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

Electronic Supplementary Information

Excited-state proton transfer in protonated adrenaline revealed by cryogenic UV photodissociation spectroscopy

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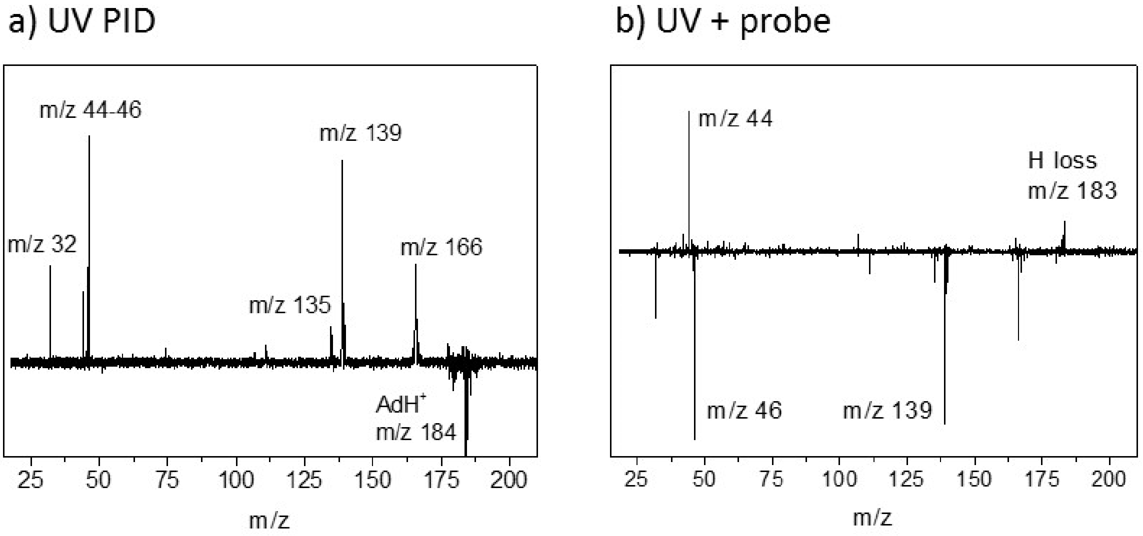

Fig. S1 Difference mass spectra of the UV photodissociation of AdH^+ (m/z 184) recorded for a short fragmentation time of 1 µs with (a) UV only (laser on – laser off) and (b) in the pump-probe scheme (pump and probe laser – pump only). The C_α-C_β bond cleavage fragments are m/z 139, m/z 46 and m/z 44, the water loss (m/z 166) and its secondary fragment at m/z 135. On the pump-probe scheme, the probe photon (550 nm) opens the H loss channel at m/z 183 along with its secondary fragment at m/z 44 and depletes all the fragmentation channels initially observed by the pump only.

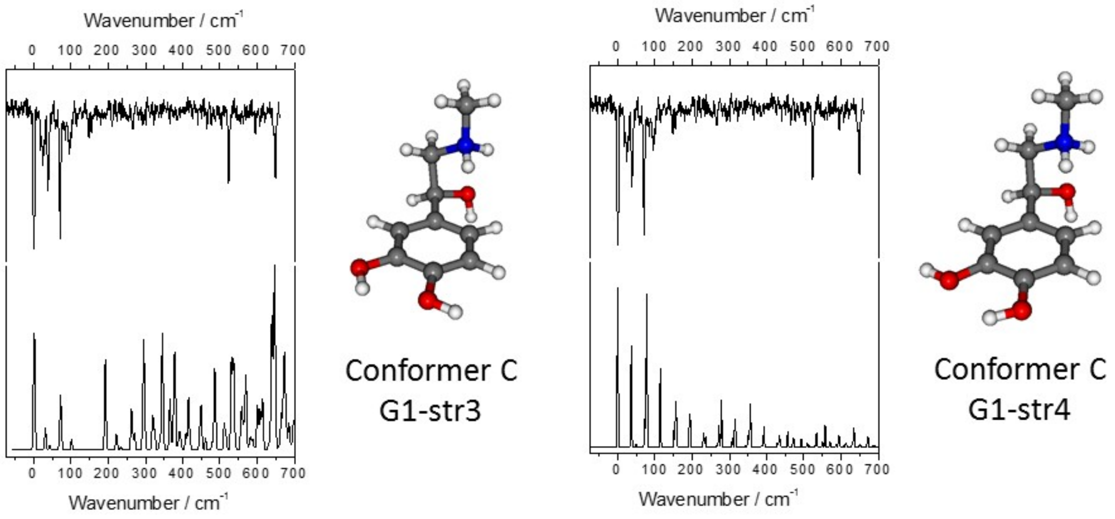

Fig. S2 Comparison of the simulated vibronic spectra of the G1-STR3 and G1-STR4 structure with the spectroscopy of conformer C. G1-STR3 provides a better agreement in the low frequency region below 200 cm^{-1}.

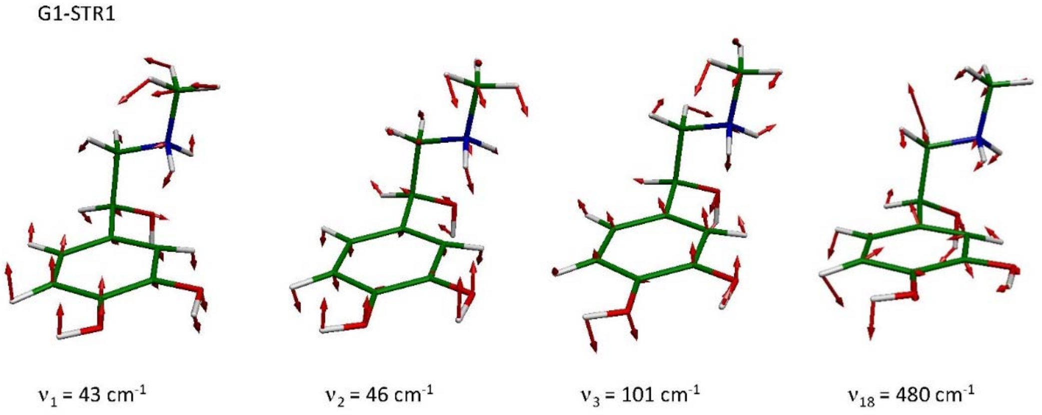

Fig. S3 Franck-Condon active modes in the vibronic spectrum of the AdH$^+$ G1-STR1 conformer. The frequency modes below 100 cm^{-1} involve motion of the methyl-amino moiety above the catechol ring. The ν_{18} mode is the first in-plane breathing mode of the catechol ring.

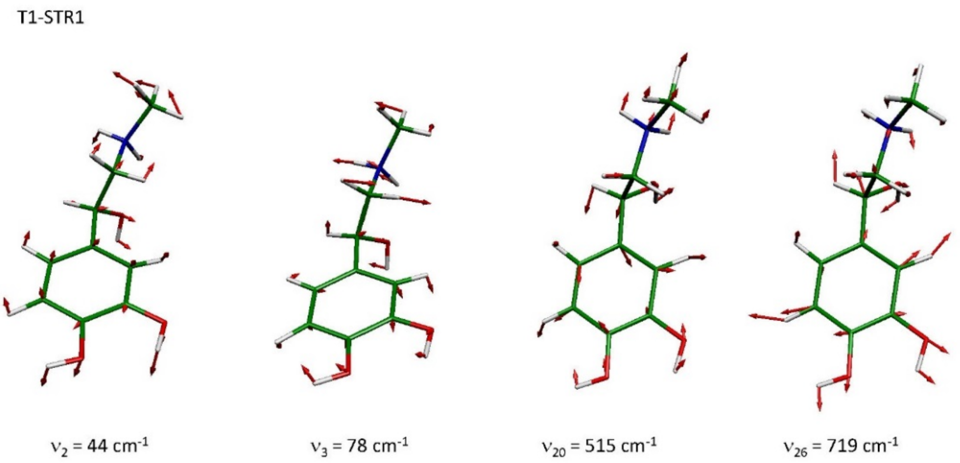

Fig. S4 Franck-Condon active modes in the vibronic spectrum of the AdH$^+$ T1-STR1 conformer.

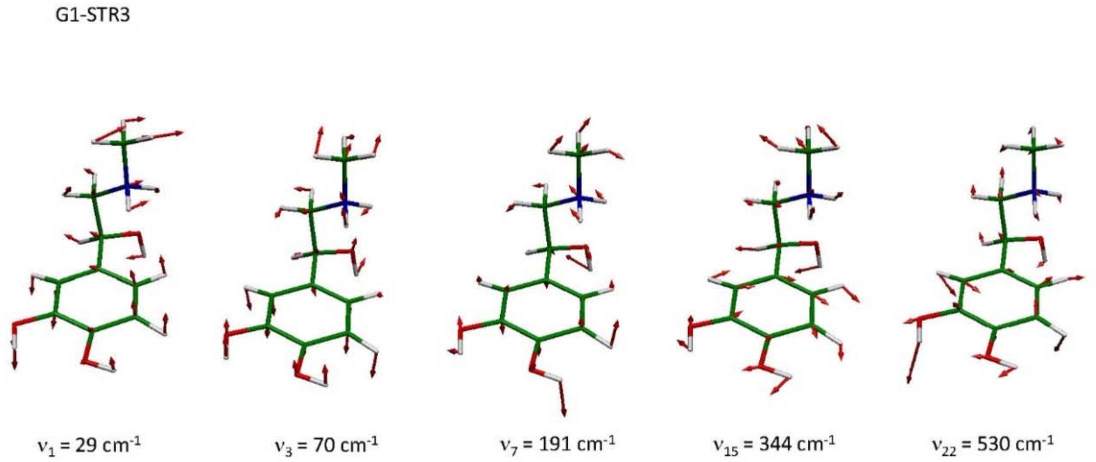

Fig. S5 Franck-Condon active modes in the vibronic spectrum of the AdH$^+$ G1-STR3 conformer.

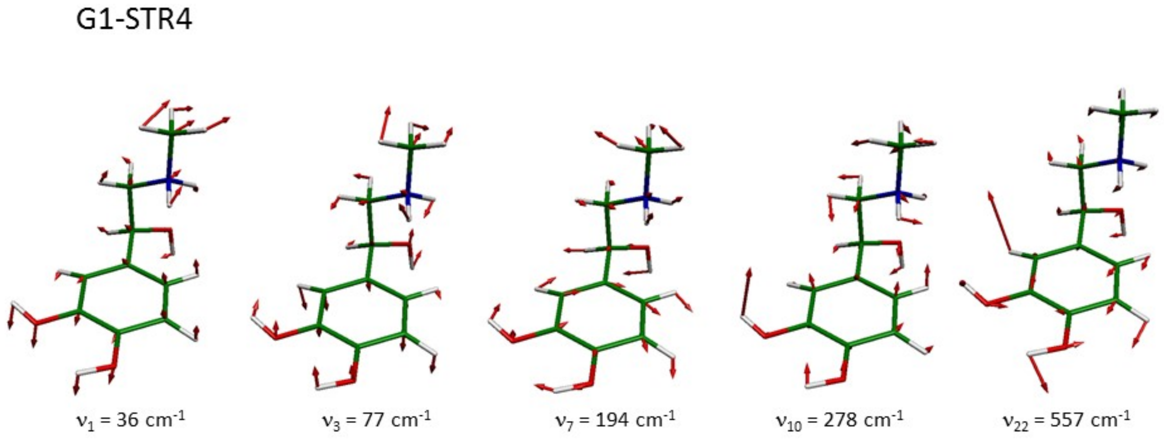

Fig. S6 Franck-Condon active modes in the vibronic spectrum of the AdH$^+$ G1-STR4 conformer.

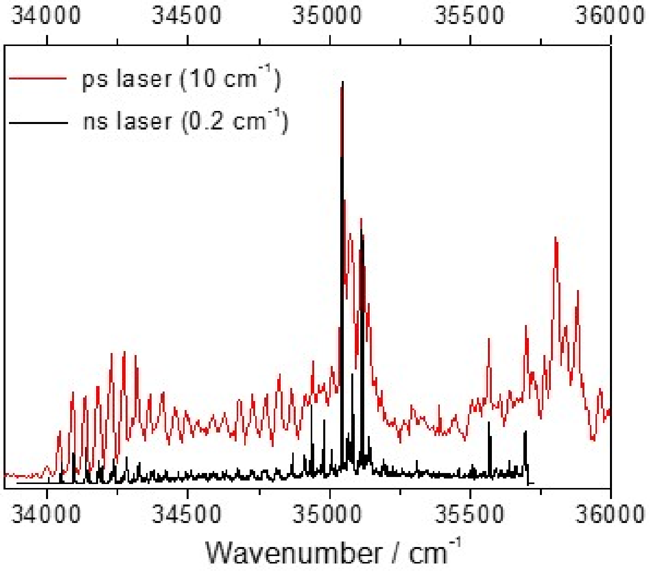

Fig. S7 UV photodissociation spectroscopy of AdH^+ recorded with the ns dye laser (0.2 cm^{-1} resolution) and the ps OPA laser (10 cm^{-1} resolution) recorded on the C_α-C_β bond break fragment.

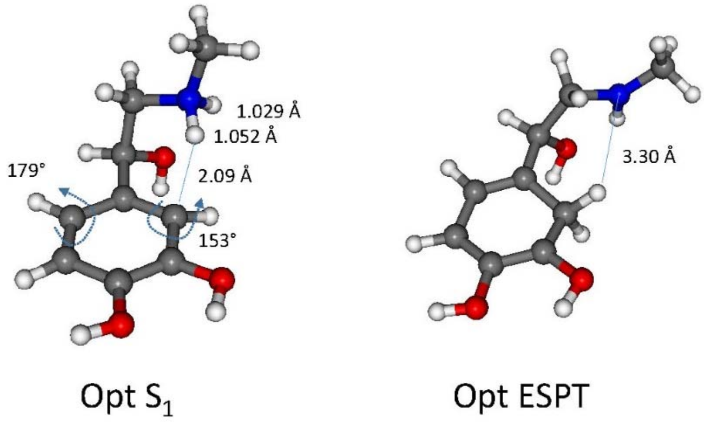

Fig. S8 Optimized structure of the $^1\pi\pi^*$ state and ESPT form of AdH^+ G1-STR1 conformer along with the most relevant bond distances and dihedral angles. In the S_1 structure, the lengthening of the N-H bond along with the slight ring puckering favor the ESPT reaction.