Discrimination of Rotational Isomers of 2-Phenylethanol by Dispersed Fluorescence Spectroscopy

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Received: October 8, 2003

Laser-induced dispersed fluorescence (DF) spectra for excitations of several low-energy bands near the S_1 origin (0_0^0) of 2-phenylethanol have been measured in a supersonic free jet expansion. The spectrum measured for excitation of a weak band at 0_0^0+48 cm^{-1} has been found to resemble the 0_0^0-excited emission spectrum. This weak band has been assigned to the $S_1 \leftarrow S_0$ origin of a higher energy conformer. Spectral analyses with the aid of ab initio (DFT/B3LYP/6-311++G**) calculations reveal that the frequencies of the benzenoid 6a and a few other ring vibrational modes are sensitive to molecular shape. Comparisons of these frequencies with those obtained by theoretical calculations suggest that the higher energy species is the anti conformer of the molecule. This conformational assignment based on vibronic analysis agrees with the quantum chemistry predictions at the MP2/cc-pVTZ level of theory that the anti is the second preferred conformational isomer having 7.03 kJ/mol more energy than the most stable gauche form. No spectral feature corresponding to emission from an excited 1:1 water complex of the molecule was apparent in the dispersed fluorescence when the exciting laser was tuned across the 0_0^0+48 cm^{-1} band. This behavior is in contrast to conclusions of two previous studies that the 48 cm^{-1} band in the LIF excitation spectrum is due to a 1:1 water complex.

Introduction

2-Phenylethanol is the hydroxy analogue of the simplest aromatic amine neurotransmitter 2-phenylethylamine. Following the predictions of the ab initio quantum chemistry calculations, Dickinson et al.[1] assigned five weak bands in the vicinity of the $S_1 \leftarrow S_0$ electronic origin in a mass-selected jet-cooled resonance enhanced two-photon ionization (R2PI) spectrum to five rotational isomers of the molecule. The basis for assignments was the simulations of the experimentally observed rotational contours of these bands using the ab initio predicted structural parameters corresponding to different conformers. The most intense band in the excitation spectrum at 37 633.2 cm^{-1} was assigned to a gauche form in which the hydroxyl hydrogen is in a position suitable for formation of a nonclassical π-type hydrogen bond with the aromatic π-electron cloud. However, in a subsequent investigation using UV−UV and fluorescence detected IR (FDIR)-UV double resonance techniques, Guchhait et al.[2] assigned those weak bands to low-frequency vibronic transitions of the major conformer and absorptions due to a 1:1 hydrogen-bonded water complex. The authors proposed that only one isomeric form of the molecule was present in the jet environment.

In a more recent report, the former group revised their assignments on the basis of UV−UV and IR−UV double resonance experimental results.[3] A weak band 48 cm^{-1} above the S_1 origin of the major (gauche) conformer was noticed to be present in the R2PI spectrum for probing the molecular ion as well as cluster ion signals, and the band was assigned as an overlap for transitions due to an isomeric species of 2-phenylethanol and a 1:1 water cluster. Moreover, in the IR−UV double resonance spectra, four different O−H stretching frequencies were noticed when the 48 cm^{-1} band was probed: one frequency for the free 2-phenylethanol molecule (molecular ion mass channel) and three for the 1:1 H-bonded complex. In contrast, in the FDIR measurement probing the same band, Guchhait et al. observed only the three O−H stretching frequencies of the 1:1 complex, but no O−H vibration corresponding to the free 2-phenylethanol molecule was observed.

A conformational study of flexible biomolecules and their hydrated clusters in the gas phase is currently a highly topical area of research,[4−10] and single and double resonance spectroscopic methods such as R2PI, UV−UV, and IR−UV are widely used in combination with mass spectrometric methods to discriminate the isomers. However, the apparently contradicting results of the three studies cited above on a relatively simpler system indicate that further investigation is required to resolve the issue. For this purpose, we have employed here a nonionizing conventional method, dispersed fluorescence spectroscopy, to discriminate the conformers.

The existence of a second conformational species of 2-phenylethanol in supersonic expansion has been suggested recently by Brown et al.[11] by use of Stark-modulated microwave spectroscopy. By combining the experimental results with predictions of ab initio calculations at the MP2/6-311++G-(d,p) level, the species was identified as the anti conformer. However, to detect the species in supersonic jet expansion, the preexpansion temperature of the sample vapor was elevated to as high as 300 °C. Under that preexpansion condition, several of the higher energy conformers, as predicted by theory,[1,11] could be appreciably populated. Therefore, the conclusion of this experimental study is likely to be of little significance to the present as well as other three investigations (ref 1−3), which are concerned in probing the second conformational species in the jet expansion that occurs from a room-temperature gas mixture.

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10.1021/jp037025f CCC: $25.00

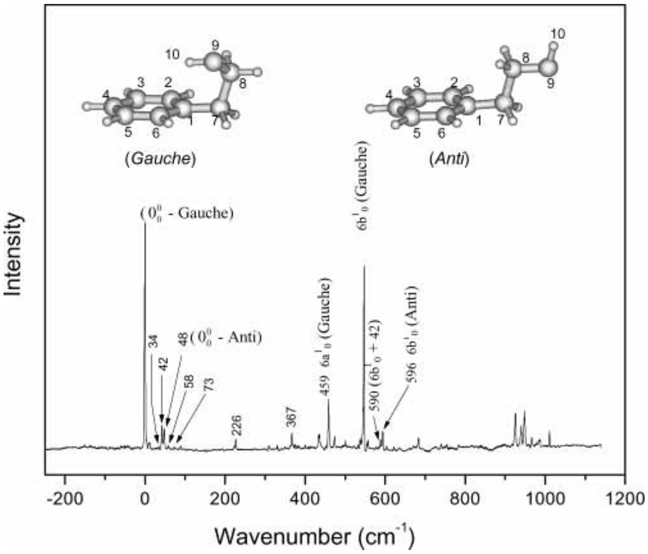

Figure 1. Fluorescence excitation spectrum of jet-cooled 2-phenylethanol. The two optimized geometries of the molecule as obtained by the ab initio calculations at the MP2/cc-pVTZ level are also shown. Positions of the electronic origin bands of the conformers are indicated.

Experimental Section

The experimental setup used to measure the laser-induced fluorescence excitation and dispersed fluorescence spectra has been described previously.[12] Briefly, the 2-phenylethanol vapor is mixed with helium at a pressure of 2 atm and expanded into a vacuum through a pulsed nozzle (General Valve) of orifice diameter 0.5 mm to generate a supersonic free jet. The jet-cooled molecules were excited by a tunable UV laser obtained as the doubled output of an optical parametric oscillator (Spectra Physics, MOPO-SL) pumped by the third harmonic of an injection seeded Nd:YAG laser (Spectra Physics, PRO-210). To measure the dispersed fluorescence spectra, a 0.75 m monochromator (Spex, Model 750M) with a grating of groove density of 2400/mm was used to disperse the fluorescence before detection. Typical spectral resolution of the results presented here is 5−7 cm^{-1}. The fluorescence was detected using a Hamamatsu R928 photomultiplier tube, and the output signal of the photomultiplier was processed by a boxcar averager (SRS 250) and the data were stored in a personal computer.

2-Phenylethanol (98%) was procured from Lancaster and purified further by vacuum distillation.

Results and Discussion

The fluorescence excitation (FE) spectrum for $S_1 \leftarrow S_0$ transition of 2-phenylethanol cooled in a supersonic jet expansion of helium is presented in Figure 1. The strongest band in the spectrum at 37 633.2 cm^{-1} has been assigned earlier to the electronic origin of the most stable gauche conformer.[1] The low-frequency features near the electronic origin band (34, 42, and 48 cm^{-1}) are also similar to those in the R2PI spectra of previous reports.[1,3]

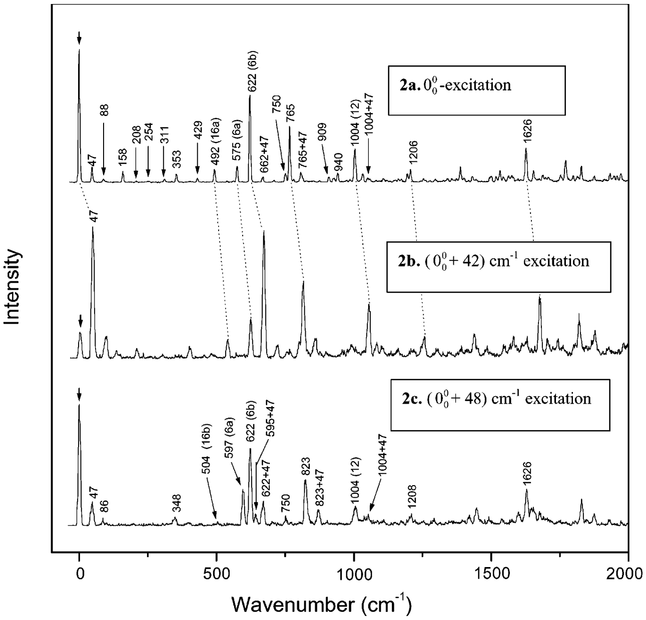

Figure 2. Dispersed fluorescence spectra for excitations at the (a) electronic origin (0^0_0) band of the major conformer and (b) 0^0_0+ 42 cm^{-1} and (c) 0^0_0+ 48 cm^{-1} bands.

The dispersed fluorescence (DF) spectra for excitations of the electronic origin band and two other weaker bands at 42 and 48 cm^{-1} are presented in Figure 2. The major vibronic features in the first case (Figure 2a) can be assigned as fundamentals and combinations of the ground-state vibrations common in many of the monosubstituted benzene derivatives.[13] The low-frequency bands (47 and 88 cm^{-1}) are assigned to torsional progression of the $-CH_2CH_2OH$ group with respect to the phenyl ring, and the same progression appears again in the DF spectrum when the 42 cm^{-1} band is excited, but with a different Franck−Condon profile. The sequence origin band (ν^1_1) in Figure 2b is 47 cm^{-1} displaced from the excitation frequency. This confirms that the 42 cm^{-1} band in the FE spectrum is due to a vibronic transition over the electronic origin of the same species, and the frequency for the corresponding transition in the ground state is 47 cm^{-1}. However, when the 48 cm^{-1} band is excited, the DF spectrum (2c) does not show any intense ν^1_1 type transition (sequence origin) at a comparable frequency. Instead, the vibronic pattern is similar to that in the emission spectrum from the electronic origin (0^0_0) of the gauche conformer, although there are distinct differences (discussed below). Thus, we assign the 48 cm^{-1} band in the FE spectrum to the $S_1 \leftarrow S_0$ origin of a second conformer and provide below further evidences in support of this assignment.

Figure 3 shows the dispersed spectra for excitation of the most intense 548 cm^{-1} vibronic band and a weaker band at 596 cm^{-1}, which is exactly 48 cm^{-1} above the former in the FE spectrum. In the first case, the ν^1_1 type transition in fluorescence is 622 cm^{-1} displaced from the excitation frequency, and most of the other prominent features in the spectrum can be interpreted as a combination of this band with all of the transitions in Figure 2a (presented here again to make a comparison). For monosubstituted benzene derivatives, 622 cm^{-1} is a characteristic frequency for the nontotally symmetric 6b mode in the ground state.[13] Therefore, the 548 cm^{-1} band in the FE spectrum must be due to the $6b^1_0$ transition of the major (gauche) conformer. Interestingly, in the second case also, the ν^1_1 transition is 622 cm^{-1} displaced from the excitation frequency, and the remaining features of the spectrum closely match as combination of this band with those in Figure 2c (shown here again to make a comparison). Therefore, the 596 cm^{-1} band in the FE spectrum is most likely the $6b^1_0$ band of the second conformational species.

It has already been pointed out that, although the vibronic features in Figure 2c are similar in many respects to those in the emission spectrum from the main origin (Figure 2a), there are distinct differences. For example, the frequencies for the $6b^0_1$ (622 cm^{-1}) and 12^0_1 (1005 cm^{-1}) transitions are same in

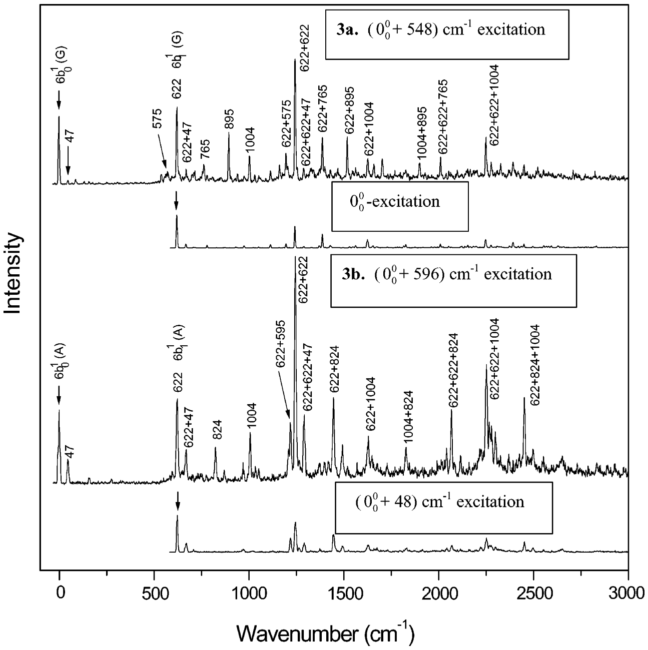

Figure 3. Dispersed fluorescence spectra for exciting the (a) 0_0^0+ 548 cm^{-1} and (b) 0_0^0+596 cm^{-1} bands. Emission spectra from the0_0^0 and 0_0^0+ 48 cm^{-1} bands are presented again in 3a and 3b, respectively, for better comparison.

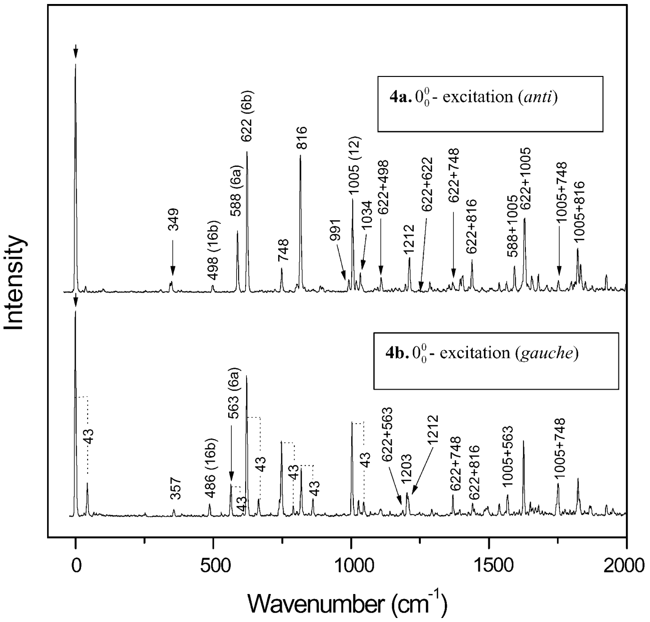

Figure 4. Dispersed fluorescence spectra for exciting the electronic origin bands of the (a) anti and (b) gauche conformers of *n*-propylbenzene.

both the spectra, but the 575 cm^{-1} band in Figure 2a, which can be assigned to the $6a_1^0$ transition, is shifted to 595 cm^{-1} in Figure 2c. Further, the bands at 765 and 823 cm^{-1} appear to be mutually exclusive in the two spectra. That these similarities and dissimilarities in spectral features between parts a and c in Figure 2 are indicative of emissions from electronic origins of two different conformers become more apparent when compared with the DF spectra of a nearly similar system, *n*-propylbenzene, for which the presence of two almost equally stable conformers, gauche and anti, are established beyond doubt by use of rotationally resolved UV[7] and microwave spectroscopy.[14] In Figure 4, we have presented the dispersed fluorescence spectra from the S_1 origin bands of *n*-propylbenzene conformers. It is clearly seen that the spectral features have many similarities to those in Figure 2, parts a and 2c. The frequencies for $6b_1^0$ (622 cm^{-1}) and 12_1^0 (1005 cm^{-1}) are same as 2-phenylethanol, but the position of $6a_1^0$ band is conformation dependent, 563 cm^{-1} for the gauche but 588 cm^{-1} for the anti conformer.[16] Moreover, the relative intensities of 748 and 816 cm^{-1} bands are reversed in two conformers. In monosubstituted benzene derivatives, the atomic displacements for the 6b and “12” modes do not involve the ring carbon atom to which a substituent is attached.[15] Therefore, the frequencies for these modes are unaffected by the conformation of the substituent. However, the 6a mode does involve the ring carbon atom to which a substituent is attached and also the atomic motions of the substituent. As a result, the frequency for the 6a mode is affected by the conformation of the substituent, and similar behavior has also been noticed in case of two conformers of allylbenzene.[17] Therefore, the resemblance in spectral features between the DF spectra of two molecules implies that the 48 cm^{-1} band in the FE spectrum is the electronic origin of a second conformational isomer of 2-phenylethanol.

Although the DF spectral data do not provide direct information about molecular shape; nevertheless, a comparison between theoretically predicted and experimentally observed vibrational frequencies for the modes which are sensitive to molecular shape is thought to be useful to provide further evidences for uncovering the conformational identity of the species. For this purpose, the energy ordering of the conformers has been reinvestigated by an ab initio quantum chemistry method at the MP2 level using Dunning correlation consistent cc-pVTZ basis set.[18] However, the predictions are not different from those obtained previously at the MP2/6-311++G(d,p) level of theory.[11] The anti conformer happens to be the second most stable species of energy 7.03 kJ/mol more than the most stable gauche conformer. The ground-state normal vibrational frequencies for these two conformers have been calculated ab initio by the DFT/B3LYP/6-311++G(d,p) method, and those are presented in Table 1 to make a comparison with the measured frequencies. It is seen that there are remarkable agreements between the experimental frequencies and theoretical predictions. For the 6b mode, predictions exactly match with experiment for both the conformers, and the same behavior is also noticed for the mode “12”. Most interestingly, for the 6a mode, the theory predicts that the frequencies for the gauche and anti conformers are significantly different, 570 and 595 cm^{-1}, and the corresponding measured frequencies are 575 and 597 cm^{-1}. Such correlation between theory and experiment has also been observed for the shape-sensitive vibrational modes of *n*-propylbenzene conformers.

It has been mentioned before that Mons et al.[3] assigned the 48 cm^{-1} band to an overlap for absorption by a 1:1 complex and a higher energy conformer of 2-phenylethanol, but Guchhait et al.[2] disagreed with this and assigned the band for only the 1:1 complex. In the present case, to be sure that the vibronic spectrum observed in dispersed fluorescence (Figure 2c) for excitation at this band position is not for the 1:1 complex, we have calculated the ground-state vibrational frequencies of the complex for the most favored geometry suggested in ref 3 (Figure 5) by the DFT/B3LYP/6-311++G(d,p) method and a few of those are presented in column VI of Table 1. The results suggest that the complex formation should not significantly alter the ring vibrational frequencies of the gauche conformer, and particularly, the predicted frequencies for the benzenoid 6a mode of the complex are far off from the observed frequency in Figure 2c. Furthermore, the dispersed fluorescence spectra do not

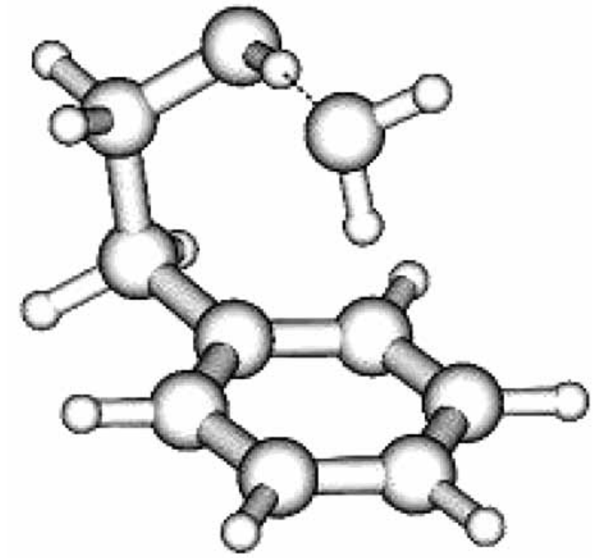

Figure 5. Optimized geometry for the most stable conformer of the 2-phenylethanol−water complex at the MP2/6-31G** level of ab initio calculations.

TABLE 1: Comparison between Observed and Calculated Frequencies (DFT/B3LYP/6-311++G Level) for the Two Conformers of 2-Phenylethanol in the Range of ∼500−1000 cm^{-1}[a]**

gauche		anti		assign-ments	water complex
obs. freq	cal. freq[b]	obs. freq	cal. freq[b]		cal. freq[b]
492	493	504	496	16b	497
575	570	597	595	6a	574
622	622	622	622	6b	622
765	764			ring mode	764
		823	827	ring mode	841
1004	998	1004	1003	“12”	995

[a] The calculated frequencies for the Water complex are also presented here to make a comparison. [b] A scaling factor of 0.98 has been used.

exhibit any new feature, which can be assigned to emission from the 1:1 complex when the laser frequency is tuned across the 48 cm^{-1} band. Therefore, we eliminate the possibility that the 48 cm^{-1} band in our LIF excitation spectrum has an overlap with the 1:1 water complex.

The apparent disagreement between the reports of previous two REMPI measurements can be interpreted with the results of the present laser-induced fluorescence study in the following way. A comparison of the low-frequency bands in our LIF excitation spectrum (Figure 1) to those reported in the R2PI spectrum of ref 2 (Guchhait et al.) clearly shows that the intensity of the 34 cm^{-1} band, which has been assigned to the 1:1 complex in both the refs 2 and 3 is very weak in the present case. Thus, the expansion condition of our experiment is not conducive for efficient formation of a water complex, and emission occurs only from the excited higher-energy conformational species when the laser frequency is tuned to 0_0^0 +48 cm^{-1} position. On the other hand, under the expansion condition of Guchhait *et al.'s* experiment the water complex formed efficiently, but most likely, the condition facilitated also the relaxation of the higher-energy conformer to the more stable gauche conformer.[19] As a result, the O−H stretching frequency corresponding to the free anti conformer is absent in their FDIR spectrum. However, this relaxation is partial under the expansion condition of Mons et al.'s experiment.

Acknowledgment. The authors gratefully acknowledge the financial support received from the Department of Atomic Energy Commission, Govt. of India, under the Grant No. 99/37/8/BRNS, and the Department of Science and Technology (DST). S.S.P. thanks the University Grant Commission, Govt. of India for the Research Fellowship.

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