\mathbf{E}_3 - 2\delta_{35}, \\ {}^3\mathbf{E}_4 &= {}^1\mathbf{E}_4 - 2\delta_{24}. \end{aligned} \tag{21}$$

The integrals, ε_i, γ_{ij} and δ_{ij} in these expressions are

$$\begin{aligned} \varepsilon_i = \int \tilde{\varphi}_i(\nu)\Big(&-\frac{h^2}{8\pi^2 m}\triangle_\nu \\ &+\sum_{f=1}^{8}\mathbf{V}_{f\nu}\Big)\varphi_i(\nu)\,\mathrm{d}\tau_\nu, \end{aligned} \tag{22}$$

$$\gamma_{ij} = \iint \frac{\mathrm{e}^2}{r_{\nu\mu}} |\varphi_i(\nu)|^2 |\varphi_j(\mu)|^2 \mathrm{d}\tau_\nu \mathrm{d}\tau_\mu, \tag{23}$$

$$\delta_{ij} = \iint \frac{\mathrm{e}^2}{r_{\nu\mu}} [\overline{\varphi_i(\nu)\varphi_j(\mu)}]\ \varphi_j(\nu)\varphi_i(\mu)\mathrm{d}\tau_\nu \mathrm{d}\tau_\mu. \tag{24}$$

Then, ε_i, γ_{ij} and δ_{ij} are expanded in terms of A_i, B_i, $\mathrm{B'}_i$, R_i, C_i, Q, d_i, for instance,⁽⁷⁾

$$\left.\begin{aligned} \varepsilon_2 = \mathrm{E}_{2p} + \frac{1}{\sigma_2}\Big[&-\mathbf{A}' - \mathrm{Q} - \frac{1}{\mathrm{S}}\mathrm{R}_1 - \frac{k}{S}\mathrm{R}_7 \\ &-\frac{1}{\mathrm{S}}\Big\{\mathrm{B}_1 + 2(\mathrm{B}_3+\mathrm{B}_5+\mathrm{B}_7)\Big\} \\ &-\frac{k}{S}\Big\{\mathrm{B}_8 + 2(\mathrm{B}_2+\mathrm{B}_4+\mathrm{B}_6)\Big\}\Big], \\ \gamma_{33} = \frac{1}{8\sigma_3^2}\Big\{&\mathbf{A} + 4(\mathrm{B}_1+\mathrm{B}_3+\mathrm{B}_5+\mathrm{B}_7) \\ &-4(\mathrm{B}_2+\mathrm{B}_4+\mathrm{B}_6+\mathrm{B}_8) - 8\mathrm{B}_2' \\ &+4\mathrm{B}_3' + 2\mathrm{B}_5' + 2\mathrm{C}_1 + 2\mathrm{C}_7\Big\}, \\ \delta_{34} = \frac{1}{8\sigma_3\sigma_4}\Big\{&\mathrm{A}_0 - \mathrm{A}_1 - \mathrm{A}_7 + 2\mathrm{A}_2 \\ &-\mathrm{A}_3 - \mathrm{A}_5 + \mathrm{A}_4\Big\}, \\ \sigma_2 &= 1 + \frac{1}{\mathrm{S}}\mathrm{d}_1 + \frac{k}{S}\mathrm{d}_7, \\ \sigma_3 &= 1 + \mathrm{d}_1 - \mathrm{d}_7 - 2\mathrm{d}_2, \end{aligned}\right\} \quad (25)$$

where

$$\left.\begin{aligned} \mathrm{A}_i &= \iint \frac{\mathrm{e}^2}{r_{\nu\mu}} \psi_1(\nu)^2 \psi_{i+1}(\mu)^2 \mathrm{d}\tau_\nu \mathrm{d}\tau_\mu, \\ &\sum_{i=0}^{7}\mathrm{A}_i = \mathbf{A}, \quad \sum_{i=1}^{7}\mathrm{A}_i = \mathbf{A}', \\ \mathrm{B}_i &= \iint \frac{\mathrm{e}^2}{r_{\nu\mu}} \psi_1(\nu)^2 \\ &\qquad \times \psi_i(\mu)\psi_{i+1}(\mu)\mathrm{d}\tau_\nu \mathrm{d}\tau_\mu, \\ \mathrm{B}_i' &= \iint \frac{\mathrm{e}^2}{r_{\nu\mu}} \psi_1(\nu)\psi_2(\nu)\psi_i(\mu) \\ &\qquad \times \psi_{i+1}(\mu)\mathrm{d}\tau_\nu \mathrm{d}\tau_\mu, \\ \mathrm{C}_i &= \iint \frac{\mathrm{e}^2}{r_{\nu\mu}} \psi_1(\nu)\psi_{i+1}(\nu)\psi_1(\mu) \\ &\qquad \times \psi_{i+1}(\mu)\mathrm{d}\tau_\nu \mathrm{d}\tau_\mu, \\ \mathrm{R}_i &= \int \psi_{i+1}(\nu)\,\mathbf{H}_{i+1}(\nu)\psi_1(\nu)\mathrm{d}\tau_\nu, \\ \mathrm{Q} &= \int \psi_1(\nu)\big(\mathbf{H}_2(\nu) + \mathbf{H}_8(\nu)\big)\psi_1(\nu)\mathrm{d}\tau_\nu, \\ \mathrm{d}_i &= \int \psi_1(\nu)\psi_{i+1}(\nu)\mathrm{d}\tau_\nu. \end{aligned}\right\} \quad (26)$$

$\mathbf{H}_i(\nu)$ is the potential of a neutral carbon atom.⁽⁵⁾ The $2p\pi$ orbital of a carbon atom is

$$\psi_{2p\pi}(r.\theta.\varphi) = \sqrt{\frac{Z^5}{32\pi}}\, r\sin\theta\cos\varphi\exp[-Zr/2], \tag{27}$$

where Z is the effective nuclear charge 3.18, calculated by Zener.⁽⁸⁾ The numerical values of A_i, B_i, $\mathrm{B'}_i$, R_i, C_i, Q, d_i⁽⁹⁾ are determined from the values of Parr and Crawford's calculation.⁽¹⁰⁾

The results of calculation are shown in Table 2 and 3.

Table 2

$\mathrm{A}_0=$	16.94 e.V.	$\mathrm{B}_3=$	1.39 e.V.	$\mathrm{C}_1=$	1.11 e.V.
$\mathrm{A}_1=$	9.31 ″	$\mathrm{B}_4=$	0.56 ″	$\mathrm{C}_7=$	0.78 ″
$\mathrm{A}_2=\mathrm{A}_6=$	5.61 ″	$\mathrm{B}_5=$	1.23 ″	$\mathrm{R}_1=$	2.12 ″
$\mathrm{A}_3=$	4.63 ″	$\mathrm{B}_6=$	0.66 ″	$\mathrm{R}_7=$	0.88 ″
$\mathrm{A}_4=$	4.33 ″	$\mathrm{B}_7=$	1.81 ″	Q $=$	1.66 ″
$\mathrm{A}_5=$	4.78 ″	$\mathrm{B}_8=$	1.84 ″	$\mathrm{d}_1=$	0.28
$\mathrm{A}_7=$	8.60 ″	$\mathrm{B}_2'=$	0.36 ″	$\mathrm{d}_7=$	0.13
$\mathrm{B}_1=$	3.60 ″	$\mathrm{B}_3'=$	0.46 ″	$\mathrm{d}_2=$	0.02
$\mathrm{B}_2=$	0.92 ″	$\mathrm{B}_5'=$	0.36 ″	k $=$	0.44

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(7) In convenience we put $k = \dfrac{\beta_s}{\beta_d}$ and $S = \sqrt{1+k^2}$.

(8) Zener, *Phys. Rev.*, **36**, 51 (1930).

(9) The integral

$$\iint \frac{\mathrm{e}^2}{r_{\nu\mu}} \phi_a(\nu)\phi_b(\nu)\phi_c(\mu)\phi_d(\mu)\mathrm{d}\tau_\nu \mathrm{d}\tau_\mu$$ was

approximated by

$$\mathrm{d}_{ab}\cdot\mathrm{d}_{cd} \times \iint \frac{\mathrm{e}^2}{r_{\nu\mu}} \mathrm{K}_{ab}(\nu)^2\cdot\mathrm{K}_{cd}(\mu)^2 \mathrm{d}\tau_\nu \mathrm{d}\tau_\mu.$$

Rf. A. London, *J. Chem. Phys.*, **13**, 417 (1945).

(10) R. G. Parr and B. L. Crawford, *J. Chem. Phys.*, **16**, 1049 (1948); *cf.* C. C. J. Roothaan and R. G. Parr, *J. Chem. Phys.*, **17**, 1001 (1949).

Table 3

$\gamma_{12}=$ 7.16 e.V.	$\gamma_{35}=$ 7.63 e.V.	$\delta_{25}=$ 1.31 e.V.
$\gamma_{13}=$ 7.38 〃	$\gamma_{44}=$ 8.97 〃	$\delta_{34}=$ 0.72 〃
$\gamma_{14}=$ 7.73 〃	$\delta_{12}=$ 2.37 e.V.	$\delta_{35}=$ 1.39 〃
$\gamma_{15}=$ 7.35 〃	$\delta_{13}=$ 1.44 〃	
$\gamma_{22}=$ 7.37 〃	$\delta_{14}=$ 1.49 〃	$\varepsilon_1=$ $E_{2p}-45.57$ e.V.
$\gamma_{23}=$ 7.64 〃	$\delta_{15}=$ 1.04 〃	$\varepsilon_2=$ $E_{2p}-46.38$ 〃
$\gamma_{24}=$ 7.87 〃	$\delta_{-22}=$ 1.50 〃	$\varepsilon_3=$ $E_{2p}-46.85$ 〃
$\gamma_{25}=$ 7.52 〃	$\delta_{23}=$ 1.94 〃	$\varepsilon_4=$ $E_{2p}-45.73$ 〃
$\gamma_{33}=$ 8.03 〃	$\delta_{24}=$ 1.58 〃	$\varepsilon_5=$ $E_{2p}-41.00$ 〃
$\gamma_{34}=$ 7.84 〃	$\delta_{-25}=$ 0.85 〃	

4. Considerations

The energy levels of the ground state and the lower excited states of cycloöctatetraene are shown in Fig. 2. The ground state is the singlet state of $^1A_1$, and then this is in agreement with the experimental result that the magnetic susceptibility of cycloöctatetraene is diamagnetic. The intensity of the shoulder of the absorption curve⁽¹¹⁾ (max. 2800 Å.) is relatively weak, so this absorption band seems to be due to a forbidden transition.

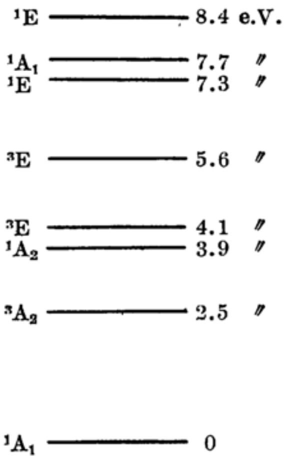

Fig. 2.

The transitions from the ground state $^1A_1$ to the excited states ^1E are allowed. According to our calculation, the wave lengths for these transitions are 1700 Å. (7.3 e.V.) and 1470 Å. (8.4 e.V.). The $^1A_1 \sim {}^1A_2$ forbidden transition is 3.9 e.V. (about 3100 Å.) and the $^1A_1 \sim {}^1A_1$ forbidden transition is 7.7 e.V. (about 1600 Å). The results of the calculation by the HLSP method⁽²⁾ show that the $^1A_1 \sim {}^1E$ transition is about 2100 Å. and the $^1A_1 \sim {}^1A_1$ forbidden transition is about 2800 Å. band. So the strong band below 2000 Å. may be due to the $^1A_1 \sim {}^1E$ transition and the 2800 Å. weak band to the $^1A_1 \sim {}^1A_1$ or the $^1A_1 \sim {}^1A_2$ transition.

The energy levels of cycloöctatetraene are also calculated by the authors, as having the symmetry of D_4, in a similar procedure to that in the case of D_{2d} by the GMS method. But the results calculated assuming as D_4 are not in agreement with the observed values of absorption spectra and magnetic properties.

5. Summary

The energy levels of cycloöctatetraene as D_{2d} were calculated byt he GMS method. Then it was shown by the authors that the ground state of cycloöctatetraene may be diamagnetic, and that the wave length of the absorption spectra calculated assuming as D_{2d} is approximately in agreement with the expetimental results.

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(11) S. Miyagawa and I. Tanaka, unpublished.