Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

IR spectrum of the protonated neurotransmitter 2-phenylethylamine: dispersion and anharmonicity of the NH_3^+-π interaction

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Table T1. Relative energies of stationary points on the potential of H^+PEA calculated at the B3LYP and B3LYP-D3 levels using the aug-cc-pVTZ basis set.

Figure S1. Structures of the most stable isomers of H^+PEA (**G**, **A**) compared to those of the most stable neutral PEA conformers (**B**, **C**) evaluated at the B3LYP-D3/aug-cc-pVTZ level. Bond distances are given in Å.

Figure S2. NBO charge distributions (in me) of the most stable isomers of H^+PEA (**G**, **A**) compared to those of the most stable neutral PEA conformers (**B**, **C**) evaluated at the B3LYP-D3/aug-cc-pVTZ level.

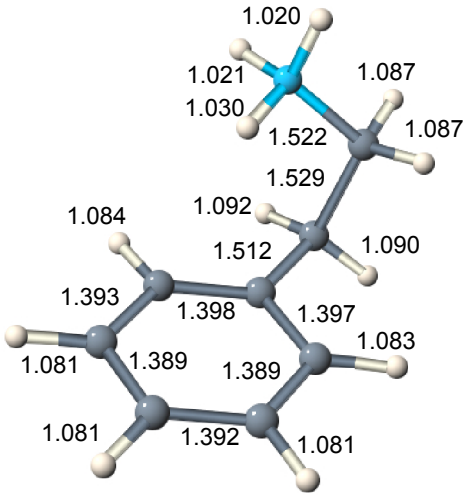
Figure S3. (top) Lengths and scaled harmonic stretch frequencies of the three N-H bonds of H^+PEA (and corresponding average values) as a function of the dihedral angle θ=θ(C1C7C8N). The plots are symmetric with respect to θ=0°. (bottom) Scaled harmonic linear IR spectra of H^+PEA as a function of selected dihedral angles θ=θ(C1C7C8N).

Figure S4. Expanded view of the linear harmonic and anharmonic IR absorption stick spectra of the **G** conformer of H^+PEA (unscaled) calculated at the B3LYP-D3/cc-pVTZ level.

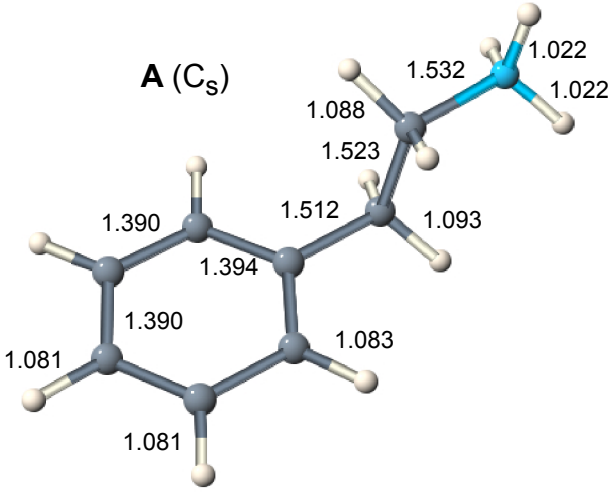
Figure S5. IRPD spectrum of H^+PEA-Ne_2 in the C-H/N-H stretch range compared to linear harmonic IR absorption stick spectrum of the **G** conformer of H^+PEA at the B3LYP-D3/aug-cc-pVTZ level. Isomer-selective IR (M. Schütz et al., unpublished) and Raman spectra (Golan et al., J. Chem. Phys. 131, 024305, 2009) of the **C** conformer of PEA compared to linear harmonic IR absorption stick spectrum at the B3LYP-D3/aug-cc-pVTZ level.

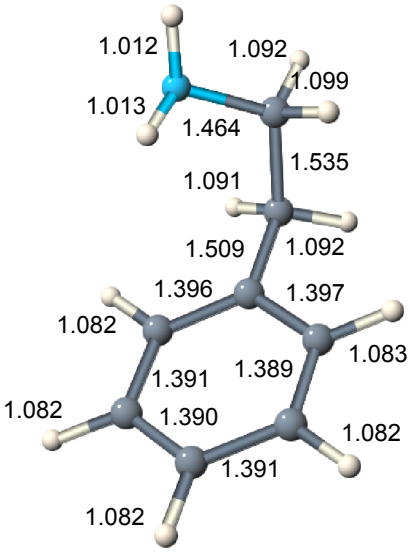
Table T1. Relative energies of stationary points on the potential of H^+PEA calculated at the B3LYP-D3 and B3LYP (in parentheses) levels using the aug-cc-pVTZ basis set.

	E_0 in cm^{-1}	E_0 in kJ/mol
G	0 (0)	0 (0)
A	1564 (1202)	18.7 (14.4)
TS1	1090 (1169)	13.0 (14.0)
TS2	2786 (2392)	33.3 (28.6)

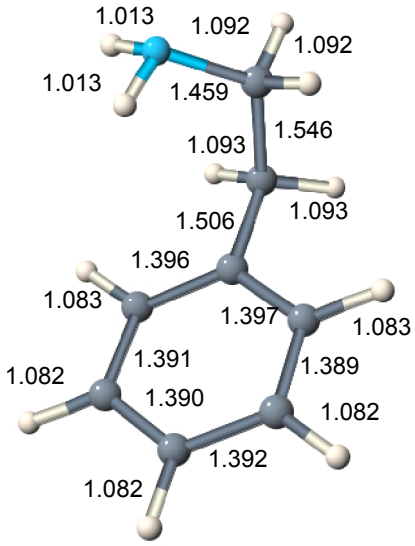


G



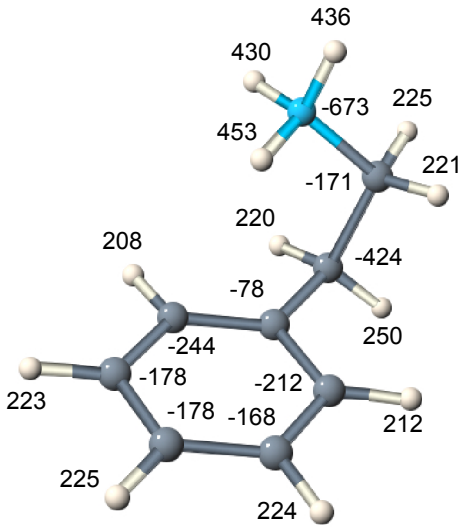


C

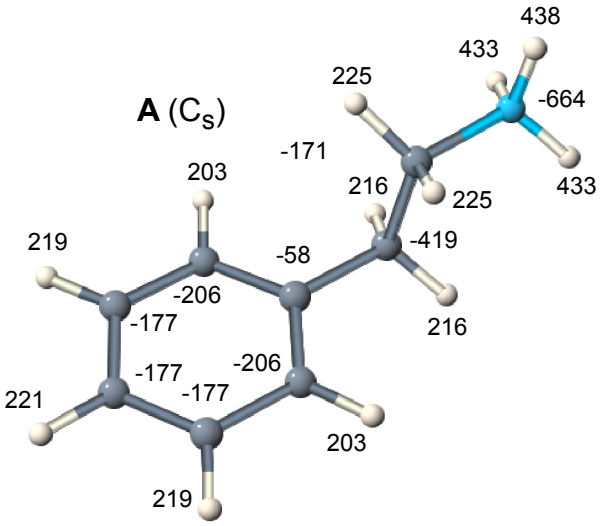


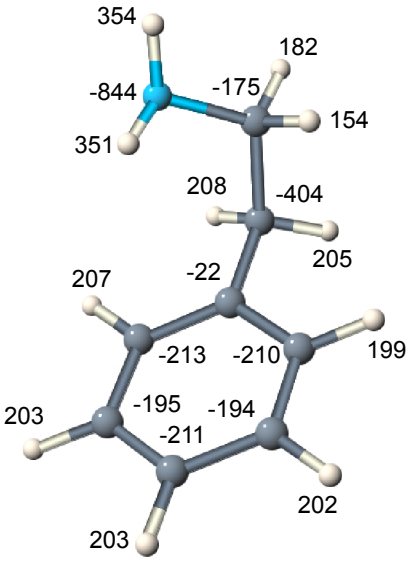
B

Figure S1

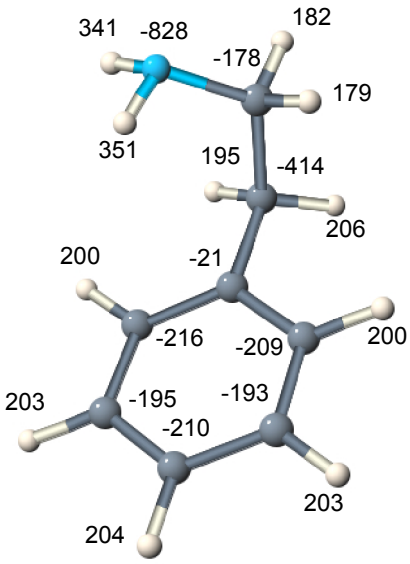


G





C



B

Figure S2

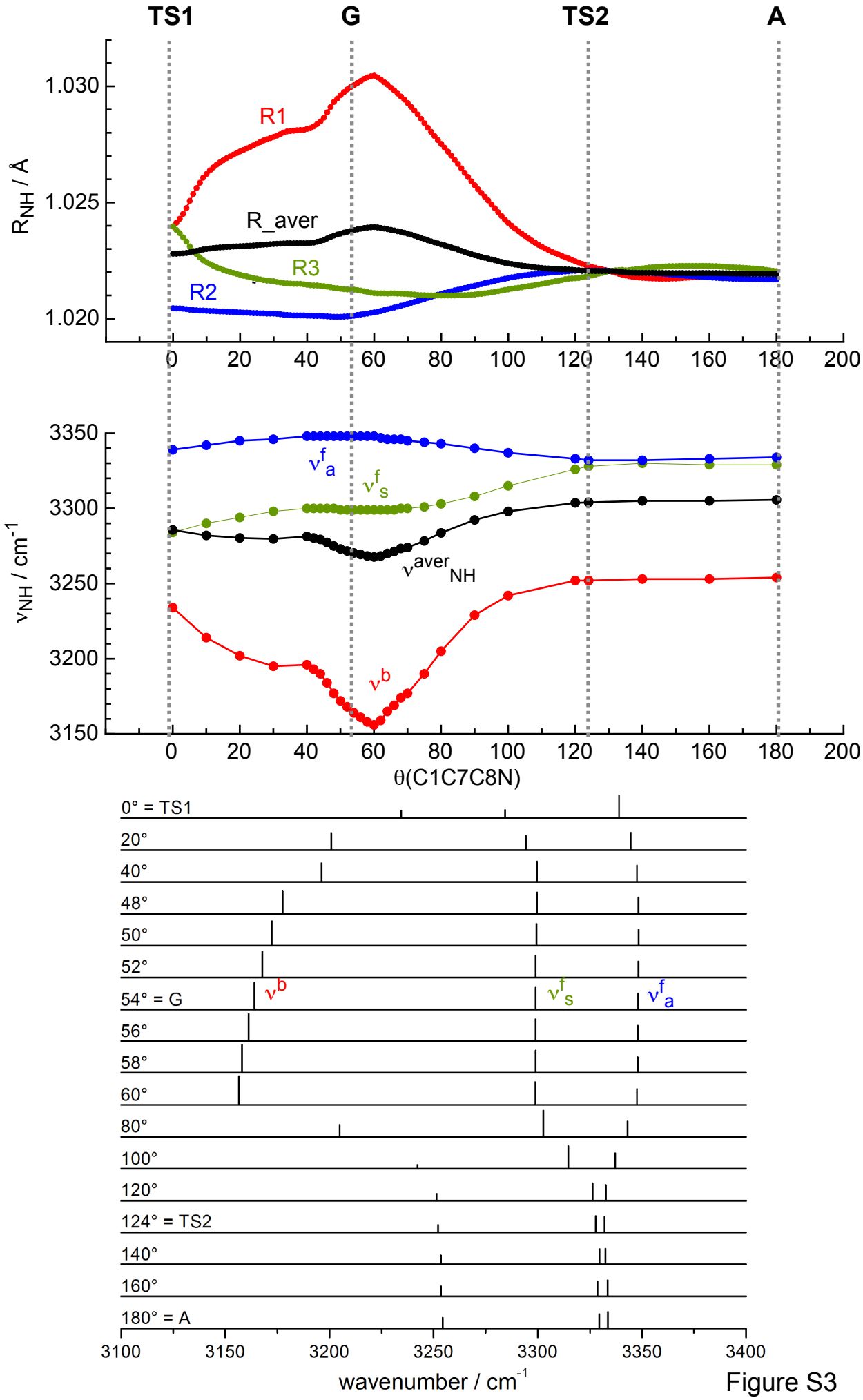

TS1
G
TS2
A
R1
R_aver
R3
R2
R_{NH} / Å
1.030
1.025
1.020
0
20
40
60
80
100
120
140
160
180
200
ν^f_a
ν^f_s
ν^{aver}_{NH}
ν^b
ν_{NH} / cm^{-1}
3350
3300
3250
3200
3150
θ(C1C7C8N)
0° = TS1
20°
40°
48°
50°
52°
54° = G
56°
58°
60°
80°
100°
120°
124° = TS2
140°
160°
180° = A
3100
3150
3200
3250
3300
3350
3400
wavenumber / cm^{-1}

Figure S3

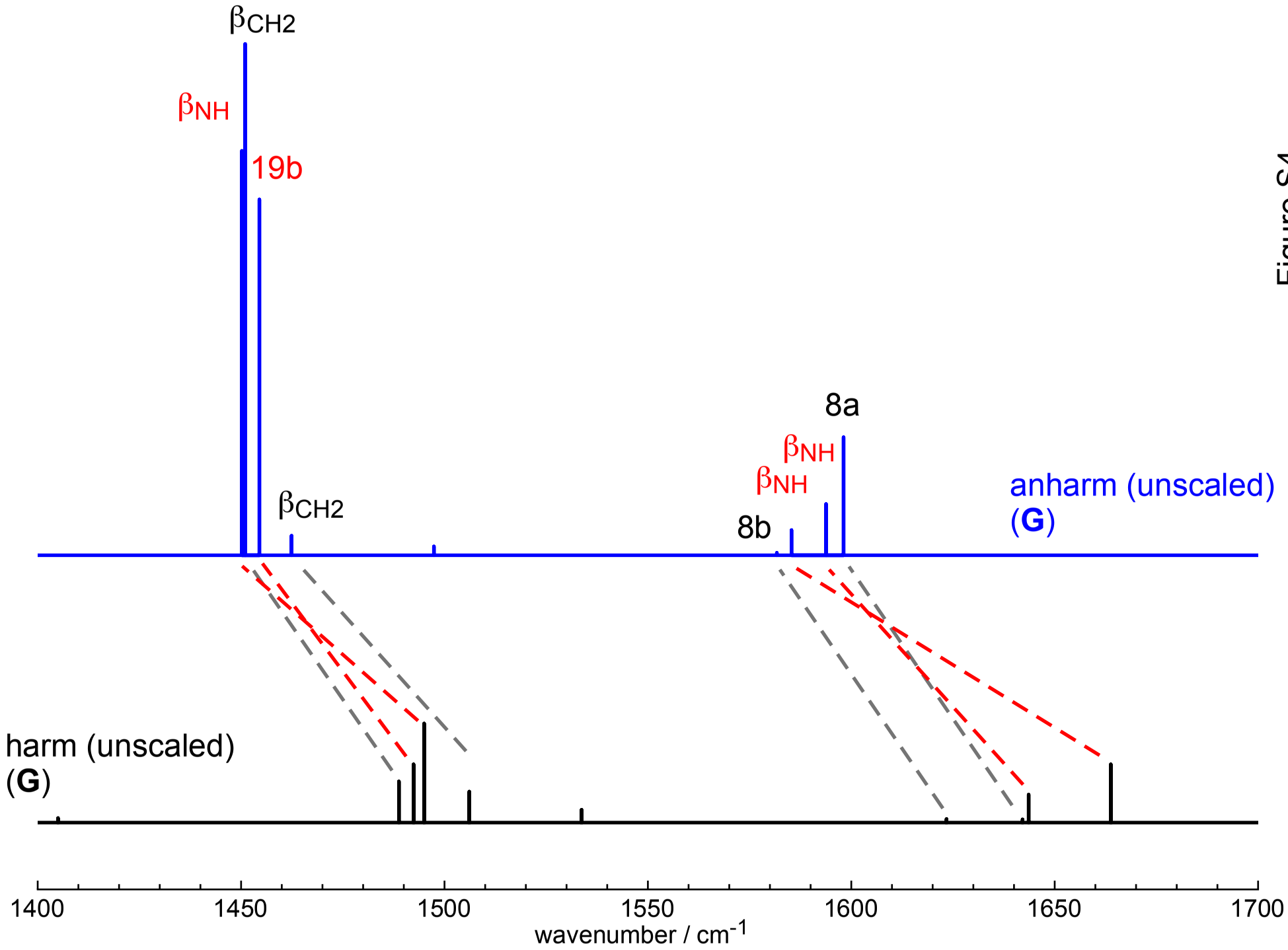

βCH2
βNH
19b
βCH2
8a
βNH
βNH
8b
anharm (unscaled)
(G)
harm (unscaled)
(G)
1400
1450
1500
1550
1600
1650
1700
wavenumber / cm-1

Figure S4

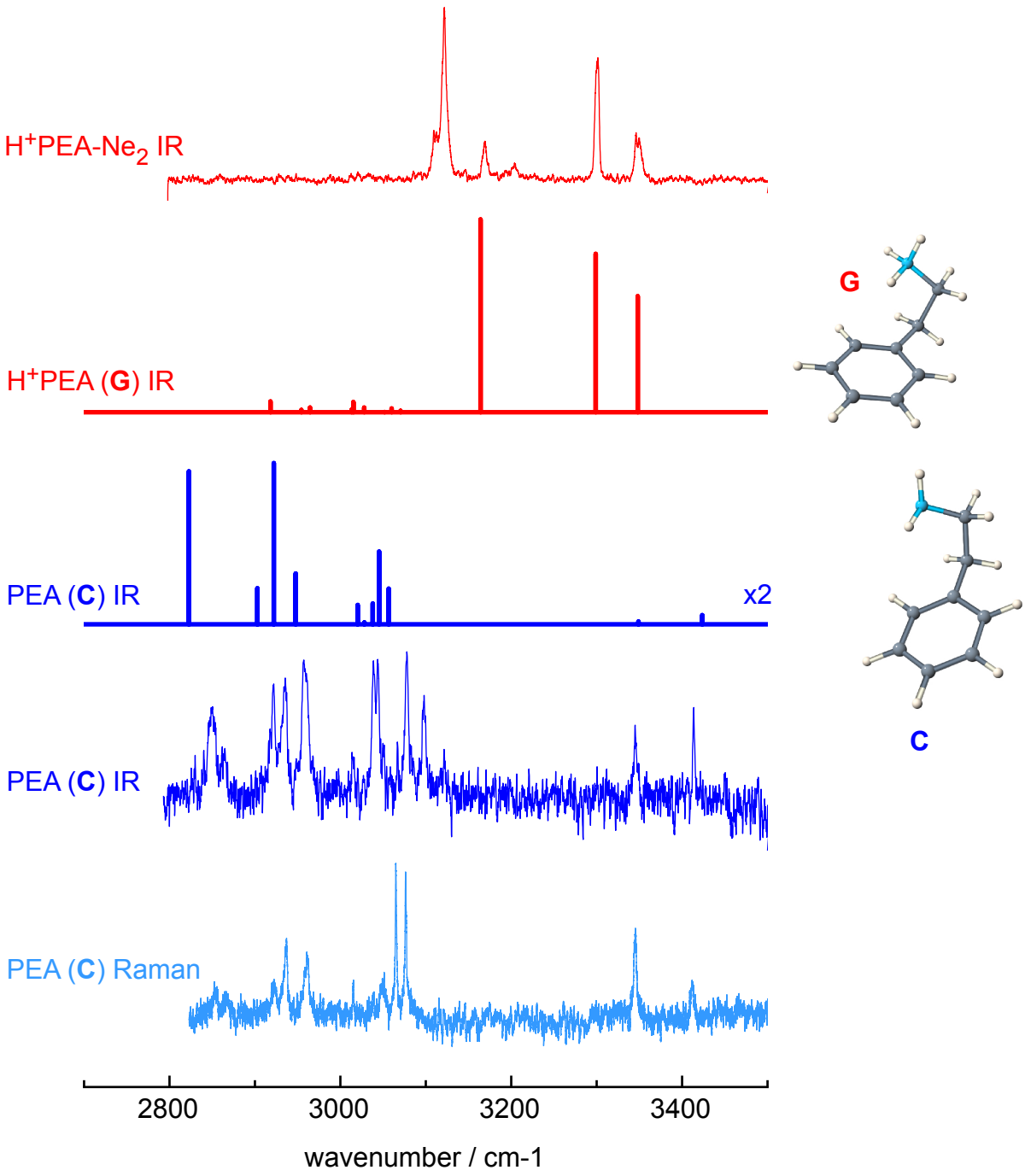

H+PEA-Ne2 IR
H+PEA (G) IR
G
PEA (C) IR
x2
C
PEA (C) IR
PEA (C) Raman
2800
3000
3200
3400
wavenumber / cm-1

Figure S5