

Charge-Transfer Molecular Compounds in Biological Systems

Sigeo YOMOSA

Department of Physics, Nagoya University, Nagoya

In order to investigate the feature of the charge-transfer molecular compound formed in biological environment, we develop a simple theory on the charge-transfer molecular compound in a local field; the polarization or the dipole moment, the binding energy and the maximum wave length and the oscillator strength of the spectrum are estimated as functions of the strength of the local field. In the biological system the local field consists of the Coulombic field due to free charges and permanent dipoles in the structural biopolymers and the reaction field due to the polarization induced in the surrounding medium by the dipole moment of the compound. By the additional effect of these two sorts of local fields the compound in biological system can be polarized strongly. Especially, an interesting phenomenon can be expected where the polarization and the absorption maximum change discontinuously for the variation of the Coulombic field or the dielectric constant of the medium. Such a strongly polarized state is considered as the first important stage of the biochemical reaction and the abrupt polarization initiated by a small change of the Coulombic field or of the dielectric constant of the surroundings seems to suggest a control mechanism in the biological functions.

§1. Introduction

The metabolic cycle of life is driven by the energy given off by the electrons which make transitions from the higher to lower levels. In the participation of enzymes the electrons transfer one by one from molecule to molecule throughout oxido-reductive series of biomolecules. To clarify the feature of these charge-transfers in biological systems is one of the essential works in quantum biophysics.

Szent Györgyi¹⁾ emphasized the role of Mulliken's charge-transfer molecular compounds in the biochemical processes and presented the existence of such compounds as tryptophan-FMN, DPNH-FMN etc.²⁾

In the biological systems the charge-transfer molecular compound is formed in a special environment constructed by the structural biopolymer, where the local fields act on the compound as shown schematically in Fig. 1. Such a local field is produced by the anionic and cationic charges q_i in the residues of amino acids of protein and by the permanent dipole moments μ_j in pe-

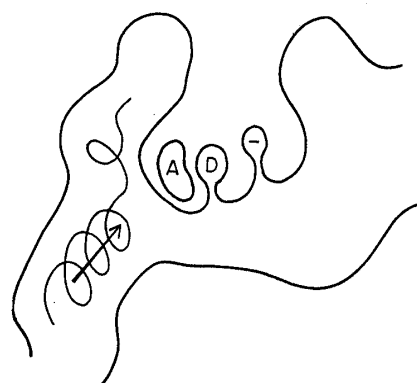


Fig. 1. Schematic model of a charge-transfer molecular compound in biological local field, where A and D represent acceptor and donor molecules of a molecular compound.

ptide groups and aromatic residues of protein and also by the dipole moments in the dielectric medium induced by the charges q_i , the dipoles μ_j and the ground state dipole moment μ_g of the molecular compound. Then the local field \mathbf{E}_L which acts upon the compound may approximately be given as the sum of the Coulombic field \mathbf{E}_C due to the charges and the dipoles in structural biopolymer surrounding the compound and the reaction field \mathbf{E}_R due to the electric displacements in a surrounding medium induced by the presence of dipole moment of the compound;

$$\begin{aligned} \mathbf{E}_L &= \mathbf{E}_C + \mathbf{E}_R, \\ \mathbf{E}_C &= -\sum_i \frac{1}{\epsilon(\rho_i)} \nabla_r \left(\frac{q_i}{\rho_i} \right) - \sum_j \frac{1}{\epsilon(\rho_j)} \frac{\rho_j^2 \mu_j - 3(\mu_j \cdot \rho_j) \rho_j}{\rho_j^5}, \\ \mathbf{E}_R &= \frac{2(\epsilon - 1)}{2\epsilon + 1} \frac{\mu_g}{a^3}, \end{aligned} \quad (1)$$

where $\rho_i = \mathbf{r}_i - \mathbf{r}$ and \mathbf{r}_i and \mathbf{r}_j are the coordinates of the charge q_i and the dipole μ_j respectively and these are given by the conformation of biopolymer, $\epsilon(\rho_i)$ denotes the static dielectric constant of the medium which may be regarded as a function of ρ_i , a is a radius of the cavity in the concept of Onsager's reaction field³⁾ and ϵ is mean static dielectric constant of the medium outside the cavity. The region except the parts belonging to the charges q_i , the dipoles μ_j and the compound are considered here as a continuous medium of dielectric constant ϵ . In the processes of the biochemical reactions the local field is controlled by the changes of pH, the temperature and the dielectric constant of the solvent.

In this paper we want to describe as simply as possible the electronic feature of charge-transfer compounds in the local field, and especially we intend to emphasize the roles of this local field in the biological functions.

When the local field acts on the compound in the direction from the acceptor molecule A to the donor molecule D, the ground state of the compound is furthermore polarized, and when the local field reaches a critical value the electronic structure of the ground state strongly changes and the dipole moment increases abruptly. In the local field exceeding the critical value the electronic structure resembles that of the excited state of the compound in no local field and this is characterized by the overwhelming weight of the charge-transfer configuration. In §2 we develop a simple theory of the charge-transfer compound in the local field and summarize the results on the local field dependencies of the quantities; the degree of polarization in the ground state, the binding energy or stabilization energy, the maximum wave length and the oscillator strength of the charge-transfer spectrum. In §3, in order to illustrate quantitatively the feature of the compound in the local field, we take well-known benzene-iodine and Try-FMN compounds as examples and make numerical estimations for the above-mentioned quantities.

In §4 we apply our theory to the biological system and investigate in detail on the local field especially on the reaction field. By virtue of a large dielectric constant of the biological medium, it is expected that the reaction field has an appreciable value and enhances the polarization of the compound. Since the effect of Coulombic and reaction fields are added in biological system it is of great advantage to realize a strongly polarized compound. By the circumstance that the local field is given as the function of μ_g which is determined with a given local field, there give rise to an interesting phenomenon that the quantities such as the polarization and the maximum wave length of absorption spectrum change discontinuously with the variation of Coulombic field or the dielectric constant of the medium.

The realization of intense polarization in the ground state without an appreciable expense of activation energy may be considered as the first step of the enzymatic oxido-reductive reaction or as the initiator of a separation of charge and hole and more generally as a cause of the allosteric effect, and the discontinuous or spontaneous increase of polarization at the critical Coulombic field or the critical dielectric constant of solvent seems to suggest an effective control mechanism in biochemical processes. From these point of view, it can be thought that the formation of the charge-transfer compound in the biological system under the action of local field constitutes an essential stage in the processes of enzymatic reaction and the compound in the local field corresponds to the ES complex in the biochemical scheme of the reaction $E + S \rightleftharpoons ES \rightarrow E + P$.

§2. Charge-transfer molecular compound in the local field

The Hamiltonian of the charge-transfer molecular compound in the local field can be written as

$$H = H^0 + V,$$

$$H^0 = H_A + H_D + V_{AD}, \quad V = V_C + V_R \quad (2)$$

with the use of the individual Hamiltonians H_A , H_D of acceptor and donor molecules, the interaction potential V_{AD} between these molecules and the potential energy V of the electrons in the compound due to the local field \mathbf{E}_L in which V_C and V_R represent the potential parts due to the permanent or Coulombic field \mathbf{E}_C and the reaction field \mathbf{E}_R respectively.

The electronic configurations of molecular compound can be represented by the antisymmetrized product functions constructed with the MO's of each component molecule A and D . In the case of Mulliken's⁴⁾ charge-transfer compound, there is a strong interaction between the nonbond configuration $\psi_1(AD)$ and the charge-transfer configuration $\psi_2(A^-D^+)$ arising from the overlap of the donor and acceptor molecular orbitals. Then, usually the wave

function Ψ of the compound is simply approximated as follows by the linear combination of the two configurations alone

$$\Psi = c_1\psi_1(AD) + c_2\psi_2(A^-D^+) \quad (3)$$

The polarization effects are not included in the above expression. If necessary, this effect can be taken into account approximately by regarding ψ_1 and ψ_2 as the first order wave functions in the perturbation by V_{AD} and V .

In order to extract the effect of local field on the molecular compounds in the simplest manner in comparison with the case of Mulliken's compounds in no local field, we treat our compound in the same approximation as that of Mulliken's treatment. Then we represent the wave function of the compound in the local field simply as a linear combination of the two interacting non-orthogonal configurations as given in Eq. (3), where we neglect the molecular polarization of component molecules and the interaction between the charge and the induced dipole as well as the London's dispersion interaction between component molecules.

The eigenvalues of the Schrödinger equation $H\Psi = E\Psi$ are given by solving the secular determinant

$$\begin{vmatrix} H_{11} - E & H_{12} - S_{12}E \\ H_{12} - S_{12}E & H_{22} - E \end{vmatrix} = 0, \quad (4)$$

where

$$H_{ij} = \int \psi_i H \psi_j d\tau, \quad S_{ij} = \int \psi_i \psi_j d\tau. \quad (5)$$

We approximate the matrix elements and the overlap integral as follows by using the matrix elements in zero local field which are represented by the superscripts zero;

$$\begin{aligned} H_{11} &\simeq H_{11}^0 + V_{11} \simeq H_{11}^0, & H_{22} &\simeq H_{22}^0 + V_{22} \equiv H_{22}^0 + \mathcal{V}, \\ H_{12} &\simeq H_{12}^0, \text{*)} & S_{12} &\simeq S_{12}^0 \equiv S. \end{aligned} \quad (6)$$

Here $\mathcal{V} \equiv V_{22} < 0$ represents the potential energy when the compound takes the structure $\psi_2(A^-D^+)$ in the local field and this is approximated by the quantity;

$$\mathcal{V} \simeq -e \int_{\langle r_A \rangle}^{\langle r_D \rangle} \mathbf{E}_L(\mathbf{r}) \cdot d\mathbf{r}, \quad (7)$$

where $\langle r_A \rangle$ and $\langle r_D \rangle$ are geometrical centers of acceptor and donor molecules respectively. Inserting (6) into (4) we obtain the energy E_1 of the ground state $\Psi_1 = c_{11}\psi_1 + c_{12}\psi_2$ and that E_2 of excited state $\Psi_2 = c_{21}\psi_1 + c_{22}\psi_2$ as the functions of \mathcal{V} as follows:

*) Following Mulliken's approximation, H_{12} may be expressed as follows: $H_{12} \simeq H_{12}^0 + V_{12} \simeq H_{12}^0 + S(V_{11} + V_{22})/2 \simeq H_{12}^0 + S\mathcal{V}/2$, but we neglect the term $S\mathcal{V}/2$. By this neglect the numerical results are not influenced appreciably.

$$\left. \begin{matrix} E_1 \\ E_2 \end{matrix} \right\} = \left. \begin{matrix} E_- \\ E_+ \end{matrix} \right\} = H_{11}^0 + \frac{1}{2(1-S^2)}(\gamma + \mathcal{V}) \mp \sqrt{(\gamma + \mathcal{V})^2 + 4(1-S^2)\beta^2}, \quad (8)$$

where

$$\gamma = \alpha - 2\beta S; \quad \alpha = H_{22}^0 - H_{11}^0, \quad \beta = H_{12}^0 - H_{11}^0 S. \quad (9)$$

Then the binding or the stabilization energy is given as follows:

$$W = H_{11}^0 - E_1 = -\frac{1}{2(1-S^2)} \left[(\gamma + \mathcal{V}) - \sqrt{(\gamma + \mathcal{V})^2 + 4(1-S^2)\beta^2} \right]. \quad (10)$$

In Fig. 2 the matrix elements H_{11} and H_{22} , the eigenvalues E_1 and E_2 and the binding energy W are plotted as the function of \mathcal{V} , where the curves E_1 , E_2 are obtained from (8) by using the parameter values for benzene-iodine compound; $\gamma = 4.15$ eV, $\beta = -0.50$ eV, which will be estimated in §3. Two lines H_{22} and H_{11} intersect at $\mathcal{V} = -\alpha$ where the ground and excited states have equal weights of two configurations;

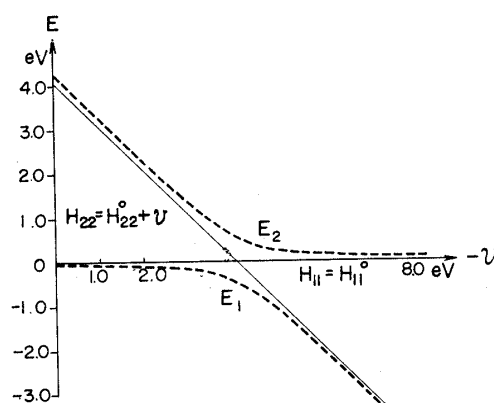


Fig. 2. Matrix elements H_{11} and H_{22} and eigenvalues E_1 and E_2 are plotted as the function of \mathcal{V} .

$$\begin{aligned} \psi_1 &= \frac{1}{\sqrt{2(1+S)}}(\psi_1 + \psi_2), & E_1 &= \frac{1}{1+S}(H_{11}^0 + H_{12}^0), \\ \psi_2 &= \frac{1}{\sqrt{2(1-S)}}(\psi_1 - \psi_2), & E_2 &= \frac{1}{1-S}(H_{11}^0 - H_{12}^0). \end{aligned} \quad (11)$$

The ratios of the coefficients of the wave functions of ground and excited states; $k_g = c_{12}/c_{11}$ and $k_e = c_{22}/c_{21}$, are given as the function of \mathcal{V} ;

$$\begin{aligned} k_g &= \frac{(\gamma + \mathcal{V}) - \sqrt{(\gamma + \mathcal{V})^2 + 4(1-S^2)\beta^2}}{2(1-S^2)\beta - S[(\gamma + \mathcal{V}) - \sqrt{(\gamma + \mathcal{V})^2 + 4(1-S^2)\beta^2}]}, \\ k_e &= \frac{(\gamma + \mathcal{V}) + \sqrt{(\gamma + \mathcal{V})^2 + 4(1-S^2)\beta^2}}{2(1-S^2)\beta - S[(\gamma + \mathcal{V}) + \sqrt{(\gamma + \mathcal{V})^2 + 4(1-S^2)\beta^2}]}. \end{aligned} \quad (12)$$

The dipole moment of the ground and excited states can be written as

$$\begin{aligned} \mu_g &= c_{11}^2 \mu_1 + c_{12}^2 \mu_2 + 2c_{11}c_{12} \mu_{12}, \\ \mu_e &= c_{21}^2 \mu_1 + c_{22}^2 \mu_2 + 2c_{21}c_{22} \mu_{12}, \end{aligned} \quad (13)$$

where

$$\mu_1 = \int \psi_1 \mathbf{M} \psi_1 d\tau, \quad \mu_2 = \int \psi_2 \mathbf{M} \psi_2 d\tau, \quad \mu_{12} = \int \psi_1 \mathbf{M} \psi_2 d\tau. \quad (14)$$

Here $\mathbf{M} = \sum_{\mu} Z'_{\mu} e \mathbf{R}_{\mu} - \sum_i e \mathbf{r}_i$ is the dipole moment operator in which Z'_{μ} , R_{μ} and \mathbf{r}_i are the effective charges of ion cores, the nuclear coordinates and the electron coordinates of the compound. Using the normalization conditions $(\Psi_i, \Psi_i) = 1$ and approximating as $\mu_1 \approx 0$, $\mu_2 - \mu_1 \approx e(\mathbf{r}_D - \mathbf{r}_A)$, $\mu_{12} - \mu_1 S \approx eS(\mathbf{r}_D - \mathbf{r}_{AD})$ with the use of $\mathbf{r}_{AD} = (\mathbf{r}_A + \mathbf{r}_D)/2$, we obtain

$$\begin{aligned} \mu_g &\approx c_{12}^2 e(\mathbf{r}_D - \mathbf{r}_A) + 2c_{11}c_{12} S e(\mathbf{r}_D - \mathbf{r}_{AD}), \\ \mu_e &\approx c_{22}^2 e(\mathbf{r}_D - \mathbf{r}_A) + 2c_{21}c_{22} S e(\mathbf{r}_D - \mathbf{r}_{AD}). \end{aligned} \quad (15)$$

With the increase of the local field or the potential energy $(-\mathcal{V})$, the quantities k_g^2 and μ_g increase and near $\mathcal{V} = -\alpha$ these quantities show such rapid increases as shown in Fig. 3.

The excitation energy or the absorption maximum of the charge-transfer spectrum is given by

$$h\nu = E_2 - E_1 = \frac{1}{1-S^2} \sqrt{(\gamma + \mathcal{V})^2 + 4(1-S^2)\beta^2}. \quad (16)$$

This represents a hyperbola in the $h\nu - \mathcal{V}$ plane as shown in Fig. 4;

$$\frac{(h\nu)^2}{\left(\frac{4\beta^2}{1-S^2}\right)} - \frac{\gamma + \mathcal{V}}{4(1-S^2)\beta^2} = 1. \quad (17)$$

With the increase of the local field the absorption spectrum shows a red shift, but on further increase this change into a blue shift. The turning occurs at $-\mathcal{V} = \gamma \approx \alpha$ ($\gamma > \alpha > 0$).

The transition dipole moment of charge-transfer spectrum can be written as

$$\mathbf{M}_{C-T} = c_{11}c_{21}\mu_1 + c_{12}c_{22}\mu_2 + (c_{21}c_{12} + c_{11}c_{22})\mu_{12}. \quad (18)$$

Using the orthogonal condition $(\Psi_1, \Psi_2) = 0$, we obtain

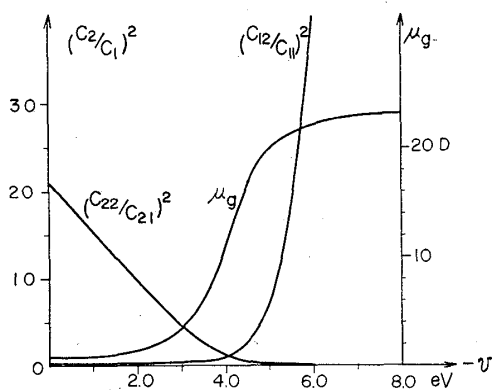


Fig. 3. Local field dependence of $(c_2/c_1)^2$ and μ_g in benzene-iodine compound.

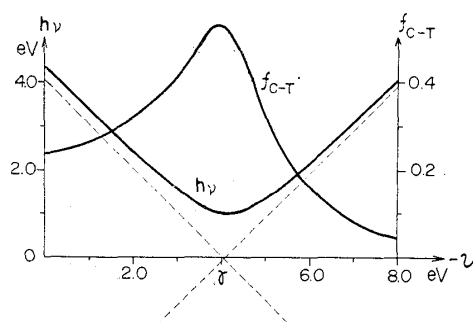


Fig. 4. Local field dependence of $h\nu$ and f_{C-T} of the charge-transfer spectrum in benzene-iodine compound.

$$\begin{aligned} M_{C-T} &= c_{12}c_{22}(\boldsymbol{\mu}_2 - \boldsymbol{\mu}_1) + (c_{21}c_{12} + c_{11}c_{22})(\boldsymbol{\mu}_{12} - S\boldsymbol{\mu}_1) \\ &\simeq c_{12}c_{22}e(\mathbf{r}_D - \mathbf{r}_A) + (c_{21}c_{12} + c_{11}c_{22})Se(\mathbf{r}_D - \mathbf{r}_{AD}). \end{aligned} \quad (19)$$

Then the oscillator strength are given as

$$f_{C-T} = 0.379 \times 10^{-2} (E_2 - E_1) M_{C-T}^2, \quad (20)$$

where $E_2 - E_1$ and M are expressed in eV and Debye unit respectively. With the increase of the local field f_{C-T} increases first and reaches the maximum at the turning point and then decreases as shown in Fig. 4.

§3. Numerical estimation

Since many theoretical and experimental studies for benzene-iodine compound in zero local field have been carried out, we take first this compound to illustrate the quantitative feature of the charge-transfer compound in the local field. Using the parameter values obtained in this case, we make the numerical calculation on the local field dependences of the various quantities mentioned before by assuming that the local field acts on the compound in the direction satisfying an inequality $\overrightarrow{AD} \cdot \mathbf{E}_L > 0$.

In the case of no local field; $\mathcal{V} = 0$, two simultaneous equations can be obtained from Eqs. (16) and (10);

$$\begin{aligned} (1 - S^2)h\nu &= \sqrt{\gamma^2 + 4(1 - S^2)\beta^2}, \\ (1 - S^2)(h\nu - 2W) &= \gamma. \end{aligned} \quad (21)$$

Assuming the value $S \simeq 0.1$ for the overlap integral in reference to Mulliken's estimation⁴⁾ $S = 0.1$ and Aono's value⁵⁾ $S = 0.11$ calculated for the model of axial symmetry C_{6v} , and using the experimental value of absorption maximum $h\nu = 4.31$ eV⁶⁾ and of the binding energy $W = 0.060$ eV,⁷⁾ we can solve the Eq. (21) and obtain the values $\gamma = 4.15$ eV and $\beta = -0.50$ eV. From these values we find $H_{22}^0 - H_{11}^0 = 4.05$ eV. Inserting this value for α and the experimental value for the ionization potential of benzene $I_p(D) = 9.24$ eV⁸⁾ and the mean distance between benzene and iodine $\langle r_{AD} \rangle = 4.80$ Å⁹⁾ into the following relation:

$$H_{22}^0 - H_{11}^0 = -E_A(A) + I_p(D) - \frac{e^2}{\langle r_{AD} \rangle}, \quad (22)$$

we obtain the value of the electron affinity of iodine $E_A(A) = 2.19$ eV which is compared with the value 1.8 eV estimated by Mulliken.⁴⁾ Moreover, using Eqs. (12), (15), (19) and (20) together with normalization condition, the values of the dipole moment and the oscillator strength in no local field are calculated as $\mu_g(\mathcal{V} = 0) = 0.59$ D and $f_{C-T}(\mathcal{V} = 0) = 0.24$, which are compared with the slightly larger values $\mu_g = 0.94$ D and $f_{C-T} = 0.34$ estimated by Aono.⁵⁾ These values are in fairly good agreement with experimental

ones; $\mu_g^{(\text{exp})} = 0.72 D$ and $f_{c-T}^{(\text{exp})} = 0.30$. Then our parameter values γ and β seem to be reasonable.

Using these α and β we can evaluate the following quantities as the function of $\mathcal{C}\mathcal{V}$. The energies of the ground and the excited states and the stabilization energy are obtained from Eqs. (8) and (10) respectively and these results are shown in Fig. 2. The ratio of the coefficients in the wave functions k_g , k_e and the ground state dipole moment are calculated from Eqs. (12) and (15) and the results are shown in Fig. 3. The absorption maximum of charge-transfer spectrum and the oscillator strength are calculated from Eqs. (16) or (17), (19) and (20) respectively and the results are shown in Fig. 4.

Next we take FMN-Try as an example of the biological compound. We suppose that the compound is formed with a parallel arrangement of molecular planes of these component molecules and the distance between acceptor (FMN) and donor (Try) is assumed as 3.3 \AA . And we suppose the local field acts on the compound along the direction \overrightarrow{AD} perpendicular to the planes of the molecules and we consider only the polarization of the compound in this direction.

The diagonal matrix elements for this compound are estimated as follows:

$$\begin{aligned} H_{11} &= E_A + E_D + (V_{AD})_{11} + V_{11} \simeq H_{11}^0, \\ H_{22} &= E_{A^-} + E_{D^+} + (V_{AD})_{22} + V_{22} \\ &= H_{11} + (E_{A^-} - E_A) + (E_{D^+} - E_D) \\ &\quad + (V_{AD})_{22} - (V_{AD})_{11} + (V_{22} - V_{11}) \\ &\simeq H_{11}^0 - E_A(A) + I_p(D) - \frac{e^2}{\langle r_{AD} \rangle} + \mathcal{C}\mathcal{V}, \end{aligned} \quad (23)$$

where E_A , E_{A^-} and E_{A^+} denote the total Hartree-Fock energies of π -electrons in the molecule A in the neutral, negative radical and positive-hole configurations respectively, and these are calculated by means of ASMO SCF method.* From our calculation we estimate the values $E_A(A) = E_A - E_{A^-} = 3.0 \text{ eV}$ and $I_p(D) = E_{D^+} - E_D = 10.5 \text{ eV}$. From these values we obtain $\alpha = H_{22}^0 - H_{11}^0 \simeq 3.13 \text{ eV}$. Then as a reasonable value of the interaction parameter β we try to assume alternate values $\beta = -0.30 \text{ eV}$ and -0.50 eV . Then, assuming $S=0.1$, we have two sets of parameters;

$$\begin{aligned} \text{case (a)} \quad & \gamma = 3.19 \text{ eV}, \quad \beta = -0.30 \text{ eV}, \quad S = 0.1; \\ \text{case (b)} \quad & \gamma = 3.23 \text{ eV}, \quad \beta = -0.50 \text{ eV}, \quad S = 0.1. \end{aligned}$$

Now we can calculate the quantities k_g^2 , μ_g , $h\nu$ and f_{c-T} as the functions of $-\mathcal{C}\mathcal{V}$ by making use of the Eqs. (12), (15), (16) and (20) respectively.

* The author is indebted to Mr. T. Miyata of Waseda University in programming of MO calculations.

These results are plotted in Figs. 5 and 6. In both cases of benzene iodine and FMN-Try the rapid increase of μ_g and the turning from a red to a blue shift of the charge-transfer spectra can be seen at the region near $\mathcal{C}\mathcal{V} = -\gamma$. We can find a strong polarization and a remarkable change of the maximum wave length of absorption spectrum compared with the case of no local field;

in the case (a)

$$\begin{aligned} \mu_g(\mathcal{C}\mathcal{V}=0) &\equiv \mu_g^0 = 0.29 \text{ D}, \\ h\nu(\mathcal{C}\mathcal{V}=0) &\equiv h\nu^0 = 3.28 \text{ eV} \\ &\quad (379 \text{ m}\mu); \end{aligned}$$

in the case (b)

$$\begin{aligned} \mu_g^0 &= 0.60 \text{ D}, \\ h\nu^0 &= 3.41 \text{ eV} (364 \text{ m}\mu). \end{aligned}$$

In order to grasp the potential energy $\mathcal{C}\mathcal{V}$ without any considerations about the surrounding dielectric medium we consider simply a local field caused by an anionic charge which is $x \text{ \AA}$ apart from Try in the arrangement $A \leftarrow 3.3 \text{ \AA} \rightarrow D \leftarrow x \text{ \AA} \rightarrow \ominus$, and we mark on an axis parallel to $-\mathcal{C}\mathcal{V}$ -axis in Figs. 5 and 6 the values of x related with the values of $-\mathcal{C}\mathcal{V}$ by the equation $-\mathcal{C}\mathcal{V} = e^2/x - e^2/(\langle r_{AD} \rangle + x)$.

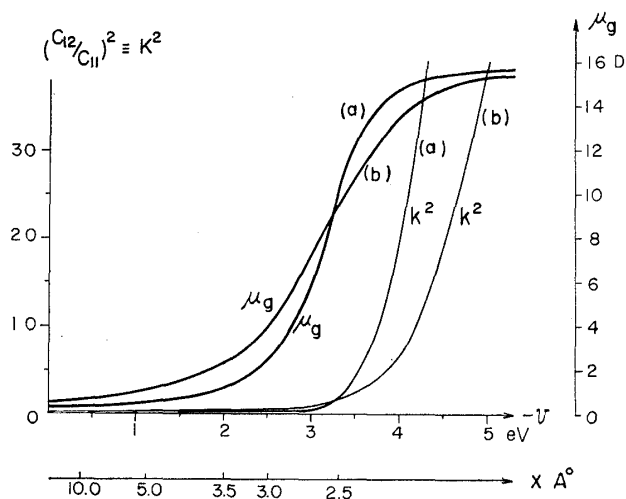


Fig. 5. Local field dependence of $(c_2/c_1)^2$ and μ_g in FMN-Try compound.

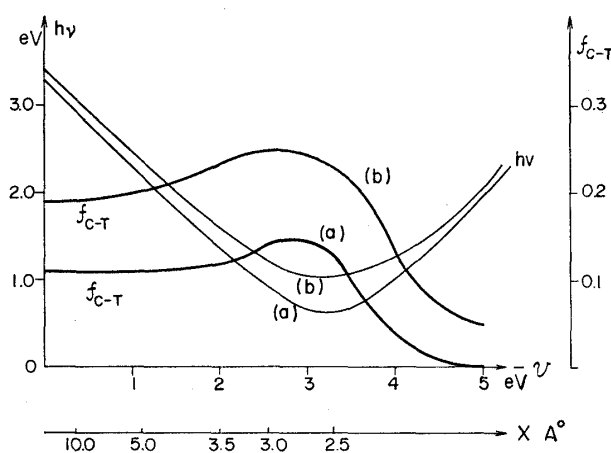


Fig. 6. Local field dependence of $h\nu$ and f_{C-T} in the charge-transfer spectrum of FMN-Try compound.

§4. Charge-transfer molecular compound in the biological system

On applying the idea of the local field to the biological system, we must consider now explicitly the polarization effect of the surrounding medium which is similar to the concept of some solvent effect^{(11)~(13)} in chemistry, and we will refine our local field theory on charge-transfer compound. In order to take account of the dielectric effect of the biological medium we can use the concept of Onsager's reaction field³⁾ E_R obtained by scooping out in the

medium a spherical cavity of radius a surrounding the compound. The reaction field arising from the dipole moments in the surrounding dielectric medium induced by the dipole μ_g of the compound is given by \mathbf{E}_R in Eq. (1). Since the local field which acts on the compound can be given by the sum of the Coulombic field \mathbf{E}_C and the reaction field \mathbf{E}_R , the potential of the electrons in the compound in the local field can be correspondingly expressed as the sum of two parts $V = V_C + V_R$. Then the diagonal matrix element of the potential corresponding to the structure $\psi_2(A^-D^+)$ can be given by

$$\mathcal{V} = V_{22} = (V_C)_{22} + (V_R)_{22} = \mathcal{V}_C + \mathcal{V}_R = \mathcal{V}_C - \mu_2 \mathbf{E}_R(\mu_g),^*) \quad (24)$$

or in the form

$$-\mathcal{V} = \phi(\mu_g; \mathcal{V}_C, \lambda) \equiv -\mathcal{V}_C + \lambda \mu_g, \quad (25)$$

where

$$\lambda(\epsilon) = \frac{2(\epsilon - 1)}{2\epsilon + 1} \frac{\mu_2}{a^3}. \quad (26)$$

In the $\mathcal{V} - \mu_g$ plane we have a group of lines corresponding to different values of $-\mathcal{V}_C$ and λ . Here \mathcal{V}_C is calculated from given \mathbf{E}_C as

$$\mathcal{V}_C = -e \int_{(r_A)}^{(r_D)} \mathbf{E}_C \cdot d\mathbf{r} \quad (27)$$

and this value can be changed by pH, the temperature etc. of the medium. The slope λ of the line (25) is given by the function of the dielectric constant ϵ of the medium and this varies with the polarity of the solvent.

Here we must notice that for a certain value of \mathcal{V} , we can solve the secular equation and find μ_g , then inserting it into (25), we obtain \mathcal{V} and this must agree with its initially assumed value. This condition of consistency leads to find the value of μ_g for a given \mathcal{V}_C and λ . In fact, μ_g can be determined by means of Eqs. (13) or (15) and is expressed in terms of \mathcal{V} , or inversely $-\mathcal{V}$ can be expressed as a function of μ_g in the form

$$-\mathcal{V} = \varphi(\mu_g). \quad (28)$$

We can decide μ_g as well as \mathcal{V} simultaneously by finding the intersection point of the line (25) and the curve (28) on the $\mathcal{V} - \mu_g$ plane.

The concrete process of solving the problem is carried out as follows. From the secular equation

$$\begin{aligned} -\epsilon + (\beta - S_\epsilon)k &= 0, \\ (\beta - S_\epsilon) + (-\epsilon + \alpha + \mathcal{V})k &= 0 \end{aligned} \quad (29)$$

we obtain the relation

*^o If we assume that a uniform local field acts on the compound in the direction AD , the potential V can be expressed as $V = -\mathbf{M} \cdot \mathbf{E}_L$, then \mathcal{V} can be given by $\mathcal{V} = V_{22} = -(\psi_2, \mathbf{M} \psi_2) \cdot \mathbf{E}_L = -\mu_2 \cdot \mathbf{E}_L = -\mu_2(E_C + E_R)$.

$$\beta + (\alpha + \mathcal{C}\mathcal{V})k + \{-\beta + S(\alpha + \mathcal{C}\mathcal{V})\}k^2 = 0, \quad (30)$$

where $-\varepsilon = H_{11}^0 - E$, $k = k_g = c_{12}/c_{11}$. Concerning the normalization condition the ground state dipole moment is given by (13); viz.

$$\mu_g = c_{12}^2 \mu_2 + 2c_{11}c_{12} \mu_{12} = \frac{k}{1 + 2Sk + k^2} (k\mu_2 + 2\mu_{12}). \quad (31)$$

Then, $\mathcal{C}\mathcal{V}$ can be expressed as

$$\mathcal{C}\mathcal{V} = \mathcal{C}\mathcal{V}_c - \lambda\mu_g = \mathcal{C}\mathcal{V}_c - \frac{\lambda k(k\mu_2 + 2\mu_{12})}{1 + 2Sk + k^2}. \quad (32)$$

Equations (30) and (32), which correspond to Eqs. (28) and (25), constitute a set of simultaneous equations to decide $\mathcal{C}\mathcal{V}$ and μ_g , viz.

$$\begin{aligned} -\mathcal{C}\mathcal{V} &= \xi(k) = \frac{\beta + \alpha k - (\beta - S\alpha)k^2}{k(1 + Sk)}, \\ -\mathcal{C}\mathcal{V} &= \eta(k) = -\mathcal{C}\mathcal{V}_c + \frac{\lambda k(2\mu_{12} + k\mu_2)}{1 + 2Sk + k^2}. \end{aligned} \quad (33)$$

Using the root of the equation $\xi(k) = \eta(k)$, which can be solved numerically, we obtain from (31) the consistent value of μ_g for a given set of $\mathcal{C}\mathcal{V}_c$ and $\lambda(\varepsilon)$.

We illustrate the nature of the solution by showing the results of numerical calculation for the compound FMN-Try with the parameter values in the

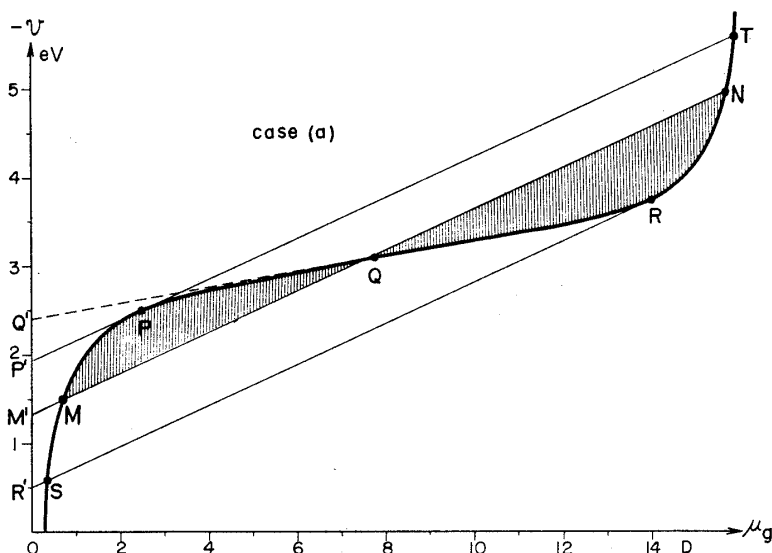


Fig. 7. $-\mathcal{C}\mathcal{V}$ versus μ_g ; the curve $-\mathcal{C}\mathcal{V} = \varphi(\mu_g)$ and the lines $-\mathcal{C}\mathcal{V} = -\mathcal{C}\mathcal{V}_c + \lambda\mu_g$ are drawn. The consistent solution is obtained by the intersection of two curves.

case (a). In Fig. 7 the curve $-\mathcal{C}\mathcal{V} = \varphi(\mu_g)$ and the lines $-\mathcal{C}\mathcal{V} = \phi(\mu_g)$ for this compound are drawn. Denoting by $\lambda^* = \varphi'(\mu_g^*)$ the slope of the tangent at the inflexion point $Q(-\mathcal{C}\mathcal{V}^*, \mu_g^*)$ of the curve, two cases should be distinguished:

$$(i) \quad \lambda \leq \lambda^*, \quad (ii) \quad \lambda > \lambda^*,$$

where $\lambda = \lambda^*$ is satisfied with the value $\epsilon^* = 1.45$.*) In the former case (i) where the medium has a value of dielectric constant smaller than critical one $\epsilon \leq \epsilon^*$, we have one intersecting point for each line $\phi(\mu_g; \mathcal{V}_c)$ with different values of \mathcal{V}_c . The value of μ_g is determined continuously with the variation of \mathcal{V}_c , then the relation between μ_g and $-\mathcal{V}_c$ is similar to that of μ_g versus \mathcal{V} as shown in Fig. 8. In this case the reaction field only slightly make the effect due to the Coulombic field \mathbf{E}_c increase.

In the latter case (ii) where the medium has a value of dielectric constant larger than critical one $\epsilon \geq \epsilon^*$, an interesting circumstance arises. When we denote by RR' and PP' in Fig. 8 the two parallel tangents of the curve $\phi(\mu_g)$ with a given slope $\lambda(\epsilon)$ and by R' and P' the points where the tangents RR' and PP' cut the \mathcal{V} -axis respectively, each line with same slope in the region below RR' and beyond PP' intersects with the curve at one point and each line being in the region between PP' and RR' intersects with the curve at three points; these three regions correspond respectively to three ranges; $-\mathcal{V}_c < R'$, $-\mathcal{V}_c > P'$ and $R' < -\mathcal{V}_c < P'$. Among three solutions corresponding to a given value of \mathcal{V}_c in the range $R' < -\mathcal{V}_c < P'$, the most stable one is determined by the minimum condition of free energy. The Gibbs' free energy G of the total system which consists of the compound and the surrounding medium is given by the sum of the free energies G_1 of the compound, G_{12} due to the interaction between compound and medium and G_2 of the medium. The sum of the former two parts and the latter are given respectively by

$$G_1 + G_{12} = - \int_{E_C}^{E_L} \mu_g dE_L = - \frac{1}{\mu_2} \int_{-\mathcal{V}_c}^{-\mathcal{V}} \mu_g d(-\mathcal{V}), \quad (34)$$

$$G_2 = \frac{1}{2} \mu_g E_R = \frac{1}{\mu_2} \left[\frac{1}{2} \mu_g (-\mathcal{V}_R) \right]. \quad (35)$$

Denoting the total free energy in the state M by $G((E_L)_M) \equiv G(M)$, we can show that $G(M) = G(N)$ when the relation of equal area holds and both states M and N correspond to the minimum points of free energy.

) Here we have assumed rather small value of $a = 3.0 \text{ \AA}$, then the effect of reaction field may be overestimated. When we assume $a = 4.0 \text{ \AA}$, we have $\epsilon^ = 2.81$.

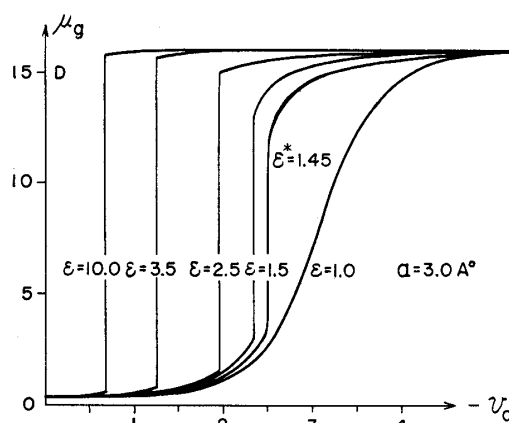


Fig. 8. $-\mathcal{V}_c$ -dependence of μ_g for various values of ϵ . At $\epsilon = \epsilon^*$ the jumping of μ_g disappears.

When $-\mathcal{V}_c$ reaches M' the value of μ_g jumps from $(\mu_g)_M$ to $(\mu_g)_N$ which represent the values of μ_g corresponding to the points M and N respectively. We show in Fig. 8 the quantity μ_g as a function of $-\mathcal{V}_c$ for various values of ϵ .

In preceding two sections we have studied generally the local field dependence of the quantities such as μ_g , $h\nu$, f_{c-T} etc. as functions of \mathcal{V} , but it must be noticed here that for the polar medium with $\epsilon \gg \epsilon^*$ the values of these quantities cannot exist for the values of $(-\mathcal{V})$ being in the region $(-\mathcal{V})_M < (-\mathcal{V}) < (-\mathcal{V})_N$. Then, when we plot these quantities as functions of $(-\mathcal{V}_c)$ we can see that a jump for μ_g and a discontinuity for $h\nu$ appear at $-V_c = M'$. Figure 9 shows the $(-\mathcal{V}_c)$ -dependence of $h\nu$ for various values of ϵ .

In the above we have considered the \mathcal{V}_c -dependence of μ_g or $h\nu$ by fixing the value of ϵ . Similarly we can study the ϵ -dependence of the quantities μ_g , $h\nu$, etc. by fixing the value of \mathcal{V}_c . Here, two cases are distinguished:

- (i) $-\mathcal{V}_c \leq Q'$, (ii) $-\mathcal{V}_c > Q'$.

In the former, we have different number of intersections with the curve according with the slope of the line and we can investigate on the solution in a similar way that we have made previously. There appears a jump for μ_g at a certain critical value of ϵ . At this critical value the parameter $\lambda(\epsilon)$ given by (26) becomes equal to the slope of the line $\overline{R'Q}$ in Fig. 7, where OR' represent the value of $-\mathcal{V}_c$.

Recently Oshika¹⁴⁾ has pointed out such a solvent effect accompanying similar jump. In Figs. 10 and 11 we plot the ϵ -dependence of μ_g and $h\nu$ respectively for various values of $-\mathcal{V}_c$ in which the jumps or discontinuities disappear at $-\mathcal{V}_c^* = Q' = 2.45$ eV. Assuming

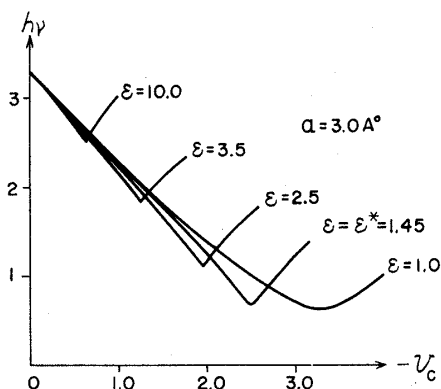


Fig. 9. $-\mathcal{V}_c$ -dependence of $h\nu$ for various values of ϵ . At $\epsilon = \epsilon^*$ the discontinuity disappears.

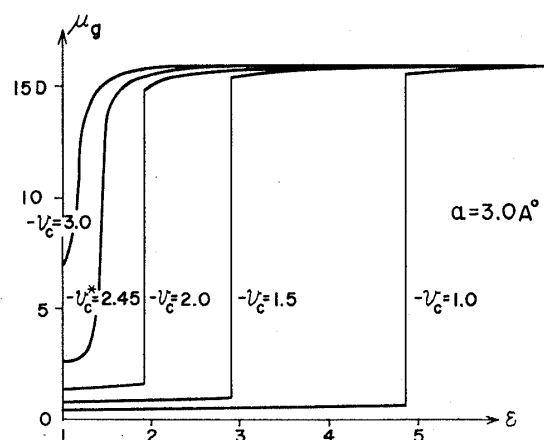


Fig. 10. ϵ -dependence of μ_g for various value of $-\mathcal{V}_c$. At $-\mathcal{V}_c = -\mathcal{V}_c^*$ the jump of μ_g disappears.

that the mean dielectric constant of biological medium is about 3.0~3.5, it may be expected from Fig. 8 or Fig. 10 that a strongly polarized state of the compound may be realized with the Coulombic potential of the order of 1.0 eV and this order of Coulombic local field can be obtained by the single anionic charge at $x \approx 5 \text{ \AA}$ in the arrangement of FMN-Try $\leftarrow x \rightarrow \ominus$.

The spontaneous jumping described above seems to have certain important biological implications. By a small increase of the Coulombic field controlled by changing of pH or the polarity of the medium, an abrupt and drastic change of polarization of the molecular compound can be realized and these polar state may be coupled with a successive oxido-reductive reactions or a allosteric change in the proteins.

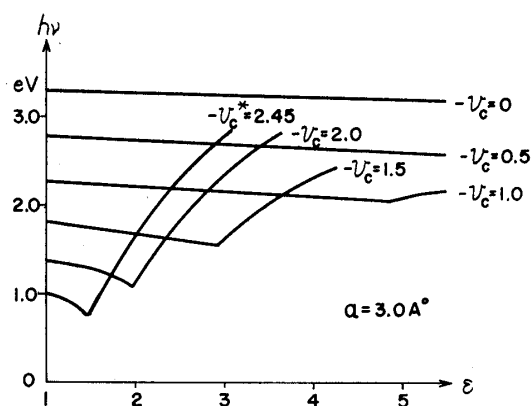


Fig. 11. ϵ -dependence of $h\nu$ for various values of $-V_C$. At $-V_C = -V_C^*$ the discontinuity disappears.

§5. Discussion

As a simple source of Coulombic local field and in order to show the order of magnitude of possible Coulombic field, we took previously an anionic charge of amino acid residue near the compound. As another possible source of the Coulombic local field we can consider a set of permanent dipoles of peptide groups in ordered arrangement. Then it is biologically important to show the order of magnitude of such a dipole field. The estimation of this can be obtained from the results of the calculation made by Arridge and Cannon¹⁵⁾ on the energy of dipole interaction for the α -helical and β -form polypeptides; for example, the interaction energy of a dipole in the α -helix of poly-L-alanine is given in converging limit by $W = -0.016\mu^2 \times 10^{24}$ ergs. Assuming the magnitude of a dipole as $\mu = 3.9$ debyes,¹⁵⁾ we can expect the helix field at the dipole in question of the order of magnitude $E_c^{\text{helix}} \approx 0.062 \times 10^6$ (cgs esu), then the corresponding potential energy $-V_c^{\text{helix}} \approx -e\langle r_{AD} \rangle E_c \approx 0.99$ eV. Therefore at a position in the molecular compound too a considerable amount of local field can be expected.

In order to clarify the existence of the local field effect in biological system it is hoped to look for some experimental verifications for some model systems. As a simplest model of the charge-transfer molecular compound in the local field, we can consider a solution in which solute molecules consist of FMN and dimer of amino acid. Dimer may be tryptophan-aspartic acid as an example. Then our system symbolized as FMN-Try- \ominus . A verification will be obtained by comparing our theoretical predictions

with the experimental measurements on the local field dependence of the absorption spectrum of such a simple model system.

A Coulombic local field can be produced in this model by the anionic charge of aspartic acid. The proton dissociation in this acid is controlled by pH of the solvent. It is expected from Fig. 9 that in the alkaline side of the solvent we shall have a red-shifted wave length and a more intense absorption spectrum. The theoretical plots of f_{c-T} versus $-V_c$ and f_{c-T} versus ϵ can be obtained easily, though these are not shown in our figures.

The local reaction field may be controlled by changing the polarity of the solvent, for example by diluting the non-polar or poor-polar substance with water. It is expected from Fig. 11 that there is a red shift and then successive weak blue shift on going from a polar to a non-polar solvent. These experiments on the model system are being planned in our laboratory.

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