

SINGLET AND TRIPLET n,π^* TRANSITIONS OF JET-COOLED p-BENZOQUINONE

ISAMU SUZUKA, MASAOMI SANEKATA*, MITSUO ITO*

*Department of Industrial Chemistry, College of Engineering, Nihon University,
Koriyama, 963, Japan*

**Institute for Molecular Science, Myodaiji, Okazaki, 444, Japan*

NOBUHIRO OHTA

*Department of Chemical Engineering, Faculty of Engineering, Hokkaido
University, Sapporo, 060, Japan*

(Received 14 May 1993)

The fluorescence/phosphorescence excitation spectra, the dispersed fluorescence/phosphorescence spectra and the sensitized phosphorescence excitation spectrum have been measured for jet-cooled p-benzoquinone. The assignments of vibronic bands in the ${}^1B_{1g}(n,\pi^*) \leftarrow {}^1A_g$ and ${}^1A_u(n,\pi^*) \leftarrow {}^1A_g$ transitions have been definitely established. The phosphorescence spectra from vibronic levels of 3A_u exhibit a feature of single vibronic level emission. The ${}^3A_u \leftarrow {}^1A_g$ transition was also vibrationally analyzed.

KEY WORDS: p-Benzoquinone, singlet-triplet transition, singlet-singlet transition, jet spectroscopy, vibrational analysis, $n-\pi^*$ transition.

INTRODUCTION

p-Benzoquinone (PBQ) has two equivalent non-bonding orbitals on the oxygen atoms. Their symmetric and antisymmetric combinations give rise to two non-bonding molecular orbitals $n_+(a_g)$ and $n_-(b_{1u})$, respectively, under the molecular symmetry of D_{2h} . The excitation of an electron from the nonbonding molecular orbital to the lowest vacant π orbital ($\pi^*(a_u)$) gives rise to two n,π^* electronic states, A_u and B_{1g} , in both the singlet and triplet manifolds. The singlet n,π^* states have been studied by many workers. ter Horst and Kommandeur observed the fluorescence excitation spectrum of the jet-cooled molecule and determined the origins of dipole forbidden ${}^1A_u \leftarrow {}^1A_g$ transition and magnetic dipole allowed ${}^1B_{1g} \leftarrow {}^1A_g$ transition at 19,991 and 20,045 cm^{-1} , respectively.¹ The frequency difference between the two origins is only 54 cm^{-1} , indicating a weak interaction between the two nonbonding orbitals localized on the oxygen atoms. On the other hand, $T(n,\pi^*) \leftarrow S_0$ transitions have been studied by absorption and phosphorescence

excitation techniques in the bulk vapor phase²⁻⁵ and in the low temperature matrix.⁶ The origin of ${}^3A_u \leftarrow {}^1A_g$ transition was located at 18682 cm^{-1} from the vapor absorption study by Hollas.² However, the orbital as well as spin forbidden ${}^3B_{1g} \leftarrow {}^1A_g$ transition has never been observed in the gas phase, although its origin seems to lie near the origin of ${}^3A_u \leftarrow {}^1A_g$.^{3,6}

The purpose of the present work is to examine the assignments of the singlet and triplet n,π^* transitions by observations of the dispersed fluorescence and phosphorescence spectra originating from various vibronic levels in the singlet and triplet excited states. The dispersed fluorescence spectra will be most powerful in establishing the assignments of the individual vibronic bands, but they have never been reported for the isolated molecule except for the spectrum from a particular vibronic level in ${}^1B_{1g}$ by ter Horst and Kommandeur.¹ We also observed the fluorescence excitation and sensitized phosphorescence excitation spectra of the jet-cooled molecule. A comparison of these two spectra provides us with information about the intersystem crossing rates of the individual vibronic levels. In PBQ, the two singlet n,π^* states 1A_u and ${}^1B_{1g}$ lie close in energy and vibronic bands belonging to these two states appear in the same energy region. The vibronic bands belonging to one of the states might be discriminated from the other by using the difference in their intersystem crossing rate. Moreover, we succeeded in observing single vibronic level (SVL) phosphorescence spectra, which have never been observed for polyatomic molecules. We could assign unambiguously the vibrational levels of the ${}^3A_u(n,\pi^*)$ state from these dispersed phosphorescence spectra.

EXPERIMENTAL

PBQ (Tokyo Kasei) was purified by vacuum sublimation. PBQ- d_4 was synthesized from hydroquinone- d_6 . PBQ vapor saturated at about 90°C was mixed with carrier gas of helium. The seeded gas with 350~760 torr stagnation pressure was expanded into a vacuum chamber through a pulsed nozzle of 0.4 mm orifice at a repetition rate of 10 Hz. The jet-cooled PBQ was excited by a XeCl excimer pumped dye laser (Lambda Physik EMG50E+FL2002 dye, coumarin 102 and 307) 15 mm downstream from the nozzle. The fluorescence or phosphorescence excitation spectrum was measured by detecting total fluorescence or phosphorescence, respectively, with a photomultiplier (Hamamatsu Photonics R562) by using a suitable cut-off filter (Toshiba O-55, O-57). A boxcar averager (Stanford Research Systems SRS 250) was employed as the signal converter. The SVL fluorescence and phosphorescence spectra were obtained by a 0.75 m Nalumi monochromator with a spectral resolution of 0.1 nm.

We also measured the sensitized phosphorescence excitation spectrum of jet-cooled PBQ. Following the technique developed by Abe *et al.*,⁷ we placed an appropriate solid phosphor downstream from the jet. Triplet state molecules produced by intersystem crossing from a laser-excited singlet state travel downstream in the jet at a high speed and hit the solid phosphor. Collision-induced energy transfer to the phosphor then results in sensitized phosphorescence. When the sensitized

phosphorescence is detected by a detector placed near the solid phosphor as the laser frequency is scanned, the sensitized phosphorescence excitation spectrum of the jet-cooled molecule is obtained. The apparatus used for the observation of the sensitized phosphorescence excitation spectrum has been described elsewhere.⁸ Solid PBQ itself, prepared on a cooled copper surface by deposition of the jet-cooled PBQ, served as a phosphor.

RESULTS AND DISCUSSION

A. Fluorescence excitation spectra and dispersed fluorescence spectra.

Figure 1 shows the fluorescence excitation spectrum of jet-cooled PBQ in the singlet n,π^* region. The spectrum is essentially the same as that reported by ter Horst and Kommandeur.¹ Their assignments of the main vibronic bands are shown in the figure. The origin of the magnetic dipole transition ${}^1B_{1g} \leftarrow {}^1A_g$ is located at 20,045 cm^{-1} . Bands at 126, 380 and 926 cm^{-1} above this origin (denoted by ${}^1B_{1g}(0,0) + 126, 380$ and 926 cm^{-1}) were assigned by ter Horst and Kommandeur to ones belonging to the same electronic transition based on their rotational contours. They gain their intensities through vibronic coupling of $\nu_{26}(b_{3u})$, $\nu_{23}(a_u)$ and $\nu_{22}(a_u)$ modes, respectively, between the ${}^1B_{1g}$ state and higher excited π,π^* states. The singlet n,π^* transition ${}^1A_u \leftarrow {}^1A_g$ is dipole-forbidden and its origin does not appear in the spectrum. ter Horst and Kommandeur located, however, the forbidden origin at 19,991 cm^{-1} , i.e., at 54 cm^{-1} below the origin of ${}^1B_{1g} \leftarrow {}^1A_g$, based on an analysis of hot band. They assigned the band at 20,312 cm^{-1} as one belonging to the ${}^1A_u \leftarrow {}^1A_g$ transition, induced by vibronic coupling through $\nu_{30}(b_{2g})$ mode.

In order to examine the above assignments, we observed the dispersed fluorescence spectra. Figure 2 shows the dispersed fluorescence spectrum from the zero-point

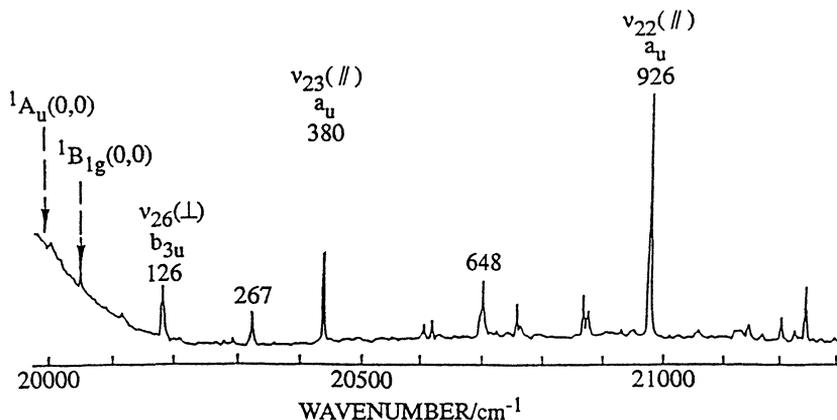


Figure 1 Fluorescence excitation spectrum of jet cooled PBQ in the singlet n,π^* region. The wave-number of vibronic band in the figure shows frequency difference from ${}^1B_{1g}(0,0)$.

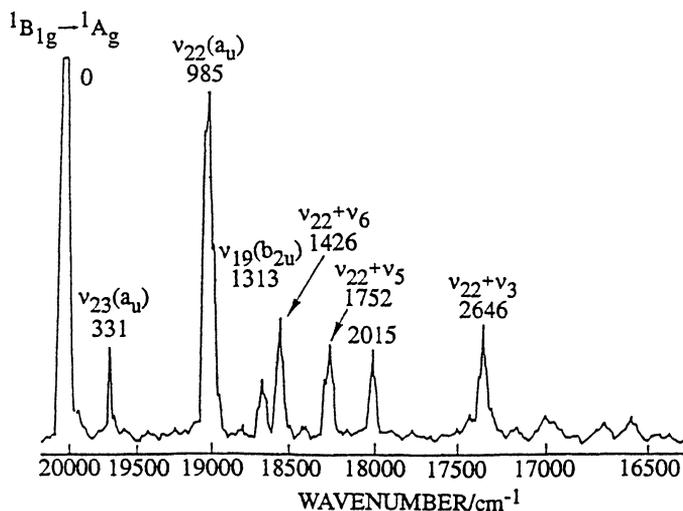


Figure 2 Dispersed fluorescence spectrum of ${}^1B_{1g}(0,0)$ of PBQ.

level of the ${}^1B_{1g}(n,\pi^*)$ state. As shown in the figure, almost all the bands can be readily assigned with ground state fundamentals of $\nu_{23}(a_u)$ of 331 cm^{-1} and $\nu_{22}(a_u)$ of 985 cm^{-1} and their combinations with totally symmetric modes $\nu_3(1,661\text{ cm}^{-1})$, $\nu_5(767\text{ cm}^{-1})$ and $\nu_6(441\text{ cm}^{-1})$. The result indicates that the ${}^1B_{1g}(n,\pi^*)$ state couples mainly through the a_u mode with higher excited ${}^1B_{1u}(\pi,\pi^*)$ states, in accord with ter Horst and Kommandeur's assignment. Strong appearance of the bands involving the a_u mode and weak appearance of the origin band as well as its rotational contour of type A in the absorption spectrum^{2,9} definitely support the assignment of the magnetic dipole allowed ${}^1B_{1g} \leftarrow {}^1A_g$ transition for the band at $20,045\text{ cm}^{-1}$. This band is denoted by ${}^1B_{1g}(0,0)$.

Figure 3 shows the dispersed fluorescence spectra obtained by exciting vibronic bands of ${}^1B_{1g}(0,0) + 126, 380$ and 926 cm^{-1} in the fluorescence excitation spectrum. The fluorescence spectrum from the 380 cm^{-1} level (Figure 3b) is readily explained with even quanta of $\nu_{23}(a_u)$ having the ground state fundamental frequency of 331 cm^{-1} and their combinations with totally symmetric modes, as indicated in the figure. The observed spectral features are consistent with the assignment as 23_0^1 belonging to the ${}^1B_{1g} \leftarrow {}^1A_g$ transition for the 380 cm^{-1} band. Similarly, the spectrum obtained by exciting the ${}^1B_{1g}(0,0) + 926\text{ cm}^{-1}$ band gives strong bands involving the overtone of $\nu_{22}(a_u)$ having a ground state fundamental frequency of 985 cm^{-1} as shown in the figure. A similar spectrum also was reported by ter Horst and Kommandeur.¹ Therefore, the assignment of ${}^1B_{1g}22_0^1$ is conclusively established for the 926 cm^{-1} band.

Since the ground state a_u vibrations (ν_{22} and ν_{23}) are inactive in both Raman and infrared, their frequencies had been inferred by indirect ways such as vibrational analysis of the vapor absorption spectrum, IR and Raman spectra of substituted PBQ

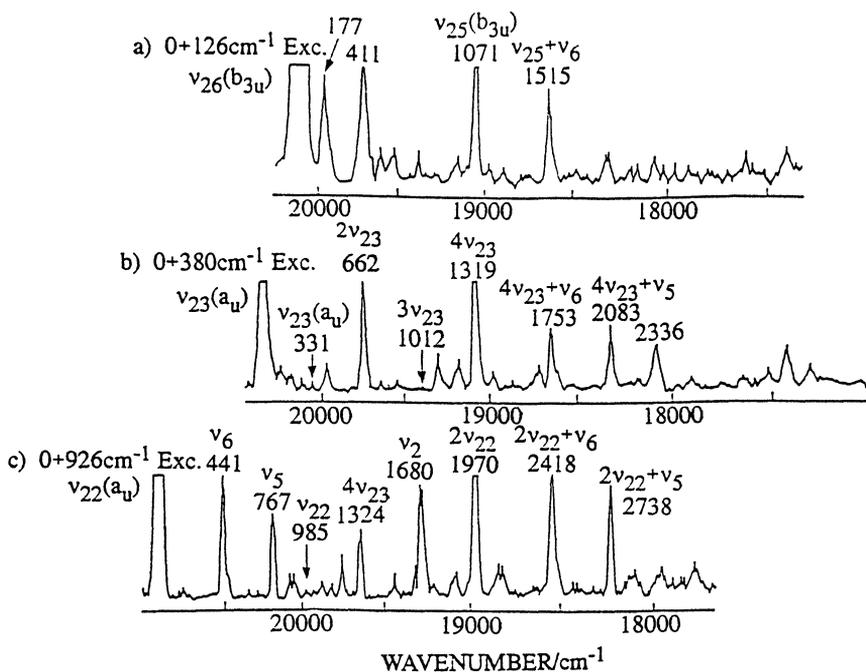


Figure 3 Dispersed fluorescence spectra obtained by exciting vibronic bands of a) ${}^1B_{1g}(0,0) + 126\text{ cm}^{-1}$, b) 380 cm^{-1} and c) 926 cm^{-1} in the fluorescence excitation spectrum.

and normal coordinate calculation. However, the estimated frequencies varied widely from author to author. Our dispersed fluorescence spectra put an end to the controversy and finally determined the frequencies of 985 and 331 cm^{-1} for ν_{22} and ν_{23} , respectively. They can be compared with the calculated frequencies of $958(\nu_{22})$ and $397(\nu_{23})\text{ cm}^{-1}$.¹⁰ ν_{22} and ν_{23} are described approximately as an out-of-plane CH bend and an out-of-plane ring distortion, respectively.

The dispersed fluorescence spectrum obtained by exciting the $B_{1g}(0,0) + 126\text{ cm}^{-1}$ band exhibits features somewhat different from those described above. For the latter the strongest band was the overtone of the ground state a_u vibration corresponding to the excited state vibration involved in a vibronic band excited. In the fluorescence spectrum obtained by exciting the $B_{1g}(0,0) + 126\text{ cm}^{-1}$ band, the strongest band occurs at $1,071\text{ cm}^{-1}$ from the exciting position. The frequency of $1,071\text{ cm}^{-1}$ can be ascribed to an overtone of $\nu_{25}(b_{3u})$, whose fundamental frequency is calculated to be 539 cm^{-1} .¹⁰ Since this ground state frequency is very different from the excited state frequency of 126 cm^{-1} involved in the exciting band, the vibration of 126 cm^{-1} is not the excited state counterpart of $\nu_{25}(b_{3u})$. It is found in the spectrum (Figure 3), however; there exists a lower frequency band at 177 cm^{-1} . This may be assigned to the overtone of the ground state vibration of $\nu_{26}(b_{3u})$, whose fundamental frequency was derived by Hollas from his vapor absorption study to be 87 cm^{-1} .

Admitting this assignment, the 126 cm^{-1} band can be assigned to ${}^1B_{1g}26_0^1$ in agreement with the assignment given by ter Horst and Kommandeur.¹ The rotational contour of the 126 cm^{-1} band in the fluorescence excitation spectrum observed by Ohta *et al.*,¹¹ also supports this assignment. The fact that the bands involving $\nu_{25}(b_{3u})$ appear more strongly than those involving $\nu_{26}(b_{3u})$ in the dispersed fluorescence spectrum indicates the existence of a large Duschinsky rotation of the b_{3u} normal coordinates in going from the ground state to the excited state.

It is concluded from the above that the assignments proposed by ter Horst and Kommandeur for the $B_{1g}(0,0) + 126, 380$ and 926 cm^{-1} bands are firmly confirmed by the dispersed fluorescence spectra. The vibrational frequencies in the ground state and the ${}^1B_{1g}$ state are summarized in Table I. It is interesting that the low frequency out-of-plane modes $\nu_{23}(a_u)$ and $\nu_{26}(b_{3u})$ increase their frequencies in going from the ground state to the excited state in contrast to other modes which generally show frequency decreases.

Table I Vibrational frequencies in the ground and the ${}^1B_{1g}$ excited states of PBQ

cm^{-1}	$S_1({}^1B_{1g})$	$S_0({}^1A_g)$	<i>IR and Raman*</i>
$\nu_{22}(a_u)$	926	985	988
$\nu_{23}(a_u)$	380	331	325
$\nu_{26}(b_{3u})$	126	88	87

* from references 10

We also obtained the dispersed fluorescence spectrum by exciting the band at 267 cm^{-1} above ${}^1B_{1g}(0,0)$ (see Figure 1) which is at 321 cm^{-1} above the forbidden origin of the ${}^1A_u \leftarrow {}^1A_g$ transition. The dispersed fluorescence spectrum obtained by exciting this band shows a broad background on which weak bands involving the ground state frequencies of $173, 479$ and 698 cm^{-1} appear. The frequency of 479 cm^{-1} can be assigned to the overtone of $\nu_{30}(b_{2g})$, whose fundamental frequency is 244 cm^{-1} in the ground-state. The appearance of this overtone band confirms the assignment of this band as ${}^1A_u 30_0^1$ in agreement with ter Horst and Kommandeur. The frequency of 173 cm^{-1} is probably the overtone of $\nu_{26}(b_{3u})$. We also observed the dispersed fluorescence spectra by exciting other vibronic bands which were assigned as bands belonging to the ${}^1A_u \leftarrow {}^1A_g$ transition. However, all the spectra were weak and broad, and no structure could be found. The results suggest an emission property of the 1A_u state quite different from that of the ${}^1B_{1g}$ state, that is, the former gives a broad and structureless emission while the latter shows a structured emission. The broadness in the fluorescence resulting from the 1A_u state may be correlated to a strong interaction between this state and triplet states. In fact, inter-system crossing from vibronic levels belonging to 1A_u was shown to be much more effective than that from levels belonging to ${}^1B_{1g}$, based on the sensitized phosphorescence excitation spectrum that will be described in the next section.

B. Sensitized phosphorescence excitation spectra.

The difference in the emission property mentioned above might be useful in discriminating vibronic bands belonging to ${}^1B_{1g} \leftarrow {}^1A_g$ from those belonging to ${}^1A_u \leftarrow {}^1A_g$. For this purpose, we observed the sensitized phosphorescence excitation spectrum of the jet-cooled molecule and compared it to the corresponding fluorescence excitation spectrum. The sensitized phosphorescence excitation spectrum and the fluorescence excitation spectrum were simultaneously observed for the jet-cooled molecule and they are shown in Figure 4. We see from the figure that the relative intensities of the vibronic bands are different between the two spectra. For example, the bands at $20,171\text{ cm}^{-1}$ (${}^1B_{1g}26_0^1$), $20,312\text{ cm}^{-1}$ (${}^1A_u30_0^1$) and $20,425\text{ cm}^{-1}$ (${}^1B_{1g}23_0^1$) have comparable intensities in the sensitized phosphorescence excitation spectrum, but the band at $20,312\text{ cm}^{-1}$ is much weaker than the other two bands in the fluorescence excitation spectrum. Since the band at $20,312\text{ cm}^{-1}$ belongs to 1A_u and the other two bands to ${}^1B_{1g}$, the result suggests that ratio of the intensity of a vibronic band in the sensitized phosphorescence excitation spectrum to that in the fluorescence excitation spectrum (I_p/I_f) is useful for the discrimination of the electronic states. Actually, I_p/I_f is a measure of the intersystem crossing rate of the vibronic level associated with a vibronic band.¹² It is conceivable that the intersystem crossing rate is quite different between the vibronic levels belonging to 1A_u and ${}^1B_{1g}$. In Table II, we listed I_p/I_f of the individual vibronic bands of PBQ and PBQ- d_4 in which the ratio was taken to be one for the origin band of ${}^1B_{1g} \leftarrow {}^1A_g$. The ratio varies greatly from band to band, but there seems to exist common tendency. First, we shall see the values of I_p/I_f for the vibronic bands of PBQ whose assignments are already

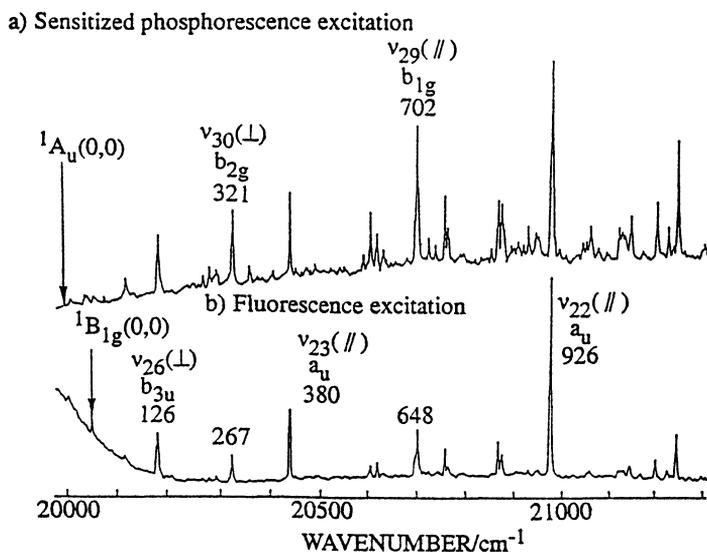


Figure 4 a) Sensitized phosphorescence excitation spectrum of jet-cooled PBQ, and b) fluorescence excitation spectrum simultaneously measured.

Table II I_p/I_t of the individual vibronic bands obtained from the fluorescence/phosphorescence excitation spectra

PBQ				PBQ- d_4					
Frequency (cm^{-1})	ΔE (cm^{-1}) [${}^1B_{1g}(0,0)$]-]	Assignment	I_p/I_t	Origin	Frequency (cm^{-1})	ΔE (cm^{-1}) [${}^1B_{1g}(0,0)$]-]	Assignment	I_p/I_t	Origin
(19991)		${}^1A_u(0,0)$			(19991)		${}^1A_u(0,0)$		
20045	0	${}^1B_{1g}(0,0)$	1.0		20045	0	${}^1B_{1g}(0,0)$	1.0	
20171	126	$\nu_{26}(b_{3u})$	1.5	${}^1B_{1g}$	20168	123	$\nu_{26}(b_{3u})$	0.9	${}^1B_{1g}$
20312	267	$\nu_{30}(b_{2g})$	2.4	1A_u	20298	253	$\nu_{30}(b_{2g})$	4.2	1A_u
20425	380	$\nu_{23}(a_u)$	1.3	${}^1B_{1g}$	20380	335	$\nu_{23}(a_u)$	1.6	${}^1B_{1g}$
20595	550	${}^1A_u + 602$	4.5	1A_u	20390	345	${}^1A_u + 399$	3.1	1A_u
20608	563	$\nu_{26} + \nu_6(a_g)$	2.1	${}^1B_{1g}$	20579	534	$\nu_{27}(b_{1g})$	8.9	1A_u
20688	643	$\nu_{30} \times 2$	1.2	${}^1B_{1g}$	20591	546	${}^1A_u + 600$	11.1	1A_u
20693	648	$\nu_{29}(b_{1g})$	3.1	1A_u	20610	565	$\nu_{25}(b_{3u})$	3.8	${}^1B_{1g}$
20749	704	$\nu_{27}(b_{1g})$	2.8	1A_u	20666	621	$\nu_{30} \times 2$	5.7	${}^1B_{1g}$
20755	710	$\nu_{30} + \nu_6$	2.5	1A_u	20683	638	$\nu_{29}(b_{2g})$	12.5	1A_u
20862	817	$\nu_{23} + \nu_6$	1.9	${}^1B_{1g}$	20739	694	$\nu_{30} + \nu_6(a_g)$	14.6	1A_u
20869	824	$\nu_{24}(b_{3u})$	2.8	${}^1B_{1g}$	20752	707	$\nu_{24}(b_{3u})$	7.8	${}^1B_{1g}$
20971	926	$\nu_{22}(a_u)$	0.9	${}^1B_{1g}$	20788	743	$\nu_{22}(a_u)$	1.6	${}^1B_{1g}$

established. The bands of ${}^1B_{1g}0_0^0$, ${}^1B_{1g}26_0^1$ (126 cm^{-1}), ${}^1B_{1g}23_0^1$ (380 cm^{-1}) and ${}^1B_{1g}22_0^1$ (926 cm^{-1}) have I_p/I_f of 1.0, 1.5, 1.3 and 0.9, respectively. On the other hand, the band of ${}^1A_u30_0^1$ (321 cm^{-1}) shows a large value of 2.4. Referring to the assignments of the individual vibronic bands given by ter Horst and Kommandeur which are shown in the table, there is an apparent tendency; both in PBQ and in PBQ- d_4 the vibronic level in ${}^1B_{1g}$ have small values of I_p/I_f but the levels in 1A_u have rather large values. This implies a general trend that the intersystem crossing rate of 1A_u is larger than that of ${}^1B_{1g}$. This trend might be related to the emission property mentioned before that the emission from the vibronic level in 1A_u gives a broad and structureless spectrum but the emission from the level in ${}^1B_{1g}$ gives a well-resolved spectrum.

C. Phosphorescence excitation spectrum and dispersed phosphorescence spectra.

Now, we shall turn our attention to the triplet n,π^* region. Figure 5 shows the phosphorescence excitation spectrum of PBQ in a supersonic jet. The lowest frequency band at $18,683\text{ cm}^{-1}$ has been assigned as the 0,0 band of the ${}^3A_u \leftarrow {}^1A_g$ transition.² The vibrational structure of the spectrum is rather simple. Sharp bands are located at 443, 807 and $1,128\text{ cm}^{-1}$ above the 0,0 band. At still higher frequencies, the bands belonging to ${}^1B_{1g} \leftarrow {}^1A_g$ and ${}^1A_u \leftarrow {}^1A_g$ described previously appear in the spectrum, together with many weak bands (cf. Figures 1 and 5). These weak bands are probably vibronic bands belonging to ${}^3A_u \leftarrow {}^1A_g$. It is noticed that the intensity of the 0,0 band of ${}^3A_u \leftarrow {}^1A_g$ is stronger than that of the 0,0 band of the magnetic dipole allowed ${}^1B_{1g} \leftarrow {}^1A_g$ transition and is comparable to the intensities of several vibronically induced vibronic bands belonging to ${}^1B_{1g} \leftarrow {}^1A_g$ or ${}^1A_u \leftarrow {}^1A_g$. This comparison suggests an oscillator strength of the ${}^3A_u \leftarrow {}^1A_g$ transition unusually much larger than that of a typical $T \leftarrow S$ transition of an aromatic molecule.

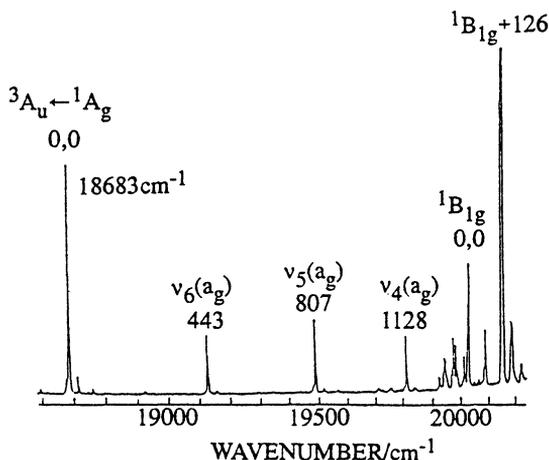


Figure 5 Phosphorescence excitation spectrum of jet-cooled PBQ in a supersonic jet.

In fact, the oscillator strength of the ${}^3A_u \leftarrow {}^1A_g$ transition of PBQ is reported to be 6×10^{-6} or 4×10^{-6} which is much larger than, for example, 8×10^{-8} for the $T_1 \leftarrow S_0$ transition of pyrazine.¹³

Figure 6 shows the dispersed phosphorescence spectrum obtained by exciting the 0,0 band of the ${}^3A_u \leftarrow {}^1A_g$ transition. The spectrum exhibits a good mirror image of the phosphorescence excitation spectrum. From the good mirror image, the bands at 443, 807 and 1,128 cm^{-1} in the excitation spectrum can be readily related to the ground state totally symmetric vibrations of 441(ν_6), 767(ν_5) and 1,148 cm^{-1} (ν_4) appearing in the dispersed phosphorescence spectrum. In the dispersed phosphorescence spectrum, the ground state totally symmetric mode ν_2 of 1,680 cm^{-1} appears strongly. However, its excited state counterpart cannot be found in the excitation spectrum. Instead, several weak bands are found at around the origin of ${}^1B_{1g} \leftarrow {}^1A_g$ in the excess vibrational energy region of 1,200–1,400 cm^{-1} above the origin of ${}^3A_u \leftarrow {}^1A_g$. These weak bands probably correspond to the strong band at 1,680 cm^{-1} in the dispersed phosphorescence spectrum, implying that the ground state normal coordinate of $\nu_2(a_g)$ is distributed by Duschinsky rotation over several normal coordinates in the excited state. Such a large Duschinsky effect is very probable because the C = O stretching frequency of 1,680 cm^{-1} will greatly decrease to 1,100–1,300 cm^{-1} in going from the ground state to the n,π^* state and the contribution of the C = O stretch to the normal mode will be quite different between the ground state and excited state.

In Figure 7 are shown phosphorescence spectra obtained by exciting the vibronic bands of ${}^3A_u(0,0) + 443(\nu_6)$, 807(ν_5) and 1,128(ν_4) cm^{-1} in the excitation spectrum. Each spectrum shows a very simple pattern. When exciting a vibronic band involving a particular totally symmetric vibration in the excited state, bands involving the cor-

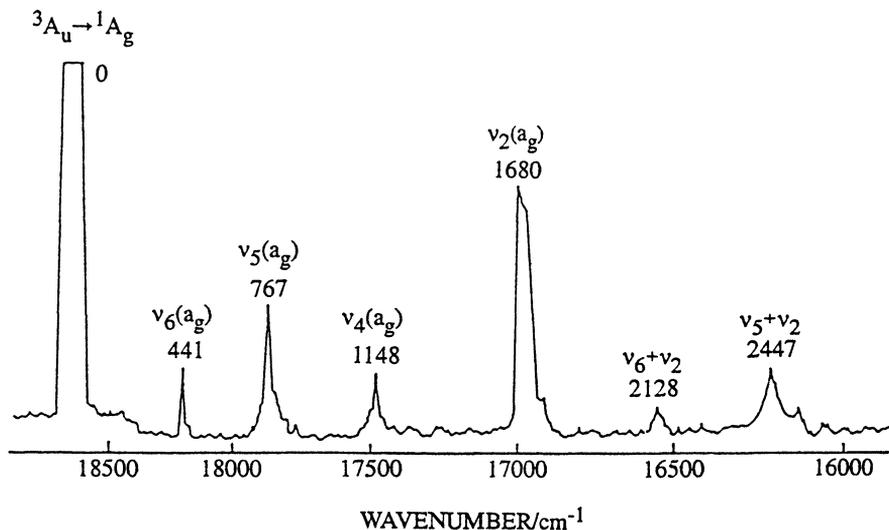


Figure 6 Dispersed phosphorescence spectrum obtained by ${}^3A_u(0,0)$ excitation.

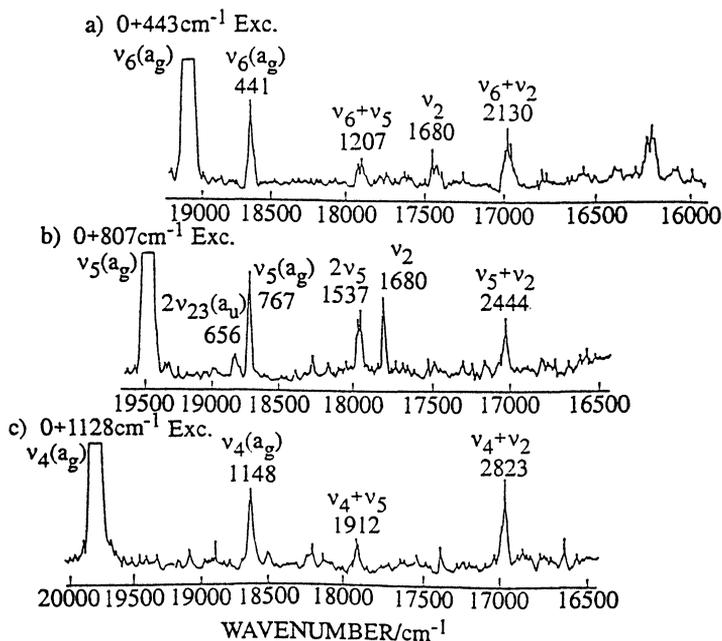


Figure 7 Dispersed phosphorescence spectra obtained by a) ${}^3A_u(0,0) + 442(\nu_6)$, b) $807(\nu_5)$ and c) $1,128(\nu_4) \text{ cm}^{-1}$ excitation.

responding ground state vibration appear strongly in the phosphorescence spectrum, supporting the assignments made for the vibronic bands in the excitation spectrum. A more interesting fact is that the observed phosphorescence spectrum exhibits a feature of resonance emission from the single vibronic level excited and the emission from other levels distributed by vibrational relaxation cannot be found even with an excess vibrational energy of as large as $1,128 \text{ cm}^{-1}$. The single vibronic level phosphorescence spectra of PBQ are probably the first observed for such a large organic molecule.

Finally, we have to mention another triplet n,π^* state, ${}^3B_{1g}$. We could not find any evidence for the ${}^3B_{1g}$ state in the spectral region studied. The failure of the detection is not due to the location of ${}^3B_{1g}$ far from 3A_u , since the energy separation between B_{1g} and A_u in the triplet state as well as in the singlet state is considered to be very small. The failure of the detection is probably ascribed to extremely weak intensity of the ${}^3B_{1g} \leftarrow {}^1A_g$ transition compared with the intensity of the ${}^3A_u \leftarrow {}^1A_g$ transition. The latter is allowed by direct spin-orbit coupling, but the former can occur only by vibronic spin-orbit coupling. Therefore, the ${}^3B_{1g} \leftarrow {}^1A_g$ transition should be very weak and its detection seems to be beyond our detection limit.

Acknowledgment

The research was partially supported by the Nihon University Research Grants.

References

1. G. ter Horst and J. Kommandeur. (a) *Chem. Phys.*, **44**, 287 (1979) (b) *J. Chem. Phys.*, **76**, 137 (1982).
2. J. M. Hollas. *Spectrochim Acta*, **20**, 1543 (1964).
3. M. Koyanagi, Y. Kogo and Y. Kanda. *Mol. Phys.*, **20**, 74 (1971).
4. L. E. Brus and J. R. McDonald. *J. Chem. Phys.*, **58**, 4223 (1973).
5. T. Itoh. *Mol. Phys.*, **55**, 799 (1985).
6. J. Goodman and L. E. Brus. *J. Chem. Phys.*, **69**, 1604 (1978).
7. H. Abe, S. Kamei, N. Mikami and M. Ito. *Chem. Phys. Lett.*, **109**, 217 (1984).
8. I. Suzuka, T. Tomioka and Y. Ito. *Chem. Phys. Lett.*, **172**, 409 (1990).
9. J. Christoffersen and J. M. Hollas. *Mol. Phys.*, **17**, 655 (1969).
10. T. Anno. *J. Chem. Phys.*, **42**, 932 (1965).
11. N. Ohta, I. Yamazaki, M. Sanekata, I. Suzuka and O. Sekiguchi. *J. Phys. Chem.*, to be submitted.
12. T. Suzuki, M. Sato, N. Mikami and M. Ito. *Chem. Phys. Lett.*, **127**, 292 (1986).
13. G. Fisher. *Chem. Phys. Lett.*, **79**, 573 (1981).