

## Electronic Supplementary Information

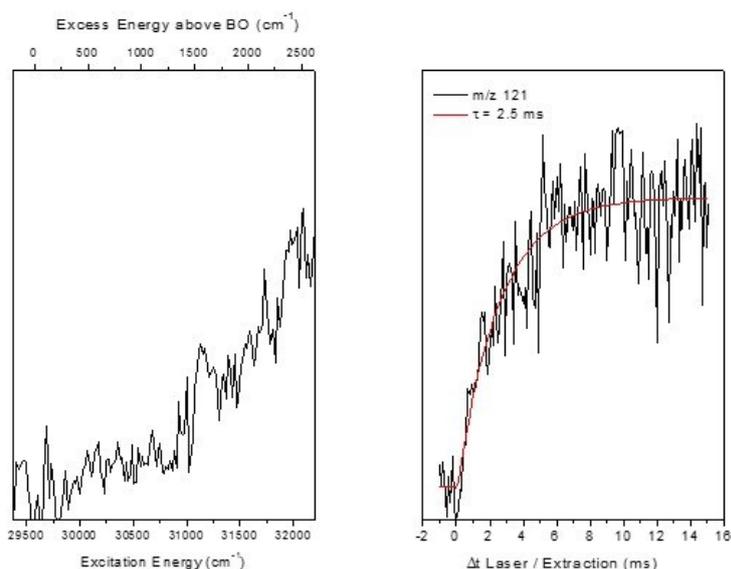
### Multiscale Excited State Lifetimes in Protonated Dimethylaminopyridines

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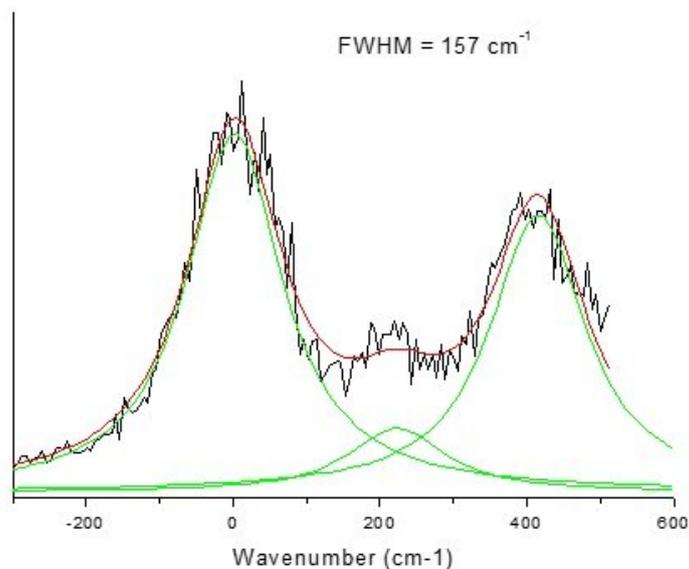
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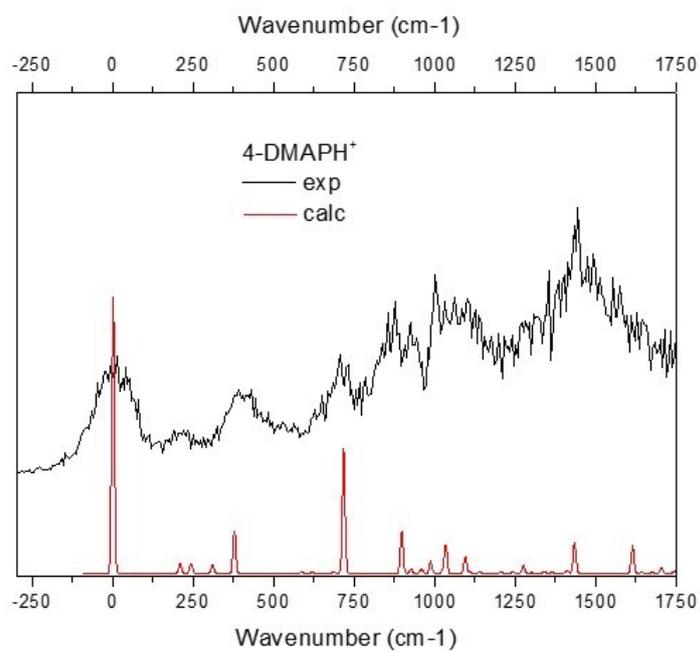
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**Fig. S11.** 1-color excitation spectrum of 2-DMAPH<sup>+</sup> recorded on the m/z 121 fragment. The onset of the fragmentation yield starts about 1500 cm<sup>-1</sup> above the band origin. (Right) Fragmentation kinetics for this fragment fitted with a time constant of  $2.5 \pm 0.2$  ms.



**Fig. SI2.** Low energy part of the electronic spectrum of 4-DMAPH<sup>+</sup> fitted with 3 Lorentzian peaks of same width (157 cm<sup>-1</sup>) centered at 0, 223 and 415 cm<sup>-1</sup>.



**Fig. SI3.** Comparison of the experimental and simulated Franck-Condon spectra of the  $\pi\pi^*$  ( $A_1$ ) excited state of 4-DMAPH<sup>+</sup>.