

# Supersonic Jet Spectroscopic Study of *p*-Methoxybenzyl Alcohol<sup>†</sup>

Min-Chul Yoon, Sun Jong Baek, Hyeongjin Cho, Young S. Choi, and Sang Kyu Kim\*

Department of Chemistry, Inha University, Incheon 402–751, Republic of Korea

Received: March 17, 2000; In Final Form: May 19, 2000

Fluorescence and mass-resolved  $S_1-S_0$  excitation spectra of *p*-methoxybenzyl alcohol in a supersonic jet are reported. The long vibrational progression bands are observed in both spectra and attributed to the modes involving torsional motion of the  $\text{CH}_2\text{OH}$  moiety with respect to the rest of the molecule. The spectral origin for the  $S_1-S_0$  transition is found to be at  $35\,701\text{ cm}^{-1}$ . Two additional distinct vibrational progression bands are observed with their pseudo origins at  $35\,785$  and  $35\,863\text{ cm}^{-1}$ . Fluorescence depletion spectroscopy shows that these three vibrational progression bands are originated not from three different conformers but from single conformer in the jet. The torsional barrier height of  $316\text{ cm}^{-1}$  in the  $S_1$  ground-vibrational state is obtained from the comparison of the experiment with the calculation assuming a sinusoidal function for the potential energy surface along the torsional angle. The comparison of the relative intensity distributions in the vibrational progression bands with the calculation of Franck–Condon factors using a free-rotor basis set suggests that the molecular geometry at the minimum energy of the  $S_1$  state is around  $45^\circ$  rotated about the  $\text{CH}_3\text{OC}_6\text{H}_4\text{---CH}_2\text{OH}$  axis compared to that of the  $S_0$  state.

## 1. Introduction

Aryl alcohols are essential molecules in many synthetic processes in organic chemistry, and their structure and reactivity have been important issues for past decades. Especially, aryl alcohols can exist in many different conformers, and a huge number of experimental and theoretical studies have been made to unravel the structures of their stable conformers in various environments.<sup>1–17</sup> Many experimental studies that have been carried out include electron diffraction, infrared, NMR, and excitation spectroscopies.<sup>1–6</sup> Among these experimental methods, supersonic jet spectroscopy using the combined technique of a molecular beam and laser has been recently found to be very useful in resolving an ambiguity regarding the conformational complexity of flexible molecules in the ground and excited electronic states.<sup>7–17</sup> In this way, it is now possible to carry out various laser spectroscopic studies of a conformer of the flexible molecule isolated in the gas phase.

However, despite recent intensive conformational studies for many aryl alcohols, it is not clearly resolved yet which conformer is the most stable one in the jet even for one of the simplest aryl alcohols, benzyl alcohol.<sup>2,7,8</sup> For example, the Bernstein group<sup>7</sup> has concluded from their mass-resolved excitation spectroscopic study that there is only one conformer of benzyl alcohol populated in the jet, and its  $\text{CH}_2\text{OH}$  moiety is perpendicular to the plane of the aromatic ring. However, Mikami and colleagues<sup>8</sup> have recently reported that, from IR–UV double-resonance spectroscopic works on the same molecule, there exist two different conformers of benzyl alcohol in the jet condition. According to them, the major rotamer is the planar one, in which the  $\text{CH}_2\text{OH}$  moiety is parallel to the aromatic ring, whereas the *gauche* form also exists as a minor population.<sup>8</sup> Theoretical predictions have not been consistent, either. Hirota et al.<sup>2</sup> used the molecular force field theory to

report the planar rotamer as a minimum energy conformer, while a hydrogen-bonded *gauche* form was predicted to be the most stable one by *ab initio* calculation.<sup>8</sup> The substituent effect on the minimum-energy conformation has also been investigated for various substituted benzyl alcohols. For instance, in ref 7, it has been concluded that *p*-ethylbenzyl alcohol exists as two different conformers in the jet, while only one conformer is populated in the jet for both *p*-methyl- and *p*-fluorobenzyl alcohols. In mass-resolved excitation spectra of various substituted benzyl alcohols, the low-frequency vibrational bands attributed to the torsional mode of the  $\text{CH}_2\text{OH}$  moiety are commonly observed.<sup>7</sup> The values of torsional barrier height and internal rotational constant deduced from the observed vibrational frequencies have been found to be little affected by the substituent if it is in the *para*-position with respect to the internally rotating  $\text{CH}_2\text{OH}$  moiety.<sup>7</sup>

Methoxy-substituted benzenes belong to another group of molecules of which the conformational studies have been well documented.<sup>9</sup> Many methoxy-substituted benzene derivatives have been investigated, and their minimum-energy conformers are found to have the planar geometry where the  $\text{CH}_3\text{O}$  group lies in the plane of the aromatic ring. No bands due to the  $\text{CH}_3\text{O}$  group torsional motion were observed in the mass-resolved excitation spectra of single methoxy-substituted benzenes, suggesting that there is no change in the minimum-energy geometry in the electronically excited state from that in the ground electronic state.

Here, we have investigated the molecule that has both methoxy and  $\text{CH}_2\text{OH}$  groups in 1,4-positions of the aromatic ring, *p*-methoxybenzyl alcohol. In principle, there could be many possible conformers of this molecule populated in the jet. Thus, we have put this molecule in the jet and carried out the laser spectroscopic study, trying to answer to following questions: (1) How many different conformers of the *p*-methoxybenzyl alcohol molecule are populated in the jet condition? (2) Which vibrational modes are optically active in the  $S_1-S_0$  electronic excitation? (3) Is there a geometrical change in the minimum-

<sup>†</sup> Part of the special issue “C. Bradley Moore Festschrift”.

\* To whom correspondence should be addressed. E-mail: skkim@inha.ac.kr. Fax: +82-32-867-5604.

energy structure of the title molecule induced by electronic excitation from the ground to the excited state?

## 2. Experimental Section

The *p*-methoxybenzyl alcohol (Aldrich 98%) and *p*-methoxy- $\alpha$ -toluenethiol (Aldrich 90%) molecules were purchased and used without further purification. The deuterated *p*-methoxybenzyl alcohol ( $p$ -CH<sub>3</sub>O-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>OD) was prepared by mixing the title molecule with CH<sub>3</sub>OD, followed by the extraction. Another deuterated *p*-methoxybenzyl alcohol ( $p$ -CD<sub>3</sub>O-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>OH) was also synthesized. The purities of the deuterated samples were checked by GC-mass and NMR spectroscopies.

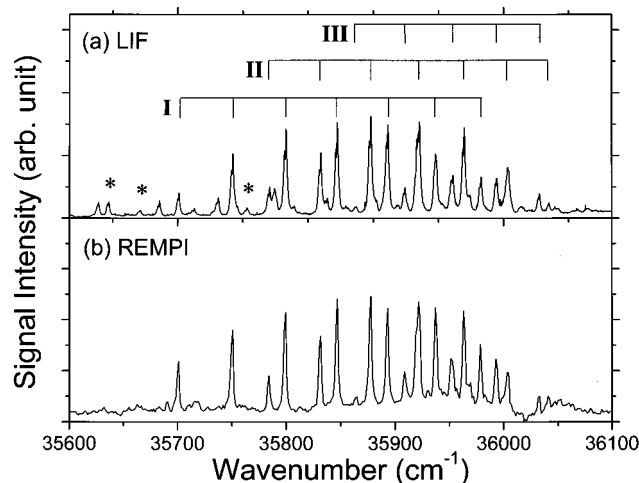
All the samples were kept at 80 °C, while the nozzle temperature was maintained at 90 °C to reduce the chance of cluster formation. The experimental setup has been given in detail elsewhere.<sup>18,19</sup> Briefly, the He carrier gas was passed on the sample, and then expanded through the nozzle orifice (General Valve, 0.5 mm diameter) into the vacuum chamber. The vacuum chamber was equipped with a 6 in. diffusion pump (Varian, VHS-6) and a liquid N<sub>2</sub> trap. The nozzle was operated at a repetition rate of 10 Hz with a typical backing pressure of 1 atm, and the background pressure was maintained at 10<sup>-5</sup> Torr when the nozzle was on.

The third harmonic output of a Nd:YAG laser (Spectra-Physics, GCR-150) was used to pump a dye laser (Lumonics, HD-500) to generate the laser pulse in the 540–560 nm range. The output of the dye laser was then frequency-doubled to produce the UV laser pulse in the 270–280 nm range with a pulse duration of  $\sim$ 7 ns and a spectral line width of  $\sim$ 0.4 cm<sup>-1</sup>. The laser frequency was calibrated using the optogalvanic signal from a hollow-cathode lamp (Ne) with an accuracy of  $\pm$ 0.5 cm<sup>-1</sup>. A BBO crystal was placed on a homemade autotracker to maintain both the intensity and direction of the frequency-doubled output. The UV laser pulse was directed into the vacuum chamber and overlapped with a molecular beam at the position of 20 mm downstream from the nozzle orifice, giving  $x/d = 40$ . For measuring fluorescence depletion spectra, another dye laser (Lambda Physik, Scanmate-II) pumped by the 532 nm output of the YAG laser was frequency-doubled to provide the UV laser pulse in the 270–280 nm range.

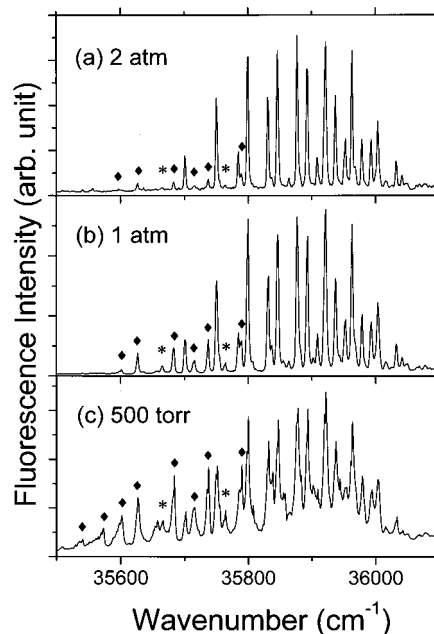
The fluorescence from the excited molecule was collected by a 2 in. diameter lens (focal length = 50 mm), imaged onto the slit, and detected by a photomultiplier tube (Hamamatsu, H-1949–50). The fluorescence signal was gate-integrated by a boxcar (SRS, SR250), A/D converted by an interface (SRS, SR245), and stored in a PC using a data-taking program. The signal was averaged over 10 shots and normalized to the laser intensity fluctuation using a photodiode detecting a small portion of the UV laser pulse. The mass-resolved excitation spectrum was taken using a time-of-flight mass spectrometry. Briefly, the molecular beam was skimmed through a 1.0 mm diameter skimmer, overlapped with an ionization laser to generate molecular ions, and these ions were repelled, accelerated, drifted along the field-free region, and detected by a multichannel-plate (MCP, Jordan) to give the appropriate mass signal.

## 3. Results and Discussion

**A. Excitation Spectra of *p*-Methoxybenzyl Alcohol.** Laser-induced fluorescence (LIF) and mass-resolved resonantly enhanced multiphoton ionization (REMPI) excitation spectra of *p*-methoxybenzyl alcohol in the supersonic jet are shown in Figure 1. Comparing these two excitation spectra, it has been found that the peaks represented as asterisks in the LIF spectrum



**Figure 1.** (a) Laser-induced fluorescence (LIF) and (b) mass-resolved excitation spectra of *p*-methoxybenzyl alcohol. The peaks noted as asterisks in (a) are due to an impurity of the sample. Three distinct vibrational progressions are denoted as I, II, and III.



**Figure 2.** LIF spectra of *p*-methoxybenzyl alcohol taken at the backing pressure of (a) 2 atm, (b) 1 atm, and (c) 500 Torr. Those peaks noted as filled diamonds grow as decreasing the backing pressure. The peaks with asterisks are due to an impurity.

(Figure 1) are due to an impurity in the sample, which has a mass different from that of the title molecule.

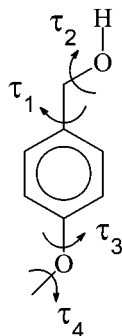
LIF spectra of *p*-methoxybenzyl alcohol taken at several backing pressures are shown in Figure 2. Intensities of the peaks denoted as filled diamonds in Figure 2 decrease as the backing pressure increases, and those peaks are ascribed to vibrational hot bands of the title molecule. Accordingly, a spectral origin is identified as the peak found at 35 701 cm<sup>-1</sup>. Taking into account the regularity of the peak positions in the spectrum, two additional pseudo-origins can be easily identified at 35 785 and 35 863 cm<sup>-1</sup>. Therefore, three distinct vibrational progressions could be identified in the S<sub>1</sub>-S<sub>0</sub> excitation spectrum and there is a spacing of  $\sim$ 50 cm<sup>-1</sup> between adjacent bands in each progression. Those progressions are denoted as I, II, and III in Figure 1, and their transition wavenumbers are listed in Table 1. The fluorescence lifetimes of the observed bands are measured to be 13  $\pm$  2 ns.

**TABLE 1: Peak Positions and Assignment for *p*-Methoxybenzyl Alcohol**

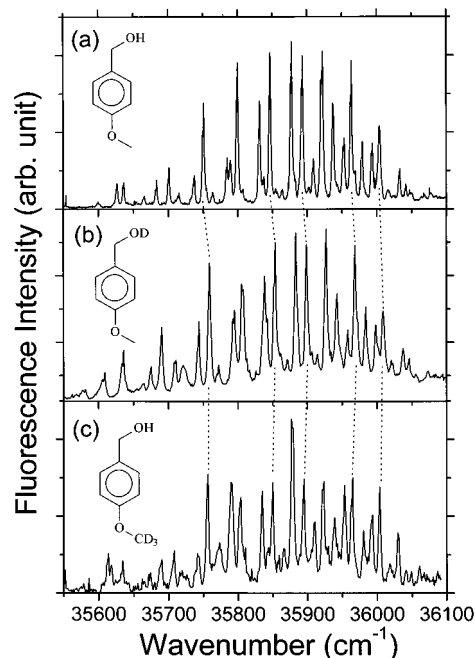
absolute <sup>a</sup> freq (cm <sup>-1</sup> )	I		II		III		assignment <sup>c</sup>
	obs	calc <sup>b</sup>	obs	calc <sup>b</sup>	obs	calc <sup>b</sup>	
35701	0						0 <sub>0</sub> <sup>0</sup>
35751	50	51					T <sub>0</sub> <sup>2</sup> <sub>0</sub>
35785			0 (84)				v <sub>0</sub> <sup>1</sup> <sub>0</sub>
35800	99	100					T <sub>0</sub> <sup>4</sup> <sub>0</sub>
35832			47	48			v <sub>0</sub> <sup>1</sup> + T <sub>0</sub> <sup>2</sup> <sub>0</sub>
35847	146	146					T <sub>0</sub> <sup>6</sup> <sub>0</sub>
35863					0 (163)		v <sub>0</sub> <sup>2</sup> (?)
35878			93	94			v <sub>0</sub> <sup>1</sup> + T <sub>0</sub> <sup>4</sup> <sub>0</sub>
35894	193	192					T <sub>0</sub> <sup>8</sup> <sub>0</sub>
35909					46	46	v <sub>0</sub> <sup>2</sup> + T <sub>0</sub> <sup>2</sup> <sub>0</sub>
35922			137	138			v <sub>0</sub> <sup>1</sup> + T <sub>0</sub> <sup>6</sup> <sub>0</sub>
35937	236	236					T <sub>0</sub> <sup>10</sup> <sub>0</sub>
35953					90	90	v <sub>0</sub> <sup>2</sup> + T <sub>0</sub> <sup>4</sup> <sub>0</sub>
35964			179	179			v <sub>0</sub> <sup>1</sup> + T <sub>0</sub> <sup>8</sup> <sub>0</sub>
35979	278	277					T <sub>0</sub> <sup>12</sup> <sub>0</sub>
35994					131	131	v <sub>0</sub> <sup>2</sup> + T <sub>0</sub> <sup>6</sup> <sub>0</sub>
36004			219	219			v <sub>0</sub> <sup>1</sup> + T <sub>0</sub> <sup>10</sup> <sub>0</sub>
36033					170	170	v <sub>0</sub> <sup>2</sup> + T <sub>0</sub> <sup>8</sup> <sub>0</sub>
36042			257	255			v <sub>0</sub> <sup>1</sup> + T <sub>0</sub> <sup>12</sup> <sub>0</sub>

<sup>a</sup> Peak positions at the maximum intensities are shown. <sup>b</sup> The calculated frequencies for only odd overtones of the torsional mode are shown for the comparison (see the text). <sup>c</sup> The assignment for v<sub>0</sub><sup>2</sup> and v<sub>0</sub><sup>1</sup> are not certain (see the text).

**B. Assignment of S<sub>1</sub> State Vibrational Bands.** Let us consider first the vibrational progression I, which has an origin at 35 701 cm<sup>-1</sup>. The optically active mode responsible for this long-vibrational progression is most likely to be one related to the torsional motion of a substituent with respect to the aromatic ring, simply because its spacing between adjacent bands is very low (~50 cm<sup>-1</sup>). There are four possible bond axes in the *p*-methoxybenzyl alcohol, about which the torsional motion of two moieties could give rise to the vibrational progression. First, the progression could be due to the torsional motion of the entire CH<sub>2</sub>OH group with respect to the rest of the molecule. The second possible torsional bond axis would be one connecting *p*-methoxybenzyl and hydroxyl moieties. The third candidate is the torsional motion of the methoxy (OCH<sub>3</sub>) group with respect to the benzyl moiety. Finally, the internally rotating CH<sub>3</sub> moiety of the methoxy group could be responsible for the vibrational progression. These four possible torsional angles are denoted as τ<sub>1</sub>, τ<sub>2</sub>, τ<sub>3</sub>, and τ<sub>4</sub>, respectively, as below.



For appropriate assignment of the observed vibrational progression, LIF spectra of several analogous molecules are

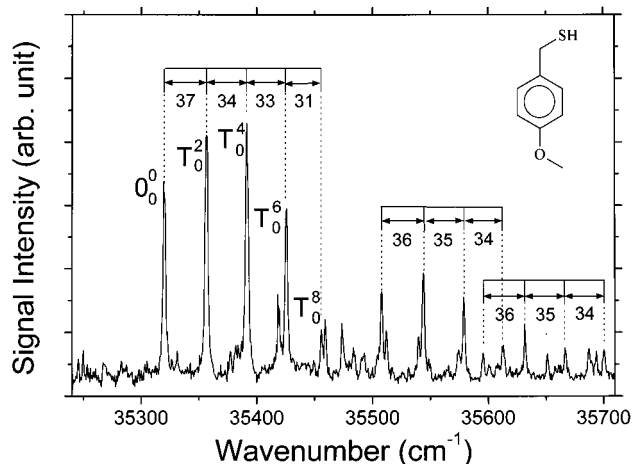


**Figure 3.** LIF spectra of deuterated analogues of the title molecule: (a) *p*-CH<sub>3</sub>O-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>OH, (b) *p*-CH<sub>3</sub>O-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>OD, and (c) *p*-CD<sub>3</sub>O-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>OH. The peak positions are listed in Table 2.

**TABLE 2: Relative Peak Positions of Deuterated Analogues**

<i>p</i> -CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -OH + 35 701 cm <sup>-1</sup>	<i>p</i> -CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -OD + 35 709 cm <sup>-1</sup>	<i>p</i> -CD <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -OH + 35 708 cm <sup>-1</sup>	progression
0	0	0	I
50	50	48	I
84	83	82	II
99	96	96	I
131	129	127	II
146	145	142	I
163	162	157	III
177	175	169	II
193	190	187	I
209	205	202	III
221	218	215	II
236	234	231	I
253	249	245	III
263	260	257	II
278	275	272	I
294	289	285	III
303	300	296	II
333	328	322	III
341	337	333	II

obtained. First, the hydroxyl hydrogen atom is substituted by a deuterium (OH → OD) to give the LIF spectrum in Figure 3. Both peak positions and relative intensities of the *p*-H<sub>3</sub>CO-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>OD LIF spectrum are almost identical to those of the title molecule, except slight red shifts of the peaks relative to the origin (Table 2). If the vibrational progression in the LIF spectrum is due to the torsional motion of the hydroxyl group along the τ<sub>2</sub> torsional angle, then substantial isotopic shifts of the peak positions should have been observed, therefore excluding the possibility of τ<sub>2</sub> torsional angle as the coordinate responsible for the optically active mode. Second, three hydrogen atoms in the methoxy group are all replaced by deuterium atoms to give the LIF spectrum of *p*-D<sub>3</sub>CO-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>OH in Figure 3. Similar to the case of the -OD analogue, the LIF spectrum of *p*-D<sub>3</sub>CO-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>OH is not much different from that of the title molecule in the relative peak positions (Table 2). Were the LIF bands assumed to be due to the torsional motion of the methoxy or methyl moieties along the τ<sub>3</sub> or τ<sub>4</sub> torsional angles, respectively, then it should be followed by the significant isotopic shift of relative peak

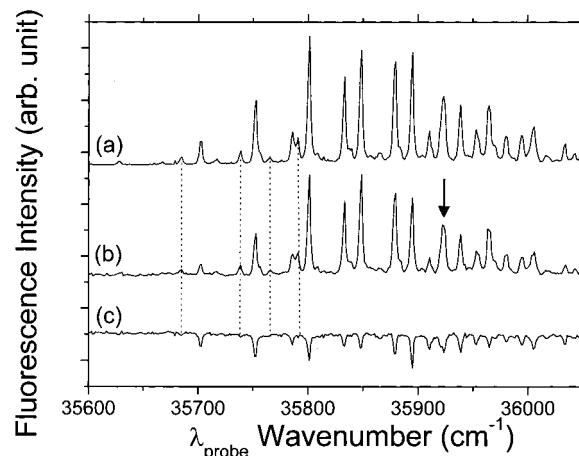


**Figure 4.** REMPI spectrum of *p*-methoxy- $\alpha$ -toluenethiol. The spacing of the adjacent peaks in the progression is red-shifted compared to that of the title molecule.

positions of the spectrum. However, as shown in Figure 3 and Table 2, the LIF spectra of the title molecule and deuterated analogues are hardly discernible among themselves. The slight red shifts of the relative peak positions in LIF spectra of deuterated analogues may come from the fact that the torsional mode should involve the motions of other nuclei not related to the local torsional motion.

Therefore, from above, the torsional motion of the entire CH<sub>2</sub>-OH moiety along the  $\tau_1$  angle is most likely to be responsible for the vibrational progression in the excitation spectrum. To confirm this, the excitation spectrum of *p*-methoxy- $\alpha$ -toluenethiol, in which the CH<sub>2</sub>OH group of *p*-methoxybenzyl alcohol is replaced by the CH<sub>2</sub>SH group, is taken in Figure 4. Since the *p*-methoxy- $\alpha$ -toluenethiol molecule does not fluoresce, the excitation spectrum has been taken using a REMPI-TOF mass spectrometry. The spectral pattern has been much changed from that of the title molecule. However, the vibrational progression starting from the origin at 35 320 cm<sup>-1</sup> is clearly identified in Figure 4. A significant red shift of the spacing between adjacent bands in the progression is observed; the spacing between first two bands of the *p*-methoxy- $\alpha$ -toluenethiol spectrum is 37 cm<sup>-1</sup>, which is about 30% less than that of the title molecule. The substantial decrease of the vibrational frequency induced by the CH<sub>2</sub>OH  $\rightarrow$  CH<sub>2</sub>SH substitution suggests that the optically active vibrational mode largely involves the torsional motion of the CH<sub>2</sub>O(or S)H moiety along the  $\tau_1$  angle. Therefore, it seems reasonable to conclude that the observed progressions I, II, and III in Figure 1 are all due to the vibrational mode involving the torsional motion of the CH<sub>2</sub>OH moiety along the  $\tau_1$  angle.

Three distinct progression bands in the excitation spectrum often suggest the existence of three different conformers in the jet. Thus, one is tempted to assign these I, II, and III progression bands in Figure 1 as those being due to three different conformers present in the supersonic jet. Hole-burning spectroscopy is one of the good ways to get an answer for whether those progression bands are originated from different conformers. Thus, we obtained fluorescence depletion spectra of the title molecule by pumping one level of a progression. When a transition corresponding to one of the three progressions is UV-pumped, the population of the ground state of a species is depopulated. Therefore, when the subsequent probe laser is given, the depopulation by the pump laser results in the decrease of fluorescence intensities of the bands that belong to the pumped species, while those belonging to other species are not



**Figure 5.** LIF spectrum of *p*-methoxybenzyl alcohol with (a) the probe laser only and (b) the pump and probe lasers. The transition corresponding to the peak with an arrow in (b) is pumped prior to detecting the fluorescence by the probe laser. The difference (b) - (a) is shown in (c). All the peaks show dips in the similar extent. It should be noted that vibrational hot bands (shown as dotted lines) show no difference in their LIF intensities in (a) and (b).

affected by the depopulation laser pulse. Accordingly, if there are three different conformers in the jet giving three distinct I, II, and III progression bands and one of the I progression bands is pumped, then only I progression bands would show the decrease in their fluorescence intensities without affecting those of II and III progressions. However, as shown in Figure 5, intensities of all three progression bands decrease by a similar extent when the transition belonging to a progression is pumped prior to detecting fluorescence by the probe laser. It is interesting to note that the fluorescence intensities of vibrational hot bands are little affected in the fluorescence depletion spectrum, verifying the validity of our experimental condition, Figure 5. Thus, it can be concluded that all the peaks in the LIF spectrum of the title molecule are originated from a single conformer in the jet. In other words, there is only one conformer of *p*-methoxybenzyl alcohol populated in the jet.

From the fact that the II and III progressions have their pseudo origins at 84 and 163 cm<sup>-1</sup>, respectively, it seems that the former is combined with the fundamental while the latter is combined with the first overtone of the same vibrational mode. It is not certain yet, however, which vibrational motion is responsible for this optically active mode. The relative peak positions of pseudo-origins in LIF spectra of deuterated analogues are almost identical to those of the title molecule. Therefore, the I, II, and III progressions are not likely combined with another torsional mode along the  $\tau_2$ ,  $\tau_3$ , or  $\tau_4$  angles. It is interesting to note, though, that the relative peak positions of the pseudo-origins in the LIF spectrum of *p*-methoxy- $\alpha$ -toluenethiol are quite different from those of *p*-methoxybenzyl alcohol. However, the full assignment of the *p*-methoxy- $\alpha$ -toluenethiol spectrum seems to be not plausible at the present time.

**C. Torsional Barrier and a Geometrical Change with Electronic Excitation.** A simple sinusoidal function with a 2-fold symmetry is often used to model one-dimensional potential energy curve along the torsional angle ( $\phi$ ).<sup>7,20</sup> The *p*-methoxybenzyl alcohol molecule is expected to have a 2-fold symmetry with respect to the CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>OH axis in its equilibrium structure of the excited state, and thus the potential and Hamiltonian are assumed to be as follows.

$$V(\phi) = V_2/2(1 - \cos 2\phi)$$

$$H = -F(d^2/d\phi^2) + V(\phi)$$

Here,  $V_2$  is the torsional barrier height and  $F$  is the internal rotational constant. A  $40 \times 40$  Hamiltonian matrix is constructed using free-rotor wave functions,  $|m\rangle = (2\pi)^{-1/2} \exp(-im\phi)$ , as a basis set. The matrix is then diagonalized to give eigenvalues and corresponding eigenvectors for the torsional energy levels. The torsional barrier height ( $V_2$ ) and internal rotational constant ( $F$ ) are two adjusting parameters used for reproducing the experimental values. The torsional angle ( $\phi$ ) is defined as the angle between the  $\text{CH}_2\text{OH}$  moiety and the ring plane. The eigenvalues calculated when  $V_2 = 316 \text{ cm}^{-1}$  and  $F = 0.55 \text{ cm}^{-1}$  reproduce the experimental values nicely, Table 1. The tunnel-splitting of the torsional energy levels is calculated to be less than  $0.5 \text{ cm}^{-1}$  and could not be resolved in the present work. It should be noted that since *p*-methoxybenzyl alcohol has a  $C_{2v}$  (MS) symmetry in its equilibrium geometry, only odd overtones are allowed.<sup>20</sup> The peak positions of those bands belonging to the second and third progressions are well reproduced when  $(V_2, F) = (286 \text{ cm}^{-1}, 0.55 \text{ cm}^{-1})$  and  $(266 \text{ cm}^{-1}, 0.54 \text{ cm}^{-1})$ , respectively, Table 1. It is interesting to note that the torsional barrier height becomes smaller as the torsional mode is combined with another vibrational mode. Therefore, in the zeroth-order picture, it is likely that the 84 and  $163 \text{ cm}^{-1}$  bands are associated with the vibrational mode, which is at least modestly coupled to the  $\text{CH}_2\text{OH}$  torsional mode. The experimental finding that the  $163 \text{ cm}^{-1}$  band is more effective in lowering the torsional barrier compared to the  $84 \text{ cm}^{-1}$  band is consistent with our tentative assignment that the  $163 \text{ cm}^{-1}$  band is the first overtone of the  $84 \text{ cm}^{-1}$  band.

The relative intensity distribution of the peaks in each progression should reflect the Franck–Condon factor distributions in the optical transition.<sup>12</sup> As shown in Figure 6, all three progression bands show the similar pattern in their intensity distributions when they are plotted versus the torsional quantum number. The Franck–Condon factor distribution often gives information about the geometrical change of the molecule upon electronic excitation. For instance, if there is little difference between the minimum-energy structures of the ground and excited electronic states, the origin band would have a maximum intensity. Meanwhile, a long progression band would be observed if a large geometrical change occurs upon electronic excitation along the corresponding vibrational coordinate. The Franck–Condon factors of the bands in a progression are calculated using the following relations.

$$\text{excited state: } V'(\phi) = V'_2/2[1 - \cos 2(\phi - \theta)]$$

$$\text{ground state: } V''(\phi) = V''_2/2[1 - \cos 2\phi]$$

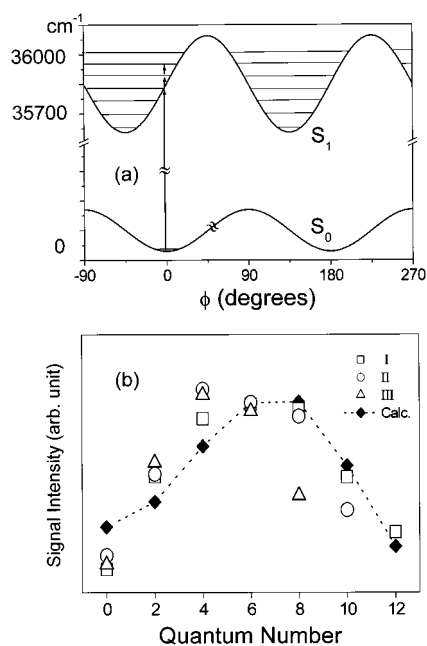
eigenfunction of the  $i$ th level in the excited state:

$$\psi'_i = \sum_m (a_{im} \pm ib_{im}) |m\rangle$$

eigenfunction of the  $j$ th level in the ground state:

$$\psi''_j = \sum_m (c_{jm}) |m\rangle$$

Here, the ground state is assumed to have an energy minimum at  $\phi = 0$ , while the minimum energy of the excited state is when the torsional angle  $\phi = \theta$ . The torsional barrier height of the ground state does not affect the eigenfunction of the ground vibrational state. Thus, the ground-state eigenfunction is calculated assuming the same barrier height as that in the excited state. In the excited state, the  $i$ th level eigenfunction is a complex linear combination of free-rotor basis functions. Therefore, from



**Figure 6.** (a) Potential energy curves of the ground and excited states along the torsional angle ( $\phi$ ). (b) Intensity distribution of the peaks in the I, II, and III progressions with a fit (filled diamonds connected with a line). The intensities of the peaks are arbitrarily scaled for the comparison. See the text for detail.

above, the Franck–Condon factors are obtained by calculating the overlap integral as follows.

$$\text{FC} \propto |\langle \psi''_j | \psi'_i \rangle|^2 = (\sum_m a_{im} c_{jm})^2 + (\sum_m b_{im} c_{jm})^2$$

The best fit to the experimental Franck–Condon distribution is obtained when  $\theta = 45^\circ$ , Figure 6. This indicates that the  $\text{CH}_2\text{OH}$  moiety is rotated about  $45^\circ$  with respect to the aromatic ring in the minimum-energy geometry of the excited state, compared to that of the ground state as shown in potential energy curves of ground and excited states, Figure 6. This means that if the molecule in the ground state has the minimum-energy geometry where the  $\text{CH}_2\text{OH}$  group is parallel (or perpendicular) to the aromatic ring, then the minimum-energy geometry of the title molecule in the excited state should be the gauche form in which the  $\text{CH}_2\text{OH}$  moiety is  $\sim 45^\circ$  rotated with respect to the aromatic ring. The intensity distribution pattern as a function of the torsional quantum number in the LIF spectrum of *p*-methoxybenzyl alcohol is very similar to that of the *p*-fluorobenzyl alcohol.<sup>7</sup> This might suggest that the electron-withdrawing group on the para position of the aromatic ring is responsible for the structural change of the molecule upon electronic excitation along the optically active mode. Further investigation including IR–UV double resonance experiment would be desirable for resolving the remaining conformational issues of the title molecule.

#### 4. Conclusion

LIF and mass-resolved REMPI excitation spectra of *p*-methoxybenzyl alcohol are reported. The long progression bands are observed, and these are ascribed to vibrational mode involving the torsional motion of the  $\text{CH}_2\text{OH}$  moiety with respect to the rest of the molecule. Three distinct progression bands are found to be originated from single conformer from the fluorescence depletion spectroscopy. The simple model calculation gives the torsional barrier height and internal rotational constant. The peak intensity distribution in each

progression gives the information about the geometrical change of the molecule induced by the electronic excitation. The Franck–Condon factor calculation suggests that the minimum-energy geometry of the molecule in the excited state is about 45° rotated compared to that in the ground state. It is not certain yet, however, which conformer is the most stable one in the ground state. The more detail spectroscopic study with more rigorous theoretical calculation would be desirable.

**Acknowledgment.** This work was financially supported by Korea Research Foundation (Project No. 1998-001-D00425) and the Brain Korea 21 program.

## References and Notes

- (1) Anderson, G. M.; Kollman, P. A.; Domelsmith, L. N.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 2344.
- (2) Ito, M.; Hirota, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2093.
- (3) Makriyannis, A.; Fesik, S. *J. Am. Chem. Soc.* **1982**, *104*, 6462.
- (4) Nyquist, R. A. *Appl. Spectrosc.* **1991**, *45*, 1649.
- (5) Turro, N. J.; Wan, P. *J. Photochem.* **1985**, *28*, 93.
- (6) Visser, T.; Van Der Maas, J. H. *Spectrochim. Acta* **1986**, *42A*, 599.
- (7) Im, H.-S.; Bernstein, E. R.; Secor, H. V.; Seeman, J. I. *J. Am. Chem. Soc.* **1991**, *113*, 4422.
- (8) Guchhait, N.; Ebata, T.; Mikami, N. *J. Am. Chem. Soc.* **1999**, *121*, 5705.
- (9) Breen, P. J.; Bernstein, E. R.; Secor, H. V.; Seeman, J. I. *J. Am. Chem. Soc.* **1989**, *111*, 1958.
- (10) Breen, P. J.; Warren, J. A.; Bernstein, E. R.; Seeman, J. I. *J. Chem. Phys.* **1987**, *87*, 1917.
- (11) Breen, P. J.; Warren, J. A.; Bernstein, E. R.; Seeman, J. I. *J. Chem. Phys.* **1987**, *87*, 1927.
- (12) Okuyama, K.; Mikami, N.; Ito, M. *J. Phys. Chem.* **1985**, *89*, 5617.
- (13) Grassian, V. H.; Bernstein, E. R.; Secor, H. V.; Seeman, J. I. *J. Phys. Chem.* **1989**, *93*, 3470.
- (14) Breen, P. J.; Warren, J. A.; Bernstein, E. R.; Seeman, J. I. *J. Am. Chem. Soc.* **1987**, *109*, 3453.
- (15) Dickinson, J. A.; Hockridge, M. R.; Kroemer, R. T.; Robertson, E. G.; Simons, J. P.; McCombie, J.; Walker, M. *J. Am. Chem. Soc.* **1998**, *120*, 2622.
- (16) Breen, P. J.; Bernstein, E. R.; Seeman, J. I. *J. Chem. Phys.* **1987**, *87*, 3269.
- (17) Breen, P. J.; Bernstein, E. R.; Seeman, J. I.; Secor, H. V. *J. Phys. Chem.* **1989**, *93*, 6731.
- (18) Yoon, M.-C.; Choi, Y. S.; Kim, S. K. *J. Chem. Phys.* **1999**, *110*, 7185.
- (19) Yoon, M.-C.; Choi, Y. S.; Kim, S. K. *J. Chem. Phys.* **1999**, *110*, 11850.
- (20) Bucker, P. R. *Molecular Symmetry and Spectroscopy*; Academic Press: New York, 1979.