A sting in the tail of flexible molecules: spectroscopic and energetic challenges in the case of *p*-aminophenethylamine

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Supplementary Data Tables

Table S1. *Ab initio* calculated relative energies of PEA conformers in kJ mol^{-1}.

Conformer alternative label [a]	Aa (V)	Ag (IV)	Ga (II)	Gg (III)	Gg' (I)
Electronic					
B3LYP/aug-cc-pVTZ	-0.08	0.56	0.43	0.00	5.81
MP2/6-311+G**	5.32	5.23	0.98	0.00	8.32
MP2/TZVP	6.10	6.39	0.36	0.00	8.12
MP2/TZVPP	5.11	6.74	1.26	0.00	8.21
CCSD-F12b/cc-pVDZ-F12 [b]	2.55	2.50	1.25	0.00	6.91
CCSD-F12b/cc-pVTZ-F12 [b]	2.63	2.54	1.28	0.00	7.01
CCSD-F12b/CBS [b,c]	2.66	2.56	1.29	0.00	7.05
CCSD(T)-F12b/cc-pVDZ-F12 [b]	3.05	3.30	1.14	0.00	7.22
CCSD(T)-F12b/cc-pVTZ-F12 [b]	3.23	3.45	1.16	0.00	7.40
CCSD(T)-F12b/CBS [b,c]	3.30	3.51	1.17	0.00	7.47
Zero point correction					
B3LYP/aug-cc-pVTZ	-0.55	-0.53	-0.18	0.00	-0.76
MP2/6-311+G**	-1.00	-1.00	0.24	0.00	-1.18
MP2/TZVP	-1.46	-1.30	-0.21	0.00	-0.63
MP2/TZVPP	-0.67	-0.66	-0.23	0.00	-0.78
Gibbs free energy correction					
B3LYP/aug-cc-pVTZ	-1.13	-1.22	-0.28	0.00	-1.99
MP2/6-311+G**	-3.38	-3.24	0.35	0.00	-2.89
MP2/TZVP	-5.69	-3.79	-0.13	0.00	-2.17
MP2/TZVPP	-2.04	-2.19	-0.50	0.00	-2.09
Gibbs Free Energy 298K					
CCSD(T)-F12b/cc-pVDZF12 [d]	1.92	2.08	0.87	0.00	5.23
CCSD(T)-F12b/cc-pVTZF12 [d]	2.10	2.23	0.89	0.00	5.41
CCSD(T)-F12b/CBS [d]	2.18	2.29	0.89	0.00	5.48
CCSD(T)-F12b/cc-pVDZF12 [e]	1.01	1.11	0.64	0.00	5.13
CCSD(T)-F12b/cc-pVTZF12 [e]	1.19	1.26	0.66	0.00	5.31
CCSD(T)-F12b/CBS [e]	1.26	1.33	0.67	0.00	5.38

[a] Alternative nomenclature CF1, CF2 …for conformers of APEA,[6] and in parentheses the labels I-V for corresponding conformers of PEA.[4, 9-11]

[b] Single-point energy at MP2/6-311+G** optimized geometries.

[c] CBS extrapolation from cc-pVDZ-F12 and cc-pVTZ-F12 relative energies.

[d] B3LYP/aug-cc-pVTZ Gibbs correction.

[e] MP2/aug'-cc-pVTZ Gibbs correction.

Table S2. *Ab initio* calculated energy differences (in kJ mol^{-1}) between APEA with the aromatic amine in 'up' and 'down' configurations. A positive value indicates that the 'down' configuration is lower in energy.

Conformer	Aa	Ag	Ga	Gg	Gg'
alternative label [a]	CF1 (V)	CF2 (IV)	CF3 (II)	CF4 (III)	CF5 (I)
Electronic energy (E_e)					
B3LYP/6-31+G*	-0.08	0.14	0.13	0.36	-0.02
B3LYP/6-31++G**	-0.04	0.17	0.14	0.36	0.01
B3LYP/6-311+G**	-0.05	0.14	0.12	0.31	0.00
MP2/TZVPP	-0.08	0.14	0.04	0.33	-0.12
CCSD-F12b/cc-pVDZ-F12 [b]	0.22	0.39	0.43	0.68	-0.14
CCSD(T)-F12b/cc-pVDZ-F12 [b]	0.18	0.35	0.37	0.63	-0.15
E_0 (including Zero-point correction)					
B3LYP/6-31+G*	-0.08	0.10	0.04	0.27	0.00
B3LYP/6-31++G**	-0.06	0.10	0.03	0.23	0.01
B3LYP/6-311+G**	-0.04	0.11	0.04	0.23	0.04
MP2/TZVPP	-0.04	0.14	0.08	0.31	-0.16
ΔG_{298K} (Gibbs free energy)					
B3LYP/6-31+G*	-0.11	0.07	0.01	0.14	0.22
B3LYP/6-31++G**	-0.08	0.06	0.00	0.10	0.05
B3LYP/6-311+G**	-0.09	0.04	-0.03	0.05	0.04
MP2/TZVPP	-0.05	0.12	0.09	0.28	-0.31
CCSD(T)-F12b/cc-pVDZ-F12 [b,c]	0.16	0.30	0.27	0.44	-0.04
CCSD(T)-F12b/cc-pVDZ-F12 [b,d]	0.21	0.33	0.42	0.57	-0.34

[a] Alternative nomenclature CF1, CF2 …for conformers of APEA,[6] and in parentheses the labels I-V for corresponding conformers of PEA.[4, 9-11]

[b] Single-point energy at MP2/6-311+G** optimized geometries.

[c] B3LYP/6-311+G** zero-point energy and Gibbs energy correction.

[d] MP2/TZVPP zero-point energy and Gibbs energy correction.

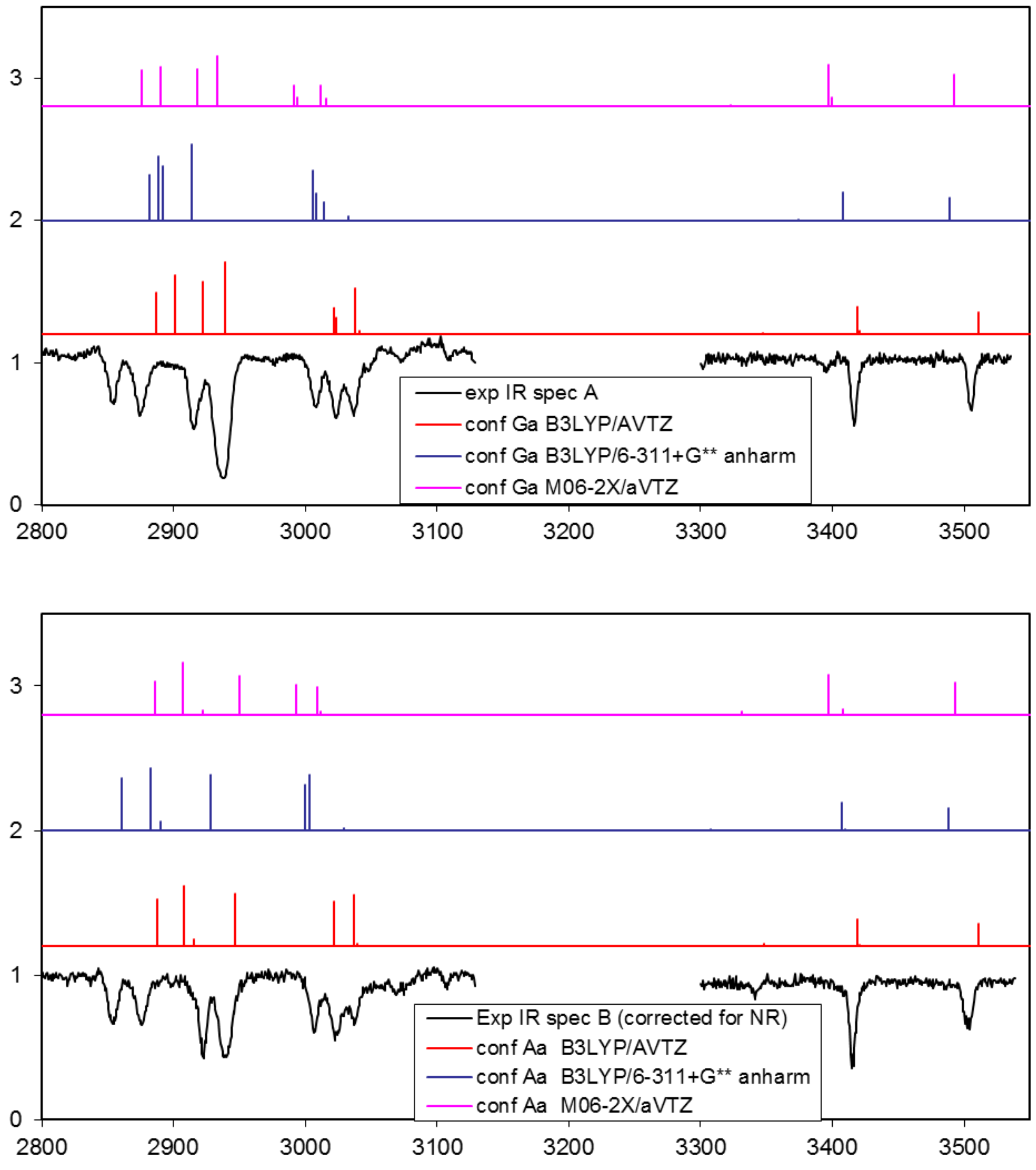
Table S3. MP2/6-311+G** calculated barrier heights (in kJ mol^{-1}) for rotational between conformers. Data is presented as Gibbs free energy (ΔG) differences between minima and transition state and refers to the energy difference from the conformer labelled on the left. Values in parentheses are B3LYP/6-311+G** results.

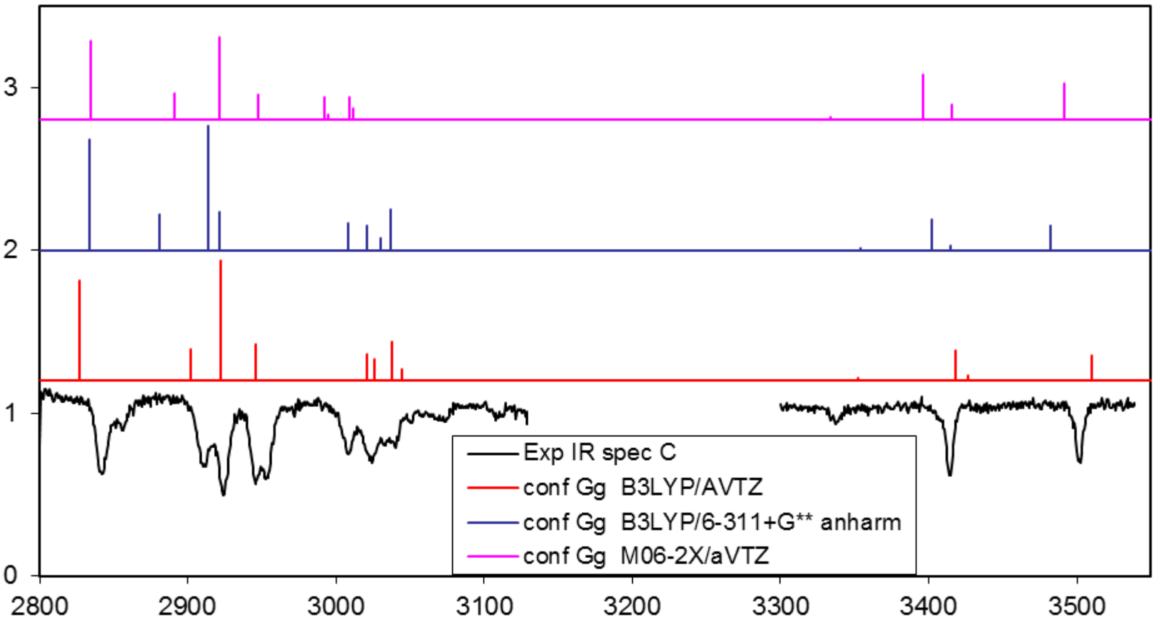
Conformer	Aa	Ag	Ga	Gg	Gg'
alternative label [a]	CF1 (V)	CF2 (IV)	CF3 (II)	CF4 (III)	CF5 (I)
Aa (CF1)	-	10.4 (9.4)	20.0 (18.4)	20.0 (18.4)	19.6 (17.5)
Ag (CF2)	10.2 (8.6)	-	13.1 (13.0)	19.4 (17.1)	16.7 (16.9)
Ga (CF3)	21.3 (17.7)	14.7 (13.1)	-	10.7 (10.9)	13.4 (13.1)
Gg (CF4)	22.9 (17.4)	22.6 (17.5)	12.3 (11.2)	-	8.0 (8.5)
Gg’ (CF5)	14.3 11.3)	11.5 (11.4)	6.8 (7.5)	2.7 (2.7)	-

[a] Alternative nomenclature CF1, CF2 …for conformers of APEA,[6] and in parentheses the labels I-V for corresponding conformers of PEA.[4, 9-11]

Supplementary Data Figures

Figure S1. Comparison of experimental IR spectra of APEA with computed stick spectra in which IR intensities in km mol^{-1} are divided by 100. Top trace: harmonic M06-X2/aug-cc-pVTZ (scaled 0.946). 2nd trace: unscaled anharmonic B3LYP/6-311+G**. 3rd trace: harmonic B3LYP/aug-cc-pVTZ (scaled 0.96).

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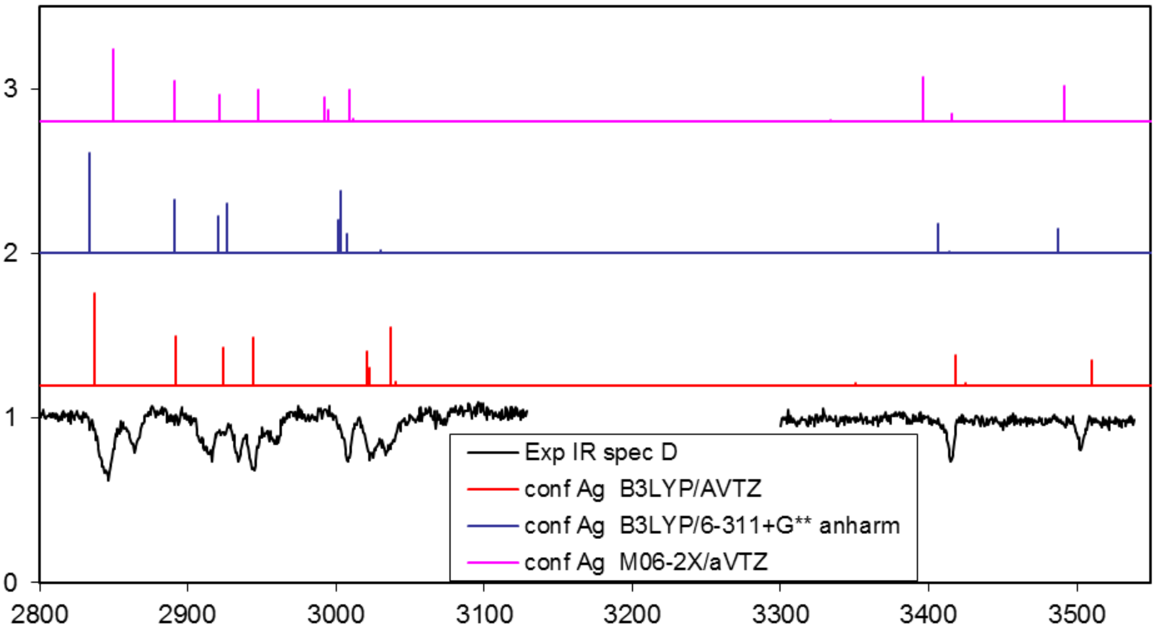
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Notes on the vibrational scaling factors used in spectral simulations

A preliminary investigation of suitable scaling factors for MP2 and B3LYP with a 6-311+G** basis, using spectroscopic data from aniline, ethylbenzene, methylamine and ethylamine determined the following set of empirical scaling factors for the different types of stretch modes:

Method	aliphatic-CH	aromatic-CH	aliphatic-NH	aromaticC-NH
MP2	0.9387	0.9484	0.9425	0.9536
B3LYP	0.9614	0.9602	0.9568	0.9580

1. MP2/TZVPP (scaled 0.94)

As stated in the table 2 footnote, MP2/TZVPP wavenumber values were scaled by 0.94. This value was selected to allow the best prediction of aliphatic CH stretch modes, and is also identical to the value chosen for CH and OH stretch modes computed at the MP2/aug-cc-pVTZ level in the study of Myshakin et al.[ref 64]. We note however that this does not match the optimal scaling factor for the anilinic NH stretch modes from the list above, and the predictions for the corresponding vibrations in figure 5 are correspondingly too low.

2. B3LYP/aug-cc-pVTZ (scaled 0.96).

Unlike the MP2 case, for B3LYP a single scaling factor of 0.96 is broadly suited to all the CH and NH stretch modes.
Note that in the study of Halls *et. al.*, a similar scaling factor of 0.9659 is recommended for modes over 1800 cm-1 computed at the B3LYP/pVTZ level, and is reported to produce a standard deviation of 39 cm^{-1}.

[Halls, M. D.; Velkovski , J.; Schlegel, H. B., "Harmonic Frequency Scaling Factors for Hartree-Fock, S-VWN, B-LYP, B3-LYP, B3-PW91 and MP2 with the Sadlej pVTZ Electric Property Basis Set," *Theor. Chem. Acc.*, **2001**, *105*, 413-421]

3. M06-2X/aug-cc-pVTZ (scaled 0.946)

The scaling factor of 0.946 is consistent with those reported in Alecu *et. al.* for fundamental wavenumber values:

M06-2X/aug-cc-pVTZ	0.946	standard deviation 48 cm^{-1}
M06-2X/def2-TZVPP	0.945	standard deviation 48 cm^{-1}

[I. M. Alecu, Jingjing Zheng, Yan Zhao, and Donald G. Truhlar, *J. Chem. Theory Comput.* **2010**, 6, 2872–2887]