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Ultrafast photodynamics and detection of the elusive twist-wagged intramolecular charge transfer (TWICT) state of N^6,N^6-dimethyladenine (DMAde) by transient vibrational absorption spectroscopy

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The DNA nucleobase derivative N^6,N^6-dimethyladenine (DMAde) stands out for its dual fluorescence, i.e. it shows short-lived emission in the near-ultraviolet from a $^1\pi\pi^*$ local excited (LE) state and longer-lived emission in the visible spectrum from a supposed twisted intramolecular charge transfer (TICT) $^1\pi\pi^*$ state. Experimental studies using time-resolved fluorescence up-conversion spectroscopy (TFLS) and time-resolved electronic absorption spectroscopy (TEAS) on the molecules in acetonitrile (ACN) solution confirmed corresponding previous works. Much deeper insight into the molecular dynamics of electronically excited DMAde has now been gained by the application of transient vibrational absorption spectroscopy (TVAS) as state- and structure-sensitive method, and interpreted by the aid of quantum chemical calculations. Vibrational marker bands have been observed in the fingerprint region of the IR spectrum that showcase the evolution of the excited state population from the initially accessed Franck–Condon region (FC) via the LE state with a lifetime of τ_1 ~ 0.3 ps to subsequent (partially) twisted (pTICT) and twist-wagged (TWIST) conformations. En route, a number of vibrational bands show characteristic broadenings and wavenumber shifts indicating an extended, shallow and nearly barrierless region on the potential energy hypersurface (PEHS) during these transformations, which appear to take up to ~ 20 ps (τ_3). The excited distorted molecules can return to their ground state (GS) in τ_2 ~ 1.2 to 2.0 ps, or they can undergo an intersystem crossing (ISC) transition from the TWICT state to a much longer-lived (τ_4 ~ 1.0 –1.1 ns) state of $^3\pi\pi^*$ character. These data give first direct spectroscopic evidence for the elusive TICT/TWICT structures of DMAde and for the importance of a triplet state in the dynamics.

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