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Dispersed fluorescence spectra of jet-cooled benzophenone ketyl radical: Assignment of the low-frequency vibrational modes

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We measured the laser-induced fluorescence (LIF) and dispersed fluorescence (DF) spectra of jet-cooled benzophenone ketyl radical (BPK), which was generated by the 248 nm photolysis of α -phenyl benzoin or benzhydrol. The several single vibronic level (SVL) DF spectra of BPK were obtained to analyze the low-frequency vibrational modes. We identified three low-frequency vibrations of 47, 74, and 98 cm⁻¹ in the ground state, which are assigned to the out-of-phase torsional motion, the in-phase torsional motion and Ph–C–Ph bending motion, respectively, with the aid of the density functional theory (DFT) calculation. The corresponding vibrational frequencies are 60, 65 and 84 cm⁻¹, respectively, in the excited state. The geometries of BPK in the ground and excited states are discussed based on the experimental results, *ab initio* calculations, and one-dimensional Franck–Condon simulation.

Introduction

Benzophenone ketyl (BPK) radical is an important and well-known intermediate generated in the photoreduction of benzophenone (BP). After photoexcitation, BP in the electronically-excited singlet state rapidly undergoes intersystem crossing with a unity quantum yield, and BP in the lowest triplet state $(^{3}n\pi^{*})$ abstracts a hydrogen atom from hydrogen donor molecule, which can be alkane, alkene, alcohol, or amine, to yield BPK. Many studies on BPK have been carried out through absorption and emission methods to elucidate the excited state dynamics and electronic structure in the condensed phase.1-22 Flexible molecules such as BPK may be characterized by large-amplitude low-frequency vibrational motions. The hyperfine coupling constant derived from the ESR spectrum of BPK strongly depends on the solvent employed, which is understood in terms of the flexible internal motions of OH and two phenyl rings and the conformational change by the solvents with different dielectric constants. Recently, Kawai et al. have revealed that the conformation is also an important factor to control the complex formation reaction of BPK with amines.²³ However, little is known about the equilibrium orientation of the two phenyl rings along the torsional coordinate and the frequencies of the low-frequency torsional vibrations in the ground and excited states. The equilibrium orientation is controlled by the conjugated π interactions in the phenyl-carbon-phenyl skeleton and the steric repulsions between ortho-hydrogen atoms belonging to different rings and between the hydrogen atom of OH and a phenyl ring. The overall geometry including the central carbon, OH, and two phenyl rings depends on the electronic state. The geometry change upon the photo-excitation is richer in diversity in these flexible molecules than in rigid molecules like benzene.

Supersonic-jet spectroscopy is one of the most powerful means for studying such low-frequency vibrations of OH and two phenyl rings. Matsushita *et al.* studied the hydrogen abstraction reaction of BP in the gas phase.²⁴ In their subsequent work, they reported the fluorescence excitation and dispersed emission spectra of BPK generated by the intracluster

reaction between BP and 1,4-cyclohexadiene in the supersonic free jet.²⁵ These observed spectra were not sharp enough to resolve the vibronic structure of BPK because of the congestion of low-frequency van der Waals modes of BPK-1,4-cyclo-hexadiene clusters. Kawai *et al.*²⁶ have also investigated photoreaction of BP in various BP/solvent molecule clusters and observed emissions of BPK and exciplexes. Recently, Wada et al. produced the jet-cooled BPK by photolysis of α phenyl benzoin and obtained the vibrationally resolved structures in the laser-induced fluorescence (LIF) and dispersed fluorescence (DF) spectra for the first time.²⁷ A few lowfrequency vibrations in the first excited state were observed and assigned on the basis of the vibrational assignments of BP.^{28–32} Only one low-frequency vibration was observed in the ground state due to the limitation of their low spectral resolution. There is little information about the geometries of BPK in the ground and excited states; whether the twist angle between two phenyl rings upon the excitation becomes large or small?

In this work, we measured several single vibronic level (SVL) DF spectra of BPK with higher spectral resolution and found in total three low-frequency vibrations in the ground state, which are significantly important in the assignment of vibrations in the excited state. The vibrational frequencies of BPK in the ground state are calculated by means of the DFT method. Those low-frequency vibrations in the ground and excited states are assigned by comparison with those of the DFT calculation. The geometrical change between the ground and excited states is discussed with the aid of an *ab initio* calculation.

Experiment

The experimental setup is essentially the same as described in detail elsewhere.^{27,33} α -Phenyl benzoin and benzhydrol (Tokyo Kasei, EP grade) are used as parent molecules to generate BPK by photolysis. The Ne carrier gas containing the sample vaporized at *ca.* 420 K was expanded into a vacuum chamber through a 400 μ m diameter orifice of a pulsed valve (Parker

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Hannifin, General Valve Ser. 9) operated at 10 Hz. A KrF excimer laser (Lambda Physik, COMPex 102) was collimated with a 1000 mm focal length lens and used to photolyze the sample just after the nozzle. A XeCl excimer laser (Lambda Physik, COMPex 102) pumped dye laser (Lambda Physik, SCANMATE) was collimated with another 1000 mm focal length lens and crossed the supersonic jet beam at 10 mm downstream from the orifice to probe the jet-cooled photolysis products by the LIF method. The wavenumbers in the LIF spectra were calibrated by the opto-galvanic lines of Ne recorded simultaneously. The LIF signals were measured with a photomultiplier (Hamamatsu Photonics, R-928) and averaged by a boxcar integrator (JY, 500M, 1800 gr/mm) was used for the DF measurements.

 α -Phenyl benzoin was synthesized as described in detail elsewhere.³⁴ 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 by recrystallization in appropriate solvents. The production of α -phenyl benzoin was confirmed by the NMR and IR spectra. α -Phenyl benzoin-*d* was prepared by deuteration of the hydroxyl group of α -phenyl benzoin with deuterium oxide in THF solution. The reagents used in the synthesis were purchased from Aldrich and Kanto Chemicals.

The MO calculations were performed for the ground and excited states of BPK using a Gaussian 98 program.³⁵ The geometries of the ground and excited states were optimized at the UB3LYP/6-31G(d,p) level of theory, and at the UCIS/6-31G(d) and 6-31G(d,p) levels, respectively. The vibrational calculations of BPK in the ground state were performed at the UB3LYP/6-31G(d,p) and 6-311+G(d,p) levels.

Results and discussion

LIF spectra

Fig. 1a shows the LIF spectrum of jet-cooled BPK prepared by the photolysis of α -phenyl benzoin (α -PB), which coincides with a previously reported one.²⁷ Fig. 1b also shows the LIF spectrum of jet-cooled BPK prepared by photolysis of benzhydrol (BH). It is confirmed that the fluorescent chemical species is BPK because the same species is generated by the photolysis of α -PB or BH.

The absorption of the diphenylmethyl radical³⁶ does not occur in this spectral region because the 0_0^0 band of the diphenylmethyl radical prepared by the photolysis of BH is located at 19 369 cm⁻¹. The 18 451 cm⁻¹ band is concluded to be the 0_0^0 band of the D₁–D₀ transition of BPK. Several progressions were observed on the higher energy side of the 0_0^0 band. The



Scheme 1



Fig. 1 LIF spectra of jet-cooled BPK generated by photolysis of (a) α -phenyl benzoin and (b) benzhydrol. The symbols of α , β and γ denote the out-of-phase torsional, in-phase torsional and Ph–C–Ph bending modes, respectively.

main progression (β_0^n) with an interval of about 65 cm⁻¹ starts from the 0_0^0 band. The other progressions ($\beta_0^n \gamma_0^1$ and $\beta_0^n \gamma_0^2$) with the 65 cm⁻¹ interval also start from the 18 535 cm⁻¹ band (γ_0^1) and the 18 619 cm⁻¹ band (γ_0^2), respectively. The γ_0^1 band is blue-shifted by 84 cm⁻¹ from the 0_0^0 band. Another weak progression starts from the 18 511 cm⁻¹ band (α_0^1), which is blueshifted by 60 cm⁻¹ from the 0_0^0 band. Three vibrational modes of 60, 65, and 84 cm⁻¹ make a series of progressions in the D₁–D₀ transition of BPK. On the basis of the spectral similarity observed in the LIF spectra of BP^{28–30} and BPK, the vibrations of 65 and 84 cm⁻¹ have been assigned to the in-phase and out-of-phase torsional motions, respectively.²⁷ Fig. 2 shows



Fig. 2 (a) Representation of BPK with the position numbers of carbon atoms. Two phenyl rings (Ph and Ph') rotate by θ and θ' around C_1-C_2 and $C_1-C'_2$ bonds, respectively, from a hypothetical geometry that the Ph and Ph' rings and the C_1 atom are on a plane. The Ph' ring is defined to be located on the hydrogen atom side on the OH group. Two arrows indicate the positive rotational direction of θ and θ' . (b) Two torsional motions. The in-phase torsional motion corresponds to conrotatory twisting motion (left), while the out-of-phase torsional motion corresponds to disrotatory twisting (right). The signs of "+" and "-" indicate the directions of the phenyl ring motions.

these torsional modes of BPK. The in-phase torsional motion is a conrotatory twisting motion of the two phenyl rings along the C–C bonds between a center carbon atom and phenyl rings, while the out-of-phase torsional is another disrotatory twisting motion.

Dispersed fluorescence (DF) spectra

Wada *et al.*²⁷ reported the DF spectrum (*ca.* 40 cm⁻¹ resolution) obtained by the 0_0^0 band excitation of BPK, which showed only one progression with the vibrational interval of about 74 cm⁻¹. The 74 cm⁻¹ vibration was assigned to the in-phase torsional mode. In order to study the low-frequency vibrations in detail, we measured several SVL-DF spectra of BPK with a higher resolution of 8 cm⁻¹.

Fig. 3a shows the DF spectrum obtained by the 0_0^0 band excitation. The spectrum is characterized by three progressions with a vibrational interval of *ca*. 74 cm⁻¹. The primary progression starts from the excitation wavenumber, as reported previously.²⁷ The progression is recognized up to six quanta with a maximum at two quanta. A peak located at 47 cm⁻¹ from the excitation wavenumber was observed for the first time. The second progression starting from the 47 cm⁻¹ band is also recognized. Another progression starts at 172 cm⁻¹ from the excitation wavenumber. The third progression seems to start from the position of 98 cm⁻¹, which is indicated by a dotted line, though the 98 cm⁻¹ peak is negligibly weak in Fig. 3a. The reason why we set the position of 98 cm⁻¹ for the third progression will be discussed later.

Fig. 3b shows the SVL-DF spectrum obtained by the 18 516 cm⁻¹ band $(0_0^0 + 65 \text{ cm}^{-1} \text{ band}, \beta_0^1)$ excitation. A progression with the 74 cm⁻¹ interval starts from the excitation wavenumber. The progression is recognized up to nine quanta with an intensity minimum at three quanta. The Franck-Condon pattern is different from that observed in the DF spectrum obtained by the 0_0^0 band excitation. These facts indicate that the vibration of 65 cm⁻¹ in the ground state. On the basis of the Franck-Condon analysis, this correspondence will be discussed later. Another weak 74 cm⁻¹ progression starts at 98 cm⁻¹ from the excitation wavenumber, though the 98 cm⁻¹ band has negligibly weak intensity.

Fig. 3c shows the SVL-DF spectrum obtained by the 18 535 cm⁻¹ band $(0_0^0 + 84 \text{ cm}^{-1} \text{ band}, \gamma_0^1)$ excitation. The intense peak obviously appears at 98 cm⁻¹ from the excitation wavenumber, which corresponds to the negligibly weak 98 cm⁻¹ bands in Figs. 3a and 3b. The 74 cm⁻¹ progression starting from the 98 cm⁻¹ band in Fig. 3c is similar to those starting from the excitation wavenumbers in Figs. 3a and 3b. Another weak 74 cm^{-1} progression starting from the 196 cm^{-1} band, the lower state of which corresponds to two quanta of the 98 cm⁻¹ vibration, is also recognized in Fig. 3c. These facts indicate that the 84 cm⁻¹ vibrational mode in the excited state corresponds to that of 98 cm⁻¹ in the ground state. Now we are sure that there is a vibrational level at 98 cm^{-1} in the ground state of BPK, which supports our vibrational assignment of the 98 cm⁻¹ bands made in Figs. 3a and 3b. Fig. 3c also shows a relatively weak 74 cm⁻¹ progression starting from the excitation wavenumber, which is quite different in an intensity pattern from the corresponding progression observed in Fig. 3a. This point will be discussed later.

Three low-frequency vibrational modes

As described above, we found three low-frequency vibrations of 47, 74, and 98 cm⁻¹ in the ground state. From the analysis of the SVL-DF spectra, it was also found that the 65 and 84



(b) β_0^1 excitation



(c) γ_0^1 excitation



Fig. 3 Dispersed fluorescence spectra. The signals at the excitation wavenumbers are very intense due to laser scattering. (a) The 0_0^0 band excitation. (b) The $0_0^0 + 65$ cm⁻¹ band corresponding to the β_0^1 excitation. (c) The $0_0^0 + 84$ cm⁻¹ band corresponding to the γ_0^1 excitation.

 cm^{-1} vibrations in the excited state correspond to the 74 and 98 cm^{-1} vibrations in the ground state, respectively.

In order to assign these vibrational modes, the vibrational frequencies in the ground state were calculated by the DFT method. Three vibrational modes were calculated to have low frequencies below 100 cm⁻¹. The values obtained for the UB3LYP/6-311+G(d,p) level are 48.4, 72.2, and 98.6 cm⁻¹

 Table 1
 Vibrational modes and frequencies (cm⁻¹) of BPK

Mode (symbol in text)	D ₀			D_1	
	Exp.	Calc. ^a		Exp.	A
		6-31G(d,p)	6-311+G(d,p)		description
Out-of-phase torsion (a)	47	50.0	48.4	59.8	
In-phase torsion (β)	74	72.4	72.2	65.4	
Ph–C–Ph bend (γ)	98	97.6	98.6	84.3	
^{<i>a</i>} Scaled by 0.95 and 0.99 for t	he UB3LYP/6-31	G(d,p) and 6-311+G(d,p) levels of theory, respective	ly.	. –

corresponding to the out-of-phase torsion, the in-phase torsion, and the in-plane Ph-C-Ph bend, respectively, which are listed in Table 1. Two sets of frequencies calculated on the UB3LYP/6-31G(d,p) and UB3LYP/6-311+G(d,p) levels of theory are essentially the same. The experimental frequency of 74 cm⁻¹, which was previously assigned to the in-phase torsion, is close to the calculated value of 72.2 cm⁻¹. The DF spectrum obtained by the 0_0^0 band excitation shows a long main progression with the 74 cm^{-1} interval, which suggests that the D_1-D_0 transition of BPK brings the structural change along the coordinate of the in-phase torsional motion. The other two experimental frequencies of 47 and 98 cm⁻ coincide well with the calculated values of 48.4 and 98.6 cm⁻¹, respectively. On the basis of the good agreement between the measured and calculated values, the vibrational modes of 47 and 98 cm⁻¹ are assigned to the out-of-phase torsion and the Ph-C-Ph bend, respectively. In the previous report,²⁷ the vibrational energy of the out-of-phase torsion of BPK was estimated to be higher than that of the in-phase torsion because of steric hindrance. However, the present DFT calculation suggests that the frequencies of the out-ofphase and in-phase torsions are the first and second lowest, respectively, and the third lowest vibration is the Ph-C-Ph bend.

As described above, the 65 and 84 cm⁻¹ vibrations in the excited state correspond to those of 74 and 98 cm⁻¹ in the ground state, respectively. Thus, the 65 and 84 cm⁻¹ vibrations in the excited state are assigned to the in-phase torsion and the Ph–C–Ph bend, respectively. Table 1 summarizes the vibrational modes and frequencies in the ground and excited states determined in the present work. Wada *et al.*²⁷ assigned the 84 cm⁻¹ vibration in the excited state as the out-of-phase torsion, which does not agree with our assignment. They carried out the vibrational analysis under the assumption that the geometries and normal modes of BPK and BP are similar. It might be of note that the vibration assigned to the out-of-phase torsion of BP could be the Ph–C–Ph bend.³⁷

We also produced BPK-*d* with a deuterated hydroxy group and measured the LIF spectrum, which coincides with a previously reported one.²⁷ The observed BPK-*d* frequencies of 59.4, 65.0 and 84.0 cm⁻¹ in the excited state are essentially the same as the corresponding BPK-*h* frequencies of 59.8, 65.4 and 84.3 cm⁻¹. According to our DFT calculation, three low-frequencies of BPK-*h* in the ground state (48.4, 72.2 and 98.6 cm⁻¹) correspond to the 48.4, 72.3 and 98.4 cm⁻¹ frequencies of BPK-*d*, respectively. It implies that three low-frequencies are not affected by the deuteration of the OH group. These results also support that three low-frequency vibrations of BPK are due to the out-of-phase torsion, the in-phase torsion, and the Ph–C–Ph bend.

Equilibrium geometries

The in-phase torsional motion of 65 cm^{-1} makes the main long progression in the LIF spectrum. This observation implies that the structural change between the ground and excited states takes place along the coordinate of the in-phase torsional motion. In order to confirm this interpretation, we calculated the geometries of BPK in the ground and excited states.

The geometries of BPK were optimized using the UB3LYP/ 6-31G(d,p) level in the ground state, and the UCIS/6-31G(d) and UCIS/6-31G(d,p) levels in the excited state, respectively. Fig. 4 shows these optimized geometries with geometry parameters. The bonds connected to the center carbon atom, C_1 ,



Fig. 4 Optimized geometries of BPK (a) in the ground D_0 state (UB3LYP/6-31G(d,p)) and (b) in the excited D_1 state (UCIS/6-31G(d) and 6-31G(d,p)). The bonds connected to C_1 are almost sp²-hybridized and the four atoms (C_1 , C_2 , C'_2 , O) are in a coplanar conformation. This plane is called " C_2 – C'_2 –O plane". Two phenyl rings (Ph and Ph') are twisted to the θ and θ' angles, respectively, from the " C_2 – C'_2 –O plane". Bond length (Å) and bond angle (degrees).

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of BPK are almost sp²-hybridized and the four atoms (C_1 , C_2 , C'_{2} , O) are in a coplanar conformation (C_{2} – C'_{2} –O plane). The twist angles, θ and θ' , of two phenyl rings (Ph and Ph') from the C2-C'2-O plane are not equal, because of the different steric repulsions of a hydrogen atom on the OH group against Ph and Ph'. In the ground state, the twist angles θ' (for the Ph' ring on the hydrogen atom side of OH) and θ (for the Ph ring on the other side) are calculated to be 31° and 21°, respectively. Upon the electronic excitation to the D_1 state, the θ' and θ angles become 40-42° and 29-31°, respectively, which are larger by $8-11^{\circ}$ than the corresponding angles in the ground state. Wada *et al.*²⁷ estimated the angle change between the ground and excited states by means of a one-dimensional Franck-Condon simulation for the in-phase torsional mode. Onedimensional oscillators of 74 and 65 cm⁻¹ were used for the ground and excited states, respectively. Assuming that the angle changes of $\Delta\theta$ and $\Delta\theta'$ are the same, the observed excitation spectrum of BPK was reproduced with $\Delta \theta \ (\equiv \Delta \theta') \cong 8^{\circ}$. This angle change is a little bit smaller than the $\Delta\theta$ value (8-11°) obtained by our *ab initio* calculation, though they might be essentially the same by considering that the comparison is based on a simple excited state calculation and a onedimensional Franck-Condon simulation. The one-dimensional simulation only gives the magnitude of the angle change but not the direction of the angle change. In our ab initio calculation, it turns out that the interplanar angles increase with the excitation. This fact is unusual as the π - π * excitation cases.

In biphenyl, two phenyl rings are twisted to an interplanar angle of *ca*. 44° in the ground state, but adopt a coplanar conformation upon the transition to the first excited state.^{38,39} The equilibrium orientation of two rings would be determined by a subtle balance between the steric repulsion of *ortho*-hydrogen atoms and the strength in π -electron conjugation covering the molecule. It is interpreted that the repulsion is a major factor to determine the nonplanar geometry in the ground state, while upon the excitation the increased strength in the π -electron conjugation makes two phenyl rings to be planar. According to *ab initio* calculation of 3-aminobiphenyl,⁴⁰ the C–C bond length and the dihedral angle between the phenyl rings are 1.492 Å and 45.8°, respectively, in the ground state. Upon excitation the bond length decreases to 1.412 Å and the dihedral angle decreases to 5.4°.

In BPK, the bond lengths between the center carbon and two phenyl rings (the C_1 - C_2 and C_1 - C'_2 lengths) decrease (from 1.439 Å to 1.417 Å, and from 1.446 Å to 1.407 Å, respectively) upon excitation, as shown in Fig. 5. On the contrary, the twist angles between two phenyl rings (θ and θ') increase (from 21 to 29-31°, and from 31 to 40-42°, respectively) upon excitation. In comparison with the biphenyl molecules, the BPK radical has a carbon atom existing between two phenyl rings. The main contribution in the D_1-D_0 transition of BPK is found to be composed of the LUMO \leftarrow SOMO transition (UCIS/6-31G(d,p), 90%). The node of the LUMO exists on the center carbon C₁ and two phenyl rings are more twisted upon excitation. The π -orbitals on C₂ and C'₂ have opposite signs and tend to induce hyperconjugation accompanied by more twisting two phenyl rings. As a result of the hyperconjugation, the distance between the two phenyl rings becomes closer and the C_1 - C_2 and C_1 - C'_2 bond lengths become shorter. The predictions of the ab initio calculation coincide with our observation.

Vibrational intensity patterns

The Franck-Condon factors in the SVL-DF spectra obtained by the 0_0^0 , β_0^1 ($0_0^0 + 65 \text{ cm}^{-1}$) and β_0^2 ($0_0^0 + 130 \text{ cm}^{-1}$) band excitations were estimated by means of a one-dimensional Franck-Condon simulation for the in-phase torsional mode. The results are shown in Fig. 5. One-dimensional oscillators of 74 and 65 cm⁻¹ were used for the ground and excited states,



Fig. 5 Observed (black bars) and calculated (white bars) Franck-Condon factors for the in-phase torsional mode in SVL-DF spectra obtained by the excitations of (a) the 0_0^0 band, (b) the β_0^1 band $(0_0^0 + 65 \text{ cm}^{-1})$ and (c) the β_0^2 band $(0_0^0 + 130 \text{ cm}^{-1})$. Gray bars represent the measured signals involving laser scattering.

respectively. The calculated intensity patterns, which are reproduced with $\Delta\theta \ (\equiv \Delta\theta') \cong 8^\circ$, are consistent with the observed ones. It is confirmed that the 65 cm⁻¹ vibration in the excited state corresponds to the 74 cm⁻¹ vibration in the ground state, and the 65 and 130 cm⁻¹ bands are the transitions to first and second excited levels for the in-phase torsional mode.

According to the *ab initio* calculation, the $\langle (C_5C_1C'_5)$ angle is 131° and 120° in the ground and excited states, respectively. The $\langle (C_5C_1C'_5)$ angle is not equal to the $\langle (C_2C_1C'_2)$ angle because three bonds of the carbon atom, C'_2 , in the excited state are almost coplanar but slightly pyramidal. In contrast with the twist angle, the $\langle (C_5C_1C'_5)$ angle is smaller in the excited state than in the ground state. The change in the $\langle (C_5C_1C'_5)$ angle indicates that the Ph–C–Ph bending mode (γ) is active in the emission and excitation spectra, which coincides with the observation shown in Figs. 1 and 3.

The Ph-C-Ph bending mode has relatively strong intensity in the LIF spectrum as shown in Fig. 1. On the other hand, this γ mode does not have appreciable intensity in the DF spectrum obtained by the 0_0^0 band excitation. The LIF spectrum was measured under the unsaturated conditions of laser power. The mirror image was not observed on the Ph-C-Ph bending mode in the excitation and emission spectra. The vibrational normal coordinates in the excited state are thought to be different from those in the ground state, which is described as Duschinsky rotation. In the SVL-DF spectrum obtained by the $\gamma_0^1~(0_0^0+84~cm^{-1}$ band) excitation, the progressions due to the in-phase torsional mode appear together with the Ph-C-Ph bending mode, which makes the progression intensity pattern different from that in the DF spectrum obtained by the 0_0^0 band excitation. If a mode mixing between the in-phase torsion and the Ph-C-Ph bend does not occur, then the progression of the in-phase torsion shown in this spectrum has

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