Conformational Choice, Hydrogen Bonding, and Rotation of the $S_1 \leftarrow S_0$ Electronic Transition Moment in 2-Phenylethyl Alcohol, 2-Phenylethylamine, and Their Water Clusters

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Abstract: Laser-induced fluorescence and one- and two-color, mass- selected R2PI excitation spectra of the $S_1 \leftarrow S_0$ electronic transitions in 2-phenylethyl alcohol and 2-phenylethylamine have been recorded in a jet-cooled environment. Five conformers of 2-phenylethyl alcohol and four of 2-phenylethylamine have been identified, together with a number of 1:1 hydrated water clusters. The fifth origin band in the excitation spectrum of 2-phenylethylamine has been reassigned to a water cluster, primarily on the basis of its ion fragmentation pattern. Analysis of their partially resolved rotational band contours has been aided by ab initio molecular orbital calculations, conducted at levels of theory ranging from MP2/3-21G* to MP2/6-311G** for the ground state and CIS/6-311G** for the first electronically excited singlet state. The reliability of the CIS method has also been tested through benchmark calculations, including computations on a related, experimentally known conformational system, methyl 3-hydroxybenzoate. 2-Phenylethylamine and 2-phenylethyl alcohol both display anti and gauche conformations (distinguished by their orientation about the $C_\alpha - C_\beta$ bond) but the folded, gauche conformations, which allow the terminal hydroxyl or amino hydrogen atoms to be hydrogen bonded to the aromatic ring, are found to be the most stable. Their intramolecular binding energies are ~ 5.5 kJ mol^{-1}. The anti conformers display b-type rotational band contours, reflecting the ^1L_b character of their first excited singlet states. In contrast, the band contours of the gauche conformers display a hybrid character, which reflects a strong rotation of the electronic transition moment in the molecular frame, attributed to electronic state mixing. The rotation of the transition moment is strongly modulated by the binding of a water molecule to the folded molecular conformer and, in the bare molecule, by changes in the orientation of the terminal hydroxyl or amino group. This effect allows a ready distinction to be made between the hydrogen-bonded and the non- hydrogen-bonded gauche conformers.

Introduction

The low-temperature environment of a free jet expansion or a molecular beam provides an excellent “laboratory” for probing the conformational structures of flexible organic molecules, attached to an optical chromophore.[1−11] The rotational band contours of their laser-induced fluorescence (LIF) or resonantly enhanced, two-photon ionization (R2PI) spectra are sensitive to conformationally induced changes, not only in the rotational constants and the inertial axes but, more interestingly, in the alignment of the electronic transition moment, TM, in the *molecular* frame. Recent studies, conducted at very high resolution in Pratt’s laboratory[4] and at lower resolution in our own,[5,6] have focused on a rapidly growing range of substituted aromatic molecules and have identified the occurrence of strong, conformationally induced changes in the alignment of the $S_1 \leftarrow S_0$ TM. Molecular orbital calculations, conducted at the HF/6-31G* and CIS/6-31G* levels, have been remarkably successful at reproducing the experimental results[5,6] and suggest that the changes in TM alignment are associated with differing degrees of electronic state mixing in their first excited singlet state.[12]

Many of the systems under current investigation provide models for simple biological molecules, for example, 2-phenylethylamine, which is the simplest member of a range of aromatic amine neurotransmitters. They each possess an aromatic chromophore, a flexible side chain containing two (or

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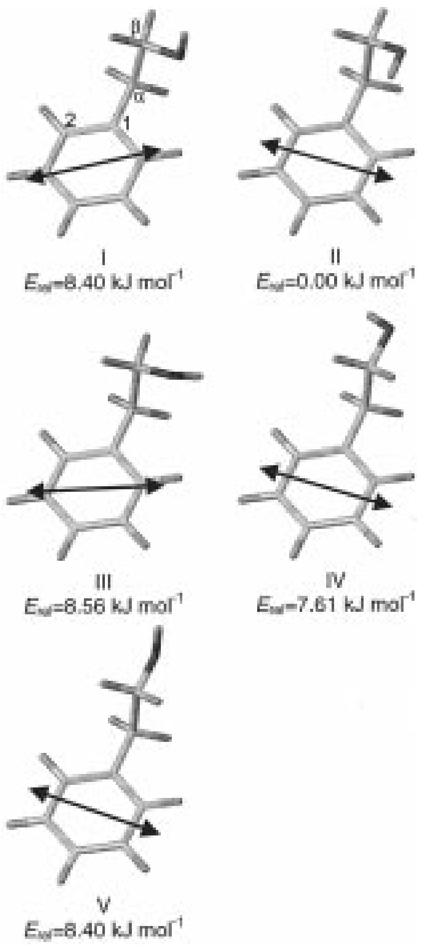

Figure 1. Conformers of 2-phenylethyl alcohol predicted by MP2/6-311G** calculations. The arrows show the TM alignments predicted by CIS/6-31G* calculations.

more) methylene groups, and a polar (or nonpolar) terminal group, e.g., an amide, carboxylic acid, alkyl, amino, or hydroxy group. The amino acids phenylalanine and tyrosine and the amine neurotransmitter dopamine, for example, are all variants on this theme. Understanding their conformational preferences is important in helping to understand the structures and properties of larger biosystems, in particular, the role of *intra*molecular hydrogen bonding. A further bonus provided by free jet expansion is the opportunity of generating solvated molecular clusters and probing the influence of bound solvent molecules, for example, water, on conformational choice. Investigations of individual clusters, identifying solvent binding sites, and the effect of solvation on conformational choice have been greatly facilitated by the use of mass-selected R2PI and hole-burning spectroscopy.[8] The use of variable intensity, two-color R2PI techniques has been particularly helpful in avoiding spectral saturation as well as the fragmentation of the excited cluster ions.[5]

To our knowledge, no studies of 2-phenylethyl alcohol have been reported, to date. The first LIF studies[7,9] of 2-phenylethylamine identified four separate origin bands, in the $S_1 \leftarrow S_0$ transition, which were assigned by Martinez et al.,[9] on the basis of power saturation measurements and relative spectral shifts, to two pairs of extended (anti) and folded (gauche) conformers, each split by alternative orientations of the terminal amino group. (The designations anti and gauche refer to the conformation of the methylene chain about the $C_\alpha-C_\beta$ bond; see Figure 1.) A similar study of tyramine (*p*-hydroxy-2-phenylethylamine) identified six conformer origin bands, consistent with the provisional spectral assignment of 2-phenylethylamine.[9] In subsequent microwave experiments, Godfrey et al.[10] were able to characterize the structures of the two gauche conformers of 2-phenylethylamine, each of which appeared to be stabilized by hydrogen bonding to the π-electron system of the aromatic ring. Ab initio molecular orbital calculations, conducted at the HF/4-21G, HF/6-31G**, and MP2/6-31G** levels of theory, supported these assignments but also predicted three other less stable conformers, one gauche and two anti.[10] Most recently, Sun and Bernstein,[8] using a combination of LIF, mass-selected R2PI, and hole-burning spectroscopy, found evidence for five origin bands. Four of these were assigned in a manner consistent with the earlier LIF and microwave studies, while the fifth and weakest band was assigned to the "missing" gauche conformer predicted by the ab initio calculations. This assignment ran counter to its earlier association with a water cluster.[7]

The present paper describes new structural studies of 2-phenylethyl alcohol and 2-phenylethylamine. The rotational band contours of the origin bands of both the bare molecular conformers and their hydrated clusters have been recorded for the first time, both in the LIF and in the R2PI, $S_1 \leftarrow S_0$ spectra of jet-cooled samples. Spectral analyses and assignments have been supported by mass-selected, one- and two-color R2PI experiments and aided by ab initio molecular orbital calculations, conducted at levels of theory ranging up to MP2/6-311G** for the ground state and CIS/6-311G** for the first excited singlet state. The reliability of the ab initio computations has been explored through a series of benchmark calculations, including computations on a related, experimentally known conformational system, methyl 3-hydroxybenzoate.[13] The new experiments allow a detailed exploration of the molecular conformational landscapes and, in particular, of the importance of *intra*molecular hydrogen-bonded interactions between the terminal group and the aromatic ring.

Analytical and Experimental Procedures

Molecular Orbital Calculations. The conformational landscapes of 2-phenylethylamine and 2-phenylethyl alcohol were explored initially, in the electronic ground state, by performing a series of ab initio molecular orbital calculations using Gaussian 94[14] at five different levels of theory: MP2/3-21G*, HF/6-31G*, HF/6-31+G**, HF/6-311G**, and MP2/6-311G**. The following procedures were pursued.

(i) The torsion angle around the C_1(benzene)$-C_\alpha$(alkyl) bond was set at 90°, while the remaining torsion angles were set initially to 180° to generate the "all-trans", anti conformer; see Figure 1. The latter angles were subsequently modified in 120° steps, to generate the full series of possible gauche conformations.

(ii) Each one of these geometries was then submitted to full ab initio optimization, beginning at the MP2/3-21G* level of theory. When the symmetry of some of the conformers was taken into account, this procedure predicted five distinct stable conformers for each molecule (see section 3). Zero-point energy corrections were also computed, except in the highest level calculations (MP2/6-311G**).

(iii) The ground state structures were subsequently optimized for the first electronically excited singlet state, at the CIS/6-31G* level of theory, to yield sets of rotational constants for the electronically excited,

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Table 1. Ab Initio Rotational Constants and Relative Energies of 2-Phenylethylamine Conformers

conformer	constant	MP2/3-21G*	HF/6-31G*	HF/6-31+G**	HF/6-311G**	MP2/6-311G**	exptl[a]
I	A''/MHz	3629.9	3537.7	3521.4	3553.0	3444.0	
	B''/MHz	1031.8	1045.9	1038.7	1045.5	1070.7	
	C''/MHz	837.4	888.6	888.5	885.5	899.0	
II	A''/MHz	3194.7	3370.1	3374.4	3377.1	3249.0	3287.7
	B''/MHz	1091.6	1053.8	1043.1	1052.2	1091.1	1066.4
	C''/MHz	949.9	943.6	939.8	942.6	970.2	957.6
III	A''/MHz	3258.2	3405.2	3400.3	3409.1	3286.5	3313.7
	B''/MHz	1099.7	1064.8	1055.9	1063.1	1105.9	1079.3
	C''/MHz	944.8	940.8	939.7	940.1	969.2	959.2
IV	A''/MHz	4298.1	4493.7	4492.7	4502.8	4350.8	
	B''/MHz	846.7	855.5	853.5	855.4	860.8	
	C''/MHz	758.5	766.3	764.3	766.2	770.3	
V	A''/MHz	3250.1	4463.1	4462.9	4475.0	4313.5	
	B''/MHz	844.3	853.8	851.9	853.7	858.6	
	C''/MHz	756.6	764.5	762.6	764.3	768.3	
I	E_{rel}/kJ mol^{-1}	2.49 [1.13][b]	6.67 [5.99]	6.98 [8.56]	5.70 [5.20]	6.88	
II	E_{rel}/kJ mol^{-1}	0.00 [0.00]	1.23 [0.84]	1.92 [3.83]	0.81 [0.55]	0.16	
III	E_{rel}/kJ mol^{-1}	0.81 [0.97]	0.00 [0.00]	0.00 [0.00]	0.00 [0.00]	0.00	
IV	E_{rel}/kJ mol^{-1}	5.93 [5.22]	1.21 [0.37]	0.58 [2.15]	0.81 [0.08]	5.85	
V	E_{rel}/kJ mol^{-1}	2.97 [2.34]	1.70 [0.69]	1.37 [1.52]	1.21 [0.30]	4.65	

[a] From ref 10. [b] The first figure quoted is the relative equilibrium energy; the figure in brackets includes zero-point corrections scaled by 0.9.

S_1 state of each conformer, together with the magnitudes and directions of the $S_1 \leftarrow S_0$ TM. In two of the conformers of 2-phenylethyl alcohol, these calculations were performed using a variety of basis sets to investigate convergence.

(iv) As a prelude to this series of calculations, similar procedures were also used to predict the equilibrium structures and the $S_1 \leftarrow S_0$ TM orientations of the four stable conformers of methyl 3-hydroxybenzoate, each one of which has already been fully characterized experimentally, through analysis of their rotational resolved fluorescence excitation spectra.[13]

Fluorescence Excitation Spectroscopy. Samples of 2-phenylethyl alcohol and 2-phenylethylamine were heated to temperatures in the range 70−100 °C and entrained in helium at stagnation pressures of 2−4 bar, before their free jet expansion into a vacuum chamber through a pulsed nozzle valve (General Valve, Series 9, 0.8 mm orifice) operating at 10 Hz. The expansion axis was intersected by a tunable UV laser beam, at selected distances lying 2−12 mm from the nozzle aperture, allowing the spectrum to be recorded at different rotational temperatures. The fluorescence was collected along a third, mutually perpendicular axis. The laser source was a grating-tuned, frequency-doubled dye laser (Lambda Physik FL3002) pumped by an excimer laser at 308 nm, and operating at wavelengths of ca. 265 nm. An intracavity Etalon provided a spectral line width of ca. 0.08 cm^{-1}. The LIF signals (detected by a photomultiplier through a 295 nm high pass filter) and the excitation beam intensities (monitored by a photodiode) were both averaged using a boxcar integrator (Stanford SRS 250) and recorded on a PC.

Mass-Selected R2PI Spectroscopy. Mass-selected, one-color R2PI spectra were recorded using a grating-tuned, frequency-doubled dye laser (Lambda Physik FL2002) pumped by a Nd:YAG laser at 532 nm and a similar nozzle expansion system (aperture, 0.5 mm) and vacuum chamber, but this time equipped with a differentially pumped time-of-flight mass spectrometer (R.M. Jordan). Water vapor could be incorporated into the gas stream by passing the helium through a water sample held in a bypass system at room temperature. Photoionization signals were sampled using a digitizing oscilloscope (Tektronix TDS 520) and recorded on a PC as a function of the pump laser wavelength and the flight time (mass). Two-color experiments were also conducted using a second, Nd:YAG-pumped and frequency- doubled dye laser (LAS LDL 20505) to provide the photoionization source. The two, doubled, dye laser beam outputs were combined coaxially to intersect the axis of the nozzle beam expansion but were separated by a time delay of ca. 30 ns, to facilitate separation of the one- and two-color ionization signals.

Ab Initio Calculations

Benchmark Calculations. To assess the reliability of the ab initio calculations for predicting the conformational landscape of the ground electronic state, the results for 2-phenylethylamine, obtained at the HF/6-31G*, HF/6-31+G**, HF/6-311G**, and MP2/6-311G** levels, were compared with the available microwave data[10] for two of its gauche conformers, II and III; see Table 1 and Figure 2. Although the best agreement was found at the highest level of theory, the predicted structures remain close to experiment even at the lower levels. The calculations predict five stable conformers in all, with the structures shown in Figure 2. These are consistent with the

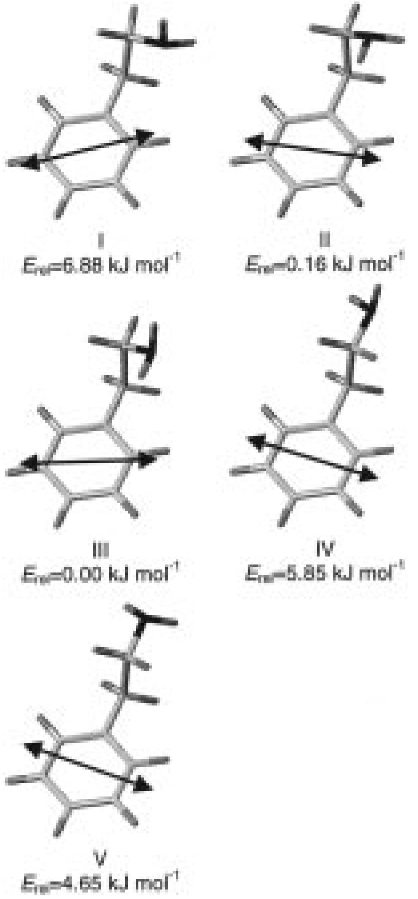

Figure 2. Conformers of 2-phenylethylamine predicted by MP2/6-311G** calculations. The arrows show the TM alignments predicted by CIS/6-31G* calculations.

Table 2. Ab Initio Rotational Constants and Relative Energies of 2-Phenylethyl Alcohol Conformers

conformer	constant	MP2/3-21G*	HF/6-31G*	HF/6-31+G**	HF/6-311G**	MP2/6-311G**
I	A''/MHz	3642.6	3565.7	3563.3	3584.5	3466.6
	B''/MHz	1049.4	1063.4	1055.8	1062.3	1085.8
	C''/MHz	847.9	901.5	897.6	897.7	911.6
II	A''/MHz	3272.7	3430.8	3427.4	3438.0	3309.1
	B''/MHz	1118.0	1077.7	1060.8	1072.9	1109.0
	C''/MHz	942.2	945.2	942.9	943.8	970.1
III	A''/MHz	3647.9	3547.3	3487.1	3558.9	3440.0
	B''/MHz	1042.5	1054.9	1040.3	1053.1	1076.2
	C''/MHz	837.7	898.1	912.2	896.4	909.1
IV	A''/MHz	4309.6	4507.0	4507.3	4520.0	4362.3
	B''/MHz	838.9	853.0	851.0	853.1	856.4
	C''/MHz	752.0	764.0	762.0	764.0	766.6
V	A''/MHz	4358.5	4535.5	4536.0	4545.9	4390.1
	B''/MHz	842.5	854.8	852.6	855.0	859.4
	C''/MHz	754.9	766.1	763.9	766.2	769.6
I	E_{rel}/kJ mol^{-1}	2.57 [3.68][a]	6.17	5.04 [5.67]	5.12 [4.31]	8.40
II	E_{rel}/kJ mol^{-1}	0.00 [0.00]	0.00	0.00 [0.00]	0.00 [0.00]	0.00
III	E_{rel}/kJ mol^{-1}	0.16 [1.84]	8.89	8.98 [9.53]	7.93 [7.35]	8.56
IV	E_{rel}/kJ mol^{-1}	7.14 [5.93]	4.09	2.97 [3.12]	3.60 [2.86]	7.61
V	E_{rel}/kJ mol^{-1}	9.14 [8.66]	3.45	1.44 [1.68]	2.49 [1.68]	8.40

[a] The first figure quoted is the relative equilibrium energy; the figure in brackets includes zero-point corrections scaled by 0.9.

Table 3. Ab Initio Transition Moment Orientations of Methyl 3-Hydroxybenzoate Conformers

conformer	θ'_{elec}(CIS/6-31G*)[a]	θ'_{elec} (exptl)[b]	conformer	θ'_{elec}(CIS/6-31G*)[a]	θ'_{elec} (exptl)[b]
A	53.2	57 ± 4	C	45.2	46 ± 4
B	73.1	72 ± 4	D	62.8	63 ± 3

[a] θ'_{elec} is defined as the angle in degrees between the *a*-axis and the TM. [b] From reference 13.

Table 4. Ab Initio Transition Moment Orientations in 2-Phenylethyl Alcohol

basis set[a]	θ_{elec}(conformer I)[b]	θ_{elec}(conformer II)[b]
STO-3G	−35.9	−6.8
3-21G	−18.9	13.5
6-31G	−30.2	1.8
6-31G*	−31.7	3.7
6-31G**	−29.0	3.3
6-311G**	−27.4	3.8

[a] Using the CIS method. [b] θ_{elec} is defined as the clockwise angle in degrees between the short axis of the benzene ring (perpendicular to the substituent) and the TM; refer to Figure 1.

Table 5. Molecular Parameters Predicted from MP2/6-311G** and CIS/6-31G* Calculations on 2-Phenylethylamine

conformer	I	II	III	IV	V
$\tau_1(C_\beta C_\alpha C_1 C_2)$[a]	101.1	80.0	84.4	87.8	87.7
$\tau_2(NC_\beta C_\alpha C_1)$[a]	69.6	59.7	61.0	177.1	180.0
$\tau_3(HNC_\beta C_\alpha)$[a]	130.3	0.9	−127.2	124.3	0.0
E_{rel}/kJ mol^{-1} [a]	6.88	0.16	0.00	5.85	4.65
A''/MHz[a]	3444.0	3249.0	3286.5	4350.8	4313.5
B''/MHz[a]	1070.7	1091.1	1105.9	860.8	858.6
C''/MHz[a]	899.0	970.2	969.2	770.3	768.3
A'/MHz[b]	3296.7	3154.7	3197.4	4179.0	4145.0
B'/MHz[b]	1058.4	1080.7	1092.4	854.6	852.7
C'/MHz[b]	900.5	953.6	951.7	762.3	760.6
$\|\mu_{trans}\| \times 10^{30}$/C m[c]	1.05	1.25	1.22	1.12	1.15
$\mu_a^2:\mu_b^2:\mu_c^2$ [c]	44:46:10	6:88:6	21:72:7	0:100:0	0:100:00
θ_{elec}[c]	−34	−10	−22	−2	0
$r_{NH\cdots\pi C}$/Å[a]		2.67	2.64		

[a] From the MP2/6-311G** calculation of the ground electronic state. $\tau_3(HNC_\beta C_\alpha)$ is the torsional angle bisecting the two amino hydrogen atoms. [b] Calculated from the MP2/6-311G** values using % ΔA, % ΔB, and % ΔC obtained from the HF/6-31G* and CIS/6-31G* calculations. [c] From the CIS/6-31G* calculations of the excited electronic state.

earlier calculations, conducted at the HF/4-21G, HF/6-31G**, and MP2/6-31G** levels, by Godfrey et al.[10] The results of a similar series of calculations for 2-phenylethyl alcohol are shown in Table 2 and Figure 1.

A second series of "benchmark" calculations addressed the reliability of the CI singles method for predicting the character of the electronic transition into the first excited state, particularly the orientation of the transition moment. Calculations at this level have been criticized in the past, because of their inability to reproduce experimental excitation energies[15] and to describe higher excited states. In the present context, however, where only the lowest, covalent, states are involved and extensive dynamic correlation corrections are not required,[16] the TM calculations should be reliable. This prediction is confirmed by the remarkable agreement between experiment[13] and theory (using a 6-31G* basis set) found for methyl 3-hydroxybenzoate and shown in Table 3. Similar levels of agreement have been reported earlier for each of the anti and gauche conformers of *n*-propylbenzene, *n*-butylbenzene,[6] and 3-phenylpropionic acid.[5] Finally, Table 4 presents the results of a series of calculations of the TM orientation in two of the gauche conformers of 2-phenylethyl alcohol, exploring the sensitivity to the choice of basis set; convergence is achieved at the 6-31G* level. Given the confirmation that the CIS/6-31G* gives very satisfactory results with respect to the TM orientation, this level of theory was applied throughout.

2-Phenylethylamine. The ab initio predictions for 2-phenylethylamine are summarized in Figure 2 and Table 5; the alignment of the TM in the molecular frame is shown by an arrow in Figure 2 and given by the angle θ_{elec} (the angle between the short axis of the benzene ring, perpendicular to the C_1-C_α bond, and the TM). The conformers I, II, and III each have a gauche side chain, associated with a different orientation of the amino group. In conformers II and III, one of the amino hydrogen atoms is directed toward the benzene ring, and at the highest level (MP2/6-311G**), these conformations are predicted to lie lowest in energy, with conformer II located slightly above conformer III. Their TM's are rotated away from the short axis of the ring, through predicted angles, $\theta_{elec} \approx -10°$ and $-22°$, respectively, and the rotational contours of their S_1

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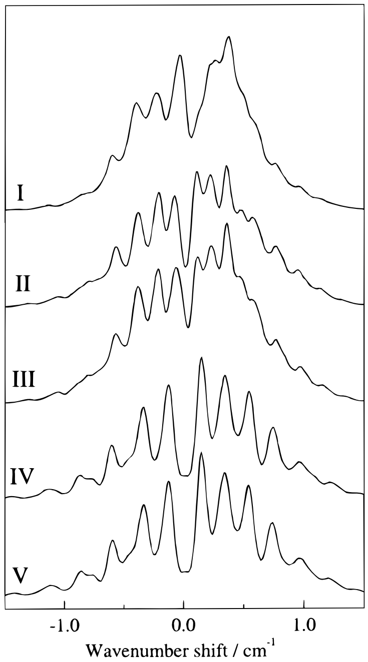

Figure 3. Simulated rotational band contours for each conformation of 2-phenylethylamine, based on the ab initio data detailed in Table 5; $T_{rot} = 2.5$ K, laser line width 0.08 cm^{-1}.

$\leftarrow S_0$ band origins are predicted to have hybrid characters; see Figure 3. The third gauche conformer (I), which has "lone pair" electron density directed toward the ring, is predicted to lie much higher in energy with its TM rotated even further away from the short axis, $\theta_{elec} \approx -34°$, leading to a strongly hybridized $S_1 \leftarrow S_0$ band origin (Figure 3). The remaining conformers, IV and V, have an anti side chain with a symmetric and a nonsymmetric orientation of the amino hydrogen atoms. At the HF level (Table 1) these two conformers are predicted to have energies comparable to those of the hydrogen-bonded gauche conformers, II and III, but with the inclusion of MP2 electron correlation the hydrogen-bonded structures become the most favored. In contrast to the gauche conformers, the TM's of the anti conformers are aligned parallel to the short axis of the ring, $\theta_{elec} \approx 0°$, and they are predicted to give rise to $S_1 \leftarrow S_0$ band origins with pure type b character, as shown in Figure 3.

2-Phenylethyl Alcohol. The ab initio results are summarized in Table 6; as with the amine, five stable conformations are predicted, with the structures shown in Figure 1. Three of them (I, II, and III) have a gauche side chain, each one distinguished by a different orientation of the terminal alcohol hydrogen atom. Conformer II, which has the terminal atom directed toward the benzene ring, is again predicted to be the most stable at all levels of theory, and particularly when electron correlation is included. Its TM is aligned close to the short axis of the benzene ring with an angle $\theta_{elec} \approx 3-4°$, and the rotational structure of its $S_1 \leftarrow S_0$ origin band is predicted to be predominantly b-type. Conformers I and III, in which the alcohol hydrogen atom is directed away from the ring, are predicted to lie at much higher energies. Their electronic TM's are now rotated away from the short axis, with $\theta_{elec} \approx -31°$ (I) and $-22°$ (III); the rotational contours of their $S_1 \leftarrow S_0$ band origins are predicted to be strongly hybridized; see Figure 4. The two remaining conformations, IV and V, each have an anti side chain with either a nonsymmetric or a symmetric orientation of the terminal OH group. They too are predicted to lie well above conformer II, and their TM's are predicted to lie parallel to the short axis of the benzene ring, $\theta_{elec} \approx 0°$; their $S_1 \leftarrow S_0$ origin bands are both expected to display pure type b character; see Figure 4.

Table 6. Molecular Parameters Predicted from MP2/6-311G** and CIS/6-31G* Calculations on 2-Phenylethyl Alcohol

conformer	I	II	III	IV	V
$\tau_1(C_\beta C_\alpha C_1 C_2)^a$	100.6	85.0	98.9	88.1	88.1
$\tau_2(OC_\beta C_\alpha C_1)^a$	67.5	60.6	65.4	176.8	180.0
$\tau_3(HOC_\beta C_\alpha)^a$	−173.5	−58.6	64.6	61.1	180.0
E_{rel}/kJ mol$^{-1\ a}$	8.40	0.00	8.56	7.61	8.40
A''/MHz^a	3466.6	3309.1	3440.0	4362.3	4390.1
B''/MHz^a	1085.8	1109.0	1076.2	856.4	859.4
C''/MHz^a	911.6	970.1	909.1	766.6	769.6
A'/MHz^b	3356.8	3238.3	3282.2	4194.3	4221.3
B'/MHz^b	1070.8	1094.3	1063.0	849.3	852.2
C'/MHz^b	901.3	943.5	914.2	757.9	760.8
$\lvert\mu_{trans}\rvert \times 10^{30}$/C m^c	0.88	1.2	0.96	0.95	0.95
$\mu_a^2:\mu_b^2:\mu_c^{2\ c}$	46:47:7	2:96:2	24:65:11	0:100:0	0:100:0
$\theta_{elec}{}^c$	−31	4	−22	−3	0
$r_{OH\cdots\pi C}$/Å^a		2.52			

[a] From the MP2/6-311G** calculation of the ground electronic state. [b] Calculated from the MP2/6-311G** values using % ΔA, % ΔB, and % ΔC obtained from the HF/6-31G* and CIS/6-31G* calculations. [c] From the CIS/6-31G* calculations of the excited electronic state.

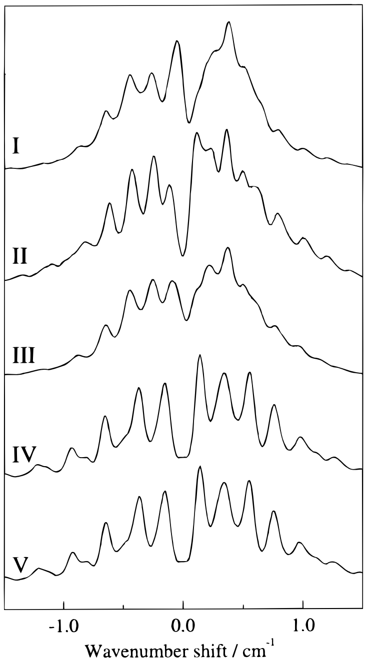

Figure 4. Simulated rotational band contours for each conformation of 2-phenylethyl alcohol, based on the ab initio data detailed in Table 6; $T_{rot} = 2.5$ K, laser line width 0.08 cm^{-1}.

Experimental Results

2-Phenylethyl Alcohol. Low-resolution MS−R2PI spectra of 2-phenylethyl alcohol and its 1:1 hydrated complex are shown in Figure 5. The four bands labeled A, B, D, and E are assigned as conformer band origins of the monomer. They appear only in the spectrum recorded in the monomer mass channel, and their relative intensities remain largely unaffected by the addition of water or changes in the stagnation pressure or laser power. Band C appears in both the monomer and 1:1 water complex mass channels. It is associated with two overlapping features arising from separate monomer and water cluster bands which are resolved on the basis of two-color Etalon scans, as discussed below. The band origin A, at 37 633.2 cm^{-1}, is by far the most intense feature in the spectrum. This encourages its assignment to conformer II, predicted by the ab initio calculations to be the most intense feature.

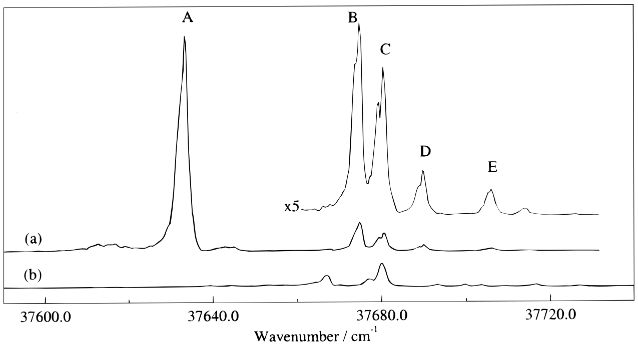

Figure 5. Mass-selected one-color R2PI spectrum of 2-phenylethyl alcohol in the region of the $S_1 \leftarrow S_0$ band origins: (a) gating the monomer mass channel ($m/z = 122$); (b) gating the 2-phenylethyl alcohol·water cluster mass channel ($m/z = 140$).

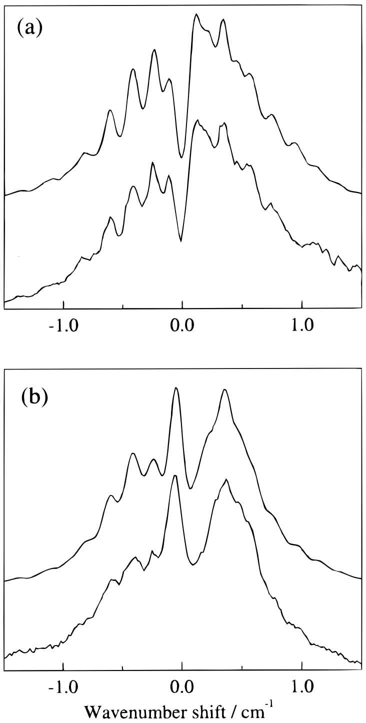

Figure 6. Partially resolved rotational band contours of 2-phenylethyl alcohol: (a) band A (b) band B. Lower traces: experimental LIF spectrum, averaged over 30 laser shots. Upper traces: best fit simulations, $T_{\rm rot} = 2$ K (data shown in Table 2).

The partially resolved rotational contours of bands A and B are shown in the lower traces of Figure 6, where they may be compared with the purely "ab initio" band contours of conformers I and II, shown in Figure 4. The striking similarities confirm the assignment of bands A and B to conformers II and I, respectively. In the case of band A, the ab initio values of A' and A'' were optimized using a simple combination difference procedure on the $^{\rm p}$Q and $^{\rm r}$Q subband heads, to give $(A-\bar{B})' = 0.0748$ cm^{-1} and $(A-\bar{B})'' = 0.0779$ cm^{-1}. A grid search performed to optimize the hybrid character (a:b:c), temperature ($T_{\rm rot}$), and the laser line width (fwhm) converged on the values 0:100:0, 2 K, and 0.10 cm^{-1}, respectively. In the case of band B, where there was insufficient K_a subband structure to employ combination differences, the values of A'' and ΔA were adjusted to fit the small amount of resolved structure in the P branch, giving $(A-\bar{B})' = 0.0769$ cm^{-1} and $(A-\bar{B})' = 0.0801$ cm^{-1}. A grid search, performed on the remaining parameters, converged on the values a:b:c = 40:40:20, $T_{\rm rot} = 2$ K, and fwhm = 0.10 cm^{-1}. This hybrid character corresponds to a TM rotation angle $\theta_{\rm elec} = -33 \pm 3°$; the corresponding higher level ab initio predictions lie in the range $-27°$ to $-32°$. The best fit simulations are shown in the upper traces of Figure 6, and the results are summarized in Table 7.

The LIF band contour of band C is presented in the lower trace of Figure 7a. Comparison of the LIF band contour with the ab initio simulations of conformer IV or V suggests that the band is due to one of the anti conformations. The best fit simulation, generated using $(A-\bar{B})' = 0.1219$ cm^{-1}, a:b:c = 0:100:0, and $T_{\rm rot} = 2.5$ K, is shown in the upper trace of Figure 7a. In this simulation all the $^{\rm p}$Q and $^{\rm r}$Q subband structure can be closely simulated with the exception of what appears to be the $^{\rm r}Q_1$ subband head. In fact, this apparent anomaly is due to an underlying band which overlaps that due to one of the anti conformers. The two-color, MS−R2PI band contour of band C, taken in both the monomer and the 2-phenylethyl alcohol·H_2O mass channels, is shown in the middle and lower traces of Figure 7b. Clearly the two mass channels give rise to very different rotational band contours. In the monomer mass channel the band contour exhibits b-type structure which, although warmer, matches the K_a subband structure in the $^{\rm p}$Q branch of the LIF band contour. The best fit simulation of the LIF band contour, calculated assuming a rotational temperature of 6 K, is shown in the upper trace of Figure 7b for comparison. The band appearing in the water complex mass channel, now labeled C*, lacks any resolved structure but has a strong central Q branch which coincides with the poorly matched $^{\rm r}$Q region of the LIF band contour. On the basis of these mass-selected spectra, it is clear that the feature C in the LIF spectrum is a composite of two bands with transitions separated by approximately 0.2 cm^{-1} and the poorly matched $^{\rm r}Q_1$ subband head is, in fact, the Q branch in the band contour of the 1:1 water complex.

The two-color, monomer mass-selected R2PI band contour of band D is shown in the lower trace of Figure 8a. It closely resembles the band contour of band C which appears in the monomer mass channel, and the best fit simulation, shown in the upper trace of Figure 8a, is identical to the warm simulation of band C shown in Figure 7. Accordingly it is assigned to the other member of the conformer pair, IV and V. Much higher experimental resolution would be needed to distinguish which contour belongs to conformer IV and which to conformer V, as the ab initio values of A'' vary by less than 1%. However, an assignment of band C to conformer IV and band D to conformer V can be made on the basis of their relative intensities. Although the intensity of band C is difficult to determine accurately, because of the presence of the overlapping water cluster, an upper limit of its intensity relative to band D is 4:1. Conformer IV is predicted to be slightly more stable than conformer V at the highest level calculation, but since conformer IV has two distinguishable forms, it is predicted to give rise to a band with 2−3 times the intensity. Although the predicted relative energies vary somewhat with the basis set and level of theory (Table 2), in each case conformer IV is expected to have a greater population than conformer V.

The two-color MS−R2PI band contour of band E is shown in Figure 8b. The $^{\rm p}$Q subband spacing is consistent with a gauche conformation, and it agrees closely with the $^{\rm p}$Q subband spacing in band A. We were not able to establish the hybrid character of this band owing to the difficulty in obtaining a well-resolved band contour of this weak feature. This band could be assigned, tentatively, to the remaining conformer III, though we cannot exclude the possibility that it is a vibronic feature based on one of the gauche band origins.

Measurements of the S_1 lifetimes of conformers I, II, and IV

Table 7. Observed and Predicted Parameters Relating to the $S_1 \leftarrow S_0$ Band Origins in 2-Phenylethyl Alcohol

	band center/cm^{-1} [a]	$(A - \bar{B})''$/cm^{-1} [b]	μ_a^2:μ_b^2:μ_c^2	rel intens (70 °C)	lifetime/ns	best fit assignment
band A	0.0 = 37 633	0.078(2)[c]	0:100:0	1.00	69(4)[c]	II
band B	42	0.080(3)[c]	40:40:20	0.10	80(6)[c]	I
band C	47	0.1219(10)[c]	0:100:0	<0.08[d]	95(10)[c]	IV
band D	57	0.1219(10)[c]	0:100:0	0.02		V
band E	73	0.078(5)[c]		0.01		(III)
PEAL I		0.0823	46:47:7	0.028		
PEAL II		0.0757	2:96:2	1.000		
PEAL III		0.0816	24:65:11	0.032		
PEAL IV		0.1184	0:100:0	0.043		
PEAL V		0.1193	0:100:0	0.016		

[a] Air wavenumbers. [b] $(A - \bar{B})'' = A'' - (B'' + C'')/2$. [c] The figure in parentheses is an error estimate in units of the least significant figure. [d] This is an upper limit on the value.

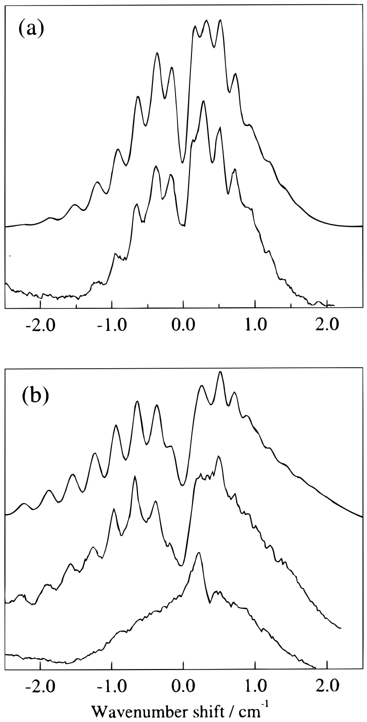

Figure 7. Partially resolved rotational band contours of 2-phenylethyl alcohol: band C. (a) Lower trace: experimental LIF spectrum, averaged over 30 laser shots. Upper trace: best fit simulation, $T_{rot} = 2.5$ K, (data shown in Table 7). (b) Experimental mass-selected two-color R2PI spectra ($h\nu_2 = 35\,090$ cm^{-1}) recorded on the $m/z = 122$ (middle trace) and $m/z = 140$ (lower trace) mass channels, averaged over 200 laser shots. Best fit simulation, $T_{rot} = 6$ K for bare conformer, $m/z = 122$, using data shown in Table 7 (upper trace).

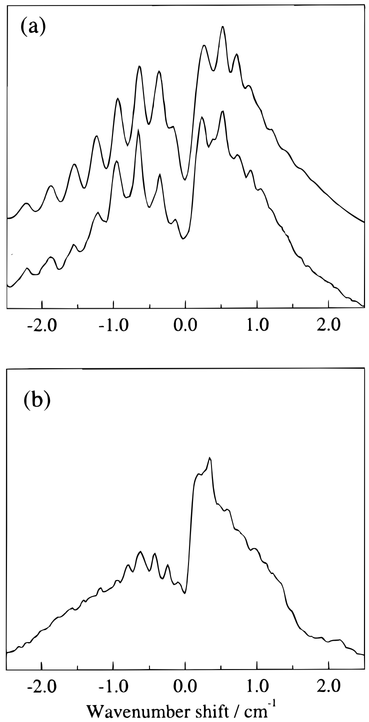

Figure 8. Partially resolved rotational band contours in the two-color R2PI spectra ($h\nu_2 = 35\,090$ cm^{-1}) of 2-phenylethyl alcohol, averaged over 160 laser shots: (a) band D (lower trace), (b) band E. Best fit simulation of band D also shown (upper trace) in (a) using data shown in Table 7, $T_{rot} = 6$ K.

were made by observing the decay in intensity of the two-color ion signal with increasing delay between the two laser pulses. The exponential decay times are summarized in Table 7. The lifetime of conformer II is shorter than that of the other two conformers as expected from the calculated dipole strengths.

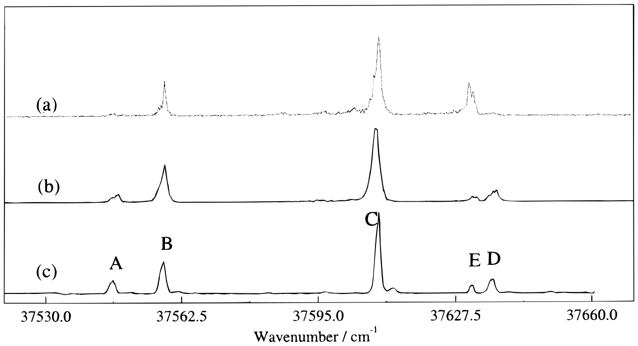

Figure 9. Excitation spectrum of 2-phenylethylamine recorded in the band origin region of the $S_1 \leftarrow S_0$ transition: (a and b) mass-selected one-color R2PI spectrum recorded on the $m/z = 121$ mass channel (a) with and (b) without water added to the He gas flow; (c) LIF spectrum recorded under the same conditions as (b).

2-Phenylethylamine. The low-resolution MS−R2PI spectrum of 2-phenylethylamine, recorded in the monomer ion mass channel, is shown in Figure 9, where it may be compared with the corresponding LIF spectrum. Five band origins, A−E, appear in both the MS−R2PI and LIF spectra, in agreement with earlier studies.[7−9] The partially resolved rotational band contours of the features A−D are shown in the lower traces of Figure 10. Their initial assignment was made by comparison of the experimental band contour with the theoretically predicted band contours described earlier. On this basis, bands A and D are assigned to the pair of anti conformers IV and V. The "best fit" simulations of both of these bands, shown in the upper traces in Figure 10a,b, were generated using $(A-\bar{B})'' = 0.1195$ cm^{-1}, a:b:c = 0:100:0, $T_{rot} = 1.5$ K, and fwhh line widths of 0.10 and 0.13 cm^{-1}, respectively. The only difference apparent in these spectra is their effective line width. This is not merely

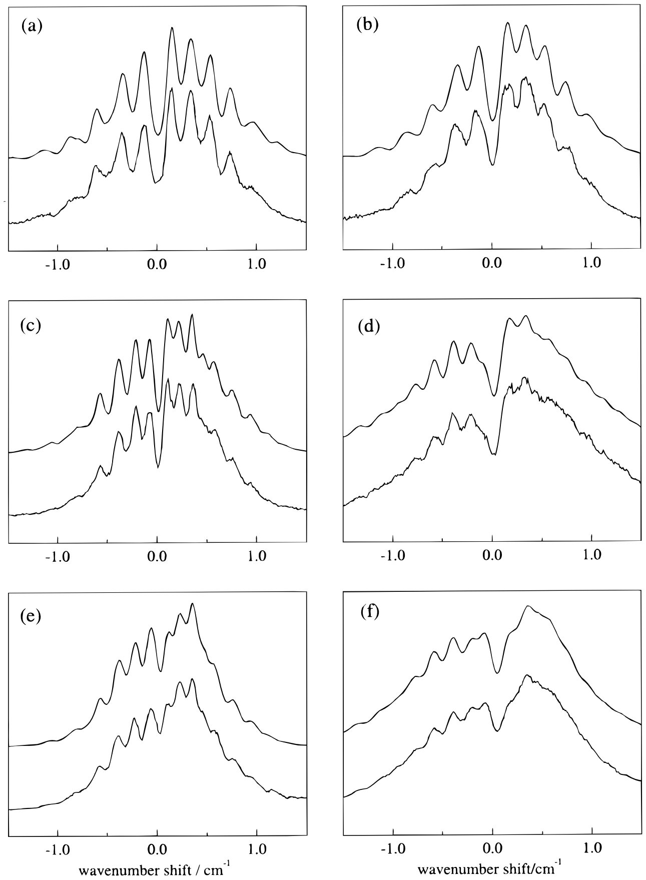

Figure 10. Partially resolved rotational band contours of 2-phenylethylamine: experimental LIF spectra (lower traces); best fit simulations, using data set in Table 8 (upper traces); (a) Band A; (b) band D, $T_{rot} = 1.5$ K; (c) band B, $T_{rot} = 1.5$ K; (d) $T_{rot} = 3.5$ K; (e) band C, $T_{rot} = 1.5$ K; (f) $T_{rot} = 3.5$ K.

an artifact of the experimental conditions, since the band contour of peak E, recorded in the same scans as peak D, shows a line width of no more than 0.10 cm^{-1}. The apparent “broadening” in peak D might arise through amino torsion/inversion splittings. The microwave spectrum of the gauche conformer of ethylamine,[17] which is equivalent to the nonsymmetric anti conformer IV of PEA, reveals amino torsion and inversion splittings of 1170 and 1391 MHz, respectively. These large splittings are evident only for c-type transitions, as a consequence of the selection rule for changes in inversion state. The equivalent axis in conformer IV of PEA is the *b*-axis, and therefore the $S_1 \leftarrow S_0$ origin might be expected to display similar splittings, depending on the barriers to torsion and inversion in both electronic states. The anti conformer of ethylamine, which is equivalent to the symmetric anti conformer V of PEA, exhibits no such splittings.[18] Peak D is therefore tentatively assigned to conformer IV and peak A to conformer V. As with 2-phenylethyl alcohol, much higher experimental resolution would be needed to confirm these findings and to explore the nature of the transitions involved in peak D. It is perhaps surprising that the band origins of the two anti conformers are separated by as much as 90 cm^{-1}. A qualitatively similar result, however, is obtained from the CIS/6-31G* calculations, which predict the $S_1 \leftarrow S_0$ band origin for conformer IV to lie 50 cm^{-1} above that for conformer V.[19]

The appearance of the band contours B and C led to their assignment to the gauche conformers II and III, respectively. The bands are the most intense in the spectrum, and their relative intensities are consistent with Godfrey et al.’s observation of these two conformations in the ratio 1:3.[10] Their rotational band contours were recorded and simulated at two different rotational temperatures, helping to better establish their hybrid character. A grid search, performed on all the parameters except the microwave rotational constants for the ground state and the values of B' and C' produced the best fit simulations shown in Figure 10c−f. Their hybrid characters were consistent with TM rotation angles $\theta_{elec} = -11°$ and $-26°$ for conformers II and III, respectively, which is in very good agreement with the ab initio predictions (see Table 5). The data confirming the assignments are summarized in Table 8.

None of the band origins, A−E, appeared in either the one- or the two-color R2PI spectra, recorded in the mass channel corresponding to the 1:1 complex with water. However, we assign band E to a 1:1 water cluster for the following reasons.

(i) Addition of water to the helium line increased the intensity of band E (compare Figures 9a,b) relative to the remaining bands. Similar behavior was observed by Sipior et al.;[7] we note also that the intensities of bands A and D were considerably reduced under these conditions.

(ii) The ion fragmentation pattern associated with the R2PI spectrum of band E was not the same as that of the other bands, A−D. In the mass spectrum of band A, which is typical of the bands A−D, the predominant ion is at *m*/*z* 121 (2-phenylethylamine). A small number of ions are also observed at *m*/*z* 30, corresponding to the $CH_2NH_2^+$ fragment ion. (In the 70 eV electron impact[20] or the photoionization mass spectrum recorded at very high laser intensities these ions are dominant, but the mass spectrum recorded at much lower intensity, through two-photon ionization (see Figure 11), lies close to the ionization threshold.) In the case of band E, although no ions are seen at *m*/*z* 139, corresponding to the 2-phenylethylamine•water complex, there is a significant ion signal at *m*/*z* 48, corresponding to $(CH_2NH_2{\cdot}H_2O)^+$; see Figure 11.

Uggerud[21] has carried out calculations, at the MP2/6-31G** level, on the stability of the $CH_2NH_2^+$ complexes with water and ammonia and found that very strong hydrogen bonds were formed, with energies of 99 and 121 kJ mol^{-1}, respectively. A binding energy of this magnitude would explain, thermodynamically, the formation of the $(CH_2NH_2{\cdot}H_2O)^+$ ion.

The partially resolved rotational band contour of band E is shown in the lower trace of Figure 12. It displays strong a-type character, with little K_a subband structure evident. While an unambiguous structural assignment of the water complex will require higher resolution studies, together with further ab initio calculations, some information can be deduced from simulations of its rotational band contour. Five possible 2-phenylethylamine•H_2O structures could be generated by binding a water molecule to the amino lone pair, at a typical hydrogen bond distance ($r_{N\cdots O} = 2.9$ Å), for each of the five predicted conformer structures. If it is assumed that binding of a water molecule does not alter the structure of the conformer or the alignment of the electronic TM in its molecular frame, none of the predicted band contours match the experimental contour. A good match can only be obtained by introducing at least 90% a-type character into the simulation. This rules out the anti

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(17) Fischer, E.; Botsker, I. *J. Mol. Spectrosc.* **1984**, *104*, 226−247.

(18) Fischer, E.; Botskor, I. *J. Mol. Spectrosc.* **1982**, *91*, 116−127.

(19) This value includes zero-point corrections to both the ground state (HF/6-31G*) and excited state (CIS/6-31G*). Although the *absolute* transition energies are overpredicted by ca. 30%, the energy *differences* may be informative, as was found recently in a similar study of *n*-butylbenzene.[6]

(20) Heller, S. R.; Milne, G. W. A. *EPA/NIH Mass Spectral Data Base*; 1978; Vol. 1.

(21) Uggerud, E. *Eur. Mass Spectrom.* **1996**, *2*, 193−195.

Table 8. Observed and Predicted Parameters Relating to the $S_1 \leftarrow S_0$ Band Origins in 2-Phenylethylamine

	band center/cm^{-1} [a]	$(A - \bar{B})''$/cm^{-1} [b]	μ_a^2:μ_b^2:μ_c^2	rel intens (70 °C)	lifetime/ns	best fit assignment
band A	−64	0.1195(10)[c]	0:100:0	0.22	72(6)[c]	IV
band B	−52	0.0759[d]	5:85:10	0.48	75(5)[c]	II
band C	0 = 37610	0.0765[d]	25:65:10	1.00	79(6)[c]	III
band D	+26	0.1195(10)[c]	0:100:0	0.21	66(14)[c]	V
PEAL I		0.0820[e]	44:46:10	0.08		
PEAL II		0.0740[e]	6:88:6	1.00		
PEAL III		0.0750[e]	21:72:7	1.00		
PEAL IV		0.1179[e]	0:100:0	0.12		
PEAL V		0.1167[e]	0:100:0	0.10		

[a] Air wavenumbers. [b] $(A - \bar{B})'' = A'' - (B'' + C'')/2$. [c] The figure in parentheses is an error estimate in units of the least significant figure. [d] Fixed to microwave values. [e] From the MP2/6-311G** calculations.

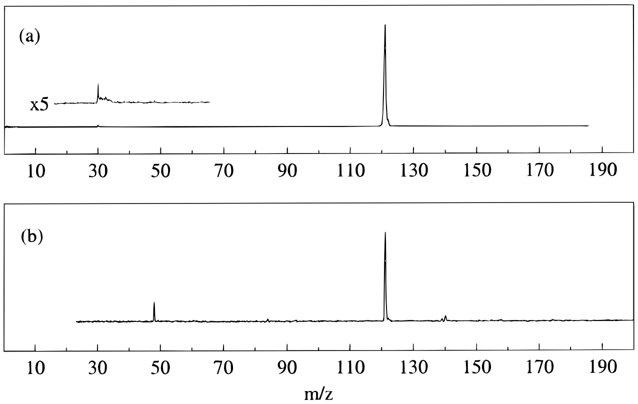

Figure 11. One-color R2PI mass spectrum of 2-phenylethylamine generated by excitation (a) at 37 610 cm^{-1} (band C) and (b) at 37 630 cm^{-1} (band E).

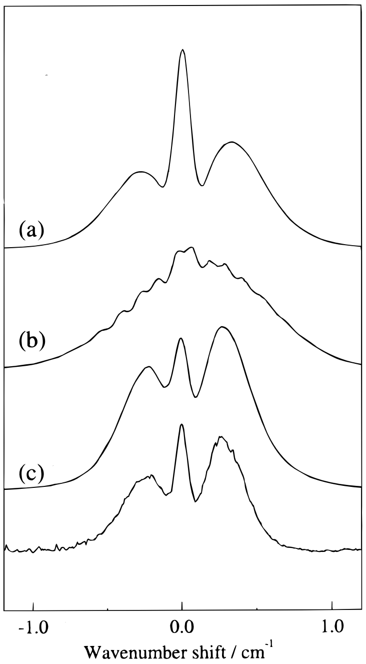

Figure 12. Partially resolved rotational band contour of the water cluster, band E, in 2-phenylethylamine. Bottom trace: experimental LIF spectrum, averaged over 40 laser shots. Upper traces: simulations based upon (a) conformer I, (b) conformer II, and (c) conformer III.

structures, where the water molecule would be a long way from the ring, since they are expected to show predominantly b-type bands. Simulations based on the gauche 2-phenylethylamine·H_2O structures I−III, using the rotational temperature obtained in the simulation of peak D (which was recorded in the same experimental spectrum as peak E), are shown in Figure 12. The simulation based on conformer III most closely resembles the experimental spectrum. If water binding promotes further rotation of the TM through 20° in the plane of the ring, the electronic transition would acquire the necessary 90% a-type character.

In 2-phenylethylamine·H_2O structures based on conformers I and II the same result can only be achieved by introducing total rotational angles of 28° and 60°, respectively, including an improbably large component *out* of the plane of the ring. Furthermore, the simulation with 90% a-type character, using the rotational constants of 2-phenylethylamine·H_2O based on conformer I, resulted in a band contour which was considerably wider than the observed spectrum. In any case, such a structure is inherently unlikely, since the H_2O molecule would be directed toward the ring in a sterically unfavorable position. Our preliminary analysis of band E strongly suggests, therefore, a water cluster based on the gauche conformer structure 2-phenylethylamine (III), which is the lowest energy conformation in the isolated molecule. Initial results from ab initio calculations on this complex support this assignment. In addition, the ring mode frequencies for band E obtained through the hole-burning experiments of Sun and Bernstein[8] are very similar to those of the gauche conformers B and C, lending further support to this conclusion.

The S_1 lifetimes measured for conformers II−IV, given in Table 4, are not significantly different from those reported earlier by Levy.[9] The corresponding lifetime of the water complex, measured on band E (τ_E = 86(4) ns), is similar to that of conformer III as well as the other three conformers.

Discussion

Isolated Conformers. The conformational landscape of 2-phenylethyl alcohol and 2-phenylethylamine has been revealed by a detailed analysis of the rotational structures of the 0−0 bands in their $S_1 \leftarrow S_0$ electronic spectra, recorded under jet-cooled conditions. The analysis has been supported by ab initio MO calculations in the minimum energy conformations of their ground and first excited singlet states. The experimental data and calculations are found to agree extremely well. All of the five predicted $S_1 \leftarrow S_0$ band origins were observed in 2-phenylethyl alcohol, and four of the five predicted bands have been observed in 2-phenylethylamine. The fifth feature, "band E", has now been correctly assigned, not to the fifth predicted conformer,[8] but to a gauche 1:1 water complex. Most strikingly, the important role played by rotation of the TM in the molecular frame and its sensitivity to both the coarse and fine details of the molecular conformational landscape have been exposed by experiment and confirmed by theory.

In both 2-phenylethyl alcohol and 2-phenylethylamine, the most stable gauche conformers are predicted to be more stable than the corresponding anti conformers. The relative intensities in the experimental spectra of both molecules suggest a gap

≥ 3 kJ mol^{-1}, which agrees with the calculations at the MP2 level on 2-phenylethylamine by Godfrey et al.[10] and by ourselves on both molecules. In the lowest energy gauche conformations one of the terminal alcohol/amine hydrogen atoms is directed toward the benzene ring. The calculated distances between these hydrogen atoms and the nearest carbon atom in the ring are ca. 2.6 Å (Tables 5 and 6), consistent with hydrogen bonding between the alcohol/amine terminal groups and the ring.[10] The remaining gauche conformers, in which the lone pair electron density is directed toward the benzene ring, are calculated to be *de*stabilized relative to the hydrogen-bonded conformers, by 7−9 kJ mol^{-1}.

The $S_1 \leftarrow S_0$ transitions of benzene chromophores in the 260−310 nm region are usually assigned as transitions to the ^1L_b state[22] and in almost all monosubstituted and para-disubstituted benzene molecules the $S_1 \leftarrow S_0$ TM has been found, or assumed to be aligned parallel to the short axis of the benzene ring, perpendicular to the axis which runs through the substituted carbon atom. Styrene, which has a strongly conjugated vinyl group and a TM polarized parallel to the *long* axis ($S_1 \equiv {}^1L_a$), provides a notable exception.[23] The present series of investigations was triggered by our earlier studies of 3-phenylpropionic acid[5] and *n*-propyl- and *n*-butylbenzene.[6] In each case, the $S_1 \leftarrow S_0$ transitions in the anti conformers were polarized parallel to the short axis (^1L_b), but in each of the gauche conformers the TM was rotated toward the long axis, suggesting the introduction of ^1L_a character through electronic state mixing. The largest effect was displayed in the gauche conformer of 3-phenylpropionic acid, where the lone pair electron density on the carbonyl oxygen is directed toward the benzene ring and the TM rotates through an angle, $\theta_{elec} = -52°$.[5] In the present study an additional effect has been discovered. The degree of "rotation" of the TM in the gauche conformation is modulated by the hydrogen-bonding interaction between the terminal, hydroxyl or amino, hydrogen atom of the side chain and the π system of the ring. In the stable gauche conformations, in which the terminal hydrogen atom is directed toward the ring, the rotation of the TM, θ_{elec}, is significantly less (alcohol II, +4°, amines II and III, −22° and −10°) than in the gauche conformations where the lone pair electron density is directed toward the ring (alcohols I and III, −22° and −32°, amine I, −34°). It is this effect that has enabled the hydrogen-bonded and non-hydrogen-bonded conformations to be distinguished. The accompanying change in the magnitude of the rotational constants alone would have been insufficient to resolve the different conformations, as is the case in the anti conformations. *It is clear that the modulated rotation* of the TM, expressed through the hybrid character of the rotational band contour, provides a powerful probe for distinguishing conformers in which there may be hydrogen bonding to the aromatic ring.

Interesting comparisons can be made with the work done by Levy's group on tryptamine[11] and by Godfrey's group on histamine.[24] Tryptamine and histamine resemble 2-phenylethylamine with the benzene chromophore replaced by indole and imidazole, respectively. It is therefore reasonable to expect that both tryptamine and histamine might exhibit sets of minimum energy side chain conformations similar to those of 2-phenylethylamine. Levy[11] has recorded five, rotationally resolved, conformer band origins in the $S_1 \leftarrow S_0$ spectrum of tryptamine and assigned them to two gauche conformations, each with two different orientations of the amino group, and one eclipsed structure. Two additional, overlapping bands were attributed to a pair of anti rotamers slightly split by rotation of the amino group. Some of these assignments are in sharp contrast to those made for 2-phenylethylamine, both in the present work and in the earlier (rotationally unresolved) studies by Levy.[9] The splitting associated with rotation of the amino group in the anti conformers was found to be ~100 cm^{-1}, and no eclipsed conformations have been detected. Although there appeared to be some variation in the alignment of the TM with change in the molecular conformation in tryptamine, the changes were not thought to lie outside the bounds of experimental error.[11] There was also no evidence of any sensitivity to the orientation of the terminal amino group. The conformational landscape of histamine has been investigated by Godfrey et al.[24] both experimentally, through microwave spectroscopy under jet-cooled conditions, and computationally, through ab initio calculations. The latter predicted 20 energy minima, 14 of which had gauche conformations but none of which were eclipsed. Four of the gauche conformers were identified in the microwave spectrum, each of which appeared to be stabilized by hydrogen bonding between the terminal amino group and the imidazole ring. It seems very likely that the role of the heteroatom should be featured in discussions of the conformational landscapes of both histamine and tryptamine.

Hydrogen bonding to π-electron systems has been the subject of much attention.[25−28] It has been found to be as important as conventional hydrogen bonding in molecular recognition of host−guest complexes in chloroform,[25,26] and the magnitude of the "π-facial" hydrogen bond has been estimated to be at least 4.5 kJ mol^{-1}.[25] It has been suggested that this interaction may have significant implications for drug design, by making drugs bind to their targets much more strongly than previously thought.[24] Our recent experimental study of *n*-propylbenzene,[6] a molecule in which there is no hydrogen bond between the non polar side chain and the benzene ring, found the gauche conformer to be 2.5 kJ mol^{-1} less stable than the anti conformer. In the present study of 2-phenylethyl alcohol and 2-phenylethylamine we find that the gauche conformers are at least 3 kJ mol^{-1} more stable than the anti conformers. This suggests a hydrogen-bonding energy of ca. 5.5 kJ mol^{-1}.

Water Clusters. Bands associated with hydrated clusters of 2-phenylethyl alcohol and 2-phenylethylamine were present in all their recorded R2PI and LIF spectra. To identify bands that were associated with the bare molecular conformers, it was essential first to eliminate all those arising from the excitation of the hydrated clusters, not to mention dimers, vibrational progressions, or impurities. Very great care is needed for an unambiguous spectral assignment, and the two systems under discussion provide an excellent illustration of this. The fluorescence excitation hole-burning experiments on jet-cooled 2-phenylethylamine, conducted by Sun and Bernstein,[8] ruled out the possibility of band E being a vibronic feature of one of the conformers A−D. A mass-resolved excitation spectrum also contained band E, and encouraged its assignment to the "remaining" predicted conformer. This was contrary to an earlier proposal by Sipior et al.[7] In the present study, no ion signal was detected in the mass channel corresponding to the

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1:1 water complex upon excitation of peak E, even near threshold. Its association with a water complex was betrayed by the presence of the fragment at *m*/*z* 48 and confirmed by its sensitivity to the purposeful addition of water to the flowing gas stream.

The value of high-resolution R2PI scans of the same spectral feature but recorded on *different* mass channels is illustrated by the analysis of the blended band "C", in the excitation spectrum of 2-phenylethyl alcohol. Low-resolution mass-selected R2PI spectra displayed signals in both the bare conformer and the 1:1 water complex ion channels, encouraging its assignment to a single feature associated with a water complex. It was only when the spectra were recorded separately, under higher resolution, on each of the two mass channels that it was possible to identify and then analyze the separate, overlapping contributions of the two components (separated by <0.3 cm^{-1}). Interestingly, neither the bare molecule nor its hydrated cluster generates the fragment ions, CH_2OH^+ (even under 70 eV EI conditions[20]) or $CH_2OH{\cdot}H_2O^+$. This is in marked contrast to the amine, where scission of the $C_\alpha-C_\beta$ bond is readily observed. The difference may be thermodynamic, since the ionization potential of CH_2OH (7.56 eV) is considerably higher than that of CH_2NH_2 (6.1 eV).[29]

The band contours of the 1:1 water complexes, band C* in 2-phenylethyl alcohol and band E in 2-phenylethylamine, each display a strong Q branch. There is very little b-type character in their electronic transitions, in striking contrast to the band composition of the corresponding bare molecular conformers. The molecular complex structure that best fits the contour of band E, in 2-phenylethylamine, does lead to a significant rotation of the inertial axis frame but not sufficient to generate the observed degree of hybrid character. An additional rotation of the TM in the molecular frame, toward the *a*-inertial axis, is clearly required, a rotation that can only have been mediated by the presence of the bound water molecule. A similar effect is likely to be required to account for the contour of the water complex band C*, in 2-phenylethyl alcohol. More detailed experimental and ab initio studies of these, and other higher water clusters, are in progress.

Conclusions

The rotational band contours of the $S_1 \leftarrow S_0$ origin bands of 2-phenylethyl alcohol and 2-phenylethylamine, recorded under jet-cooled conditions, have been analyzed with the aid of ab initio calculations. The experimental and theoretical analyses have led to the assignment of five distinct anti and gauche conformers in the alcohol but only four in the amine. The "fifth" conformer has been re-assigned to a 1:1 water complex, primarily on the basis of its mass-resolved, two-color R2PI excitation spectrum. The most stable conformers in each molecule are those in which the methylene chain is folded into a gauche structure and the terminal hydroxyl or amino hydrogen atoms are oriented toward the aromatic ring, to form weakly hydrogen-bonded structures with binding energies of ∼5.5 kJ mol^{-1}.

The anti conformers display b-type rotational band contours reflecting the ^1L_b character of their first excited singlet states. The folded, gauche conformers display hybrid band contours, however, arising from a rotation of the electronic transition moment in the plane of the aromatic ring which is attributed to electronic state mixing. The rotation angle is also strongly modulated by the orientation of the terminal hydroxyl or amino group, with the angle being at a maximum when the lone pair electron density on the O or N atom is directed toward the π electrons on the aromatic ring. This dependence has a profound influence on the rotational band contours, and it allows a clear, unambiguous and serendipitous distinction to be made between the hydrogen-bonded and non-hydrogen-bonded gauche conformers. Without such a dependence, their separate assignment would have required a combination of very high-resolution spectroscopy and D atom substitution. Several hydrated water clusters have also been identified. A preliminary analysis of the hybrid character of their partially resolved rotational band contours indicates a further rotation of the electronic transition moment, promoted by the bound solvent molecule.

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