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Electronic Spectra of Single Crystals of 1,1′-Diethyl-2,2′-Cyanine Iodide, Bromide, and Chloride

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Reflection spectra of single crystals of 1,1′-diethyl-2,2′-cyanine iodide, bromide and chloride were measured in order to find the origin of the J band. The spectra were obtained by the Kramers-Kronig transformation of reflectivity. The positions of absorption peaks and the shapes of vibronic envelope for each crystalline faces are explained by a calculation of surface exciton splitting with a weak coupling model. The intensity of each bands is interpreted by the oriented gas model, however, a peculiar anomalous band shape characteristic of J band is explained by the charge resonance (CR) and the molecular exciton interaction. The J band is found along particular crystalline direction, in which the dye molecules are stacked face to face, showing importance of interplanar π electron interaction. The molecular exciton band shape is changed significantly to give a J band because the higher vibronic bands are blurred off by the enhanced relaxation mechanism of the CR interaction.

Jelly¹⁾ and Scheibe²⁾ found a sharp electronic absorption band of cyanine dye on a concentrated solution of 1,1′-diethyl-2,2′-cyanine, and it has been called J band. The J band shows several peculiar spectral characteristics; the band appears only in an aggregate system and it is unusually sharp as an electronic transition of organic molecule modified by association. The emission spectra of the aggregate is also sharp without Stokes shift. The spectra and physico-chemical properties of cyanine dye aggregate system have been investigated by many people, particularly by Scheibe and his coworkers³⁾ in view of finding the relation between the structure and the spectra and the mechanism of spectral sensitization for silver halide crystals. Cooper⁴⁾ investigated the aggregate state in solution at low temperature and found a doublet structure in the J band and a sharp emission band. Daltrozzo *et al.*⁵⁾ studied the condition of J-aggregation in solution and proposed a model of the aggregate.

Theoretical investigation on the band shift of the aggregate was first presented by McRae and Kasha⁶⁾ based on a molecular exciton theory, and further development was proceeded by Norland, Bird and their group⁷⁾ and Kuhn and his group.⁸⁾ These authors suggested that a lateral displacement of adjacent dye molecules shifts a monomer absorption band (M band) to red and produces the J band, while a pairwise stacking of the dye causes a hypsochromic H band. A theory of the band shape of the J band was developed by Briggs and Herzenberg⁹⁾ with coherent exciton scattering (CES) method and it has been suggested that the band will be sharp when the exciton interaction is much stronger than the coupling with the molecular vibration. Sumi¹⁰⁾ extended a model calculation with coherent potential approximation (CPA) including several coupling parameters and obtained a band shape which looks like the J band. A similar calculation was carried out by Ito *et al.*¹¹⁾

In order to study the nature of the electronic transitions of the J aggregate, spectral measurement of the single crystals of these dyes will be particularly useful, because the directional properties of the electronic transition may be clearly demonstrated and a peculiar characteristics of the J band may be found. Several years ago Dr. Jörg Preuss in Münich suggested to one of the authors (J. T.) that a sharp J type absorption band could be found in the crystal of 1,1′-diethyl-2,2′-cyanine chloride along the stacking axis of the molecules. Recently Marchetti *et al.*¹²⁾ reported the crystalline spectra of the same dye iodide and chloride and correlated the J band in solution to the crystalline exciton state.

In this paper the spectra of the above dye iodide, bromide and chloride are presented with a theoretical consideration of the band splitting and the band shape, together with assignments of each band. A particular emphasis will be given on the importance of the charge resonance (CR) interaction between the dye molecules in the crystals.

Experimental

Materials. 1,1′-Diethyl-2,2′-cyanine iodide (dye iodide) was a product of Japanese Research Institute for Photosensitizing Dyes Co. (Okayama). The crystals of the dye iodide were obtained by recrystallization from methanol solution. The crystals of the dye bromide and the chloride were obtained by metathesis with potassium bromide or chloride after precipitation of the iodide by silver nitrate as silver iodide. The crystalline forms and faces were confirmed by taking X-ray photographs on Weissenberg camera and compared with the published X-ray data.¹³⁻¹⁵⁾ The shape of the crystalline forms are sketched as shown in Fig. 1.

Measurements. The reflection spectra were measured with a microscopic spectrophotometer constructed in this laboratory. It consists of an Olympus microscope, a Carl Zeiss Ultrafluar lens (×10), a Nikon crystal mount, a HTV 928 photomultiplier tube as detecting device and an Intel 8080 microcomputer for data processing. The reflectivities were converted to molar absorption coefficients by using Kramers-Kronig transformation on a FACOM 230-60 and 230-75 computers of Nagoya University Computation Center.

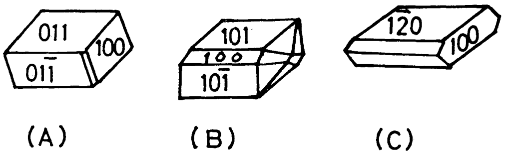

Fig. 1. Crystalline habit and developed faces of (A) dye iodide, (B) dye bromide, and (C) dye chloride.

TABLE 1. CRYSTALLINE DATA OF 1,1′-DIETHYL-2,2′-CYANINE HALIDE

	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)	Space group	Ref.
Dye iodide	10.787	11.626	16.484	90.0	107.48	90.0	$P2_1/c$	15
Dye bromide	13.530	10.500	14.070	90.0	90.6	90.0	$P2_1/n$	14
Dye chloride	13.586	19.167	10.517	90.0	90.0	134.35	$P2_1/b$	13

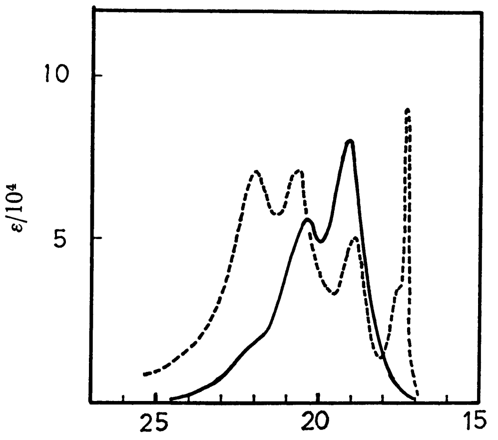

Fig. 2. Solution spectra of the dye iodide in EGW solution at 298 K (2×10^{-5} M, ——) and at 77 K (2×10^{-3} M, ----).

The spectra in a ethyleneglycol–water (EGW) solution at room temperature and 77 K were measured with a Cary 16 spectrophotometer equipped with a Cryo-tip refrigerator (Fig. 2).

Theoretical Considerations on Crystalline Excited States

Molecular Orbital and the Excited State of the Dye Molecule. The molecular orbitals of π electron system of the dye were calculated by Pariser-Parr-Pople[16] method with Nishimoto-Mataga[17] potential. The atomic coordinates determined by the X-ray crystal structure analyses were used for the calculation, and the results were nearly the same for the molecules in the iodide, bromide and chloride crystals. Two quinoline rings are twisted, hence the directions of π electron envelopes were settled along the direction perpendicular to one of the quinoline ring plane, another quinoline ring plane and the plane composed of the central carbon and the adjacent carbons of the quinoline rings. By this choice a pseudo-two-fold symmetry of the MO was conserved.

The highest occupied orbital (orbital 11, HOMO) and the lowest unoccupied orbital (orbital 12, LUMO) have a pseudo-symmetry of S_y and A_y, respectively, where the y axis is the short molecular axis, and the charge density spreads over the whole molecule. The second and the third HOMO are nearly degenerate, and the charge densities are localized on either one of quinoline rings.

The energy of the lowest allowed transition, which is composed of mainly one electron transition from the HOMO to LUMO, was calculated at 18600 cm^{-1} (2.30 eV) and the polarization is along the long axis of the molecule. The calculated value is nearly in agreement with the value found in solution spectra (*cf.* Fig. 2, peak at 19000 cm^{-1}). We consider only this transition in this paper because other bands are weak and locate at higher energy region.

Molecular Exciton States and Intermolecular Exciton Interaction. The crystals treated in this paper are all monoclinic with space groups and lattice constants as shown in Table 1 and they contain four molecules per unit cell. The molecular exciton (MX) state in the crystal, one of them is allowed along the monoclinic axis (A_u state) and another is allowed perpendicular to it (B_u state), are written as

$$\left.\begin{aligned} \mathrm{A_u}:\ \Psi_{\mathrm{b}} &= \frac{1}{\sqrt{N}}(\Psi_{1i}-\Psi_{2i}+\Psi_{3i}-\Psi_{4i})e^{i\boldsymbol{k}\cdot\boldsymbol{R}_i} \\ \mathrm{B_u}:\ \Psi_{\mathrm{ac}} &= \frac{1}{\sqrt{N}}(\Psi_{1i}-\Psi_{2i}-\Psi_{3i}+\Psi_{4i})e^{i\boldsymbol{k}\cdot\boldsymbol{R}_i} \end{aligned}\right\}, \tag{1}$$

where N is the number of molecules in the crystal under consideration, i is the numbering of unit cell and 1, 2, 3, and 4 designate the molecular site. Ψ_{1i} means the original site of the i-th cell is excited and others are in the ground state. Ψ_{2i}, Ψ_{3i}, and Ψ_{4i} are the wavefunction in which the excitation occurs at sites related by the crystal symmetries of inversion, screw-axis rotation and glide-reflection, respectively. The exponential factor shows the translational symmetry of the crystal, and if we consider N molecules with a spacing of a, then $k=2\pi n/Na$ where $n=0,1,2,\cdots N$.

The most significant term of the interaction Hamiltonian is the dipole-dipole type between the transition moment on different molecules. If we denote the HOMO by ψ_m and LUMO by ψ_n, the excitation transfer matrix element between the i-th and the j-th molecules will be written as

$$\begin{aligned} b_{ij} &= \int \psi^*_{jn}(r_j)\psi^*_{im}(r_i)\frac{e^2}{r_{ij}}\psi_{jm}(r_j)\psi_{in}(r_i)\,\mathrm{d}v_i\mathrm{d}v_j \\ &= \frac{1}{\boldsymbol{R}^3_{ij}}\left(\boldsymbol{p}_i\cdot\boldsymbol{p}_j-\frac{3(\boldsymbol{p}_i\cdot\boldsymbol{R}_{ij})(\boldsymbol{p}_j\cdot\boldsymbol{R}_{ij})}{\boldsymbol{R}^2_{ij}}\right) \end{aligned} \tag{2}$$

Here $\boldsymbol{R}_{ij}$ is the vector connecting between the i-th and the j-th molecules, $\boldsymbol{p}_i$ and $\boldsymbol{p}_j$ are the transition moments of these transitions, respectively.

For the strong molecular transition of the dye in the crystal, the dipole interaction is most significant, and the calculation of surface exciton states by a slab sum method is appropriate for the present analysis.[18] Marchetti *et al.*[12] calculated the surface exciton state of the dye iodide to explain the spectral shifts. We have calculated the surface exciton energies for the measured crystalline faces of the dye iodide and bromide and the results of calculation are shown in Table 2. Because the measured crystalline spectra showed a weak coupling type, the estimation of exciton band

Table 2. Calculated and observed band splittings

	Crystalline face	Calculated shift B_n			Observed shift (cm^{-1})	Shift used for simulation
		axis	Vib. level n	(cm^{-1})		
Dye iodide[a)]	(100)	b	0-0	−1425	−1650	−1500
			0-1	−1000	−1300	
		c	0-0	1319	1350	1500
			0-1	910	1050	
	(011)	b	0-0	−1034	−1600	
		a, c	0-0	750	1000	
			0-1	520	500	
					1000	
	(011)	b	0-0	−1633	−1600	
		a, c	0-0	123	1000	
Dye bromide[b)]	(100)	b	0-0	−1590	−1000	−1000
			0-1	−1113	−900	
			0-2	−398	−200	
		c	0-0	−974	−1040	−1000
			0-1	−682	−700	
			0-2	−244	−400	
	$(10\bar{1})$	b	0-0	−1590	−1000	
		c	0-0	−260	−200?	
	(101)	b	0-0	−1575	−1000	
		a, c	0-0	1880	2300?	3000
			0-1	1316		
			0-2	470		
Dye chloride[c)]	(100)	c	0-0	−1766	−1400	
			0-1	−1236	−1250	
		b	0-0	2184	2500	
	$(1\bar{2}0)$	c	0-0	−2092	−1400	
		a, b	0-0	−520	−500?	

a) $D=20$ Å, $R=100$ Å, and $E_0=19000$ cm^{-1}. b) $D=20$ Å, $R=200$ Å, and $E_0=18500$ cm^{-1}. c) $D=20$ Å, $R=200$ Å, and $E_0=19000$ cm^{-1}.

D=Depth of Slab. R=Radius of summation of molecules. E_0=The center of crystalline transition to compare with the observed spectra.

energies were presented for each vibronic band. The listed values B_n for each vibronic levels were obtained by using p values estimated from the oscillator strength for each vibronic band.

The summation of molecules was taken for the limited radius of sphere (100—200 Å) or the finite depth (10—20 Å) of the slab which gave a convergent result. The energy band structure for each exciton levels is illustrated in Fig. 3. The state density for the single exciton level will be given by $N/2B_n$, but when the higher vibronic exciton band overlaps with the lower ones, the density will be increased in the superposed region.

Charge Resonance State. When molecules in the crystals strongly overlap with neighboring ones, the charge transfer (CT) state becomes important. The crystals now considering are composed of same species, and the CT should occur between each other, hence the CT state should be called as the charge resonance (CR) state. The CR effect in molecular crystal will be two or three-fold; one is for the ground state to stabilize the stacked structure and others are an appearance of the CR exciton band and the modification of the molecular exciton bands.

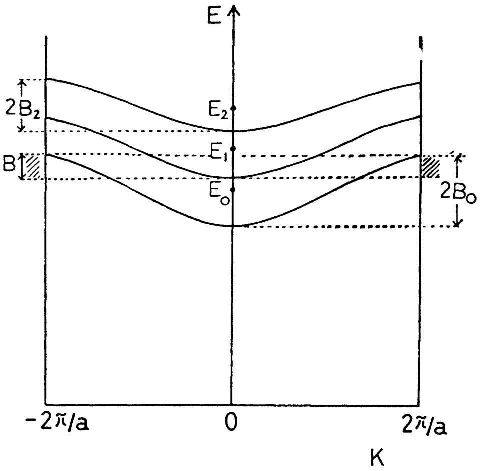

Fig. 3. Molecular exciton (MX) band structure with vibronic exciton splittings.

The CR transition in a neat molecular crystal is not so frequently found; the out of plane transition of the α form crystal of 9,10-dichloroanthracene[19–21)] is known to be the case. In anthracenophane molecules where the interplanar distances are very close, the CR absorptions are found but they are rather weak and broad.[22)] Apparently the CR transitions are found in cases where a peculiar polarization is

TABLE 3. ENERGY LEVELS OF CHARGE RESONANCE STATE

Dye halide crystals	Axis relating stacked molecules	Energy levels of CR states without polarization correction
Dye iodide	b-axis	3.33 eV
	c-axis	3.36
Dye bromide	a-axis	3.32
	b-axis	3.43
Dye chloride	a-axis	3.20
	c-axis	3.44

expected or a borrowing of intensity from nearby strong allowed transition is accessible. In the present crystals the intermolecular overlap is appreciably large along one-dimensional chain and the CR effect may be found on particular crystalline directions.

The energy level of the CR state is estimated by using the calculated MO and Nishimoto-Mataga[17] potential as shown in Table 3. The potential may underestimate the Coulomb term between molecules, hence the estimated levels may be too high. Moreover the CR state will be stabilized by a polarization force in a highly polarizable crystal as much as 1—2 eV.[23] Therefore the CR level may be at about 2.3 eV and they will be close to or coincident with the molecular exciton levels.

The mixing of the CR state wavefunction Φ to the ground state wavefunction Ψ_0 can be described by the wavefunction of the stabilized ground state as

$$\Psi_G = \Psi_0 + \frac{\langle \Psi_0 | H' | \Phi \rangle}{E_{CR} - E_0} \Phi. \tag{3}$$

The CR matrix element between the stacked molecules will be related to the transfer integral t and it is actually estimated by the overlap integrals between the π electrons of stacked molecules. Namely, the charge transfer matrix will be written, for example, between the HOMO of the i-th molecule and the LUMO of the j-th molecule as $t_{im,jn}$ or simply as t_{mn}. The calculated results of overlap integrals between the neighboring molecules are shown in Table 4, where a single exponent AO and four term expanded AO[24] were used for the calculation and compared in the Table. The empirical values of energy of t integrals are given by

$$t = kS, \tag{4}$$

where the proportional constant k is about $k = -10$ eV for S evaluated by the four term expanded AO and $k = -15$ eV for S obtained by single exponent AO. Referring to Table 2 the largest value is about -0.10—0.15 eV between the HOMO (t_{mm}) and about -0.10 eV between the HOMO and LUMO (t_{mn}). These values are fairly large as the intermolecular interaction in molecular crystal between the same species. The matrix element in Eq. 3 is relevant for t_{mn} and the coefficient of the CR configuration in the ground state is estimated as about 0.1.

The wavefunctions for the optically allowed CR exciton states are written as

$$\left.\begin{aligned} A_u\colon\ \Phi_b &= \frac{1}{\sqrt{N}} \sum_i (\Phi_{1i} - \Phi_{2i} + \Phi_{3i} - \Phi_{4i}) e^{ik\cdot R_i} \\ B_u\colon\ \Phi_{ac} &= \frac{1}{\sqrt{N}} \sum_i (\Phi_{1i} - \Phi_{2i} - \Phi_{3i} + \Phi_{4i}) e^{ik\cdot R_i} \end{aligned}\right\}. \tag{5}$$

Here Φ_{1i} implies that an electron in the 1st site of the i-th cell is transferred to the adjacent molecules. The CR exciton band width is estimated with these wavefunctions and only the nearest neighbor interactions are taken into account to give

$$C = b_{CR} + S_{mm} t_{nn} + S_{nn} t_{mm}. \tag{6}$$

Here b_{CR} is the dipole-dipole interaction between the CR transitions on different sites and it is much less as compared to the values of strong molecular HOMO to LUMO transition. The terms $S_{mm} t_{nn}$ are second order to the electron overlap, therefore the CR exciton band width C will be one or two order of magnitudes smaller than B. On this ground the CR exciton band will be much narrow than the MX band. When they are mixed the CR band will be wider than before the interaction.

Mixing of the CR State with Molecular Exciton States. When the CR level is located nearby the MX level, the interaction between the two states will be significant and it may modify the shape of MX band. The wavefunction for the mixed exciton states will be given for A_u state as

$$\left.\begin{aligned} &\Psi_b + \frac{\langle \Psi_b | H' | \Phi_b \rangle}{E_{CR} - E_{MX}} \Phi_b \\ \text{and}\quad & \\ &\Phi_b + \frac{\langle \Phi_b | H' | \Psi_b \rangle}{E_{MX} - E_{CR}} \Psi_b \end{aligned}\right\}. \tag{7}$$

The off-diagonal matrix elements between the CR and the MX states include both the dipole interaction and the transfer terms and they will be written as

$$b_{MC} + \sum_{ij} (t_{in,jn} - t_{im,jm}), \tag{8}$$

where b_{MC} is the dipole interaction between the molecular and CR exciton transitions of A_u symmetry and the transfer integrals may be taken over i and j molecules related by translation, inversion, screw-axis and glide reflection, respectively, but actually the transfer interaction between the nearest neighbors is much larger than for other type. This is one of the reason why the mixing occurs anisotropically; the electron overlap between the stacked molecules is significant along particular direction. The dipole-dipole interaction between the two type of transitions may be another probable source of the anisotropy of mixing. The b-axis of the dye iodide and bromide and the c-axis of the dye chloride are the direction along which the CR effect seems important because t_{nm} is large between the molecules stacked along these directions, hence the ground state will have an anisotropic CR character by this mechanism. The intrinsic CR band will be stronger along this direction than others, therefore the mixing through b_{MC} term will be larger along this particular crystalline directions than others.

One of the consequence of the CR and the MX mixing will appear in the exciton band structure. The CR exciton band is narrow and flat, and the

Table 4. Overlap integrals between the MO of stacked dye molecules

Molecules related by inversion symmetry Stacking directions		Overlap integrals between MO			
Dye crystals	MO	Single term AO		Four term AO	
		11	12	11	12
Chloride					
c-axis	11	0.0059	0.0049	0.0093	0.0079
	12		0.0030		0.0052
a-axis	11	0.0023	0.0002	0.0026	0.0006
	12		−0.0005		−0.0006
Bromide					
b-axis	11	0.0047	−0.0038	0.0077	−0.0066
	12		0.0024		0.0046
a-axis	11	0.0022	−0.0004	0.0027	−0.0008
	12		−0.0007		−0.0010
Iodide					
b-axis	11	0.0069	0.0043	0.0115	0.0061
	12		0.0027		0.0032
c-axis	11	0.0049	−0.0020	0.0057	−0.0016
	12		0.0006		−0.0002

state density may be greatly modified around the interacting region. For instance the energy levels in Fig. 4 show that the CR exciton level exists on the top region of the MX 0-0 band, and after the interaction, by non-crossing rule, the energy curves become plateu and the state density increases greatly in this range. If the 0-1 exciton level is located close to it, the radiationless exciton scattering may be enhanced and the higher vibronic band shape will be broadened significantly by the radiationless transitions.

One of another consequence of the CR and MX mixing may be an appearance of Fano's effect[25] in the begining of the absorption band. An interference which produces a dip or sharpening of the absorption band may be an indication of such interaction.

Band Splitting and Band Shape Analysis of Exciton States. Electronic transitions of large oscillator strength exhibit directional dispersion in anisotropic crystals. Weiser *et al.*[26] analysed the spectra of pentamethine cyanine dye crystal showing that the band shift is changed with the direction of the propagation of light to the crystalline face, however, this method is applicable only for uniaxial crystal.

For the present crystals the surface exciton state is calculated by a slab sum method.[18] The vibrational pattern of the monomer absorption band of the dye is simulated by a Lorentzian type shape function as

$$\left.\begin{aligned} \langle g\rangle &= \sum_{n=0}^{2}\langle g\rangle_n \\ \langle g\rangle_n &= Im\frac{|p_n|^2}{E-E_0-n\lambda-i\gamma_n} \end{aligned}\right\}, \tag{9}$$

where E_0 is the transition energy of the monomer dye, λ is the vibrational quanta of the coupled normal vibration and γ_n is the half-width of each band. The band width γ_n manifests the coupling of each vibronic level with other low frequency intramolecular and solvent modes. The present monomer spectrum was simulated by using $E_0=19000\ \mathrm{cm}^{-1}$, $\lambda=1300\ \mathrm{cm}^{-1}$ and $\gamma_n=500\ \mathrm{cm}^{-1}$. We took the square of the transition moment $|p_n|^2$ as proportional to the observed vibronic band intensities. Actually each absorption band has a Gaussian shape, but it was approximated by a Lorentzian shape. In the molecular exciton states, following a weak coupling model, each band peak is expected to shift as proportional to the vibronic band intensity and the shift is given by B_n, where the CR effect is not taken into account. Then the absorption shape of the molecular surface exciton states is written as follows.

$$\langle G\rangle = \sum_{n=0}^{2} Im\frac{|p_n|^2}{E-E_0-n\lambda-B_n-i\Gamma_n} \tag{10}$$

Here Γ_n is the half-width for the n-th vibronic level. The band shapes are simulated for several crystalline faces of the dye bromide and iodide and the results are shown in Fig. 5, where the crystalline Γ_n is taken equal to γ_n of solution spectra.

Results of this simulation may be summarized as follows. (1) When B_n is negative and large, the red shift of the split band is accompanied with increasing separation of the vibrational progressions. The band intensities are distributed among each vibronic levels as in solution spectra. (2) When B_n is positive and large, the blue-shifted vibronic levels are overlapped and converged into a single peak. Some of the measured spectra shown in the following section are consistent with this theoretical band shape analysis, but the J type band is different from this calculation. As regard to the sharpness of the J band, Briggs and Herzenberg[9] and also Sumi[10] attributed it solely to the increased exciton band shift, B, and B/λ was taken as a measure of the interaction, however, actually the same B/λ value does not give the same band shape. The J type absorption shape is found when the higher vibronic transitions lose intensity and the 0-0 vibronic transition becomes sharp. In fact the J type absorption band appears when the CR level is coincident or close to the MX 0-0 band and the interaction is significant.

The CR band shape is not explained in the above treatment. Apparently extra absorption bands are found in the present crystals in addition to the MX bands, because the electron overlap is appreciably large. They are regarded as the CR bands. Normally the CR transition is rather broad in many molecular crystals, but it is found to be sharp when the CR exciton band width is increased by the mixing with the MX band. Toyozawa[27] pointed out that the half-band width of the exciton absorption band is given by an exciton scattering mechanism and is proportional to the state density of the exciton band. For the localized CR exciton state the band width will be given by

$$\gamma_{\mathrm{CR}} = \frac{2\pi}{\hbar}\sum d_{\mathrm{CR}}^2/\Delta_{\mathrm{CR}}, \tag{11}$$

where d_{CR} is the matrix element with phonon and Δ_{CR} is the energy of the coupled phonon modes. When the CR level is below the MX 0-0 level and they interact each other, the mixed CR+MX states are formed, and the exciton band-width of CR state may be increased as aB_0, and γ_{CR} will be reduced significantly. The localized CR state is changed into the mobile molecular coupled exciton state. The band-width Γ_{CR} will be narrowed because $aB_0 > \Delta_{\mathrm{CR}}$ and $d_{kk'} < d_{\mathrm{CR}}$ where $d_{kk'}$ is the exciton scattering matrix. The band-width will be given by

$$\Gamma_{\mathrm{CR}} = \frac{2\pi}{\hbar}\sum d_{kk'}^2/aB_0. \tag{12}$$

The intensity of the mixed transitions is mostly due to the MX 0-0 band, and the absorption appears as a single band or separate bands depending on the coupling of the CR and MX transition dipoles.

The band-width of the MX 0-0 level may be reduced from its original molecular band-width γ_0 by several mechanisms. One is discussed by Toyozawa[27] that when B_0 is large the state density is reduced and Γ_0 will be decreased as

$$\Gamma_0 = \frac{2\pi}{\hbar}\sum d_{kk'}^2/B_0. \tag{13}$$

For the higher vibronic MX levels, when $B_0 > \lambda$, the 0-0 exciton band will overlap with the 0-1 level, and additional scattering route may be provided through the inter-band scattering and the absorption band-width may be increased as

$$\Gamma_1 = \frac{2\pi}{\hbar}\{\sum d_{kk'}^2/B_1 + \sum d_{kk'_0}^2/bB_0\} \tag{14}$$

The increase of Γ_1 is contrast to the decrease of Γ_0, thus the narrowing of the MX 0-0 band may be interpreted by the exciton band scattering mechanism and the peak intensities of higher vibronic bands will be suppressed by the increase of Γ_1.

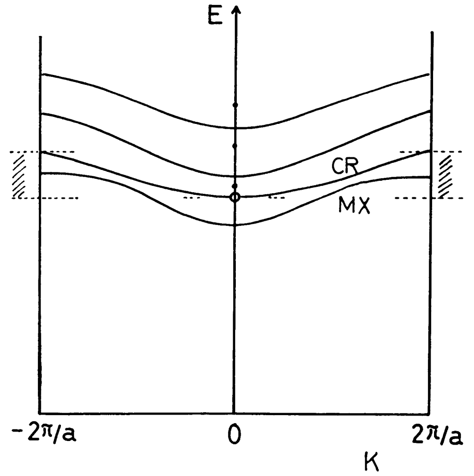

Fig. 4. Mixing of the CR and MX levels and band structures.

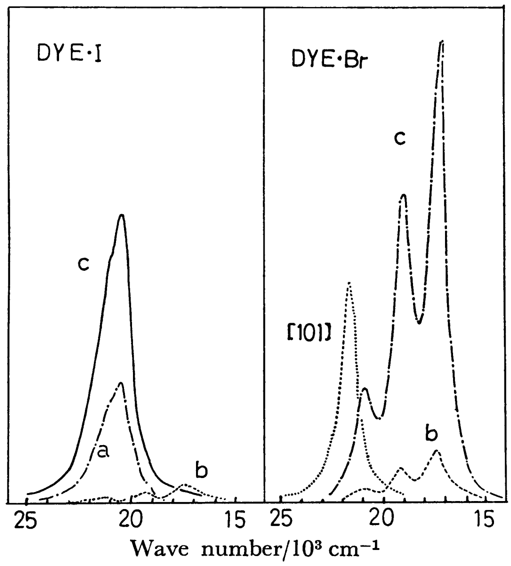

Fig. 5. Simulated absorption spectra of the dye iodide and the dye bromide. The ordinate is absorption coefficient in arbitrary unit.

However, as is described previously, the CR interaction with the MX band may change the exciton band structure. If the exciton band becomes flat by the CR mixing, the inter-band scattering will be enhanced because the state density is increased around the interacting region and higher vibronic band has additional decay terms represented by

$$\Gamma_n = \frac{2\pi}{\hbar}\sum t_{\mathrm{CR,\,MX}}^2/\delta_n,$$

where $t_{\mathrm{CR,MX}}$ is the inter-band scattering matrix between the CR and MX states and δ_n is a small energy difference of two levels of nearly iso-energetic condition. The increased Γ_n will make the higher vibronic exciton band very broad and the absorption intensity will be lost except the mixed MX 0-0 band. Moreover the band-width of the MX 0-0 band may be sharpened by the following CR interaction mechanism. When the CR level is above and close to the MX 0-0 band, another mechanism is conceivable as follows. Suppose some phonon coupled 0-0 band may have energy of $E_0 + \Delta_n$, and it is equal to that of the CR level. The mixing with the CR level will take place, and the band-width will be broadened by the inter-band scattering mechanism as is discussed above. Then the MX 0-0 band will be sharper

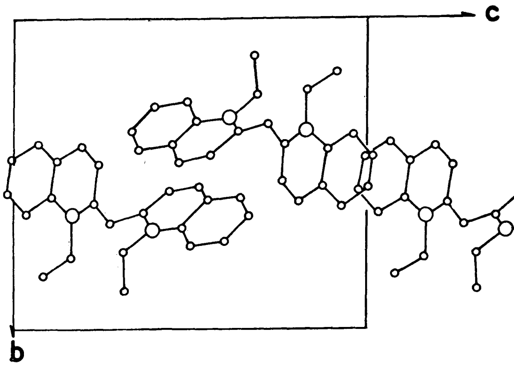

Fig. 6. Projection of molecules in the dye iodide crystal onto the (100) plane.

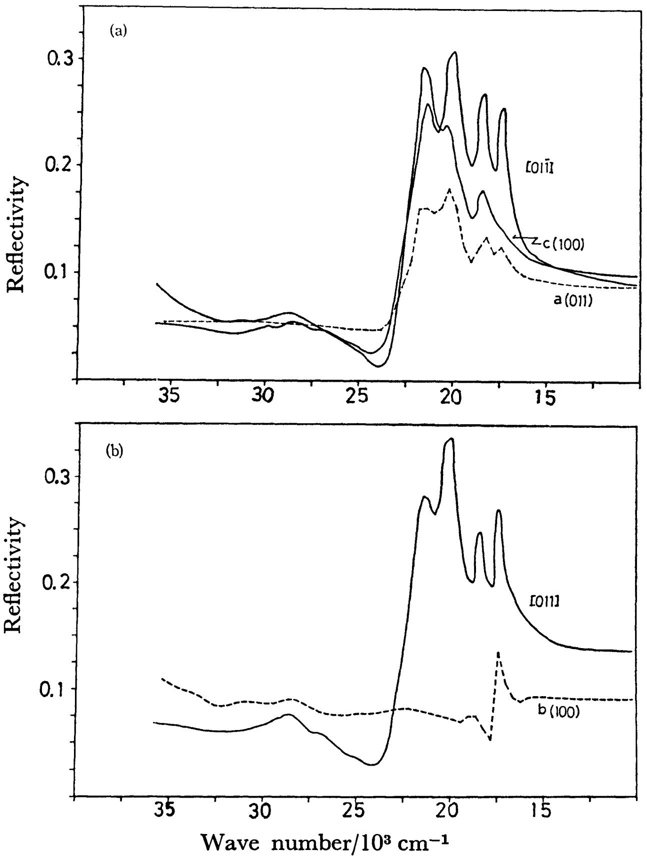

Fig. 7. Reflection spectra of the dye iodide taken with (a) (011), (a,b) (100), and (b) (01$\bar{1}$) faces.

because some phonon coupled modes lose the peak intensity. These arguments may throw some light on the peculiar band shape of the J band.

Results and Discussion

Crystalline Spectra of the Dye Iodide. The crystals obtained from methanol solution were used for the reflectivity measurement with crystalline faces, (100), (011), and (01$\bar{1}$) as shown in Fig. 1. The projection of molecules onto the (100) plane is shown in Fig. 6 according to the X-ray crystal analysis of Nakatsu *et al.*[15] Two quinoline rings of the dye molecule are twisted each other, and each ring stacks with another quinoline ring of the adjacent molecules. The double array of molecules extend along [101].

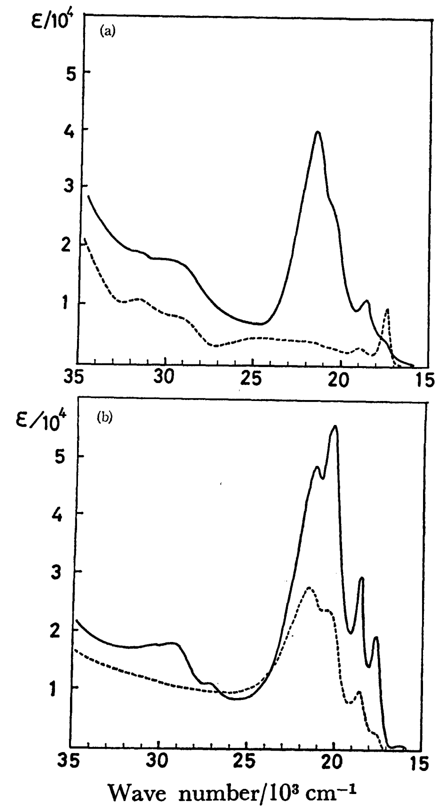

Fig. 8. Absorption spectra of the dye iodide obtained with the (100) and (011) faces.
(a) (100) face, - - - - b-axis, —— c-axis.
(b) (011) face, - - - - a-axis, —— [01$\bar{1}$] direction.

The reflection spectra with (100), (011), and (0$\bar{1}\bar{1}$) faces are shown in Fig. 7. The Kramers-Kronig transformation of the reflectivity gives the absorption spectra as shown in Fig. 8. The spectra along the [011] axis is similar to that of along the [01$\bar{1}$]. The absolute values of reflectivity and hence the molar absorption coefficients are dependent on the quality of surface of crystal, therefore the comparison of intensities with different crystalline faces may be less accurate than to obtain the dichroic ratio with the same face.

The spectra with the (100) face (Fig. 8(a)) showed a strong dichroism; the intensity is much stronger along the c-axis than along the b-axis. Actually the intensity along the b-axis is much intensified than the value expected from the oriented gas model; and it may be due to the influence of the CR state which may exist around the 17000—19000 cm^{-1} region. The exciton splitting for the (100) face is calculated as shown in Table 2; the red shift for the b-axis is well explained and the blue shift of the c-axis will be right if we take the 20350 cm^{-1} band along the c-axis as the 0-0 band because it should be fairly strong as compared to other bands. Then the band at 17400 and 18600 cm^{-1} along the c-axis is regarded as the CR band. The broad absorption bands in the 18000—26000 cm^{-1} region appeared along the b-axis are regarded as the mixed band of the CR and MX states, because an enhancement of the intensity and the

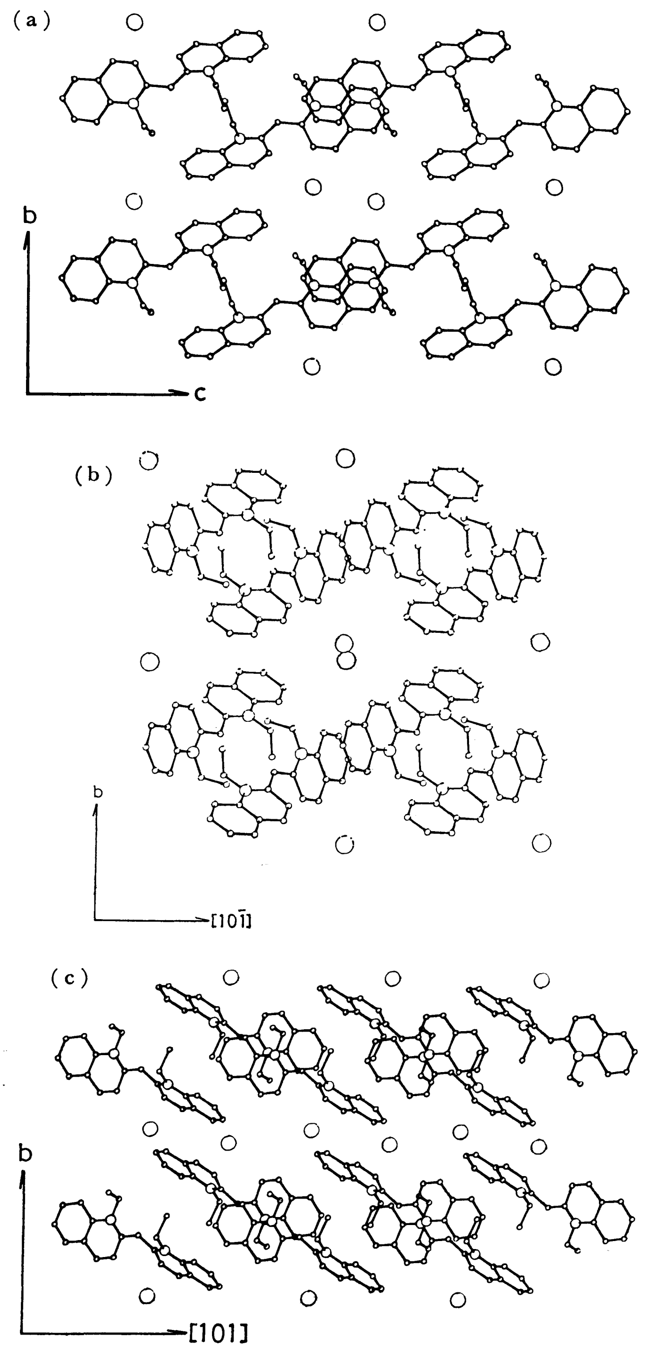

Fig. 9. Projection of molecules onto the developed crystalline faces of the dye bromide.
(a) (100) face, (b) (101) face, and (c) (10$\bar{1}$) face.

sharpening of the 0-0 band may be explained by the interaction between the CR and MX states as is discussed previously.

The spectra with the (011) face is shown in Fig. 8(b). The absorption band along the a-axis is similar to the c-axis band, and the weak humps at 17500 and 18600 cm^{-1} are regarded as the CR band. Along the [01$\bar{1}$] direction both the A_u and the B_u transitions are allowed, the peak at 17400 cm^{-1} is ascribed to the A_u type, while peaks at 18700, 20100, and 21100 cm^{-1} are ascribed to the B_u type transitions. The calculated splittings for the MX bands are approximately in agreement with the observed spectral tendency.

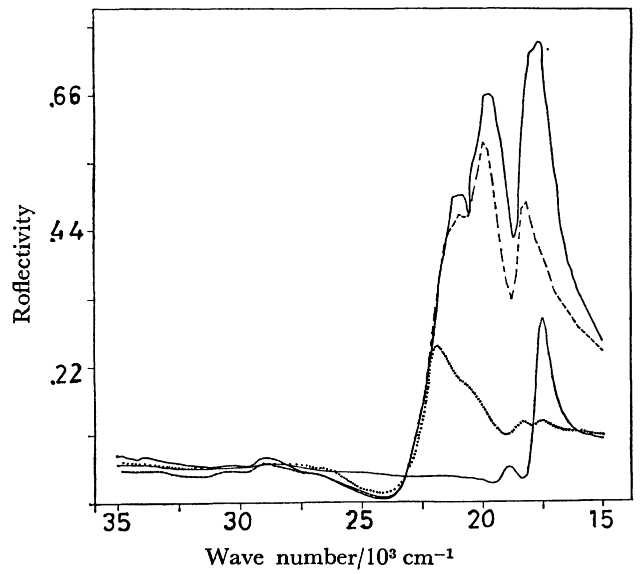

Fig. 10. Reflection spectra of the dye bromide measured with (100) face —— c-axis, —— b-axis, and (10$\bar{1}$) face---- [101] direction (101) face······ [10$\bar{1}$] direction.

The simulated absorption curve by Eq. 10 for the MX vibronic band is shown in Fig. 5, where the intensity is taken as proportional to the oriented gas value. We took the values of B_0 as -1500 cm^{-1} for the b-axis and 1500 cm^{-1} for the c-axis. The calculated curve is in agreement with the observed spectra except that the CR effect is seen along the b-axis and the CR bands are seen along other axes as extra bands. The original CR band starts at about 17000 cm^{-1} and appears in the range of 17500—27000 cm^{-1} as a broad band. Along the b-axis the CR state interacts strongly with the MX state in the 17000—19000 cm^{-1} region and a sharp mixed band is observed, because the electron overlap is largest along this direction. Examination of these spectra shows that the J-type sharp absorption can be found only along the b-axis. It means an importance of CR effect through the electron overlap, since the calculated overlap integrals given in Table 4 show that the b-axis value is larger than for the c-axis and the obtained value is large enough to give effective interaction between molecules.

Crystalline Spectra of the Dye Bromide. The projection of molecules onto the measured crystalline faces are shown in Fig. 9 according to the X-ray structural result of Nakatsu *et al.*[14] The crystalline reflection spectra were measured with (100), (101) and (10$\bar{1}$) faces as shown in Fig. 10 and the absorption spectra calculated by the Kramers-Kronig transformation are shown in Fig. 11. The simulated absorption curve (Fig. 5) is obtained with the reduced surface exciton shift of -1000 cm^{-1} and the 0-0 band origin assumed at 18500 cm^{-1}.

The transition to the A_u excited state, which is allowed along the b-axis, appears at the same position for all measured faces and the calculated value is

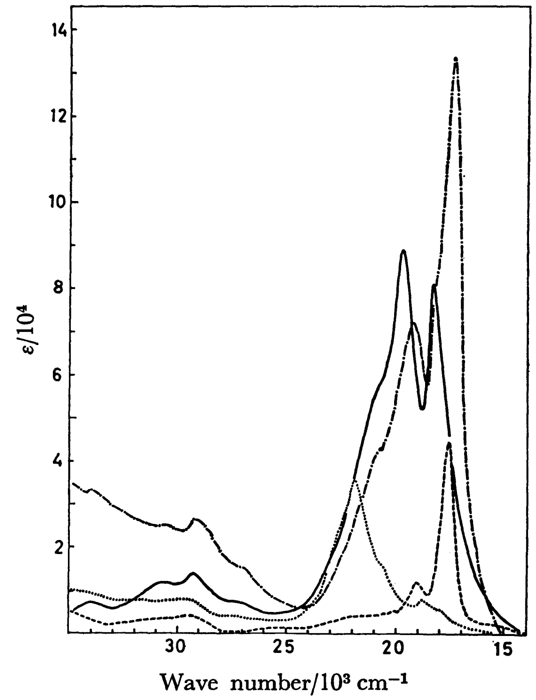

Fig. 11. Absorption spectra of the dye bromide obtained with (100) face —·—·— c-axis, ---- b-axis, $(10\bar{1})$ face —— [101] direction, and (101) face ······ $[10\bar{1}]$ direction.

—1590 cm^{-1}, while the observed shift is about —1000 cm^{-1}. Comparison of the intensity of simulated spectra with the observed spectra showed that the 0-0 band is intensified and sharpened. The CR state may exist in this region and the enhancement and the sharpening of the b-axis transition may be due to the interaction of the CR and MX states. The band shape along the b-axis is a typical of J band that the intensity is concentrated around the 0-0 transition and higher vibronic bands are broad and weak.

The transition to the B_u state on the (100) face is allowed along the c-axis, and it shows vibronic structures starting 0-0 at 17460 cm^{-1}. Although the exciton shift B_0 is almost same for b and c-axes, the band shape is different. The simulated spectra with a shift of —1000 cm^{-1} shown in Fig. 5 is in good agreement with the observed spectra, except that the 0-0 band is actually much sharp and intense than the simulated spectra. For the c-axis the mixing of the CR and MX states seems smaller than for the b-axis, presumably because the electron overlap is smaller along this direction.

The B_u type transition on the $(10\bar{1})$ face showed peaks at 18300 and 19700 cm^{-1} and a shoulder at 21000 cm^{-1}. We may assign the 18300 cm^{-1} band as the 0-0 band and the 19700 cm^{-1} band as the 0-1 band, because the calculated shift for the 0-0 band is —260 cm^{-1}, but the band progression is not normal as compared to other directions. An alternative plausible interpretation may be that the 18300 cm^{-1} band is the CR mixed band and the MX 0-0 band is shifted to 19700 cm^{-1}. The vibronic pattern is normal by this choice, and the CR band is fairly strong because of borrowing intensity from the MX 0-0 band.

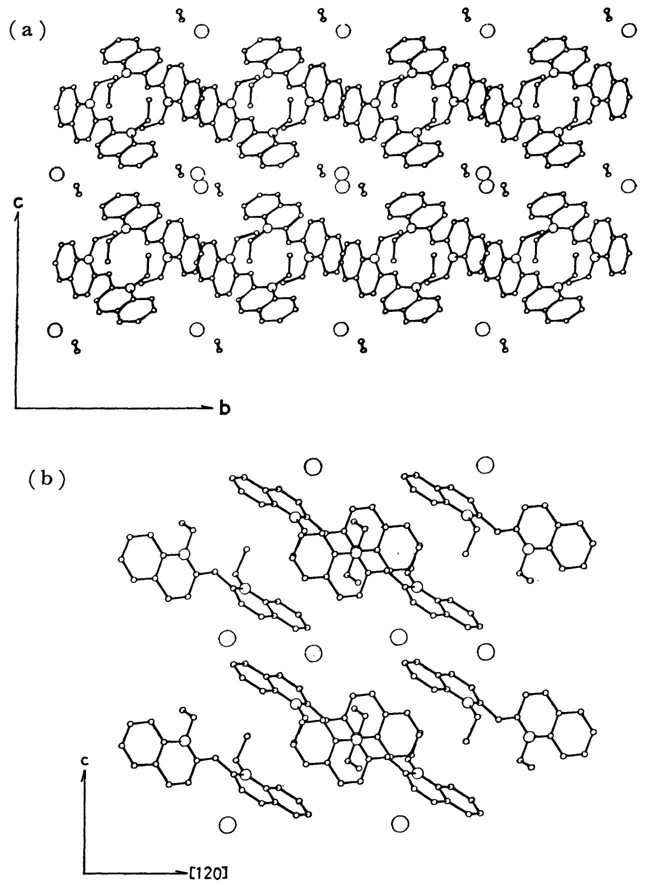

Fig. 12. Projection of molecules onto the developed crystalline faces of the dye chloride (a) (100) plane, (b) $(1\bar{2}0)$ plane.

With the (101) face along the $[10\bar{1}]$ direction a peak is found at 21800 cm^{-1}, a shoulder at 20800 cm^{-1} and weak humps around 18800 cm^{-1}. The simulated absorption spectra (Fig. 5) is in agreement if we take a shift of +3000 cm^{-1}, but actually the calculated shift is +1880 cm^{-1} for the 0-0 band. A shoulder at 20800 cm^{-1} may be the shifted 0-0 band. Thus a calculated tendency of overlap of peaks for the blue-shifted bands is actually exemplified. The weak humps around 18500 cm^{-1} region may be the CR band, and it will be weak because the strong MX band shifts to blue and does not mix with it.

In this spectra again the value of B/λ does not show a good correlation with the observed spectral bandwidth. Moreover the directional property of the J band will show the detailed mechanism of the CR and MX mixing that the electron overlap and the dipole interaction anisotropy are important.

Crystalline Spectra of the Dye Chloride. The crystalline structure of the dye chloride was analysed by Dammeier and Hoppe[13)] although the crystalline axes were chosen differently from other crystals. The crystal structure is isomorphous with the dye bromide, and the c-axis of the chloride corresponds to the b-axis of the bromide. The [120] and b-axes of the chloride are correlated to the [101] and $[10\bar{1}]$ axes of the bromide. The projection of molecules onto the measured

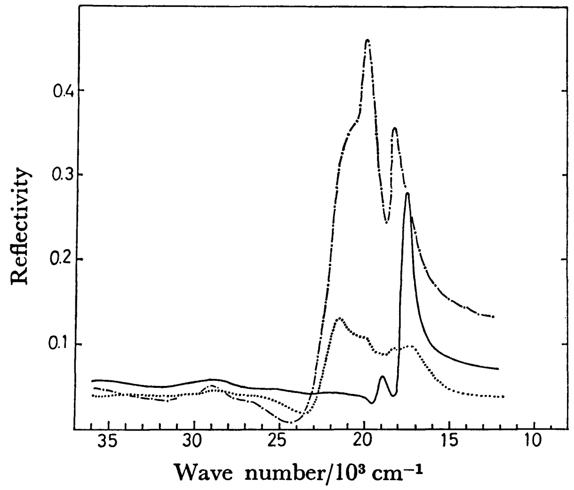

Fig. 13. Reflection spectra of the dye chloride measured with (100) face ······ b-axis, —— c-axis and $(1\bar{2}0)$ face —·—·— [120] direction.

faces are shown in Fig. 12. The reflection spectra were measured with the $(1\bar{2}0)$ and (100) faces as shown in Fig. 13.

The absorption spectra obtained by the Kramers-Kronig transformation look like the bromide spectra (Fig. 14). The surface exciton splitting on (100) and $(1\bar{2}0)$ faces were calculated as shown in Table 2. If we take the molecular 0-0 transition at 19000 cm^{-1} the agreement between the calculated and the experimental values of the shift is quite satisfactory. The transition along the c-axis is red shifted and the sharp J band appears by the interaction of the CR and the MX states, because the electron overlap is significantly large along the c-axis (Table 4). The band along the [120] axis showed several peaks and a plausible explanation for this pattern may be that the 18400 cm^{-1} band is the mixed CR state and the 19800 cm^{-1} band is the MX 0-0 vibronic transition. The spectra along the b-axis is blue-shifted at 21400 cm^{-1}, and the calculated shift is in reasonable agreement with the observed value. A single peak is appeared because the large blue-shifted vibronic transitions are overlapped as is discussed previously. Another weak shoulder around 18400 cm^{-1} may be due to the CR band. Thus the observed spectra showed a similarity with the bromide spectra reflecting isomorphous crystalline structure.

Spectra of the Dye Iodide in Solution. The J band in solution may be compared with the crystalline spectra in order to find the structure of the J aggregate in solution. The spectra of the dye iodide in a 1:1 ethyleneglycol water (EGW) solution shown in Fig. 2 are nearly in agreement with the earlier results of Zimmerman and Scheibe$^{3)}$ and Cooper;$^{4)}$ the J band appears at 77 K. However, the detail of the spectra is slightly different between independent studies and it may be due to the difference in experimental conditions such as the kind of solvent and the concentration of counter ions. For instance the intensity of the J band is varied case by case; it is strongest in water with chloride ion$^{3)}$ and is weak in ethanol with iodide ion$^{12)}$ and is intermediate in EGW solution. Cooper$^{4)}$ observed a doublet structure of the J band on the dye bromide in EGW at 77 K, but we found a weak doublet in dye iodide in the same solution at 77 K. It appears that the change of spectra reflects a variation of the fine structure of the aggregate. Marchetti *et al.*$^{12)}$ did not report the doublet presumably because their solution contained 0.1 M KI and they proposed that the spectra resemble to the crystalline spectra of the dye iodide, hence the J aggregate will have a similar structure of the iodide crystals. Our results showed that the positions of the aggregate band are very close to the bands found in the iodide crystal rather than that of the bromide, but the intensity of the J band at 17400 cm^{-1} in solution is much stronger than in the crystal. We agree with their opinion that the aggregate in solution may have a similar structure of the iodide crystal.

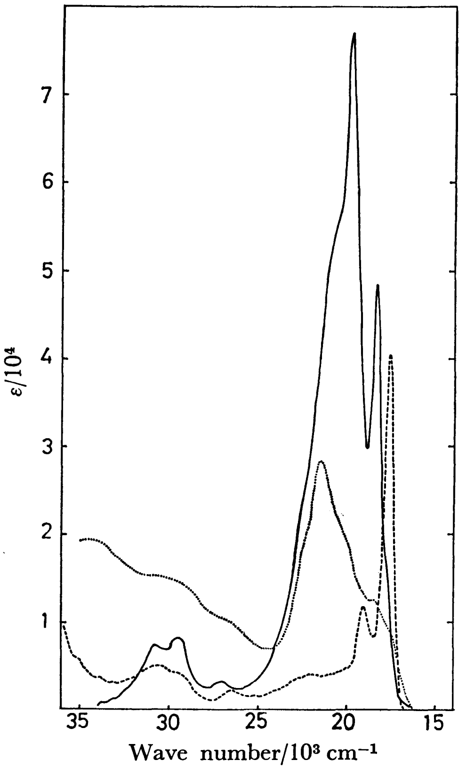

Fig. 14. Absorption spectra of the dye chloride with (100) face ······ b-axis, ---- c-axis and $(1\bar{2}0)$ face —— [120] direction.

We have estimated how many molecules might be involved in the aggregate by calculating the band splitting using the same arrangement of molecules in the crystal of the dye iodide. The splitting for the A_u and B_u transitions were calculated for the spherical assemblies of molecules of radius 10—18 Å, which includes 4 to 50 molecules inside. The results of the calculation showed that the sphere of the radius 16 Å containing 36 molecules gives a maximum splitting, the red shift of -1220 cm^{-1} and the blue shift of 1640 cm^{-1}. In solution the splitting of the J band and the blue-shifted 0-0 vibronic band is 3400 cm^{-1}, hence the calculated value is smaller than the observed value, but the agreement is not so bad. If we use the crystalline data of the dye bromide or chloride, the result is much smaller than for iodide. Although the agreement is not in perfect, but the similarity of the band shape supports the iodide structure and it may be inferred that the J-aggregate of 2,2′-cyanine in solution is conformed of at least 30 molecules assembled like the dye iodide crystal. Scheibe and his coworkers[3,5] discussed the minimum size of the J-aggregate and suggested that it might include at least 7 molecules. Further studies will be required to clarify these points.

Summary of the J Band of 2,2′-Cyanine Dye Crystals. The results of spectral investigation on 2,2′-cyanine dye iodide, bromide, and chloride crystals are summarized as follows. (1) Molecular electronic transition of the dye is split on crystalline surfaces by the exciton interaction. The splittings on the developed crystalline faces are reasonably explained by the dipole-dipole interaction with a slab sum method. The vibronic band shapes are well simulated by a weak coupling model; each vibronic level interacts individually. A red shifted band shows expanded vibronic intervals while a blue shifted one converges into a single peak. In addition, extra bands, which are not found in solution spectra, appear because of the electron overlap effect, that is the CR band.

(2) The J type band is found with particular crystalline directions of specific surfaces. A characteristic of the crystalline J band may be a sharpened 0-0 band and diminished higher vibronic bands. It appears when the CR state is mixed with the split MX state. An extensive electron overlap between the neighbor molecules is an important necessary condition for the appearance of the J band. A coincidence of the MX and CR state is another requisite for the sharp J band. It may be said that the sharp J band will be found only when these several dominating conditions are satisfied, but a widely used nomenclature for the J band may infere the red shifted strong transition with exciton sharpening without the CR mixing. We believe our view is more extensive.

Anyhow, several conditions, a lateral displacement of molecules, which is necessary for a large red shift, an extensive stacking of molecules to give a strong electron overlap, and a coincidence of the MX and CR levels, are satisfied only for rare cases. Therefore the appearance of the J band may be an unusual spectral phenomena associated with specific aggregation of cyanine dyes.

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