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Microsolvation Effects on the Excited-State Dynamics of Protonated Tryptophan MATTEO GUGLIELMI, SEBASTIEN MERCIER, OLEG BOYARKIN, ANTHI KAMARIOTIS, IVANO TAVERNELLI, MICHELE CASCELLA, URSULA ROETHLISBERGER, THOMAS RIZZO, LCPC COLLABORATION — To better understand the complex photophysics of the amino acid tryptophan, which is widely used as a probe of protein structure and dynamics, we have measured electronic spectra of protonated, gas-phase tryptophan solvated with a controlled number of water molecules and cooled to $\sim$10 K. We observe that, even at this temperature, the bare molecule exhibits a broad electronic spectrum, implying ultrafast, nonradiative decay of the excited state. Surprisingly, the addition of two water molecules sufficiently lengthens the excited-state lifetime that we obtain a fully vibrationally resolved electronic spectrum. Quantum chemical calculations at the RI-CC2/aug-cc-pVDZ level, together with TDDFT/pw based first-principles MD simulations of the excited-state dynamics, clearly demonstrate how interactions with water destabilize the photodissociative states and increase the excited-state lifetime.

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