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Laser-Induced Fluorescence Spectroscopy of Jet-Cooled Benzophenone Ketyl Radical

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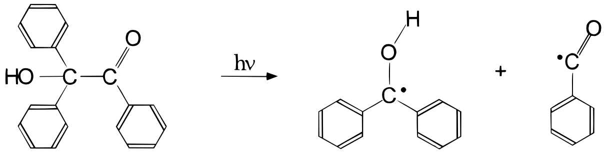
The $D_1 \leftarrow D_0$ transition of jet-cooled benzophenone ketyl radical (BPK) and its deuteride was studied by using laser-induced fluorescence (LIF) spectroscopy. BPK was generated by the 248 nm photolysis of α-phenylbenzoin, and its vibrationally resolved LIF excitation and emission spectra were obtained for the first time. The 18 451 cm^{-1} band was assigned to the 0^0_0 band of the $D_1 \leftarrow D_0$ transition of BPK. Two vibrational modes of BPK with 65 and 84 cm^{-1} in the first excited state were assigned to the in-phase and out-of-phase torsional motions of the phenyl rings, respectively. The vibrational mode with 980 cm^{-1} was tentatively assigned to the C−O stretching mode. The mode of 74 cm^{-1} in the ground state was assigned to the in-phase torsional mode. It was confirmed that the torsional motions do not couple with the C−O stretching and O−H rotational motions. The force field analysis and the simple Franck−Condon calculation were made. The measured fluorescence lifetimes of BPK and its deuteride are short and consistent with those in the gas and liquid phases at room temperature.

Introduction

Benzophenone ketyl radical (BPK) is known to be an important intermediate in the photoreduction of benzophenone. After photoexcitation, benzophenone rapidly undergoes intersystem crossing with a unity quantum yield, and the lowest triplet state abstracts a hydrogen atom from hydrogen donor molecules, such as alkanes, alkenes, alcohols, and amines yielding BPK. Many studies on BPK have been carried out in absorption and emission to elucidate the excited state dynamics and the electronic structure in the condensed phase.[1−17] The temperature dependence and the deuterium isotope effect on the fluorescence lifetime are interpreted by chemical reactions;[13−15] the excitation of BPK induces the cleavage of the O−H bond to yield benzophenone and hydrogen atom.[15] A few MO calculations were done about the $D_1 \leftarrow D_0$ transition, and the transition moment was suggested to be parallel to the molecular long axis.[16,17] Recently, the complex formation between BPK and amines was reported.[18]

Until recently, there have been no spectroscopic data of BPK in the gas phase. Matsushita et al.[19] studied the hydrogen abstraction reaction in the gas phase for the first time and reported the fluorescence excitation and dispersed emission spectra of BPK. The spectra observed were broad and are in good agreement with those of BPK in the condensed phase. In a subsequent work, they also measured the spectra of BPK in the supersonic free jet,[20] where BPK was generated by the intracluster reaction between benzophenone and 1,4-cyclohexadiene. Though the spectra obtained in a supersonic free jet expansion are generally vibrationally resolved due to molecular cooling, the reported spectra are broad. They tried to resolve the vibrational structure by varying experimental conditions, such as the pressure of hydrogen donor molecules and the distance between the nozzle orifice and laser beams. However, the spectral profile did not change significantly. They interpreted the broad spectra due to the congestion of low-frequency van der Waals modes of BPK−1,4-cyclohexadiene clusters which survived after photoreaction. To investigate the vibrational structure of free BPK, it is necessary to produce the cold BPK by another method.

SCHEME 1



The photolysis of α-phenylbenzoin gives BPK and benzoyl radical by α-cleavage in solution.[21,22] (See Scheme 1.) Baumann et al.[21] demonstrated that N_2 laser photolysis of α-phenylbenzoin resulted in homolytic cleavage of the ketone, and the fluorescence spectrum of BPK was identical to that observed in the photoreduction of benzophenone. The fluorescence lifetime was 3.7 ns, and the reaction rate constants with some quenchers were reported.

In this work, α-phenylbenzoin is used as a parent molecule to produce the jet-cooled BPK by the photolysis. Vibrationally resolved structures are obtained for the first time in the laser-induced fluorescence (LIF) excitation and dispersed emission spectra. The fluorescence lifetime of BPK and its deuteride is also measured. Vibrational modes of BPK are assigned in the ground and first excited states. The potential function and the geometrical change between the ground and the excited states are discussed.

Experimental Section

The conventional LIF technique in a supersonic free jet was used, whose details were described elsewhere.[23] α-Phenylbenzoin and its deuteride were heated to 420 K and were seeded in Ne or Ar carrier gas. The sample was expanded through a pulsed solenoid nozzle (General Valve Corp. P/N 9-279-900, with a 400 μm diameter orifice) into a vacuum chamber. The 248 nm output of a KrF excimer laser (Lambda Physik EMG 103E) was focused with a 500 mm focal length lens and used to photolyze the sample just after the nozzle. A XeCl excimer laser (Lambda Physik EMG 52 MSC) pumped dye laser (Lambda Physik FL 2002) irradiated the molecular beam to probe the photolysis products by LIF. The output of the probe laser was attenuated through a neutral density filter and focused with a 1000 mm focal length lens. Spectral resolution was

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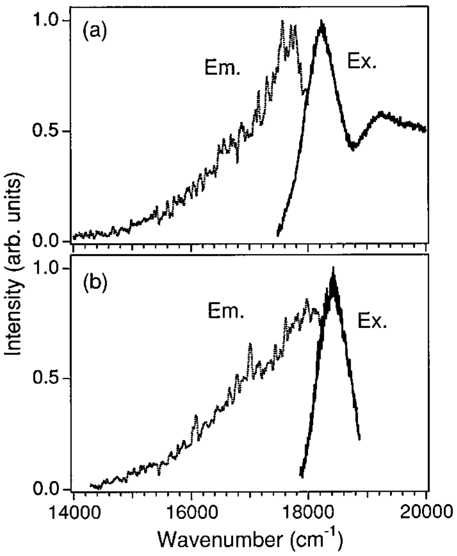

Figure 1. LIF excitation (Ex.) and dispersed emission (Em.) spectra of the D_1-D_0 transition of BPK. (a) Spectra of BPK obtained by the intracluster hydrogen abstraction reaction of benzophenone and 1,4-cyclohexadiene (ref 20). The dispersed emission spectrum was obtained by 18 518 cm^{-1} excitation. (b) Spectra of BPK obtained by the photodissociation of α-phenylbenzoin at *X*/*D* = 5 in the Ar jet. The dispersed emission spectrum was obtained by 18 692 cm^{-1} excitation.

restricted by the dye laser and about 0.3−0.5 cm^{-1} full width at half-maximum (fwhm).

The fluorescence signals were collected with a lens system and focused onto a photomultiplier tube (Hamamatsu R-928) through appropriate cutoff filters (Toshiba color filter). A monochromator (Nikon P-250, 1200 grooves/mm) was used to measure the dispersed fluorescence spectrum, of which the spectral resolution was about 1 nm (fwhm). The output signals terminated with a 500 ohm resistance were integrated with a gated integrator (Stanford SR-250), digitized by an A/D converter (Stanford SR-245), and transferred to a personal computer. To obtain the time profile of the fluorescence decay, the photomultiplier signals were accumulated by a digital storage oscilloscope (Tektronix TDS640). The signal intensities were calibrated to the dye laser power.

α-Phenylbenzoin was synthesized by the following Grinard reaction.[24] Phenylmagnesium bromide which was prepared by mixing bromobenzene, magnesium, and iodine was added to benzil dissolved in anhydrous tetrahydrofuran (THF) solution at 245 K. The product was separated through a column and purified recrystallization in appropriate solvents. The production of α-phenylbenzoin was confirmed by the NMR and IR spectra. α-Phenylbenzoin-*d* was prepared by the deuteration of the hydroxyl group of α-phenylbenzoin with deuterium oxide in THF solution. Regents used in the synthesis were purchased from Aldrich and Kanto Chemicals.

Results and Discussion

The excitation and emission spectra of BPK were reported under several experimental conditions. In the condensed phase, it has an absorption band in the visible region with a maximum at around 18 400 cm^{-1} and shows emission in the 15 400−18 200 cm^{-1} region. Recently, Matsushita et al.[20] have reported the LIF spectra of BPK, which was produced by the intracluster reaction of triplet benzophenone with 1,4-cyclohexadiene in the supersonic free jet. They reported that the first excitation band, which was broad even in the jet, lies around 18 350 cm^{-1}, and the emission was observed in the 15 000−17 800 cm^{-1} region as shown in Figure 1a.

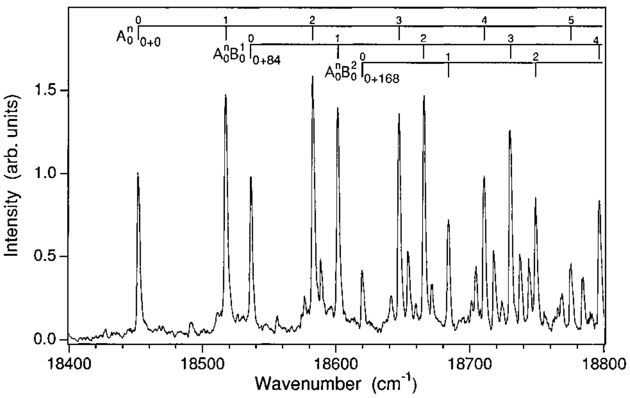

Figure 2. LIF excitation spectrum of jet-cooled BPK in the 0_0^0 band region. The carrier gas was Ne and *X*/*D* = 20. A and B denote the in-phase and out-of-phase torsional modes of two phenyl rings, respectively.

To confirm the formation of BPK by the photolysis of α-phenylbenzoin in the supersonic free jet, we performed preliminary spectroscopic measurements. α-Phenylbenzoin seeded in 1.0 atm of Ar was expanded. The photolysis and probe lasers irradiated the beam at *X*/*D* = 5, where *X* is a distance between the orifice and the observation point and *D* is the diameter of the orifice. Cooling is not complete with this small *X*/*D* value. The LIF spectra obtained are shown in Figure 1b. No fluorescence signals were detected if either the photolysis or the probe laser was not irradiated. The excitation spectrum is basically broad, with a maximum around 18 400 cm^{-1}. The dispersed emission spectrum was obtained with the 18 692 cm^{-1} excitation. The spectrum in the 15 000−18 200 cm^{-1} region shows a maximum around 17 800 cm^{-1}. The profiles and absolute wavenumber positions of the spectra in Figure 1b are very similar to those in Figure 1a. It indicates that the fluorescent chemical species generated by the photolysis of α-phenylbenzoin is BPK. The vibrationally unresolved excitation spectrum, though it was obtained in the jet, results from insufficient cooling of the product BPK due to the small *X*/*D* value. The photolysis of α-phenylbenzoin yields benzoyl radical in the same amount with BPK. (See Scheme 1.) Benzoyl radical has an absorption band extending from 14 000 to 33 000 cm^{-1} with a maximum at about 27 000 cm^{-1} and a small shoulder around 21 700 cm^{-1}.[25] However, it is an optically forbidden $\sigma-\pi^*$ transition, whose extinction coefficient[25] ($\epsilon \leq 380$ M^{-1} cm^{-1} at 27 000 cm^{-1} and 287 K) is very small compared to that of the $\pi-\pi^*$ transition of BPK[21] ($\epsilon = 5.5 \times 10^3$ M^{-1} cm^{-1} at 18 350 cm^{-1}). Therefore, the benzoyl radical does not contribute to the excitation and emission spectra.

The jet-cooled spectrum of BPK was obtained by measuring LIF at *X*/*D* = 20−25. In this case, α-phenylbenzoin was seeded in 1.0 atm of Ne. The LIF excitation spectrum obtained is shown in Figure 2. Vibrationally well resolved bands appear in the energy range from 18 451 to 18 800 cm^{-1}, and no other signal was observed in the lower energy region than the 18 451 cm^{-1} band. The spectrum mainly consists of progressions with a vibrational interval of about 65 cm^{-1}. The first and primary progression starts from the lowest wavenumber band at 18 451 cm^{-1}, which is denoted as the 0 + 0 band. The progression was observed up to five quanta with a maximum at two quanta with slight anharmonicity. Other similar progressions with the 65 cm^{-1} interval also start from 18 535 and 18 619 cm^{-1} bands, which are the 0 + 84 and 0 + 168 cm^{-1} bands, respectively. Three sets of vibrational progressions with the 65 cm^{-1} interval are separated by 84 cm^{-1}, indicating another vibration with the fundamental frequency of 84 cm^{-1}. The progression with the

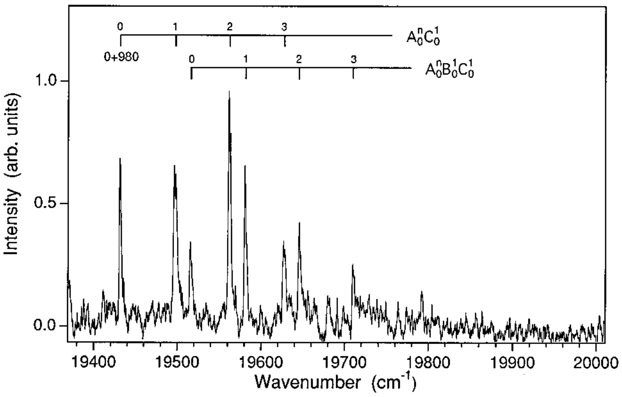

Figure 3. LIF excitation spectrum of jet-cooled BPK in the C−O stretching region. A, B, and C denote the in-phase and out-of-phase torsional modes of two phenyl rings and C−O stretching mode, respectively.

TABLE 1: Observed Vibrational Bands and Their Assignments in the LIF Excitation Spectrum of BPK in 18 400−18 800 and 19 400−20 000 cm^{-1} Regions

wavenumber/cm^{-1}	spacing/cm^{-1}	rel int^a	assignt^b
18 451	0.0	1.0	0^0_0
18 511	59.8	0.16	
18 516	65.3	1.5	A^1_0
18 535	84.2	0.97	B^1_0
18 576	124.4	0.27	$60 + A^1_0$
18 581	130.2	1.6	A^2_0
18 588	136.8	0.50	
18 596	144.4	0.20	$60 + B^1_0$
18 600	149.2	1.4	$A^1_0B^1_0$
18 619	167.7	0.42	B^2_0
18 641	189.4	0.26	$60 + A^2_0$
18 646	195.0	1.3	A^3_0
18 653	202.1	0.51	$137 + A^1_0$
18 659	208.0	0.21	$60 + A^1_0B^1_0$
18 665	213.7	1.5	$A^2_0B^1_0$
18 671	220.0	0.33	$137 + B^1_0$
18 684	232.5	0.72	$A^1_0B^2_0$
18 705	253.7	0.45	$60 + A^3_0$
18 711	259.4	0.98	A^4_0
18 718	266.8	0.53	$137 + A^2_0$
18 724	273.3	0.24	$60 + A^2_0B^1_0$
18 729	278.4	1.3	$A^3_0B^1_0$
18 737	286.0	0.50	$137 + A^1_0B^1_0$
18 744	293.3	0.50	$60 + A^1_0B^2_0$
18 748	297.2	0.86	$A^2_0B^2_0$
18 754	304.0	0.18	$137 + B^2_0$
18 769	318.0	0.26	$60 + A^4_0$
18 775	323.7	0.44	A^5_0
18 783	331.8	0.37	$137 + A^3_0$
18 789	337.8	0.16	$60 + A^3_0B^1_0$
18 794	342.6	0.83	$A^4_0B^1_0$
18 801	350.5	0.48	$137 + A^2_0B^1_0$
18 809	358.2	0.76	$60 + A^2_0B^2_0$
18 813	361.6	0.76	$A^3_0B^2_0$
18 819	368.6	0.24	$137 + A^1_0B^2_0$
19 431	979.8		C^1_0
19 496	1045.1		$A^1_0C^1_0$
19 516	1064.6		$B^1_0C^1_0$
19 562	1110.4		$A^2_0C^1_0$
19 581	1129.4		$A^1_0B^1_0C^1_0$
19 627	1175.9		$A^3_0C^1_0$
19 646	1194.6		$A^2_0B^1_0C^1_0$
19 691	1240.2		$A^4_0C^1_0$
19 710	1258.7		$A^3_0B^1_0C^1_0$

[a] Relative intensities are indicated for the intensity at the 18 451 cm^{-1} band (0^0_0 band). Relative intensities between 19 400 and 20 000 cm^{-1} were not measured correctly due to insufficient intensities. [b] A = In-phase torsion of two phenyl rings; B = out-of-phase torsion of two phenyl rings; C = C−O stretching.

84 cm^{-1} vibrational interval also indicates slight anharmonicity and loses intensity monotonously. Two vibrational modes of 65 and 84 cm^{-1} are found in the low-energy region of the first excited state of BPK. On the basis of the fact that no signal was observed in the lower energy region than the 18 451 cm^{-1} band and referring to the absorption and emission spectra in the condensed phase, we assign the 18 451 cm^{-1} band to the 0^0_0 band of the $D_1 \leftarrow D_0$ transition. Other weak progressions obviously start from the 0 + 60 and 0 + 137 cm^{-1} bands, which indicates that vibrations with 60 and 137 cm^{-1} exist.

The vibrational analysis of the excited state was also carried out in the bands lying at higher energies. The absorption spectrum of BPK in the condensed phase has a shoulder around 19 200−20 000 cm^{-1}. We measured the LIF excitation spectrum in this region, and the results are shown in Figure 3. The vibrationally well-resolved spectrum was obtained though the intensity was weaker than that of the 0^0_0 band. The spectrum shows two vibrational modes of the low frequencies, 65 and 84 cm^{-1} similar to that in the 0^0_0 band region. The two kinds of vibrational progressions start from the 19 431 cm^{-1} band, which is the 0 + 980 cm^{-1} band. The band positions, the spacings from the 0^0_0 band, and the relative intensities to the 0^0_0 band are summarized in Table 1 together with the band assignments which will be discussed later.

Figure 4 shows the dispersed fluorescence spectrum of BPK obtained by the 0^0_0 band excitation. The emission spectrum is simple and only shows the progression with a vibrational interval of about 74 cm^{-1} due to the limitation of the spectral slit width.

As described above, we found three major vibrational modes, 65, 84, and 980 cm^{-1}, in the first excited state and one vibrational mode of 74 cm^{-1} in the ground state. When we assign them, the vibrational motion of benzophenone is a good model. Murai and co-workers suggested that bonds of the center carbon atom of BPK were almost sp^2 hybridized because of the small contribution of an unpaired electron to the s orbital, that is, not tetrahedral, but coplanar conformation.[5] Therefore, BPK is considered to have a molecular conformation similar to that of benzophenone.

Ito and co-workers analyzed the n−π* transition of the jet-cooled benzophenone by sensitized phosphorescence excitation spectroscopy.[26] They observed a long progression with the 63 cm^{-1} interval and a short progression with the 101 cm^{-1} interval. The vibrations with 63 and 101 cm^{-1} were assigned to symmetric and asymmetric torsions in the S$_1$ state, respectively, of the phenyl rings about the C−C bonds connecting the carbonyl group and the phenyl rings. They assigned the vibrational bands of 1211−1250 cm^{-1} to the C═O stretching mode perturbed with other symmetric vibrations. On the other hand, Holtzclaw and Pratt suggested that the asymmetric torsion of the phenyl rings had the vibrational frequency of 70 cm^{-1} as a result of nonlinear (Fermi) resonance.[27] The excitation spectrum of BPK only shows the progressions of the low vibrational frequencies less than 100 cm^{-1} similar to that of benzophenone. The symmetric and asymmetric torsions in benzophenone become the in-phase and out-of-phase torsions in BPK due to the loss of C_2 symmetry. The O−H rotation is added to these modes as low-frequency vibrations.

To assign these vibrational modes, α-phenylbenzoin-*d* was used. Figure 5 shows the LIF excitation spectrum obtained by the photolysis of mixed compounds, α-phenylbenzoin-*d* and α-phenylbenzoin-*h*, under the same conditions described before.

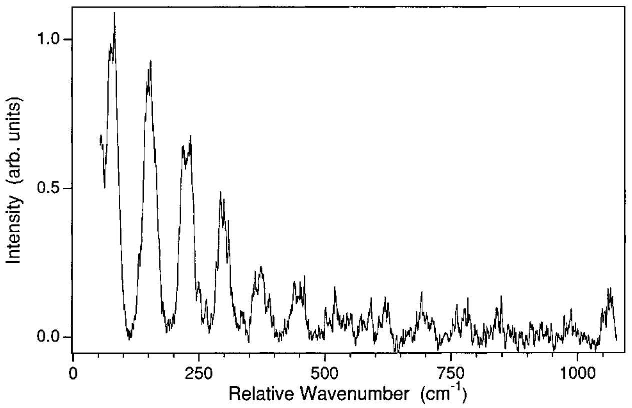

Figure 4. LIF dispersed emission spectrum of jet-cooled BPK obtained by the excitation at 18 451 cm^{-1} (the 0_0^0 band). The carrier gas was Ne and $X/D = 20$.

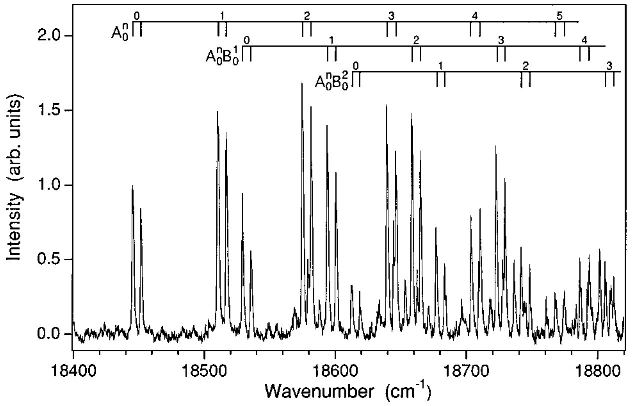

Figure 5. LIF excitation spectrum of a mixture of jet-cooled BPK-*h* and BPK-*d*. The bands originating from the 18 445 cm^{-1} band (lowest wavenumber band) belong to BPK-*d*, and the bands originating from the 18 451 cm^{-1} band (next lower band) belong to BPK-*h*. A and B denote the in-phase and out-of-phase torsional modes of two phenyl rings, respectively.

The mixture was used to make the comparison of the spectra of BPK-*d* and BPK-*h* easy. The spectral features are similar to those observed by the photolysis of α-phenylbenzoin-*h* shown in Figure 2. Progressions with the 65 and 84 cm^{-1} intervals obviously appear. Sets of progressions with the 65 and 84 cm^{-1} intervals do not start from a common band but from two different bands located at 18 445 and 18 451 cm^{-1}, and each band splits into a doublet with a 6.4 cm^{-1} spacing. It indicates that the spectrum consists of two sets of the same vibrational structure shifted by 6.4 cm^{-1}. The relative intensity of the doublet is almost same for all pairs, that is, 1.24, which agrees with the ratio of α-phenylbenzoin-*d* to α-phenylbenzoin-*h*, 1.25, determined from the NMR spectrum. The vibrational structure starting from 18 445 cm^{-1} is, therefore, assigned to BPK-*d*. The band positions and assignments of the BPK-*d* spectrum are listed in Table 2.

TABLE 2: Torsional Vibrational Bands and Their Assignments in the LIF Excitation Spectrum of BPK-*d* in the 18 400−18 800 cm^{-1} Region

wavenumber/cm^{-1}	spacing/cm^{-1}	rel int[a]	assignt[b]
18 445	0.0	1.0	0_0^0
18 510	65.0	1.7	A_0^1
18 529	84.0	1.1	B_0^1
18 574	129.7	1.9	A_0^2
18 594	148.9	1.6	$A_0^1B_0^1$
18 613	167.8	0.40	B_0^2
18 639	194.3	1.7	A_0^3
18 658	213.5	1.7	$A_0^2B_0^1$
18 677	232.2	0.87	$A_0^1B_0^2$
18 703	258.7	0.94	A_0^4
18 722	277.6	1.4	$A_0^3B_0^1$
18 741	296.6	0.68	$A_0^2B_0^2$
18 768	322.9	0.36	A_0^5
18 787	341.8	0.67	$A_0^4B_0^1$
18 806	360.9	0.57	$A_0^3B_0^2$

[a] Relative intensities are indicated for the intensity at the 18 445 cm^{-1} band (0_0^0 band). [b] A = In-phase torsion of two phenyl rings; B = out-of-phase torsion of two phenyl rings.

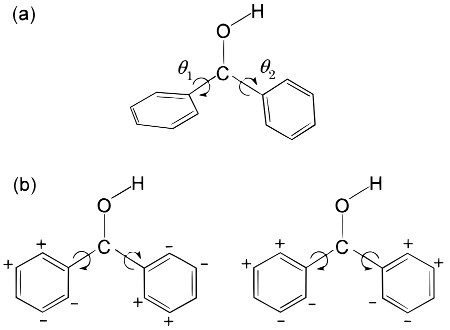

Figure 6. (a) Schematic representation of BPK whose phenyl rings are rotated by θ_1 and θ_2, respectively, along the C−C bonds between centered carbon atom and phenyl rings. The torsional motions correspond to the rotations of $\Delta\theta_1$ and $\Delta\theta_2$. (b) The in-phase and out-of-phase torsional motions. The in-phase torsional motion (left) is conrotatory twisting motion, and the out-of-phase torsional motion (right) is anticonrotatory twisting. The signs of "+" and "−" indicate the direction of the phenyl ring motions.

The vibrational frequencies of 65 and 84 cm^{-1} are not altered by the deuteration of the hydroxyl group. This indicates that there is no contribution of the O−H rotation to these low-frequency modes. Other candidates for low-frequency vibrations are the in-phase and out-of-phase torsional motions, which are schematically represented in Figure 6. The in-phase torsional motion is a conrotatory twisting motion of the two phenyl rings along the C−C bonds between center carbon atom and phenyl rings, while the out-of-phase is anticonrotatory twisting. As the torsional motions in BPK change the angle of two phenyl rings along the C−C bonds, the out-of-phase torsional mode would have a deeper potential well than the in-phase torsional mode because of steric hindrance. The vibration energy of the out-of-phase torsional mode is, therefore, thought to be higher than that of in-phase. Moreover, it is inferred from the similarity between BPK and benzophenone that the $D_1 \leftarrow D_0$ transition of BPK brings the structural change along the coordinate of the in-phase torsional motion between the ground and the excited states, that is, the conrotatory change of the angle of phenyl rings. Based on the above arguments, the vibration of 65 cm^{-1} with the long progressions is assigned to the in-phase torsional motion and that of 84 cm^{-1} to the out-of-phase torsional motion at the present stage.

The vibration of 980 cm^{-1} is tentatively assigned to the C−O stretching after the vibrational energy, about 1200 cm^{-1}, of the C=O stretching mode of benzophenone. Vibrational assignments of BPK-*h* and BPK-*d* in the excited state are listed in Tables 1 and 2, respectively.

The dispersed fluorescence spectrum also shows the long progression (Figure 4). Although two torsional modes were not clearly distinguishable due to the limitation of the spectral resolution, the vibration of about 74 cm^{-1} observed in the emission spectrum is assigned to the in-phase torsional motion in the ground state based on the Franck−Condon patterns of the torsional motions mentioned above.

The vibrational frequencies are analyzed by using the term

TABLE 3: Vibrational Constants of BPK in the D_1 State

constant	value/cm^{-1}	constant	value/cm^{-1}
T_0	18451.0 ± 0.1	χ_{22}	-0.19 ± 0.09
ω_1	65.4 ± 0.1	χ_{12}	-0.24 ± 0.04
ω_2	84.3 ± 0.2	χ_{23}	0.25 ± 0.14
ω_3	979.9 ± 0.1	χ_{13}	0.19 ± 0.05
χ_{11}	-0.12 ± 0.02		

energy

$$E_{\nu_1,\nu_2,\nu_3} = \sum_{i=1}^{3}\omega_i\nu_i + \sum_{i\geq j}^{3}\chi_{ij}\nu_i\nu_j \qquad (1)$$

where ν_1, ν_2, and ν_3 are the vibrational quantum numbers of the in-phase and out-of-phase torsional and C−O stretching modes, respectively, and the results of a least-squares fit analysis are listed in Table 3. The observed and calculated energies agree very well within the laser bandwidth, about 0.4 cm^{-1}. The anharmonicity constant due to the coupling of two phenyl rings, χ_{12}, is -0.24 cm^{-1}, which is smaller than that for benzophenone,[26] -1.50 cm^{-1}.

A force field analysis was done for the torsional motions of phenyl rings in the first excited state of BPK. The vibrational quanta of torsional motions show little change in the $\nu_3 = 0$ vibrational levels of BPK-*h* and BPK-*d* and the $\nu_3 = 1$ level of BPK-*h*. This suggests that the torsional motions do not couple with other molecular motions, such as the C−O stretching and O−H rotational motions. Figure 6 shows a simple sketch of these vibrational motions of phenyl rings in which the phenyl rings are rotated by the angles θ_1 and θ_2 about the plane composed of the center carbon atom and two carbon atoms of the phenyl rings bonded with the center carbon atom. The kinetic energy T for torsional motions of two phenyl rings is expressed by

$$T = \frac{I}{2}(\Delta\dot{\theta}_1)^2 + \frac{I}{2}(\Delta\dot{\theta}_2)^2 \qquad (2)$$

where I is the moment of inertia of the phenyl ring about the axis connecting the center carbon atom and the adjacent carbon atom of phenyl ring. The in-phase, Q_{in}, and the out-of-phase, Q_{out}, torsional coordinates are rewritten by

$$\begin{pmatrix} Q_{\mathrm{in}} \\ Q_{\mathrm{out}} \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \Delta\theta_1 \\ \Delta\theta_2 \end{pmatrix} \qquad (3)$$

Equation 2 is replaced with eq 3.

$$T = \frac{I}{2}\dot{Q}_{\mathrm{in}}{}^2 + \frac{I}{2}\dot{Q}_{\mathrm{out}}{}^2 \qquad (4)$$

On the other hand, the potential energy V is written as

$$V = \frac{k_1}{2}\Delta\theta_1{}^2 + \frac{k_2}{2}\Delta\theta_2{}^2 + k'\Delta\theta_1\Delta\theta_2 \qquad (5)$$

where k_1 and k_2 are the torsional force constants and k' is the interaction force constant. Since the coupling of the O−H rotation with the torsional motions is weak as discussed above, two torsional motions are assumed to be equivalent and $k_1 = k_2 = k$. Then, eq 5 is written as

$$V = \frac{1}{2}(k + k')Q_{\mathrm{in}}{}^2 + \frac{1}{2}(k - k')Q_{\mathrm{out}}{}^2 \qquad (6)$$

using eq 3. Based on the obtained vibrational energies of torsional motion, 65 and 84 cm^{-1}, and assuming that the moment of inertia I is the same as that of benzene, the force constants are derived as follows

$$k = 2.98 \times 10^{-12} \ \ \text{dyn cm rad}^{-1}$$

$$k' = -7.40 \times 10^{-13} \ \ \text{dyn cm rad}^{-1} \qquad (7)$$

The force constants of the excited singlet benzophenone were reported[26] as $k = 3.61 \times 10^{-12}$ and $k' = -1.58 \times 10^{-12}$ dyn cm rad^{-1}. The k and k' values of BPK are 20 and 50% smaller than those of benzophenone, respectively. A fairly large decrease of the k' value is consistent with the small anharmonicity constant χ_{12} of BPK, which reflects that the coupling of vibrational motions of phenyl rings is fairly weak compared with benzophenone. The torsional force constant of benzophenone is known to increase by the electronic excitation ($k = 1.70 \times 10^{-12}$ dyn cm rad^{-1} for the ground state). Ito and coworkers[26] suggested that the C−Ph bonds gained more double-bond character in the first excited state than that in the ground state. Since the torsional force constant of BPK is close to that of benzophenone in the excited state, it is considered that the C−Ph bonds of BPK and benzophenone have similar double-bond character in the excited state.

The angle change caused by the excitation is estimated from the observed excitation and emission spectra by means of simple one-dimensional Franck−Condon calculations for the in-phase torsional mode. Assuming that the angle changes, $\Delta\theta_1$ and $\Delta\theta_2$, are the same, the observed excitation spectrum of BPK is reproduced with $\Delta\theta \cong 8°$. This calculation only gives the magnitude of angle changes but cannot suggest whether the angle between the two phenyl rings opens or closes with the excitation. The angle of twist in benzophenone radical anion[28] was calculated to be 22°−23°. Considering that BPK and benzophenone radical anion are isoelectronic and that BPK has a molecular conformation similar to benzophenone radical anion, the equilibrium angles of BPK are thought to be similar to that of benzophenone radical anion. The change of the equilibrium angle of BPK (8°) is, therefore, not large compared to the angle of twist.

The fluorescence lifetime of BPK was measured by monitoring total fluorescence. Because the lifetime was short and close to the duration of the probe laser pulse (8 ns fwhm), the time profiles of fluorescence were fitted by the convolution technique. The lifetimes were measured for several bands including the 0_0^0 band, in which a dominant change was not observed. The lifetimes of BPK-*h* and BPK-*d* in the supersonic free jet were estimated to be less than 4 and 10 ns, respectively. Matsushita et al. reported that the fluorescence lifetimes of BPK formed by the photoreduction of benzophenone were less than 5 ns in the gas phase at room temperature[19] and less than 10 ns in a supersonic free jet.[20] The fluorescence lifetimes of BPK-*h* were reported to be less than 5 ns[8,9,14,15,21] in several solutions, and that of BPK-*d* was 8.7 ns[15] in toluene-d_8 at room temperature. The fluorescence lifetimes of jet-cooled BPK-*h* and BPK-*d* formed by the photolysis of α-phenylbenzoin agree with those in the gas phase and in solution at room temperature. Scaiano and co-workers[15] suggested that transfer of the hydrogen atom from the hydroxyl group played an important role in the transition state of a reaction judging from the lengthening of the fluorescence lifetime by the deuteration of the hydroxyl group. The isotope effect was attributed to the cleavage of the O−H bond to yield benzophenone and hydrogen atom. The results obtained in this work are consistent with their conclusion.

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