Supporting information for :

Discrimination of 4-Hydroxyproline Diastereomers by Vibrational Spectroscopy of the Gaseous Protonated Species

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Contents :

Figure 7S. Calculated IR spectra of protonated (2S,4R)-4-hydroxyproline ($HypH^+$) structures **R-$_{endo}$ IIc**, **R-$_{endo}$ IIIa**, **R-$_{endo}$ IIIc** at the MP2/6-311+G** level.

Figure 8S. Calculated IR spectra of protonated (2S,4S)-4-hydroxyproline ($hypH^+$) structures **S-$_{endo}$ Ic**, **S-$_{exo}$ Ic**, **S-$_{endo}$ IIIa**, **S-$_{exo}$ IIa**, **S-$_{endo}$ IIIb** at the MP2/6-311+G** level.

Figure 9S. Calculated IR spectra of protonated (2S,4S)-4-hydroxyproline ($hypH^+$) structures **S-$_{exo}$ IIc**, **S-$_{exo}$ IIIa**, **S-$_{endo}$ IIIc**, **S-$_{exo}$ IIIc** at the MP2/6-311+G** level.

Figure 10S. Experimental IRMPD spectra of protonated (2S,4R)-4-hydroxyproline ($HypH^+$) enlarged in the higher frequency OH stretch region, showing all data points.

Figure 11S. Experimental IRMPD spectra of protonated (2S,4S)-4-hydroxyproline ($hypH^+$) enlarged in the higher frequency OH stretch region, showing all data points.

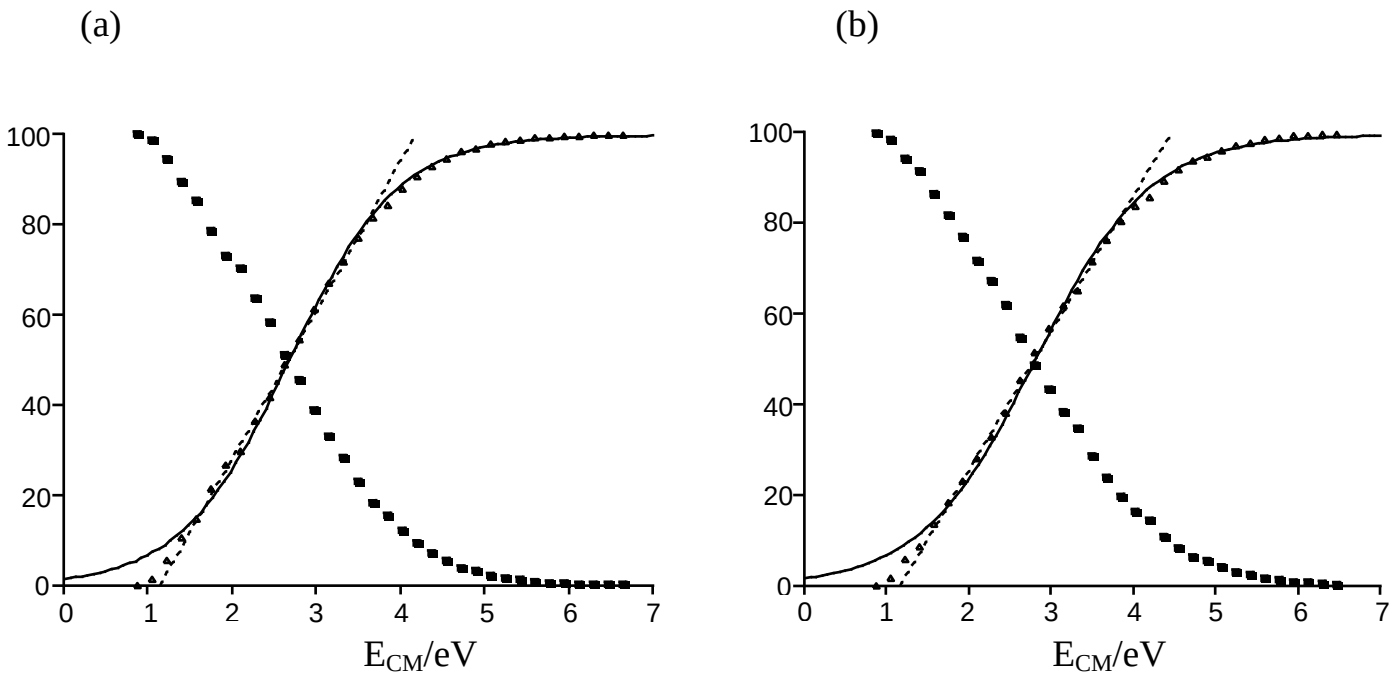


Figure 1S. Relative abundances of mass selected (a) HypH+ and (b) hypH+ ions (■, m/z 132) to afford daughter ion (▲, m/z 86) as a function of collision energy (center of mass, E_{CM}/eV).

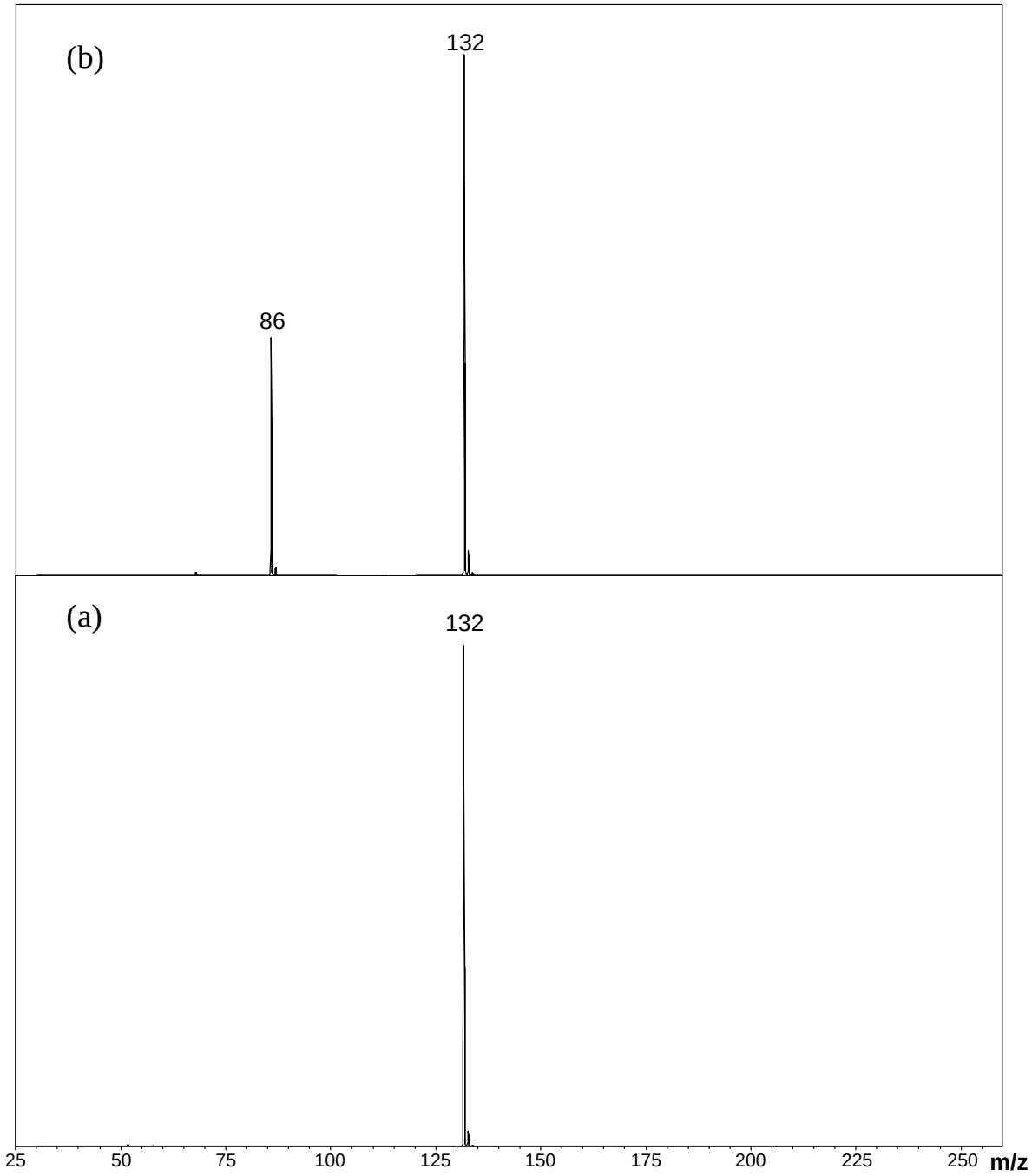


Figure 2S. Photodissociation mass spectrum of protonated (2S,4R)-4-hydroxyproline ($HypH^+$) ions at *m/z* 132 before (a) and after (b) irradiation with OPO/OPA IR frequency fixed at 3550 cm^{-1}.

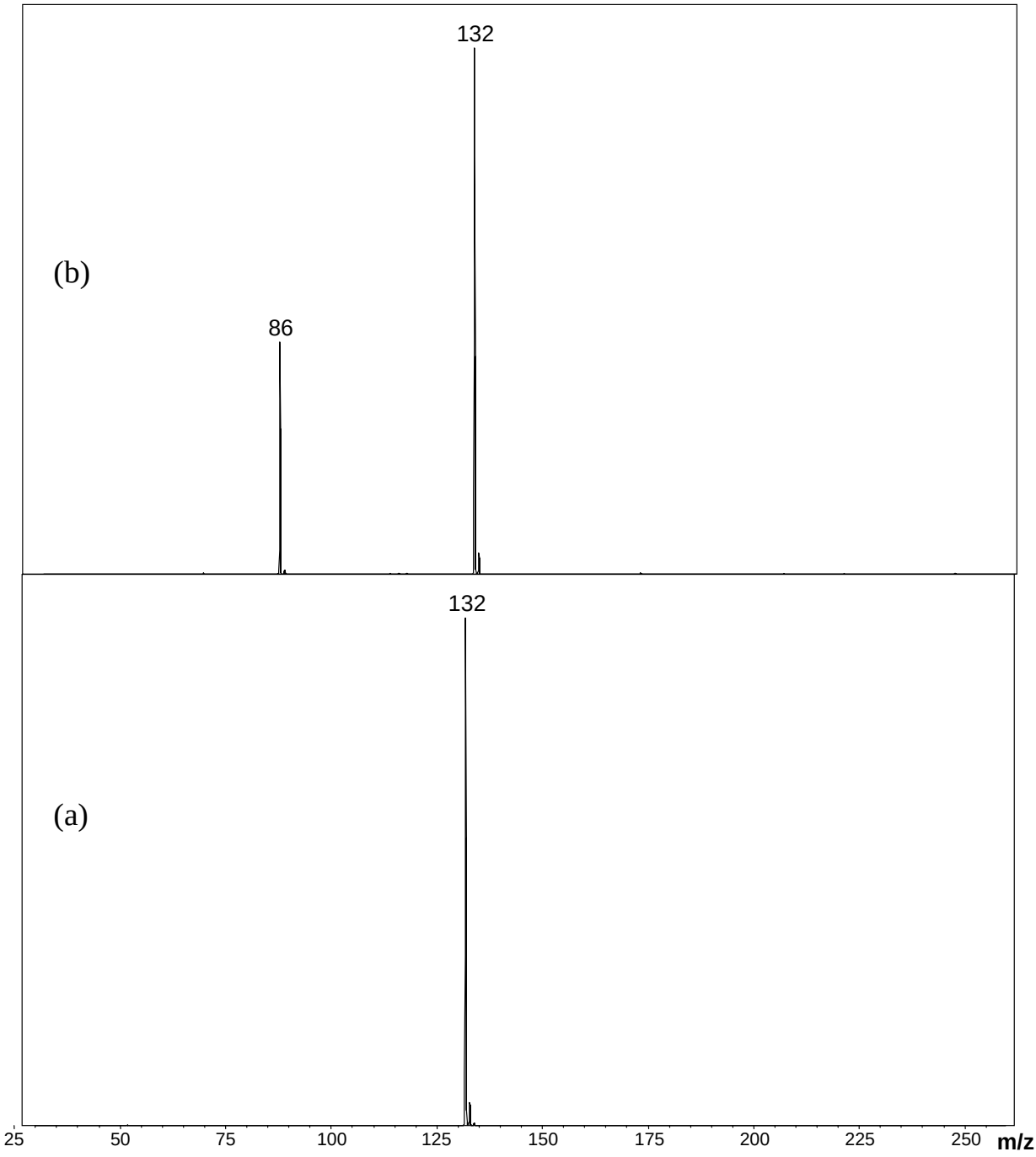
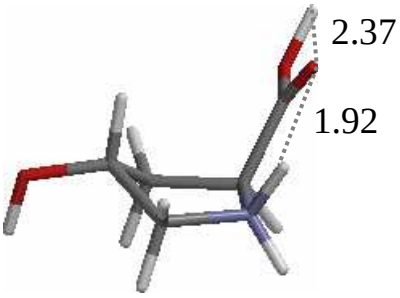
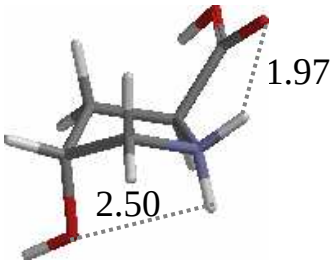


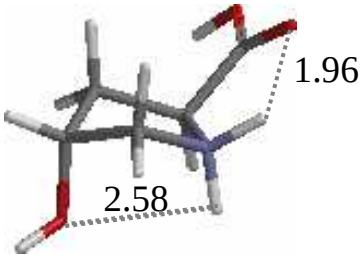
Figure 3S. Photodissociation mass spectrum of protonated (2S,4S)-4-hydroxyproline ($hypH^+$) ions at *m/z* 132 before (a) and after (b) irradiation with CLIO FEL IR frequency fixed at 1770 cm^{-1}.



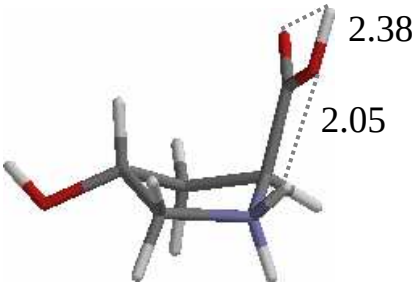
R-$_{endo}$ Ic (33.6)



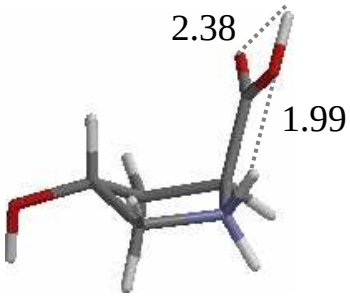
R-$_{exo}$ IIIa (34.8)



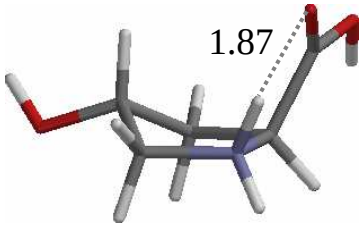
R-$_{exo}$ IIIb (35.2)



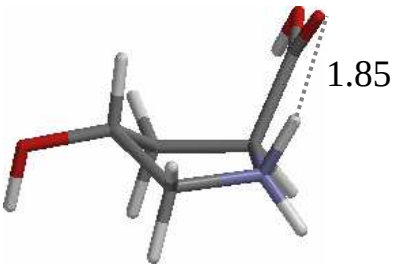
R-$_{endo}$ IIa (37.4)



R-$_{endo}$ IIc (51.1)

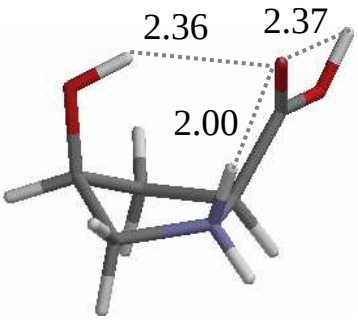


R-$_{endo}$ IIIa (55.5)



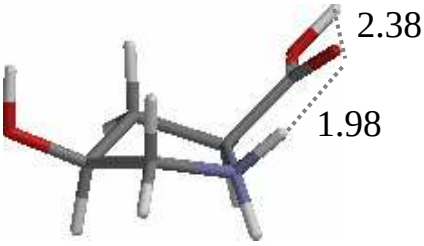
R-$_{endo}$ IIIc (69.1)

Figure 4S. Optimized structures and relative free energies (kJ mol^{-1}, in parentheses) at 298 K of protonated (2S,4R)-4-hydroxyproline (HypH^{+}) conformers **R-$_{endo}$ Ic, R-$_{exo}$ IIIa, R-$_{exo}$ IIIb**, **R-$_{endo}$ IIa**, **R-$_{endo}$ IIc**, **R-$_{endo}$ IIIa**, **R-$_{endo}$ IIIc**, calculated at MP2/6-311+G** level of theory.



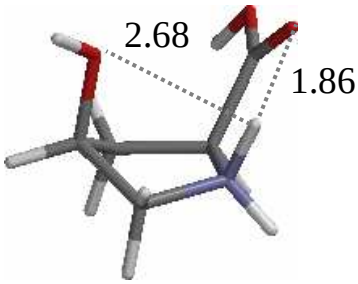
S-$_{endo}$ Ic

(27.9)

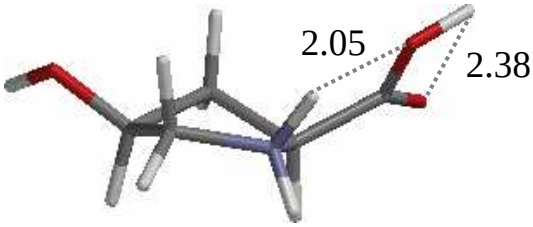


S-$_{exo}$ Ic

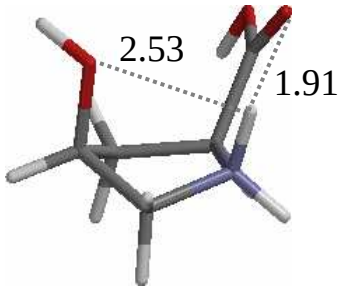
(32.5)



S-$_{endo}$ IIIa
(36.9)

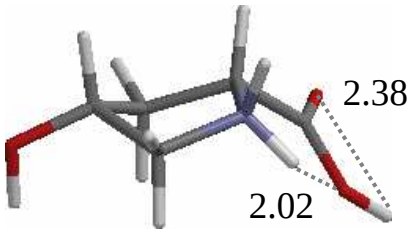


S-$_{exo}$ IIa
(37.1)



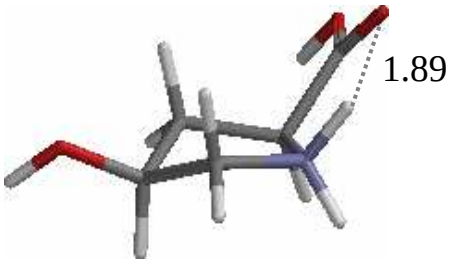
S-$_{endo}$ IIIb

(37.2)



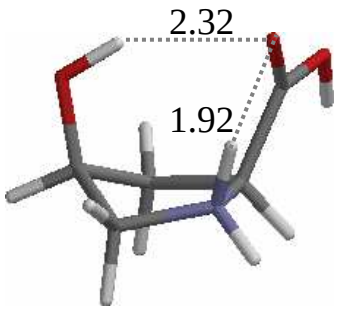
S-$_{exo}$ IIc

(49.4)



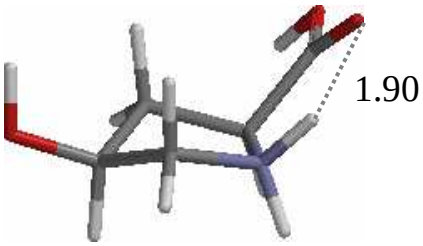
S-$_{exo}$ IIIa

(55.9)



S-$_{endo}$ IIIc

(62.7)



S-$_{exo}$ IIIc

(67.0)

Figure 5S. Optimized structures and relative free energies (kJ mol^{-1}, in parentheses) at 298 K of hypH$^+$ conformers **S-$_{endo}$ Ic**, **S-$_{exo}$ Ic**, **S-$_{endo}$ IIIa**, **S-$_{exo}$ IIa**, S-$_{endo}$ **IIIb**, **S-$_{exo}$ IIc**, **S-$_{exo}$ IIIa**, **S-$_{endo}$ IIIc**, **S-$_{exo}$ IIIc**, calculated at MP2/6-311+G** level of theory. Hydrogen bond lengths, marked by dashed lines, are given in Å.

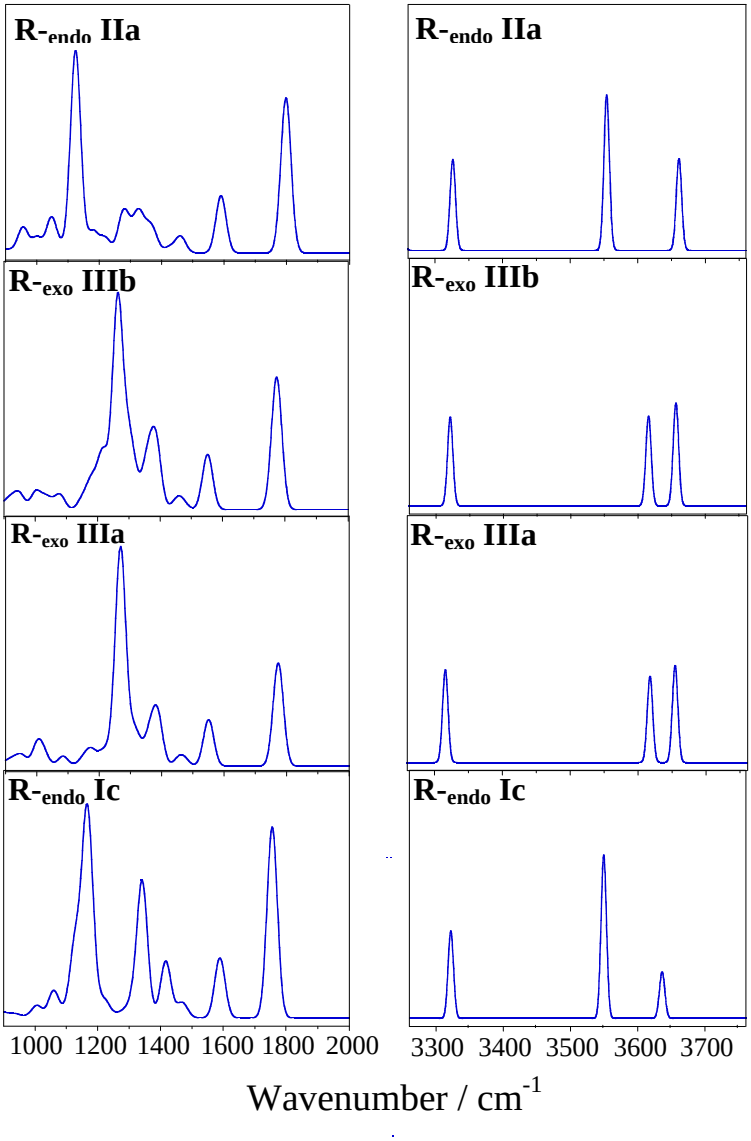


Figure 6S. Calculated IR spectra of protonated (2S,4R)-4-hydroxyproline ($HypH^+$) structures $\mathbf{R_{endo}}$ **Ic**, $\mathbf{R_{exo}}$ **IIIa**, $\mathbf{R_{exo}}$ **IIIb**, $\mathbf{R_{endo}}$ **IIa**, at the MP2/6-311+G** level.

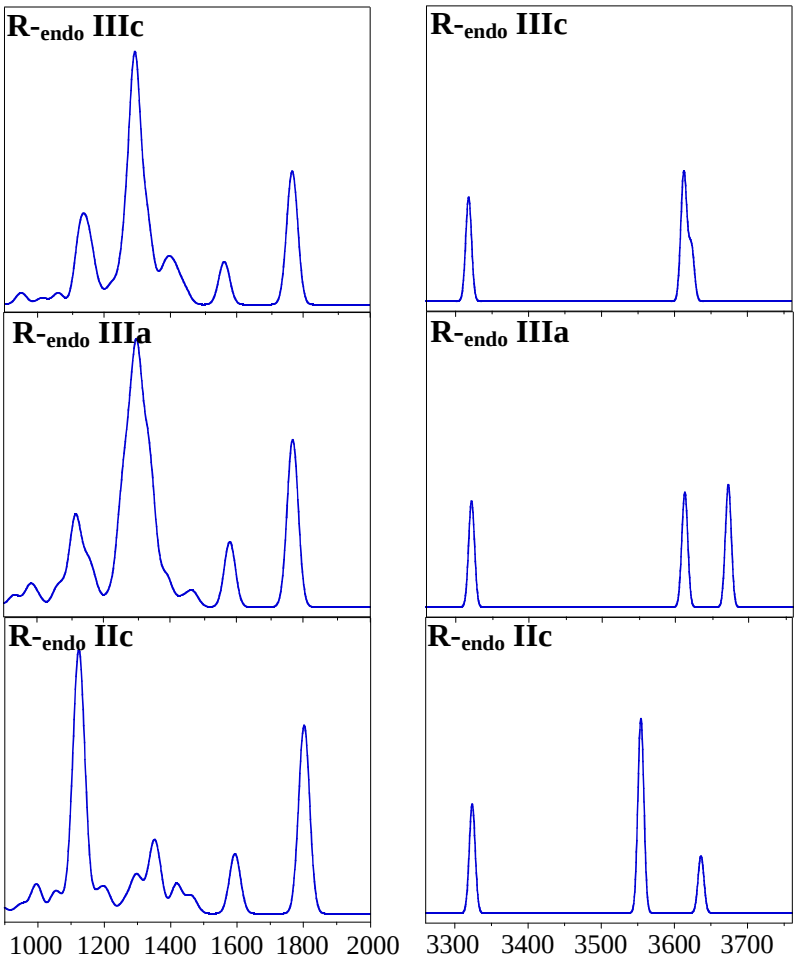
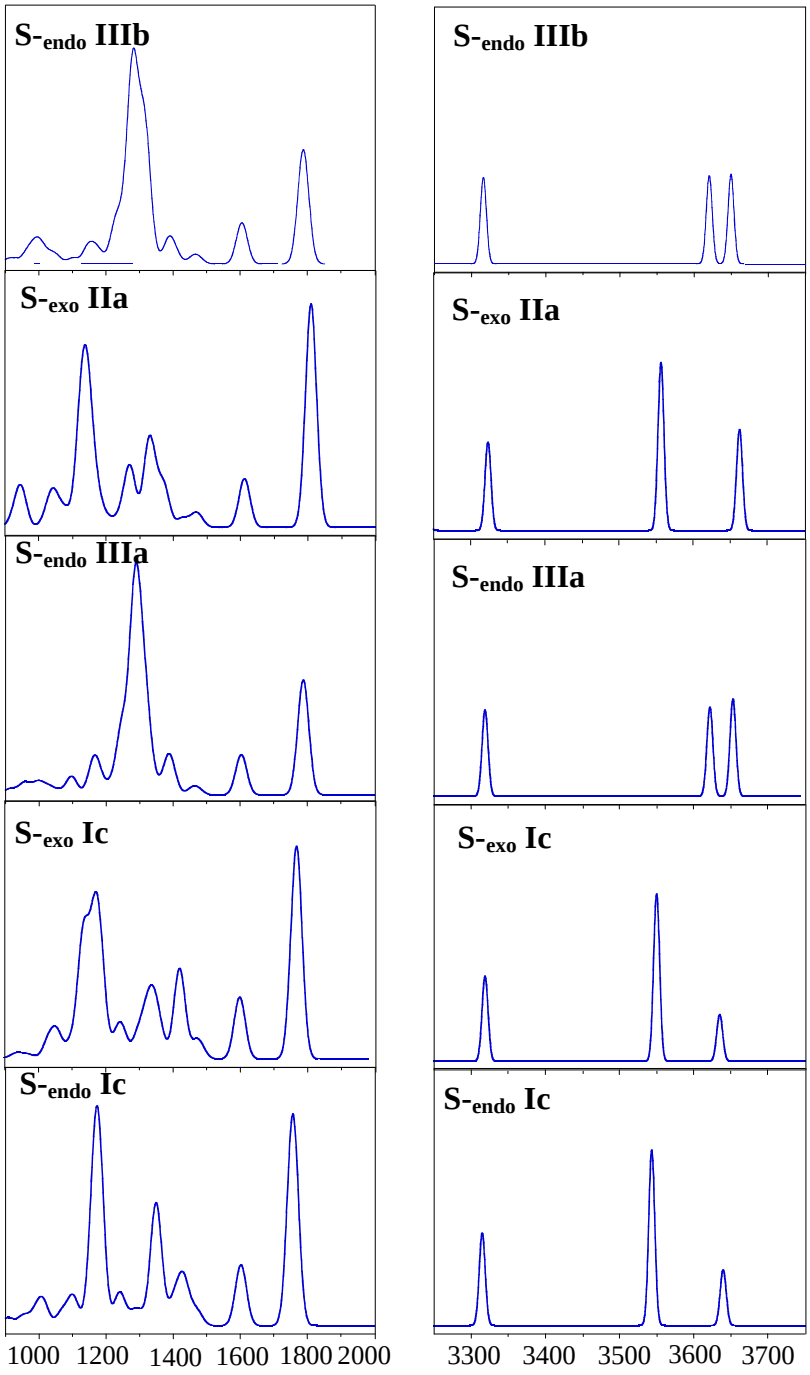


Figure 7S. Calculated IR spectra of protonated (2S,4R)-4-hydroxyproline ($HypH^+$) structures **R-endo IIc**, **R-endo IIIa**, **R-endo IIIc** at the MP2/6-311+G** level.



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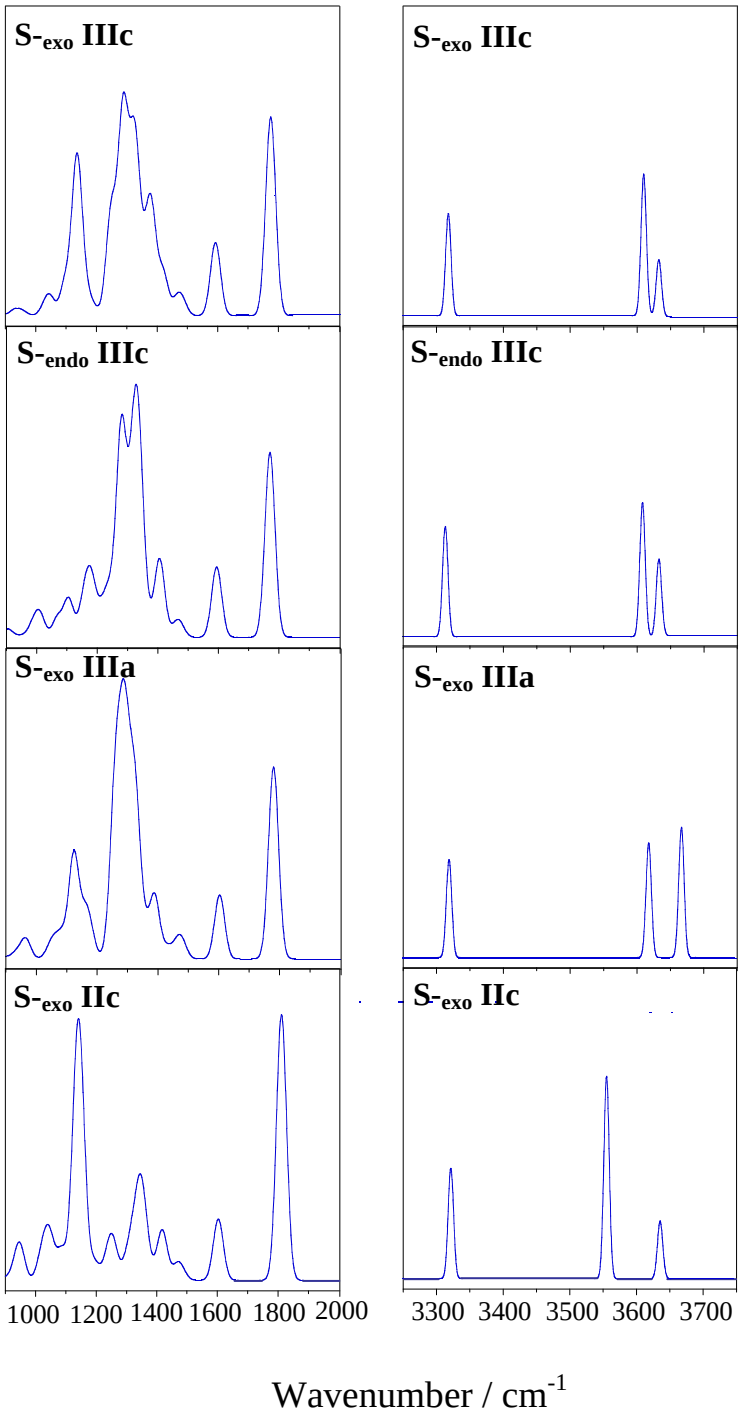

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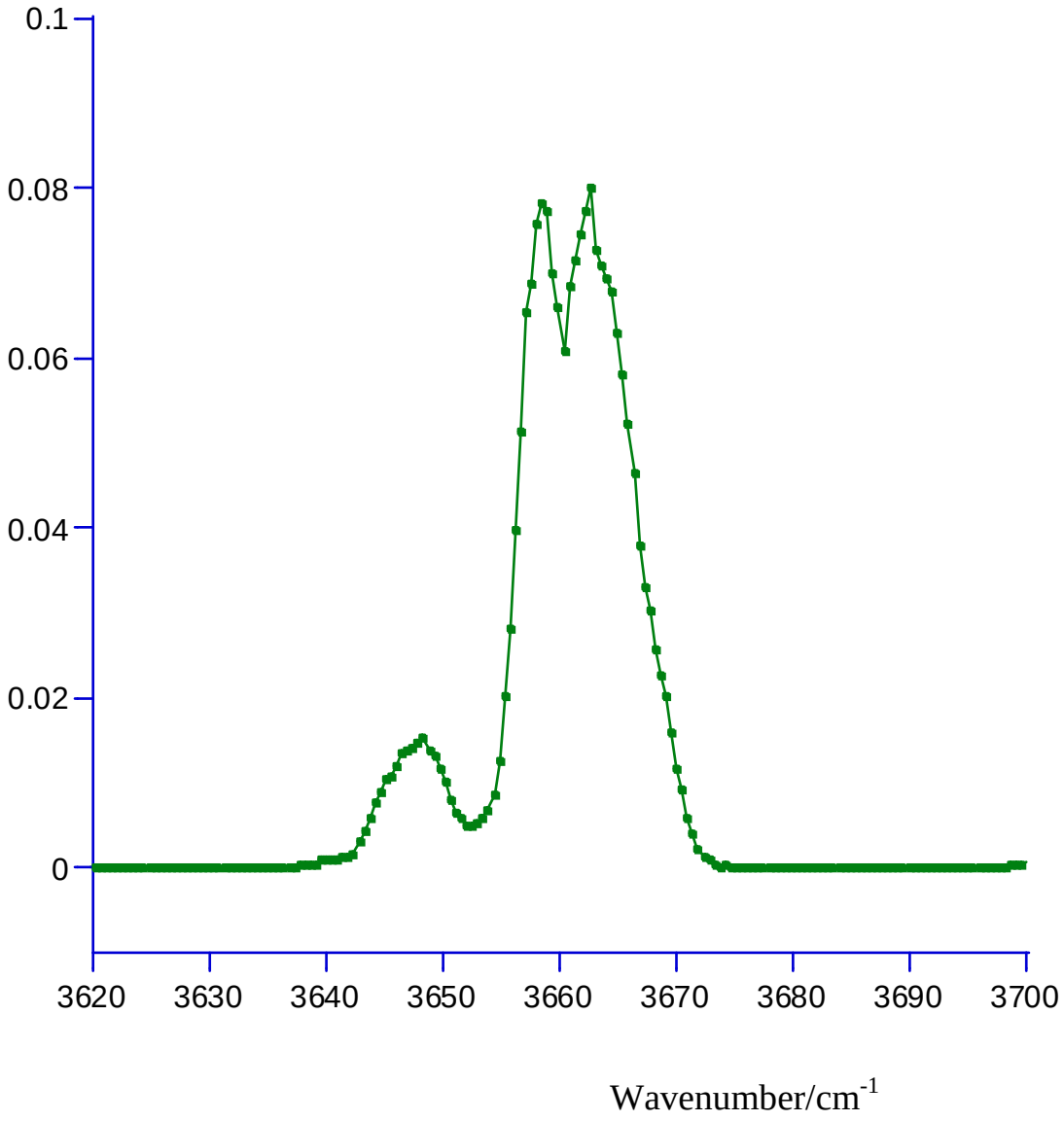

Figure 10S. Experimental IRMPD spectra of protonated (2S,4R)-4-hydroxyproline ($HypH^+$) enlarged in the higher frequency OH stretch region, showing all data points.

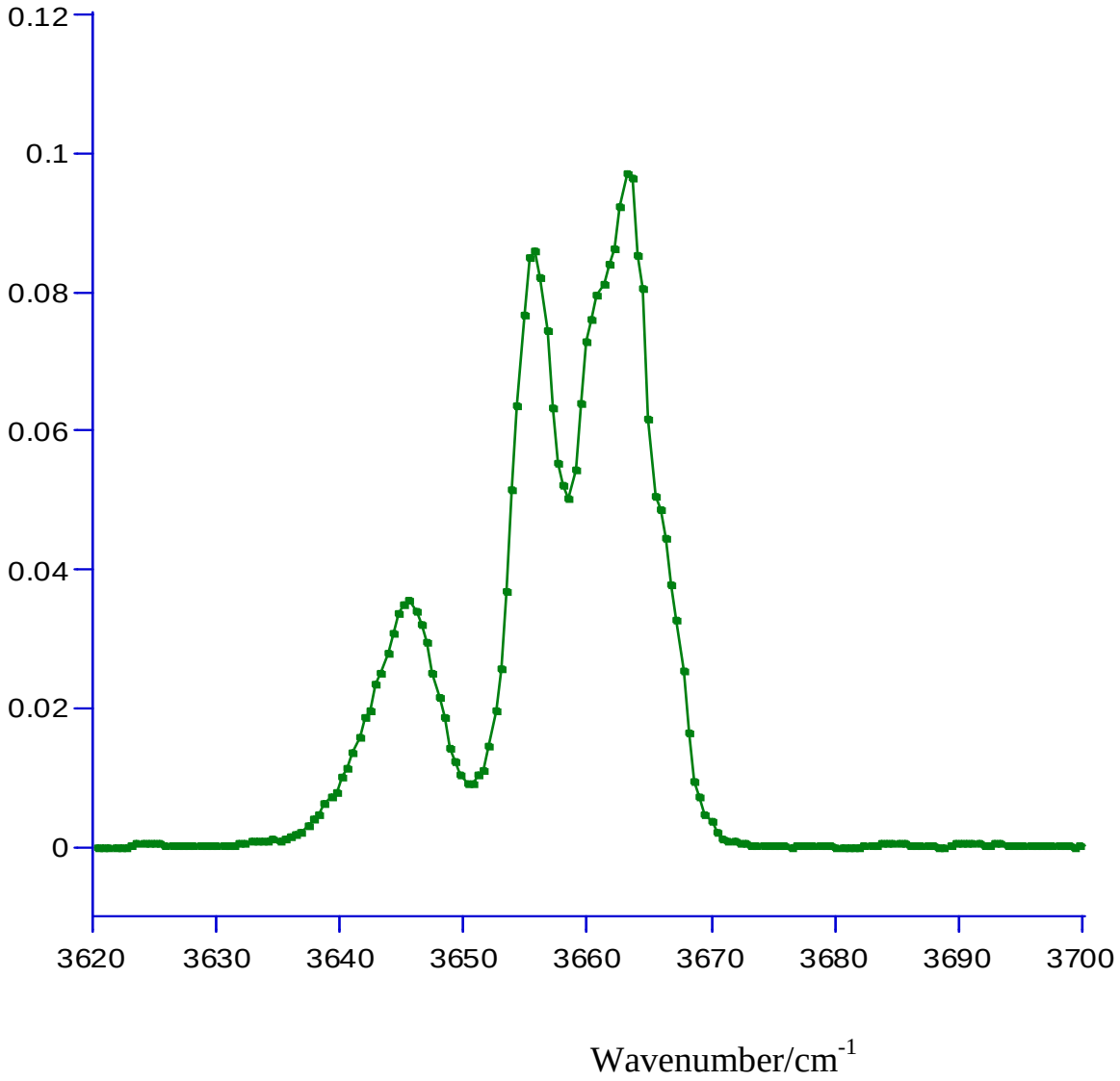

Figure 11S. Experimental IRMPD spectra of protonated (2S,4S)-4-hydroxyproline ($hypH^+$) enlarged in the higher frequency OH stretch region, showing all data points.