Theoretical Study of Optical Absorption Curves of Molecules. I

—Feasible Method to Calculate Optical Absorption Curves of Large Molecules—

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(Received July 12, 1972)

A feasible method to obtain theoretically optical absorption curves of large molecules is developed using Franck-Condon factors. To make calculations simple, we calculate Franck-Condon factors exactly only for those vibrational modes whose displacements of normal coordinates accompanying the electronic transition are larger than a certain value, and put those of the remainder modes into one. We have examined the case where frequency shift accompanying the transition is very large, and discussed how the intensity distribution is altered by them. Theoretical basis of the Coulson's relation and the criterion to be safely applied to molecules are studied, and this relation is found to be very useful to evaluate the magnitude of the displacement of the normal coordinate. In the end, as an example, the optical absorption curve of \( \beta \)-carotene is calculated.

§ 1. Introduction

There is great variety of shapes in optical absorption spectra of molecules. Thus, it is a very interesting problem to reproduce respective spectral curves theoretically from the electronic and vibronic properties of molecules. It was as early as 1930 that the band spectra intensities for symmetrical di-atomic molecules were calculated by Hutchisson. But, until recent times, there have been few theoretical studies on the spectral shape of the molecule larger than di- or tri-atomic molecules. This comes from the following situation: As the molecule becomes large, the number of the vibrational mode increases very much, and it becomes tedious to calculate concretely the Franck-Condon factors for these modes.

Recently, Lin and Hill made a rather compact but not so much exact formulation to calculate the spectral curve of any molecules in dense media. Their final formula involves four independent parameters, which are properly averaged over all vibrational modes. Applying this theory to acetone, they obtained a surprisingly good result. We think this theory is not good for molecules in non-polar solvent. In such systems, the nature of the electron-vibration interaction straightly reflects in the spectral shape. Thus, the naive property of each vibrational mode will essentially determine the spectral shape. Indeed, in the spectra of aromatic molecules, marked structures are seen. These structures
T. Kakitani

originate from the special mode of the vibration which is prescribed by the molecular structure and the vibronic properties in the excited and ground states. These minute investigations are impossible by the theory of Lin et al.

On the other hand, McCoy and Ross investigated the relation between the intensity distribution in spectra and the bond length changes accompanying the electronic transition for polycyclic aromatic molecules. Their theory are based on the Franck-Condon principle and only the displacement of the equilibrium point of the normal coordinate in the electronic transition is taken into account. This corresponds to an approximation of the first-order perturbation of the electron-vibration interaction. Without solving the vibrational problem in the excited and ground states, they intuitively assumed that the displacement of the normal coordinate, which plays the most important role, is a root of sum of squares of bond length changes. They calculated the bond length changes using Coulson’s relation of bond order and bond length. By this, they obtained comparatively good results of the intensity distribution for benzene, naphthalene and anthracene. We think that their theory involves the following difficulties: The force constant or the effective mass of the important vibrational mode is unknown, and all the bond length changes accompanying the transition are not necessarily concerned with only the displacement of the important normal mode. Thus the calculation of the Franck-Condon factor becomes an approximate one and/or a roughly estimated one.

From these considerations, it can be said that if we intend to elucidate the origin of the wide variety of spectral shapes and to get spectral curves theoretically which are so quantitative as to be comparable with experiments, we should precisely solve the vibrational problem in the excited and ground states to some extent, and take into account many modes of the vibration in the calculation of the Franck-Condon factor. Formerly, we have calculated the intensity distribution of the optical absorption spectrum of benzene in gas phase, considering almost all the vibrational modes, but using some parameters. The result was very good. This is rather a special case because the molecular structure of benzene has high symmetry.

In this paper, we intend to show a convenient method to pick out some important vibrational modes and develop a concrete procedure by which we make numerical calculations of spectral curves for various molecules. In §2 we formulate the oscillator strength within the Franck-Condon principle, using an approximation of the first-order perturbation for the electron-vibration interaction. In §3 we propose a method for evaluating semiempirically the magnitude of the displacement of the normal coordinate. In §4 we examine the criterion of the applicability of our theory. In §5 we investigate a theoretical basis for Coulson’s relation. In §6 we give some discussions and try to apply our theory to linear polyenes.
§ 2. Formulation of oscillator strength

The total Hamiltonian of a molecule $H(r, R)$ is written as

$$H(r, R) = H_e(r) + H_{\text{ion}}(R) + H_{\text{int}}(r, R),$$

(2.1)

$$H_e(r) = -\sum_i \frac{1}{2m} \varepsilon_i^2 + \frac{1}{2} \sum_{ij} \frac{\varepsilon_i^2}{\left| r_i - r_j \right|},$$

(2.2)

$$H_{\text{ion}}(R) = -\sum_a \frac{1}{2M_a} \varepsilon_a^2 + \frac{1}{2} \sum_{ab} \frac{Z_a \varepsilon_a^2}{|R_a - R_b|},$$

(2.3)

$$H_{\text{int}}(r, R) = -\sum_i \sum_a \frac{Z_a \varepsilon_a^2}{|r_i - R_a|},$$

(2.4)

where $H_e(r)$, $H_{\text{ion}}(R)$ and $H_{\text{int}}(r, R)$ are energies of electrons, ions and interaction between them, respectively. The symbols $m$ and $r_i$ are the mass of the electron and the coordinate of the $i$-th electron. The symbols $M_a$, $R_a$ and $Z_a$ are the mass, coordinate and valency of the $a$-th ion, respectively. Variables $r$ and $R$ denote all the coordinates of the electrons and ions. The Planck constant $\hbar$ is taken to be 1. We decouple the total wave function into two parts as follows:

$$\Psi(r, R) = \psi(r, R) \cdot \zeta(R),$$

(2.5)

where $\psi$ and $\zeta$ are the electronic and vibrational wave functions, respectively. Our procedure of calculation in the following is as follows: Assuming that the electronic ground state and all the vibrational states in the ground state are solved exactly, we go to obtain the electronic excited state and the vibrational states in the excited state by the perturbation method. We rearrange the total Hamiltonian as

$$H(r, R) = H_e'(r) + H_{\text{vib}}(R) + H_{\text{int}}'(r, R),$$

(2.6)

$$H_e'(r) = -\sum_i \frac{1}{2m} \varepsilon_i^2 + \frac{1}{2} \sum_{ij} \frac{\varepsilon_i^2}{\left| r_i - r_j \right|} - \sum_{i} \sum_a \frac{Z_a \varepsilon_a^2}{|r_i - R_a|},$$

(2.7)

$$H_{\text{vib}}(R) = -\sum_a \frac{1}{2M_a} \varepsilon_a^2 + U(R),$$

(2.8)

$$H_{\text{int}}'(r, R) = -\sum_i \sum_a \left( \frac{Z_a \varepsilon_a^2}{|r_i - R_a|} - \frac{Z_a \varepsilon_a^2}{|r_i - R_a^0|} \right)$$

$$+ \frac{1}{2} \sum_{ab} \frac{Z_a Z_b \varepsilon_a^2}{|R_a - R_b|} - U(R).$$

(2.9)

In the above equations, $H_e'(r)$ is the unperturbed Hamiltonian of the electron which satisfies

$$H_e'(r) \psi_i^{(0)}(r) = \varepsilon_i^{(0)} \psi_i(r),$$

(2.10)
where $\psi_1^{(0)}$ and $\varepsilon_1^{(0)}$ are the electronic wave function and the energy in the unperturbed state $l$. The constant $R_x^0$ is the equilibrium position of the $a$-th ion in the ground state. $U(R)$ is the adiabatic potential of the ion in the ground state. $H_{\text{int}}(r, R)$ is the perturbation Hamiltonian for the electron system. We do this so that the perturbation energy may become the smallest. The equation of the electronic part becomes

$$\{H_1'(r) + H_{\text{int}}(r, R)\} \psi_1(r, R) = W_1(R) \psi_1(r, R). \quad (2\cdot11)$$

In the ground state, the energy $W_1(R)$ becomes a constant $\varepsilon_1^{(0)}$ because the adiabatic potential in the ground state is subtracted from our electronic Hamiltonian. In the excited state, the energy $W_1(R)$ becomes an unperturbed energy $\varepsilon_1^{(0)}$ plus a potential energy with small $R$-dependence which comes from the difference of the adiabatic potentials between the excited and ground states. Thus the perturbation energy is very small compared with the electronic energy difference. The equation for the vibration is written as

$$\{H_{\text{vib}}(R) + W_1(R)\} \zeta_{1\nu}(R) = E_{1\nu} \zeta_{1\nu}(R), \quad (2\cdot12)$$

where $\zeta_{1\nu}$ and $E_{1\nu}$ are the vibrational wave function and the energy in the electronic state $l$ and the vibrational state $\nu$, respectively. In the ground state, this vibrational equation is solved from our assumption. In the harmonic approximation, it is solved as

$$H_{\text{vib}}(R) = \frac{1}{2} \sum_{j=1}^{N} (P_j^2 + \omega_j^2 Q_j^2), \quad (2\cdot13)$$

where $Q_j$, $P_j$, $\omega_j$, and $N$ are the $j$-th normal coordinate of the vibration in the ground state, canonical momentum to it, normal frequency and number of the total vibrational modes, respectively. We expand $H_{\text{int}}'(r, R)$ by a polynomial of $Q_j$ and stop in the first order of it as follows:

$$H_{\text{int}}'(r, R) = -\sum_{j=1}^{N} u_{ji}(r) Q_j. \quad (2\cdot14)$$

The limitation due to this approximation is discussed in § 4. From Eqs. (2\cdot11) and (2\cdot14), we obtain $\psi_1(r, R)$ and $W_1(R)$ in the first-order approximation as follows:

$$\psi_1(r, R) = \psi_1^{(0)}(r) - \sum_j \sum_{l'} u_{j1l'} \psi_1^{(0)}(r) Q_{jl'}/(\varepsilon_1^{(0)} - \varepsilon_1^{(0)}), \quad (2\cdot15)$$

$$W_1(R) = \varepsilon_1^{(0)} - \sum_j u_{ji} Q_j, \quad (2\cdot16)$$

where

$$u_{j1l'} = \int \psi_1^{(0)}(r)^* u_j(r) \psi_1^{(0)}(r) \, dr. \quad (2\cdot17)$$

Of course, in the ground state, the second term in Eqs. (2\cdot15) and (2\cdot16) drops out. The adiabatic potential in the excited state becomes
Theoretical Study of Optical Absorption Curves of Molecules. I

\[ U(R) + W_i(R) \equiv \epsilon_i^{(0)} + \frac{\hbar}{2} \sum_{j=1}^{N} \omega_j (Q_j - \Delta Q_j)^2, \]  

(2.18)

where \( \Delta Q_j \) is defined by

\[ \Delta Q_j = \omega_j / \omega_j. \]  

(2.19)

From this, we see that the vibrational frequency does not alter but the normal coordinate shifts by \( \Delta Q_j \) in the excited state compared with those of the ground state.

The transition dipole moment of the electron due to the transition from a state \( lv \) to a state \( l'v' \) is

\[ M_{lv,lv'} = \int \sum_{i} \psi_{lv}(r_0) \psi_{lv'}(r) dr dR. \]  

(2.20)

In the allowed transition, we can write as follows:

\[ (M_{lv,lv'})^2 = (m_{lv}^{(0)})^2 F_{lv,lv'}, \]  

(2.21)

where

\[ F_{lv,lv'} = \left( \sqrt{\int_{R}(R) \psi_{lv'}(R) dR} \right)^2, \]  

(2.22)

\[ m_{lv}^{(0)} = \sqrt{2} \int \psi_{lv}^{(0)}(r) (\sum_{i} r_i) \psi_{lv}^{(0)}(r) dr. \]  

(2.23)

Here we call \( F_{lv,lv'} \) total Franck-Condon factor (abbreviation: TFC factor).

The vibrational wave function is written as

\[ \psi_{lv} = \prod_{j} \chi_{n_j}(z_j - \Delta z_j), \]  

(2.24)

\[ \chi_{n_j}(z_j - \Delta z_j) = N_{n_j} \exp \left[ -\frac{1}{2} (z_j - \Delta z_j)^2 \right] H_{n_j}(z_j - \Delta z_j), \]  

(2.25)

\[ N_{n_j} = \left( \frac{\pi}{\omega_j 2^{n_j}} \right)^{1/2}, \]  

(2.26)

where \( z_j \) and \( \Delta z_j \) are the dimensionless variable and parameter defined by

\[ z_j = \sqrt{\omega_j} Q_j, \]  

(2.27)

\[ \Delta z_j = \sqrt{\omega_j} \Delta Q_j, \]  

(2.28)

respectively, \( n_j \) is the quantum number of the vibrational mode \( j \) and \( H_{n_j} \) is the \( n_j \)-th Hermite polynomial. In the following, we assume that states \( l \) and \( l' \) denote the ground and excited states, respectively. Then we get from Eqs. (2.22) and (2.24)

\[ F_{lv,lv'} = \prod_{j=1}^{N} \tilde{F}_{lv,lv'}(\Delta z_{l'j}), \]  

(2.29)

\(^{\text{*) For the forbidden transition, see Ref. 8.}}\)
where
\[ F_{i\nu,\nu'} (dz_{i\nu}) = \frac{1}{\omega_j} \left( \int \chi_{\nu'} (z_j - \Delta z_{i\nu}) \chi_{\nu_j} (z_j) dz_j \right)^2 , \]  \hspace{1cm} (2.30)

where \( n_j \) and \( n'_j \) are the quantum number of the vibration in the ground and excited states, respectively. We call \( F_{i\nu,\nu'} (dz_{i\nu}) \) mode Franck-Condon factor (abbreviation: MFC factor). The oscillator strength for the transition \( lv-l'v' \) is written as
\[ f_{lv,l'v'} = (B_v \sum B_v) \frac{\hbar}{m} \Delta E_{lv,l'v'} (M_{lv,l'v'}) , \]  \hspace{1cm} (2.31)

where \( B_v \) is the Boltzmann factor for the vibrational state \( v \), and \( \Delta E_{lv,l'v'} \) is the energy difference between the states \( lv \) and \( l'v' \), which is defined by
\[ \Delta E_{lv,l'v'} = \varepsilon^{(v)}_l - \varepsilon^{(v)}_l + \sum (n'_j - n_j) \omega_j . \]  \hspace{1cm} (2.32)

Calculating the oscillator strength, we put \( \Delta E_{lv,l'v'} \) into constant, because the electronic energy difference is much larger than the vibrational energy. Then, the oscillator strength becomes proportional to the product of \( B_v \) and the TFC factor. In the latter part of this paper, we do not concern ourselves with the absolute value of the oscillator strength, but with the relative amplitude.

§ 3. **Displacement parameter and Coulson's relation**

In this section, we state how we use the formulas of § 2 in a concrete calculation and show how well our simple theory catch the most essential point in the optical absorption curve. The oscillator strength (2.31) is rewritten as
\[ f_{lv,l'v'} = AB_v F_{lv,l'v'} \]
\[ = A \prod_{j=1}^{N} \exp ( - n_j \omega_j / kT ) F_{i\nu,\nu'} (dz_{i\nu}) , \]  \hspace{1cm} (3.1)

where \( A \) is a constant. From Eq. (3.1) we find that the essential factor which determines spectral shapes is only the parameter \( \Delta z_{i\nu} \). We call it the displacement parameter because it relates only to the difference of molecular structures between the ground and excited states. Experimentally, optical spectra are often got in a liquid state. In such a condition, each spectral line should become broader. Then we modulate our equation as follows:
\[ \mathcal{J}_{i,\nu} (E, T) = A' \sum_{v} \sum_{v'} \frac{B_v F_{lv,l'v'}}{(E - \Delta E_{lv,l'v'})^2 + \Gamma^2} \]
\[ = A' \prod_{i=1}^{N} \sum_{n_i} \sum_{n_i'} \sum_{n_v} \sum_{n_v'} \frac{\prod_{j=1}^{N} \exp ( - n_j \omega_j / kT ) F_{i\nu,\nu'} (dz_{i\nu})}{(E - \varepsilon^{(v)}_l + \varepsilon^{(v')}_{l'} - \sum (n'_j - n_j) \omega_j)^2 + \Gamma^2} , \]  \hspace{1cm} (3.2)

where \( \mathcal{J}_{i,\nu} (E, T) \), \( \Gamma \) and \( A' \) are the molar extinction coefficient, the line width in each absorption line and a constant, respectively.
Next we consider methods to evaluate $\Delta z_{\mu'}$. The first is to calculate it from the first principle. From Eqs. (2.19) and (2.27), $\Delta z_{\mu'}$ is written as

$$\Delta z_{\mu'} = u_{\mu'\nu} \omega_{\nu}^{-3/2}. \quad (3.3)$$

In this expression, it is not difficult to evaluate $\omega_{\nu}$ by properly formulating the equation of motion for ions and adopting force constants determined semiempirically. The quantity of interaction $u_{\mu'\nu}$ is written as follows from Eqs. (2.9), (2.14) and (2.17):

$$u_{\mu'\nu} = \int \Psi_{\nu}^{(g)}(r)^* \left( \sum_{\alpha} \frac{Z_{\alpha} e^{i(\mathbf{R}_{\alpha} - \mathbf{r}_{\nu})}}{|\mathbf{r}_{\nu} - \mathbf{R}_{\alpha}|^{3/2}} \right) \psi_{\mu}^{(g)}(r) \frac{\partial R_{\alpha}}{\partial Q_{\nu}}. \quad (3.4)$$

Numerical calculations of Eq. (3.4) for benzene were made by Murrell and Pople, Liehr and others. But the results are unsatisfactory. This is because it is necessary to use much improved electronic wave functions, and screening effect by $\sigma$- and $\pi$-electrons on the induced dipole moment is important. Thus, at present, to evaluate $u_{\mu'\nu}$ from Eq. (3.4) is said to be very difficult.

The second method to evaluate $\Delta z_{\mu'}$ is to use the molecular structures in the ground and excited states determined either experimentally or theoretically. The procedure of calculation is as follows: The normal coordinate of the vibration in the ground state is written as

$$Q_{\nu} = \sum_{(a,b)} v_{a,b} l_{a,b} + \sum_{(a,b,c)} \omega_{a,b,c} \theta_{a,b,c}, \quad (3.5)$$

where $l_{a,b}$, $\theta_{a,b,c}$, $v_{a,b}$ and $\omega_{a,b,c}$ are displacement of the bond length $R_{a,b}$ from the equilibrium bond length $R_{a,b}^{(g)}$, displacement of the angle between two consecutive bonds $ab$ and $bc$ from the equilibrium ones, coefficients of them, respectively. The summations over $(a,b)$ and $(a,b,c)$ denote that the sums are made for all bonds and angles between two consecutive bonds. If molecular structures differ by $\Delta R_{a,b}$ and $\Delta \theta_{a,b,c}$ between the excited and ground states, $\Delta z_{\mu'}$ is written as

$$\Delta z_{\mu'} = \sqrt{\omega_{\nu}} \left\{ \sum_{(a,b)} v_{a,b} \Delta R_{a,b}^{(e)} + \sum_{(a,b,c)} \omega_{a,b,c} \Delta \theta_{a,b,c} \right\}. \quad (3.6)$$

This is the final equation to get $\Delta z_{\mu'}$ from the knowledge of the molecular structures. In conjugated hydrocarbons, it often happens that the bond length changes but the angle is unchanged when the molecule is excited. In that case, we can easily calculate $\Delta z_{\mu'}$. We state it in the following. The electronic wave function in the LCAO-ASMO* of $\pi$-electrons is written as

$$\psi_{\mu}^{(g)} = \prod_{e}^{\infty} \varphi_{e}^{(g)}, \quad (3.7)$$

$$\varphi_{e}^{(g)} = \sum_{a} C_{e,a} \tilde{\varphi}_{a}, \quad (3.8)$$

* LCAO-ASMO is the abbreviation of the antisymmetrized molecular orbital obtained by the linear combination of the atomic orbital.
where \( \mathcal{A}, \varphi_k^{(0)}, C_{k,a} \) and \( \phi_a \) are the antisymmetricizing operator, \( k \)-th unperturbed molecular orbital, coefficient of the atomic orbital and atomic orbital at site \( a \), respectively. Here state \( k \) includes the spin state. The bond order due to \( \pi \)-electrons is defined by

\[
P_{ab} = \sum_k C_{a_k} C_{b_k}.
\]

(3.9)

If a \( \pi \)-electron is excited from the \( s \)-th occupied molecular orbital to the \( t \)-th unoccupied molecular orbital, the change in the bond order is

\[
\Delta p_{ab} = C_{s_a} C_{t_b} - C_{s_b} C_{t_a}.
\]

(3.10)

Here we use Coulson's relation, which is the empirical relation between the bond order and the bond length approximately written by

\[
R_{ab}^0 = \eta - \gamma p_{ab}^0,
\]

(3.11)

where \( \eta \) and \( \gamma \) are the constant of length (1.54Å) and coefficient (\( \sim 0.20\)Å). Then, the change of the bond length is written as

\[
\Delta R_{ab}^0 = -\gamma \Delta p_{ab} = -\gamma (C_{s_a} C_{t_b} - C_{s_b} C_{t_a}).
\]

(3.12)

Substituting Eq. (3.12) into Eq. (3.6), we obtain

\[
\Delta x_{ft} = -\gamma \sqrt{\omega f} \sum_{(a,b)} \alpha_{f,ab} (C_{s_a} C_{t_b} - C_{s_b} C_{t_a}).
\]

(3.13)

This formula is very useful because all the coefficients are easily calculated.

Next we qualitatively examine how intensity distribution of absorption spectra changes according to the variation of the displacement parameter. In Table I, formulas of the MFC factor are listed for some values of \( n_j \). In Fig. 1, intensity distributions of the MFC for various values of \( \Delta x_{ft} \) and \( n_j \) are plotted. From

Table I. The mode Franck-Condon factor as a function of the displacement parameter. \( \Delta x_{ft} \), and \( n_j \) are replaced by \( \Delta \) and \( n \), respectively. The constant \( S_{n,i} \) is defined by \( S_{n,i} = \Pi_{k=n-i}^i x_k \) for \( n > i \) and \( S_{n,i} = 0 \) for \( n \leq i \).
these graphs it is found that absorption lines for \( n_j \neq n_j' \) appear with considerable intensity when \( \Delta \varepsilon_{\mu'} \) is larger than 0.3, and that the intensity distribution becomes very broad when \( \Delta \varepsilon_{\mu'} \) is 2.0. In the graphs of \( n_j = 1 \) and 2, very peculiar intensity distributions are seen as \( \Delta \varepsilon_{\mu'} \) becomes large. In absorption spectra of many molecules, the intensity distribution such as that of \( n_j = 2 \) and \( \Delta \varepsilon_{\mu'} = 2.0 \) is scarcely seen. This will be due to the following facts: Almost all the vibrational frequencies are much larger than \( kT \), and thus almost all the vibrational states are at \( n_j = 0 \) owing to the Boltzmann factor. Even in the case that there are vibrational modes with a very low frequency which is less than \( kT \), it is usual that its \( \Delta \varepsilon_{\mu'} \) becomes very small chiefly due to the factor \( \sqrt{\omega_j} \) in Eq. (2·28). Thus, the intensity distribution becomes rather normal one. Next we consider intensity distributions of the TFC factor. We set \( n_j = 0 \) for all modes. For brevity of calculation, we assume that the number of the mode is three. In Fig. 2, we have plotted the intensity distribution of the TFC factor for various values of \( \Delta \varepsilon_{\mu'} \). From these it is found that the largest value of \( \Delta \varepsilon_{\mu'} \) essentially determines the spectral shape, and especially, when the vibrational mode with the largest frequency has the largest value of \( \Delta \varepsilon_{\mu'} \), absorption lines with an interval of that frequency markedly appear. Indeed, this is often seen in many conjugated molecules.

Now using the characteristics of the intensity distribution of the MFC faction as a function of \( \Delta \varepsilon_{\mu'} \), we can pick up some vibrational modes which are important in the calculation of the absorption spectrum. That is, we choose those modes whose \( \Delta \varepsilon_{\mu'} \) is larger than 0.24. The error in doing this is less than 3%. Using some important modes, we calculate the TFC factor and omit those lines the amplitude of which are less than 3% of the highest one. By this, our calculation becomes feasible even for large molecules.

§ 4. Examination of the approximation in our theory

Our first approximation is the adiabatic approximation. This approximation may be bad for the motion of a proton in the hydrogen-bond and for the nuclear
The non-diagonal terms in regard to $Q_j$ on the right side of Eq. (4.1) play a role to mix the vibrational modes defined in the ground state. But, when we solve the vibration in the excited state by the perturbation method, the non-diagonal terms act as a higher order than $Q_{H'}$ does. Thus we omit them here. We shall examine those effects on the absorption curve elsewhere. Then, we find that the normal coordinate and normal frequency become $Q_j - \Delta Q_{H'}$ and $\omega_j^3 + \omega_{H'}^3$, respectively. Further, the bottom of the adiabatic potential is decreased by $2\sum_j \omega_j^3 (\Delta Q_R)^3$ from that of the unperturbed excited state. Usually this value is several quanta of the vibrational frequency. In this approximation, the MFC factor and the energy difference are rewritten as

$$\mathcal{F}_{\omega_j, \nu' \nu'} (\Delta \varepsilon_{j \nu'}, \Delta \varepsilon_{j' \nu'}) = \frac{1}{\omega_j} \left( \int \chi_{\nu'} (\xi_{j \nu'} \varepsilon_{j \nu'} - \Delta \varepsilon_{j \nu'}) \cdot \chi_{\nu_j} (\varepsilon_{j \nu}) d\varepsilon_{j \nu} \right)^2,$$

where $\varepsilon_{j \nu} = \varepsilon_{j \nu}^{(0)} - \sum_j \omega_j (\Delta Q_{R})^3$. (4.4)
Theoretical Study of Optical Absorption Curves of Molecules. I

\[ \Delta E_{10,1'0'} = \varepsilon_1^{(0)} - \varepsilon_1^{(0)} + \frac{1}{2} \sum_{j=1}^{N} (\omega_j - \omega_j') + \sum_{j=1}^{N} (n_j' \omega_j - n_j \omega_j), \]  

where \( \omega_j \) and \( \omega_j' \) are vibrational frequencies of the mode \( j \) in the ground and excited states. The distortion parameter \( \xi_{1'} \) is defined by

\[ \xi_{1'} = (\omega_j'/\omega_j)^{1/2}. \]

The integral of Eq. (4·4) was analyzed by Hutchisson. Using his result, we have plotted \( \mathcal{F}_{10,1'0'}(\Delta z_{1'}, \xi_{1'}) \) in Fig. 3. From this graph we find the following properties:

1. When the value of \( \Delta z_{1'} \) is varied, the intensity distribution changes very much,
2. when the value of \( \xi_{1'} \) is varied, the intensity distribution does not change so much as the case of \( \Delta z_{1'} \),
3. when the value of \( \Delta z_{1'} \) is small, intensity distribution becomes very narrow regardless of the value of \( \Delta z_{1'} \)
4. when \( \xi_{1'} \) is larger than 1, the intensity distribution becomes a stumpy form and when \( \xi_{1'} \) is smaller than 1, it becomes a slim form (see graphs of \( \Delta z_{1'} = 1.0 \)). In most molecules, \( |\Delta z_{1'}| \leq 1.5 \) and \( \xi_{1'} \leq 1.3 \). Thus, it is found from properties (1) ~ (3) that the intensity distribution is essentially determined by \( \Delta z_{1'} \), and \( \xi_{1'} \) plays a minor role in it. Then, it can be said that our theory in §§ 2 and 3 is fairly good for most molecules.

The third approximation is the neglect of anharmonic terms in the molecular vibration. Generally speaking, the anharmonicity introduces a life time to the vibration, and thus the line width to the absorption line. Further, the frequency of higher quanta deviates from \( n_{j0j} \) or \( n_j' \omega_j' \). But the role which the anharmonicity plays in the absorption spectrum in many molecules is thought to be very small at the room temperature. Indeed, our previous calculation of the absorption spectrum of benzene neglecting the anharmonicity agrees very well with that of the experiment.

The fourth approximation is to use the empirical law, Coulson's relation, for conjugated molecules. This empirical law is very simple and thus convenient to
use. In the next section, we prove this law by HMO theory.

The limitations of our theory are as follows: a) The difference of vibrational frequencies between the ground and excited states should not be large. This is because our theory is constructed by the perturbational method. b) Mixing of the vibrational mode in the excited state should be small. When the mixing is large, exchange of the vibrational quanta among the vibrational mode occurs accompanying the electronic transition. Then, the structure in the absorption curve will be more or less smeared out. We are now examining what relation there is between the mixing effect and the line width.

§ 5. Theoretical basis of Coulson’s relation

Within the HMO theory, the total energy $E^T$ of the conjugated hydrocarbon is approximately written as

$$E^T = E^0 + E^e + E^\pi,$$

(5·1)

$$E^0 + E^e = \sum_{(a,b)} \frac{1}{2} K^e (R_{ab} - R^e),$$

(5·2)

$$E^\pi = \sum_a \alpha_a + \sum_{(a,b)} \rho_{ab} \beta_{ab},$$

(5·3)

where

$$\alpha_a = \int \phi_a^* (r) H_{\text{core}} (r, R) \phi_a (r) \, dr,$$

(5·4)

$$\beta_{ab} = \int \phi_a^* (r) H_{\text{core}} (r, R) \phi_b (r) \, dr.$$  

(5·5)

In the above equations, $E^0$, $E^e$ and $E^\pi$ are energies of the nuclear-nuclear interaction, $\sigma$-electrons and $\pi$-electrons, respectively. $K^e$ and $R^e$ are the force constant and bond length of the single bond, respectively. The form of Eq. (5·2) is valid as far as $R_{ab} - R^e$ is much smaller than $R^e$. This assumption is the same as that of Longuet-Higgins and Salem. Hcore$(r, R)$ is the Hamiltonian for $\pi$-electrons in the ion-core field. The Coulomb integral $\alpha_a$ is usually assumed to be independent of the site $a$, and the resonance integral $\beta_{ab}$ is assumed to depend upon only the bond length $R_{ab}$. Differentiating $E^T$ by $R_{ab}$, we get

$$\frac{\partial E^T}{\partial R_{ab}} = K^e (R_{ab} - R^e) + \rho_{ab} \frac{\partial \beta_{ab}}{\partial R_{ab}},$$

(5·6)

where $\varepsilon_i$ and $\varepsilon_j$ are energies of the $i$-th and $j$-th molecular orbitals of the $\pi$-HMO is the abbreviation of Hückel molecular orbital.

**Coulson derived his relation also by the HMO theory.** However, he assumed the resonance integral as a quadratic form of the bond length and an abnormally large value of $K^e/K^d$, where $K^e$ and $K^d$ are force constants of single and double bonds, respectively. Our theory in this section is improved in it.
Theoretical Study of Optical Absorption Curves of Molecules. I

electron. In the equilibrium position of atoms, $\partial E^T/\partial R_{ab}=0$. Then, the bond order is expressed by the bond length as follows:

$$p^0_{ab} = -\frac{K(R^0_{ab} - R^*)}{(\partial \beta_{ab}/\partial R_{ab}^0)}.$$  

(5.7)

Equation (5.7) involves the variables concerning only the bond $ab$. Thus, we omit the suffix $ab$ in the following part of this section. At present, we do not know the exact form of $\beta(R)$. Then, we assume the following two types of $\beta(R)$:

- Type I: $\beta(R) = -A_1 \exp(-B_1 R)$,  
- Type II: $\beta(R) = A_{II} \exp(B_{II} R) - C_{II}$,

(5.8I)  
(5.8II)

where $A_1, B_1, A_{II}, B_{II}$ and $C_{II}$ are positive constants. Type I is the function most widely used by many investigators. Substituting Eq. (5.8) into Eq. (5.7), we get

$$p^0 = \frac{K^*}{A_1 B_1} (R^* - R^0) \exp(B_1 R^0),$$  

(5.9I)

$$p^0 = \frac{K^*}{A_{II} B_{II}} (R^* - R^0) \exp(-B_{II} R^0).$$  

(5.9II)

Equation (5.9) exhibits the relation between bond order and bond length. To determine values of the constants in Eq. (5.8), we use the following empirical and/or experimental data:

$$K^* = 4.5 \times 10^6 \text{ dyne/cm,}$$  

(5.10)

$$R^* = 1.54 \text{Å,}$$  

(5.11)

$$\beta = -3.25 \text{ eV for } R^0 = 1.335 \text{Å (ethylene),}$$  

(5.12)

$$p^0 = 1 \text{ for } R^0 = 1.335 \text{Å (ethylene),}$$  

(5.13)

$$p^0 = \frac{2}{3} \text{ for } R^0 = 1.397 \text{Å (benzene).}$$  

(5.14)

$A_1$ and $B_1$ are determined so that Eqs. (5.8I) and (5.9I) may satisfy Eqs. (5.12) and (5.13). $A_{II}, B_{II}$ and $C_{II}$ are determined so that Eqs. (5.8II) and (5.9II) may satisfy Eqs. (5.12) $\sim$ (5.14). The result is as follows:

$$A_1 = 34.5 \text{ eV,} \quad B_1 = 1.77 \text{Å}^{-1},$$  

(5.15I)

$$A_{II} = 2.32 \text{ eV,} \quad B_{II} = 0.831 \text{Å}^{-1}, \quad C_{II} = -10.29 \text{ eV.}$$  

(5.15II)

Using these values and Eq. (5.8), we have plotted $\beta$ as a function of $R$ in Fig. 4. It should be noticed that the curvature in the $\beta - R$ curve of Type I is opposite to that of Type II. Using Eq. (5.9), we have plotted the graph of bond length vs. bond order in Fig. 5. The graph is drawn only in the region...
0 \leq p \leq 1$, because our theory cannot be applied to the molecule with a triple bond, where correlation between $\pi$-electrons is very large. From Fig. 5, we find that the theoretical curve using $\beta$ of Type II fits the experimental values very well. Thus, it can be said that if we use an appropriate function of $\beta$, we can derive Coulson’s relation by HMO method.

In Eq. (5·9), we approximate as

$$\exp(B_\Pi R^0) = \exp(B_\Pi R^d) \cdot \exp(B_\Pi (R^0 - R^d)) \approx \frac{K^\prime}{A_\Pi B_\Pi} \{1 + B_\Pi (R^0 - R^d)\},$$

(5·16)

where $R^d$ is the length of the double bond. Then we get

$$R^0 = R^* - \frac{R^* - R^d}{1 + K(1 - \rho^5)/\rho^5},$$

(5·17)

where $K = 1/(B_\Pi (R^* - R^d) + 1)$. Equation (5·17) is of the same form as that of Coulson. Our value of $K$ is 0.855, which is a little larger than Coulson’s 0.765. If we approximate in Eq. (5·9) as follows:

$$\exp(B_\Pi R^0) \approx \frac{K^\prime}{A_\Pi B_\Pi},$$

(5·18)

we get

$$R^0 = R^* - (R^* - R^d) \rho^5,$$

(5·19)

This is the same form as Eq. (3·11).
Coulson's relation holds for the molecular structure in an equilibrium form, but not for that in nonequilibrium forms. In this respect, we will point out the error in the study of Longuet-Higgins and Salem. In calculating the force constant of the conjugated molecule, they used the following equation (5.20) which is obtained by differentiating Eq. (3.11) by $R_{ab}$:

$$\left(\frac{\partial \rho}{\partial R}\right)_0 = -\frac{1}{\gamma}.$$  (5.20)

To differentiate by the bond length is to deviate the bond length from the equilibrium length, where Coulson's relation does not hold. Thus, Eq. (5.20) is not valid. Actually, in ethylene the bond order does not change when the bond length between two carbon atoms is altered.

§ 6. Discussion

We summarize the process to calculate the spectral curve in the following. (1) We solve the Schrödinger equation of the unperturbed Hamiltonian of the electron (2.10). (2) We obtain normal coordinates and normal frequencies of the vibration in the ground and excited states. (3) We obtain the molecular structure in the ground and excited states. (4) We calculate displacement parameters from Eq. (3.6) and select those modes whose $\Delta \varepsilon_{\mu}$'s are larger than 0.24. (5) We calculate the MFC factors for the selected modes using Table I. The MFC factors of the other modes are put as 1. We omit those spectral lines the amplitudes of which are less than 3% of the highest one. (6) We calculate the TFC factor defined by Eq. (2.29). We omit those spectral lines the amplitudes of which are less than 3% of the highest one. (7a) For the molecule in a gas phase, we calculate the oscillator strength from Eq. (2.31). (7b) For the molecule in a liquid phase, we calculate the molar extinction coefficient from Eq. (3.2).

In the process (1), we solve the Schrödinger equation by either LCAO-ASMO or simple LCAO-MO. We need not a very accurate wave function of the electron, because we must venture to adopt many approximations in our calculation. In the process (2), if it is troublesome to solve the vibration exactly in large molecules, we may simplify the molecule as a model molecule by grouping some atoms into a point. In the process (3), the molecular structure in the ground state is available from the data of the X-ray study. In conjugated molecules, we obtain the molecular structure in the excited state from Coulson's relation. In non-conjugated molecules, there is no simple rule such as Coulson's relation. Thus, we must get the molecular structure by calculating the total energy as a function of the bond length and angle between two consecutive bonds. In the process (7b), we treat $\Gamma$ as a parameter, which is determined by the process that the calculated spectral curve may best fit the experimental curve. The line width $\Gamma$ involves many effects, such as anharmonicity in the vibration, intermolecular in-
teraction, solvent-solute interaction, etc. Thus, the value of $\Gamma$ may be somewhat larger than $kT$. We state this once more in the latter part of this paper.

In §§ 2 and 3, we have shown that the spectral shape is essentially determined by the largest value of $\Delta \varepsilon_{j'}$. Then, what mode of the vibration has the largest value? From Eq. (3·6), it is found that this mode should satisfy the following condition: (i) $\omega_j$ should be large and (ii) signs of $\nu_{j,ab}$ and $\nu_{j,abc}$ should be the same as those of $\Delta R_{ab}^a$ and $\Delta R_{abc}^{abc}$, respectively for all $(a, b)$ and $(a, b, c)$. In other words, the molecular structure in the ground state should become similar to that in the excited state by borrowing the vibration of that mode.

In the alternant conjugated molecule, the coefficient $C_{ka}$ of the HMO has the following property:

\[ C_{2L-k+1,a} = -C_{k,a} \quad \text{for the starred site}^*) \]
\[ C_{2L-k+1,b} = C_{k,b} \quad \text{for the unstarred site}^*) \]

where $2L$ is the total number of $\pi$-electrons. When a $\pi$-electron is excited from the occupied $k$-th orbital to the unoccupied $2L-k+1$-th orbital, we can rewrite Eq. (3·13) within the Hückel approximation in a simpler form as follows:

\[ \Delta \varepsilon_{j'} = 2\Gamma \sqrt{\omega_j} \sum_{(a, b)} \nu_{j,ab} p_{k,ab}, \]

where $p_{k,ab}$ is the $k$-th orbital-bond-order defined by

\[ p_{k,ab} = C_{ka} C_{kb}. \]

To ascertain the utility of Eq. (6·2), we apply it to the linear polyene. For brevity, we assume the system as one dimension. In Table II, we have listed the signs of $C_{k,a}$, $p_{k,ab}$ and $\nu_{j,ab}$ for the molecule with $10 \pi$-electrons. From this, we find that the sign of $\nu_{j,ab}$ of the mode with the highest frequency (top mode) is the same as that of $p_{k,ab}$ of the highest-occupied molecular orbital (HOMO). In the same way, the sign of $\nu_{j,ab}$ of the mode with the third highest frequency (third top mode) is the same as that of $p_{k,ab}$ of the second-highest-occupied molecular orbital (SHOMO). We also find that as the distribution of the sign of $p_{k,as}$ is symmetric with regard to the center of the molecule, $\Delta \varepsilon_{j'}$ of the antisymmetric mode ($Q_a$ in Table II) becomes zero. Properties stated above generally apply to symmetric linear polyenes.

To see more quantitatively, we calculate the absorption spectrum of $\beta$-carotene, as an example. The molecular structure is shown in Fig. 6(a). The electronic state is solved by HMO theory. We adopt the following values for the resonance integrals

\[ \beta_a = -4.282 \text{ eV}, \quad \beta_s = -3.233 \text{ eV}, \]

with which the distribution of the absorption wave lengths of the linear polyenes

*) The starred and unstarred sites are alternatively labeled for atoms in the molecule.
Theoretical Study of Optical Absorption Curves of Molecules. I

Table II. Signs of $C_{k,i}$, $P_{k,ab}$ and $V_{j,ab}$ of a linear conjugated molecule with 10 $\pi$-electrons.

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<th>$C_{k,2}$</th>
<th>$C_{k,3}$</th>
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Fig. 6. (a) Molecular structure of $\beta$-carotene. The methyl group is represented by a line.

(b) Simplified model molecule of $\beta$-carotene. The masses $m_1$, $m_2$ and $m_3$ are represented by symbols $\circ$, $\bullet$ and $\blacksquare$, respectively. The bold and fine lines denote the double- and single-like bonds, and the force constants of them are $k_d$ and $k_s$, respectively.

with various length is excellently explained by Suzuki. The suffixes $d$ and $s$ denote the double and single bonds. Regarding the vibration, the one-dimensional model molecule in Fig. 6(b) is considerably good because the deformation of the bond angle scarcely affects bond stretching modes with high frequency, in which
we are most interested. We assume the following two force constants and masses

\[ k_x = 5.3 \times 10^5 \text{ dyne/cm}, \quad k_y = 4.0 \times 10^5 \text{ dyne/cm}, \]

\[ m_1 = 13m_p, \quad m_2 = 27m_p, \quad m_3 = 123m_p, \quad (6.5) \]

where \( m_p \) is the proton mass. The displacement parameter for each vibrational modes solved is evaluated as shown in Table III.

In this calculation, the coefficient of Coulson's relation \( \gamma \) is chosen to be 0.29, which is a little larger than the value usually used. The normal modes of the odd number labelled are antisymmetrical ones. The vibrational mode for the largest value of the displacement parameter is found to be that of the largest frequency as expected. Using these displacement parameters, we calculate the intensity distribution of the absorption spectrum following the method stated before. The result is plotted in Fig. 7 for some values of \( \Gamma \). The temperature is 80°K (55.6 cm\(^{-1}\)). From these graphs, it is found that four peaks appear with an interval of about 1480 cm\(^{-1}\), which is the highest frequency of the vibration. We also see that spectral curves vary very much for variation of \( \Gamma \). Especially, when \( \Gamma \) becomes larger than 600 cm\(^{-1}\), the position of the highest peak shifts from zero to 1500 cm\(^{-1}\). In Fig. 8, we have compared our theoretical curve for

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Table III. Vibrational frequencies and displacement parameters of our modelized \( \beta \)-carotene. Accidentally the frequency of the mode number 15 is almost the same as that of the mode number 16.
Theoretical Study of Optical Absorption Curves of Molecules. I

Fig. 7. Theoretical absorption spectra for the various values of $\Gamma$. The abscissa is the transition energy taking $\epsilon^{(9)} - \epsilon^{(10)}$ as the origin. The amplitude is taken arbitrarily.

$\Gamma = 300 \text{ cm}^{-1}$ with that of the experiment. From this we find that the position of four peaks agrees very well between them. Furthermore the intensity distribution of the four peaks in the theoretical curve qualitatively fits that of the experiment. It can be said that our theory well explains the absorption curve of $\beta$-carotene.

But our calculation so far involves some abnormal values of the parameters. One of them is that the most plausible value of $\Gamma$ is too large compared with the temperature. The others are the large value of $\gamma$ and rather small values...
of the force constants chosen. In the author's opinion, these are chiefly due to the assumption of the too simple model for the molecular structure and the neglection of the vibrational frequency shift accompanying the electronic transition, etc. In a subsequent paper, we investigate them in more detail. We have also calculated the absorption curve, varying the temperature for a fixed $\Gamma (=300 \text{ cm}^{-1})$. The result is that absorption curves little change from 0°K up to 1000°K. Experimentally the absorption curves vary very much according to the temperature. Thus we must consider that $\Gamma$ changes remarkably for the variation of the temperature. We should investigate further the meaning of $\Gamma$.

Our theory in this paper can be applied to the emission spectrum by choosing the unperturbed state as a certain excited state, and can be extended to the spectrum of the forbidden transition. It can be expected that there is a wider variety of shapes in the emission spectrum. That is, there are many emissions from high-quantum states of the vibration in the excited state. This will be seen in the emission spectrum of molecules excited by laser. It is also interesting to investigate the spectrum of the molecule which suffers from the Jahn-Teller deformation either in the excited or gound states. In a forthcoming paper, we make numerical calculation of the spectrum in respective molecules.

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Theoretical Study of Optical Absorption Curves of Molecules. I