Electronic Supplementary Information

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

Jordan Dezalay,a Michel Broquier,a Satchin Soorkia,a Keisuke Hirata,b,c Shun-ichi Ishiuchi,b,c Masaaki Fujii*b,c,d and Gilles Grégoire*a,d

a Université Paris-Saclay, CNRS, Institut des Sciences Moléculaires d’Orsay, F-91405 Orsay, France. E-mail: gilles.gregoire@universite-paris-saclay.fr

b Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology, 4259, Nagatsuta-cho, Midori-ku, Yokohama, 226-8503, Japan. Email: mfujii@res.titech.ac.jp

c School of Life Science and Technology, Tokyo Institute of Technology. 4259 Nagatsuta-cho, Midori-ku, Yokohama, Kanagawa, 226-8503, Japan.

d Tokyo Tech World Research Hub Initiative (WRHI), Institute of Innovation Research, Tokyo Institute of Technology, 4259, Nagatsuta-cho, Midori-ku, Yokohama, 226-8503, Japan

*Corresponding authors: mfujii@res.titech.ac.jp; gilles.gregoire@universite-paris-saclay.fr

**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 Cα-Cβ 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 $v_{18}$ 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 Cα-Cβ bond break fragment.

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