

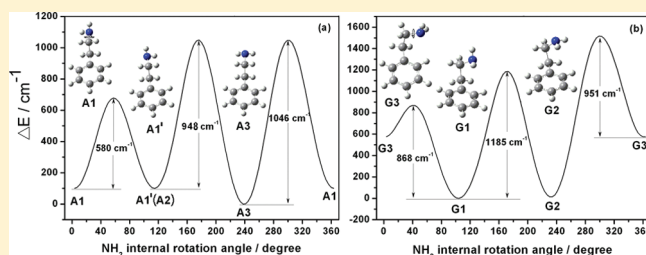
Conformational Equilibrium and Hydrogen Bonding in Liquid 2-Phenylethylamine Explored by Raman Spectroscopy and Theoretical Calculations

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Supporting Information

ABSTRACT: 2-Phenylethylamine (PEA) is the simplest aromatic amine neurotransmitter, as well as one of the most important. In this work, the conformational equilibrium and hydrogen bonding in liquid PEA were studied by means of Raman spectroscopy and theoretical calculations (DFT/MP2). By changing the orientation of the ethyl and the NH₂ group, nine possible conformers of PEA were found, including four degenerate conformers. Comparison of the experimental Raman spectra of liquid PEA and the calculated Raman spectra of the five typical conformers in selected regions (550–800 and 1250–1500 cm⁻¹) revealed that the five conformers can coexist in conformational equilibrium in the liquid. The NH₂ stretching mode of the liquid is red-shifted by ca. 30 cm⁻¹ relative to that of an isolated PEA molecule (measured previously), implying that intermolecular N–H···N hydrogen bonds play an important role in liquid PEA. The relative intensity of the Raman band at 762 cm⁻¹ was found to increase with increasing temperature, indicating that the anti conformer might be favorable in liquid PEA at room temperature. The blue shift of the band for the bonded N–H stretch with increasing temperature also provides evidence of the existence of intermolecular N–H···N hydrogen bonds.



1. INTRODUCTION

Raman scattering spectroscopy, which identifies substances from their characteristic spectral patterns (fingerprinting), is widely used to provide information on chemical structures and physical forms.¹ Theoretical calculations, especially density functional theory (DFT) and Møller–Plesset second-order perturbation theory (MP2) calculations, usually have been used to optimize the structures and predict the energies and frequencies of molecules or ions.^{2–9} Recently, Raman spectroscopy combined with theoretical calculations was found to be an excellent method for investigating the conformations of flexible molecules in liquid phase.^{10–19} By comparing the experimental Raman spectrum of the liquid and the calculated Raman spectra of isolated molecules, the conformational equilibrium in the liquid can be explored.^{13–19} With this method, Ishiguro and co-workers studied several flexible molecules. They first found that two conformers coexist in the liquid of bis(trifluoromethanesulfonyl)imide (TFSI⁻) and concluded that conformational equilibrium of TFSI⁻ in the liquid is established between the C₁ and C₂ conformers.¹³ They obtained similar results when they studied the ionic liquid 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide (EMI⁺FSI⁻).¹⁴ Thereafter, it was found that the Raman and IR spectra, over a wide frequency range, of liquid *N,N*-dimethylacrylamide (DMAA) and *N,N*-dimethylpropionamide (DMPA) could be satisfactorily explained in terms of planar cis and nonplanar staggered conformers.¹⁵ Very recently, Dobrowolaki and co-workers studied

the liquid allyl acrylate with a similar method and found that all 10 of the predicted conformers might coexist in the liquid.¹⁷

Recently, temperature-dependent Raman spectroscopy has been employed to probe the conformational preferences of flexible organic molecules.^{10,12–18,20} Lassègues and co-workers found that the C₂ conformer is more stable than the C₁ conformer in bis(perfluoroethanesulfonyl)imide anion (BETI⁻) solution.¹⁰ Durig and co-workers revealed that the cis conformer is more stable than the gauche conformer in both the gaseous and liquid phases of 3,3-difluorobutene.¹⁸ Moreover, studies have also indicated that vibrational spectroscopy, especially temperature-dependent vibrational spectroscopy, can be used as a tool for studying the hydrogen bonding of H-bond liquids.^{20–22}

2-Phenylethylamine (PEA, C₆H₅–CH₂–CH₂–NH₂), which contains a rigid skeleton ring and a flexible ethylamine side chain, is one of the most important flexible organic molecules and the simplest member of a range of aromatic amine neurotransmitters. It has been found that PEA can cross the blood–brain barrier and concentrate in the mammalian brain^{23,24} and can modulate the affective behaviors.²⁵ To conduct basic research on PEA is valuable for the study of its biological functions in its native environment. Additionally, the exploration of the conformational

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preferences of PEA is helpful to understand the structures and properties of some other neurotransmitters, such as amphetamine, dopamine, serotonin, and histamine.^{2,5}

Conformations of PEA and other flexible molecules in the gas phase have been studied by many spectroscopic methods combined with theoretical calculations.^{2–7,26} As early as 1995, Godfrey and co-workers theoretically predicted that PEA has two types of stable conformations (two anti and three gauche conformations) that mainly differ in terms of the orientation of the amine group. Moreover, two of them can be characterized by millimeter-wave spectroscopy.² Thereafter, Simons et al.³ and Alonso et al.⁴ revealed that four PEA conformers coexist in the gas phase. These studies^{2–4} also indicated that, as an isolated molecule, gauche PEA, which can form an aromatic hydrogen bond (a weak N–H··· π interaction between the amine group and the aromatic ring), is more stable than anti conformers.⁴ Recently, Bar and co-workers explored the Raman spectral features of four conformers of PEA using the novel method of ionization-loss stimulated Raman spectroscopy (ILSRS)⁵ and found that the calculated Raman spectra of the PEA molecules agreed with the observed spectra very well.⁵ However, to our knowledge, no studies on conformational equilibrium in liquid PEA have been performed.

In this work, the conformational equilibrium and hydrogen bonding in liquid PEA were explored by Raman spectroscopy combined with theoretical calculations (DFT/MP2). To acquire more information on the conformational preferences and hydrogen bonding in the liquid PEA, the temperature-dependent Raman spectra of PEA were also measured.

2. METHODS

2.1. Experimental Details. Liquid 2-phenylethylamine (PEA) (>98% pure) was purchased from Aladdin Reagent Company (Shanghai, China) and used as received.

All Raman spectra of liquid PEA were recorded in the full spectral range with a confocal micro-Raman spectrometer (HORIBA Jobin Yvon HR800) and with a 532-nm solid-state laser as the excitation source. The exposure time during the measurements was 30 s. The power density was kept about 1 mW at the sample location, which is low enough to avoid heating effects. The temperature-dependent Raman spectra of liquid PEA were obtained while raising the temperature from 223 to 393 K, using a Linkam TMS 94 hot stage with a temperature stability of ± 0.1 K. The temperature was held at each selected value for at least 5 min. The freezing and boiling points of liquid PEA are ca. 213 and 470 K, respectively; thus, PEA was in the liquid phase throughout all measurements.

2.2. Computational Details. The geometry optimizations, one-dimensional potential energy scans (PESs), transition state searches, and harmonic frequency and Raman scattering activity calculations of PEA molecules were performed with the Gaussian 03 package.²⁷ Compared to the MP2 method, the B3LYP method is inexpensive, and its prediction of normal-mode frequencies are reliable.^{28,29} The harmonic frequencies of all PEA conformers were calculated at the B3LYP/aug-cc-pvdz level, and the geometries of all conformers were optimized at this theoretical level before the harmonic frequencies and Raman activities were calculated. The harmonic frequencies calculated with the basis set were scaled with two scaling factors that were successfully used in the similar systems before:^{30,31} 0.959 for the C–H and N–H stretching vibrations (derived from the previously reported scaling factor for valence A–H stretching force

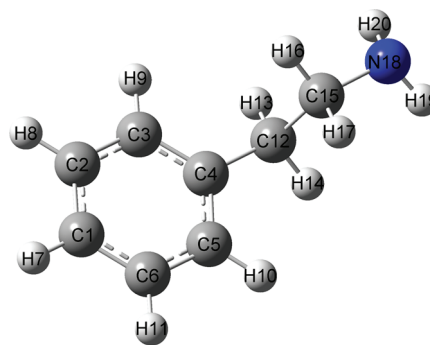


Figure 1. Molecular structure of PEA.

constants³⁰) and 0.987 for all other vibrations. It can be seen that these scaling factors yielded good agreement between the observed and calculated frequencies for the PEA conformers. However, the MP2 method, which accounts for electron–electron correlation, can obtain more reliable results for correlation energies than the B3LYP method.²⁸ Therefore, the one-dimensional potential energy scans, transition state searches, and correlation energies (thermal energies and Gibbs energies) of PEA were predicted by MP2/6-311G(d,p).³ The calculations were performed for isolated molecules, without taking into account intermolecular interactions.

The Raman intensities (I_i) of PEA can be derived from the calculated Raman scattering activities (S_i) of the normal modes. The intensity of a Stokes Raman band (I_i) is proportional to its differential scattering cross section ($\partial\sigma/\partial\Omega$)^{32,33}

$$I_i \propto [\partial\sigma/\partial\Omega]_i$$

The theoretical differential scattering cross section associated with normal mode Q_i is given by^{33,34}

$$[\partial\sigma/\partial\Omega]_i = D(\nu_0 - \nu_i)^4 [1 - \exp(-h\nu_i c/kT)]^{-1} S_i$$

where the constant D is the suitably chosen common normalization factor for all peak intensities; ν_0 is the wavenumber of exciting laser radiation (in our calculations, we used $\nu_0 = 18796.0 \text{ cm}^{-1}$, which corresponds to the laser radiation used); ν_i is the theoretical wavenumber of normal mode Q_i ; h , c , k , and T are the Planck constant, speed of light, Boltzmann constant, and temperature in Kelvin (298.15 K), respectively; and S_i is the theoretical Raman scattering activity of normal mode i ($\text{\AA}^4 \text{ amu}^{-1}$). For the plots of simulated Raman spectra, the harmonic frequencies were convoluted with pure Lorentzian lines with a full width at half-maximum (fwhm) of 10 cm^{-1} .

3. RESULTS AND DISCUSSION

3.1. Theoretical Calculations. Figure 1 shows the chemical structure of the PEA molecule with atom labeling. By changing the internal rotation angle of the ethyl group (C12–C15), three types of conformations can be found, which include one anti and two gauche conformations. Several possible conformations, associated with the rotation of the phenyl ring, were ignored because of their high energy. Using starting structures proposed in previous works,^{2–5} one-dimensional potential energy scans of the anti and gauche conformers were performed by changing the NH_2 internal rotation angle in 3.6° steps between 0° and 360° at the MP2/6-311G(d,p) level of theory. The potential energy curves as a function of the NH_2 internal rotation angle are shown

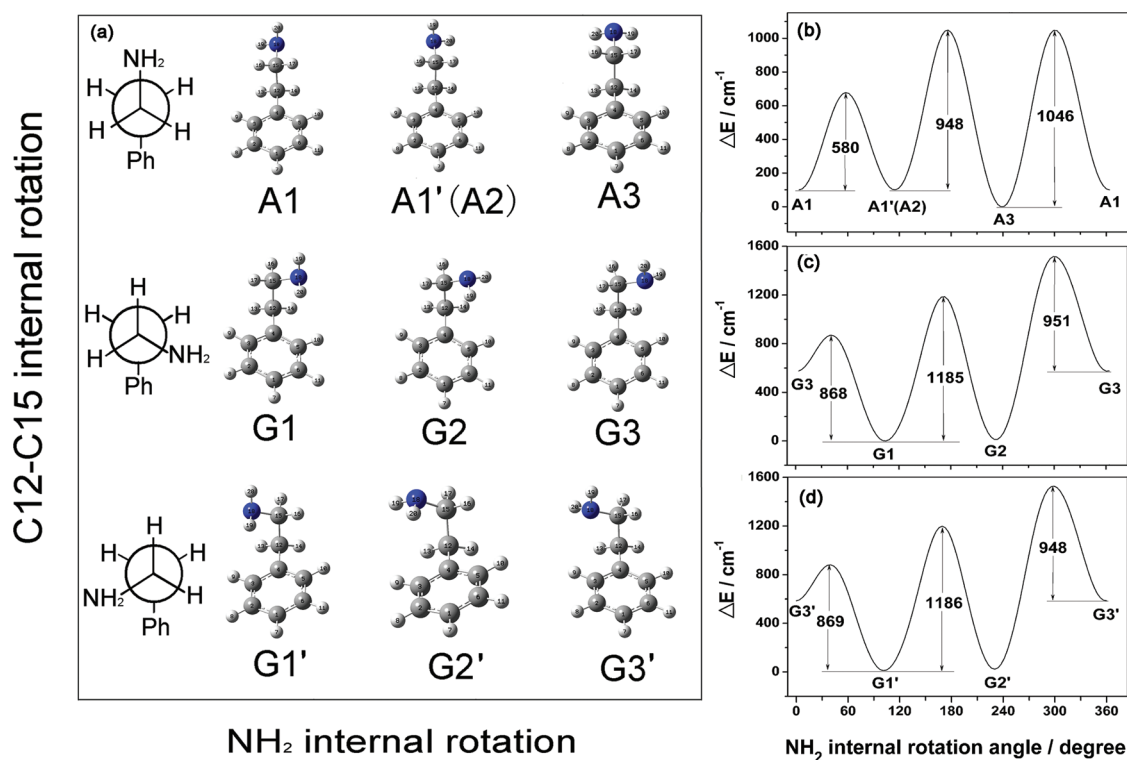


Figure 2. (a) Nine possible conformations of PEA obtained by changing the ethyl group and the NH₂ group. (b–d) Potential energy curves of the (b) anti and (c,d) gauche conformers of PEA as a function of the NH₂ internal rotation angle obtained at the MP2/6-311G(d,p) level.

in Figure 2b–d. It was found that each torsion energy potential curve has three stationary points. The nine different stationary points suggest that there are nine possible conformations. It can be concluded that all nine conformers are local minimum-energy conformations because of the absence of imaginary harmonic frequencies. The nine conformers are shown in Figure 2a.

From Figure 2a, one can see that all nine conformations can be approximately described by two flexible internal coordinates: the C12–C15 internal angle that specifies the position of the NH₂ group relative to the phenyl ring and the C15–N internal rotation angle that specifies the orientation of the NH₂ group. The position of the NH₂ group is defined as anti (A, with the NH₂ group pointing away from the phenyl ring) or gauche (G, with the NH₂ group pointing toward the phenyl ring). The nine conformers are labeled as A1, A1' (A2), A3, G1, G2, G3, G1', G2', and G3'. It was found that the conformer pairs A1 and A1' (A2), G1 and G1', G2 and G2', and G3 and G3' have the same energies and frequencies. Therefore, there are four degenerate conformers among the nine conformers. Thus, only five typical conformers (A1, A3, G1, G2, and G3) were considered in this report, which is consistent with previous reports.^{2–5}

In Figure 2b–d, the barrier of A3 → A1 interconversion was calculated to be ca. 1046 cm⁻¹, and the A1 → A1' (A2) and A1' (A2) → A3 barriers were calculated as ca. 580 and 948 cm⁻¹, respectively. The G1 → G3, G1 → G2, and G3 → G2 barriers are ca. 868, 1185, and 951 cm⁻¹, respectively. The G1' → G3', G1' → G2', and G3' → G2' barriers are ca. 869, 1186, and 948 cm⁻¹, respectively. It is well-known that the flexible molecules can easily change from one conformation to another when the freedom barrier heights between the conformers are below 2.9 kcal/mol (ca. 1000 cm⁻¹).³⁵ Because the interconversion barriers between the PEA conformers are slightly higher or lower than 1000 cm⁻¹,

the anti and gauche conformers are expected to interchange easily. In contrast, the A3 → G1 (G1') and A3 → G2 (G2') barriers are ca. 1470 cm⁻¹, and the A3 → G3 (G3') barriers are ca. 1385 cm⁻¹. The barriers of A1 → G1 (A1' → G1'), A1 → G2 (A1' → G2'), and A1 (A1') → G3 (G3') are ca. 1282, 949, and 1282 cm⁻¹, respectively. The barriers of A1 → G1' (A1' → G1) and A1 → G2' (A1' → G2) are ca. 1349 cm⁻¹ [obtained by transition state searches that were conducted employing the synchronous transit-quasi-Newton (STQN) QST2 method^{36–38}]. This indicates that the interchange between anti and gauche conformers should overcome a higher barrier.

A selection of geometrical parameters and the corresponding relative energies (values of the thermal energy, ΔE, and Gibbs energy, ΔG, relative to the G1 conformer) of the five conformers of PEA are shown in Table 1, which were obtained from MP2/6-311G(d,p) calculations. From the data in Table 1, one can also see that the differences among the conformers of PEA molecules mainly exist in the terminal flexible side chain. The anti and gauche conformers essentially differ in the internal rotation angle of the ethyl group (namely, the C4–C12–C15–H16 dihedral angle). The three gauche conformers mainly differ in the orientation of the NH₂ group (namely, the C12–C15–N18–H19 dihedral angle) from the anti conformers. On the other hand, Table 1 shows that G1 and G2, which have a N–H···π hydrogen bond, are much more stable than G3. In Table 1, the order of the thermal energy of the five conformers is G1 < G2 < A3 < A1 < G3. G1 is the most stable structure among the five isolated conformers, and the stability of the five conformers is in line with previous results.^{2,3,5} In addition, the differences in energy between the conformers are less than 1.6 kcal/mol (see Table 1). These indicate that all five conformers can coexist in conformational equilibrium in liquid PEA.

Table 1. Geometrical Parameters of the Five Conformers and Their Corresponding Relative Energies^a

	five predicted conformers				
	A1	A3	G1	G2	G3
bond lengths (Å)					
N18–H19	1.0163	1.0163	1.0155	1.0165	1.0165
N18–H20	1.0158	1.0163	1.0165	1.0164	1.0155
bond angles (deg)					
H13–C12–H14	107.50	107.31	108.18	107.49	106.98
H16–C15–H17	107.05	106.57	107.51	107.07	107.50
H19–N18–H20	105.83	105.72	106.19	105.80	106.08
dihedral angles (deg)					
C3–C4–C12–H13	–32.90	–33.18	–36.50	–41.22	–29.78
C4–C12–C15–H16	–57.03	–57.84	179.06	–178.16	–165.28
C12–C15–N18–H19	67.04	–57.46	174.89	–56.62	72.89
relative energies ^b (kcal·mol ^{–1})					
ΔE	1.34	1.06	0.00	0.05	1.58
ΔG	0.80	0.62	0.00	0.08	1.35

^a Labeling of atoms is provided in Figure 1. The data were predicted at the MP2/6-311G(d,p) level. ^b Thermal energies, ΔE, and Gibbs energies, ΔG, relative to the G1 conformer.

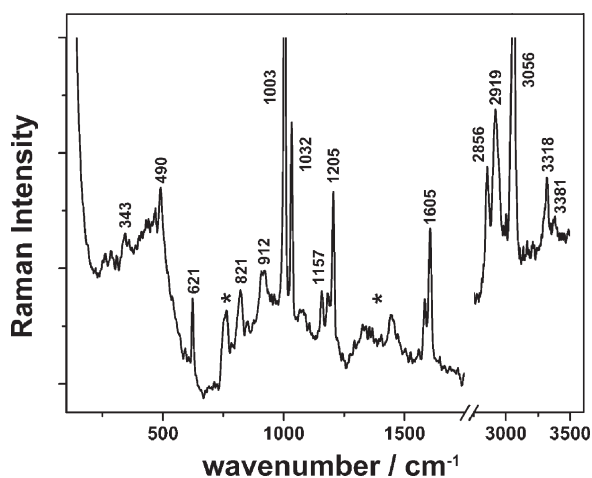


Figure 3. Measured Raman spectrum of liquid PEA (at 303 K) in the regions of 100–1800 and 2700–3500 cm^{–1}.

3.2. Conformational Equilibrium in Liquid PEA. Figure 3 shows the Raman spectrum of liquid PEA at 303 K in the regions 100–1800 and 2700–3500 cm^{–1}. Comparisons of the observed and calculated frequencies are presented in Table S1 of the Supporting Information. The scaling factor 0.987 was applied to the calculated frequencies in the range of 100–1800 cm^{–1}, and 0.959 was applied in the range of 2700–3500 cm^{–1}. Comparison of the observed and calculated Raman frequencies indicates that different conformers of PEA are present in the liquid.

Previous experimental and computational results showed that at least four conformers coexist in the conformational equilibrium of gas-phase PEA.^{3–5} Comparison (see Table S1 of the Supporting Information) indicates that different conformers have different characteristic bands in the 550–800 and 1250–1500 cm^{–1} regions, as marked by asterisks in Figure 3. To find some vibrational modes related to specific molecular

structures of the calculated conformers, we juxtaposed the selected (550–800 and 1250–1500 cm^{–1} regions) experimental Raman spectra of liquid PEA at 303 K and the calculated Raman spectra of all five conformers (A1, A3, G1, G2, and G3) (see Figure 4).

Figure 4 shows the experimental Raman spectra and the theoretical predicted spectra of the five conformers in the selected ranges of 550–800 and 1250–1500 cm^{–1}. Wavenumbers of all of the experimental Raman bands of the liquid and the calculated Raman bands of the five conformers in the selected region are also listed in Table 2, together with rough assignments of the bands. The assignments were done by the assistance of the theoretical predictions, and some of them are based on the previous studies.^{5,39–41}

In the range of 550–600 cm^{–1}, two weak bands at 568 and 592 cm^{–1} can be seen in the experimental Raman spectrum. The band located at 568 cm^{–1} can be seen in the predicted spectra of only gauche conformers, and the band at 592 cm^{–1} corresponds only to anti conformers. By the assistance of the theoretical predictions, the band at 568 cm^{–1} can be attributed to C–H out-of-plane bending and C15H₂ rocking of the gauche conformers, and the band at 592 cm^{–1} can be attributed to ring phenyl in-plane deformations of the anti conformers. Both of these bands appear in the measured Raman spectra, suggesting that at least one of the gauche conformers and one of the anti conformers exist in the liquid PEA.

In the range of 700–800 cm^{–1}, the bands at ca. 752 and 762 cm^{–1} can be observed in the experimental spectrum of liquid PEA. The band at ca. 752 cm^{–1} is assigned to C–H out-of-plane bending. It appears in the Raman spectra of all five predicted conformers. However, the band at ca. 762 cm^{–1}, which mainly corresponds to C15H₂ rocking and C–H out-of-plane bending, evidently exists only in the spectra of gauche conformers, which confirms that at least one of the gauche conformers exists in liquid PEA.

In the range of 1250–1500 cm^{–1}, conformers of PEA can be distinguished by the characteristic bands of their Raman spectra.

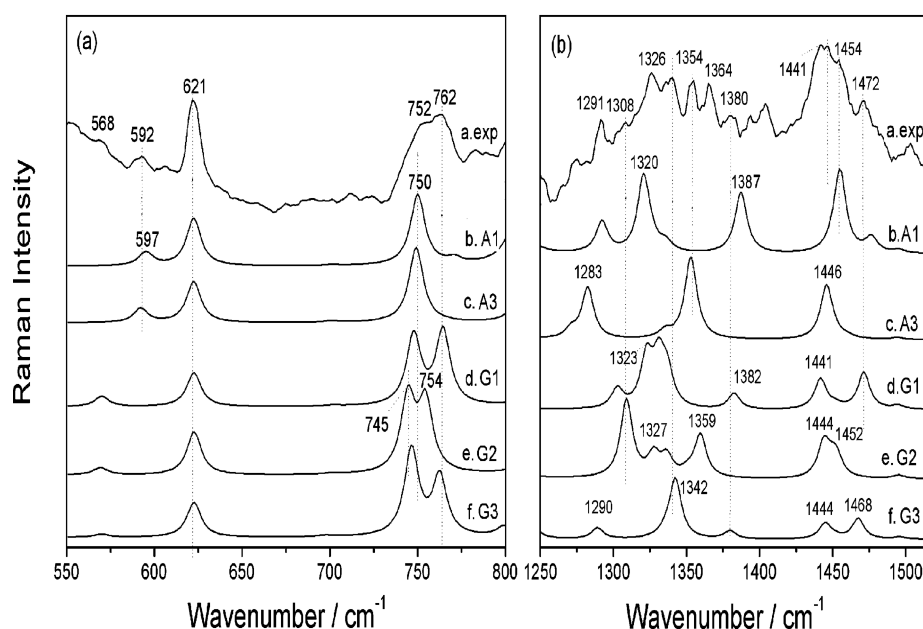


Figure 4. Comparison of the experimental Raman spectra of liquid PEA with the calculated Raman spectra of the five PEA conformers in the regions of (a) 550–800 and (b) 1250–1500 cm^{-1} .

Table 2. Wavenumbers of All Experimental Raman Bands in the Selected Regions (550–800 and 1250–1500 cm^{-1}) and Corresponding Predicted (B3LYP/aug-cc-pvdz) Raman Bands of the Five Conformers, with Rough Assignments of the Bands^a

exp (cm^{-1})	five predicted conformers					assignment
	A1	A3	G1	G2	G3	
568 (w)	–	–	568	568	568	$\beta(\text{CH})$ op + $\gamma(\text{C15H}_2)^{b,c}$
592 (w)	597	592	–	–	–	ring def ip ^b
621 (m)	621	622	622	621	621	ring def ip ^{b,c}
752 (m)	750	749	748	745	747	$\beta(\text{CH})$ op ^{b,c}
762 (m)	–	–	764	754	760	$\gamma(\text{C15H}_2)$ + $\beta(\text{CH})$ op ^b
–	–	1283	–	–	–	$\omega(\text{C12,15H}_2)^{b,c}$
1291 (w)	1291	–	–	–	1290	$\tau(\text{C12,15H}_2)^b$
1326 (w)	1320	–	1323	1327	–	$\tau(\text{C15H}_2, \text{NH}_2)$ + $\omega(\text{C12H}_2)^{b,c}$
1336 (w)	1334	1336	1331	1335	–	$\beta(\text{CH})$ ip + $\omega(\text{C12H}_2)^{b,c}$
1340 (w)	–	–	–	–	1342	$\tau(\text{C15H}_2)$ + $\omega(\text{C12H}_2)^b$
1354 (w)	–	1353	–	–	–	$\omega(\text{C12,15H}_2)^{b,c}$
1364 (w)	–	–	–	1359	–	$\tau(\text{C15H}_2)$ + $\tau(\text{NH}_2)^b$
1380 (w)	–	–	1382	–	1380	$\omega(\text{C15H}_2)$ + $\tau(\text{NH}_2)^{b,c}$
1393 (w)	1386	–	–	–	–	$\omega(\text{C12,15H}_2)$ + $\tau(\text{NH}_2)^{b,c}$
1404 (w)	–	–	–	–	–	–
1441 (m)	–	–	1441	–	–	$\delta(\text{C12H}_2)^{b,c}$
1446 (m)	–	1446	–	1444	1444	$\delta(\text{C12,15H}_2)^{b,c}$
1454 (w)	1454	–	–	1452	–	$\delta(\text{C12,15H}_2)^{b,c}$
1472 (w)	–	–	1472	–	1468	$\delta(\text{C15H}_2)^b$
1480 (w)	1477	–	–	–	–	$\delta(\text{C12,15H}_2)^b$

^a Abbreviations used: m, medium; w, weak; β , bending; γ , rocking; τ , twisting; ω , wagging; δ , scissoring; op, out of plane; ip, in plane; def, deformation. ^b From the DFT calculation results in this work. ^c From refs 5, 39, 40, and 41.

The band located at 1441 cm^{-1} , which is assigned to C12H₂ scissoring, is related only to G1 conformer. Furthermore, G1 is the lowest-energy conformer among the five. Thus, the G1 conformer should exist in the liquid. The band at 1354 cm^{-1} , which is assigned to the C12H₂ and C15H₂ wagging, can be explained by only the A3 conformer. Additionally, A3 is the lowest-energy conformer among the anti conformers. This indicates that A3 conformer cannot be excluded in liquid PEA. The weak band observed at 1291 cm^{-1} is attributed to the C12H₂ and C15H₂ twisting, which is related to conformer A1 or G3. Furthermore, the band at 1340 cm^{-1} assigned to C15H₂ twisting and C12H₂ wagging is related to only the G3 conformer. Therefore, G3 exists in liquid PEA. As A1 is lower in energy than G3, A1 can exist in the conformational equilibrium of liquid-phase PEA. The weak band at 1364 cm^{-1} , which is related to the C15H₂ and NH₂ twisting modes, can be found only in the G2 conformer, which indicates that the G2 conformer is also present in liquid PEA. These results confirm that all five conformers coexist in the conformational equilibrium of liquid PEA.

3.3. Hydrogen Bonding in Liquid PEA. Two kinds of hydrogen bonds (i.e., N–H··· π and N–H···N hydrogen bond) can form in liquid PEA. Wavenumbers of the NH₂ symmetric stretching band of liquid PEA at 303 K, of isolated PEA in the gas phase,⁵ and of the five predicted conformers are listed in Table 3.

In Table 3, the Raman spectra of the isolated PEA molecules in the gas phase show that the Raman band of the nonbonded or N–H··· π hydrogen-bonded NH₂ symmetric stretch can be observed in the range of 3340–3350 cm^{-1} . The NH₂ symmetric stretching mode of gauche conformers (at ca. 3345 cm^{-1}) is red-shifted by about 5 cm^{-1} compared to that of anti conformers (at ca. 3350 cm^{-1}), because of the presence of weak intramolecular N–H··· π hydrogen bonds in the former.⁵ However, no obvious band in the range of 3340–3350 cm^{-1} can be observed in the experimental Raman spectrum of liquid PEA. Note that only two kinds of hydrogen bonds, i.e., N–H··· π and

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