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Vibrational Signature of the Conformers in Tyramine Studied by IR Dip and Dispersed Fluorescence Spectroscopies

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Dispersed fluorescence and IR dip spectra of seven conformers of tyramine were measured in a supersonic jet. Observed vibrational bands are assigned based on quantum chemical calculations. The vibrational frequency of out-of-plane CH bending in the benzene ring shows characteristic shifts according to the conformation of $C_\beta-C_\alpha$, while that of CH stretching in the methylene chain reflects the conformation of $N-C_\beta$. From these vibrational frequencies, assignments of the conformers observed in the S_1-S_0 laser induced fluorescence spectrum are discussed.

1. Introduction

Tyramine is a member of the family of neurotransmitters, including dopamine and noradrenalin, which contain an ethylamino chain and a phenolic OH. Their flexible structures may be essential for their biological activity as the binding affinity of transmitters to receptors may differ for different conformers. To further delineate the mechanism of molecular recognition in flexible neurotransmitters, it is important to understand their conformational structures in detail. Laser spectroscopy in a supersonic jet is a powerful tool for studying the details of molecular conformations without perturbation by solvent molecules. Recently, many biologically relevant molecules and clusters have been studied by various supersonic-jet laser spectroscopies.[1−26]

The first LIF spectrum of a jet-cooled biogenic amine, tyramine, was reported together with a dispersed fluorescence spectrum from the strongest peak by Teh et al. in 1991.[27] Martinez et al. also measured the LIF spectrum and assigned the bands to six different conformers based on analogy with the spectra of 4-propylphenol. They also reported the dispersed fluorescence spectra from the six conformers, but only the spectral similarity to *p*-cresol was mentioned,[28] which may be due to the low resolution of the spectra (50 cm^{-1}). Simons and co-workers proposed different assignments in the electronic spectrum of tyramine. On the basis of analogy with the LIF spectrum of the phenylethylamine molecule, they classified the observed six origins into four conformational species with different positions of the ethylamine side chain. They also proposed splitting of the origins due to different orientations of the phenolic OH.[29] In a theoretical study, Richardson et al. reported seven structures of tyramine determined by ab initio calculations at the MP2/6-31G** level.[30] Melandri and Maris recorded a free-jet microwave spectrum of tyramine, analyzed with the help of ab initio MO calculations at the MP2/6-31G* level.[31] In their observation, four stable conformational species were assigned based on the relative value of the permanent dipole moment components. However, this number of conformers is less than that proposed in the LIF spectrum and thus the conformational analysis of the LIF spectrum remains unclear. Most recently, Yoon et al. reported R2PI and UV−UV hole-burning spectra of tyramine and its water clusters.[32] They assigned all seven stable conformers of tyramine on the basis of UV rotational band contour spectra and ab initio MP2/6-31G** calculations. Rotational analysis is highly reliable only in the case that all the rovibronic structures are well-resolved; ambiguity remains in the rotational contour analysis.[33] For example, the rotational contour in the LIF spectrum of the nonreactive 7-azaindole dimer was consistently fit with a T-shape structure;[33] however, it was finally reassigned to the dimer with H_2O from the IR spectrum.[34,35] Contour analysis of rotational bands should not be seen as unequivocal and it is essential that alternative methods are used in tandem to ensure correct assignment. Vibrational spectroscopy provides an excellent complementary technique for such confirmation and is preferable in many cases. In spite of the extensive studies to date, an infrared spectrum of each conformer has not been reported. IR spectroscopy plays a key role in the conformational studies of biologically relevant molecules and clusters,[1,4,7−10,13−17,20−24] and therefore IR spectra of tyramine are desirable.

In the present work, we report the IR spectra of jet-cooled tyramine measured by IR dip spectroscopy. The dispersed fluorescence spectra of seven conformers are also observed with resolution sufficient to resolve vibrational bands in S_0 (15 cm^{-1}). From the observed vibrations in the IR and dispersed fluorescence spectra, we discuss the conformations of the ethylamine chain, which enables us to assign systematically all seven stable conformers of tyramine.

2. Experimental Section

The experimental setup for the LIF and dispersed fluorescence instruments has been described elsewhere.[36] Briefly, the exciting light was the second harmonic of a dye laser (Sirah, Cobra

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stretch) pumped by the third harmonic of a Nd^{3+}:YAG laser (Spectra-Physics, INDI-20). The LIF spectrum was measured by monitoring the total fluorescence with a photomultiplier (Hamamatsu Photonics, 1P28). The signal was transferred to a personal computer on each trigger and integrated. The intensity was continuously averaged and recorded as a function of the laser wavelength. The dispersed fluorescence spectra were measured with a 0.75 m single monochromator (Spex) having a grating of 2400 lines mm^{-1}. The typical resolution of the dispersed fluorescence spectrum was ~14 cm^{-1} with a slit of 200 μm. To measure the dispersed fluorescence spectrum, a photomultiplier with high-gain (Hamamatsu photonics, R955) was used, and the fluorescence signal was amplified by a preamplifier (Keythley, model 427) before integration.

The setup for the IR dip spectroscopy is essentially the same as that employed in a previous study.[37] The UV radiation was generated by a frequency-doubled dye laser (Lumonics, HD-500) pumped by the second harmonic of a Nd^{3+}:YAG laser (Spectra-Physics, INDI-20). Tunable IR radiation was generated by difference-frequency mixing, using the output of a dye laser (Sirah, Cobra stretch/DCM) pumped by the second harmonic of a Nd^{3+}:YAG laser (Spectra-Physics, Laboratory 190-10) and 532 nm radiation in a $LiNbO_3$ crystal. Both the IR laser and UV laser were introduced into the vacuum chamber coaxially to cross the molecular beam. The produced cations were extracted to a linear time-of-flight mass spectrometer by a Wiley−McLaren electrode and detected by an Even-cup dynode converter.[38,39] The signal, amplified by a preamplifier (NF, BX-31A), was recorded by a fast digitizer board (acqiris, DP240) and integrated by a PC as a function of the IR laser frequency. The sample was heated in a nozzle chamber to 120 °C and seeded in 2 atm of He gas. The mixture was expanded into a vacuum chamber through a pulsed valve (General Valve, series 9), producing a supersonic jet of tyramine. We employed the valve designed by Carney and Zwier, which enables us to heat the sample without temperature-induced instability.[40] Tyramine was purchased from Aldrich and used after purification by vacuum sublimation.

We carried out quantum chemical calculations to obtain probable structures of tyramine. Geometry optimization and vibrational analysis of the tyramine monomer were done at the B3LYP/aug-cc-pVDZ level of theory. All the calculations were performed with GAUSSIAN 03.[41] For comparison of experimental IR spectra with calculated ones, calculated vibrational frequencies were scaled by a scaling factor of 0.958.

3. Results and Discussion

3.1. IR Dip Spectra. Prior to the measurement of the IR dip spectra, we measured the LIF spectrum of tyramine in a supersonic jet. Figure 1a shows the LIF spectrum of tyramine in the region of the $S_1 \leftarrow S_0$ origin bands. The LIF spectrum well reproduced the spectrum reported by Levy and co-workers[28] and the REMPI spectrum reported by Yoon et al.[32] Six strong bands in the LIF spectrum are assigned to at least six stable conformers from UV−UV hole-burning spectra of tyramine by Yoon et al.[32] The origin bands of the conformers are labeled by letters A−G. The broadband labeled F&G is tentatively assigned to overlapped origin bands of the two conformers F and G.[30,32]

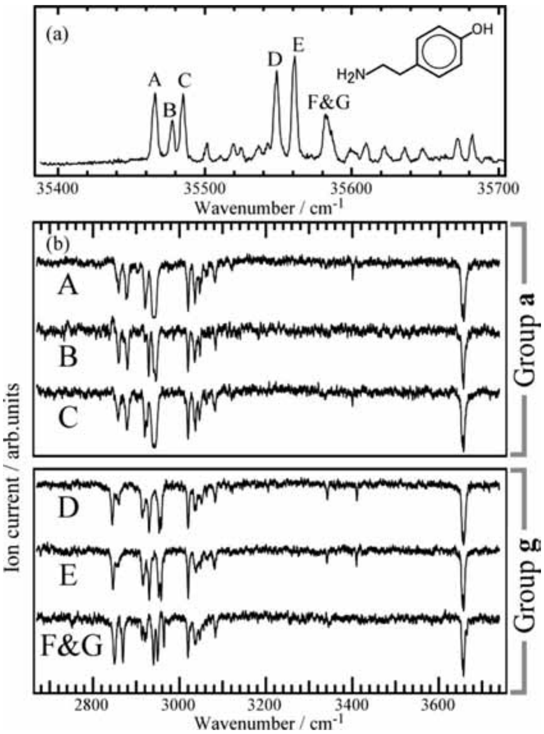

Figure 1. (a) LIF spectrum of jet-cooled tyramine. (b) IR dip spectra observed by probing bands A−G in the LIF spectrum.

TABLE 1: Vibrational Assignment of "Group a" Conformers of Tyramine in the IR Dip Spectra

conformer A		conformer B		conformer C		
obsd/ cm^{-1}	calcd[a]/ cm^{-1}	obsd/ cm^{-1}	calcd[a]/ cm^{-1}	obsd/ cm^{-1}	calcd[a]/ cm^{-1}	assignment[b]
2860	2890	2860	2891	2859	2890	ν_{11}: methylene CH sym stretching
2876	2904	2879	2910	2879	2904	ν_{10}: methylene CH sym stretching
2921	2932	2929	2926	2920	2931	ν_9: methylene CH antisym stretching
2941	2948	2945	2955	2942	2948	ν_8: methylene CH antisym stretching
3021	3022	3020	3021	3020	3023	ν_7: aromatic CH stretching
3036	3036	3036	3032	3037	3033	ν_6: aromatic CH stretching
3047	3039	3047	3039	3047	3042	ν_5: aromatic CH stretching
3061				3064		Fermi resonance[c]
3083	3064	3084	3064	3083	3064	ν_4: aromatic CH stretching
				3337	3332	ν_3: NH sym stretching
3401	3411			3400	3411	ν_2: NH antisym stretching
3656	3656	3656	3656	3656	3656	ν_1: OH stretching

[a] For calculated frequencies, a scaling factor of 0.958 is used. [b] Calculated frequencies are labeled as ν_i: $i = 1-57$ from higher to lower frequency to obey the IUPAC recommendation. Vibrational motions are described by the combination of the vibrational mode of the benzene ring (Load notation) and motion of the chain. [c] Tentative assignment for the split band.

Figure 1b shows IR dip spectra of tyramine with probing bands A−G in the LIF spectrum. From frequencies, one can assign the IR dip spectra of tyramine in Figure 1b as follows. First, all the spectra have a band at 3656 cm^{-1}. This band is the stretching vibration of the phenolic OH bond. Weak bands at ~3342 and ~3410 cm^{-1} are assigned to the symmetric and antisymmetric NH stretching vibrations of the NH_2 group, respectively. The NH stretching vibrations were relatively weak and were not observed in some conformers. The CH stretching vibration of the benzene ring emerges in the region of 3000−3100 cm^{-1} in all the spectra. Finally, bands in the region of 2800−3000 cm^{-1} are attributed to the CH stretching vibration of the methylene chain. Observed vibrational frequencies are listed in Tables 1 and 2.

IR dip spectra can be divided into two groups because of spectral similarity in the region of the CH stretching vibration of the methylene chain (2800−3000 cm^{-1}). The IR dip spectra

TABLE 2: Vibrational Assignment of "Group g" Conformers of Tyramine in the IR Dip Spectra

conformer D		conformer E		conformer F		conformer G		
obsd/ cm^{-1}	calcd[a]/ cm^{-1}	obsd/ cm^{-1}	calcd[a]/ cm^{-1}	obsd/cm^{-1}	calcd[a]/ cm^{-1}	obsd/ cm^{-1}	calcd[a]/ cm^{-1}	assignment[b]
2845	2831	2846	2833	2849	2841	2849	2840	ν_{11}: methylene CH sym stretching
2860		2559		2869		2869		Fermi resonance[c]
2914	2907	2916	2907	2920	2896	2920	2897	ν_{10}: methylene CH sym stretching
2930	2932	2930	2932	2940	2930	2940	2931	ν_9: methylene CH antisym stretching
2953	2956	2952	2956	2950	2953	2950	2953	ν_8: methylene CH antisym stretching
2958		2958		2964		2964		Fermi resonance[c]
3020	3021	3020	3024	3020	3022	3020	3021	ν_7: aromatic CH stretching
3035	3038	3039	3032	3037	3032	3037	3034	ν_6: aromatic CH stretching
3051	3043	3048	3048	3047	3040	3047	3039	ν_5: aromatic CH stretching
3063		3065		3057		3057		Fermi resonance[c]
3082	3064	3081	3063	3083	3063	3083	3063	ν_4: aromatic CH stretching
3342	3339	3341	3339	3345	3337	3345	3337	ν_3: NH sym stretching
3411	3418	3410	3418					ν_2: NH antisym stretching
3656	3656	3656	3656	3656	3656	3656	3656	ν_1: OH stretching

[a] For calculated frequencies, a scaling factor of 0.958 is used. [b] Calculated frequencies are labeled as ν_i: $i = 1-57$ from higher to lower frequency to obey the IUPAC recommendation. Vibrational motions are described by the combination of the vibrational mode of the benzene ring (Load notation) and motion of the chain. [c] Tentative assignment for the split band.

of conformers A, B, and C are very similar to each other in this region and are thus assigned to the same group. The IR dip spectra of conformers D, E, F, and G show similar spectral features which differ from the former group (A, B, and C). The IR dip spectrum obtained by probing the band F&G shows more peaks than the spectrum of conformers D and E. This can be explained by the overlap of two origins of the conformers F and G. Therefore, on the basis of the IR dip spectra, we categorized the conformers A, B, and C into the same group (Group **a**) and conformers D, E, F, and G into another group (Group **g**). In Section 3.4, we will discuss assignments of vibrations and relation to the conformation based on quantum chemical calculations.

3.2. Dispersed Fluorescence Spectra. Figure 2 shows dispersed fluorescence spectra of tyramine obtained by exciting bands A−G in the LIF spectrum. The spectra are drawn with respect to the relative wavenumbers from the excitation position. The gross features of our dispersed fluorescence spectra are similar to those measured by Levy and co-workers.[28] However their spectral resolution was only 50 cm^{-1}, which is not enough to distinguish vibrational differences among conformers. Our spectral resolution is about three times higher than theirs thus we can discuss the detailed vibrational structure clearly.

We can classify the dispersed fluorescence spectra into two groups because of vibrational structures at ∼500 cm^{-1}, which is in the region of the out-of-plane CH bending mode in the benzene ring. The dispersed fluorescence spectra obtained by exciting bands A, C, D, and E are very similar to each other in this region. Thus we can classify the four conformers in the same group. On the other hand, the dispersed fluorescence spectra from bands B, F, and G show similar structure, which differs from that in the former group (bands A, C, D, and E). Therefore, we classify conformers A, C, D, and E in one group (Group **G**) and conformers B, F, and G in another group (Group **A**). This classification must be related to the conformational difference that affects the out-of-plane CH bending in the benzene ring. Frequencies of the observed bands are listed in Tables 3 and 4. Assignments and relation to the conformation will be discussed later based on quantum chemical calculations.

3.3. Theoretical Calculation. Figure 3 shows the optimized structures of the nine lowest energy conformers of tyramine at the B3LYP/aug-cc-pVDZ level. The conformational structure of tyramine is determined by both the structure of the ethylamine chain and the relative orientation of the OH group. The ethylamine chain can rotate about two bonds: $C_\beta-C_\alpha$ and $N-C_\beta$ bonds. Thus, tyramine has three bonds that determine its conformation. Hence, we can classify the nine conformers of tyramine systematically in three phases. In the first phase, rotation about the $C_\beta-C_\alpha$ bond in the ethylamine chain gives **Gauche** or **Anti** conformations. This conformation is denoted as **G** and **A**, respectively. Second, the **Gauche** conformers are divided into three groups; **gauche**, **gauche′**, and **anti**, according to the orientation of nitrogen lone pair (denoted **g**, **g′**, and **a**, respectively). Here, conformations of **g**, **g′**, and **a** are shown in the figure. **Anti** conformers are categorized into two groups, **gauche** and **anti**, according to the rotation about $N-C_\beta$. Finally, each group is classified into **cis** or **trans** conformation (denoted **c** and **t**) depending on the relative orientation of the NH_2 and

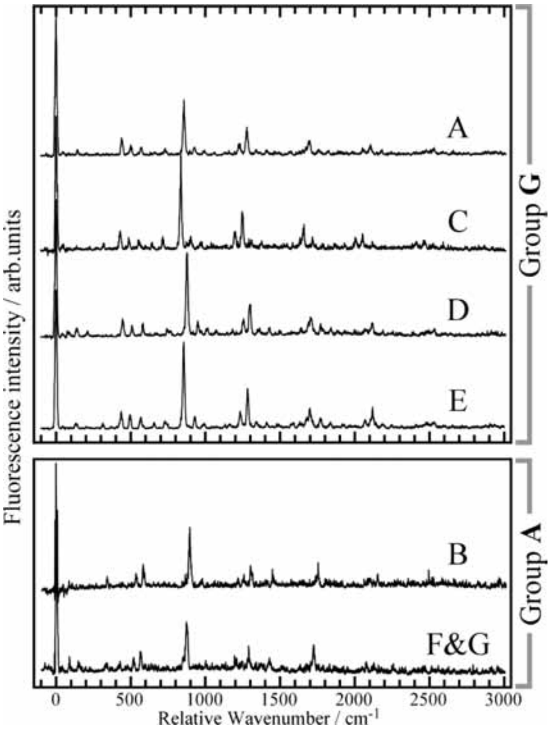

Figure 2. Dispersed fluorescence spectra obtained by exciting bands A−G in the LIF spectrum. The spectra are presented with respect to the relative wavenumbers from the excitation position.

TABLE 3: Vibrational Assignment of "Group G" Conformers of Tyramine in the Dispersed Fluorescence Spectra

conformer A		conformer C		conformer D		conformer E		
obsd/ cm^{-1}	calcd/ cm^{-1}	obsd/ cm^{-1}	calcd[a]/ cm^{-1}	obsd/ cm^{-1}	calcd[a]/ cm^{-1}	obsd/ cm^{-1}	calcd[a]/ cm^{-1}	assignment[b]
44	39	43	38	43	44	43	43	ν_{57}: Ph-C_α torsion
77	73			76	77			ν_{56}: ethylamine wagging
143	130	138	131	136	132	134	133	ν_{55}: C_α-C_β torsion
204	197	221	195	208	202	201	201	ν_{54}: C_α-C_β torsion + ethylamine wagging
		315	312			313	304	ν_{53}: $C_\alpha-C_{\beta A}$ torsion + $N-C_\beta$ torsion
437	431	429	431	445	435	436	436	ν_{47}: 17b + ethylamine wagging
498	490	485	491	507	490	496	490	ν_{46}: 17b + $C_\alpha-C_\beta$ torsion
568	561	550	560	576	562	567	561	ν_{45}: 17b + $C_\alpha-C_\beta$ torsion
658	652	643	652	670	652	655	651	ν_{44}: 6b
728	737	713	714	740	745	729	744	ν_{42}: 4
854	847	833	847	874	843	855	843	ν_{38}: 1 + NH_2 wagging
923	916	900	915	947	919	928	920	ν_{36}: 1 + $C_\beta H_2$ rocking
992	966	965	968	1003	971	992	968	ν_{34}: 17a
1053	1081			1065	1100	1133	1101	ν_{31}: 18b + $C_\beta H_2$ wagging
				1141	1156	1164	1156	ν_{29}: NH_2 twisting + $C_\beta H_2$ twisting
1220	1220	1190	1219	1252	1223	1233	1222	ν_{26}: 19a ($Ph-C_\alpha$)
1275	1273	1242	1274	1294	1272	1282	1272	ν_{24}: 19a ($Ph-O$)
1331	1327	1303	1325	1342	1319	1340	1339	ν_{23}: 3
1405	1377	1373	1377	1427	1402	1409	1402	ν_{19}: NH_2 twisting + $C_\beta H_2$ wagging
1487	1463	1463	1463	1489	1465	1477	1465	ν_{17}: 14 + $C_\alpha H_2$ scissors
1562	1537	1579	1538	1570	1537	1569	1537	ν_{15}: 19a ($Ph-C_\alpha$ and $Ph-O$)
1643	1635	1628	1634	1634	1634	1634	1635	ν_{14}: 8b + NH_2 scissors
1666	1658	1649	1657	1689	1657	1679	1658	ν_{12}: 8a + NH_2 scissors
1694	1694	1655	1695	1697	1686	1698	1686	$2\nu_{38}$
1751	1763	1710	1762	1766	1762	1769	1763	$\nu_{38} + \nu_{36}$
1820	1813	1787	1815	1835	1814	1837	1811	$\nu_{38} + \nu_{34}$
1896	1928			1874	1943	1924	1944	$\nu_{38} + \nu_{31}$
2046	2067	2002	2066	2063	2066	2069	2065	$\nu_{38} + \nu_{26}$
2099	2120	2045	2121	2112	2115	2120	2115	$\nu_{38} + \nu_{24}$
2176	2174	2111	2172	2182	2162	2188	2182	$\nu_{38} + \nu_{23}$
						2247	2245	$\nu_{38} + \nu_{19}$
2470	2482	2407	2481	2477	2477	2475	2478	$\nu_{38} + \nu_{14}$
2522	2541	2462	2542	2526	2529	2529	2529	$3\nu_{38}$

[a] No scaling factor has been applied to the frequencies in this case. [b] Calculated frequencies are labeled as ν_i: $i = 1-57$ from higher to lower frequency to obey the IUPAC recommendation. Vibrational motions are described by the combination of the vibrational mode of the benzene ring (Load notation) and the motion of the chain.

OH groups, except for conformer **Aa**(**Anti**−**anti**). We denote each conformer according to the conformation about $C_\beta-C_\alpha$, $N-C_\beta$, and orientation of OH, such as **Gg′c**. This classification is shown graphically in Figure 3.

Table 5 shows the calculated relative energies for the nine stable conformers and those reported in previous studies.[31,30,32] While seven stable conformers were observed in the LIF spectrum, the theoretical calculation predicted nine conformers. Table 5 indicates relative energies of **Gg′c** and **Gg′t** conformers are significantly high, and this tendency is consistent with all previous works.[31,30,32] These two conformers have the amino lone pair oriented toward the π-electron system on a benzene ring. Richardson et al. considered that these two conformers were not in minima on the potential energy surface.[30] Consequently, it is conceivable that **Gg′c** and **Gg′t** conformers do not exist under the present conditions and we can exclude them from the assignment of the observed conformational structures of tyramine. There is no regular pattern to the relative energies of the other seven conformers in the theoretical calculations and thus it is difficult to assign the seven conformers in the spectrum by using only relative energies. To reliably assign the observed conformers, it is necessary to directly compare observed vibrational signatures with those obtained from theoretical calculations. Such an analysis is discussed in the next section.

3.4. Conformational Analysis. Figure 4 displays a comparison of the IR dip spectra of tyramine with those calculated for the seven stable conformers. As described previously, we classified the IR dip spectra into Group **a** (conformers A, B, and C) and Group **g** (conformers D, E, F, and G) based on the CH stretching vibration of the methylene chain in the 2800−3000 cm^{-1} region. Accordingly, here we show the observed spectra of conformers A and D representing Group **a** and Group **g**, respectively. The IR dip spectra agree well with the calculated spectra throughout the observed region. The comparison in CH stretching vibration of the methylene chain suggests that Group **a** (conformers A, B, and C) corresponds to the conformers **Gac**, **Gat**, and **Aa**, and those of Group **g** (D, E, F, and G) correspond to the conformers "**Ggc**, **Ggt**, **Agc**, and **Agt**". Specifically, the lowest frequency CH stretching bands of the methylene chain of conformers "**Ggc**, **Ggt**, **Agc**, **Agt**" are located at a frequency (∼2840 cm^{-1}) distinctly lower than those of conformers "**Gac**, **Gat**, **Aa**" (∼2890 cm^{-1}). The IR dip spectra reflect the conformation of $N-C_\beta$; that is, the group **a** "conformers A, B, and C" and the group **g** "conformers D, E, F, and G" are assigned to **anti** and **gauche** conformers, respectively. It should be highlighted that the chemical environment of the methylene chain mainly depends on the rotation of $N-C_\beta$.

Figure 5 displays a comparison of the dispersed fluorescence spectra of tyramine in the region of 350−650 cm^{-1} (region of out-of-plane CH bending vibration of the benzene ring) with calculated spectra for the seven stable conformers. As previously stated, we also classified the dispersed fluorescence spectra into two groups: Group **G** (conformers A, C, D, and E) and Group

TABLE 4: Vibrational Assignment of "Group A" Conformers of Tyramine in the Dispersed Fluorescence Spectra

conformer B		conformer F		conformer G		
obsd/ cm^{-1}	calcd[a]/ cm^{-1}	obsd/ cm^{-1}	calcd[a]/ cm^{-1}	obsd/ cm^{-1}	calcd[a]/ cm^{-1}	assignment[b]
43	44	40	42	40	42	ν_{57}: Ph−C_α torsion
84	78	88	79	88	79	ν_{56}: ethylamine wagging
101	95	101	92	101	93	ν_{55}: C_α−C_β torsion
132	122	148	121	148	121	$\nu_{57} + \nu_{56}$
339	318	335	329	335	329	ν_{51}: NH_2 wagging
531	512	517	514	517	514	ν_{46}: 17b + ethylamine wagging
579	557	571	559	571	559	ν_{45}: 17b + ethylamine wagging
890	862	870	863	870	863	ν_{37}: 1 + NH_2 wagging
973	968	1000	966	1000	973	ν_{34}: 17a
1211	1222	1208	1221	1208	1221	ν_{26}: 19a (Ph−C_α)
1252	1273	1239	1273	1239	1252	ν_{25}: 19a (Ph−O)
1295	1286	1288	1286	1288	1273	ν_{24}: $C_\alpha H_2$ twisting + $C_\beta H_2$ twisting
		1426	1402	1426	1402	ν_{19}: $C_\alpha H_2$ wagging + $C_\beta H_2$ wagging
1441	1463					ν_{17}: 14 + $C_\alpha H_2$ scissors + $C_\beta H_2$ scissors
1746	1724	1722	1726	1722	1727	$2\nu_{37}$
2090	2084	2073	2084	2073	2085	$\nu_{37} + \nu_{26}$
2144	2148	2126	2149	2126	2136	$\nu_{37} + \nu_{24}$

[a] No scaling factor has been applied to the frequencies in this case. [b] Calculated frequencies are labeled as ν_i: $i = 1-57$ from higher to lower frequency to obey the IUPAC recommendation. Vibrational motions are described by the combination of the vibrational mode of the benzene ring (Load notation) and the motion of the chain.

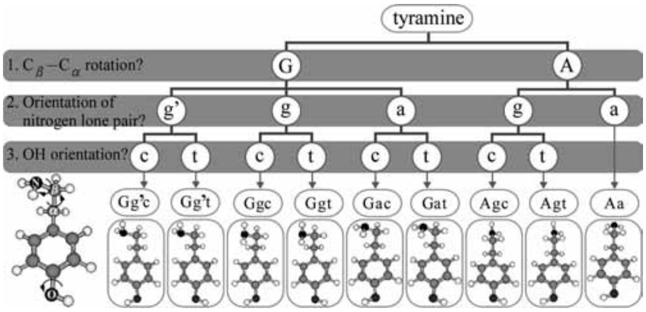

Figure 3. Optimized structures of the nine lowest energy conformers of tyramine at the B3LYP/aug-cc-pVDZ level. **G**, **A**, **g**, **g′**, **a**, **c**, and **t** represent **Gauche**, **Anti**, **gauche**, **gauche′**, **anti**, **cis**, and **trans** conformations, respectively.

TABLE 5: Total Energy of Conformers of Tyramine Calculated from ab Initio Calculations

	Gg′c	**Gg′t**	**Ggc**	**Ggt**	**Gac**	**Gat**	**Agc**	**Agt**	**Aa**
E_{rel}/cm^{-1}[a]	425	451	67	68	0	23	35	26	14
E_{rel}/cm^{-1}[b]	576	605	0	28	53	49	424	411	302
E_{rel}/cm^{-1}[c]			30	55	59	0	496	483	353
E_{rel}/cm^{-1}[d]	668	704	0	32	84	79	515	529	412

[a] Our work from the B3LYP/aug-cc-pVDZ calculation. [b] Reference 32. [c] Reference 30. [d] Reference 31.

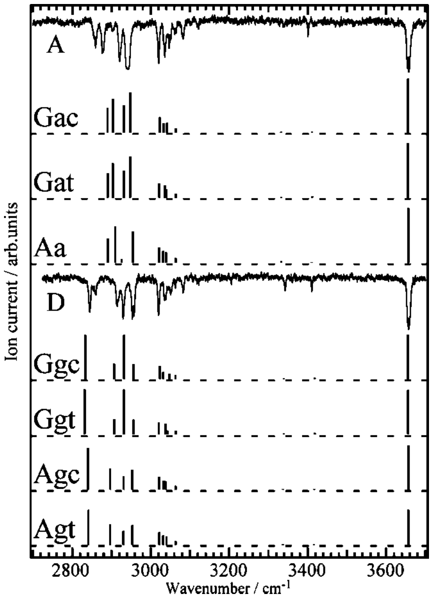

Figure 4. Comparison of the IR dip spectra of tyramine with calculated spectra of the seven stable conformers. For calculated frequencies, a scaling factor of 0.958 is used.

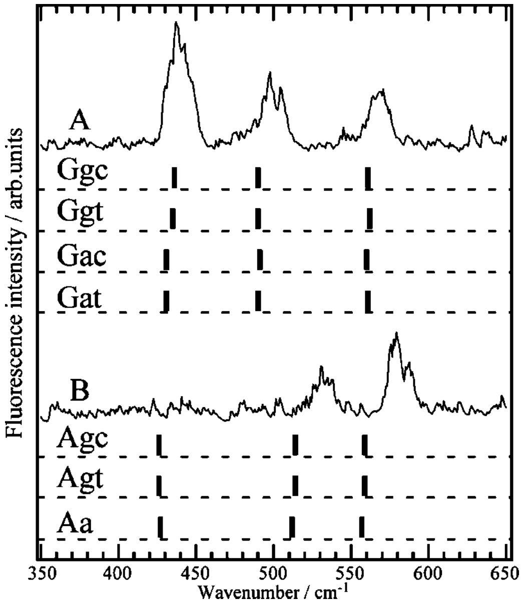

Figure 5. Comparison of the dispersed fluorescence spectra of tyramine in the region of 350−650 cm^{-1} (region of out-of-plane CH bending vibration of the benzene ring) with calculated spectra of the seven stable conformers. No scaling factor has been applied to the frequencies in this case.

A (conformers B, F, and G). The observed spectra of conformers A and B are presented as representatives of groups **G** and **A**, respectively. The dispersed fluorescence spectra match well the calculated spectra in the out-of-plane CH bending regions of the benzene ring. Noticeably, the CH bending bands at 533 and 579 cm^{-1} of the spectrum of conformer B are blue-shifted from bands at 498 and 568 cm^{-1} of the spectrum of conformer A, respectively. This characteristic shift is well reproduced in the calculated spectra. In particular, the central band at ~510 cm^{-1} of conformers **Agc**, **Agt**, and **Aa** corresponds well with the observed band at 533 cm^{-1} in the spectrum of conformer B. Additionally, in the spectrum of conformer B, no band is observed that corresponds to the band at 440 cm^{-1} in the spectrum of conformer A. This is likely due to the difference in the Franck−Condon factors. Therefore, on the basis of the clear correspondence with the theoretical vibrational frequencies, conformers of Group **G** and Group **A** are assigned to the conformers "**Ggc**, **Ggt**, **Gac**, and **Gat**" and "**Agc**, **Agt**, and **Aa**", respectively. It is confirmed that the dispersed fluorescence spectra reflect the conformation of C_β−C_α. The **Gauche** conformers (**Ggc**, **Ggt**, **Gac**, and **Gat**), i.e., Group **G**, have a NH···π hydrogen bond, whereas the **Anti** conformers (**Agc**, **Agt**, and **Aa**), Group **A**, do not have such an interaction. The reason why the dispersed fluorescence spectra clearly reflect the C_β−C_α conformation is due to the interaction with the π

TABLE 6: Band Position and Assignment of Conformers of Tyramine

band	position/cm^{-1}	assignment[a]	assignment[b]
A	35 466	Gac or Gat	Gat
B	35 478	Aa	Aa
C	35 485	Gac or Gat	Gac
D	35 549	Ggc or Ggt	Ggt
E	35 561	Ggc or Ggt	Ggc
F	35 583	Agc or Agt	Agt
G	35 583	Agc or Agt	Agc

[a] Our work. [b] Reference 32.

ring. The vibrational intensity distribution reflects the Franck−Condon factor between the S_1 excited electronic state and the S_0 ground state. Here S_1 is a $\pi\pi^*$ electronic transition and thus the molecular vibration that contains the bond interacting with the π ring will be activated in the dispersed fluorescence spectra. All the calculated vibrational frequencies and assignments are listed in Tables 1−4. Here, vibrational modes are numbered according to the order of frequencies. Vibrational motions are described by the combination of vibrational modes of the benzene ring (Lord notation) and the motion of the methylene chain, which are noted beside the mode number in the tables.

It is now possible to assign conformers A to G based on the above discussion. The LIF spectrum of conformer A is **Gauche** on the rotation of C_β−C_α from the dispersed fluorescence spectra and is **anti** on the rotation of N−C_β from the IR dip spectra. Therefore conformer A is assigned to **Gauche−anti**, that is, either **Gac** or **Gat**. Similarly, conformer B is assigned to **Aa**. Conformer C is assigned to either **Gac** or **Gat**. Conformers D and E are assigned to either **Ggc** or **Ggt**. Conformers F&G are assigned to either **Agc** or **Agt**. However, the assignment of the relative orientation of the phenolic OH (**cis** or **trans**) is not possible at present because the conformers which vary only in this respect have similar relative energies and vibrational structures. Table 6 summarizes our assignments of conformers. The previous assignments reported by Yoon et al.[32] are also shown. Our assignments are consistent with the previous ones obtained by rotational band contour spectra. Although the vibrational spectra reported here were not able to determine the orientation of the phenolic OH group, the good agreement with the previous assignment means it is now reasonable to take the conformational assignments by Yoon et al. According to the assignments, the splitting due to the different orientation of the OH group causes splitting of 19 (A&C), 12 (D&E), and 0 cm^{-1} (F&G) in tyramine. The splittings due to the OH orientation are also found in a related molecule, tyrosine, which are assigned to 31, 21, 5, and 0 cm^{-1}.[17] We also would like to highlight the fact that the key vibrational frequencies, the CH stretching vibration of the methylene chain (2800−3000 cm^{-1}) and the out-of-plane CH bending mode in the benzene ring (∼500 cm^{-1}), are good signatures for distinguishing the conformation of the chain in tyramine. Vibrational spectroscopy is available not only in the gas phase but also in the condensed phase and thus the vibrational signature of the conformers is potentially useful for future studies of molecular interactions with tyramine and related molecules.

In conclusion, we have measured the IR dip spectra and the relatively high resolution dispersed fluorescence spectra of jet-cooled tyramine. From observed and calculated vibrational frequencies of out-of-plane CH bending of the benzene ring and the CH stretching vibrations of the methylene chain, it was possible to assign the seven conformers observed in the S_1−S_0 laser induced fluorescence spectrum with a high degree of confidence.

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