The Electronic Spectra of Anthraquinone in Shpol'skii Matrices and in Crystals at 4.2 K

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The lower excited singlet and triplet states of 9,10-anthraquinone-d_0 and -d_8 are examined in normal alkanes and in crystals at 4.2 K with the phosphorescence excitation method. The $S \leftarrow S_0$ and $T \leftarrow S_0$ excitation spectra are analyzed by considering environmental effects on and isotopic changes in the vibrational structure. The low energy region of the spectra can be explained without taking the A_u origin in close proximity of the B_{1g} origin into account. The latter origin band in the singlet and triplet spectra in hexane and in crystals, respectively, is weaker by a factor of 10^{-3}—10^{-2} than the strongest vibronic band in the respective regions. No clear evidence has been found about the location of the singlet and triplet A_u states in the excitation spectra.

The investigation of the energy separation between the two low lying n,π^* states of quinones has attracted much interest,$^{1-8)}$ because its determination measures the magnitude of the electronic interaction of the nonbonding orbitals. In a *p*-quinone molecule, only the through bond interaction is dominant, as in the cases of pyrazine and quinoxaline,$^{9)}$ in which the two interacting nonbonding orbitals are concluded to have an energy separation of the order of 1 eV ($\simeq$8067 cm^{-1}), in good agreement with the theoretical calculation.$^{9,10)}$

Although there is a discrepancy in the assignment of the He-I photoelectron spectrum of *p*-benzoquinone between the two groups,$^{2,10,11)}$ the energy levels of the two nonbonding orbitals are separated by 0.9$^{10)}$ or 0.3 eV.$^{2,11)}$ The Coulomb integrals for the n_+,π^* and n_-,π^* states, J_{n_+,π^*} and J_{n_-,π^*}, may differ from each other and modify the energy separation between the two zero-order n,π^* states. From the absorption experiments on *p*-benzoquinone crystals, the separation has been reported to be about 225 cm^{-1} in the singlet state$^{3)}$ and 320 cm^{-1} in the triplet state.$^{6)}$ Recently Goodman and Brus$^{12)}$ have examined excitation spectra of *p*-benzoquinone in a neon host. They could not observe the broad band, which had been assigned to a different electronic origin, but observed very strong origin bands which they assigned to the ^1A_u and ^3A_u states. Their conclusion is that the two n,π^* states are nearly degenerate in *p*-benzoquinone. Although we do not agree with their conclusion, because they did not consider the possibility of a structural change induced by the host, their results give us very important information about the assignment of the two origins.

The assignment of the lowest triplet state of anthraquinone (AQ) has also attracted much attention from many workers.$^{13-17)}$ The polarization measurement indicates that the phosphorescence of AQ has the transition dipole moment along the oxygen-oxygen direction(z).$^{13)}$ Thus, it is concluded that the radiative transition from the lowest triplet state of AQ borrows its activity from the z axis polarized $^1B_{1u}(\pi,\pi^*) \rightarrow {}^1A_g$ transition.

The phosphorescence spectrum of AQ in hexane is known to arise from the $^3B_{1g}(n,\pi^*) \rightarrow {}^1A_g$ transition. The AQ molecules in this matrix seem to retain the inversion symmetry, because the 0,0 band is missing.$^{17)}$ On the other hand, the spectrum in pentane was analyzed to be a two-site emission. One of the sites produces a strong origin band induced by breakdown of the inversion symmetry.$^{17)}$

The $T \leftarrow S_0$ absorption spectrum of crystalline AQ has been obtained and the Zeeman experiment has been performed on the individual bands in the spectrum. From the very weak intensity and the Zeeman patterns of the 0,0 band, the lowest triplet state of AQ is assigned to $^3B_{1g}(n,\pi^*)$, which is located at 22154 cm^{-1} $^{14)}$ or at 22150 cm^{-1}. $^{15)}$ The vibronic bands appearing in the spectrum are ascribed to the ungerade-type vibrations, since the inversion symmetry of the molecule is conserved even in the crystal.$^{18)}$

The purpose of this work is to analyze the excitation spectra of AQ-d_0 and AQ-d_8 in the above two Shpol'skii matrices and to find evidence for the location of the A_u state. We will also discuss the structure of the $T \leftarrow S_0$ excitation spectra of both isotope crystals.

Experimental

9,10-Anthraquinone (AQ-d_0) and spectrograde hexane were purchased from Tokyo Kasei Co., Ltd. Merck Uvasol pentane was used without further purification. 2,3-Dichloroquinoxaline (DCQ) and 9,10-anthraquinone-d_8 (AQ-d_8) were from Eastman Kodak and Merck Sharp and Dohme Ltd., respectively.

An Ushio UXL-1000DO 1 kW xenon lamp was used as a light source for excitation and absorption experiments. A Molectron DL-200 tunable dye laser equipped with a Molectron UV-1000 1 MW N_2 laser was used to detect the origin bands in the $T \leftarrow S_0$ excitation spectra. Most of the high resolution spectra were observed through a Jobin Yvon HR 1000 monochromator fitted with a 1800 grooves/mm, 120 × 140 mm^2 grating, and a Spex 1700-III 3/4 m or a Bausch & Lomb 1/2 m monochromator was used to isolate a specific band of emission for excitation studies or microwave experiments.

Results and Discussion

Phosphorescence. The spectra of AQ-d_0 in hexane and pentane showed sharp bands. These spectra were essentially the same as those reported by Khalil and Goodman.$^{17)}$ The high resolution spectra of AQ-d_8 in these matrices are shown in Fig. 1. We could detect

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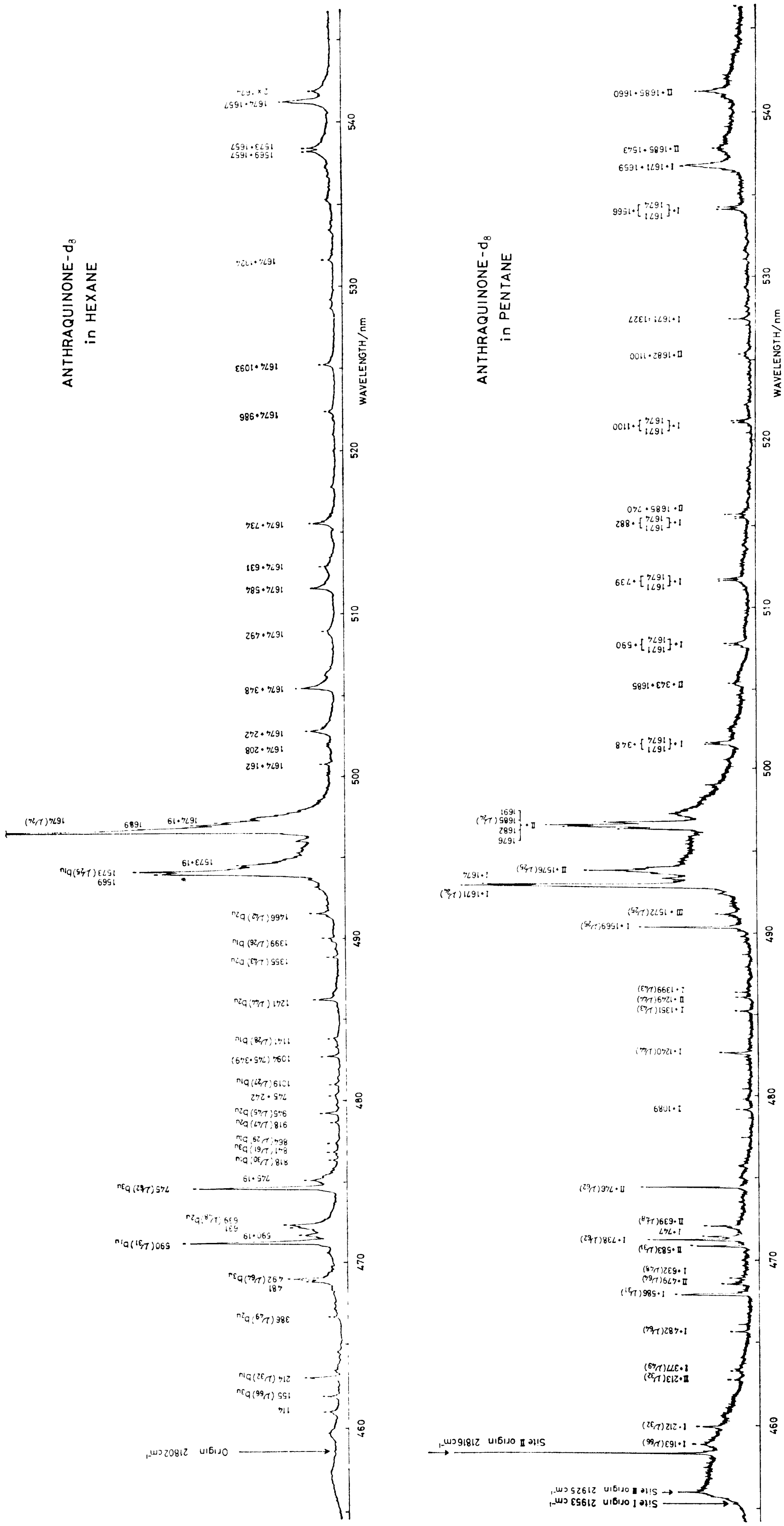

Fig. 1. The phosphorescence spectra of 9,10-anthraquinone-d_8 in hexane (top) and in pentane (bottom) at 4.2 K.

the origin band at 21802 cm^{-1} in hexane, the intensity of which was about 10^{-3} of that of the strongest band assigned as being due to the b_{1u} C=O stretching vibration(ν_{24}). This vibronic band has a single peak and is accompanied with a broad tail towards the low energy side. This feature is also seen in its combination bands with totally symmetric vibrations. The shape of this tail is apparently different from that seen in the band at 0—745 cm^{-1}. The band assigned to ν_{25} shows a doublet structure at 0—1569 and 0—1573 cm^{-1}. Most of the b_{1u} and b_{2u} vibrations, except for the two C–D stretching modes, are found in the spectrum.

Three-site emission is observed in pentane at 4.2 K. Most of the active bands were analyzed to be bands originating from two sites. The emission from site I has a very, very weak origin at 21953 cm^{-1}. The vibrational structure is almost the same as that in hexane. The origin band of the emission from site II reveals the strongest intensity in the spectrum. The energy of this origin band is close to that in hexane. The most intense vibronic band due to ν_{24} splits into two lines for site I and into four or more for site II. The combination bands with a_g vibrations show a similar band shape, which is very helpful for the analysis.

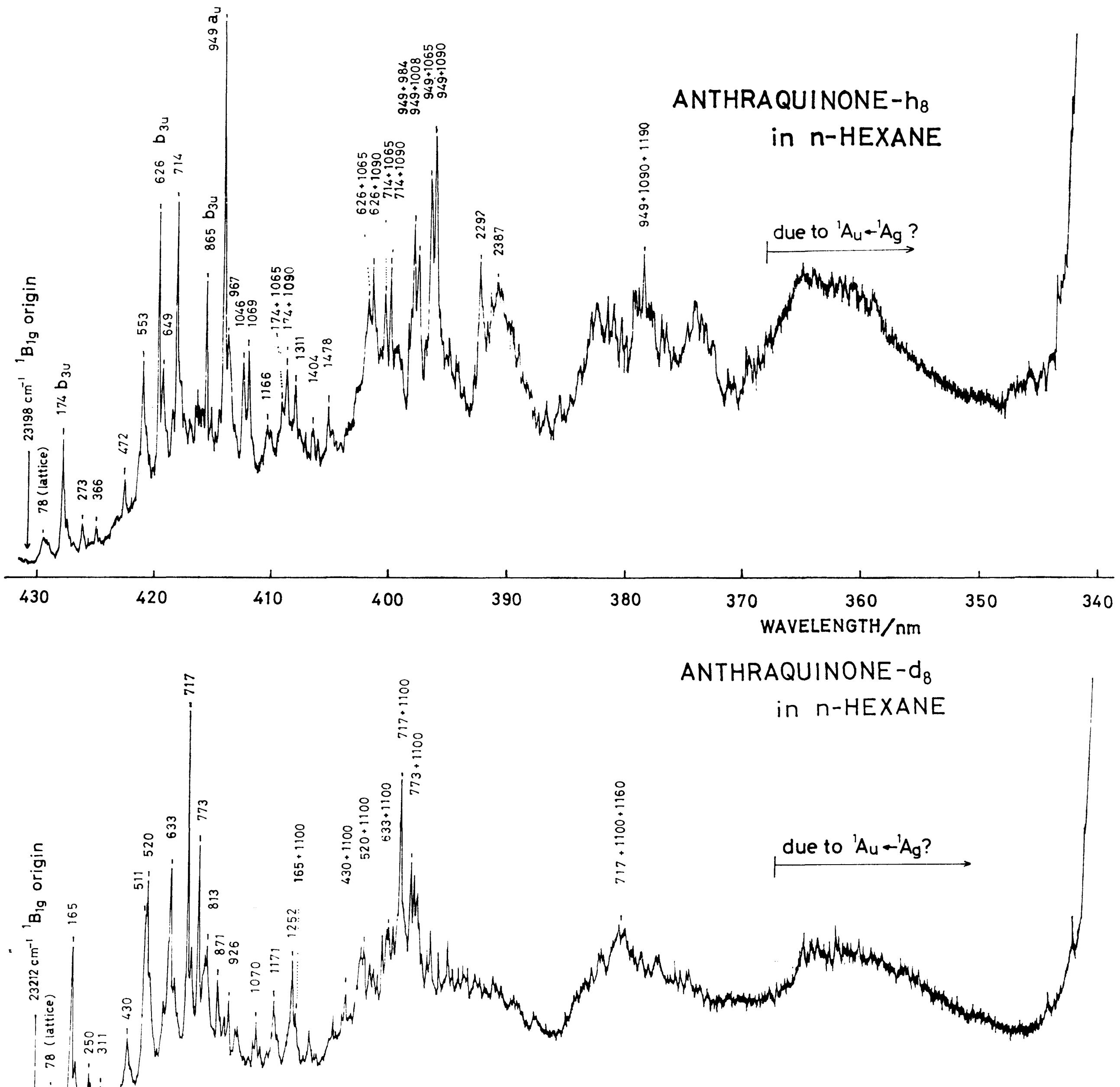

Fig. 2. The S←S$_0$ excitation spectra of 9,10-anthraquinone-d_0 and -d_8 in hexane at 4.2 K. Detection bandwidth is 4 nm centered at 497 nm.

The band width of the site II origin is about 2 cm^{-1} and those of other bands are generally much narrower in pentane than those in hexane. In spite of the very strong intensity of the origin band of site II, no other a_g fundamental band shows distinguishable activity in the spectrum. This indicates that any distortion of the site II molecules is not very large.

$S(n,\pi^*)\leftarrow S_0$ Excitation. The two n,π* states in question are $^1B_{1g}$ and ^1A_u in the low energy region of AQ. The transitions from the ground state to both of these n,π* states are symmetry forbidden processes, and would become allowed by borrowing intensities mainly from $^1B_{1u}(\pi,\pi^*)\leftarrow{}^1A_g$ and $^1B_{2u}(\pi,\pi^*)\leftarrow{}^1A_g$ transitions through u-type out-of-plane vibrations for the transition to the $^1B_{1g}$ state and g-type vibrations for that to the ^1A_u state, or by molecular distortion to a lower symmetry.

Spectra in Hexane: The excitation spectra of AQ-d_0 and -d_8 in hexane are shown in Fig. 2. A very, very weak but distinct band at 23198 cm^{-1} in the spectrum of AQ-d_0 and at 23212 cm^{-1} in that of AQ-d_8 was observed in the hexane matrix. The vibrational structures were analyzed by taking these bands as an electronic origin and the results are given in the figure.

The spectrum of AQ-d_0 has a structure quite similar to that of crystalline *p*-benzoquinone observed by Trommsdorff.[3] The bands in the spectra of AQ-d_0 and *p*-benzoquinone exhibit a good correspondence with each other, except for the strong bands, which have been assigned to the $^1B_{1g}$ and ^1A_u origins of *p*-benzoquinone. The strongest band in the *p*-benzoquinone spectrum is the one at 0+946 cm^{-1}. The corresponding band also appears as the strongest band in the AQ-d_0 spectrum in hexane at 0+949 cm^{-1}. Other bands seen in the *p*-benzoquinone spectrum at 0+141, 0+597, 0+679, 0+836, 0+1044, 0+1069, and 0+1161 cm^{-1} correspond well to the bands at 0+174, 0+553, 0+626, 0+865, 0+1046, 0+1066, and 0+1166 cm^{-1}, respectively, in the spectrum of AQ-d_0. These frequencies are surprisingly closely related to each other. In the case of AQ-d_0, however, there is no strong band in the lower energy region which corresponds to the strong broad band assigned as the ^1A_u origin of *p*-benzoquinone.

The broad band at 0+78 cm^{-1} and the sharp band at 0+174 cm^{-1} of AQ-d_0 correspond well with the first two vibrational bands of AQ-d_8 at 0+78 and 0+165 cm^{-1} in their intensity and frequency. The corresponding bands are also observed in the phosphorescence spectra of AQ-d_0 and -d_8 in hexane (at 0*−76 and 0*−167 cm^{-1} for AQ-d_0, where 0*=21783 cm^{-1}) and assigned to a lattice mode and a b_{3u} out-of-plane vibration, respectively.[17] The vibration of 141 cm^{-1} found in the spectrum of a *p*-benzoquinone crystal was also assigned to a b_{3u} skeletal mode by Trommsdorff.[3] The appearance of the b_{3u} vibration clearly indicates that these bands are associated with the $^1B_{1g}\leftarrow{}^1A_g$ transition.

The spectra of the two isotopes show different structures in the region from 0+500 to 0+1200 cm^{-1} mainly in their intensity relation. The strongest band of AQ-d_0 at 0+949 cm^{-1} shifts to 0+717 cm^{-1} for AQ-d_8. This frequency lowering by about 230 cm^{-1} excludes an assignment of these bands to vibrations belonging to another electronic state. The isotopic ratio of 1.32 (=949/717) indicates that these vibrations are to be assigned to a C–H(D) bending mode. Considering the assignment of the 946 cm^{-1} vibration of *p*-benzoquinone,[3] we also assign the 949 cm^{-1} vibration tentatively to an a_u out-of-plane C–H bending vibration. However, we could not eliminate the possibility of a b_{3u} vibration, because the band observed at 970 cm^{-1}

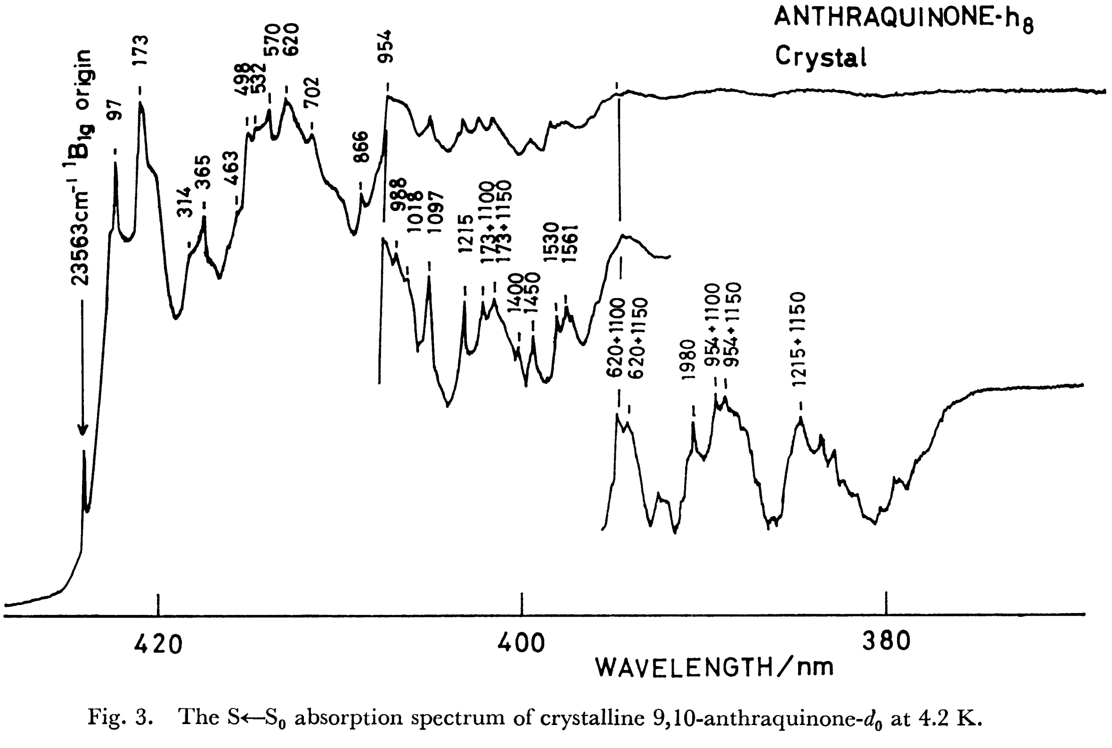

Fig. 3. The S←S_0 absorption spectrum of crystalline 9,10-anthraquinone-d_0 at 4.2 K.

in the infrared spectrum was assigned to ν_{61}, a b_{3u} C–H bending mode.[18]

Other strong bands of AQ-d_0 at 0+553, 0+626, 0+714, and 0+865 cm^{-1} correspond with those of AQ-d_8 at 0+511, 0+520, 0+633, and 0+813 cm^{-1}, respectively. The combination bands of these strong lines with the 1065 and 1090 cm^{-1} vibrations of AQ-d_0 and the 1100 cm^{-1} vibration of AQ-d_8 are found strongly and this proves that these bands do not belong to a different electronic transition. Such combination bands were also observed in the spectrum of a *p*-benzoquinone crystal by Trommsdorff,[3] who assigned the 1100 cm^{-1} vibration as being due to the totally symmetric C=O stretching vibration.

Spectrum of Neat Crystal: The absorption spectrum of the AQ-d_0 crystal is shown in Fig. 3. The origin band was observed at 23563 cm^{-1}, which is about 360 cm^{-1} higher in energy than the $^1B_{1g}$ origin in hexane. The

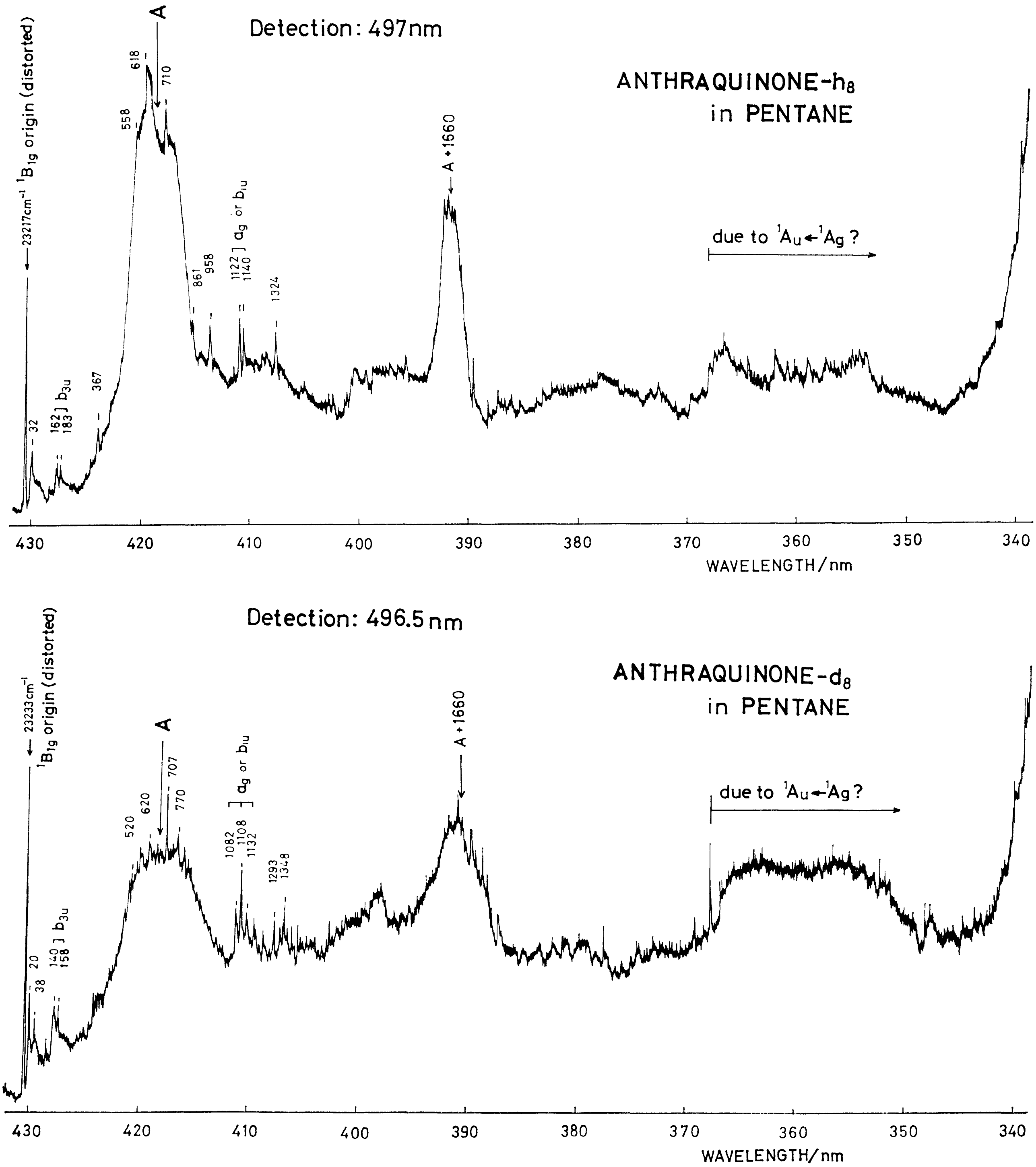

Fig. 4. The S←S$_0$ excitation spectra of 9,10-anthraquinone-d_0 and -d_8 in pentane at 4.2 K. Detection bandwidth is 5 nm centered at 497 nm.

band at $0+97\ \mathrm{cm}^{-1}$ corresponds with a lattice mode. and the band at $0+173\ \mathrm{cm}^{-1}$ to the b_{3u} mode found in the hexane system. The vibrational structure of the strong bands in this spectrum coincides quite well with that in hexane. Combination bands with a_g vibrations of 1100 and $1150\ \mathrm{cm}^{-1}$ are also active in the crystal.

Spectra in Pentane: The excitation spectra of AQ-d_0 and -d_8 in pentane were observed by monitoring the strong bands around 497 nm of the phosphorescence from site II with a detection bandwidth of 4—5 nm The observed spectra in Fig. 4 show a strong origin band to the higher energy side by about $20\ \mathrm{cm}^{-1}$ with respect to the origin band in hexane. The appearance of the strong origin band is consistent with that observed at $21790\ \mathrm{cm}^{-1}$ for AQ-d_0 and at $21816\ \mathrm{cm}^{-1}$ for AQ-d_8 in the phosphorescence in pentane. Therefore, we are really observing the same species with a distorted structure.

Apart from the intense broad bands around 420 and 390 nm, which will be shown to be due to molecular aggregates, the spectra consist of a number of sharp bands and a hump around 365 nm. The sharp bands in the lower energy region may be classified into two groups. One of the groups consists of the bands which correspond to those found in the hexane system; these bands can be assigned to b_{3u} and a_u vibrations. Since the fundamental frequencies measured from the origin band fit quite well to those observed in hexane, there is no possibility that these bands belong to the ${}^1A_u \leftarrow {}^1A_g$ transition which could be observed for the distorted species. If the bands belonging to the ${}^1A_u \leftarrow {}^1A_g$ transition appeared in the same region, the vibrations should be assigned to b_{1g} or b_{2g} symmetry.

The bands in the other group are characteristic of a distorted species, for which a_g and b_{1u} in-plane vibrations may show some activity. The bands appearing around $0+1100\ \mathrm{cm}^{-1}$ do not have a corresponding band in the spectrum in hexane. The vibration of about $1100\ \mathrm{cm}^{-1}$ is known to form combination bands with b_{3u} and a_u vibrations in hexane and is assigned to the a_g C=O stretching vibration. The b_{1u} C=O stretching vibration is also expected to acquire activity, if the molecular symmetry is reduced by the environment to C_{2v} with the C_2 axis along the C=O bonds.

In pentane, the phosphorescence emission shows strong sharp bands overlapping a very broad background. The broad background was assigned to molecular aggregates.[17] As a matter of fact, the strong broad bands also appear at 420 and 390 nm in the excitation spectra monitored at 497 nm. The position and relative intensity of the broad band around 420 nm were found to change markedly when the wavelength setting of the detecting monochromator was changed; some examples are shown in Fig. 5. The energy shift of the band center seems to be just equivalent to the difference in the wavelength of the monitored light. Furthermore, the intensity of the broad band relative to that of the origin band at $23217\ \mathrm{cm}^{-1}$ also changes with cooling condition of the sample and initial guest concentration. The spectra of the two isotopes in Fig. 4 were taken at the concentrations differing by a factor of three. These results suggest that the broad band around 420 nm arises from molecular aggregates. The broad band around 390 nm (about $1660\ \mathrm{cm}^{-1}$ higher in energy) seems to be its combination band, although the bandwidth is about half.

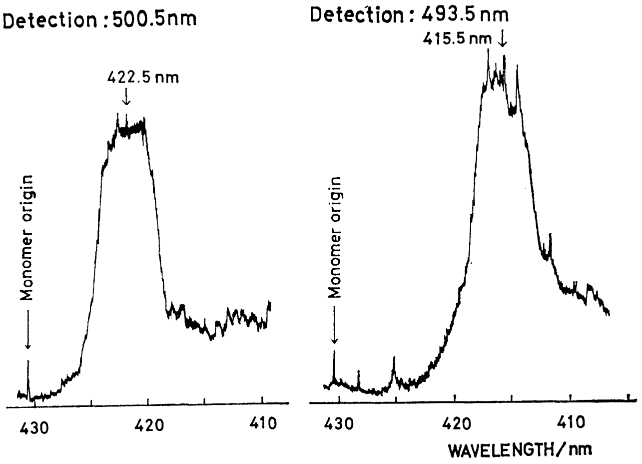

Fig. 5. Variation of the broad band position in the excitation spectrum with detection wavelength of the emission from anthraquinone-d_0 in pentane at 4.2 K.

The ${}^1A_u \leftarrow {}^1A_g$ Transition: It was expected that the forbidden ${}^1A_u \leftarrow {}^1A_g$ transition would appear in the excitation spectrum in pentane, when the phosphorescence from the distorted species was monitored. For this purpose, we have carefully adjusted the detecting monochromator to a desired wavelength. In this respect, it is of great interest to pay attention to the sharp band appearing at 367.65 nm in the excitation spectrum of AQ-d_8 in pentane. The band lies at 4033 cm^{-1} from the strong origin and could not be assigned to a combination band or an overtone band. Furthermore, the hump with weak but sharp bands is commonly found around 365 nm in all the four spectra in Figs. 2 and 4. As the ${}^1B_{1g}$ origin lies within $35\ \mathrm{cm}^{-1}$ in the four systems, the origin of the ${}^1A_u \leftarrow {}^1A_g$ transition in these systems is also expected to appear at nearly the same position. The region where the hump is observed clearly satisfies this condition. The sharp band at 367.65 nm in the spectrum of AQ-d_8 is quite within the reasonable bounds of possibility of the ${}^1A_u$ origin. A weak similar band is also seen at 367.7 nm in the spectrum of AQ-d_0 in pentane.

$T(n,\pi^*) \leftarrow S_0$ Excitation. A mixed crystal of AQ with 0.1% of 2,3-dichloroquinoxaline (DCQ) emits a strong phosphorescence from the lowest triplet state of DCQ. The vibrational structure of the phosphorescence spectrum is in good agreement with the result reported by Tinti and El-Sayed.[19] The excitation spectrum of crystalline AQ was observed by monitoring this emission. The spectra for the AQ-d_0 and -d_8 crystals are shown in Fig. 6. The excitation spectrum of AQ-d_0 is essentially the same as the absorption spectrum reported by Drabe *et al.*[14] and Narisawa *et al.*,[15] except for minor details. Carefully comparing the spectra of the two isotopes, we could notice a structural difference around 443 nm. AQ-d_8 shows an intensity increment of the broad band around $0+327\ \mathrm{cm}^{-1}$. Another obvious

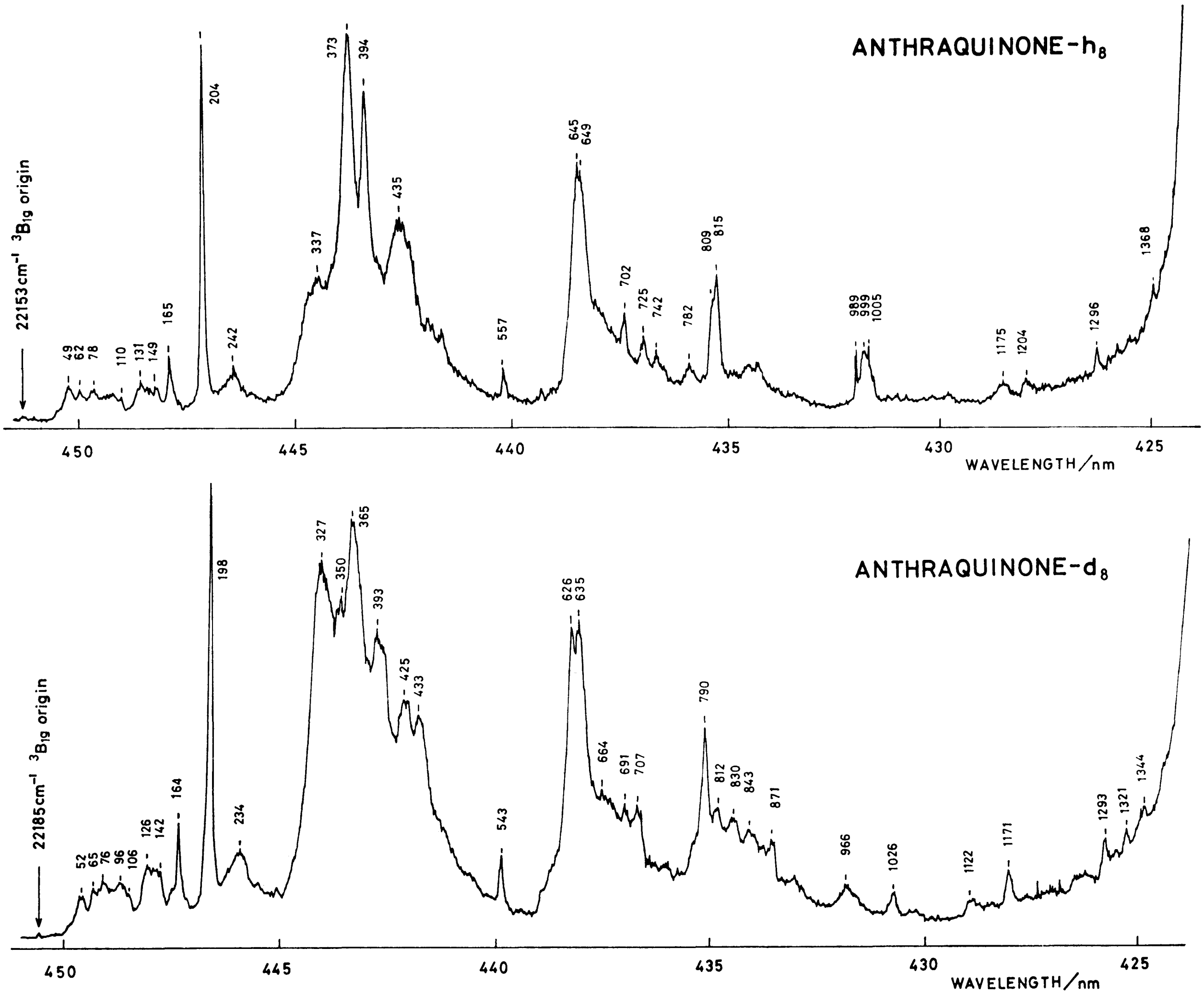

Fig. 6. The $T \leftarrow S_0$ excitation spectra of crystalline 9,10-anthraquinone-d_0 (top) and -d_8 (bottom) at 4.2 K. The whole phosphorescence from the doped 2,3-dichloroquinoxaline was monitored.

difference can be found around 0+830 and 0+1000 cm^{-1}. This difference can be attributed to an isotopic frequency shift of vibrations, thereby suggesting some participation of hydrogen bending vibrations in the transition mechanism.

MIDP Excitation Spectra: Since each of the transitions from the ground state to the three spin states in a single vibronic level of an excited triplet state has a different selection rule, depending on the spin-orbit coupling processes involved, microwave induced delayed phosphorescence (MIDP)[20] signals in an isolated molecule reflect the transition probability characteristic of each sublevel excitation. In a mixed crystal, however, the selective populations of the spin states are sometimes not maintained during energy transfer processes, and MIDP signals show a modified spin population depending on the relative orientations of the molecular spin axes between the guest and host and between the host molecules.[20,21]

The short axes(z) of the AQ molecules in a crystal are nearly parallel to each other, but the long axis(y) of an AQ molecule is approximately parallel to the normal axis(x) of the translationally inequivalent molecules.[22] In the mixed crystal of AQ with DCQ, it is reasonably assumed that the guest molecules replace the host molecules substitutionally. Therefore, it is expected that the population of T_z produced in DCQ by direct $T \leftarrow S_0$ excitation of the mixed crystal may not be affected very much by energy transfer and trapping processes, whereas the populations of T_y and T_x may or may not mix with each other depending on whether the main energy transfer mechanism is one-dimensional or not. A single band excitation of the AQ-d_0 crystal yielded the steady state population ratios of N_z: N_y: N_x to be approximately 1.9: 2.1: 1 for the 0+165 cm^{-1} band and 5.5: 0.55: 1 for the 0+204 cm^{-1} band. From these results, it was concluded that the mechanism is mainly one-dimensional and that the mixing of the populations of T_y and T_x during the energy transfer has a minor effect on the relative populations in our systems.

The excitation spectrum shown in the upper part of Fig. 7 was taken by sampling the DCQ phosphorescence in the AQ-d_8 crystal for a period of 110 ms just after excitation lasting 30 ms. The repetition rate was 2 Hz. Since the decay times of T_z, T_y, and T_x were observed

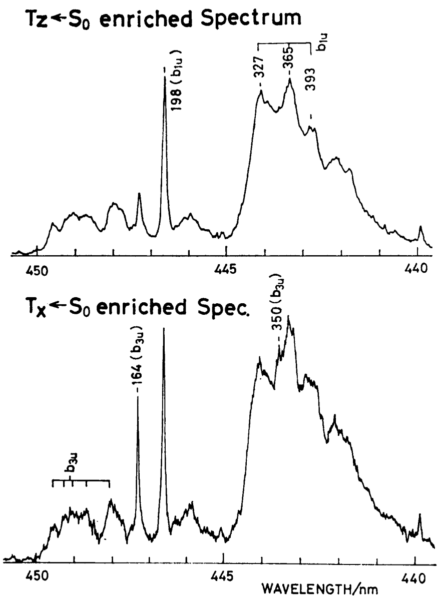

Fig. 7. The T←S_0 excitation spectra of crystalline 9,10-anthraquinone-d_8 at 1.4 K. The absorption to T_z is enhanced in the upper spectrum by choosing the sampling time, while that to T_x is enhaced in the lower spectrum by using microwave modulation.

to be 150, 260, and 2700 ms, respectively, this spectrum contains an enhanced contribution from the T_z←S_0 transition of AQ-d_8, by comparison with an excitation spectrum taken under steady state condition.

The lower spectrum of Fig. 7 is an MIDP excitation spectrum taken by sampling only the portion of the MIDP signal on sweeping the microwave frequency through the T_y↔T_x transition of DCQ 950 ms after excitation. The microwave sweep increases the T_y emission in proportion to the population of T_x produced mostly by the T_x←S_0 transition of the host molecules The assignments of the vibronic bands were performed according to the selection rule that a b_{1u} vibration is actively involved in the excitation to the T_z sublevel in the $^1B_{1g}$ state and a b_{3u} vibration is involved in the excitation to the T_x sublevel. Some of the results are shown in Fig. 7.

The sharp band at 0+164 cm^{-1} is notably enhanced by the T_y↔T_x pumping and assigned to a b_{3u} vibration. The vibration of 165 cm^{-1} has also appeared in the S←S_0 excitation spectrum of AQ-d_8 in hexane. This was assigned to the $\nu_{66}(b_{3u})$ mode. The intensity of the band at 0+350 cm^{-1} is markedly increased by the T_y↔T_x pumping, and this band can be assigned to a b_{3u} vibration. At first sight, the broad bands at 0+365 and 0+393 cm^{-1} also seem to be intensified by the microwave transition, but this could be due to their overlapping with the band at 0+350 cm^{-1}. The broad low frequency bands which should be considered as being due to lattice modes behave like b_{3u} vibrations. Murao and Azumi[23] also found that the fundamental lattice band is exceedingly active in the emission spectrum from the T_x sublevel of AQ-d_0 in octane.

Except for several broad bands around 0+400 cm^{-1}, most of the strong bands in Fig. 6 were assigned on the basis of the relation of the isotopic ratio of the vibrational frequency and the relative intensity found in the phosphorescence spectra of both isotopes in hexane and in octane.[23] The fundamental frequencies obtained are summarized in Table 1, together with those found in the emission[17] and in the infrared absorption spectra.[18] The frequency changes of these vibrations in the $^3B_{1g}$ state are not very large, except for the C–H(D) bending mode(ν_{45}), which shows a frequency reduction of 16—17 per cent.

The antisymmetric C=O stretching mode(ν_{24}) and the out-of-plane C–H bending mode(ν_{63}) are found to be active in the phosphorescence spectrum.[17] However, we are not certain whether these vibrations appear in the T←S_0 excitation spectrum. If the frequency of ν_{24} is increased for any reason in the $^3B_{1g}$ state or is decreased by less than 16 per cent, then the vibronic band due to ν_{24} would be hidden in the region of S←S_0 absorption. The symmetric C=O stretching mode(ν_3) of about 1100 cm^{-1} is known to form several combination bands in the S←S_0 excitation in hexane, as discussed above. Therefore, we may also expect the appearance of its combination bands in the T←S_0 excitation spectrum. The band appearing at 0+1295 cm^{-1} might be attributed to a combination band with the ν_{32} mode. However, this band seems to be too weak to be assigned to the combination band of ν_3.

Any strong vibronic interaction between the $^3B_{1g}$

TABLE 1. THE VIBRATIONAL FREQUENCIES OBSERVED IN THE $^3B_{1g}$←^1A_g EXCITATION SPECTRA OF THE ANTHRAQUINONE CRYSTALS WITH THE CORRESPONDING FREQUENCIES FOUND IN THE PHOSPHORESCENCE SPECTRA IN HEXANE AND IN THE INFRARED ABSORPTION SPECTRA OF CRYSTALS

Assignment	9,10-Anthraquinone-d_0			9,10-Anthraquinone-d_8		
	T_1(cryst.)	S_0(hexane)[a]	IR(cryst.)[b]	T_1(cryst.)	S_0(hexane)	IR(cryst.)[b]
ν_{66} b_{3u} skel. def.	165 cm^{-1}	167	167	164	155	161
ν_{32} b_{1u} skel. def.	204	228	237	198	214	222
ν_{64} b_{3u} C=O bend.	—	(517)	491	350	492	(398)
ν_{31} b_{1u} skel. def.	645	620	626	626	590	605
ν_{62} b_{3u} skel. def.	815	791	816	790	745	744
ν_{45} b_{2u} C–H bend.	999	1155	1207	812	945	965
ν_{44} b_{2u} ring str.	1204	1339	1335	1122	1241	1246

a) Ref. 17, b) Ref. 18; skel., skeletal; def., deformation; bend., bending; str., stretching.

and ^3A_u states through the ν_{24} mode would have a possibility of causing a frequency shift of this vibration. The strong band at 0+373 cm^{-1} for AQ-d_0 and at 0+365 cm^{-1} for AQ-d_8 might be considered to be due to ν_{24} of reduced frequency, as a result of the pseudo-Jahn-Teller effect. However, the PMDR studies of *p*-benzoquinone[24) and AQ-d_0[23) did not demonstrate any detectable molecular distortion along the b_{1u} coordinate. These results are therefore consistent with the fact that the origin band is vanishingly weak in the excitation spectra of the AQ crystals and in the emission spectra of AQ-d_0 and -d_8 in hexane. The frequency reduction from 1676 cm^{-1} in the ground state to 373 (or 365) cm^{-1} in the $^3B_{1g}$ state would be too large to explain the absence of molecular distortion along the b_{1u} direction. The above discussion suggests that the frequency of the ν_3 vibration and possibly that of the ν_{24} vibration are higher than 1100 cm^{-1} in the $^3B_{1g}$ state.

The Broad Band Cluster: Drabe *et al.* assigned the center of the broad band cluster from 445 to 441 nm (*i.e.*, 22560±10 cm^{-1}) as the origin of the ^3A_u state.14) Instead of taking the origin at the center of the cluster, the strongest band position may be a more adequate choice for the origin, that is, 22526 cm^{-1} (0+373 cm^{-1}) for AQ-d_0 and 22550 cm^{-1} (0+365 cm^{-1}) for AQ-d_8. This assignment was proposed mainly from analogy with the absorption spectrum of a *p*-benzoquinone crystal, which exhibited a strong broad absorption at 320 cm^{-1} to the higher energy side from the $^3B_{1g}$ origin. However, this broad band assigned as the ^3A_u origin was not found in the excitation spectrum of the isolated *p*-benzoquinone molecule in a neon matrix.12) Goodman and Brus concluded that this broad band might be vibronic absorption induced by the environment.12) Therefore, it seems that the assignment of the cluster is still inconclusive. The cluster may be interpreted in several ways.

In the first place, we examine the possibility that the ^3A_u origin may be in the cluster and the vibronic bands thereafter would belong to the $^3A_u \leftarrow {}^1A_g$ transition. In this case, a vibronic band is expected to have a band shape similar to that of the origin, because the ^3A_u origin band has an allowed character and coupling with a non-totally symmetric phonon is not expected in this transition. The shapes of the clusters are different in the spectra of the two isotopes, although the spectral positions of the clusters are coincident. Therefore, the vibrational bands coupled with the origin band would give rise to a more complex spectrum for AQ-d_8 than for AQ-d_0. The observed spectrum of AQ-d_8, however, does not include such a complicated structure and the difference between the two spectra is thus attributed to the involvement of C–H(D) bending vibrations. This cluster does not seem to behave as an origin in the spectrum.

The second case is that the strongest band in the cluster would be assigned to the ^3A_u origin as before, but the vibronic bands in the cluster are built on the $^3B_{1g} \leftarrow {}^1A_g$ transition and are induced by a strong interaction between the vibronic levels in $^3B_{1g}$ and the ^3A_u origin. In this case, the fact that the intensity of the band at 0+327 cm^{-1} is comparable with that at 0+365 cm^{-1} in the spectrum of AQ-d_8 indicates that the coupling should be very strong in AQ-d_8. However, the intensity of the corresponding band at 0+337 cm^{-1} in the spectrum of AQ-d_0 is less than half of that of the strongest band at 0+373 cm^{-1} and the energy gap between the two bands is nearly the same as that for AQ-d_8. This fact probably eliminates the possibility that the strong interactions exist between the vibrational levels in $^3B_{1g}$ and the ^3A_u origin.

Thirdly, the coupling of a vibronic band with phonon modes may be considered. Vibrational frequencies of 350—450 cm^{-1} correspond to those of in-plane C=O bending vibrations in the ground state. A b_{2u} mode is found at 387 cm^{-1} in the infrared absorption spectrum and assigned to ν_{49}.18) A Raman band at 485 cm^{-1} was attributed to the b_{3g} C=O bending mode.25) The former b_{2u} vibration was also found in the phosphorescence spectrum of AQ-d_8 in hexane (Fig. 1) and in that of an isotopically mixed crystal.14) Since the triplet state is n,π^* in character, frequency reduction of C=O bending vibrations can be expected, although delocalization of the nonbonding orbitals over the whole σ framework probably decreases this effect to some extent. Such a change in the force field around the C=O groups is considered to induce an interaction with local lattice modes. Here, we have to attach importance to the fact that the lattice modes coupled with the very weak $^3B_{1g}$ origin band appear with different relative intensities among the bands in the spectra of the two isotopic crystals. It would then be possible that these b_{2u} and b_{3g} vibrations couple with some lattice modes of b_g and b_u symmetries, respectively, resulting in the same behavior as b_{1u} vibrations. This explains the similarity in frequency and the difference in relative intensity of the peaks in the broad band clusters in the two excitation spectra. This idea is consistent with the interpretation suggested by Goodman and Brus12) that the broad absorption band of *p*-benzoquinone may be vibronically induced by the environment.

Finally, it is also possible to consider that the Duschinsky effect26,27) is prominent in the triplet manifold and that the transition intensity shared by ν_{24} is distributed over several bands with b_{1u} symmetry, including the bands coupled with lattice modes. This allows some strong bands to appear in the low frequency region, where the fundamental band of the ν_{24} mode in the ground state coordinate cannot be expected to appear.28)

As discussed above, the assignment of the ^3A_u origin to the broad band around 443 nm does not explain satisfactorily the intensity relation among the near lying bands. We conclude that no tangible evidence for that assignment has been found in the excitation spectra of the AQ crystals. From analogy with the singlet system, we presently lean towards the possibility that the ^3A_u state in the AQ crystal lies outside the region accessible by the $T \leftarrow S_0$ excitation technique. Further studies are indispensable to draw a final conclusion.

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