

## FEMTOSECOND TIMESCALE EVOLUTION OF PYRROLE ELECTRONIC EXCITATION

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Pyrrrole is a simple aromatic molecule with relevant chromophoric properties in biology. Although its apparent simplicity, it shows a complicated dynamics after excitation in the near part of the UV absorption spectrum, which results from the interplay between the bright  $\pi\pi^*$  and the dark dissociative  $\pi\sigma^*$  electronic transitions.<sup>a</sup> Herein, we present a time resolved study with ultrafast resolution on the relaxation dynamics of isolated pyrrole, after excitation in the 265-217 nm range. Two lifetimes of 19 and 15 fs, which are associated with the internal conversion from the bright  $^1B_2 \pi\pi^*$  state and the propagation of the wavepacket on the  $\pi\sigma^*$  state, respectively, are found in the studied energy interval. The work also explores the consequences of non resonant adiabatic excitation of the system when broadband femtosecond pulses are employed to prepare the molecule in the targeted electronic states, revealing the key implication of this type of coherent phenomena. The collected data reveal that the bright  $^1B_2 \pi\pi^*$  state is adiabatically populated at excitation wavelengths far away from resonance, providing an efficient way to reach the  $\pi\sigma^*$  state. The recorded transients are fit employing a coherent model that provides a comprehensive view of the dynamical processes pyrrole undergoes after excitation by ultrashort light pulses.

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<sup>a</sup>M. N. R. Ashfold, B. Cronin, A. L. Devine, R. N. Dixon and M. G. D. Nix *Science*, **312**, 1637-1640, 2006.