Discrimination of Rotamers of Aryl Alcohol Homologues by Infrared−Ultraviolet Double-Resonance Spectroscopy in a Supersonic Jet

Nikhil Guchhait, Takayuki Ebata,* and Naohiko Mikami*

Contribution from the Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

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Abstract: Infrared−ultraviolet double-resonance spectroscopy has been applied to discriminate rotamers of jet-cooled aryl alcohol homologues, ϕ-$(CH_2)_n$OH, where ϕ represents phenyl group and $n = 1$, 2, and 3 correspond to benzyl, phenethyl, and 3-phenylpropyl alcohols, respectively. Experimental results indicate that different OH stretching frequencies are associated with different rotamers and that the ability of intramolecular hydrogen bonding with the benzene π-electron decreases with an increase in alkyl chain length. In each aryl alcohol, the most prominent species in jets corresponds to the non-hydrogen-bonded rotamer having higher OH stretching frequency.

I. Introduction

Aryl alcohols are of particular interest with respect to their significance in synthetic utilities for organic chemistry as well as their important roles in natural products.[1−4] Since they belong to a typical class of flexible molecules exhibiting various conformational complexity, a huge number of investigations of their conformers have been performed by various methods and sophisticated spectroscopies, such as electron diffraction,[5] NMR,[6,7] infrared (IR),[8−11] and electronic spectroscopies.[12−14] Despite extensive studies, the ambiguity regarding possible conformational isomers of aryl alcohol homologues ϕ-$(CH_2)_n$-OH has not yet been resolved. Iwamura's group reported IR spectra of aryl alcohols at room temperature and assigned the bands with different OH stretching frequencies to different structural isomers.[15−17] They also interpreted that the dominant conformer having a lower OH stretching frequency corresponds

to the hydrogen-bonded form and that the other conformer having a higher OH frequency is assigned to the free form without a hydrogen bond. NMR[6,7] and electron diffraction[5] studies for benzyl alcohol supported the high abundance of the hydrogen-bonded form compared to the free form. Spectroscopic techniques involving high-resolution IR,[18] microwave,[19] laser-induced fluorescence,[20,21] multiphoton ionization,[22] and rotationally resolved fluorescence excitation[23] spectroscopies are also very much useful to throw light into the conformational complexity of flexible molecules in the ground and excited states.

In a recent study for benzyl alcohol in a supersonic jet, Bernstein's group predicted that only the perpendicular free form is populated in the jet, and they assigned several low-frequency bands to be the torsional motion of hydroxy alkyl group.[13] Hirota et al. employed molecular force field calculations proposed by Allinger and co-workers and predicted that the planar form is the minimum energy form of the molecule.[24] However, ab initio calculations suggested a hydrogen-bonded gauche form corresponding to the low-energy stable form.[25] So, despite such a large number of experimental and theoretical results, the structural ambiguity for benzyl alcohol is still not resolved. Very

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recently, Dickinson et al.[14] predicted five conformers of phenethyl alcohol by performing high-resolution spectroscopy in a jet together with ab initio calculations. Thus, it is necessary to find an appropriate method to investigate the conformational analysis of the rotamers of aryl alcohols.

Recent development of multiresonance laser spectroscopic techniques in combination with the molecular beam method allows us to apply vibrational spectroscopy even to jet-cooled molecules as well as size -selected molecular clusters.[26−31] In the case of neutral jet-cooled species, IR spectroscopy is often performed by the population labeling method. This is known as infrared−ultraviolet (IR−UV) double-resonance spectroscopy, in which the UV laser light is used to monitor the population changes caused by the IR absorption. This method has been used to observe OH stretching vibrations of hydrated organic compounds, such as phenol−$(H_2O)_n$ clusters. The observed OH bands exhibit characteristic spectral shifts depending on intermolecular hydrogen-bonding structures, and their cluster structures have been analyzed on the basis of ab initio quantum chemical calculations.

In this paper, we apply IR−UV double-resonance spectroscopic technique to the conformational investigation of rotamers of aryl alcohols. Our main interest in this paper is to produce and discriminate different structures of aryl alcohol homologues by putting stress on the OH stretching vibration, which untangles the structural ambiguity and provides information regarding the acidity of different structures and the intramolecular hydrogen-bonding ability in different electronic states.

II. Experimental Procedures

The details of the experimental setup were described elsewhere.[31] The jet-cooled molecules were generated by the expansion of the gaseous samples mixed with helium carrier gas into vacuum through a pulsed nozzle. The samples were heated to 330 K to obtain enough vapor pressure. For the measurement of resonant enhanced multiphoton ionization (REMPI) spectra, the jet-cooled molecules were ionized by (1+1) REMPI with a UV light generated by second harmonics of a Nd:YAG pumped dye laser (Continuum PL 9000/Lumonics HD500) and the ion of desired mass was selected by a Q-mass filter and detected by an electron multiplier (Murata Ceratron). Then the output signal was processed by a boxcar intregator (PAR 4420) and finally was stored in a personal computer.

The IR spectra for the electronically ground state (S_0) molecules were measured by IR−UV double-resonance spectroscopy, and those of the excited state (S_1) molecules were measured by UV−IR double-resonance spectroscopy.[38] In these measurements, the population of a particular species in a supersonic jet was monitored by laser-induced fluorescence (LIF) via the S_1 state with the tunable UV light. For the measurements of the IR spectra in S_0, the tunable IR pulse is introduced 50 ns prior to the UV pulse. In this case, the LIF intensity is the measure of the population in S_0. When the IR frequency is resonant to the vibrational transition of S_0, a part of the S_0 molecules are pumped to the vibrational level, resulting in the depletion of the fluorescence signal. Thus, by scanning the IR laser frequency while monitoring the fluorescence intensity, a fluorescence-detected IR (FDIR) spectrum is obtained.

In case of the measurement of the IR spectra in S_1, the IR laser pulse is introduced 5 ns after the UV pulse. Here, the LIF intensity is the measure of the population in S_1 state. When the IR frequency is resonant to the vibrational transition of S_1 state and the fluorescence quantum yield of the vibronic level is smaller than that of the lower level, the total fluorescence intensity is weakened. Thus, the fluorescence-dip IR spectrum of the molecule in S_1 state is obtained by scanning the IR laser frequency while monitoring the total fluorescence.

The tunable UV light was a second harmonic of a XeCl excimer laser pumped dye laser (Lambda Physik LPX 100/FL 2002). The IR beam was generated with a $LiNbO_3$ crystal by a difference frequency mixing between a part of the second harmonic of a Nd:YAG laser (Quanta Ray GCR 230) and the output of another dye laser (Continuum ND-6000) pumped by the same Nd:YAG laser. The tunable IR output passed through a CaF_2 Brewster angle window and dichroic mirrors to eliminate the visible light. Both the UV and IR beams were introduced into the vacuum chamber in a counter propagating way and coaxially focused by lenses ($f = 250$ mm for IR and $f = 500$ mm for UV) on the supersonic jet. The fluorescence signal was detected by a photomultiplier tube, processed through the boxcar integrator, and finally accumulated by the same computer described above.

For the IR population labeling spectral measurements,[32] two LIF spectra were measured: (1) the LIF spectrum with the IR laser frequency is resonant to the particular vibrational transition, and (2) the LIF spectrum with the IR frequency is off-resonant. Since the LIF band intensity of the IR laser labeled species in the spectrum (1) becomes very weak, the IR population labeling spectrum can be obtained by subtracting the spectrum (1) from the spectrum (2).

Samples of benzyl, phenethyl, and 3-phenylpropyl alcohols were purchased from Aldrich Chemical Co and were used without further purification.

All of the theoretical ab initio calculations for different equilibrium conformers were done by Gaussian 94 program at HF/6-31G level.[33]

III. Ab Initio Calculated Structures

A. Benzyl Alcohol. Benzyl alcohol is essentially a phenyl-substituted methanol. However, the presence of π electrons on the benzene ring put a special emphasis on stable structures involving intramolecular hydrogen bonding. Several conformers having different orientations of the OH group with respect to the C−C_α bond and the benzene ring are possible, where C_α is the carbon atom to which the hydroxyl group is attached. These are planar, perpendicular, and gauche conformers, as well as freely rotating isomer. Figure 1 illustrates the two stable structures of benzyl alcohol obtained by ab initio (HF/6-31G) calculations. Conformer I is the planar form where the OH group is lying in the plane of the benzene ring, so that the molecule has no possibility of intramolecular hydrogen bonding. On the other hand, in conformer II, called the gauche conformer, the OH group is lying out-of-plane of the benzene ring and is pointing to the π-electron. So, this conformer has a possibility of intramolecular hydrogen bonding between alcoholic hydrogen and the benzene π-electron. The perpendicular conformer, which was suggested by Bernstein's group, was not obtained as a stable form. As seen in Table 1, the calculated OH stretching frequency for the gauche conformer is slightly lower than that of the planar conformer. It is also seen that the gauche conformer is more stable than the planar conformer by 482 cm^{-1}.

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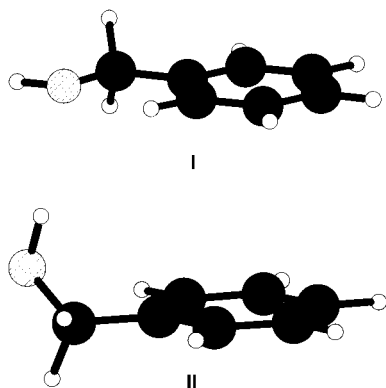
Figure 1. Ab initio calculated geometries (HF/6-31G) for benzyl alcohol: (I) planar form, (II) minimum energy gauche conformer. See Table 1 for calculated ΔE and ν_{OH}.

Table 1. Observed and ab Initio (HF/6-31G) Calculated OH Stretching Frequencies (ν_{OH}) and Energies[a] (ΔE) for Aryl Alcohols in the S_0 State

S_1-S_0 transition energy[a]	intensity[b]	ν_{OH}(obsd)	ν_{OH}(calcd)	ΔE[c]	calcd conformer
Benzyl Alcohol					
37527(0-0)	vs	3650	4043	+482	I
(−46)	w	3585	4013	minimum	II
Phenethyl Alcohol					
37622(0-0)	vs	3627	4021	minimum	I
(+42)	vs	3627	4032	+130	II
			4021	+288	III
			4036	+361	IV
			4016	+761	V
Phenethyl Alcohol−Water (1:1) Cluster					
(+34)	s	3723			
	s	3608			
	s	3521			
(+48)	s	3727			
	s	3608			
	s	3551			
3-Phenylpropyl Alcohol					
37546(0-0)	vs	3680	4018	minimum	I
(−142)	w	3630	4017	+72	II
(+23)	m	3659	4027	+178	III
(+35)	s	3682	4031	+226	IV
(+45)	w	3662	4019	+228	V
			4039	+409	VI

[a] Values are in cm^{-1}. [b] Intensity: vs, very strong; s, strong; m, medium; w, weak. [c] ΔE is the difference in energy with respect to the minimum energy conformer.

B. Phenethyl Alcohol. Phenethyl alcohol is the next higher homologue of benzyl alcohol, which is a phenyl-substituted ethyl alcohol. A number of possible conformers are expected with respect to the rotation of the C−C single bonds. The ab initio (HF/6-31G) calculated equilibrium geometries of phenethyl alcohol are shown in Figure 2. The relative energies and the OH frequencies of the conformers are also listed in Table 1. The ab initio calculation of phenethyl alcohol has been recently done by Dickinson et al., who performed higher level calculation including electron correlation.[14] Though our level of calculation is lower than that done by them, we obtained all the possible isomers reported by them. The difference between their results and the present calculation is the relative energies among the conformers. Since their relative energies are so small with each other, it is hard to conclude which isomer is the most stable form with this calculation level. In all structures, the C_α atom is lying out of plane and mostly perpendicular to the benzene ring. All the tetrahedral centers are oriented in such a way that
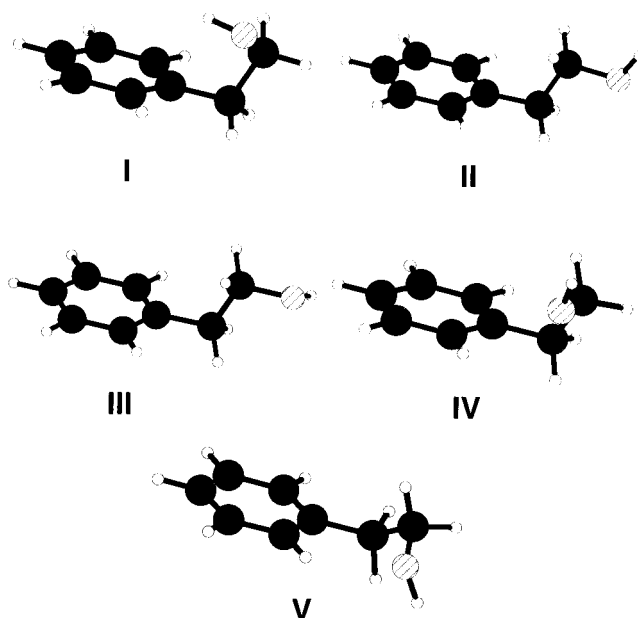

Figure 2. Ab initio calculated geometries (HF/6-31G) for phenethyl alcohol: (I) minimum energy conformer, (II−V) other calculated conformers. See Table 1 for calculated ΔE and ν_{OH}.

the bonds are staggered at both the carbon centers. Major differences among the isomers are whether the position of the OH group is inside or outside with respect to the benzene π-ring. The minimum energy conformer I, in Figure 2, has the OH group facing toward the benzene ring. Conformer I is also the minimum energy conformer reported by Dickinson et al. Although this conformer has the possibility of the intramolecular hydrogen bond to the π electrons, its calculated OH frequency is not the lowest one. The lowest OH frequency is associated with the conformer V in Figure 2, in which the hydroxyl hydrogen is far from the π electrons, and so there is no probability of intramolecular hydrogen bonding.

C. 3-Phenylpropyl Alcohol. The next higher homologue, 3-phenylpropyl alcohol, has three tetrahedral carbon centers, and it forms a large number of possible conformers by rotating the bonds at the alkyl carbon centers and the OH group. Figure 3 shows the ab initio (HF/6-31G) calculated stable conformers of 3-phenylpropyl alcohol. As can be seen in Figure 3, in the lowest energy conformer I, the OH group is not directed toward the benzene ring, i.e., this conformer may not have the intramolecular hydrogen bonding. In almost all other lower energy conformers, the hydroxy hydrogen atom is far from the π-electron of the benzene ring and there is no chance of making the hydrogen bond with the benzene π-electron. The possible hydrogen-bonded conformer VI in Figure 3 is about ~409 cm^{-1} higher in calculated energy than the minimum energy conformer I and has much higher OH stretching vibrational frequency compare to the free conformer I.

IV. Experimental Results

A. Benzyl Alcohol. Figure 4 shows the (1+1) REMPI spectrum of benzyl alcohol ($m/z = 108$), representing an intense peak at 37 527 cm^{-1} (band A) and some other moderately strong bands. Bernstein's group assigned the band A as the 0−0 band of the perpendicular conformer.[13] The prominent bands in the spectrum are more or less same with their result, except for a new band at −46 cm^{-1} (band B) with respect to the 0−0 band. This new band was not reported by Bernstein's group. We carefully examined the band B by mass analysis and confirmed
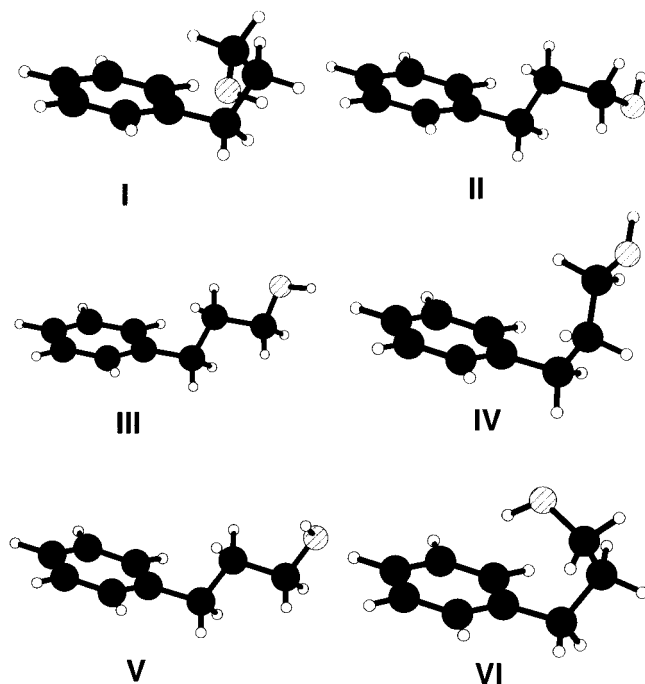
Figure 3. Ab initio calculated geometries (HF/6-31G) for 3-phenyl-propyl alcohol: (I) minimum energy conformer, (II–VI) other calculated conformers. See Table 1 for calculated ΔE and ν_{OH}.

Figure 4. (1+1) REMPI spectrum of jet-cooled bare benzyl alcohol in the origin region of the S_1–S_0 transition. The bands with asterisk are hot bands,[13] and the number of very low intense bands are due to benzyl alcohol–water clusters.[2,45]

that this band B is not due to the clusters with water but due to the bare benzyl alcohol molecule. The bands due to the clusters with water appear at different positions.[2,34] Parts a and b of Figure 5 show the FDIR spectra obtained by fixing the UV light to bands A and B, respectively. The OH stretching frequency for the band A appears at 3650 cm^{-1}, whereas the band B has its OH stretching frequency at 3585 cm^{-1}. The observed IR frequencies are summarized also in Table 1.

The IR dip intensity of the OH band at 3585 cm^{-1} was found to be ∼90% and was much greater than that at the 3650 cm^{-1} band (∼50% dip). We also measured the fluorescence lifetimes of the two bands. The lifetimes of the band A and the band B were found to be 50 and 30 ns, respectively. These results indicate that species associating with the two bands should be different conformers to each other. To confirm these, population labeled LIF spectra were observed, which are shown in Figure 6. Here, the IR laser frequencies were fixed to each OH stretching bands and the LIF spectra were observed. When the IR light was fixed at 3585 cm^{-1} and the UV light was scanned, only the band B decreases its fluorescence intensity as shown in Figure 6a. On the other hand, when the IR light was fixed at 3650 cm^{-1}, the band A and all the blue-side bands decrease their fluorescence intensities, while the intensity of the band B is unchanged as shown in Figure 6b. This means that band A and all the blue-sided bands belong to the same isomer and band B belongs to other isomer.

B. Phenethyl Alcohol. Figure 7 shows the (1+1) REMPI spectrum for the S_1–S_0 excitation of phenethyl alcohol (m/z = 122). The strongest band A at 37 622 cm^{-1} is assigned to the 0–0 band of the dominant species. Other low intense bands appear at +34, +42, and +48 cm^{-1} in the blue side of the band A. Figure 8 shows the FDIR spectrum of the OH stretching vibrations of phenethyl alcohol. As shown in Figure 8a, the OH stretching band of the dominant species corresponding to band A was observed at 3627 cm^{-1} (∼90% dip). Figure 9a shows the IR population labeled LIF spectrum obtained by fixing the
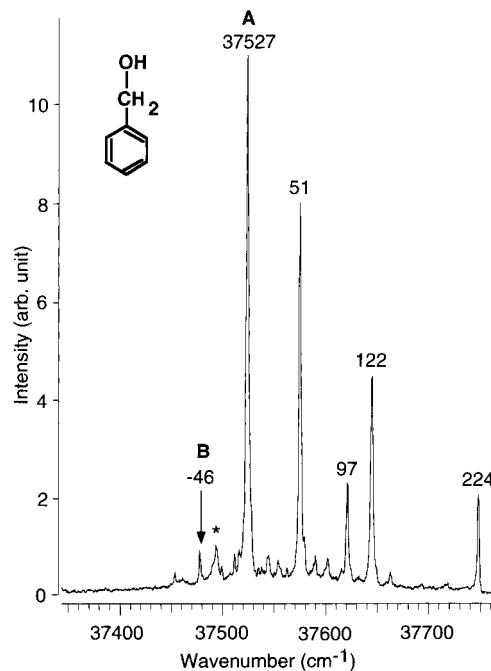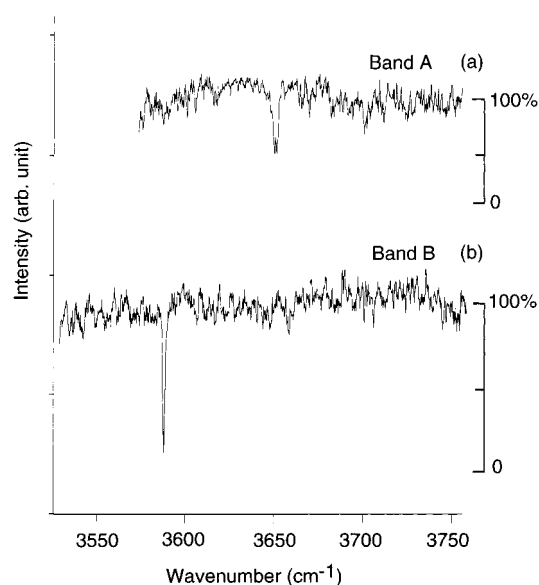

Figure 5. FDIR spectra for benzyl alcohol for the S_0 state. The exciting UV laser was fixed to (a) 37 527 cm^{-1} (band A) and (b) −46 cm^{-1} (band B) bands of the S_1–S_0 LIF spectrum. In all cases, the IR laser was irradiated for ∼50 ns prior to the UV laser light.

IR frequency to 3627 cm^{-1}. It is seen that band A and band B (+42 cm^{-1} band) simultaneously decrease their intensities, representing that both bands correspond to the same conformer. Figure 8b shows the S_1 state IR spectrum of the OH stretching band obtained by fixing the UV frequency at band A. Here, the IR pulse was introduced 5 ns after the UV pulse. A similar spectrum was obtained for band B, and it was found that both bands have same OH stretching frequency at 3612 cm^{-1} in the S_1 state. These results represent that the dominant species of the molecule exhibits the band A and B. Parts c and d of Figure 8 show the FDIR spectra when the UV frequencies are fixed to band C and band D, respectively. As seen in the figures, three

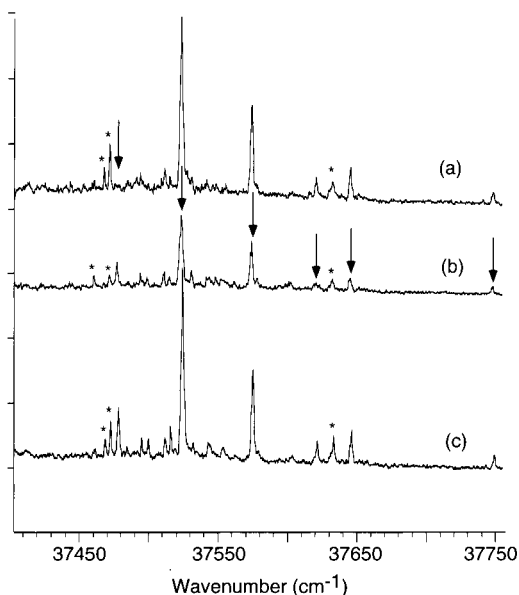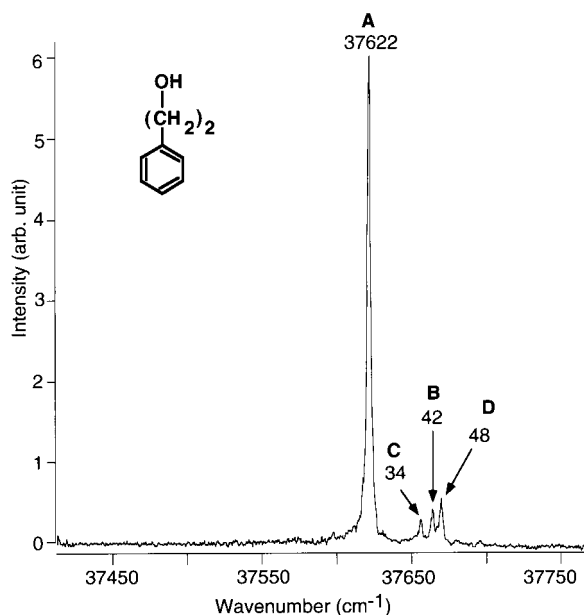(34) Guchhait, N.; Ebata, T.; Mikami, N. Manuscript in preparation.

Discrimination of Rotamers of Aryl Alcohol Homologues

J. Am. Chem. Soc., Vol. 121, No. 24, 1999 5709

Figure 6. IR population labeled LIF spectra of jet-cooled benzyl alcohol obtained by fixing ν_{IR} (a) to 3585 cm^{-1} and (b) to 3650 cm^{-1}, where ν_{IR} is IR laser frequency. (c) The LIF spectrum of benzyl alcohol (a few impurity bands which we could not remove in the LIF spectrum are marked by asterisks). The bands that showed depletion by ν_{IR} are indicated by arrows. For the IR population labeled spectra, the fixed frequency IR laser was irradiated for ~50 ns prior to the tunable UV laser light.

Figure 8. FDIR spectra for phenethyl alcohol for the S_0 state. The exciting UV laser was fixed to (a) 37 622 cm^{-1} (strongest band, band A), (c) +34 cm^{-1} band (band C), (d) +48 cm^{-1} band (band D) of the excitation spectrum lines. In all cases, ν_{IR} was irradiated for ~50 ns prior to the UV laser light. (b) S_1 state FDIR spectra, when UV light was fixed at band A and ν_{IR} was irradiated for ~5 ns after UV light.

Figure 7. (1+1) REMPI spectrum of jet-cooled bare phenethyl alcohol in the origin region of the S_1–S_0 transition.

Figure 9. (a) Population labeled LIF spectra of phenethyl alcohol obtained by fixing ν_{IR} to 3627 cm^{-1}. Here, ν_{IR} was irradiated for ~50 ns prior to the tunable UV laser light. (b) LIF spectrum of phenethyl alcohol without the IR laser light.

OH stretching bands are observed for bands C and D. The results mean that band C and band D correspond to an phenethyl alcohol–water (1:1) cluster. Details are discussed in a later section.

C. 3-Phenylpropyl Alcohol. Figure 10 shows the (1+1) REMPI spectrum of 3-phenylpropyl alcohol ($m/z = 136$). The spectrum shows an intense band at 37 546 cm^{-1} (band A) with a moderately strong band at +35 cm^{-1} (band C). In addition, several weak bands are observed at −142 cm^{-1} (band F), −43 cm^{-1} (band B), +23 cm^{-1} (band D), and +45 cm^{-1} (band E). FDIR spectra obtained by monitoring these bands are shown in Figure 11. All of these bands show only one OH stretching
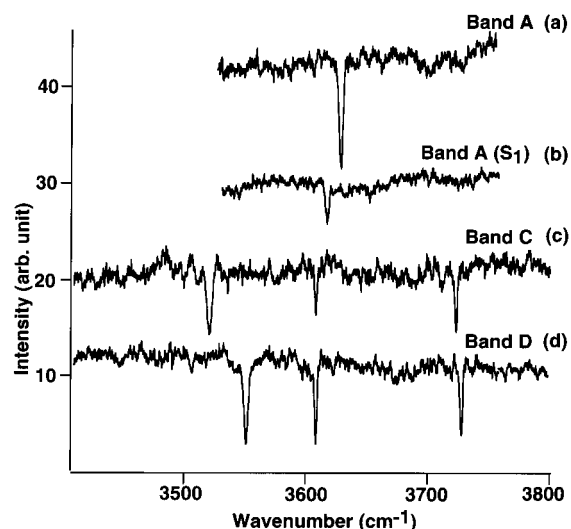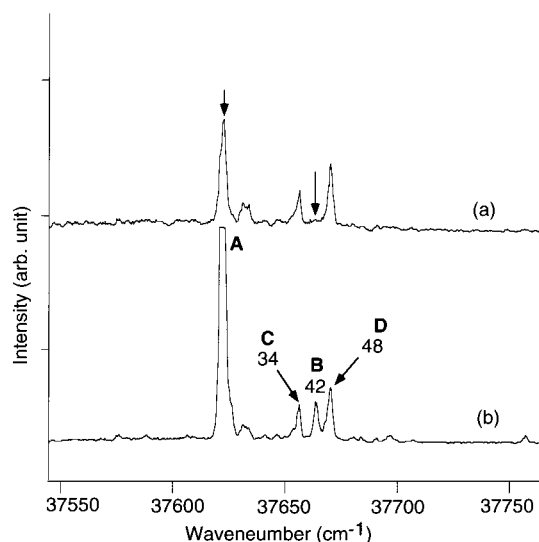
frequency in the IR dip spectra. The splitting of the OH band for the band E is due to the fact that the IR intensity becomes weak at this frequency due to the absorption of water vapor. Band A and band B show their OH stretching frequency at 3680 cm^{-1} (Figure 11a,b). However, the observed IR dip intensity for band A is larger than that of band B. Figure 11c shows the highest observed OH stretching at 3682 cm^{-1}, which was obtained for the band C. As shown in Figures 11d−f, the IR dip spectra of bands D, E, and F show OH stretching bands at 3659, 3661, and 3630 cm^{-1}, respectively. Overall, all of the observed OH stretching frequencies of 3-phenylpropyl alcohol are higher than those of lower homologues of aryl alcohol.

V. Discussions

A. Benzyl Alcohol. A number of experimental and theoretical works have been done to solve the structural ambiguity of benzyl
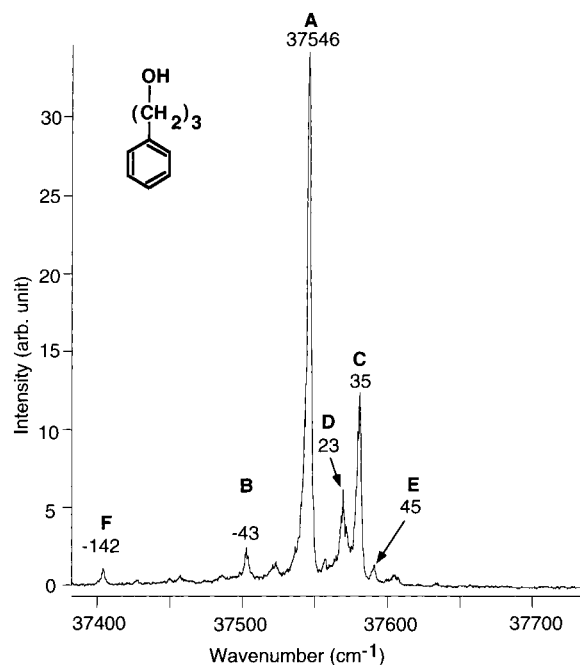
Figure 10. (1+1) REMPI spectrum of jet-cooled bare 3-phenylpropyl alcohol in the origin region of the S_1–S_0 transition.
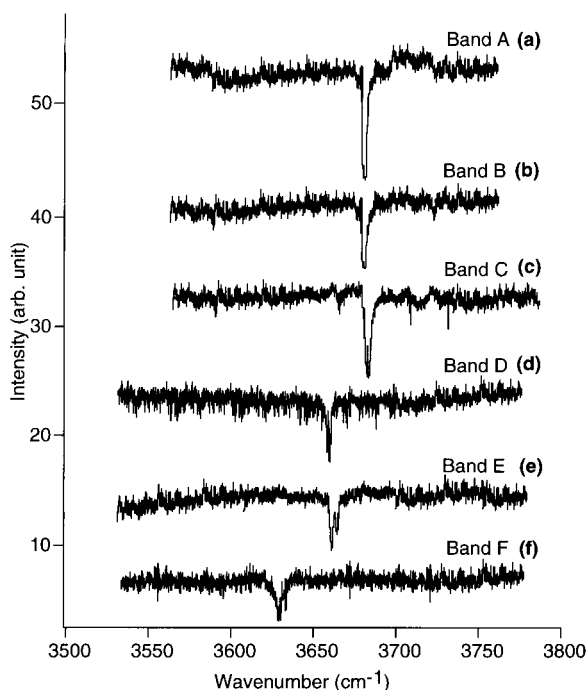

Figure 11. FDIR spectra for 3-phenylpropyl alcohol for the S_0 state. Exciting UV laser was fixed to (a) 37 546 cm^{-1} (band A), (b) −43 cm^{-1} (band B), (c) +35 cm^{-1} (band C), (d) +23 cm^{-1} (band D), (e) +45 cm^{-1} (band E), and (f) −142 cm^{-1} (band F) of the excitation spectrum lines. In all cases, the IR laser was irradiated for ~50 ns prior to the UV laser light. The splitting in some spectra is not due to the vibrational structure but due to the change of the IR laser intensity owing to the absorption by water vapor in the room.

alcohol. The IR spectrum in the condensed phase at room temperature shows two OH stretching vibrations, one of which was assigned to the freely rotating conformer and the other highly populated one to the intramolecular hydrogen-bonded conformer.[15–17] Bernstein's group measured mass-resolved S_1–S_0 REMPI spectra of jet-cooled benzyl alcohol.[13] They considered that only the free perpendicular form is populated in jet, which has a low-frequency torsional mode of the hydroxy alkyl

group. Their study on D-atom-substituted derivatives of benzyl alcohol strongly supported their assignment for the torsional mode. As was described previously, we observed new species corresponding to −46 cm^{-1} band (band B). This band was not observed by Bernstein's group. Though we do not have a reasonable answer of this discrepancy, this species might be sensitively dependent on the expansion condition since the band B is very weak compared to band A.

Two different OH stretching frequency of 3650 and 3585 cm^{-1} for band A and band B means that they are coming from two different conformers. Both spectra represent a single IR absorption band with different OH frequency, suggesting that they are due to a different conformer of the bare benzyl alcohol and not due to any clusters with water. The difference in the lifetimes of two bands also supports that these bands correspond to two different species. Comparatively the red-shifted OH frequency of band B indicates a weak hydrogen bonding. Our results indicate that the observed OH frequency at 3585 cm^{-1} is due to the conformer having a hydrogen bond and correlates with the calculated minimum energy gauche form (conformer II) which has lower OH stretching frequency due to the possibility of hydrogen bonding. However, the OH band of 3650 cm^{-1} is associated with the calculated high-energy conformer I having higher OH stretching frequency. In addition, the REMPI spectrum shows that the conformer with hydrogen bond is much less populated compared to the other without hydrogen bond. The results suggest that the intramolecular hydrogen bond formation may induce the extra energy elevation due to the rotation at C_α from the planar conformer which is supposed to be the minimum energy form.

B. Phenethyl Alcohol. Dickinson et al. observed LIF and mass-selected R2PI spectroscopies of phenethyl alcohol in jets along with high-level MP2 calculations and interpreted their spectra by considering five conformers.[14] They discriminated different conformers by comparing the rotational band contour of experimental electronic transition bands with simulated spectra. Our REMPI spectrum (Figure 7) of phenethyl alcohol is similar to the reported spectrum by Dickinson et al. The strongest band A shows its ground-state OH stretching frequency at 3627 cm^{-1}. The IR population labeled LIF spectrum (Figure 9a) indicates that band B also has the same OH stretching frequency at 3627 cm^{-1} in the ground state. So, simply, we can say that bands A and B belong to the same conformer. But, Dickinson et al. interpreted that bands A and B correspond to two different conformer because the rotational contours of these bands are slightly different from each other and their simulated spectra reproduced well the observed ones. So, at this moment, it is hard for us to conclude whether band A and band B belong to same conformer or different conformers having the same OH stretching frequency in the S_0 state. However, we found that the OH stretching frequencies of bands A and B in the S_1 state occur at the same frequency of 3612 cm^{-1} (Figure 8b). It is very hard to describe that it would be an accidental coincidence that the two conformers have the same OH stretching frequency both in the ground and excited states. Therefore, our experimental results lead us to conclude that band A and band B correspond to same conformer as both bands have same OH stretching frequency in the ground and excited states. Band B may be a low-frequency torsional mode belonging to the band A.

A reported condensed phase study supplied three OH stretching frequencies at 3636, 3626, and 3607 cm^{-1}, where the higher frequencies corresponding to free OH and lower frequencies are for the hydrogen-bonded forms.[16] The observed strongest

band in the REMPI spectrum of phenethyl alcohol, having the higher OH stretching frequency (3627 cm^{-1}), may be assigned to the free form. It should be noted, however, that this OH frequency is rather low for the non-hydrogen-bonded form, since the non-hydrogen-bonded OH stretching usually exhibits its frequency in the range $3680-3650$ cm^{-1}, as seen in the cases of benzyl and 3-phenylpropyl alcohols.

Three observed OH stretching frequencies in the FDIR spectra of bands C and D (Figure 8c,d) indicate that these bands correspond to phenethyl alcohol−water (1:1) cluster. By the comparison with the phenol−water[30] and benzyl alcohol−water[34] (1:1) clusters, we assigned two higher observed bands to the OH bands of the water site and the lowest one to the hydrogen-bonded OH stretch band of the phenethyl alcohol site. Dickinson et al.[14] reported that band D in the excitation spectrum is the overlapped by the transitions of bare phenethyl alcohol and its 1:1 cluster with water. If band D is the overlapped band (one for the bare molecule and the other for the 1:1 water cluster), we should expect four OH stretching bands in the IR dip spectrum, one from the bare molecule and three from the 1:1 cluster. However, as seen in Figure 8d, only three bands appeared in the IR dip spectrum. So we have to conclude that band D is due to the 1:1 cluster with water. The differences in the OH stretching frequencies for bands C and D indicate the existence of the two isomers for water 1:1 clusters. Although Dickinson et al. reported two other bands at $+57$ and $+73$ cm^{-1} in their excitation spectrum for two other conformers, those bands are very weak in our REMPI spectrum, which does not allow us to perform IR dip spectroscopy for those bands.

Thus, the experimental results for phenethyl alcohol lead us to the conclusion that only one conformer is dominant in the jet which has high OH stretching vibrational frequency. Although the present ab initio calculations predict that the intramolecular hydrogen-bonded conformer is the minimum energy conformer, its OH frequency (calculated) is not so different from that of other conformers. The HF/6-31G level calculation seems to be insufficient to obtain resonable OH frequency involving intramolecular hydrogen bonding. Band C and band D are coming from two different conformers of phenethyl alcohol−water (1:1) cluster.

C. 3-Phenylpropyl Alcohol. The FDIR spectra of 3-phenylpropyl alcohol in Figure 11 show different OH stretching frequencies. Table 1 shows the observed OH frequencies. Bands A and B have the same OH stretching frequency at 3680 cm^{-1} in the S_0 state, and at a first glance, they belong to the same conformer. However, if band B is the origin of the conformer and band A is its low-frequency vibronic band, a progression of this mode will be expected from the intensity pattern. However, the next progression is absent in the REMPI spectrum (Figure 10). Furthermore, the IR dip intensity of band A is different from that of band B. So, we conclude that band A

and band B belong to different conformers having the same OH stretching frequency in the S_0 state. Bands D, C, E, and F show their OH bands at 3659, 3682, 3661, and 3630 cm^{-1}, respectively. Among them, band F has lowest OH stretching vibrational frequency. Since the intensity of band F is very weak, the results suggest a small population of the conformer having intramolecular hydrogen bond. The observed variety of the OH stretching frequencies indicates that these bands correspond to different conformers, i.e. a number of conformers are populated in the jet.

So, the measured REMPI and IR dip spectra of 3-phenylpropyl alcohol represent that at least six conformers are populated in the jet. Here, the most prominent band in the REMPI spectrum corresponds to the conformer which has the high OH stretching frequency. Another noticeable point is that all of the observed OH stretching frequencies are higher than those of lower homologues, i.e. benzyl and phenethyl alcohols. The result indicates that the ability of the intramolecular hydrogen bonding is less in 3-phenylpropyl alcohol. Such high OH stretching frequencies indicate that these conformers do not have the possibility of intramolecular hydrogen bonding with benzene π-electron. However, due to the limited experimental results, it is difficult to assign which OH band corresponds to which conformer and it is tough to correlate the calculated geometries and frequencies with the experimental results.

VI. Conclusion

We discussed the discrimination of different rotamers of the aryl alcohol homologues from their OH stretching vibrational spectra and theoretical calculations. It is clearly demonstrated that different conformers have different OH stretching frequencies. It is concluded that in all aryl alcohols the most dominant conformer is the non-hydrogen-bonded free form having a high OH stretching frequency. In general, the calculated structures and frequencies have a poor correlation with the experimental results and we need to improve our calculation so that we can solve the remaining ambiguity regarding the structures of these molecules. It is also concluded that the strength of the intramolecular hydrogen bond with benzene π-electron decreases with an increase in alkyl chain length.