

# Ultrafast Relaxation in Isolated and Aqueous Nucleobases: Substituent and Solvent Effects

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## ABSTRACT

Nucleobases display remarkable photostability due to ultrafast internal conversion (IC) from the optically bright  $1\pi\pi^*$  excited state to the electronic ground state ( $S_0$ ), enabling rapid dissipation of excess electronic energy and limiting photochemical damage.<sup>1</sup> In pyrimidine nucleobases, an additional relaxation pathway involves an optically dark  $1n\pi^*$  state with a longer lifetime, which can mediate intersystem crossing to the triplet  $3\pi\pi^*$  state.<sup>1-5</sup> The quantum yield of the  $1n\pi^*$  state is therefore a key parameter for understanding nucleobase photolesion mechanisms.

Here, we performed ultrafast extreme ultraviolet time-resolved photoelectron spectroscopy (EUV-TRPES) measurements of 6-methyluracil (6mUra) and 5-fluorouracil (5FUra) in the gas phase, as well as 6mUra and 5-fluorouridine (5FUrd) in aqueous solution to investigate the substituent and solvent effects on the ultrafast relaxation dynamics. In the gas phase, IC from the  $1\pi\pi^*$  to the  $1n\pi^*$  state occurs within tens of femtoseconds, followed by ISC to the  $3\pi\pi^*$  state on a picosecond timescale. In contrast, in aqueous solution 6mUra relaxes almost exclusively to  $S_0$  within  $\sim 100$  fs, closely resembling the dynamics of unsubstituted uracil and proceeding significantly faster than in thymine (5-methyluracil).<sup>6</sup> The distinct relaxation dynamic for C5 and C6-substituted molecules indicates that IC from the  $1\pi\pi^*$  state to  $S_0$  is facilitated by out-of-plane motion of the C5 substituent.<sup>7</sup>

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