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Polarized Absorption Spectrum of the Second S → T Transition of Phenazine Crystals

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Polarized absorption spectrum of the second S→T transition of phenazine single crystal was measured at 4.2°K. The transition moments of the individual vibronic bands were determined uniquely from their polarization characteristics. The 0—0 band at 20470 cm^{-1} was found to be polarized along the N-N axis of the molecule and assigned as ${}^3B_{3u}\leftarrow{}^1A_g$ (n-π^*) transition. The vibronic bands other than the 0—0 band was found to be exclusively polarized along the long axis of the molecule, and they were assigned as the vibronic bands induced by a nontotally symmetric vibration in the ${}^3B_{3u}$ state. The possible routes of vibronic spin orbit coupling mechanism are discussed on the basis of the observed results.

Recently, high resolution photo-excitation technique becomes popular for detection of extremely weak singlet-triplet absorption spectrum of aromatic molecules. This indirect method[1] has real advantages for the crystals which have delayed fluorescence produced by triplet-triplet annihilation,[2] or in such a case that the excitation energy of triplet state of host crystal transfers well to phosphorescent molecules doped in the crystal.[3,4] In other cases, however, the direct observation of singlet-triplet absorption spectrum always gives unambiguous results. The polarization characteristic of singlet-triplet transition of aromatic molecules is important not only in assignment of the triplet state but also in elucidation of the spin orbit coupling mechanism of the molecules. Especially if the polarization characteristic of individual vibronic bands is determined, it provides reliable information on the mechanism of so called vibronic spin orbit interaction. Many works along this line were performed mainly by measurements of polarization degrees of the phosphorescence spectra.[5] In the absorption studies, however, only a few works have been reported.

The lowest singlet-triplet absorption spectrum of phenazine crystal was first observed by Clarke and Hochstrasser[6] at about 6400 Å and it was assigned by them as ${}^3B_{1u}\leftarrow{}^1A_g$ (π–π^*) transition on the basis of Zeeman splitting pattern of the factor group components.[7] This assignment for the lowest triplet state is reasonable because of good correspondence to the assignment for anthracene.[8,9] Later, Hochstrasser and Mazzacco[10] reported another weak abosption system in the region of 4800 Å and assigned it to be due to a second singlet–triplet transition. But

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[1] P. Avakian, E. Abramson, R. G. Kepler, and J. C. Caris, *J. Chem. Phys.*, **39**, 1127 (1963).

[2] G. Durocher and D. F. Williams, *ibid.*, **51**, 5405 (1969).

[3] G. Castro and G. W. Robinson, *ibid.*, **50**, 1159 (1969).

[4] D. M. Burland, G. Castro, and G. W. Robinson, *ibid.*, **52**, 4100 (1970).

[5] For example, S. M. Ziegler, and M. A. El-Sayed. *J. Chem. Phys.* **52**, 3257 (1970).

[6] R. H. Clarke and R. M. Hochstrasser, *ibid.*, **47**, 1915 (1969).

[7] R. M. Hochstrasser and T. S. Lin, *ibid.*, **49**, 4929 (1968).

[8] R. Pariser, *ibid.*, **24**, 250 (1956).

[9] R. H. Clarke and R. M. Hochstrasser, *ibid.*, **46**, 4532 (1967).

[10] R. M. Hochstrasser and C. Marzzacco, *ibid.*, **49**, 971 (1968).

their spectrum was too obscure to ensure detail analysis.

In the present work, the polarized measurements of the 4800 Å absorption were carried out for the single crystal at 4.2°K, and the assignments and the possible routes of vibronic spin orbit coupling mechanism are discussed on the basis of the observed results.

Experimental

The single crystal of phenazine was grown in a high vacuum Pyrex tube by conventional Bridgman method after sample purification by chromatographic extraction followed by extensive zone refinning. The crystal was cleaved along the *bc*-plane, and cut down perpendicular to it. Thickness of the crystal used for spectral measurements was 5 to 30 mm. The polarized absorption spectra were taken on the *bc*-plane with the light polarized along the *b*-axis and with light perpendicular to it. The *b*-axis of the crystal was identified by X-ray diffraction method.

We were also able to obtain another crystal which exposes the *ac*-plane. Polarizing microscopic observation of this crystal through the *b*-axis showed that the angles between the *c*-axis and the directions of the minimum and maximum refractive indices α, γ, were about 50° and 40°, respectively, in agreement with the crystallographic data cited in the literature.[11]

The crystals used were so large that it was difficult to cool them to 4.2°K without cracking. Therefore, we constructed a cryostat having a specially designed thermal exchange tube. With this cryostat, the crystal was cooled very slowly to liquid helium temperature. After many failures, we succeeded in obtaining very clear crystals having no cracking at 4.2°K, and they were subject to the spectral measurements.

The absorption spectra were photographed on Kodak 103a-O plates with a Shimadzu GE-100 grating spectrograph having reciprocal linear dispersion of 8.4 Å/mm in the first order. Continuum from a 500 W xenon arc lamp and/or a tungsten iodine lamp was condensed on the crystal after passing through a water filter of 100 mm path length and a Toshiba UV-39 glass filter. The light passed through the crystal was focussed on a slit of the spectrograph. A Glan-Foucault prism was placed in front of the slit for polarization measurements.

To serve in vibrational analysis of the spectrum, we observed also the Raman spectrum of the crystal. The Raman spectrum was measured with a Narumi double monochromator combining with a He-Ne gas laser. The single crystal cube whose edges are parallel to *a*,*b* axes was used for plarization measurements at room temperature. The depolarization degrees of the Raman lines were also measured for molten phenazine with a high temperature liquid cell.

Results and Discussion

The absorption spectra of the first and the second singlet-triplet transitions are reproduced in Fig. 1. The first singlet-triplet absorption spectrum obtained in this work is the same as that reported by Clarke and Hochstrasser.[6] The half band widths of this absorption region were about 0.5 cm^{-1}. Davydov splittings were observed for the 0—0 band at 15447.5 cm^{-1} and the 0+1328 cm^{-1} vibronic band. The observed frequencies of fundamental vibrations in the first triplet excited state are 415, 452, 599, 740, 1044, and 1384 cm^{-1}.

The second singlet-triplet absorption consists of many bands whose half widths are about 3 cm^{-1},

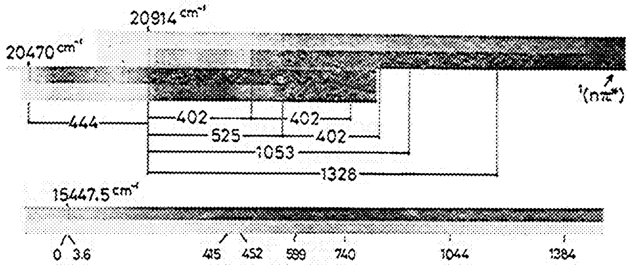

Fig. 1. Absorption spectra of phenazine crystal at 4.2°K. The upper is the second S→T absorption spectrum at about 4885 Å, and the lower is the first S→T transition at 6470 Å.

Table 1. Vibrational analysis of main absorption bands in 2nd S → T transition of phenazine crystal (cm^{-1})

ν	Intensity[a)]	Remarks	
20470	w	0	
20498	vw, b	0+28	phonon
20554	vw, b	0+84	phonon
20586	vw, b	0+116	phonon
20815	w	0+345	
20839	w	0+369	
20876	vw, b	0+369+28	phonon
20914	s	0′(0+444)	
20943	m, b	0′+28	phonon
20974	w	0+504	
21035	w	0+565	
21208	m	0+738	
21315	s	0′+402	
21343	m, b	0′+402+28	phonon
21439	s	0′+525	
21464	m	0′+525+28	phonon
21498	w	0+504+525	
21520	w	0′+606	
21546	w	0′+606+26	phonon
21639	w, b	0′+725	
21719	m	0′+2×402	
21744	w, b	0′+2×402+26	phonon
21843	m	0′+525+402	
21869	w	0′+525+402+26	phonon
21920	m	0′+606+402	
21958	w	0+1488	
21967	m	0′+1053 or 2×525	
21993	m	0′+1053+26	phonon
22023	w, b	0+504+2×525	
22243	w	0′+1329	
22270	vw	0′+1329+26	phonon
22368	w	0′+1053+402 or 2+525+402	
22394	vw	0′+1053+402+26 or 2×525+424+26	
22645	w	0′+1329+402	
22742	m	0′+1628	
22809	m	vibronic band belonging to $^1B_{3u} \leftarrow {}^1A_g(n\pi^*)$ transition	

a) Relative intensity
s: strong, m: medium, w: weak, vw: very weak, b: broad

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[11] R. G. Wood and G. Williams, *Phil. Mag.*, **31**, 115 (1941).

Davydov splitting was not observed. The longest wavelength band at 20470 cm^{-1}, which was considered as a 0—0 band of this absorption system, was weak compared with the bands at higher frequencies than 20914 cm^{-1}. Frequencies of the main bands and their tentative vibrational analysis are shown in Table 1. Five fundamental frequencies, 402, 525, 606, 1053, and 1328 cm^{-1} were found which start from the band at 20914 cm.$^{-1}$ Of these frequencies, 402 and 525 cm^{-1} belong to totally symmetric vibrations in the excited state, since they form short progressions. The other frequencies 606, 1053, and 1328 cm^{-1} are also probably due to totally symmetric vibrations. On the other hand, no prominent progression starting from the 20470 cm^{-1} band was observed. The frequency difference between this band and the 20914 cm^{-1} band is 444 cm^{-1}. It is probably due to a fundamental frequency in the excited state, but it is not repeated anywhere except the above difference. This fact and the weak intensity of the 20470 cm^{-1} band suggest that the 20914 cm^{-1} band and the higher ferquency bands followed to it are attributed to "*forbidden bands*" induced by a nontotally symmetric vibration.[12] If this interpretation would be correct, 444 cm^{-1} should be a nontotally symmetric vibration in the excited state and the strong intensity of the 20914 cm^{-1} band is explained as the results of intensity borrowing from higher excited states through this perturbing vibration. This situation is very similar to that of the (n-π^*) singlet-singlet absorption spectrum of this crystal at about 4200 Å where a vibronic band perturbed by a b_{1g} vibration occurs[13].

In order to determine the directions of the transition moments of the individual vibronic bands, we observed polarized absorption spectrum. Phenazine forms a monoclinic crystal of space group $P2_{1/a}$ having two molecules in a unit cell, as shown in Fig. 2.[14] It is seen from Fig. 2 that projection of the long axis of the molecules on *ac*-plane is nearly parallel to the [201] direction shown by **L** in the figure. This direction is easily identified from the direction of the largest refractive index on the *ac*-plane and the angle made between it and the cleavage plane. It is also seen from the figure that projection of the molecular normal axis on the *ac*-plane is also almost parallel to **L** because the molecular short axis is nearly parallel to the *ac*-plane. Thus, polarization measurements were made on the *ac*-plane with incident light polarized parallel to **L** and with light polarized perpendicular to it. A part of the observed spectrum for a crystal of 28 mm thickness is reproduced in Fig. 3. The weak 0—0 band at 20470 cm^{-1} (which is not shown in the figure) and the band at 21208 cm^{-1} appear dominantly in the $\mathbf{L}_\perp$ component. Then, the transition moments of these bands are parallel to the short axis of the molecule. On the other hand, all the bands above 20914 cm^{-1} except the band at 21208 cm^{-1} is exclusively polarized in the $\mathbf{L}_{/\!/}$ direction. Therefore, we may conclude that their transition moments are parallel to the long or normal axis of the molecule. In order to distinguish between the two possiblities for the latter, we measured the polarized spectrum on the *bc* crystal plane. The observed intensity ratio $\frac{I(b)}{I(c)}$ was 3 for all the bands exclusively polarized along the **L** direction. The calculated ratios for the long and normal axis transition moments should be 2.7 and 18, respectively, in oriented gas approximation. Therefore, we may conclude that the transition moments of the 20914 cm^{-1} band and its relatives are parallel to the long axis of the molecule.

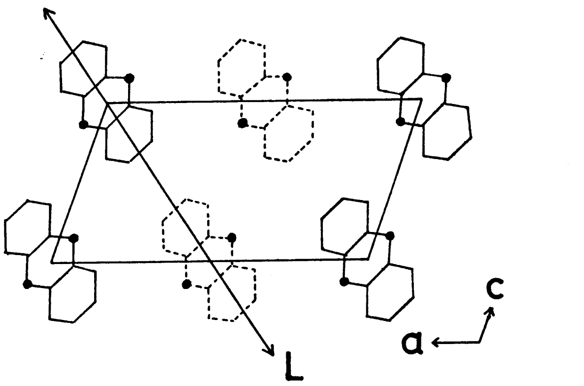

Fig. 2. Projection of the molecules onto the *ac* plane of the crystal. The molecules which are translationally inequivalent in a unit cell are indicated by the broken line. The direction **L** indicates the [201] in the crystal.

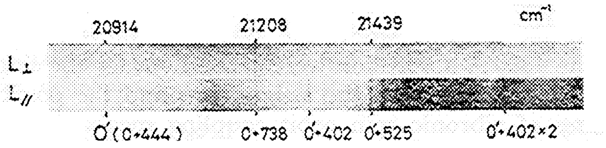

Fig. 3. Polarized absorption spectrum of the second S→T transition of phenazine single crystal at 4.2°K. The 0—0 band at 20470 cm^{-1} is not shown but its polarization characteristices is same as that of the band 0+738 at 21208 cm^{-1}.

Now, we proceed to assignment of the 0—0 band at 20470 cm^{-1} of the second triplet state which is polarized along the short axis (z) of the molecule. $^3B_{1u}$, $^3B_{2u}$, and $^3B_{3u}$ states are considered as candidates. All g-states are excluded because of appearance of the 0—0 band. In Table 2 are listed possible perturbing singlet states coupled with the triplet state by usual spin orbit interaction. It is found from this table that the triplet states which can couple with the $^1B_{1u}$ state of the short axis (z) transition moment must be $^3B_{3u}$ (n–π^*) or B_{2u} (π–π^*). Within the limit of LCAO MO consideration for the one electron spin orbit matrix elements, $^3B_{2u}$ (π–π^*) state can never couple with any short axis polarized singlet state, since operation of the operator l_x on an atomic orbital p_x from which the molecular orbitals are constructed always gives zero eigenvalue[15]. Hence, we have a unique

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[12] A. C. Albrecht, *J. Chem. Phys.*, **33**, 156 (1960).

[13] N. Mikami, *J. Mol. Spectrosc.*, **37**, 147 (1971).

[14] F. H. Herbstein and G. M. Schmidt, *Acta, Cryst.* **8**, 406 (1955).

[15] For example, S. P. McGlynn, T. Azumi, and M. Kinoshita, "*Molecular spectroscopy of the triplet state*" Prenice-Hall, Inc. 1969 New Jersey.

assignment of ${}^3B_{3u}$ $(n\ \pi^*)$ for this triplet state. This assignment is supported from the theoretical predictions of the location of the $(n\ \pi^*)$ triplet state[16] and from the smaller energy separation between the singlet and triplet $(n\ \pi^*)$ states of this molecule than that of pyrazine.

Table 2. Spin orbit coupling selection rule for the triplet state

Γ(T)		$\Gamma(l_\xi)$		Γ(S)
${}^3B_{3u}(n\pi^*)$	<	$B_{1g}(l_z)$	—	${}^1B_{2u}(y)$
		$B_{2g}(l_y)$	—	${}^1B_{1u}(z)$
${}^3B_{2u}(\pi\pi^*)$	<	$B_{1g}(l_z)$	—	${}^1B_{3u}(x)$
		$B_{3g}(l_x)$	—	${}^1B_{1u}(z)$
${}^3B_{1u}(\pi\pi^*)$	<	$B_{2g}(l_y)$	—	${}^1B_{3u}(x)$
		$B_{3g}(l_x)$	—	${}^1B_{2u}(y)$

Γ(T), $\Gamma(l_\xi)$, and Γ(s) indicate irreducible representations of triplet state, angular momentum operator and singlet state of the molecule having D_{2h} symmetry, respectively.

As mentioned before, the band at 20914 cm^{-1} has its transition moment parallel to the long axis (y) of the molecule. If it would be an electronic band origin of another triplet state, it should have the symmetry of ${}^3B_{3u}$ $(n\ \pi^*)$ or ${}^3B_{1u}$ $(\pi\ \pi^*)$ as is seen from Table 2. However, ${}^3B_{1u}$ $(\pi\ \pi^*)$ can not couple with any ${}^1B_{2u}$ states within the limit of LCAO MO approximation, while ${}^3B_{3u}$ $(n\ \pi^*)$ can couple only with ${}^1B_{2u}$ $(n\ \sigma^*)$. Such $(n\ \sigma^*)$ singlet state lies in general in far ultraviolet region and the corresponding absorption is not so intense. Therefore, contribution from the ${}^1B_{2u}$ $(n\ \sigma^*)$ seems not to be important. From these reasons, we exclude the possibility that the 20914 cm^{-1} band is a band origin of another triplet state. As already suggested before we interprete the band at 20914 cm^{-1} as a vibronic band induced by a nontotally symmetric vibration of the frequency 444 cm^{-1} in the excited state. In the Raman spectral measurement, we observed seven bands in the frequency range from 400 to 750 cm^{-1}. Of them, the Raman bands at 414, 582, 610, and 734 cm^{-1} are readily assigned as due to totally symmetric vibrations from their depolarization degrees observed for the molten sample. Furthermore, the experiment on the polarized Raman spectrum of the single crystal of phenazine indicated that the Raman spectrum of the single crystal of phenazine indicated that the Raman band at 494 cm^{-1} belongs to b_{1g} species and the bands at 449 and 512 cm^{-1} to b_{3g}. It is then very probable that the excited state vibration of 444 cm^{-1} is b_{3g} which corresponds to 449 cm^{-1} in the ground state.[17]

Now, we shall discuss the origin of the 20914 cm^{-1} on the vibronic-spin-orbit interaction scheme.[18] The Hamiltonian containing spin orbit coupling[19] is written to first order in nuclear displacement by

$$\mathbf{H} = \mathbf{H}_o{}^o + \mathbf{H}^o{}_{so} + \sum_a \left\{\left(\frac{\partial \mathbf{H}_o}{\partial \mathbf{Q}_a}\right)^0 + \left(\frac{\partial \mathbf{H}_{so}}{\partial \mathbf{Q}_a}\right)^0\right\}\mathbf{Q}_a$$

where, $\mathbf{H}_o$ is unperturbed term, $\mathbf{H}_{so}$ spin orbit coupling operator and $\mathbf{Q}_a$ indicates normal coordinate, the superscript zero referring to the equilibrium nuclear configurations. The vibronic wave function of the triplet state with which we are concerned is thus written in second order perturbation theory by

$$\begin{aligned}{}^T\theta = {}^T\theta_o &+ \textstyle\sum_S \frac{\langle S|\mathbf{H}^o{}_{so}|T\rangle}{E_{ST}} {}^S\theta_o + \sum_S \frac{\langle S|\mathbf{H}'{}_{so}|T\rangle}{E_{ST}} {}^S\theta_o \\ &+ \textstyle\sum_S \sum_{S'} \frac{\langle S|\mathbf{H}'{}_o|S'\rangle}{E_{SS'}} \frac{\langle S'|\mathbf{H}^o{}_{so}|T\rangle}{E_{S'T}} {}^S\theta_o \\ &+ \textstyle\sum_S \sum_{T'} \frac{\langle S|\mathbf{H}^o{}_{so}|T'\rangle}{E_{ST'}} \frac{\langle T'|\mathbf{H}_o'|T\rangle}{E_{TT'}} {}^S\theta_o\end{aligned}$$

where $\mathbf{H}'_o$ and $\mathbf{H}'_{so}$ represent $\left(\frac{\partial \mathbf{H}_o}{\partial \mathbf{Q}_a}\right)^0 \mathbf{Q}_a$ and $\left(\frac{\partial \mathbf{H}_{so}}{\partial \mathbf{Q}_a}\right)^0 \mathbf{Q}_o$ respectively. S′ and T′ indicate intermediate states. The second term indicates the usual spin orbit coupling for pure electronic state. The third term represents "the direct spin vibronic coupling." The fourth term is called "vibronic coupling in the singlet manifold with spin orbit coupling" and the last term is called "spin orbit coupling with vibronic coupling in the triplet manifold."

As is already described, the vibrationless triplet state is ${}^3B_{3u}$ $(n\ \pi^*)$ which couple with a ${}^1B_{1u}$ state through spin-orbit interaction, while the states corresponding to the vibronic band at 20914 cm^{-1} and its relatives must be perturbed by ${}^1B_{2u}$ state on the same interaction scheme. The selection rule for the spin-orbit coupling with vibronic coupling in the singlet manifold (the fourth term of the above equation) is same as that of the usual spin orbit coupling. Hence, the coupling by this mechanism between the ${}^3B_{3u}$ $(n\ \pi^*)$ state and the intermediate singlet state ${}^1B_{2u}$ are almost forbidden from the reason mentioned previously. On the other hand, the last term of the above equation, for which selection rule is shown in Table 3, will be non-zero when the intermediate triplet state is ${}^3A_u$ because it interacts vibronically with the ${}^3B_{3u}$, ${}^3B_{2u}$, or ${}^3B_{1u}$ by vibrations of b_{3g}, b_{2g}, or b_{1g} species, respectively and also it interacts with ${}^1B_{2u}$ by the spin-robit coupling. Since the perturbing vibration to the ${}^3B_{3u}$ $(n\ \pi^*)$ electronic state is the

Table 3. Selection rule for vibronic spin orbit coupling with the ${}^1B_{2u}(y)$ singlet state

Γ(T)	×	Γ(vib)	=	Γ(vibronic)		$\Gamma(l_\xi)$		$\Gamma^{obs}_{(S)}$
${}^3B_{3u}$	×	b_{3g}	>	${}^3A_u$	——	$B_{2g}(l_y)$	—	${}^1B_{2u}(y)$
${}^3B_{2u}$	×	b_{2g}						
${}^3B_{1u}$	×	b_{1g}						
${}^3B_{2g}$	×	b_{1u}	—	${}^3B_{3u}$	——	$B_{1g}(l_z)$	—	
	×	b_{2u}	—	${}^3A_u$	——	$B_{2g}(l_y)$	—	

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[16] L. Goodman and R. W. Harrell, *J. Chem. Phys.*, **30**, 1131 (1959).

[17] In the previous paper,[13] we correlated the vibration of 413 cm^{-1} of the excited $(n\ \pi^*)$ singlet state with the ground state vibration of 449 cm^{-1}. However, polarized Raman spectrum reveals that the 449 cm^{-1} must be a b_{3g} vibration and the 494 cm^{-1} belongs to b_{1g} vibration. Then, we revise that the 413 (b_{1g}) vibration of the singlet $(n\ \pi^*)$ state corresponds to the 494 cm^{-1} in the ground state.

[18] T. Pavlopoulos and M. A. El-Sayed, *J. Chem. Phys.*, **41**, 1082 (1964).

[19] A. C. Albrecht, *ibid.*, **38**, 354 (1963).

b_{3g} vibration of 444 cm^{-1}, the "*forbidden band*" at 20914 cm^{-1} and its relatives borrow their intensities from ^3A_u intermediate state which interacts with $^1B_{2u}$ (π π^*) state by spin orbit coupling. Hence, the following scheme is considered as the most possible coupling route,

$$^3B_{3u}(n\pi^*)\overset{Vib}{\underset{b_{3g}}{\text{——}}}{}^3A_u(n\pi^*)\overset{SO}{\underset{l_y}{\text{——}}}{}^1B_{2u}(\pi\pi^*)$$

Group theoretically, the coupling route by the third term of the equation is not excluded, but it gives the same result as that given above.

The MO calculation[20) indicates that the symmetry of the highest occupied π obrital (π_7) of phenazine molecule is b_{2g} and the lowest and the second lowest vacant orbitals (π_8* and π_9*) are of b_{3u} and a_u, respectively. The two nonbonding orbitals resulting from the two nitrogen atoms are of $a_g(n_+)$ and $b_{1u}(n_-)$. The first singlet-singlet transition at about 2.9 eV is mainly described as $n_+\to\pi_8^*$, while the second singlet-singlet transition at 3.2 eV is due predominantly to $\pi_7\to\pi_8^*$. Roughly speaking, the n_+ orbital is slightly higher in energy than the π_7 orbital. Then, the A_u excited state ($n_+\to\pi_9^*$), which is forbidden optically, may have almost same excitation energy as that of the $^1B_{2u}$ ($\pi_7\to\pi_9^*$) state observed at about 5 eV. The singlet–triplet separation of ($n\to\pi^*$) transition is generally not so large that the ^3A_u ($n_+\to\pi_9^*$) state state will locate near the $^1B_{2u}$ ($\pi_7\to\pi_9^*$) state. Therefore, strong spin-orbit coupling between them is expected. The fact that the intensity of the 0—0 band is much weaker than the vibronic bands may be explained from absence of the short axis polarized singlet state in vicinity of this spectral region. This is in accord with the result obtained from the polarized absorption spectrum of (n π^*) singlet state of this crystal.13)

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20) W. R. Carper and J. Stengl, *Mol. Phys.*, **15**, 121 (1968).
Figure Captions