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# Spectroscopy of Neurotransmitters and Their Clusters. 1. Evidence for Five Molecular Conformers of Phenethylamine in a Supersonic Jet Expansion

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**Abstract:** The neurotransmitter molecule phenethylamine (PEA) is studied by fluorescence excitation, mass-resolved excitation, hole burning, and dispersed emission spectroscopies. The excitation spectrum of PEA exhibits a group of five transition bands in the $S_1 \leftarrow S_0\ 0_0^0$ region. This group of transitions appears repetitively with the same spectral separations and intensity pattern in the higher energy regions up to 1000 cm$^{-1}$ above the origin. The hole burning spectra of these five bands show different independent spectral hole depletion features. With the observation of no blue shifted emission bands higher than the excitation energy in the dispersed emission spectra, these five transition bands can be assigned to five different molecular conformers of PEA. These molecular conformers are distinguished from each other in their alkylamine side chain conformations and the amino group spatial orientations. With the assistance of *ab initio* calculations, we are able to identify the conformations of these five isomers. The effects of the alkylamino chain conformation, as well as the amino group orientation, on the relative potential energies of these conformers are discussed. The significance of this work for future studies of PEA/solvent molecule clusters and the other neurotransmitters is demonstrated by the amphetamine (AMP) excitation spectrum. The conformation of the alkylamine side chain is found to have little impact on in-plane vibrational modes of the phenyl ring such as $\nu_{6b}$ and $\nu_{12}$.

## Introduction

The electronic spectroscopy and photophysics of many biological molecules are under continued scrutiny by numerous new and sophisticated experimental techniques.[1−7] With the development of laser spectroscopy and supersonic expansion techniques, high-resolution spectra and structural information on many biological molecules have been obtained. For example, Levy's group has studied the fluorescence spectra of the basic components of proteins−amino acids and their basic and acidic analogs.[8−10] Employing laser desorption[11] and high-pressure solution injection[12] techniques, Lubman's group improved the laser mass spectrometry method for nonvolatile or thermally labile biomolecules. Among the various systems investigated, one type of biomolecule−the neurotransmitter−is of particular interest. Even though they are present in living systems in only trace amounts, they have important biological functions and play significant roles in human emotions and behavior. Many neurotransmitters are aromatic amine compounds, which have relatively unambiguous and easy-to-assign spectral features.

A number of years ago we studied the spectra of phthalocyanine clustered with various small solvent molecules.[13] We are continuing to investigate the spectroscopic and photophysical properties of various biomolecules and their solvation clusters with the study of various aromatic amine neurotransmitters. Among these neurotransmitters, phenethylamine (PEA) is the simplest and has a readily accessible $S_1 \leftarrow S_0$ transition. To analyze the spectral features of PEA clusters, a clear understanding of its molecular spectrum is, of course, necessary. Unfortunately, this understanding has not been realized, despite the previous work on this molecule.[9] The problem arises from the fact that quite a few molecular conformers exist for PEA, and the spectral assignments to these conformers are less than unambiguous. During the investigations of amino acids, Levy's group studied the fluorescence excitation spectra of PEA, which is the basic analog of phenylalanine.[9] In the $0_0^0$ region of the $S_1 \leftarrow S_0$ excitation, they observed at least five prominent transition bands. With the help of carrier gas backing pressure dependence and laser power saturation studies, they identified four different conformers of PEA. By comparison of the PEA fluorescence excitation spectrum with the fluorescence excitation spectra of tyramine,[9] alkylbenzenes,[14,15] and 4-propylphenol,[16,17] they assign the four conformers to two *gauche* and two *anti* structures. The dispersed emission spectra of these four conformer bands also verify the assignments. Employing

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millimeter wave spectroscopy, Godfrey et al. assign the majority of the PEA rotational transition bands to two *gauche* conformers, both of which have an amino hydrogen atom close to the phenyl ring.[18] The $\pi$-system amino hydrogen atom proximity apparently provides extra stabilization to appropriate PEA conformations. High-quality *ab initio* calculations on PEA yield five stable molecular conformers—three *gauche* and two *anti*.[18] The different conformers have their alkylamine side chain taking different conformations. These conformers are suggested to affect only slightly the electronic transitions associated with the phenyl ring. PEA offers us a model system in which to study the structure of molecular conformers and isomerization processes connecting them.

We have performed fluorescence excitation, dispersed emission, hole burning, and mass resolved excitation spectroscopy on PEA and its clusters with simple solvent molecules. The $S_1 \leftarrow S_0$ excitation spectrum of the PEA molecule shows five fully resolved prominent transition bands in the $0_0^0$ region. The intensity ratio of these five bands is quite sensitive to the cooling conditions in the supersonic jet and varies from one experiment to another. The backing pressure dependence and laser power saturation studies carried out in ref 9 are therefore not able to distinguish unambiguously between hot band features and conformer transitions. To derive a clear assignment for the five component bands of the origin and most intense vibronic features, we employ both hole burning and dispersed emission spectroscopy techniques. The hole burning spectra of these five bands in the same wavelength region display independent and distinct spectra. This observation indicates that the five bands originate either from PEA molecules in different ground state potential minima (conformers) or from different ground state vibrational levels (hot bands). Since subsequent dispersed emission experiments exhibit no blue shifted emission features above the excitation energy for each of the five bands, the latter assumption of hot band transitions can be excluded. Furthermore, the dispersed emission spectra imply that the conformers are of two classes, each class with its own spectral characteristics. At energies up to 1000 cm$^{-1}$ above the origin band transitions, the PEA excitation spectrum shows complicated features which again can be ambiguously assigned as arising from the above five different conformers with the aid of hole burning spectroscopy.

Hole burning spectroscopy was first introduced in the context of supersonic jet studies by Lipert and Colson in 1989.[19] Within a few years, this technique has been widely applied in molecular and cluster isomer studies and its potential has been fully demonstrated.[20] In this method, an intense pump laser beam first saturates a transition band of a specific species, thus causing a ground state population depletion. A delayed probe laser beam detects this saturation by exciting the saturated species from the same ground state vibrational level. Any transition accessed by the probe laser that inolves the same ground state level as the pump laser will show a change in the probe generated spectrum. In practice, the probe beam is usually fixed at one transition band and the pump laser is scanned through the wavelength region of interest. Should the two laser excited transitions share the same ground state vibrational level, the pump beam induced depopulation is manifested by a decrease in the transition intensity (spectral "hole") induced by the probe beam. If the two lasers excite different ground state potential minima (conformers) or different ground state vibrational levels (hot bands), the intensity of the probe beam induced transition should not be affected and thus no spectral hole will be observed. In supersonic jet expansions, the cooling effect eliminates most of the hot band transitions, therefore by examining the "holes" in a hole burning spectrum one can typically resolve the correlation of different excitation transitions and identify different isomer species. This technique is complementary to mass resolved excitation spectroscopy since it is able to distinguish the spectral features from different isomer species of the same mass.

## Experimental Procedures

The experiment setup has been described in full previously.[21] In this report, we give a brief overview of the employed techniques and apparatus with some emphasis on the technical differences between this and previous studies.

In fluorescence excitation experiments, the doubled output of a Nd/YAG pumped dye laser (Quanta Ray, DCR II/PDL-1/WEX-1) is employed as the excitation source. Only one dye, Coumarin 500 (Exciton), is used to cover the wavelength region of interest (258.8−267.5 nm). The laser beam is slightly focused through a 1 m focal length lens at about 1.5 cm downstream from the nozzle throat. The supersonic nozzle (General Valve, Series 9) has an orifice diameter of 0.7 mm. The fluorescence signal is detected by a photomultiplier tube (PMT) (RCA, C31034).

In dispersed emission experiments, the excitation laser source is the same as above. The excitation beam is slightly focused at about 0.7 cm downstream from the nozzle throat, where the sample concentration is higher but the cooling effect is still not complete. A 1 m scanning monochromator (GCA/Mcpherson Instrument, Model 2051) with a 2400 groves/mm grating is used as the dispersing element. Different spectral resolutions are tried during the experiment. In the dispersed emission spectra presented in this paper, the monochromator entrance and exit slit widths are set to ∼0.15 mm achieving a spectral resolution of ≤10 cm$^{-1}$. A PMT (RCA, C31000M) with high sensitivity and low noise is placed at the exit slit of the monochromator.

In hole burning experiments, two laser systems as described above are utilized. The intensity ratio of the pump beam to the probe beam is about 3:1; this ratio is able to generate spectral holes up to 50% intensity depletion of the probe laser induced fluorescence. The time delay between the two laser beams is set to 500 ns which is about 7 times the fluorescence lifetimes of the PEA origin bands.[9] This setup ensures that pump laser induced fluorescence does not interfere with the described signal induced by the probe laser.

For the investigations of the PEA clusters, MRES is also performed for the PEA bare molecule. The mass detected excitation spectra are similar to the fluorescence excitation spectra. A one-color ionization scheme is employed in which the same laser beam served as both excitation and ionization sources. A Wiley-McLaren type time-of-flight (TOF) mass spectrometer is used with a Jordan pulsed valve as the supersonic nozzle. The excitation laser beam is not focused and the ion signal is quite intense due to the large extinction coefficient of PEA.

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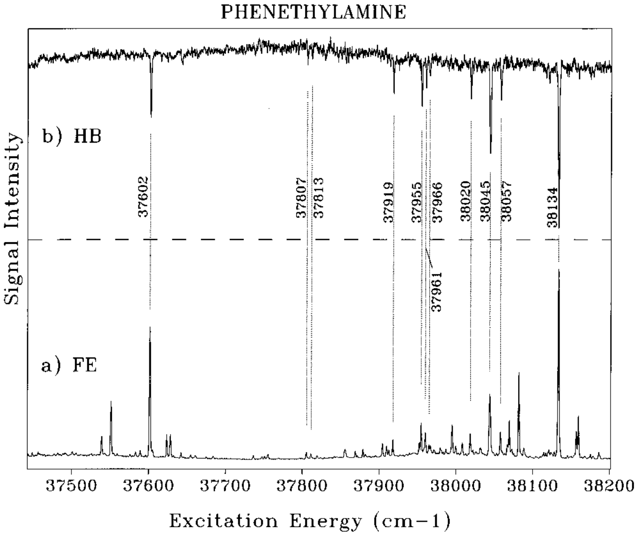

**Figure 1.** (a) Fluorescence excitation spectrum of PEA from 37 440 to 38 200 cm$^{-1}$ (from the origin band to ~800 cm$^{-1}$ above). (b) The hole burning spectrum of PEA conformer C obtained by monitoring the fluorescence signal depletion of the 37 602-cm$^{-1}$ band and scanning the pump laser beam. The maximum signal depletion ratio is greater than 50%. The intensity ratio of the pump to the probe beams is about 3:1, with a time delay between them of ~500 ns. The dotted lines indicate the correspondence of the vibronic transitions in both spectra.

The fluorescence signal from the PMT and the ion signal from the micro-channel plate (MCP) are sent through a fast preamplifier (EG&G, 9301) to either a boxcar integrator (Standard, SR250) for spectra analysis or a transient digitizer (Tektronix, 7912AD) for temporal investigation. All timings are controlled by two digital pulse/delay generators (Stanford, DG535).

PEA is purchased from Aldrich (99+%) and used without additional purification. The sample is placed close to the nozzle throat without any active heating. He is used as the carried gas in all experiments with a backing pressure of about 50 psi.

## Results

**A. Excitation and Hole Burning Spectroscopy.** Figure 1a displays the fluorescence excitation spectrum of PEA from its $S_1 \leftarrow S_0$ origin band to ~800 cm$^{-1}$ above it. In the origin band region there is a major peak at 37 602 cm$^{-1}$, with four other less prominent features in the energy range from 37 539 to 37 629 cm$^{-1}$. A mass resolved excitation spectrum for this region also exhibits these five peaks at the same positions, thus confirming that the five features are due to vibronic transitions of the PEA molecule. These five bands were observed previously by Martinez et al.[9] They assigned four of them, located at 37 538, 37 551, 37 602 and 37 629 cm$^{-1}$, as the $S_1 \leftarrow S_0$ origin band transitions of four different PEA conformers—A, B, C, and D, respectively. The fifth conformer transition at 37 624 cm$^{-1}$, which in their spectrum partially overlaps conformer D's origin band at 37 629 cm$^{-1}$, was probably taken as a hot band transition and neglected.[9] Their assignments followed a logical reasoning by comparing these features with the different conformer origin bands of tyramine and 4-propylphenol;[9,17] however, no direct and unambiguous proof for their assignments was offered. Our excitation spectrum shows a spectral line width of about 1.5 cm$^{-1}$ (fwhm) for the origin band transitions, which is at least twice as sharp as the ref 9 result. Furthermore, in our spectrum, the fifth band at 37 624 cm$^{-1}$ is fully resolved from the origin band of conformer D. We assign this fifth peak as the origin band of yet another conformer, E. The proof for this assignment will be given in the following presentation.

The overall excitation spectrum (Figure 1a) is quite complicated, especially in the higher energy region in which the aggregates of transition features are beyond ready comprehension without resorting to other spectroscopic methods. Since the PEA molecule has multiple conformers, the total excitation spectrum is an overlap of all the vibronic transition features from the different conformers. Hole burning spectroscopy seems to be the ideal method by which to untangle this collection of features. Figure 1b shows the hole burning spectrum for the probe laser beam fixed at the most intense origin band, the 37 602 cm$^{-1}$ band of the conformer C, and the pump laser beam scanned through the whole excitation wavelength region. This hole burning spectrum clearly displays all the transition features starting from the ground state vibrationless level of the PEA conformer C, and unambiguously distinguishes these bands from the rest of the features which belong to other conformers. The fluorescence signal depletion ratio is more than 50% in the strongest band at 38 134 cm$^{-1}$. This latter feature in both the fluorescence excitation and the hole burning spectra, which is 532 cm$^{-1}$ above the origin band, is assigned as the $6b_0^1$ vibronic band; this is a typical intense feature in many substituted single ring benzene-like aromatic compounds.[15,23] Other major intensity bearing vibronic transitions can be assigned in a similar manner to the vibrational modes of the phenyl ring. The energies of these modes show only small variations from those of alkyl-substituted benzenes. Ethylamine substitution also relaxes the symmetry restrictions imposed on the vibronic transitions, since the PEA molecule has either $C_s$ or $C_1$ point group symmetry. The intensity patterns of the vibronic bands in these two types of spectra (hole burning and fluorescence excitation) are generally similar to each other, with some minor exceptions. For example, the intensity ratio of the three most intense bands at 37 602, 38 045, and 38 134 cm$^{-1}$ is roughly 2:1:3 in the fluorescence excitation spectrum, but about 2:3:5 in the hole burning spectrum. This difference may be due to differences in quantum yields for these three bands.

Hole burning spectroscopy on the other conformer bands of PEA is also shown in Figure 2 for the origin band region from 37 500 to 37 700 cm$^{-1}$. Figure 2a gives the fluorescence excitation spectrum in this region for comparison. Figures 2b to 2f display the hole burning spectra obtained by monitoring the fluorescence signal depletion of the five transition bands in the order of decreasing excitation energy. Following Martinez et al.'s convention,[9] we attribute the vibronic transitions at 37 539, 37 551, 37 602, and 37 629 cm$^{-1}$ to the $S_1 \leftarrow S_0$ origin bands of conformers A, B, C, and D, respectively. The fifth band at 37 624 cm$^{-1}$ is assigned to the origin band of another conformer E, since it shows an independent single spectral hole just as the other four bands. These five hole burning spectra clearly indicate the different origins of the five vibronic transitions in the origin band region. The hole burning spectra of conformers A, B, D, and E all display signal depletion at 37 602 cm$^{-1}$, which is the origin band position of conformer C; however, this is just a false "spectral dip" originating from the saturation of the PMT due to the pump laser induced intense fluorescence signal to the conformer C origin band. The feature is therefore a single-laser effect, as can be verified by observing the dip signal even with the probe beam blocked. The weaker the origin band transitions (such as those of conformers A, D, and E), the more prominent this false dip signal (due to the required higher detection sensitivity) becomes. Increasing the time delay between pump and probe laser pulses results in the diminishing of this dip signal. A closer inspection of Figure 2e reveals another real spectral hole corresponding to a weak transition at 37 590 cm$^{-1}$, while the other four hole burning

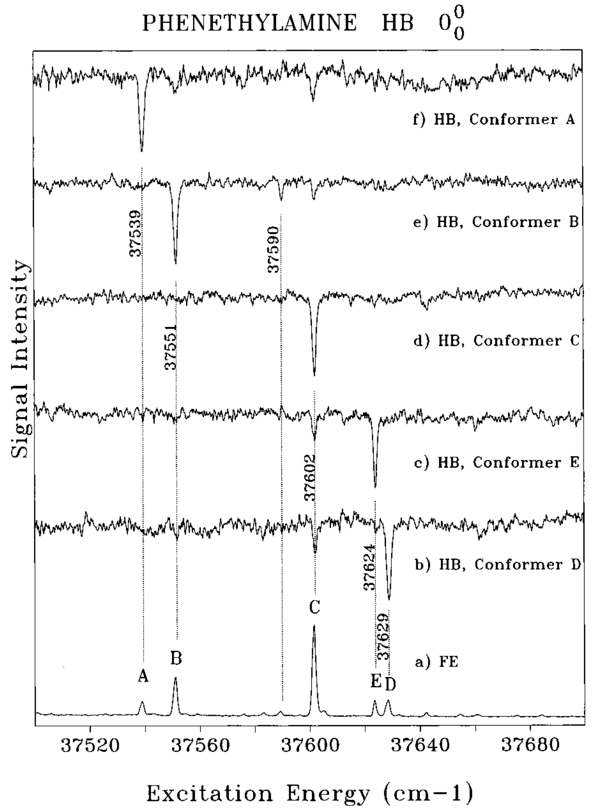

**Figure 2.** (a) Fluorescence excitation spectrum of PEA in its origin band region (37500−37700 cm$^{-1}$). (b−f) The hole burning spectra of PEA conformers obtained by scanning the pump laser and monitoring the fluorescence signal depletion of the origin bands of conformers D, E, C, B, and A at 37 629, 37 624, 37 602, 37 551, and 37 539 cm$^{-1}$, respectively.

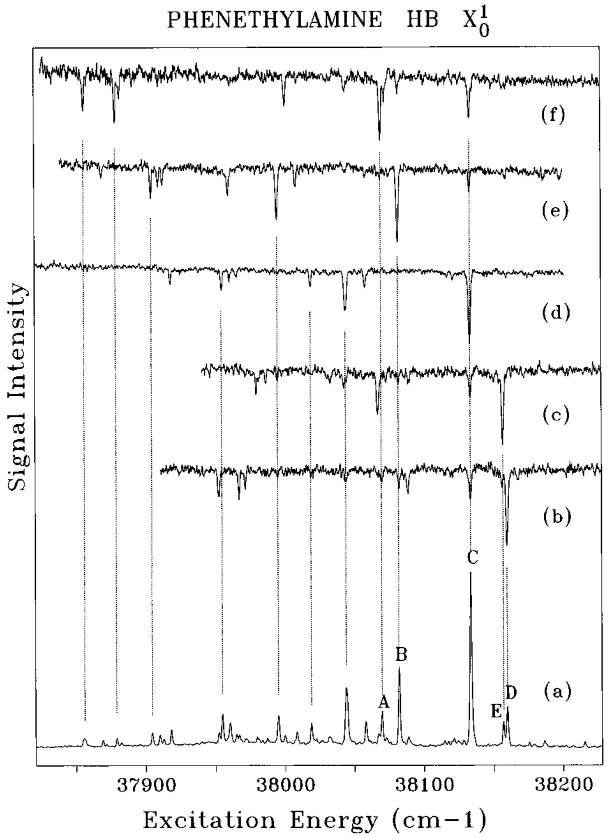

**Figure 3.** (a) Fluorescence excitation spectrum of PEA in the higher energy region (37820−38230 cm$^{-1}$). (b−f) The hole burning spectra of PEA conformers obtained by scanning the pump laser and monitoring the fluorescence signal depletion of the origin bands of conformers D, E, C, B, and A at 37 629, 37 624, 37 602, 37 551, and 37 539 cm$^{-1}$, respectively.

spectra exhibit only a single spectral hole over this wavelength range within the limit of the noise fluctuation level.

Figure 3 is the continuation of Figure 2 in the higher energy region from 37 820 to 38 230 cm$^{-1}$. The excitation spectrum in Figure 3a shows quite complicated vibronic transition features; however, with the assistance of the hole burning spectra of conformers D, E, C, B, and A, displayed in Figures 3b to 3f, respectively, each single vibronic feature in the excitation spectrum can be found corresponding to a conformer transition band in one of the hole burning spectra. All the hole burning spectra are obtained by monitoring the origin band fluorescence signal depletion of the corresponding conformer. The transition energy of each vibronic band is tabulated in Table 1, along with the appropriate vibrational energy in the excited $S_1$ state. From Figure 3 and Table 1 we find that the strongest feature in each hole burning spectrum corresponds to the $6b_0^1$ vibronic transition of each conformer. These five $6b_0^1$ bands have the same spectral separations between each other (within ±1 cm$^{-1}$) as the five origin bands, and their relative intensity pattern is also quite similar to that of the origin bands. This suggests that the conformation of the ethylamine side chain has little effect on the $\nu_{6b}$ vibrational mode of the phenyl ring; indeed, all the conformers have their $\nu_{6b}$ vibrational energy in the $S_1$ state at ∼532 ± 1 cm$^{-1}$. This insensitivity has been observed before by Hopkins et al.:[15] for various alkylbenzenes, the in-plane vibrational modes $\nu_{6b}$, $\nu_{12}$, and $\nu_{18a}$ of the phenyl ring are found to be invariant to the side chain substitution. On the other hand, other modes, such as $\nu_{6a}$ and $\nu_1$, change with the alkyl chain length as well as its conformation.[15] As in Figure 2, pump laser induced false signal dips in the hole burning spectra, which correspond to the intense $6b_0^1$ transitions of both conformers C and B, are also present in Figure 3.

Figures 3b and 3f, which exhibit the vibronic features of conformers D and A, respectively, show a strong resemblance to one another, but are slightly different from the other three hole burning spectra. As listed in Table 1, both hole burning spectra (A, D) have singlet and doublet features in the lower energy region, at vibrational excess energies ($X_0^1$ − $0_0^0$) of about 320 and 340 cm$^{-1}$. Another vibronic transition with excess energy of 462 cm$^{-1}$ is observed in both spectra, but it does not appear in the other three hole burning spectra. On the other hand, Figures 3c, 3d, and 3e show similarities to each other. As an example, they all have a relatively strong vibronic transition with an excess energy of ∼444 cm$^{-1}$. In fact, Figures 3d and 3e share additional common features. For instance, both spectra have a triplet progression starting at an excess energy of 353 cm$^{-1}$ with a separation of about 5 cm$^{-1}$ (see Table 1). Some of these common vibronic bands may also exist in Figure 3c, but they are submerged in the noise due to the weak fluorescence intensity of conformer E.

The above analysis strongly suggests that PEA conformers can be divided into two classes: one consisting of conformers B, C, and E, and the other consisting of conformers A and D. Martinez et al. proposed that conformers A and D are of *anti* conformation while conformers B and C are of *gauche* conformation. The similarity of the various hole burning spectra is one of the verifications presented in this paper. We will discuss the conformer structures in the next section.

Hole burning spectra of the higher energy region are presented in Figure 4. The fluorescence excitation and hole burning

**Table 1.** $S_1 \leftarrow S_0$ Excitation Transitions of the Five Phenethylamine Conformers

| conformer A | | conformer B | | conformer C | | conformer D | | conformer E | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| transition energy ($cm^{-1}$) | rel position ($cm^{-1}$)[a] | transition energy ($cm^{-1}$) | rel position ($cm^{-1}$)[a] | transition energy ($cm^{-1}$) | rel position ($cm^{-1}$)[a] | transition energy ($cm^{-1}$) | rel position ($cm^{-1}$)[a] | transition energy ($cm^{-1}$) | rel position ($cm^{-1}$)[a] | assignment[b] | |
| 37 539 | 0 | 37 551 | 0 | 37 602 | 0 | 37 629 | 0 | 37 624 | 0 | $0_0^0$ | * |
| | | | | 37 807 | 205 | | | | | | |
| | | | | 37 813 | 211 | | | | | | |
| 37 857 | 318 | 37 870 | 319 | 37 919 | 317 | 37 953 | 324 | | | | |
| 37 880 | 341 | | | | | 37 968 | 339 | | | | |
| 37 883 | 344 | | | | | 37 972 | 343 | | | | |
| | | 37 905 | 354 | 37 955 | 353 | | | | | | |
| | | 37 910 | 359 | 37 961 | 359 | | | 37 980 | 356 | | |
| | | 37 914 | 363 | 37 866 | 364 | | | 37 987 | 363 | | |
| | | 37 960 | 418 | 38 020 | 418 | | | | | | |
| | | 37 996 | 445 | 38 045 | 443 | | | 38 068 | 444 | | * |
| | | 38 009 | 458 | 38 057 | 455 | | | | | | |
| 38 001 | 462 | | | | | 38 090 | 461 | | | | |
| | | | | 38 122 | 520 | | | | | | |
| 38 070 | 531 | 38 083 | 532 | 38 134 | 532 | 38 160 | 531 | 38 157 | 533 | $6b_0^1$ | * |
| | | | | 38 331 | 729 | | | | | | |
| | | | | 38 491 | 889 | | | | | | |
| | | | | 38 493 | 891 | | | | | | |
| | | | | 38 524 | 922 | | | | | | |
| | | | | 38 526 | 924 | | | | | | |
| 38 471 | 932 | 38 484 | 933 | 38 536 | 934 | 38 562 | 933 | 38 557 | 933 | $12_0^1$ | * |
| | | | | 38 574 | 972 | | | | | $18a_0^1$ | |
| | | | | 38 588 | 986 | | | | | | |

[a] Spectral shift is relative to the $S_1 \leftarrow S_0$ origin band of each conformer, i.e., the vibrational energy in the excited state. [b] Assignments follow the benzene vibration notation, an asterisk (*) denotes the intense transition bands.

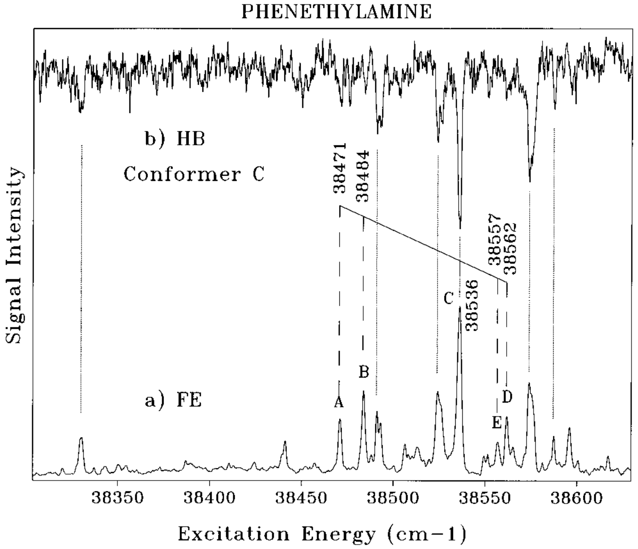

**Figure 4.** (a) Fluorescence excitation spectrum of PEA from 38 300 to 38 630 $cm^{-1}$. (b) The hole burning spectrum of PEA conformer C obtained by monitoring the fluorescence signal depletion of the origin band at 37 602 $cm^{-1}$. The dotted lines indicate the correspondence of the vibronic transitions of conformer C in the two spectra, while the dashed lines depict the $12_0^1$ vibronic bands of the five conformers.

spectra from 38 300 to 38 630 $cm^{-1}$, about 1000 $cm^{-1}$ above the origin band, are shown. In the fluorescence excitation spectrum (Figure 4a), the transition features display a more complicated and less resolved pattern than in the spectra displayed in Figure 3a. Due to the high $S_1$ vibrational energy, the line widths of these vibronic bands have increased to ~3 $cm^{-1}$ (fwhm); nonetheless, this convoluted pattern can still be analyzed and the major transitions can be assigned with the assistance of the hole burning experimental results. Figure 4b shows the hole burning spectrum obtained by monitoring the fluorescence signal depletion of the origin band of PEA conformer C. Although in this hole burning spectrum the signal-to-noise ratio (S/N) is reduced compared to former spectra, one can still unambiguously determine half a dozen vibronic transitions of conformer C. The strongest feature in both spectra is located at 38 536 $cm^{-1}$, which has an excess vibrational energy of 934 $cm^{-1}$ and is assigned to the in-plane $\nu_{12}$ vibrational mode of the phenyl ring in the $S_1$ state. To the red and blue of the $12_0^1$ band, one can also locate the $12_0^1$ vibronic transitions of the other four conformers, as labeled in Figure 4a. The five $12_0^1$ bands have a similar intensity pattern to those of the $0_0^0$ and $6b_0^1$ transitions, and their excess vibrational energy is the same, $933 \pm 1$ $cm^{-1}$. This indicates the conformation of the alkylamine side chain has little effect on the $\nu_{12}$ vibrational mode of the aromatic ring. The transition energies of the various vibronic bands can be found in Table 1. The assignment of $\nu_{12}$ follows Hopkins et al.'s convention.[15] In benzene, the in-plane vibrations $\nu_1$ and $\nu_{12}$ are of $a_{1g}$ and $b_{1u}$ symmetry ($D_{6h}$ point group), respectively, and their frequencies are quite similar ($\nu_1 = 993$ $cm^{-1}$ and $\nu_{12} = 1010$ $cm^{-1}$ in the ground state);[23] however, with the side chain substitution, the symmetry restriction is relaxed and both vibrational modes are reduced to $a_1$ symmetry in $C_{2v}$ or lower symmetry point groups. These two modes have identical motions except for the phase of the adjacent carbon displacements,[15] and therefore the strong Fermi resonance of these two vibrational levels results in two new levels represented as 1+12 and 1−12. Following Vasanyi's convention,[24] Hopkins assigned the former as "$\nu_1$" and the latter as "$\nu_{12}$"; however, the opposite choice is also seen in the literature.[25,26] In propylbenzene, the $\nu_{12}$ mode has an energy of 933 $cm^{-1}$, which is exactly the value for $\nu_{12}$ in PEA.

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(24) Varsanyi, G. *Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives*; Wiley: New York, 1974.

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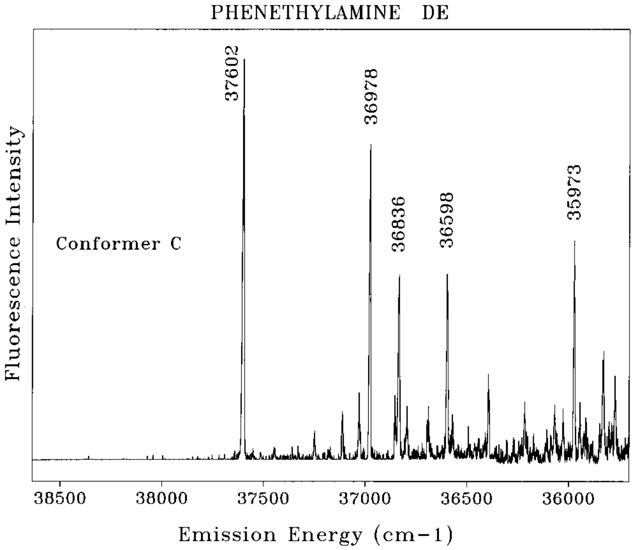


**Figure 5.** Dispersed emission spectrum of the origin band of the PEA conformer C from 38 635 to 35 700 cm$^{-1}$. The excitation energy is at 37 602 cm$^{-1}$. The spectral resolution in this spectrum is about 8.8 cm$^{-1}$.

**B. Dispersed Emission Spectroscopy.** Although the hole burning spectra verify that the vibronic transitions of the five conformers start from different origins, and the mass-resolved excitation spectrum confirms all the features do belong to PEA, a small possibility still exists that some of these transitions originate from different vibrational levels of an $S_0$ conformer state instead of different local potential wells (conformers) in the ground electronic state; that is, the observed transitions are not all due to cold conformer vibronic bands but that some are hot band transitions associated with fewer conformers. For example, the intensity of the vibronic bands assigned to conformer E is quite sensitive to the jet expansion conditions. Martinez et al. therefore did not assign the band at 37 624 cm$^{-1}$ to a conformer origin band, but presumably treated it as a hot band transition.[9] Dispersed emission spectroscopy can be employed to resolve this ambiguity. Since PEA is a low-symmetry molecule (either $C_s$ or $C_1$ point group), all its vibronic transitions (certainly $X_1^0$ and $0_0^0$) ought to be active in the $S_1 \leftrightarrow S_0$. Therefore, should any of the vibronic bands be a hot band transition which originates from a different ground state vibrational level of a common conformer, the dispersed emission spectrum of this band will definitely exhibit blue shifted emission features relative to the excitation transition.

Figure 5 shows the $S_0 \leftarrow S_1$ dispersed emission spectrum of the PEA conformer C from 38 635 to 35 700 cm$^{-1}$ following the excitation of its origin band at 37 602 cm$^{-1}$. No blue-shifted emission bands are observed to nearly 1000 cm$^{-1}$ above the excitation energy. Similar dispersed emission spectra are obtained for the excitation of origin bands of the other four conformers; none of these conformers exhibits blue shifted emission features above its excitation energy. This clearly dismisses the suspicion of hot band transitions mistaken for a new conformer transition, and proves that the five origin bands do arise from different conformers.

The emission features in Figure 5 are clustered about 37 000 to 36 000 cm$^{-1}$ and are quite numerous. The transition energies of the most intense bands have been labeled in the figure. Since our focus is not on the assignments of the spectral features in this presentation, we only point out some of the quite obvious assignments: the intense emission bands at 37 602, 36 978, 36 598, and 35 973 cm$^{-1}$ correspond to the $0_0^0$, $6b_1^0$, $12_1^0$, and $6b_1^0 12_1^0$ vibronic transitions of PEA conformer C, respectively. The weak progressions about 37 000 and 36 000 cm$^{-1}$ are probably due to motion of the ethylamine group.

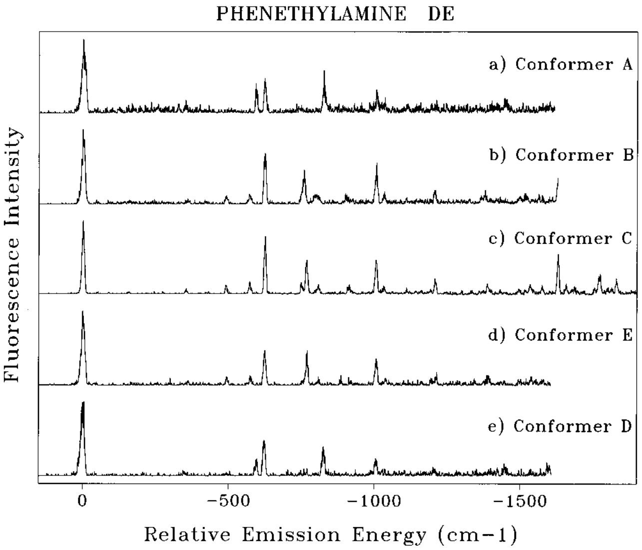


**Figure 6.** (a−e) Comparison of the dispersed emission spectra of the five PEA conformers following their origin band excitation. The excitation energies are 37 539, 37 551, 37 602, 37 624, and 37 629 cm$^{-1}$ for conformers A, B, C, E, and D, respectively. The horizontal axis displays the emission energy relative to its origin band energy, i.e., the negative of the ground state vibrational energy. The spectral resolution is about 10 cm$^{-1}$ for all the spectra.

Stimulated by the successful comparisons depicted in Figure 3, we try to compare the dispersed emission spectra of the five conformers in detail. Figures 6a−6e display all five dispersed emission spectra following the excitations of the conformer origin bands at 37 539, 37 551, 37 602, 37 624, and 37 629 cm$^{-1}$. Choosing the excitation energy of each origin band as the reference energy, the horizontal axis in this figure is the relative emission energy, i.e., the negative of the ground state vibrational energy of each conformer. In this way, we are able to align the five dispersed emission spectra and to compare the ground state vibrational levels of the different conformers. Table 2 lists all the emission energies of the vibronic bands, along with their vibrational energies in the ground electronic state. From Figure 6 and Table 2 one can again see that the conformation of the ethylamine side chain has almost no effect on the $\nu_{6b}$ and $\nu_{12}$ vibrational modes of the phenyl ring. All five dispersed emission spectra yield the same vibrational energies for the $\nu_{6b}$ mode (623 ± 1 cm$^{-1}$) and $\nu_{12}$ mode (1005 ± 1 cm$^{-1}$) for the five conformers. As a comparison, in the analog molecule propylbenzene, $\nu_{6b}$ and $\nu_{12}$ vibrations have the energies of 624 and 1013 cm$^{-1}$, respectively.[15b] The emission features in the dispersed emission spectra exhibit patterns similar to excitation spectra.

A close inspection of Figure 6 and Table 2 suggests that the five dispersed emission spectra can again be divided into two groups. Figures 6b, 6c, and 6d show similarity while Figures 6a and 6e resemble each other. Therefore, conformers B, C, and E belong to one class of conformers, while conformers A and D form another class. This again verifies the results and conclusions obtained from Figure 3. In Figures 6a and 6e, there is a doublet emission feature just below the $6b_1^0$ transition with the vibrational energy of ~593 cm$^{-1}$. On the other hand, Figures 6b, 6c, and 6d exhibit at least two separate weak bands located at about −491 and −571 cm$^{-1}$ in this region. In the spectral region between $6b_1^0$ and $12_1^0$ transitions, Figures 6a and 6e have another emission band at −825 cm$^{-1}$, while Figures 6b, 6c, and 6d display similar multipeak features scattered in

**Table 2.** $S_0 \leftarrow S_1$ Dispersed Emission Transitions of the Five Phenethylamine Conformers

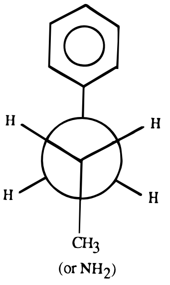
| conformer A | | conformer B | | conformer C | | conformer D | | conformer E | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| transition energy ($cm^{-1}$) | vib energy ($cm^{-1}$)[a] | transition energy ($cm^{-1}$) | vib energy ($cm^{-1}$)[a] | transition energy ($cm^{-1}$) | vib energy ($cm^{-1}$)[a] | transition energy ($cm^{-1}$) | vib energy ($cm^{-1}$)[a] | transition energy ($cm^{-1}$) | vib energy ($cm^{-1}$)[a] | assignment[b] | |
| 37 539 | 0 | 37 551 | 0 | 37 602 | 0 | 37 629 | 0 | 37 624 | 0 | $0_0^0$ | * |
| | | | | 37 249 | 353 | | | | | | |
| | | 37 060 | 491 | 37 112 | 490 | | | 37 131 | 493 | | |
| | | 36 980 | 571 | 37 031 | 571 | | | 37 051 | 573 | | |
| 36 948 | 591 | | | | | 37 039 | 590 | | | | * |
| 36 944 | 595 | | | | | 37 032 | 597 | | | | * |
| 36 917 | 622 | 36 928 | 623 | 36 978 | 624 | 37 006 | 623 | 37 002 | 622 | $6b_1^0$ | * |
| | | | | 36 854 | 748 | | | | | | |
| | | 36 794 | 757 | 36 836 | 766 | | | 36 856 | 768 | | * |
| | | 36 750 | 801 | 36 796 | 806 | | | 36 818 | 806 | | |
| 36 714 | 825 | | | | | 36 804 | 825 | | | | |
| | | 36 652 | 899 | 36 691 | 911 | | | | | | |
| 36 533 | 1006 | 36 546 | 1005 | 36 598 | 1004 | 36 624 | 1005 | 36 620 | 1004 | $12_1^0$ | * |
| | | 36 519 | 1032 | 36 570 | 1032 | | | | | $18a_1^0$ | |
| | | 36 346 | 1205 | 36 394 | 1208 | | | 36 413 | 1211 | $9a_1^0$ | |
| | | | | 36 216 | 1386 | | | 36 236 | 1388 | | |
| | | | | 36 069 | 1533 | | | | | | |
| | | | | 36 028 | 1574 | | | | | | |
| | | 35 922 | 1629 | 35 973 | 1629 | | | | | $6b_1^0 12_1^0$ | * |
| | | | | 35 834 | 1768 | | | | | | |
| | | | | 35 829 | 1773 | | | | | | |
| | | | | 35 773 | 1829 | | | | | | |

[a] Spectral shift is relative to the $S_0 \leftarrow S_1$ origin band of each conformer, i.e., the vibrational energy in the ground state. [b] Assignments follow the benzene vibration notation, an asterisk (*) denotes the intense transition bands.

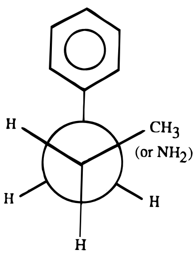
this region. These examples again support the contention that conformers A and D are of *anti* conformations while B, C, and E are *gauche* conformations, as will be discussed below.

## Discussion

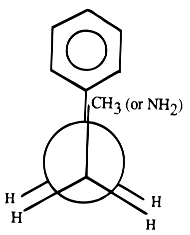
**A. The Conformers.** From the hole burning experimental results we conclude that the five transitions at each vibronic level start from different independent origins. With the dispersed emission spectra we are certain that none of them are hot band transitions which originate from different vibrational levels in the ground state of a single conformer. Therefore the only explanation for the hole burning results is that five different conformers exist for the PEA molecule. These conformers are distinguished in their conformational variations of the ethylamine side chain and amino group orientations. From the studies of ethylbenzene and other similar molecules, the $C_\alpha-C_\beta$ bond of the alkyl side chain is well established to almost always lie in the plane perpendicular to the phenyl ring, i.e., $\tau_1 = 90°$.[14] Therefore for both propylbenzene and PEA, the side chain conformational variations have three possibilities: *anti*, *gauche*, and *eclipsed*.



*anti*



*gauche*



*eclipsed*

In the propylbenzene fluorescence excitation spectrum, only two conformer transition bands of nearly equal intensity have been observed in the $S_1 \leftarrow S_0\, 0_0^0$ region.[14a,15] Hopkins et al. compare this spectrum with that of ethylbenzene and concluded that one band corresponds to the *anti* conformation (*trans* in their paper). The other band, which is suggested to be red shifted due to the attractive van der Waals (vdW) interactions between the alkyl group and the phenyl ring $\pi$-electrons,[14c,26] may correspond to either a *gauche* or an *eclipsed* conformation.[15a] By studying the conformers in the *m*-(*n*-propyl)toluene, Breen et al. determined that this red shifted origin band arises from the *gauche* conformation.[14a] Thus the propylbenzene molecule has two conformers in the jet expansion: one is *gauche* and the other is *anti*.

PEA conformational possibilities are more complex than those of propylbenzene due to the different possible orientations for the amino group hydrogen atoms. One expects, of course, that the major chain conformations will follow those for propylbenzene and that those interactions that force the propylbenzene conformational preferences ($C_\alpha-C_\beta$ bond perpendicular to the ring, *anti*, and *gauche* terminal methyl group) will be satisfied first. Following this, the $NH_2$ group can express its conformational preferences through its hydrogen atom positions relative to the rest of the molecule. Thus, the gross *anti* and *gauche* chain conformations of PEA represent the two main classes of conformers and the members of each class can be distinguished by their $NH_2$ hydrogen atom orientation. The rapid cooling attendant a supersonic expansion allows the various higher energy conformers to be trapped and "frozen out" in their local potential energy wells. Based on comparisons with spectra of other molecules, the authors of ref 9 have assigned the A and D conformers as *anti* and the B and C conformers as *gauche*. We accept this assignment in the following discussion.

Hole burning and dispersed emission spectra offer experimental verification of the above assignments, while theoretical calculations also support these assignments. Quite a number of calculational studies have appeared on the conformations of PEA and its analog molecules. This body of work includes empirical,[14,29] semiempirical,[30] and *ab initio* calculations[18,31] at various levels of sophistication. The results of these studies

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(28) Tsoucaris, G. *Acta Crystallogr.* **1961**, *14*, 909.

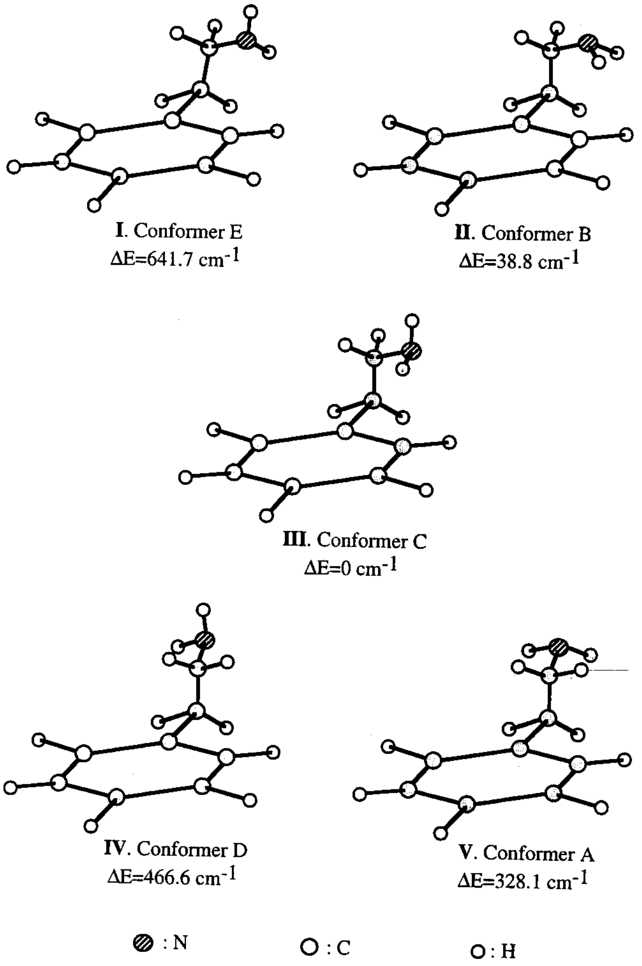

**Figure 7.** Qualitative diagram of the five PEA conformer configurations. The Roman numeral numbering is the same as in ref 18, followed by our conformer assignment. The $\Delta E$ in parentheses is the conformer potential energy of the ground state local minimum relative to that of conformer C, which is calculated to be the global minimum. These values are the *ab initio* calculational results at the MP2/6-31G level quoted from Table 3, ref 18.

often depend on the calculational technique employed. Here we introduce the results of the latest *ab initio* calculation, which is carried out at the MP2/6-31G(d,p) level and is thus so far the most potentially reliable and insightful.[18] In this paper by Godfrey et al., the possible conformers of PEA are searched first at the RHF/4-21G level, and five domains of local potential minima are found. Among them, three correspond to *gauche* and two correspond to *anti* conformations. Starting at these structures, they employ RHF/6-31G(d,p) and MP2/6-31G(d,p) algorithms to determine more accurate potential energies for the five conformers. Their results are presented in Figure 7. At the RHF/4-21G level, conformer II is found to be the global minimum, while at the RHF/6-31G and MP2/6-31G levels, conformer III has the largest stabilization energy. The relative energies of these five conformers are listed in Table 3 of ref 18 and quoted here in Figure 7. In addition to *ab initio* calculations, they also perform millimeter wave spectroscopy on PEA and identify two of these five conformers (II and III): they are unable to resolve spectral features of the other three conformers, probably due to their low concentrations in the experiment.[18]

This *ab initio* calculation satisfactorily explains our experimental results and adds crucial support to the conformer assignments. Structures **IV** and **V** have *anti* conformations in which the $NH_2$ group extends away from the phenyl ring, while conformations **I**, **II**, and **III** correspond to *gauche* conformations. In the calculation, conformations **II** and **III** have the lowest potential minima and their relative energy difference is quite small ($\Delta E \sim 38$ cm$^{-1}$). Therefore both conformers **II** and **III** ought to generate stronger transition intensities relative to the other three conformers since in the jet expansion their ground state population should be enhanced. Based on the arguments above, we assign structure **III** to conformer C and structure **II** to conformer B, as conformers B and C have the most intense spectra. Conformers A and D must therefore be *anti* and the only *gauche* structure remaining, **I**, is assigned to conformer E. Structure **I** has the highest relative energy and E has the weakest spectrum.

To find the correspondence of *anti* structures **IV** and **V** with conformers A and D, we must consider the similarities of these structures and the spectral separations of the conformer vibronic bands. In the excitation spectra, bands A and B are relatively close ($\Delta\nu \sim 12$ cm$^{-1}$) and more than 50 cm$^{-1}$ to the red of the other three bands. Thus conformers A and B should have similar structures. The separations between bands C and D, E and D are 27 and 5 cm$^{-1}$, respectively. This implies that conformer D should structurally resemble conformers C and E. In Figure 7, structures **II** and **V** have both amino hydrogens pointing down toward the aromatic plane, while the other three, **I**, **III**, and **IV**, have only one amino hydrogen pointing down toward the aromatic plane and the other pointing away from the phenyl ring. Therefore we assign the two *anti* structures IV and V to conformers D and A, respectively. These assignments also agree with those made by Martinez et al.; they suggest that conformers A and D are a pair of *anti* structures, and conformers B and C are a pair of *gauche* structures, with the energy differences between members of these two pairs corresponding to the amino group spatial orientation.

From the above results and discussion based on our studies and those of others[9,18] we can firmly conclude that two groups of conformers exist, *anti* and *gauche*, and that transitions A(V) and D(IV) belong to the *anti* classification and transitions B(II), C(III), and E(I) belong to the *gauche* classification. These conclusions are based on hole burning studies, transition intensities, calculations, and comparisons with other model compound studies. One would now like to associate the energy of each transition with a clear mechanism for side chain−ring interaction: such interactions could include hydrogen bonding interactions, lone-pair−$\pi$-system repulsion or attraction, etc. Calculations would suggest that hydrogen bonding interactions between the amine hydrogens and the $\pi$-system of $S_0$ stabilize the ground state structures C and B. In fact, this is why we have assigned them to the largest intensity transitions in the spectra. One might thereby hope to find an excitation sequence such as A,D...B,C,E, or B,C,E...A,D, etc., which would correlate nicely with such ideas. Clearly this is not the case, as the actual sequence is A,B...C...E,D. We note in passing that *n*-propylbenzene transitions are at 37 534 (g) and 37 583 (a) cm$^{-1}$,[15] close to the AB set of features. We thus conclude that the order of the transitions is based simply on zero point energy changes in the conformers for $S_0$ to $S_1$, or that the transition ordering is far more complex and subtle than simple ground state hydrogen bonding/lone pair−$\pi$ repulsion ideas would suggest.

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(29) Pauling, P. In *Conformation of Biological Molecules and Polymers*; Bergmann, E. D., Pullman, B.; Eds.; The Jerusalem symposia on Quantum Chemistry and Biochemistry V; Academic: New York, 1973; pp 505−516.

(30) For example: Martin, M.; Carbo, R.; Petrongolo, C.; Tomasi, J. *J. Am. Chem. Soc.* **1975**, *97*, 1338.

(31) For example: Choi, Y.; Lubman, D. M. *Anal. Chem.* **1992**, *64*, 2726.

Conformer E was neglected by Martinez et al.[9] and this is probably due to three factors: (1) their molecular analog derived assignment precludes a fifth conformer configuration; (2) the sensitivity of its transition band intensity with respect to the jet expansion conditions; and (3) lower resolution than presented in this work.[9] We have also observed such band intensity variations in different excitation scans, and the intensity ratio of bands D or E varies from 1:2 to 2:1. Besides band E, bands A and D also exhibit similar intensity variations under different expansion conditions in the experiment. In the *ab initio* calculations, the potential energies of the local minima of conformers A, D, and E are 328.1, 466.6, and 641.7 $\mathrm{cm}^{-1}$ above that of conformer C (the global minimum).[18] For a Maxwell–Boltzmann distribution ($P \propto e^{-E/kT}$), such high energy local potential minima should have very small population. For example, $P_E:P_C \sim 9.6 \times 10^{-9}$, assuming a PEA vibrational temperature of 50 K. Since the alkylamine chain conformation should have little effect on the intensity of the vibronic transitions localized on the aromatic ring, such ground state population distributions would result in negligibly weak transition bands for conformers A, D, and E even though the calculated energies may not be exact. The actual intensities of A, D, and E bands are of the same order as bands B and C, which suggests that an equilibrium population distribution (characterized by a temperature) of these conformers has not developed in the expansion. This gives a plausible explanation of the intensity variances of bands A, D, and E. Each slight change in the jet expansion conditions, in the laser excitation and signal detection positions, may result in the observation of different conformer population distributions and hence the variations of the relative intensities of these transition bands. The various conformers must be trapped at a relatively high temperature early in the expansion cooling process.

The potential barriers separating these conformers are also of particular interest. In several alkylbenzenes, the potential barriers separating local potential minima are not large enough to prevent isomerization between different alkyl chain conformations, as the large amplitude contortional motions result in molecular nonrigidity.[32,33] A typical example is the toluene molecule in which the methyl group is virtually a free rotor.[15,34] In the $S_1 \leftarrow S_0$ origin band region of propylbenzene, an additional weak feature is observed and assigned to the torsions of the propyl group;[14a] but no molecular nonrigidity is found for this molecule. The hole burning experiments in this study indicate clearly that no molecular nonrigidity occurs in the ground state of PEA, since each conformer has its independent single spectral hole in the hole burning spectra. Should there be an isomerization process between these conformer configurations, one ought to be able to observe the vibronic bands of the different conformers in a hole burning spectrum. The relatively strong interactions of the amino hydrogens and the ring $\pi$-electrons may add additional stiffness to the PEA molecule. The potential barriers between different conformations in alkylbenzenes are usually around 5–20 kJ/mol.[14] Such barriers are high enough to confine the molecular conformers within their potential minima in a jet expansion; however, if a molecular conformer were excited to a high vibronic state above its origin band with enough excess vibrational energy to overcome the potential barriers separating its conformation from others, one should be able to observe the $S_0 \leftarrow S_1$ vibronic transition features of the different conformers in the dispersed emission spectrum, provided that the conformer isomerization rate is comparable to the vibrational relaxation rate of the conformer. A dynamics study of such isomerization processes is bound to offer more insight into the potential barrier height and the conformer isomerization rates.

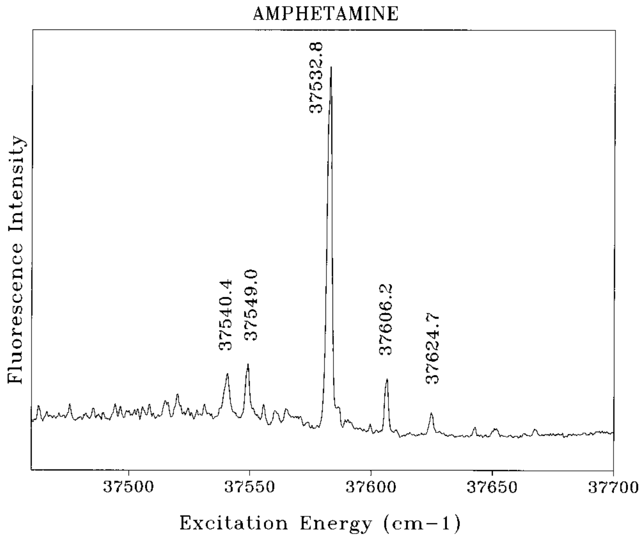

**Figure 8.** Fluorescence excitation spectrum of amphetamine ($C_6H_5$-$CH_2CHCH_3NH_2$), another neurotransmitter molecule, in its $S_1 \leftarrow S_0$ origin band region. The excitation energies of the five major transition bands have been marked on the spectrum.

**B. Other Neurotransmitter Molecules—Amphetamine.** The identification of the PEA conformers is just the first step in our studies of neurotransmitters and their clusters. Only with a clearly assigned spectrum of PEA and a solid knowledge of its conformer spectral features can we proceed to study the excitation spectra of its clusters with various solvent molecules. Different PEA conformers may bind solvent molecules to form clusters of different configurations and/or solvation may force molecular conformations to changes. By studying cluster spectra and structures, one may be able to access and assess the microenvironment of neurotransmitters in solution.

In addition to PEA, jet studies can be extended to other neurotransmitter molecules and their clusters, further expanding the collection of microscopic information on these species. As an example, Figure 8 displays a preliminary scan of the fluorescence excitation spectrum of amphetamine (AMP), another neurotransmitter and a controlled drug, in the region of its $S_1 \leftarrow S_0$ origin band. Compared to PEA, AMP has an extra methyl group at the $C_\beta$ position of the alkylamine chain ($C_6H_5CH_2CHCH_3NH_2$). As a result, both molecules have their $S_1 \leftarrow S_0$ origins less than 100 $\mathrm{cm}^{-1}$ apart. Similar to PEA, AMP also has five major transition features in the origin band excitation region, with the center peak of the strongest intensity. This excitation spectrum can again be analyzed with hole burning and dispersed emission spectroscopy, and the five bands may well correspond to the transitions of the AMP conformers with different alkylamine conformations and amino group hydrogen orientations. The effects of the extra methyl group on conformer structures and functional properties can be further explored with this molecule.

## Conclusion

We have performed mass resolved excitation, fluorescence excitation, hole burning, and dispersed emission spectroscopy on the neurotransmitter molecule PEA. The excitation spectrum displays a group of five transition features in the $S_1 \leftarrow S_0$ origin band region as well as in the higher energy regions up to 1000 $\mathrm{cm}^{-1}$ above. The hole burning spectra of these five bands show

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(32) Ito, M. *J. Phys. Chem.* **1987**, *91*, 517.

(33) Hollas, J. M. *Chem. Soc. Rev.* **1993**, *22*, 371.

(34) Breen, P. J.; Warren, J. A.; Bernstein, E. R.; Seeman, J. I. *J. Chem. Phys.* **1987**, *87*, 1917.

different independent spectral hole features. With the observation of no blue shifted emission bands higher than the excitation energy in the dispersed emission spectra, we conclude that these five transition bands arise from five different molecular conformers of PEA. Referring to the prior experimental studies and *ab initio* calculations, we are able to identify unambiguously the structures of these five conformers. Transitions B, C, and E are due to *gauche* conformers and transitions A and D are due to *anti* conformers. Detailed structural assignments for these conformers are given in Figure 7 based on the latest most elaborate *ab initio* calculations.

The effects of the amino group orientation as well as the alkyl chain conformation on the conformer spectral shifts and the relative potential energies are discussed. The possibilities of investigating the potential barriers and the conformer isomerization process are explored. The significance of this work for future studies of clusters and other neurotransmitters is demonstrated by the AMP excitation spectrum. The conformation of the alkylamine side chain is found to have little impact on the in-plane vibrational modes of the phenyl ring such as $\nu_{6b}$ and $\nu_{12}$. Future work with these two molecules will include clustering studies in which the effect of cluster formation on molecular conformation will be elucidated. Investigations of a similar nature on catechol based neurotransmitters (3,4-dihydroxyphenylamine−dopamine and norepinephrine) and others are presently underway.

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