THE EFFECT OF VIBRATIONAL ENERGY ON THE ISOMERIZATION REACTION OF TRANS-STILBENE IN THE CONDENSED PHASE

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We study the effect of vibrational energy on the isomerization reaction of *trans*-stilbene in deuterated chloroform. We first excite a ground-state C-H stretch overtone or a stretch-bend combination and allow vibrational relaxation to occur within the molecule before photoinitiating the excited-state isomerization with an ultraviolet photon. Once the stilbene molecule is on the excited state, we monitor the isomerization dynamics via broadband transient absorption spectroscopy. We measure an excited-state lifetime of 55 ± 9 ps when exciting through the C-H stretch overtone and a lifetime of 56 ± 7 ps for excitation through the stretch-bend combination. The *trans*-stilbene excited-state lifetime after single photon vertical excitation is 52 ± 6 ps with the total added energy being the same for all measurements. Unlike in gas phase studies, where vibrational motion can change the outcome of a chemical reaction, there is no observed difference in the reaction dynamics when exciting this condensed phase system with a single photon versus exciting through a ground-state vibrational mode. Interactions with the solvent cause fast vibrational relaxation on the excited state, though the insensitivity of the rate to vibrational energy may also be due to excess vibrational energy not being promptly partitioned into modes along the isomerization coordinate.