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RPA Method Applied to Molecular Crystals

Masashi Tanaka and Jiro Tanaka

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, 464, Nagoya, Japan

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A new theory is presented on the excited states of molecular crystals by using the random phase approximation (RPA). The method is applied to the analysis of the absorption spectrum of anthracene crystal. The Davydov splitting for the long axis polarized band is calculated as about 9200 cm^{-1} while the observed value is 9000 ~ 12000 cm^{-1}. In the earlier theories, much larger values are reported and a simple dipole-dipole approximation gives the value of 32000 cm^{-1}. The general feature of the crystalline spectra is well predicted.

Es wird eine neue Theorie der angeregten Zustände von Molekülkristallen vorgelegt, die mit Hilfe des RPA-Verfahrens gewonnen wurde. Die Methode wird zur Interpretation des Absorptionsspectrums von Anthracenkristallen verwendet. Die Davydow-Aufspaltung des polarisierten Bandes (lange Achse) wird mit 9200 cm^{-1} berechnet (der beobachtete Wert beträgt 9000 ~ 12000 cm^{-1}). Nach den älteren Theorien erhält man viel größere Werte, und eine einfache Dipol-Dipol-Approximation liefert 32000 cm^{-1}. Das charakteristische Bild des kristallinen Spektrums wird gut wiedergegeben.

1. Introduction

The theory of the random-phase (RPA) approximation widely used in nuclear and solid state physics has been applied to the study of electronic correlation in molecules [1–2]. The method uses the Bose second quantization for the electron-hole pair to describe the excited state and the excitation energy is given by diagonalizing the Hamiltonian matrix for these sets. It covers the effect of electron correlation than earlier theories and gives better results in the calculation of energy and oscillator strength of complex molecules.

In the study of the molecular exciton states, Agranovitch [3–4] was the first who used the second quantized version of the electron-hole pair Hamiltonian. Although a formal theoretical treatment has been published, actual calculations by this method has not been appeared as yet. Philpott [5] derived a similar equation as Agranovitch [3] starting from a classical theory of light and investigated the contribution of dipole-dipole interactions to the Davydov splitting of anthracene, tetracene, naphthalene and phenanthrene crystals.

In our previous paper [6] an alternative new approach was presented to the analysis of the electronic absorption spectra of molecular crystal, in which the crystal exciton configuration is constructed from the one-electron excited configurations of the SCF molecular orbitals in the constituent molecules and the mixing between the different exciton configurations has been taken into account using the complete Hamiltonian of the crystal. In the present paper, we consider the effect of electron correlation by using the RPA method and derive the equation which is non-Hermitian. The equation is applied to the calculation of excited states of anthracene molecule and crystal [7].

2. Theory

The Hamiltonian for a crystal containing N unit cells and σ identical molecules per unit cell may be written by

$$\mathscr{H} = \sum_{\mu} \left\{ -\frac{\hbar^2}{2m} \Delta_\mu + \sum_{p\alpha a} V(\boldsymbol{R}_{p\alpha a} - \boldsymbol{r}_\mu) \right\} + \frac{1}{2} \sum_{\mu\nu}{}' \frac{e^2}{r_{\mu\nu}} \tag{1}$$

where the summation is taken over all π-electrons in the σ N molecules of the crystal and the prime in the third summation indicates that the terms for which $\mu = \nu$ is omitted. $V(\boldsymbol{R}_{p\alpha a} - \boldsymbol{r}_\mu)$ is the attraction potential energy between the μ-th electron and the a-th core atom at the α-th site of the p-th unit cell and $e^2/r_{\mu\nu}$ is the electrostatic repulsion between π-electrons μ and ν. Then, the Hamiltonian of electron field in the second quantized form is:

$$\begin{aligned} \mathscr{H} &= \int \psi^*(\mu) \left\{ -\frac{\hbar^2}{2m} \Delta_\mu + \sum_{p\alpha a} V(\boldsymbol{R}_{p\alpha a} - \boldsymbol{r}_\mu) \right\} \psi(\mu)\, d\tau_\mu \\ &\quad + \frac{1}{2} \iint \psi^*(\mu)\, \psi^*(\nu) \frac{e^2}{r_{\mu\nu}} \psi(\nu)\, \psi(\mu)\, d\tau_\mu\, d\tau_\nu \end{aligned} \tag{2}$$

where $\psi^*(\mu)$ and $\psi(\mu)$ are the creation and annihilation operators of the electron field which will be given by the one-electron molecular orbital as shown below, the argument denotes both of the space coordinates and the spin of the electron, and $d\tau$ is the volume element including spin.

Let $\varphi_{p\alpha i}$ be the i-th SCF-MO of the $p\alpha$-th molecule written as linear combinations of Löwdin's orthogonalized atomic orbitals [8]:

$$\varphi_{p\alpha i} = \sum_{a=1}^{m} X'_{p\alpha a}\, C'_{ai} \tag{3}$$

where

$$X'_{q\beta b} = \sum_{q=1}^{N} \sum_{\beta=1}^{\sigma} \sum_{a=1}^{m} (1+S)^{-1/2}_{p\alpha a, q\beta b}\, X_{q\beta b}\,.$$

$X_{q\beta b}$ is the $2p\pi$ atomic orbital on the atom b in the molecule $q\beta$ and $(1+S)$ is the overlap matrix with elements:

$$S_{p\alpha a, q\beta b} = -\delta_{p\alpha a, q\beta b} + \int X^*_{p\alpha a}(\mu)\, X_{q\beta b}(\mu)\, dv_\mu\,. \tag{4}$$

Then, all the MO's in the crystal are orthonormalized to each other:

$$(\varphi_{p\alpha i} | \varphi_{q\beta j}) = \int \varphi^*_{p\alpha i}(\mu)\, \varphi_{q\beta j}(\mu)\, dv_\mu\,. \tag{5}$$

These MO's satisfy the Hartree-Fock equations as follows:

$$\left\{-\frac{\hbar^2}{2m}\Delta_\mu+\sum_a V(\boldsymbol{R}_{p\alpha a}-\boldsymbol{r}_\mu)+\sum_h^{\mathrm{occ}}(2J_{p\alpha h}(\mu)-K_{p\alpha h}(\mu))\right\}\varphi_{p\alpha i}(\mu)=\varepsilon_i\varphi_{p\alpha i}(\mu)\,. \tag{6}$$

Here, ε_i is the orbital energy and $J_{p\alpha h}(\mu)$ and $K_{p\alpha h}(\mu)$ are the Coulomb and the exchange operators defined by Roothaan [9]:

$$J_{p\alpha h}(\mu)\,\varphi_{p\alpha i}(\mu)=e^2\int\frac{\varphi^*_{p\alpha h}(\nu)\,\varphi_{p\alpha h}(\nu)}{r_{\mu\nu}}\,\varphi_{p\alpha i}(\mu)\,dv_\nu$$

and

$$K_{p\alpha h}(\mu)\,\varphi_{p\alpha i}(\mu)=e^2\int\frac{\varphi^*_{p\alpha h}(\nu)\,\varphi_{p\alpha i}(\nu)}{r_{\mu\nu}}\,\varphi_{p\alpha h}(\mu)\,dv_\nu\,. \tag{7}$$

Now, the field operator $\psi(\mu)$ can be expanded as linear combinations of spin-orbitals $\phi_{p\alpha i}(\mu)=\varphi_{p\alpha i}(\mu)\,\eta(\mu)$ were $\eta(\mu)$ is the spin function:

$$\psi(\mu)=\sum_{p\alpha i}a_{p\alpha i}\,\phi_{p\alpha i}(\mu)\,. \tag{8}$$

The operators $a^+_{p\alpha i}$ and $a_{p\alpha i}$ are the creation and annihilation operators of the electron which satisfy the following Fermi commutation relations:

$$\begin{gathered} a^+_{p\alpha i}\,a^+_{q\beta j}+a^+_{q\beta j}\,a^+_{p\alpha i}=0\\ a_{p\alpha i}\,a_{q\beta j}+a_{q\beta j}\,a_{p\alpha i}=0\\ a^+_{p\alpha i}\,a_{q\beta j}+a_{q\beta j}\,a^+_{p\alpha i}=\delta_{p\alpha i,q\beta j}\,. \end{gathered} \tag{9}$$

Substituting Eq. (8) into Eq. (2), the Hamiltonian becomes:

$$\begin{aligned} \mathscr{H}=&\sum_{p\alpha i}\varepsilon_i\,a^+_{p\alpha i}a_{p\alpha i}\\ &+\sum_{p\alpha i}\sum_{q\beta j}\left(\phi_{p\alpha i}\middle|\sum_{s\gamma\neq p\alpha}\sum_a V(\boldsymbol{R}_{s\gamma a}-\boldsymbol{r}_\mu)\middle|\phi_{q\beta j}\right)a^+_{p\alpha i}a_{q\beta j}\\ &-\sum_{p\alpha i}\sum_{q\beta j}\left(\phi_{p\alpha i}\middle|\sum_h^{\mathrm{occ}}(2J_{p\alpha h}(\mu)-K_{p\alpha h}(\mu))\middle|\phi_{q\beta j}\right)a^+_{p\alpha i}a_{q\beta j}\\ &+1/2\sum_{p\alpha i}\sum_{q\beta j}\sum_{s\gamma k}\sum_{t\delta l}(\phi_{p\alpha i}\phi_{q\beta j}|\phi_{s\gamma k}\phi_{t\delta l})\,a^+_{p\alpha i}a^+_{s\gamma k}a_{t\delta l}a_{q\beta j} \end{aligned} \tag{10}$$

where

$$(\phi_{p\alpha i}|\,V(\boldsymbol{R}_{s\gamma a}-\boldsymbol{r}_\mu)\,|\,\phi_{q\beta j})=\int\phi^*_{p\alpha i}(\mu)\,V(\boldsymbol{R}_{s\gamma a}-\boldsymbol{r}_\mu)\,\phi_{q\alpha j}(\mu)\,d\tau_\mu$$

and

$$(\phi_{p\alpha i}\phi_{q\beta j}|\,\phi_{s\gamma k}\phi_{t\delta l})=\iint\phi^*_{p\alpha i}(\mu)\,\phi_{q\beta j}(\mu)\,\frac{e^2}{r_{\mu\nu}}\,\phi^*_{s\gamma k}(\nu)\,\phi_{t\delta l}(\nu)\,d\tau_\mu\,d\tau_\nu\,. \tag{11}$$

Denoting the ground and excited states of the Hamiltonian $\mathscr{H}$ by $|0\rangle$ and $|E\rangle$, the excitation operator $A^+(E)$ and the Hermitian conjugate operator $A(E)$ are defined as follows:

$$\begin{aligned} A^+(E)\,|0\rangle &= |E\rangle \\ A(E)\,|0\rangle &= 0\,. \end{aligned} \tag{12}$$

Then, the operators $A^+(E)$ and $A(E)$ satisfy the Bose commutation relation [Eq. (13)] and the equation of motion [Eq. (14)].

$$\begin{aligned} \langle 0|\,[A(E), A^+(E')]\,|0\rangle &= \langle 0|\,A(E)\,A^+(E') - A^+(E')\,A(E)\,|0\rangle \\ &= \langle E|E'\rangle \\ &= \delta_{E,E'} \end{aligned} \tag{13}$$

and

$$[\mathscr{H}, A^+(E)]\,|0\rangle = \Delta E\, A^+(E)\,|0\rangle \tag{14}$$

where ΔE is the energy difference $(E - E_0)$ between the excited state and ground state and is usually called as the elementary excitation energy. The Hamiltonian can be diagonalized by using the operator $A^+(E)$ and $A(E)$ as follows:

$$\mathscr{H} = E_0 + \sum_E \Delta E\, A^+(E)\, A(E)\,. \tag{15}$$

This may be easily proved by substituting Eq. (15) into Eq. (14).

In molecular crystals, the exciton states can be characterized by three indices $f, \mu, \boldsymbol{k}$ [6] and the operator $A(E)$ is rewritten as $A(E) = A_{f\mu}(\boldsymbol{k})$ where $\boldsymbol{k}$ is the wave vector, μ characterizes the exciton state and f numbers the excited states of molecules in the crystal. Then, the exciton state function $\Psi_{f\mu}(\boldsymbol{k})$ and the locally excited configuration $\theta_{p\alpha}^{i\to j}$ can be expressed in terms of the operator representation:

$$\begin{aligned} \Psi_{f\mu}(\boldsymbol{k}) &= A_{f\mu}^+(\boldsymbol{k})\,|0\rangle\,, \\ \theta_{p\alpha}^{i\to j} &= a_{p\alpha j}^+ a_{p\alpha i}\,|0\rangle\,. \end{aligned} \tag{16}$$

It was shown in our previous paper [6] that the wave function $\Psi_{f\mu}(\boldsymbol{k})$ can be approximated by the linear combinations of the configuration $\theta_{p\alpha}^{i\to j}$:

$$\Psi_{f\mu}(\boldsymbol{k}) = (N\sigma)^{-1/2} \sum_{ij} \sum_{p\alpha} e^{i\boldsymbol{k}\cdot\boldsymbol{R}_p}\, C_{i\to j}^{f\mu}(\boldsymbol{k})\, B_{\alpha\mu}(\boldsymbol{k})\, \theta_{p\alpha}^{i\to j}\,. \tag{17}$$

Comparing Eqs. (16) and (17), the operator $A_{f\mu}^+(\boldsymbol{k})$ can be given by the unitary transformation of creation operator $a_{p\alpha j}^+ a_{p\alpha i}$ for the electron-hole pair as follows:

$$\begin{aligned} A_{f\mu}^+(\boldsymbol{k}) &= (N\sigma)^{-1/2} \sum_{ij} \sum_{p\alpha} e^{i\boldsymbol{k}\cdot\boldsymbol{R}_p}\, C_{i\to j}^{f\mu}(\boldsymbol{k})\, B_{\alpha\mu}(\boldsymbol{k})\, a_{p\alpha j}^+ a_{p\alpha i} \\ &= \sum_{ij} \sum_{p\alpha} e^{i\boldsymbol{k}\cdot\boldsymbol{R}_p}\, u_{\alpha ij, f\mu k}\, a_{p\alpha j}^+ a_{p\alpha i}\,. \end{aligned} \tag{18}$$

However, Dunning and McKoy [2] has shown that the operators $A_{f\mu}^+(\boldsymbol{k})$ and $A_{f\mu}(\boldsymbol{k})$ are defined as linear combinations of the electron-hole creation and annihilation operators $a^+_{p\alpha j}a_{p\alpha i}$ and $a^+_{p\alpha i}a_{p\alpha j}$ in order to take into account the effect of electron correlation. The ground state wave function to first order is represented by the expansion:

$$|0\rangle = C_0|\mathrm{HF}\rangle + \sum_{p\alpha ij,}\sum_{q\beta kl} C_{p\alpha ij,q\beta kl}\, a^+_{p\alpha j}\, a_{p\alpha i}\, a^+_{q\beta l}\, a_{q\beta k}|\mathrm{HF}\rangle\,. \tag{19}$$

Now, $|\mathrm{HF}\rangle$ is the Hartree-Fock ground state. The subscripts i and k are used to denote the occupied molecular orbitals, and j and l are employed to label the vacant MO's and m, n and h describe all MO's without differentiation. The second term implies a double excitation. Then, the single excited state is expressed as a linear combination of wave function obtained in two ways: (1) by exciting from the HF ground state or (2) by de-exciting from one of the doubly excited components. Then, the excitation operator $A^+_{f\mu}(\boldsymbol{k})$ is given by the following equation:

$$A^+_{f\mu}(\boldsymbol{k}) = \sum_{ij}\sum_{p\alpha} e^{i\boldsymbol{k}\cdot\boldsymbol{R}_p}\{u_{\alpha ij,f\mu \boldsymbol{k}}\, a^+_{p\alpha j}a_{p\alpha i} - v_{\alpha ij,f\mu \boldsymbol{k}}\, a^+_{p\alpha i}a_{p\alpha j}\} \tag{20}$$

and its Hermitian conjugate $A_{f\mu}(\boldsymbol{k})$ becomes as follows:

$$A_{f\mu}(\boldsymbol{k}) = \sum_{ij}\sum_{p\alpha} e^{-i\boldsymbol{k}\cdot\boldsymbol{R}_p}\{u^*_{f\mu \boldsymbol{k},\alpha ij}\, a^+_{p\alpha i}a_{p\alpha j} - v^*_{f\mu \boldsymbol{k},\alpha ij}\, a^+_{p\alpha j}a_{p\alpha i}\}\,. \tag{21}$$

The pair operators are shown to satisfy the following commutation relations by using the Fermi commutation relations (9):

$$\begin{aligned}
&[a^+_{p\alpha j}a_{p\alpha i},\, a^+_{q\beta l}a_{q\beta k}] = [a^+_{p\alpha i}a_{p\alpha j},\, a^+_{q\beta k}a_{q\beta l}] = 0\\
&[a^+_{p\alpha i}a_{p\alpha j},\, a^+_{q\beta l}a_{q\beta k}] = \delta_{p\alpha i,q\beta k}\delta_{p\alpha j,q\beta l} - \delta_{p\alpha i,q\beta k}a^+_{q\beta l}a_{p\alpha j} - \delta_{q\beta l,p\alpha j}a_{q\beta k}a^+_{p\alpha i}\\
&[a^+_{p\alpha j}a_{p\alpha i},\, a^+_{q\beta k}a_{q\beta l}] = -\delta_{p\alpha i,q\beta k}\delta_{p\alpha j,q\beta l} + \delta_{p\alpha i,q\beta k}a^+_{p\alpha j}a_{q\beta l} + \delta_{p\alpha j,q\beta l}a_{p\alpha i}a^+_{q\beta k}\,.
\end{aligned} \tag{22}$$

If the strict Bose commutation relation is used instead of the commutation relations (22), the transformation of Eqs. (20) and (21) becomes unitary and the coefficients are orthonormalized as follows:

$$\begin{aligned}
&\sum_{f\mu k}\{U^*_{f\mu\boldsymbol{k},p\alpha ij}U_{q\beta kl,f\mu kl} - V^*_{f\mu\boldsymbol{k},q\beta kl}V_{p\alpha ij,f\mu\boldsymbol{k}}\} = \delta_{p\alpha ij,q\beta kl}\\
&\sum_{p\alpha}\sum_{ij}\{U^*_{f\mu\boldsymbol{k},p\alpha ij}U_{p\alpha ij,f'\mu'\boldsymbol{k}'} - V^*_{f\mu\boldsymbol{k},p\alpha ij}V_{p\alpha ij,f'\mu'\boldsymbol{k}'}\} = \delta_{f\mu\boldsymbol{k},f'\mu'\boldsymbol{k}'}
\end{aligned} \tag{23}$$

where $U_{p\alpha ij,f\mu\boldsymbol{k}} = e^{i\boldsymbol{k}\cdot\boldsymbol{R}_p}u_{\alpha ij,f\mu\boldsymbol{k}}$ and $V_{p\alpha ij,f\mu\boldsymbol{k}} = e^{i\boldsymbol{k}\cdot\boldsymbol{R}_p}v_{a ij,f\mu\boldsymbol{k}}$.

This approximation is strict if the excitation density of the system is small, i.e. if the expectation values of the number of the electron-hole pair for the states under consideration are much smaller than the total number of electrons in the system. Then, $a^+_{p\alpha j}a_{p\alpha i}$ and $a^+_{p\alpha i}a_{p\alpha j}$ can be expressed by the operators $A^+_{f\mu}(\boldsymbol{k})$ and $A_{f\mu}(\boldsymbol{k})$ as

$$\begin{aligned}
a^+_{p\alpha j}a_{p\alpha i} &= \sum_{f\mu\boldsymbol{k}}\{u^*_{f\mu\boldsymbol{k},\alpha ij}e^{-i\boldsymbol{k}\cdot\boldsymbol{R}_p}A^+_{f\mu}(\boldsymbol{k}) + v_{\alpha ij,f\mu\boldsymbol{k}}e^{i\boldsymbol{k}\cdot\boldsymbol{R}_p}A_{f\mu}(\boldsymbol{k})\}\\
a^+_{p\alpha i}a_{p\alpha j} &= \sum_{f\mu\boldsymbol{k}}\{v^*_{f\mu\boldsymbol{k},\alpha ij}e^{-i\boldsymbol{k}\cdot\boldsymbol{R}_p}A^+_{f\mu}(\boldsymbol{k}) + u_{\alpha ij,f\mu\boldsymbol{k}}e^{i\boldsymbol{k}\cdot\boldsymbol{R}_p}A_{f\mu}(\boldsymbol{k})\}
\end{aligned} \tag{24}$$

and the Hamiltonian becomes as follows:

$$\mathscr{H} = E_0 + \sum_{f\mu k} E_{f\mu}(\boldsymbol{k})\, A^+_{f\mu}(\boldsymbol{k})\, A_{f\mu}(\boldsymbol{k})\,. \tag{25}$$

By using the Hamiltonian (10) and the Fermi commutation relation (9), the commutator $[\mathscr{H}, a^+_{p\alpha j} a_{p\alpha i}]$ becomes as follows:

$$\begin{aligned}
[\mathscr{H}, a^+_{p\alpha j} a_{p\alpha i}] = {} & (\varepsilon_j - \varepsilon_i)\, a^+_{p\alpha j} a_{p\alpha i} \\
& + \sum_{q\beta m} \sum_{s\gamma \neq q\beta} \{(\phi_{q\beta m} | U_{s\gamma} | \phi_{p\alpha j})\, a^+_{q\beta m} a_{p\alpha i} - (\phi_{p\alpha i} | U_{s\gamma} | \phi_{q\beta m})\, a^+_{p\alpha j} a_{q\beta m}\} \\
& + \sum_{q\beta m} \sum_{s\gamma n} \{(\phi_{q\beta m} \phi_{s\gamma n} | \phi_{p\alpha i} \phi_{p\alpha j}) - (\phi_{q\beta m} \phi_{p\alpha j} | \phi_{p\alpha i} \phi_{s\gamma n})\}\, a^+_{q\beta m} a_{s\gamma n} \\
& + \sum_{q\beta m} \sum_{s\gamma} \left\{ \left(\phi_{p\alpha i} \middle| \sum_{h}^{\text{occ}} (2 J_{s\gamma h} - K_{s\gamma h}) \middle| \phi_{q\beta m} \right) a^+_{p\alpha j} a_{q\beta m} \right. \\
& \left. - \left(\phi_{q\beta m} \middle| \sum_{h}^{\text{occ}} (2 J_{s\gamma h} - K_{s\gamma h}) \middle| \phi_{p\alpha j} \right) a^+_{q\beta m} a_{p\alpha i} \right\} \\
& - 1/2 \sum_{q\beta m} \sum_{s\gamma n} \sum_{t\delta h} \{(\phi_{q\beta m} \phi_{p\alpha j} | \phi_{t\delta h} \phi_{s\gamma n}) \\
& - (\phi_{q\beta m} \phi_{s\gamma n} | \phi_{t\delta h} \phi_{p\alpha j})\}\, a_{p\alpha i} a^+_{q\beta m} a^+_{t\delta h} a_{s\gamma n} \\
& - 1/2 \sum_{q\beta m} \sum_{s\gamma n} \sum_{t\delta h} \{(\phi_{p\alpha i} \phi_{s\gamma n} | \phi_{q\beta m} \phi_{t\delta h}) \\
& - (\phi_{q\beta m} \phi_{s\gamma n} | \phi_{p\alpha i} \phi_{t\delta h})\}\, a^+_{p\alpha j} a^+_{q\beta m} a_{t\delta h} a_{s\gamma n}
\end{aligned} \tag{26}$$

where $U_{s\gamma}(\mu) = \sum_{a} V(\boldsymbol{R}_{p\alpha a} - \boldsymbol{r}_\mu) + \sum_{h}^{\text{occ}} (2 J_{p\alpha h}(\mu) - K_{p\alpha h}(\mu))$.

Neglecting the interactions of the hole-hole, electron-electron, multiple electron-hole and retaining the first term and part of the second and third terms, Eq. (26) reduces to a simple form:

$$\begin{aligned}
[\mathscr{H}, a^+_{p\alpha j} a_{p\alpha i}] = {} & \sum_{kl} (\Delta \varepsilon_{ij,kl} + D_{ij,kl})\, a^+_{p\alpha l} a_{p\alpha k} \\
& + \sum_{kl} \sum_{q\beta} \{ I_{p\alpha ij, q\beta kl}\, a^+_{q\beta l} a_{q\beta k} + J_{p\alpha ij, q\beta kl}\, a^+_{q\beta k} a_{q\beta l} \}\,.
\end{aligned} \tag{27}$$

The symbols $\Delta \varepsilon_{ij,kl}$, $D_{ij,kl}$, $I_{p\alpha ij, q\beta kl}$ and $J_{p\alpha ij, q\beta kl}$ are defined as follows:

$$\Delta \varepsilon_{ij,kl} = \delta_{i,k} \delta_{j,l} (\varepsilon_j - \varepsilon_i)$$

$$D_{ij,kl} = \sum_{q\beta \neq p\alpha} \{\delta_{i,k} (\varphi_{p\alpha l} | U_{q\beta} | \varphi_{p\alpha j}) - \delta_{l,j} (\varphi_{p\alpha i} | U_{q\beta} | \varphi_{p\alpha k})\}$$

$$I_{p\alpha ij, q\beta kl} = 2 \delta_S (\varphi_{q\beta l} \varphi_{q\beta k} | \varphi_{p\alpha i} \varphi_{p\alpha j}) - (\varphi_{q\beta l} \varphi_{p\alpha j} | \varphi_{p\alpha i} \varphi_{q\beta k})$$

and

$$J_{p\alpha ij, q\beta kl} = 2 \delta_S (\varphi_{q\beta k} \varphi_{q\beta l} | \varphi_{p\alpha i} \varphi_{p\alpha j}) - (\varphi_{q\beta k} \varphi_{p\alpha j} | \varphi_{p\alpha i} \varphi_{q\beta l}) \tag{28}$$

where $\delta_S = 1$ for the singlet state and $\delta_S = 0$ for the triplet,

$$(\varphi_{p\alpha l} | U_{q\beta} | \varphi_{p\alpha j}) = \int \varphi^*_{p\alpha l}(\mu)\, U_{q\beta}(\mu)\, \varphi_{p\alpha j}(\mu)\, dv_\mu$$

and

$$(\varphi_{q\beta k} \varphi_{q\beta l} | \varphi_{p\alpha i} \varphi_{p\alpha j}) = \iint \varphi^*_{q\beta k}(\mu)\, \varphi_{q\beta l}(\mu)\, \frac{e^2}{r_{\mu\nu}}\, \varphi^*_{p\alpha i}(\nu)\, \varphi_{p\alpha j}(\nu)\, dv_\mu\, dv_\nu\, .$$

Substituting Eq. (24) into Eq. (27), Eq. (27) can be expressed in terms of the operators $A^+_{f\mu}(\boldsymbol{k})$ and $A_{f\mu}(\boldsymbol{k})$:

$$\begin{aligned}
&[\mathscr{H}, a^+_{p\alpha j} a_{p\alpha i}] \\
&\quad = \sum_{f\mu\boldsymbol{k}} \Big\{ e^{-i\boldsymbol{k}\cdot\boldsymbol{R}_p} A^+_{f\mu}(\boldsymbol{k}) \sum_{kl} \sum_{\beta} [G^*_{\beta kl,\alpha ij}(\boldsymbol{k})\, u^*_{f\mu\boldsymbol{k},\beta kl} + H^*_{\beta kl,\alpha ij}(\boldsymbol{k})\, v^*_{f\mu\boldsymbol{k},\beta kl}] \\
&\qquad + e^{i\boldsymbol{k}\cdot\boldsymbol{R}_p} A_{f\mu}(\boldsymbol{k}) \sum_{kl} \sum_{\beta} [G_{\alpha ij,\beta kl}(\boldsymbol{k})\, v_{\beta kl,f\mu\boldsymbol{k}} + H_{\alpha ij,\beta kl}(\boldsymbol{k})\, u_{\beta kl,f\mu\boldsymbol{k}}] \Big\}
\end{aligned} \tag{29}$$

where

$$G_{\alpha ij,\beta kl}(\boldsymbol{k}) = \delta_{\alpha,\beta}(\Delta\varepsilon_{ij,kl} + D_{ij,kl}) + \sum_q I_{p\alpha ij,q\beta kl}\, e^{-i\boldsymbol{k}\cdot(\boldsymbol{R}_p - \boldsymbol{R}_q)}$$

and

$$H_{\alpha ij,\beta kl}(\boldsymbol{k}) = \sum_q J_{p\alpha ij,q\beta kl}\, e^{-i\boldsymbol{k}\cdot(\boldsymbol{R}_p - \boldsymbol{R}_q)}\, . \tag{30}$$

On the other hand, by using Eqs. (24) and (25) and the Bose commutation relation of the operators $A^+_{f\mu}(\boldsymbol{k})$ and $A_{f\mu}(\boldsymbol{k})$, the commutator becomes as follows:

$$\begin{aligned}
&[\mathscr{H}, a^+_{p\alpha j} a_{p\alpha i}] \\
&\quad = \sum_{f\mu\boldsymbol{k}} E_{f\mu}(\boldsymbol{k})\, \{u^*_{f\mu\boldsymbol{k},\alpha ij} e^{-i\boldsymbol{k}\cdot\boldsymbol{R}_p} A^+_{f\mu}(\boldsymbol{k}) - v_{f\mu\boldsymbol{k},\alpha ij} e^{i\boldsymbol{k}\cdot\boldsymbol{R}_p} A_{f\mu}(\boldsymbol{k})\}\, .
\end{aligned} \tag{31}$$

By comparing Eqs. (29) and (31), the eigenvalue equation can be obtained and written in matrix notation as:

$$\begin{aligned}
\boldsymbol{U}\boldsymbol{E} &= \boldsymbol{G}\boldsymbol{U} + \boldsymbol{H}\boldsymbol{V} \\
-\boldsymbol{V}\boldsymbol{E} &= \boldsymbol{G}\boldsymbol{V} + \boldsymbol{H}\boldsymbol{U}
\end{aligned} \tag{32}$$

where the amplitudes $\boldsymbol{U}$ and $\boldsymbol{V}$ are normalized to an indefinite metrix as shown in Eq. (23):

$$\boldsymbol{U}^+\boldsymbol{U} - \boldsymbol{V}^+\boldsymbol{V} = \boldsymbol{1}\, . \tag{33}$$

Comparing the above equations to the equations used in our previous theory [6], the earlier formula corresponds to the equation $\boldsymbol{U}\boldsymbol{E} = \boldsymbol{G}\boldsymbol{U}$ by neglecting the vector $\boldsymbol{V}$. The $\boldsymbol{H}$ matrix takes into account the effect of the doubly excited configuration and allows for the contribution of the π electron correlation to the single excited state.

The excitation energies are the eigenvalues of a non-Hermitian matrix and can be obtained by transforming Eqs. (32) into a single equation:

$$(\boldsymbol{U} + \boldsymbol{V})\, \boldsymbol{E}^2 = (\boldsymbol{G} - \boldsymbol{H})(\boldsymbol{G} + \boldsymbol{H})(\boldsymbol{U} + \boldsymbol{V})\, . \tag{34}$$

Putting the vectors $\boldsymbol{U}$ and $\boldsymbol{V}$ in the following forms:

$$\begin{aligned} \boldsymbol{U} &= \tfrac{1}{2}\{(\boldsymbol{G}-\boldsymbol{H})^{1/2}\,\boldsymbol{w}E^{-1/2} + (\boldsymbol{G}-\boldsymbol{H})^{-1/2}\,\boldsymbol{w}E^{1/2}\} \\ \boldsymbol{V} &= \tfrac{1}{2}\{(\boldsymbol{G}-\boldsymbol{H})^{1/2}\,\boldsymbol{w}E^{-1/2} - (\boldsymbol{G}-\boldsymbol{H})^{-1/2}\,\boldsymbol{w}E^{1/2}\}, \end{aligned} \tag{35}$$

the new vector satisfies the orthonormalization condition by Eq. (33) as

$$\boldsymbol{w}^{+}\boldsymbol{w} = \boldsymbol{1}. \tag{36}$$

Namely, $\boldsymbol{w}$ is unitary and Eq. (34) reduces to an equation for $\boldsymbol{w}$:

$$\boldsymbol{w}E^{2} = (\boldsymbol{G}-\boldsymbol{H})^{1/2}(\boldsymbol{G}+\boldsymbol{H})(\boldsymbol{G}-\boldsymbol{H})^{1/2}\,\boldsymbol{w}. \tag{37}$$

This is a usual eigenvalue equation for a Hermitian matrix.

Defining the eigenvector $\boldsymbol{x}$ and eigenvalue $\boldsymbol{\lambda}$:

$$\begin{aligned} (\boldsymbol{G}-\boldsymbol{H})\,\boldsymbol{x} &= \boldsymbol{x}\boldsymbol{\lambda} \\ \boldsymbol{x}^{+}\boldsymbol{x} &= \boldsymbol{1} \\ (\boldsymbol{G}-\boldsymbol{H})^{n} &= \boldsymbol{x}\boldsymbol{\lambda}^{n}\boldsymbol{x}^{+}, \end{aligned} \tag{38}$$

Eqs. (36) and (37) can be expressed by using the new vector $\boldsymbol{y} = \boldsymbol{x}\boldsymbol{w}$ as follows:

$$\begin{aligned} \boldsymbol{y}E^{2} &= (\boldsymbol{\lambda}^{2} + 2\boldsymbol{\lambda}^{1/2}\boldsymbol{x}^{+}\boldsymbol{H}\boldsymbol{x}\boldsymbol{\lambda}^{1/2})\,\boldsymbol{y} \\ \boldsymbol{y}^{+}\boldsymbol{y} &= \boldsymbol{1} \end{aligned} \tag{39}$$

and

$$\begin{aligned} \boldsymbol{U}+\boldsymbol{V} &= \boldsymbol{x}\boldsymbol{\lambda}^{1/2}\boldsymbol{y}E^{-1/2} \\ \boldsymbol{U}-\boldsymbol{V} &= \boldsymbol{x}\boldsymbol{\lambda}^{-1/2}\boldsymbol{y}E^{1/2}. \end{aligned} \tag{40}$$

In order to reduce the above matrix elements to those of the integrals over the atomic orbitals, it has been shown [6] that the following approximations are valid:

$$(\varphi_{p\alpha i}\varphi_{q\beta j}|\varphi_{s\gamma k}\varphi_{t\delta l}) = \delta_{p\alpha,q\beta}\,\delta_{s\gamma,t\delta}\sum_{a}\sum_{b} C'_{ai}C'_{aj}C'_{bk}C'_{bl}\,e^{2}\ |\boldsymbol{R}_{p\alpha a}-\boldsymbol{R}_{s\gamma b}|\,. \tag{41}$$

Then, the elements $G_{\alpha ij,\beta kl}$ and $H_{\alpha ij,\beta kl}$ can be approximated as follows:

$$\begin{aligned} G_{\alpha ij,\beta kl} - H_{\alpha ij,\beta kl} &= \delta_{\alpha,\beta}\{(\Delta\varepsilon_{ij,kl} + D_{ij,kl}) + (\varphi_{p\alpha k}\varphi_{p\alpha j}|\varphi_{p\alpha i}\varphi_{p\alpha l}) - (\varphi_{p\alpha l}\varphi_{p\alpha j}|\varphi_{p\alpha i}\varphi_{p\alpha k})\} \\ H_{\alpha ij,\beta kl} &= \delta_{\alpha,\beta}\{2\delta_{S}(\varphi_{p\alpha k}\varphi_{p\alpha l}|\varphi_{p\alpha i}\varphi_{p\alpha j}) - (\varphi_{p\alpha k}\varphi_{p\alpha j}|\varphi_{p\alpha i}\varphi_{p\alpha l})\} \\ &\quad + 2\delta_{S}\sum_{q\neq p} e^{-i\boldsymbol{k}\cdot(\boldsymbol{R}_{q}-\boldsymbol{R}_{p})}(\varphi_{q\beta k}\varphi_{q\beta l}|\varphi_{p\alpha i}\varphi_{p\alpha j})\,. \end{aligned} \tag{42}$$

Using the above approximation, Eqs. (38), (39) and (40) are reduced to the simple equations:

$$\begin{aligned} &(\varepsilon_{j} - \varepsilon_{i} - \lambda_{\varrho})\,x_{ij,\varrho\alpha} \\ &\quad + \sum_{kl}\{D_{ij,kl} + (\varphi_{p\alpha k}\varphi_{p\alpha j}|\varphi_{p\alpha i}\varphi_{p\alpha l}) - (\varphi_{p\alpha l}\varphi_{p\alpha j}|\varphi_{p\alpha i}\varphi_{p\alpha k})\}\,x_{kl,\varrho\alpha} = 0 \\ &(\lambda_{\varrho}^{2} - E_{f\mu}(\boldsymbol{k})^{2})\,y_{\varrho\alpha,f\mu\boldsymbol{k}} + \sum_{\eta\beta} V_{\varrho\alpha,\eta\beta}\,y_{\eta\beta,f\mu\boldsymbol{k}} = 0 \\ &V_{\varrho\alpha,\eta\beta} = 2\lambda_{\varrho}^{1/2}\sum_{ij}\sum_{kl} x^{+}_{\varrho\alpha,ij}H_{\alpha ij,\beta kl}\,x_{kl,\eta\beta}\,\lambda_{\eta}^{1/2} \end{aligned} \tag{43}$$

and

$$\begin{aligned}(U+V)_{\alpha ij,f\mu\boldsymbol{k}} &= \sum_{\varrho} x_{ij,\varrho\alpha}\,\lambda_{\varrho}^{1/2}\,y_{\varrho\alpha,f\mu\boldsymbol{k}}\,E_{f\mu}(\boldsymbol{k})^{-1/2} \\ (U-V)_{\alpha ij,f\mu\boldsymbol{k}} &= \sum_{\varrho} x_{ij,\varrho\alpha}\,\lambda_{\varrho}^{-1/2}\,y_{\varrho\alpha,f\mu\boldsymbol{k}}\,E_{f\mu}(\boldsymbol{k})^{1/2}\,.\end{aligned} \tag{44}$$

The dipole moment operator is given in the second quantization formalism:

$$\boldsymbol{r} = \sum_{p\alpha m}\sum_{q\beta n} \boldsymbol{d}_{q\beta n,\,p\alpha m}\,a^{+}_{q\beta n}\,a_{p\alpha m} \tag{45}$$

where

$$\boldsymbol{d}_{q\beta n,\,p\alpha m} = \int \varphi^{*}_{q\beta n}(\mu)\,\boldsymbol{r}_{\mu}\,\varphi_{p\alpha m}(\mu)\,dv_{\mu}\,.$$

Again, retaining only the electron-hole interactions, this is reduced to

$$\boldsymbol{r} = \sum_{p\alpha}\sum_{ij} \boldsymbol{d}_{p\alpha j,\,p\alpha i}\,(a^{+}_{p\alpha j}\,a_{p\alpha i} + a^{+}_{p\alpha i}\,a_{p\alpha j})\,. \tag{46}$$

The dipole transition moment to the singlet state $f\mu k$ is defined as:

$$\boldsymbol{M}_{f\mu\boldsymbol{k}} = (N\sigma)^{-1/2}\,\langle 0|\boldsymbol{r}|\,f\mu\boldsymbol{k}\rangle \tag{47}$$

or, by using Eqs. (12) and taking into account the spin,

$$\begin{aligned}M_{f\mu\boldsymbol{k}} &= -\,(N\sigma)^{-1/2}\,\langle 0|\,[A^{+}_{f\mu}(\boldsymbol{k}),\boldsymbol{r}]\,|0\rangle \\ &= (2N/\sigma)^{1/2}\,\delta_{\boldsymbol{k}}\sum_{\alpha ij}(u+v)_{\alpha ij,f\mu\boldsymbol{k}}\,\boldsymbol{d}_{p\alpha i,\,p\alpha j}\end{aligned} \tag{48}$$

where $\delta_{\boldsymbol{k}} = 1$ for $\boldsymbol{k} = 0$ and $\delta_{\boldsymbol{k}} = 0$ for $\boldsymbol{k} \neq 0$. The vectors u and v may be expressed as products of two coefficients as is seen in Eq. (18):

$$u_{\alpha ij,f\mu\boldsymbol{k}} = (N\sigma)^{-1/2}\,P^{f\mu}_{i\to j}(\boldsymbol{k})\,B_{\alpha\mu}(\boldsymbol{k})$$

and

$$v_{\alpha ij,f\mu\boldsymbol{k}} = (N\sigma)^{-1/2}\,Q^{f\mu}_{i\to j}(\boldsymbol{k})\,B_{\alpha\mu}(\boldsymbol{k}) \tag{49}$$

where $P^{f\mu}_{i\to j}(\boldsymbol{k})$ and $Q^{f\mu}_{i\to j}(\boldsymbol{k})$ can be determined by solving Eqs. (43) and (44) and $B_{\alpha\mu}(\boldsymbol{k})$'s is found by the symmetry operation of the factor group of the crystal. Then, the transition moments are defined as follows:

$$\boldsymbol{M}_{f\mu\boldsymbol{k}} = \frac{\sqrt{2}}{\sigma}\sum_{ij}\left(P^{f\mu}_{i\to j}(\boldsymbol{k}) + Q^{f\mu}_{i\to j}(\boldsymbol{k})\right)\left(\sum_{\alpha} B_{\alpha\mu}(\boldsymbol{k})\,\boldsymbol{d}_{p\alpha j,\,p\alpha i}\right). \tag{50}$$

The oscillator strength f is given by:

$$f = 3\times 0.08753\,E_{f\mu}(\boldsymbol{k})\,|\boldsymbol{M}_{f\mu\boldsymbol{k}}|^{2} \tag{51}$$

where the excitation energy $E_{f\mu\boldsymbol{k}}$ is given in eV and $\boldsymbol{M}_{f\mu\boldsymbol{k}}$ is in Å.

The similar equation of molecule has been given by Dunning and McKoy [2] and is reduced to the equations suitable for numerical calculations by the same procedure as above-mentioned:

$$(\varepsilon_j - \varepsilon_i - \lambda_{\varrho})\,x_{ij,\varrho} + \sum_{kl}\{(\varphi_k\varphi_j|\varphi_i\varphi_l) - (\varphi_l\varphi_j|\varphi_i\varphi_k)\}\,x_{kl,\varrho} = 0$$

$$(\lambda_{\varrho}^{2} - E_f^{2})\,y_{\varrho,f} + \sum_{\eta} V_{\varrho,\eta}\,y_{\eta,f} = 0$$

$$V_{\varrho,\eta} = 2\lambda_{\varrho}^{1/2}\sum_{ij}\sum_{kl} x^{*}_{\varrho,ij}\,\{2\delta_S(\varphi_k\varphi_l|\varphi_i\varphi_j) - (\varphi_k\varphi_j|\varphi_i\varphi_l)\}\,x_{\eta,kl}\,\lambda_{\eta}^{1/2} \tag{52}$$

and

$$M_f = \sqrt{2} \sum_{ij} (U+V)_{ij,f} \, \boldsymbol{d}_{j,i}$$
$$f = 0.08753 \, E_f \, |\boldsymbol{M}_f|^2 \,. \tag{53}$$

The correlation effect is shown by examing the excitation energy E and transition moment $\boldsymbol{M}$ of only single electron-hole pair operator $a_j^+ a_i$. That is, Eq. (37) gives the following eigenvalue and moment:

$$\begin{aligned} E &= (\Delta - \Gamma)^{1/2} \\ &\cong \Delta - \frac{\Gamma^2}{2\Delta} \\ \boldsymbol{M} &= \sqrt{2}\, \boldsymbol{d}_{j,i} \left(\frac{\Delta - \Gamma}{\Delta + \Gamma} \right)^{1/4}, \end{aligned} \tag{54}$$

where $\Delta = G_{ij,ij}$ is the excitation energy of the single configuration and $\Gamma = H_{ij,ij}$ is the correlation term. Equations (54) show that the correlation term gives an improvement on the excitation energies and oscillator strengths. The triplet state becomes instable when $\Delta < \Gamma$. This problem may be solved by applying the higher random phase approximation [10].

3. Results and Discussions

The electronic spectra and structure of anthracene crystal is a problem of wide interest. The present theory will be applied to its analysis.

The SCF-MO's of the anthracene molecule were calculated by solving Fock's equation (6) with an approximation of the neglect of differential overlap [11–12]:

$$X_a'(\mu)\, X_b'(\mu) = 0 \quad \text{for} \quad a \neq b$$

and of two center Coulomb integrals evaluated by Nishimoto-Mataga's method [13]. The excitation energies and oscillator strengths of anthracene molecule were obtained by employing Eqs. (52) and (53) and considering thirteen electron-hole pairs. The results are shown in Table 1. Comparing the observed values

Table 1. Comparison between the calculated and observed values of transition energies (E_f in eV) and oscillator strengths of the anthracene molecule

		The present method		The usual CI method		Observed values	
		E_f	f	E_f	f	E_f	f
I	B_{1u}	3.692	0.238	3.812	0.307	3.301	0.11
II	B_{2u}	4.849	2.026	5.050	2.805	4.921	1.56
III	B_{1u}	5.826	0.353	5.968	0.478	5.603	0.21
IV	B_{1u}	6.088	0.135	6.235	0.189	6.52	0.41
V	B_{1u}	7.162	0.444	7.255	0.787		

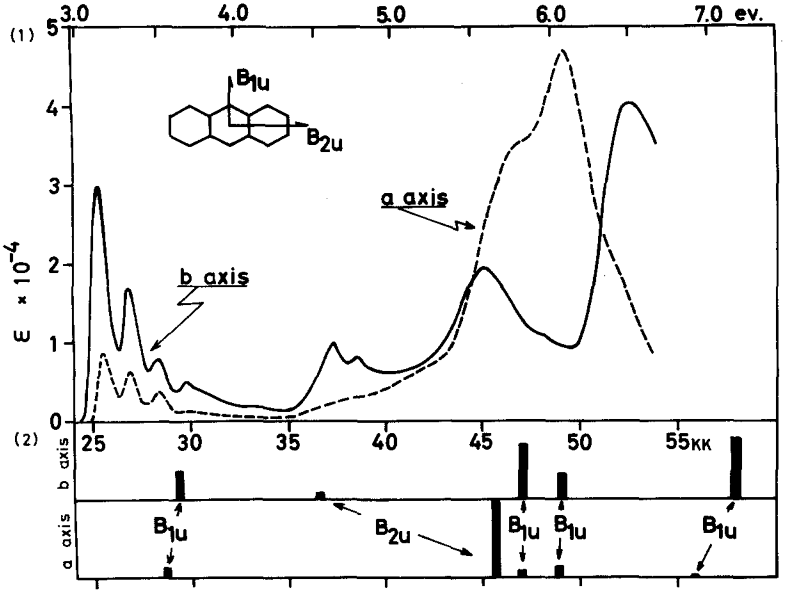

Fig. 1. Observed absorption spectra of anthracene crystal taken by Clark and Philpott with our assignment. 1 the crystalline spectra determined from reflection data [15]. 2 the calculated values by the present theory

with calculated ones, the excited states are assigned to the B_{1u}, B_{2u}, B_{1u}, B_{1u} and B_{1u} states in the region of from 4000 Å down to about 1700 Å. The B_{1u} state is polarized to the short molecular axis and the B_{2u} state to the long axis. In Table 1, the calculated values obtained by the present theory are compared with those by the usual CI method. The present theory gives better results in the calculation of excitation energies and oscillator strengths than the usual ASMO-SCF-CI method. Presumably, this improvement will be caused by the effect of electron correlation which will be efficient in decreasing the excitation energies and oscillator strengths of intense bands.

Anthracene crystallizes in the monoclinic system with the space group $C_{2h}^5 - P2_1/a$ and has two molecules per unit cell [7]. In this crystalline lattice, molecule 1 may be transformed into molecule 2 by reflection in the *ac* plane

Table 2. Character table for the group C_{2h} and the selection rule of the exciton states

	E	C_2	i	σ	Transition moment[a]	
A_g	1	1	1	1	$d_1^S + d_2^S$	
A_u	1	1	−1	−1	$d_1^A - d_2^A$	*b*
B_g	1	−1	1	−1	$d_1^S - d_2^S$	
B_u	1	−1	−1	1	$d_1^A + d_2^A$	*a, c*

[a] The lower subscript numbers the site in an unit cell and the upper subscripts S and A mean the symmetric (A_g and B_{1g}) and antisymmetric (B_{1u} and B_{2u}) electron-hole pairs with respect to inversion of the anthracene molecule.

Table 3. Comparison between the calculated and observed values of transition energies (E_f in eV) and oscillator strengths of the anthracene crystal

		The present theory					Observed values [15]			
		A_u state		B_u state			A_u state		B_u state	
		E_f	f^b	E_f	f^a	f^c	E_f	f^b	E_f	f^a
I	B_{1u}	3.627	0.508	3.531	0.152	0.010	3.137	0.248	3.161	0.076
II	B_{2u}	4.512	0.123	5.656	1.305	3.442	4.623	0.16	5.776	
III	B_{1u}	5.801	0.741	5.810	0.146	2.167	5.566	0.6		0.7
IV	B_{1u}	6.069	0.428	6.043	0.175	0.229	5.975	0.06	6.52	
V	B_{1u}	7.166	1.090	7.077	0.057	0.066	6.508	0.8		

followed by a glide at $\frac{1}{2}\boldsymbol{a}$. The coefficients $B_{\alpha\mu}(\boldsymbol{k})$'s are determined from the character table of the group C_{2h} of the wave vector $\boldsymbol{k}=0$ as displayed in Table 2. It shows that the crystal field mixing arises only between A_g and B_{3g}, B_{1u} and B_{2u} of the anthracene molecule and the allowed exciton states are A_u (polarized parallel to b axis) and B_u (polarized perpendicular to b axis) states. Table 3 gives the exciton state energies and oscillator strengths when the interactions for the inner zone were calculated to 50 Å. The absorption spectra of the anthracene crystal are reported by many workers [14, 15]. The crystalline spectra determined from reflectivity data by Clark and Philpott [15] are shown in the figure together with our assignment.

The calculated Davydov splitting ($E_{B_u}-E_{A_u}$) of the band I is $-780\,\mathrm{cm}^{-1}$ while the observed value is $360\,\mathrm{cm}^{-1}$. This result will be improved when the long range terms are included as is shown in our previous paper [6]. The intensity ratio ($f^b/f^a=3.5$) is in good agreement with the observed values (3.3) [15]. The Davydov splitting of the long axis polarized band II is a matter of controversial discussion, and the spectra [15] shown in the figure gives a value of $9300\,\mathrm{cm}^{-1}$. The earlier transmission measurement by Lyons and Morris [14] gives a value of $10000\,\mathrm{cm}^{-1}$ for this splitting. Although a correct order of magnitude for this splitting was obtained in the earlier theories, but the agreement with the observed value was not so sufficient. Our calculated value in the present theory is $9200\,\mathrm{cm}^{-1}$. The coincidence between the experiment and calculated value is quite satisfactory and it may be due to the correlation effect of π-electrons in high density solid state. Oscillator strengths are evaluated to be about 0.123 for the A_u state and 1.305 for the B_u state.

The bands III, IV and V at the higher energy region are originally derived from the molecular B_{1u} states polarized to the short axis. These bands are at 5.80, 6.07 and 7.12 eV for the A_u states and the oscillator strengths are 0.74, 0.43 and 1.09, respectively. The b-axis polarized spectrum has a peak at 5.57 eV, a weak shoulder at 5.98 eV and an intense peak at 6.51 eV and these are satisfactorily correlated with the calculated values. For the B_u exciton states, the corresponding levels are calculated at 5.81, 6.04 and 7.08 eV with f values of 0.146, 0.176 and 0.006. The shoulder at the vicinity of 6.5 eV may be assigned to the overlapped band of lower two transitions and the last band may not be observed because of its weak intensity.

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Dr. M. Tanaka
Department of Chemistry
Faculty of Science
Nagoya University
Chikusa, 464, Nagoya, Japan