© 1997 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 70, 321—327 (1997)

A Unified Theory of Uniaxially- and Biaxially-Stretched Film Methods: Three-Dimensional Reduced Spectra of Perylene

Michio Kobayashi,* Xinghai Yuan,† Norio Shinbo, Masashi Watanabe, Masunori Matsumoto, Masanori Miura, Ikuko Yoshioka, and Yoshie Tanizaki

Department of Chemistry, Nagaoka University of Technology, Kamitomioka-machi, Nagaoka 940-21

†Department of Chemistry, Harbin Teacher's University, 24 He Xing Road, Harbin, China

(Received August 1, 1996)

A unified theory of uniaxially- and biaxially-stretched film methods has been proposed. This theory allows the decomposition of the electronic absorption spectrum into three-dimensional reduced spectra polarized along the molecular orientation axes. A transformation theory has also been proposed to transform these reduced spectra to the three-dimensional reduced spectra polarized along the molecular axes, assuming that there exist a pure band and an overlapping band in the spectrum. These theories were applied to get the three-dimensional reduced spectra of perylene.

The absorption spectrum of a symmetric molecule consists of three absorption components (A_z, A_y, A_x), which are purely polarized along the three molecular axes (long axis z, short axis y, out-of-plane axis x), i.e., three-dimensional reduced spectra. It was pointed out that three-dimensional reduced spectra can be obtained if at least three independent spectra are available experimentally.[1,2] A third independent spectrum is needed in addition to the polarized absorption spectra ($A_{\parallel}$ and $A_{\perp}$) measured by the uniaxially-stretched film technique for the determination of three-dimensional reduced spectra by the stretched film method. It was demonstrated in our previous paper[3] that the biaxially-stretched film method can provide this third independent spectrum. That is, a nonunified coupling of the biaxially- and uniaxially-stretched film methods tentatively proposed by us proved to yield an approximate estimation of the three-dimensional reduced spectra of a rod-like molecule (pinacyanol, 1-ethyl-2-[3-(1-ethyl-2(1*H*)-quinolinylidene)-1-propenyl]quinolinium iodide), demonstrating the usefulness of the biaxially-stretched film technique coupled with the uniaxially-stretched film technique.[3] In this paper, a theory for the unified coupling of the biaxially- and uniaxially-stretched film methods, formulated by the use of an orientational distribution function as an extension of Tanizaki's theory[4,5] for a quantitative analysis of linear dichroism ($A_{\parallel}$ and $A_{\perp}$), is proposed to form a more accurate and self-consistent estimation of the three-dimensional reduced spectra for a symmetrical molecule of general shape. Furthermore, three-dimensional reduced spectra of perylene are obtained by this unified theory of biaxially- and uniaxially-stretched film methods.

Theoretical

A Unified Theory of Uniaxially- and Biaxially-Stretched Film Methods. The coordinates (Z,Y,X) fixed on the polymer film are defined so that the ZY-plane represents the film plane and the X-axis is the propagation direction of the light beam. Then we consider that an imaginary sphere (**IS**) in the film substrate is deformed to the spheroid **A** upon uni(Z)axial stretching and to the spheroid **B** upon bi(Z,Y)axial stretching as shown in Fig. 1. To analyze the orientational distribution of the solute molecules, which are isotropically distributed in **IS**, in the spheroids **A** and **B**, we introduce the three-dimensional (ζ, η, and ξ) molecular orientation axes (OA) inherent in the solute molecule and assume after the Tanizaki model[3] for the uniaxially-stretched film method that these OA respond without retardation to the orientations of the three-dimensional unit vectors fixed to the film substrate. The molecular orientation axes are generally not coincident with the molecular axes (MA); for a symmetrical planar molecule, ζ-OA is the main OA that is close to the longer (z-) MA, η- and ξ-OA being close to the shorter (y-) and out-of-plane (x-) MA, respectively.

On uni(Z)axial stretching of **IS**, the ζ-OA will approach the stretching direction (Z) and the angle (θ) between ζ-OA and Z-axis will become smaller (Fig. 2a; $0 \leqq \theta \leqq \theta_0 \leqq \pi/2$). Assuming that the deformation of **IS** into the spheroid **A** proceeds with a constant volume, Tanizaki[4,5] obtained the orientational distribution function of the ζ-OA in the spheroid **A** as

$$f(\theta) = R_{\mathrm{u}}^2 \sin\theta / [1 + (R_{\mathrm{u}}^2 - 1)\sin^2\theta]^{3/2}, \qquad (1)$$

where R_{u} is the uniaxial deformation ratio defined as the c/a value ($\geqq 1$) in the spheroid **A** (Fig. 1) and is equal to the uniaxial stretching ratio (R_{s}) of the film obtained experimentally. In this uniaxial stretching model, free rotation about the ζ-OA is assumed, i.e., the orientational distribution of the η-OA in the spheroid **A** is assumed to be equal to that of the ξ-OA in the spheroid **A**. The unequal distributions of

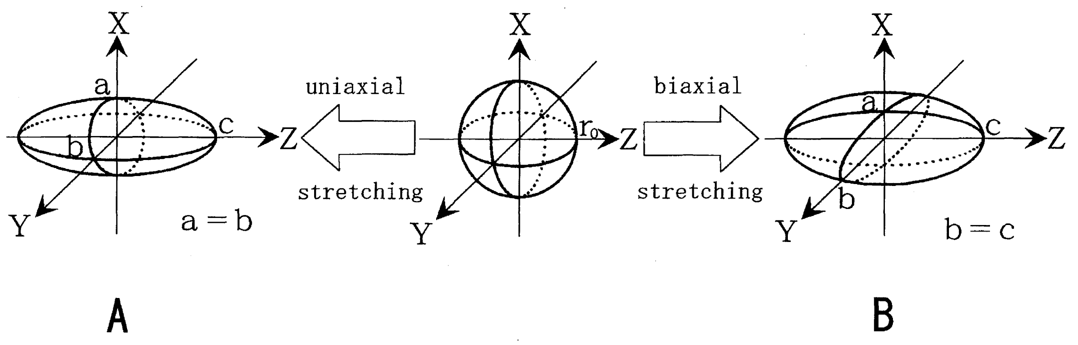

Fig. 1. Deformations of the imaginary sphere in the film substrate to the spheroids **A** and **B** on uniaxial and biaxial stretching of the film, respectively.

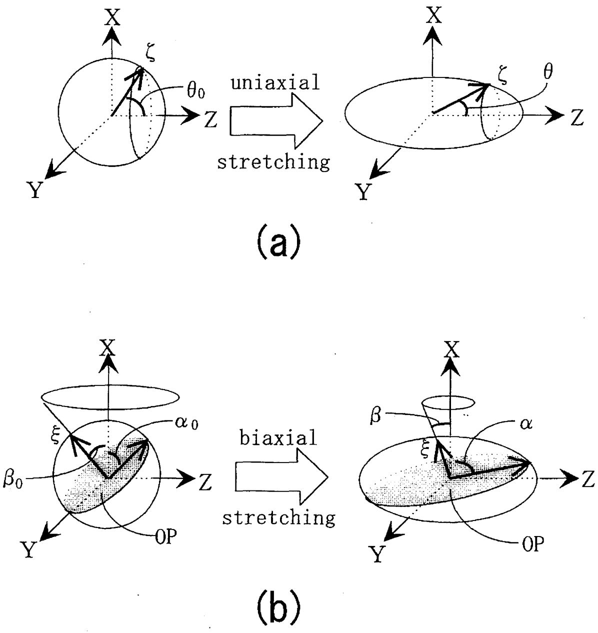

Fig. 2. Approach of (a) ζ-OA to the uniaxial stretching direction (Z-axis) on uniaxial atretching of the film and (b) ζ η-plane (OP) or ζ-OA to ZY-plane (film plane) or X-axis on biaxial stretching of the film.

the orientations of the η- and ξ-OA in the spheroid **A** can be considered by coupling the uniaxial stretching model with the biaxial stretching model described below.

On bi(Z,Y)axial stretching of **IS**, the ζ η-plane, which we call the orientational plane (OP), will approach the ZY-plane (film plane) as shown in Fig. 2b. On the other hand, ξ-OA, which is normal to OP, will approach the X-direction. In this biaxial stretching model we ignore, for simplicity, the anisotropy in OP, which can be taken into account by coupling the biaxial stretching model with the uniaxial stretching model described above. Thus, as shown in Fig. 2b, the orientational distribution of OP in the spheroid **B** is described by one parameter α which is the angle of OP from the X-axis ($\pi/2 \geqq \alpha \geqq \alpha_0 \geqq 0$), the angle between ξ-OA and X-axis being $\pi/2-\alpha \equiv \beta$ ($0 \leqq \beta \leqq \beta_0 \leqq \pi/2$). As an alternative model for the bi(Z,Y)axial stretching of **IS**, we consider that **IS** is compressed in the X-direction. We have applied this uni(X)axial compressing model for the analysis of the orientational distribution of OP in the spheroid **B**. The distribution function in the uniaxial compressing model may be the same as that in the uniaxial stretching model, the difference being only that the deformation ratio is smaller than 1 in the uniaxial compressing model, while it is larger than 1 in the uniaxial stretching model. Thus, the orientational distribution function of OP in the spheroid **B** is given as

$$f(\alpha) = R_b^2 \sin\alpha / [1 + (R_b^2 - 1)\sin^2\alpha]^{3/2}, \tag{2}$$

where R_b is the biaxial deformation ratio defined as the a/c value ($\leqq 1$) in the spheroid **B** (Fig. 1) and is equal to the minus third power of the biaxial stretching ratio (R_{sb}) of the film obtained experimentally. Since β is a complementary angle of α, we can substitute $\cos\beta$ for $\sin\alpha$ in Eq. 2 to obtain the orientational distribution function of the ξ-OA in the spheroid **B** as

$$f(\beta) = R_b^2 \cos\beta / [1 + (R_b^2 - 1)\cos^2\beta]^{3/2}. \tag{2a}$$

Availing ourselves of the Euler angles representing the spatial relations between the ZYX- and ζ η ξ-systems, and assuming free rotations about the Z- and ζ-axes, i.e., assuming equal orientational distributions for the directions perpendicular to the Z- and ζ-axes, we can obtain the following relations between the Z-, Y-, and X-polarized absorption components (A_Z, A_Y, and A_X) and the ζ-, η-, and ξ-polarized absorption components (A_ζ, A_η, and A_ξ) for the uni(Z)axial stretching model.

$$A_Z = A_\zeta \cos^2\theta + (1/2)(A_\eta + A_\xi)\sin^2\theta, \tag{3a}$$

$$A_Y = A_X = (1/2)A_\zeta \sin^2\theta + (1/4)(A_\eta + A_\xi)(\cos^2\theta + 1). \tag{3b}$$

Likewise, assuming free rotations about the X- and ξ-axes, the relations between A_Z, A_Y, A_X and A_ζ, A_η, A_ξ are given for the bi(Z,Y)axial stretching model as

$$A_Z = A_Y = (1/4)(A_\zeta + A_\eta)(\cos^2\beta + 1) + (1/2)A_\xi \sin^2\beta, \tag{4a}$$

$$A_X = (1/2)(A_\zeta + A_\eta)\sin^2\beta + A_\xi \cos^2\beta. \tag{4b}$$

As spectroscopic measures for the anisotropies of the orientational distributions of the solute molecules in the uniaxially- and biaxially-stretched films, we have experimentally determined the uniaxial absorbance ratio (R_A^u) and the biaxial absorbance ratio (R_A^b) for A_Z, A_Y, and A_X as

$$R_{\mathrm{A}}^{\mathrm{u}} = \langle A_Z \rangle_{\mathrm{u}} / [(\langle A_Y \rangle_{\mathrm{u}} + \langle A_X \rangle_{\mathrm{u}})/2] = A_{\|}/A_{\perp}, \tag{5}$$

$$R_{\mathrm{A}}^{\mathrm{b}} = \langle A_X \rangle_{\mathrm{b}} / [(\langle A_Z \rangle_{\mathrm{b}} + \langle A_Y \rangle_{\mathrm{b}})/2] = 3R_{\mathrm{b}}^{2/3} A_{\mathrm{i}}/A_{\mathrm{b}} - 2. \tag{6}$$

$A_{\|}$ and $A_{\perp}$ in Eq. 5 are the absorbances for the polarized lights the electric vectors of which are parallel to and perpendicular to the uniaxial stretching direction of the film, respectively. A_{i} and A_{b} in Eq. 6 are the absorbances before and after the biaxial stretching of the film, respectively, $A_{\mathrm{b}}/A_{\mathrm{i}}$ being denoted as $(R_{\mathrm{bi}})_{\mathrm{exp}}$ in our previous paper.[3)] $\langle A_Z \rangle_{\mathrm{u}}$ and $\langle A_Z \rangle_{\mathrm{b}}$ stand for the mean values of A_Z averaged over all the solute molecules that are anisotropically distributed in the uniaxially- and biaxially-stretched films, respectively, and are evaluated by the uses of the orientational distribution functions $f(\theta)$ (Eq. 1) and $f(\beta)$ (Eq. 2a) as $\langle A_Z \rangle_{\mathrm{u}} = \int_0^{\pi/2} A_Z f(\theta)\mathrm{d}\theta$ and $\langle A_Z \rangle_{\mathrm{b}} = \int_0^{\pi/2} A_Z f(\beta)\mathrm{d}\beta$. The second equality in Eq. 6 is derived as follows. $A_{\mathrm{i}}^{\mathrm{b}}$, which is the A_{i} value calibrated for the change in the film thickness ($t_{\mathrm{b}}/t_{\mathrm{i}}$) accompanying the biaxial stretching of a film, is evaluated as $A_{\mathrm{i}}^{\mathrm{b}} = (t_{\mathrm{b}}/t_{\mathrm{i}})A_{\mathrm{i}} = R_{\mathrm{sb}}^{-2} A_{\mathrm{i}} = R_{\mathrm{b}}^{2/3} A_{\mathrm{i}}$, where the relation of $t_{\mathrm{b}}/t_{\mathrm{i}} = R_{\mathrm{sb}}^{-2}$ is experimentally verified in Fig. 7 in Ref. 3. Considering that $\langle A_X \rangle_{\mathrm{i}} = \langle A_Y \rangle_{\mathrm{i}} = \langle A_Z \rangle_{\mathrm{i}} = A_{\mathrm{i}}^{\mathrm{b}}$ and $\langle A_X \rangle_{\mathrm{b}} \neq \langle A_Y \rangle_{\mathrm{b}} = \langle A_Z \rangle_{\mathrm{b}} = A_{\mathrm{b}}$, the relation of $\langle A_X \rangle_{\mathrm{b}} + \langle A_Y \rangle_{\mathrm{b}} + \langle A_Z \rangle_{\mathrm{b}} = \langle A_X \rangle_{\mathrm{i}} + \langle A_Y \rangle_{\mathrm{i}} + \langle A_Z \rangle_{\mathrm{i}}$ yields that $\langle A_X \rangle_{\mathrm{b}} = 3A_{\mathrm{i}}^{\mathrm{b}} - 2A_{\mathrm{b}} = 3R_{\mathrm{b}}^{2/3} A_{\mathrm{i}} - 2A_{\mathrm{b}}$. Therefore, $\langle A_X \rangle_{\mathrm{b}} / [(\langle A_Z \rangle_{\mathrm{b}} + \langle A_Y \rangle_{\mathrm{b}})/2] = (3R_{\mathrm{b}}^{2/3} A_{\mathrm{i}} - 2A_{\mathrm{b}})/A_{\mathrm{b}} = 3R_{\mathrm{b}}^{2/3} A_{\mathrm{i}}/A_{\mathrm{b}} - 2$.

Substituting Eq. 3 into Eq. 5 and Eq. 4 into Eq. 6, and evaluating the definite integrals mentioned above, we obtain the theoretical expressions for $R_{\mathrm{A}}^{\mathrm{u}}$ and $R_{\mathrm{A}}^{\mathrm{b}}$ as

$$R_{\mathrm{A}}^{\mathrm{u}} = [2 + 2(2r_{\mathrm{A}}^{\mathrm{u}} - 1)T_{\mathrm{u}}] / [2r_{\mathrm{A}}^{\mathrm{u}} + 1 - (2r_{\mathrm{A}}^{\mathrm{u}} - 1)T_{\mathrm{u}}], \tag{7a}$$

where

$$\begin{aligned} T_{\mathrm{u}} &= \int_0^{\pi/2} \cos^2\theta \; f(\theta)d\theta \\ &= [R_{\mathrm{u}}^2/(R_{\mathrm{u}}^2 - 1)][1 - (R_{\mathrm{u}}^2 - 1)^{-1/2} \sin^{-1}\{(R_{\mathrm{u}}^2 - 1)^{1/2}/R_{\mathrm{u}}\}], \end{aligned} \tag{7b}$$

$$r_{\mathrm{A}}^{\mathrm{u}} = A_{\zeta}/(A_{\eta} + A_{\xi}), \tag{7c}$$

and

$$R_{\mathrm{A}}^{\mathrm{b}} = [2r_{\mathrm{A}}^{\mathrm{b}} + (1 - 2r_{\mathrm{A}}^{\mathrm{b}})T_{\mathrm{b}}] / [1 - (1 - 2r_{\mathrm{A}}^{\mathrm{b}})T_{\mathrm{b}}/2], \tag{8a}$$

where

$$\begin{aligned} T_{\mathrm{b}} &= \int_0^{\pi/2} \sin^2\beta \; f(\beta)d\beta \\ &= [R_{\mathrm{b}}^2/(1 - R_{\mathrm{b}}^2)][(1 - R_{\mathrm{b}}^2)^{-1/2} \sinh^{-1}\{(1 - R_{\mathrm{b}}^2)^{1/2}/R_{\mathrm{b}}\} - 1], \end{aligned} \tag{8b}$$

$$r_{\mathrm{A}}^{\mathrm{b}} = A_{\xi}/(A_{\zeta} + A_{\eta}). \tag{8c}$$

Substituting the experimental values of $R_{\mathrm{A}}^{\mathrm{u}}$ and R_{u} into Eq. 7, and those of $R_{\mathrm{A}}^{\mathrm{b}}$ and R_{b} into Eq. 8, we can obtain the uniaxial absorbance ratio ($r_{\mathrm{A}}^{\mathrm{u}}$, Eq. 7c) and the biaxial absorbance ratio ($r_{\mathrm{A}}^{\mathrm{b}}$, Eq. 8c), respectively, for A_{ζ}, A_{η}, and A_{ξ}. The essential aspect of our unified theory of the uniaxially- and biaxially-stretched film methods is to assume that the three-dimensional molecular orientation axes (ζ-, η-, and ξ-OA) for the solute molecule in the uniaxially-stretched film coincide with those for the solute molecule in the biaxially-stretched film. Under this assumption, we solve Eqs. 7c and 8c along with the equation of $A_{\zeta} + A_{\eta} + A_{\xi} = A$ as simultaneous ones to evaluate A_{ζ}, A_{η}, and A_{ξ}. By this unified theory, therefore, we can reduce the electronic absorption spectrum ($A(\lambda)$; λ stands for the wavelength) of a solute into the three-dimensional reduced spectra polarized along the ζ-, η-, and ξ-OA ($A_{\zeta}(\lambda)$, $A_{\eta}(\lambda)$, $A_{\xi}(\lambda)$).

Transformation Theory: Transformation of OA-Polarized Three-Dimensional Reduced Spectra into MA-Polarized Three-Dimensional Reduced Spectra. In the next step, we must transform the OA-polarized three-dimensional reduced spectra ($A_{\zeta}(\lambda)$, $A_{\eta}(\lambda)$, $A_{\xi}(\lambda)$) into the MA-polarized ones ($A_z(\lambda)$, $A_y(\lambda)$, $A_x(\lambda)$). To perform this transformation, we need the spatial relation between OA and MA, which can be obtained by evaluating the direction cosines (DC) of MA with respect to OA ($l_{z\zeta}$, $l_{z\eta}$, $l_{z\xi}$, etc.) as follows: Since the direction of the transition moment (μ) for the pure (nonoverlapping) band of the symmetrical molecule coincides with that of MA, the reduction of all the MA-polarized pure bands (A_z, A_y, A_x) into the OA-polarized absorption components ($A_{z\zeta}$, $A_{z\eta}$, $A_{z\xi}$, etc.) by our unified theory allows the evaluation of all the above-mentioned DC squared as

$$l_{z\zeta}^2 = A_{z\zeta}/A_z; \quad l_{z\eta}^2 = A_{z\eta}/A_z; \quad l_{z\xi}^2 = A_{z\xi}/A_z; \quad \text{etc.} \tag{9}$$

Since the ideal condition of the concomitant existence of all the MA-polarized pure bands (z-, y-, and x-bands), which is assumed to be satisfied in the above discussion, is seldom fulfilled, we assume a plausible condition of the existences of an MA-polarized pure band (e.g. z-band) and an overlapping band (H-band) consisting of two MA-polarized absorption components (e.g., A_z and A_y; $A_{\mathrm{H}} = A_{\mathrm{H}z} + A_{\mathrm{H}y}$), one of which must coincide in polarization with the pure band (z-band) just assumed to exist. Under this assumption, we will show the procedures to evaluate DC squared of MA with respect to OA. If we apply the unified theory to the z-band, we obtain the values of the uniaxial and biaxial absorbance ratios ($r_{\mathrm{A}z}^{\mathrm{u}}$ and $r_{\mathrm{A}z}^{\mathrm{b}}$) for the OA-polarized absorption components of the z-band ($A_{z\zeta}$, $A_{z\eta}$, $A_{z\xi}$), yielding the following equations.

$$\begin{aligned} &r_{\mathrm{A}z}^{\mathrm{u}} = A_{z\zeta}/(A_{z\eta} + A_{z\xi}); \quad r_{\mathrm{A}z}^{\mathrm{b}} = A_{z\xi}/(A_{z\zeta} + A_{z\eta}); \\ &A_z = A_{z\zeta} + A_{z\eta} + A_{z\xi}. \end{aligned} \tag{10}$$

Solving these simultaneous equations, we can evaluate DC squared of the z-MA with respect to OA, i.e. ${l_{z\zeta}}^2(=A_{z\zeta}/A_z)$, ${l_{z\eta}}^2(=A_{z\eta}/A_z)$, and ${l_{z\xi}}^2(=A_{z\xi}/A_z)$, in terms of $r_{\mathrm{A}z}^{\mathrm{u}}$ and $r_{\mathrm{A}z}^{\mathrm{b}}$ as

$$\begin{aligned} &l_{z\zeta}^2 = (r_{\mathrm{A}z}^{\mathrm{u}} + r_{\mathrm{A}z}^{\mathrm{u}} r_{\mathrm{A}z}^{\mathrm{b}})/\Delta'; \quad l_{z\eta}^2 = (1 - r_{\mathrm{A}z}^{\mathrm{u}} r_{\mathrm{A}z}^{\mathrm{b}})/\Delta'; \\ &l_{z\xi}^2 = (r_{\mathrm{A}z}^{\mathrm{b}} + r_{\mathrm{A}z}^{\mathrm{u}} r_{\mathrm{A}z}^{\mathrm{b}})/\Delta', \end{aligned} \tag{11}$$

where $\Delta' = 1 + r_{\mathrm{A}z}^{\mathrm{u}} + r_{\mathrm{A}z}^{\mathrm{b}} + r_{\mathrm{A}z}^{\mathrm{u}} r_{\mathrm{A}z}^{\mathrm{b}}$. Likewise, the apparent DC squared for μ of the H-band with respect to OA, i.e. $L_{\mathrm{H}\zeta}^2(=A_{\mathrm{H}\zeta}/A_{\mathrm{H}})$, $L_{\mathrm{H}\eta}^2(=A_{\mathrm{H}\eta}/A_{\mathrm{H}})$, and $L_{\mathrm{H}\xi}^2(=A_{\mathrm{H}\xi}/A_{\mathrm{H}})$, are also given in the form of Eq. 11, where $r_{\mathrm{A}z}^{\mathrm{u}}$ and $r_{\mathrm{A}z}^{\mathrm{b}}$ are respectively replaced by $r_{\mathrm{AH}}^{\mathrm{u}}(=A_{\mathrm{H}\zeta}/(A_{\mathrm{H}\eta} + A_{\mathrm{H}\xi}))$ and $r_{\mathrm{AH}}^{\mathrm{b}}(=A_{\mathrm{H}\xi}/(A_{\mathrm{H}\zeta} + A_{\mathrm{H}\eta}))$, both of which can be evaluated by application of the unified theory to the H-band. These apparent

DC squared for μ of the H-band are expressed, since the H-band is assumed to consist of A_z and A_y, by linear combinations of DC squared of z- and y-MA with respect to OA as

$$L_{\mathrm{H}\zeta}^2 = \rho_z l_{z\zeta}^2 + \rho_y l_{y\zeta}^2;\quad L_{\mathrm{H}\eta}^2 = \rho_z l_{z\eta}^2 + \rho_y l_{y\eta}^2;$$
$$L_{\mathrm{H}\xi}^2 = \rho_z l_{z\xi}^2 + \rho_y l_{y\xi}^2, \tag{12}$$

where ρ_z and ρ_y are the overlapping ratios of A_z and A_y in the H-band, respectively ($\rho_{\mathrm{z}}+\rho_{\mathrm{y}}=1$). The coupling of the orthogonal relation of DC of MA with respect to OA ($l_{z\zeta}l_{y\zeta}+l_{z\eta}l_{y\eta}+l_{z\xi}l_{y\xi}=0$) with Eq. 12 can eliminate ρ_y and DC of y-MA with respect to OA, yielding the quadratic equation of ρ_z as

$$A\rho_z^2 + 2B\rho_z + C = 0, \tag{13}$$

where

$$\begin{aligned}
A &= (l_{z\xi}^4 + l_{z\eta}^4 - l_{z\zeta}^4)^2 - 4l_{z\xi}^4 l_{z\eta}^4,\\
B &= 2l_{z\xi}^2 l_{z\eta}^2 (l_{z\xi}^2 L_{\mathrm{H}\eta}^2 + l_{z\eta}^2 L_{\mathrm{H}\xi}^2)\\
&\quad -(l_{z\xi}^4 + l_{z\eta}^4 - l_{z\zeta}^4)(l_{z\xi}^2 L_{\mathrm{H}\xi}^2 + l_{z\eta}^2 L_{\mathrm{H}\eta}^2 - l_{z\zeta}^2 L_{\mathrm{H}\zeta}^2),\\
C &= (l_{z\xi}^2 L_{\mathrm{H}\xi}^2 + l_{z\eta}^2 L_{\mathrm{H}\eta}^2 - l_{z\zeta}^2 L_{\mathrm{H}\zeta}^2)^2 - 4l_{z\xi}^2 l_{z\eta}^2 L_{\mathrm{H}\xi}^2 L_{\mathrm{H}\eta}^2.
\end{aligned}$$

Since the coefficients (A, B, and C) are known, this quadratic equation can be solved for ρ_z, ρ_y being given by $1-\rho_z$. Using ρ_z and ρ_y thus evaluated, ${l_{y\zeta}}^2$, ${l_{y\eta}}^2$, and ${l_{y\xi}}^2$ can be evaluated from Eq. 12 as Eq. 14, and the values of ${l_{x\zeta}}^2$, ${l_{x\eta}}^2$, and ${l_{x\xi}}^2$ are given by Eq. 15.

$$l_{y\zeta}^2 = (L_{\mathrm{H}\zeta}^2 - \rho_z l_{z\zeta}^2)/\rho_y;\quad l_{y\eta}^2 = (L_{\mathrm{H}\eta}^2 - \rho_z l_{z\eta}^2)/\rho_y;$$
$$l_{y\xi}^2 = (L_{\mathrm{H}\xi}^2 - \rho_z l_{z\xi}^2)/\rho_y. \tag{14}$$

$$l_{x\zeta}^2 = 1 - l_{z\zeta}^2 - l_{y\zeta}^2;\quad l_{x\eta}^2 = 1 - l_{z\eta}^2 - l_{y\eta}^2;$$
$$l_{x\xi}^2 = 1 - l_{z\xi}^2 - l_{y\xi}^2. \tag{15}$$

The transformation of the OA-polarized three-dimensional reduced spectra into the MA-polarized ones can be done by substituting DC between MA and OA evaluated by Eqs. 11, 14, and 15 into Eq. 19 derived below. The apparent DC squared for μ of $A(\lambda)$ with respect to OA, i.e., $L_\zeta(\lambda)^2(=A_\zeta(\lambda)/A(\lambda))$, $L_\eta(\lambda)^2(=A_\eta(\lambda)/A(\lambda))$, and $L_\xi(\lambda)^2(=A_\xi(\lambda)/A(\lambda))$ can be given in the form of Eq. 11, where $r_{\mathrm{A_z}}^{\mathrm{u}}$ and $r_{\mathrm{Az}}^{\mathrm{b}}$ are replaced by $r_{\mathrm{A}(\lambda)}^{\mathrm{u}}(=A_\zeta(\lambda)/(A_\eta(\lambda)+A_\xi(\lambda)))$ and $r_{\mathrm{A}(\lambda)}^{\mathrm{b}}(=A_\xi(\lambda)/(A_\zeta(\lambda)+A_\eta(\lambda)))$, respectively, evaluated by application of the unified theory to $A(\lambda)$. These apparent DC squared for μ of $A(\lambda)$ are expressed by linear combinations of DC squared of z-, y-, and x-MA with respect to OA in parallel with Eq. 12 as

$$L_\zeta(\lambda)^2 = \rho_z(\lambda) l_{z\zeta}^2 + \rho_y(\lambda) l_{y\zeta}^2 + \rho_x(\lambda) l_{x\zeta}^2;$$
$$L_\eta(\lambda)^2 = \rho_z(\lambda) l_{z\eta}^2 + \rho_y(\lambda) l_{y\eta}^2 + \rho_x(\lambda) l_{x\eta}^2;$$
$$L_\xi(\lambda)^2 = \rho_z(\lambda) l_{z\xi}^2 + \rho_y(\lambda) l_{y\xi}^2 + \rho_x(\lambda) l_{x\xi}^2, \tag{16}$$

where $\rho_z(\lambda)$, $\rho_y(\lambda)$, and $\rho_x(\lambda)$ are the overlapping ratios of $A_z(\lambda)$, $A_y(\lambda)$, and $A_x(\lambda)$ in $A(\lambda)$, respectively ($\rho_z(\lambda)+\rho_y(\lambda)+\rho_x(\lambda)=1$). Solving these three equations as simultaneous ones, the values of $\rho_z(\lambda)$, $\rho_y(\lambda)$, and $\rho_x(\lambda)$ are given as

$$\rho_z(\lambda) = (1/\Delta)\begin{vmatrix} L_\zeta(\lambda)^2 & l_{y\zeta}^2 & l_{x\zeta}^2 \\ L_\eta(\lambda)^2 & l_{y\eta}^2 & l_{x\eta}^2 \\ L_\xi(\lambda)^2 & l_{y\xi}^2 & l_{x\xi}^2 \end{vmatrix}; \tag{17a}$$

$$\rho_y(\lambda) = (1/\Delta)\begin{vmatrix} l_{z\zeta}^2 & L_\zeta(\lambda)^2 & l_{x\zeta}^2 \\ l_{z\eta}^2 & L_\eta(\lambda)^2 & l_{x\eta}^2 \\ l_{z\xi}^2 & L_\xi(\lambda)^2 & l_{x\xi}^2 \end{vmatrix}; \tag{17b}$$

$$\rho_x(\lambda) = (1/\Delta)\begin{vmatrix} l_{z\zeta}^2 & l_{y\zeta}^2 & L_\zeta(\lambda)^2 \\ l_{z\eta}^2 & l_{y\eta}^2 & L_\eta(\lambda)^2 \\ l_{z\xi}^2 & l_{y\xi}^2 & L_\xi(\lambda)^2 \end{vmatrix}, \tag{17c}$$

where

$$\Delta = \begin{vmatrix} l_{z\zeta}^2 & l_{y\zeta}^2 & l_{x\zeta}^2 \\ l_{z\eta}^2 & l_{y\eta}^2 & l_{x\eta}^2 \\ l_{z\xi}^2 & l_{y\xi}^2 & l_{x\xi}^2 \end{vmatrix}. \tag{18}$$

If we multiply both sides of each equation in Eq. 17 by $A(\lambda)$, we obtain Eq. 19 using the relations $A_z(\lambda)=\rho_{\mathrm{z}}(\lambda)A(\lambda)$, $A_\zeta(\lambda)=L_\zeta(\lambda)^2A(\lambda)$, etc.

$$A_z(\lambda) = (1/\Delta)\begin{vmatrix} A_\zeta(\lambda) & l_{y\zeta}^2 & l_{x\zeta}^2 \\ A_\eta(\lambda) & l_{y\eta}^2 & l_{x\eta}^2 \\ A_\xi(\lambda) & l_{y\xi}^2 & l_{x\xi}^2 \end{vmatrix}; \tag{19a}$$

$$A_y(\lambda) = (1/\Delta)\begin{vmatrix} l_{z\zeta}^2 & A_\zeta(\lambda) & l_{x\zeta}^2 \\ l_{z\eta}^2 & A_\eta(\lambda) & l_{x\eta}^2 \\ l_{z\xi}^2 & A_\xi(\lambda) & l_{x\xi}^2 \end{vmatrix}; \tag{19b}$$

$$A_x(\lambda) = (1/\Delta)\begin{vmatrix} l_{z\zeta}^2 & l_{y\zeta}^2 & A_\zeta(\lambda) \\ l_{z\eta}^2 & l_{y\eta}^2 & A_\eta(\lambda) \\ l_{z\xi}^2 & l_{y\xi}^2 & A_\xi(\lambda) \end{vmatrix}. \tag{19c}$$

Experimental

Commercial perylene (Aldrich, GR) was used without further purification. Experimental procedures for the biaxially- and uniaxially-stretched film techniques were already described.[3,6,7] To introduce a self-consistent terminology in the theoretical section, we have changed the previous notations[3] of R_{s} (uniaxial stretching ratio of the film) and $R_{\mathrm{d}}(=A_{\parallel}/A_{\perp})$ to R_{u} and $R_{\mathrm{A}}^{\mathrm{u}}$, respectively. The spectra of perylene in the uniaxially- and biaxially-stretched films were measured on a Shimadzu UV-3100PC spectrophotometer equipped with a Rochon-type polarizer.

Results and Discussion

Figures 3a and 3b shows the $A_{\parallel}$, $A_{\perp}$, and $R_{\mathrm{A}}^{\mathrm{u}}(=A_{\parallel}/A_{\perp})$ spectra and the A_{b}, A_{i}, and $R_{\mathrm{bi}}(=A_{\mathrm{b}}/A_{\mathrm{i}}$ calibrated for the change in the film thickness accompanying the biaxial stretching of a film) spectra of perylene obtained by uniaxially- and biaxially-stretched film techniques, respectively. These spectral data were used for the unified theory proposed in the theoretical section to decompose the absorption spectrum ($A(\lambda)$) of perylene into the OA(ζ, η, ξ)-polarized three-dimensional reduced spectra ($A_\zeta(\lambda)$, $A_\eta(\lambda)$, $A_\xi(\lambda)$). The $A_\zeta(\lambda)$, $A_\eta(\lambda)$, and $A_\xi(\lambda)$ spectra of perylene thus obtained can be transformed into the MA(z,y,x)-polarized three-dimensional reduced spectra ($A_z(\lambda)$, $A_y(\lambda)$, $A_x(\lambda)$) by use of the transformation theory offered in the theoretical section. The key point in this transformation procedure is the selections of the nonoverlapping pure band and the overlapping

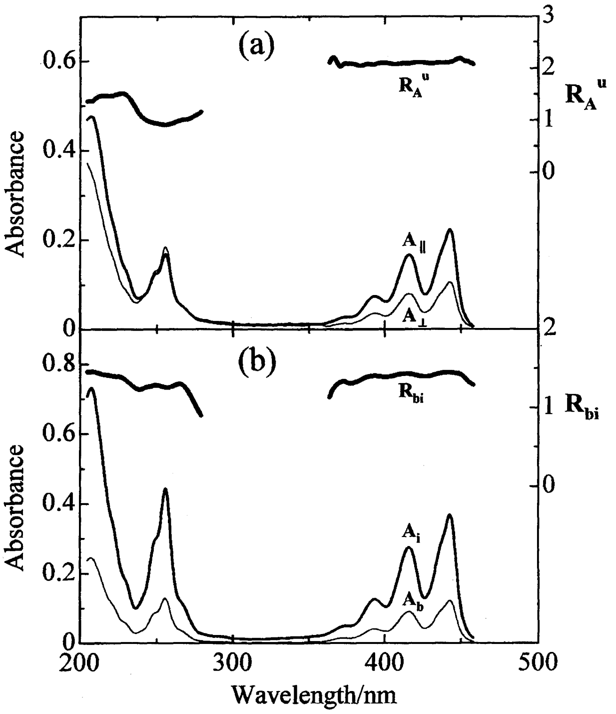

Fig. 3. Observed Spectra of perylene in (a) uniaxially- and (b) biaxially-stretched films.

band (H-band) consisting of two MA-polarized absorption components, as demonstrated below.

The R^u_A values in Fig. 3a are largest in the first (443 nm) band region and are smallest in the second (256 nm) band region. This qualitatively suggests that the first and second bands of perylene are approximately polarized along the longer (z) and shorter (y) molecular axes, respectively. Thus, there are two possibilities of selecting the first or second band as the pure band in applying the transformation theory. Selecting the first band as the z-polarized pure band and the second band as the overlapping H-band composed of A_z and A_y, we have tried to transform the $A_\zeta(\lambda)$, $A_\eta(\lambda)$, and $A_\xi(\lambda)$ spectra of perylene into the $A_z(\lambda)$, $A_y(\lambda)$, and $A_x(\lambda)$ spectra. This trial, however, has proved to be unsuccessful because the quadratic equation (Eq. 13) in the theoretical section gave a meaningless value of ρ_z or ρ_y, i.e., a negative or imaginary value or a value larger than 1.0. The alternative selection of the second band as the y-polarized pure band and the first band as the H-band composed of A_z and A_y has made the transformation in question possible. The resulting $A_z(\lambda)$, $A_y(\lambda)$, and $A_x(\lambda)$ spectra of perylene differed, however, in their relative intensities depending on which vibronic band of the first band is selected as the H-band, as shown in Figs. 4 and 5. In Figs. 4, 5a, 5b, and 5c are given the $A_z(\lambda)$, $A_y(\lambda)$, and $A_x(\lambda)$ spectra which resulted when the 0–0 peak (443 nm) and the first (416 nm), second (393 nm), and third (375 nm) vibronic peaks of the first band were selected as the H-band, respectively. It is noticed that the difference of these resulting spectra is greatest for the first band. That is, the $A_y(\lambda)$ and $A_x(\lambda)$ spectra in the first band region become regularly more intense on going from Fig. 4 to Fig. 5c, keeping the tendency that $A_y(\lambda)$ and $A_x(\lambda)$ are most intense at the 0–0 peak position and the former is always larger than the latter. We have considered that Fig. 4, which gives no A_x at the 0–0 peak position, is the correct $A_z(\lambda)$, $A_y(\lambda)$, and $A_x(\lambda)$ spectra of perylene on the ground that A_x does hardly happen to emerge at the 0–0 peak position of the first band; the minor extra absorption component (A_y or A_x) can emerge at the 0–0 position of the major electronically-allowed absorption component spectrum ($A_z(\lambda)$) by only the mechanism of the intensity borrowing from the nearby y-polarized second (256 nm) band, thus the borrowed absorption component is A_y alone.

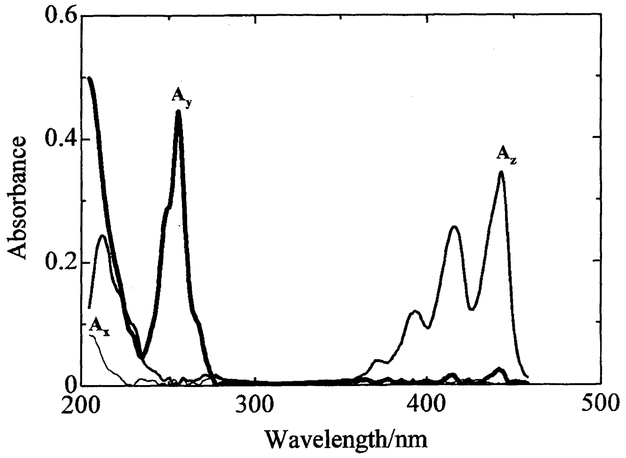

Fig. 4. Correct $A_z(\lambda)$, $A_y(\lambda)$ and $A_x(\lambda)$ spectra of perylene, which result when the second (256 nm) band and the 0–0 peak (443 nm) of the first band are selected as the y-polarized pure band and the overlapping band (H-band), respectively, in the transformation theory.

The intensity borrowing mechanism mentioned above is supported by the following results of the semiempirical MO calculations by the PPP method[8,9] modified by the Nishimoto–Mataga[10] and Nishimoto–Forster[11] equations: Between the first allowed (f (oscillator strength)$=0.843$) z-polarized electronic transition calculated at 420 nm and the second allowed ($f=1.585$) y-polarized one calculated at 255 nm, which are respectively assigned to the first (443 nm) and second (256 nm) bands, is predicted, by an MO calculation adopting the same Coulomb potentials for all the carbon atoms of perylene, no allowed electronic transition to be assigned to the minor absorption component of A_y in the first band region, or, by an MO calculation adopting the deeper Coulomb potentials (higher valence-state ionization potentials) for the carbon atoms combined with only the carbon atoms than those for the carbon atoms combined with both the carbon and hydrogen atoms, at most only a very weak ($f=0.005$) y-polarized transition, which is calculated at 353 nm far from the first allowed transition and hence is hard to assign to A_y appearing at the 0–0 position of $A_z(\lambda)$ in the first band region. In the latter MO calculation, the pairing theorem no longer applies even for the alternant hydrocarbon of perylene, and hence all the transitions, which are, despite their group-theoretical allowances, calculated to

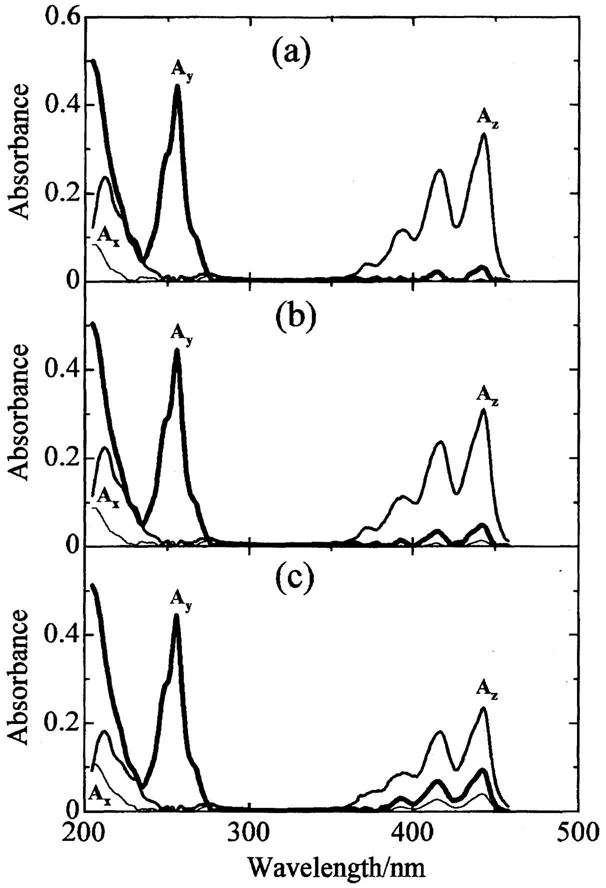

Fig. 5. Incorrect $A_z(\lambda)$, $A_y(\lambda)$ and $A_x(\lambda)$ spectra of perylene, which result when (a) the first (416 nm), (b) second (393 nm), and (c) third (375 nm) vibronic peaks of the first band are selected as the H-band in the transformation theory, the second (256 nm) band being selected as the y-polarized pure band as in Fig. 4.

be forbidden following Pariser's parity rule[12] in the former MO calculation, are computed to be allowed in violation of Pariser's parity rule, thus the very weak transition at 353 nm is calculated to be newly allowed.

Figure 6 shows the spatial relation that was used in the transformation theory to obtain Fig. 4, between molecular axes (z,y,x) and molecular orientation axes (ζ, η, ξ) of perylene. It is verified from this figure that the molecular orientation axes are not coincident with the molecular axes, and ζ-, η-, and ξ-OA are close to z-, y-, and x-MA, respectively.

The correct MA-polarized three-dimensional reduced spectra of perylene (Fig. 4) shows that the first and second bands are almost wholly contributed by A_z and A_y, respectively, throughout these respective band regions. This decomposition result is in good agreement with the two-dimensional reduced spectra of perylene obtained by Tanizaki, Yoshinaga, and Hiratsuka,[13] and by Thulstrup, Michl, and Eggers[14] by use of only the uniaxially-stretched film method.

A close inspection of the first band in Fig. 4 shows that this band contains a weak absorption component spectrum of $A_y(\lambda)$, the intensity of which is borrowed from the y-polarized second band as already discussed, with a vibronic structure the peaks of which coincide with the main vibronic band peaks of $A_z(\lambda)$. These vibronic structures of $A_z(\lambda)$ and $A_y(\lambda)$ are considered to arise from the coupling of the totally-symmetric a_{1g} vibration with the first allowed (z-polarized) electronic transition and with the borrowed (y-polarized) absorption, respectively.

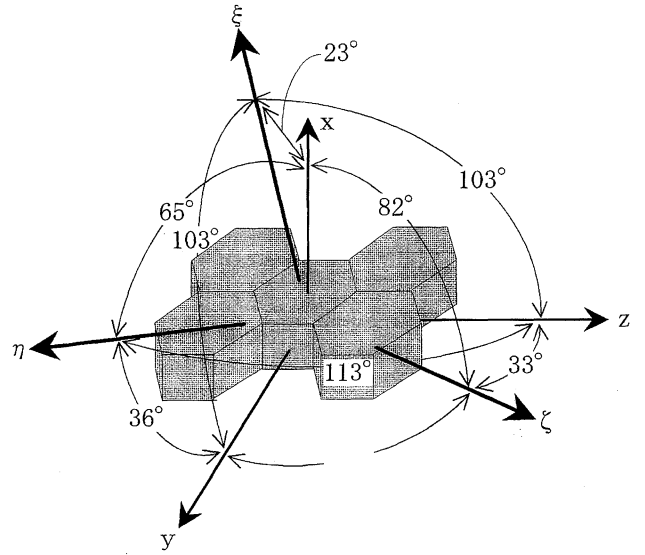

Fig. 6. Spatial relation between molecular axes (z,y,x) and molecular orientation axes (ζ, η, ξ) of perylene. This relation was used in the transformation theory to get Fig. 4.

Figure 4 shows furthermore that the third band of perylene, positioned in the wavelength region shorter than 235 nm, is a complex superimposition of A_y, A_z, and A_x with decreasing contributions in this order, A_x being most weak but nonneglible. This decomposition result differs from the two-dimensional reduced spectra[13,14] mentioned above in several points: First, A_x contributes considerably to the third band as opposed to both the two-dimensional reduced spectra; second, A_y is most intense in the third band region in contrast to the reduced spectra obtained by Tanizaki et al.[13] in which A_z is most intense in the third band region (note that the notation of the molecular axes in Ref. 13 differs from that in this paper); third, a fairly intense A_z exists in the third band region in contrast to the reduced spectra found by Thulstrup et al.[14] in which A_z is fairly weak in the third band region.

In the third band region in Fig. 4, the most intense A_y is positioned at a wavelength shorter than the fairly intense A_z with shoulders, which is well reproduced by a PPP calculation to result in the assignments of the former to the y-polarized electronic transition calculated at 201 nm (f=2.075) and the latter to the z-polarized ones calculated at 221 nm (f=0.736) and 213 nm (f=0.317). The x-polarized absorption component in the third band region is tentatively considered to emerge by intensity borrowing from the x-polarized $\pi^* \leftarrow \sigma$ band to be observed in the vacuum ultraviolet region.

Thus, it has been demonstrated that the electronic absorption spectrum of a symmetric molecule can be decomposed into three-dimensional reduced spectra polarized along three molecular axes by a unified coupling of the uniaxially- and biaxially-stretched film methods. This unified coupling has given the in-plane polarized (longer- and shorter-molecular axes polarized) absorption spectra of perylene, which are in fair agreement with those obtained by the uniaxially-stretched film method and, furthermore, has shed light on a new aspect of the out-of-plane polarized absorption spectrum of perylene, which is never clarified by the uniaxially-stretched film method alone.

References

1) E. W. Thulstrup and J. Michl, *J. Phys. Chem.*, **84**, 82 (1980).

2) E. W. Thulstrup and J. Michl, *J. Am. Chem. Soc.*, **104**, 5594 (1982).

3) M. Kobayashi, X. Yuan, H. Sakai, T. Hoshi, J. Okubo, and Y. Tanizaki, *Bull. Chem. Soc. Jpn.*, **65**, 463 (1992).

4) Y. Tanizaki, *Bull. Chem. Soc. Jpn.*, **32**, 75 (1959).

5) Y. Tanizaki, *Bull. Chem. Soc. Jpn.*, **38**, 1798 (1965).

6) Y. Tanizaki and S. Kubodera, *J. Mol. Spectrosc.*, **24**, 1 (1967).

7) H. Hiratsuka, Y. Tanizaki, and T. Hoshi, *Spectrochim. Acta, Part A*, **28**, 2375 (1972).

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

9) J. A. Pople, *Proc. Phys. Soc. (London)*, **A68**, 81 (1955).

10) N. Mataga and K. Nishimoto, *Z. Phys. Chem. Neue Folge*, **13**, 140 (1957).

11) K. Nishimoto and L. S. Forster, *Theor. Chim. Acta*, **3**, 407 (1965).

12) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).

13) Y. Tanizaki, T. Yoshinaga, and H. Hiratsuka, *Spectrochim. Acta, Part A*, **34**, 205 (1978).

14) E. W. Thulstrup, J. Michl, and J. H. Eggers, *J. Phys. Chem.*, **74**, 3868 (1970).