

# The free jet microwave spectrum of 2-phenylethylamine–water

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We observed the rotational spectrum of the 1 : 1 molecular adduct between 2-phenylethylamine and water (normal and H<sub>2</sub><sup>18</sup>O species) by free jet absorption microwave spectroscopy in the frequency region 60–78 GHz. The dominant spectrum belongs to the structure where the PEA moiety is in the most stable *gauche* conformation and the water molecule is hydrogen bound to the nitrogen lone pair. The orientation of the water molecule is such that the oxygen atom is almost equidistant (*ca.* 2.5 Å) from the closest methylenic and aromatic hydrogen atoms.

## Introduction

The investigation of the forces that determine the spatial arrangement of molecules is essential for the understanding of the molecular processes that play a central role in important biological processes like molecular recognition, neurotransmission, intracellular transport and drug–receptor interaction.<sup>1</sup> While for the isolated molecule the shape is a result of the intramolecular interactions, when the molecule is in different environments the shape is the result of a delicate balance between intra and intermolecular interactions. An understanding of this balance is particularly important for bioactive molecules.

Spectroscopic studies of molecules or small molecular complexes performed in isolated conditions (in gas phase or with supersonic jet techniques) allow the precise determination of intrinsic molecular properties that can be directly compared to high level quantum chemical calculations.<sup>2</sup> Among the possible experimental techniques, rotational spectroscopy gives the most detailed structural picture of the conformational space.

2-Phenylethylamine (hereafter abbreviated as PEA) is the parent structure of a variety of important neurotransmitters including dopamine, amphetamine, serotonin, histamine and adrenaline. PEA and the neurotransmitters cited above, all contain the ethylamino side chain which, due to its flexibility gives rise to a complex conformational surface which contains several minima at relatively low energy.

The conformational surface of PEA was studied by various spectroscopic and theoretical methods.<sup>3</sup> The lowest energy conformers of PEA are those in which the ethylamino side chain is folded into a *gauche* structure and one of the amino hydrogen atoms is oriented towards the aromatic ring to form a weakly N–H··· $\pi$  hydrogen bonded structure, while in the less stable conformers the chain is in the *anti* position (they are depicted in Fig. 1 with their relative stability). This means that the energy difference between the *gauche* and *anti* conformers (*ca.* 4 kJ mol<sup>−1</sup>) represents the energy associated with this weak interaction.

This kind of interaction is the leading force stabilizing the isolated molecule, as in similar molecules like tyramine<sup>4</sup> and

tryptamine.<sup>5</sup> If other substituents are present such as in 2-amino-1-phenylethanol and 2-methylamino-1-phenylethanol,<sup>6</sup> then the conformational preferences are controlled by different competing interactions (in those cases the OH···N intramolecular hydrogen bond).

The rotational spectrum of PEA was studied in 1995 by Godfrey *et al.* (ref. 3*b*) who detected two conformers in a free jet expansion and in 2007 by J. C. Lopez *et al.* (ref. 3*e*) who detected four of the five most stable conformers with Molecular Beam Fourier Transform Microwave spectroscopy. The fifth conformer, highest in energy, was not detected in the adiabatic expansion, since it probably relaxes to a lower energy conformer due to the low barrier to interconversion.

Water clusters of PEA were first detected by Dickinson *et al.* (ref. 3*d*) and subsequently confirmed by Hockridge and Robertson.<sup>7</sup> In their work the authors used laser induced fluorescence and mass-selected resonant two-photon ionization of the S<sub>1</sub> ← S<sub>0</sub> electronic transition to detect clusters of different stoichiometry. Within a given stoichiometry, the identification of different conformations relies on band

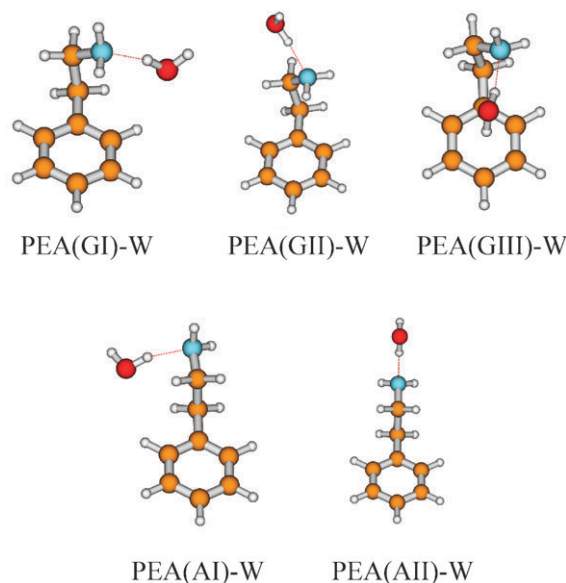


Fig. 1 The five most stable conformations of PEA-W.

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contour analysis and calculated energy differences, still leaving some degree of ambiguity.

In the present work we study the 1 : 1 complex of PEA and water. The determination of the rotational constants of the normal and isotopic species and the orientation of the dipole moment within the cluster, which can be obtained by rotational spectroscopy, allows the univocal determination of the water complex's structure thus enabling us to track down the dominant forces that are involved in the interaction of PEA and water.

## Methods

The design of the Stark and pulse modulated free jet absorption millimetre-wave spectrometer working in the frequency range 60–78 GHz used in this study has been described previously.<sup>8</sup>

Complexes of 2-phenylethylamine and water were formed by passing a stream of argon saturated with water at room temperature and at a pressure of about 3 bar over a sample of 2-phenylethylamine (purchased from Aldrich, and used without further purification) heated to about 65 °C at 500 mbar. The gas mixture was then expanded to about  $5 \times 10^{-3}$  mbar through a continuous nozzle with diameter of 0.35 mm kept at 5 °C above the reservoir temperature.

Ar was used as the carrier gas for the first searches and the measurement. Some scans were also performed using He as carrier in order to find new transitions belonging to other conformations that could have relaxed in the jet.

Measurements on PEA-H<sub>2</sub><sup>18</sup>O were performed at the same experimental conditions simply replacing normal water with and H<sub>2</sub><sup>18</sup>O.

The accuracy of the frequency measurements is estimated to be better than 0.05 MHz.

*Ab initio* calculations of the molecular structure, conformational energies, electric dipole moments and nuclear quadrupole constants at the MP2/6-311+G\*\* level of theory performed

using the GAUSSIAN 03<sup>9</sup> suite of programs, were carried out on the plausible conformers in order to assist the rotational assignment and to guide the identification of the conformers present in the jet expansion. The calculation of the vibrational frequencies in the harmonic approximation for all the optimized structures allowed us to check that the stationary points were actual minima and let us estimate the zero point correction to the electronic energy and the values of the quartic centrifugal distortion constants.

## Results

Molecular orbital calculations (MP2/6-31G\*//HF/6-31G\*), performed as an aid to experimental interpretation, for the water clusters of PEA are reported in ref. 7 based on the conformational landscape of the PEA monomer discussed in ref. 3d. The calculations are repeated here for the 1 : 1 complex of PEA-W, at a higher level of theory (MP2/6-311++G\*\*) to predict the spectroscopic parameters essential for the assignment of the rotational spectrum, that is, the rotational and centrifugal distortion constants, the components of the electric dipole moment in the principal inertia axes system of the molecule and the nuclear quadrupole coupling constants.

The optimized conformations are depicted in Fig. 1 while the spectroscopic parameters and the relative energies are reported in Table 1.

These structures are based on the five most stable conformations of PEA (see for example ref. 3e), and as it can be seen from Fig. 1, in all cases the main interaction is between the nitrogen lone pair of PEA and the hydrogen atom of the water molecule.

Based on the rotational constants and values of the dipole moment components reported in Table 1, we predicted the rotational spectra of the different conformers of PEA-W and searched for the rotational transition in the frequency range of the spectrometer.

**Table 1** *Ab initio* spectroscopic parameters of PEA-W (MP2/6-311++G\*\*)

|  | PEA(GI)-W   | PEA(GII)-W  | PEA(GIII)-W | PEA(AI)-W   | PEA(AII)-W  |
|--|-------------|-------------|-------------|-------------|-------------|
| $E/\text{Hartree}$                           | -441.496818 | -441.493550 | -441.494970 | -441.493060 | -441.491194 |
| $E_0/\text{Hartree}$                         | -441.296476 | -441.293910 | -441.295106 | -441.293441 | -441.292019 |
| $E + \text{BSSE}/\text{Hartree}$             | -441.492553 | -441.490535 | -441.489678 | -441.489403 | -441.488097 |
| $\Delta E/\text{kJ mol}^{-1}$                | 0           | 8.58        | 4.85        | 9.86        | 14.76       |
| $\Delta E_0/\text{kJ mol}^{-1}$              | 0           | 6.74        | 3.60        | 7.97        | 11.70       |
| $\Delta(E + \text{BSSE})/\text{kJ mol}^{-1}$ | 0           | 5.30        | 7.55        | 8.26        | 11.70       |
| $D_e/\text{kJ mol}^{-1}$                     | 42.5        | 35.3        | 46.4        | 38.2        | 33.6        |
| $D_0/\text{kJ mol}^{-1}$                     | 31.9        | 26.7        | 35.8        | 28.5        | 25.1        |
| $D_e^{\text{BSSE}}/\text{kJ mol}^{-1}$       | 31.3        | 27.4        | 32.6        | 28.6        | 25.4        |
| $A_g/\text{MHz}$                             | 1965        | 2319        | 1761        | 2467        | 2427        |
| $B_g/\text{MHz}$                             | 839         | 569         | 966         | 634         | 494         |
| $C_g/\text{MHz}$                             | 677         | 556         | 826         | 535         | 481         |
| $D_J/\text{kHz}$                             | 0.18        | 0.60        | 0.17        | 0.22        | 0.31        |
| $D_{JK}/\text{kHz}$                          | -0.37       | -8.13       | 0.55        | -0.73       | 4.71        |
| $D_K/\text{kHz}$                             | 1.70        | 43.83       | 0.39        | 3.50        | 3.11        |
| $\mu_a/\text{D}$                             | -0.34       | 2.82        | 1.63        | 1.32        | -0.46       |
| $\mu_b/\text{D}$                             | -1.89       | -0.96       | -3.16       | -2.55       | -3.17       |
| $\mu_c/\text{D}$                             | 2.32        | -1.42       | 0.76        | 0.72        | -0.74       |
| $\mu_{\text{tot}}/\text{D}$                  | 3.08        | 3.30        | 3.63        | 2.96        | 3.28        |
| $\chi_{aa}/\text{MHz}$                       | 0.16        | -2.77       | -3.40       | 1.54        | -0.71       |
| $\chi_{bb}/\text{MHz}$                       | -1.49       | 0.22        | 1.20        | -2.61       | -0.81       |
| $\chi_{cc}/\text{MHz}$                       | 1.33        | 2.55        | 2.20        | 1.07        | 1.52        |

We easily observed one set of coalesced (due to near prolate degeneracy)  $\mu_b$ , and  $\mu_c$  R-type transitions with high  $K_a$  values, and then a few low  $K_a$  transitions where we could distinguish between  $\mu_b$  and  $\mu_c$  components lines. This is in agreement with the calculated rotational spectra where the  $\mu_b$  and  $\mu_c$  type transitions are more intense than the  $\mu_a$  transitions which become weak for the high rotational quantum numbers involved.

For transitions with lower  $K_a$  values, when the degeneracy due to near-prolate behaviour is lost, we see a multiplet of lines due to the separation of  $\mu_b$  and  $\mu_c$  component transitions which have different intensities. This difference is mainly due to the values of  $\mu_b$  and  $\mu_c$  dipole moment components since all the other factors which contribute to the intensity are very

similar. The comparison between different  $\mu_b$  and  $\mu_c$  transitions show an intensity ratio of about 0.8, in agreement with the value  $\mu_b^2/\mu_c^2$  of 0.7 that can be calculated from the values reported in Table 1 for the most stable PEA(GI)-W.

No hyperfine splitting of the rotational lines was observed since in the scanned frequency range, the hyperfine structure due to the coupling of the nuclear quadrupole moment of the nitrogen atom is not resolvable

After the assignment of the normal species we recorded and assigned the spectrum of the isotopolog PEA-H<sub>2</sub><sup>18</sup>O. The rotational transitions' frequencies of PEA-H<sub>2</sub>O and PEA-H<sub>2</sub><sup>18</sup>O are given in Table 2 while the spectroscopic parameters of both isotopologs fitted with Watson's semirigid Hamiltonian in the

**Table 2** Measured rotational transition frequencies (MHz) of the two isotopomers of PEA-W

| $J' (K_a, K'_c) - J'' (K''_a, K''_c)$ | PEA-H <sub>2</sub> O |  | PEA-H <sub>2</sub> <sup>18</sup> O |  |
|---------------------------------------|----------------------|--|------------------------------------|--|
|                                       | $\nu$ /MHz           | $\nu_{\text{Obs.}} - \nu_{\text{Calc.}}$ | $\nu$ /MHz                         | $\nu_{\text{Obs.}} - \nu_{\text{Calc.}}$ |
| 17 (17)–16 (16) <sup>a</sup>          | 65116.25             | –0.02                                    |                                    |  |
| 18 (17)–17 (16)                       | 66595.50             | 0.03                                     |                                    |  |
| 19 (17)–18 (16)                       | 68074.50             | –0.01                                    |                                    |  |
| 22 (17)–21 (16)                       |                      |  | 70866.16                           | 0.00                                     |
| 16 (16)–15 (15)                       | 61220.07             | –0.08                                    |                                    |  |
| 17 (16)–16 (15)                       | 62699.30             | 0.03                                     |                                    |  |
| 18 (16)–17 (15)                       | 64178.27             | 0.04                                     |                                    |  |
| 20 (16)–19 (15)                       |                      |  | 65619.19                           | –0.02                                    |
| 17 (15)–16 (14)                       | 60280.95             | 0.04                                     |                                    |  |
| 18 (15)–17 (14)                       | 61759.45             | –0.04                                    | 60371.16                           | 0.01                                     |
| 19 (15)–18 (14)                       | 63237.71             | 0.04                                     |                                    |  |
| 20 (15)–19 (14)                       | 64715.31             | –0.02                                    |                                    |  |
| 19 (14)–18 (13)                       | 60816.55             | 0.09                                     |                                    |  |
| 20 (14)–19 (13)                       | 62293.03             | –0.06                                    |                                    |  |
| 21 (14)–20 (13)                       | 63768.72             | –0.07                                    |                                    |  |
| 22 (14)–21 (13)                       |                      |  | 63729.08                           | 0.04                                     |
| 23 (14)–22 (13)                       |                      |  | 65159.98                           | –0.04                                    |
| 24 (14)–23 (13)                       |                      |  | 66589.43                           | –0.04                                    |
| 25 (14)–24 (13)                       |                      |  | 68017.23                           | 0.07                                     |
| 26 (14)–25 (13)                       |                      |  | 69442.81                           | –0.02                                    |
| 20 (13)–19 (12)                       | 59867.86             | 0.02                                     |                                    |  |
| 21 (13)–20 (12)                       | 61341.62             | 0.05                                     | 59912.66                           | –0.05                                    |
| 22 (13)–21 (12)                       |                      |  | 61342.68                           | 0.06                                     |
| 23 (13)–22 (12)                       |                      |  | 62770.70                           | 0.01                                     |
| 24 (13)–23 (12)                       |                      |  | 64196.62                           | –0.02                                    |
| 25 (13)–24 (12)                       |                      |  | 65620.19                           | 0.03                                     |
| 26 (13)–25 (12)                       |                      |  | 67040.86                           | –0.03                                    |
| 22 (12)–21 (11)                       | 60377.27             | –0.05                                    |                                    |  |
| 23 (12)–22 (11)                       | 61843.03             | –0.01                                    | 60373.26                           | –0.01                                    |
| 24 (12)–23 (11)                       | 63305.66             | –0.02                                    | 61793.89                           | –0.01                                    |
| 25 (12)–24 (11)                       |                      |  | 63211.11                           | 0.03                                     |
| 27 (12)–26 (11)                       |                      |  | 66033.09                           | 0.00                                     |
| 24 (11)–23 (10)                       | 60842.61             | 0.02                                     |                                    |  |
| 25 (11)–24 (10)                       | 62291.40             | 0.04                                     |                                    |  |
| 26 (11, 15)–25 (10, 16)               | 63734.46             | –0.07                                    |                                    |  |
| 26 (11, 16)–25 (10, 16)               | 63734.46             | –0.03                                    |                                    |  |
| 26 (11, 16)–25 (10, 15)               | 63733.87             | 0.09                                     |                                    |  |
| 26 (11, 15)–25 (10, 15)               | 63733.87             | 0.01                                     |                                    |  |
| 27 (11, 16)–26 (10, 17)               | 65170.35             | 0.01                                     |                                    |  |
| 27 (11, 17)–26 (10, 17)               | 65170.85             | 0.08                                     |                                    |  |
| 27 (11, 17)–26 (10, 16)               | 65169.41             | 0.01                                     |                                    |  |
| 27 (11, 16)–26 (10, 16)               | 65169.41             | –0.05                                    |                                    |  |
| 25 (10, 16)–24 (9, 15)                | 59778.07             | –0.04                                    |                                    |  |
| 25 (10, 15)–24 (9, 16)                | 59784.27             | 0.01                                     |                                    |  |
| 25 (10, 16)–24 (9, 16)                | 59783.61             | 0.03                                     |                                    |  |
| 25 (10, 15)–24 (9, 15)                | 59778.81             | 0.02                                     |                                    |  |
| 26 (10, 17)–25 (9, 16)                | 61196.59             | 0.01                                     |                                    |  |
| 26 (10, 16)–25 (9, 17)                | 61209.29             | –0.05                                    |                                    |  |
| 26 (10, 17)–25 (9, 17)                | 61207.87             | 0.02                                     |                                    |  |
| 26 (10, 16)–25 (9, 16)                | 61198.04             | –0.02                                    |                                    |  |

<sup>a</sup> Doubly overlapped transitions due to the near prolate degeneracy of the involved levels: only  $K_a$  is given.

**Table 3** Rotational and centrifugal distortion constants (Watson's S-reduction, I<sup>r</sup> representation) of the two isotopomers of PEA-W

|                      | PEA-H <sub>2</sub> O | PEA-H <sub>2</sub> <sup>18</sup> O |
|----------------------|----------------------|------------------------------------|
| A/MHz                | 1952.313(6)          | 1909.558(6)                        |
| B/MHz                | 816.14(2)            | 793.38(4)                          |
| C/MHz                | 657.30(1)            | 637.79(3)                          |
| D <sub>J</sub> /kHz  | 0.276(4)             |                                    |
| D <sub>JK</sub> /kHz | -0.97(1)             |                                    |
| D <sub>K</sub> /kHz  | 3.46(2)              |                                    |
| N <sup>a</sup>       | 70                   | 22                                 |
| σ/MHz                | 0.05                 |                                    |

<sup>a</sup> Number of transitions in the fit.

**Table 4** H-bond parameters and *r<sub>s</sub>* coordinates of the water oxygen in PEA(G1)-W

| PEA(G1)-W                 | <i> r<sub>s</sub> </i> | <i>r<sub>0</sub></i> | <i>r<sub>e</sub><sup>a</sup></i> |
|---------------------------|------------------------|----------------------|----------------------------------|
| <i>a</i> /Å               | ±2.972(2) <sup>b</sup> | -3.014               | -2.898                           |
| <i>b</i> /Å               | ±1.751(4)              | 1.646                | 1.704                            |
| <i>c</i> /Å               | ±0.11(6)               | -0.299               | -0.281                           |
| N-H <sub>w</sub> /Å       |                        | 1.955(6)             | 1.909                            |
| ∠ H <sub>w</sub> -N-C/°   |                        | 110.8(2)             | 107.2                            |
| ∠ H <sub>w</sub> -N-C-C/° |                        | 42.0(9)              | 48.89                            |
| ∠ N-C-C-C/°               |                        | 66.8(8)              | 58.6 <sup>c</sup>                |
| A/MHz                     | 1952.313(6)            | 1952.5               | 1965.4                           |
| B/MHz                     | 816.14(2)              | 816.1                | 839.1                            |
| C/MHz                     | 657.30(1)              | 657.4                | 677.4                            |

<sup>a</sup> MP2/6-311++G\*\* values. <sup>b</sup> Error in parentheses in units of the last digit. <sup>c</sup> The same parameter in the PEA monomer is 61.3°.

“S” reduction and I<sup>r</sup> representation<sup>10</sup> are reported in Table 3. The transitions of the normal species and <sup>18</sup>O species were fitted together with Pickett's program<sup>11</sup> using a common set of centrifugal distortion constants.

The accuracy of the *ab initio* rotational constants is within 3% (closer to the ones reported in ref. 7 calculated at the MP2/6-31G\* which agree within 10%). This is good enough to attribute unambiguously the observed conformation to one of the calculated geometrical arrangements reported in Table 1: namely PEA(G1)-W, nevertheless it is advisable perform a structural refinement on the *ab initio* geometry in order to better reproduce the observed rotational constants. The choice of the most significant structural parameters is guided by the consideration that the structural parameters which are probably more affected by the approximation of the *ab initio* method are those involving the weakly bound atoms.

The *r<sub>0</sub>* structure obtained adjusting the H<sub>w</sub>···N distance, the H<sub>w</sub>···N-C valence angle and the H<sub>w</sub>···NCC and NCCC dihedral angles, is reported in Table 4 together with the starting *r<sub>e</sub>* values. The *r<sub>0</sub>* structure reproduces the rotational constants within a few MHz. In the same Table we report the *r<sub>0</sub>*, *r<sub>e</sub>* and the *r<sub>s</sub>* (substitution structure)<sup>12</sup> coordinates of the water oxygen atom.

The calculated centrifugal distortion constants agree with the experimental ones only within *ca.* 50%. For this reason, while they can be useful as an independent piece of evidence for conformational assignment, the poor agreement is evidence of the fact that the harmonic approximation used in the calculations is too crude to reproduce the experimental data.

Comparing the experimental and calculated rotational constants and the ratio of the dipole moment components which supply two independent pieces of information, we can reliably conclude that the observed conformation is PEA(G1)-W.

The coordinates of the water oxygen atom, which can be obtained from the rotational constants of the isotopic species show again a good agreement with those of PEA(G1)-W. This conformation is in turn calculated as the global minimum.

Extensive searches (also using He as the carrier gas, since it should prevent relaxation) have been performed trying to identify other conformers of PEA-W. A few lines remain unassigned in the spectrum.

## Conclusions

In this work we observe the rotational spectra of the most stable conformation of the 1:1 adduct of PEA and water.

The lowest energy conformation of PEA is that in which the ethylamine side chain is folded in a *gauche* arrangement and the amino hydrogen interacts with the aromatic π cloud. When the complex is formed, the water molecule approaches PEA with the hydrogen atom directed towards the lone pair of the nitrogen atom without disrupting the original conformation of the monomer.

The values of the rotational constants of two isotopologs of the complex show unambiguously the position of the oxygen atom and allow the determination of the orientation of the water molecule within the complex and the estimate of the hydrogen bond parameters. The bonding of the water molecule seems not to affect much the structure of the molecule and the main structural parameters of the flexible amino side chain remain basically unaltered.

The *ab initio* results suggest that the observed conformer of PEA-W is the global minimum of the conformational space for this complex. For the conformers calculated at higher energy it is interesting to note that they were not observed either using Ar or He as the carrier gas.

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