ULTRAFAST PHOTOCHEMISTRY OF BROMOFORM IN SOLUTION PROBED IN THE DEEP-UV- TO NEAR-IR SPECTRAL RANGE

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The photochemical pathways of bromoform ($CHBr_3$) in dilute (10 mM) and concentrated (500 mM) acetonitrile and methylcyclohexane solutions following excitation with ultrafast (100 fs) 255-nm laser pulses were investigated. Ultrafast transient absorption spectra manifest the formation of a $CHBr_2$ radical species within the apparatus response function through its intense deep-UV ($\sim$ 250-nm) absorption band. The formation of *iso*-bromoform (*iso*-$CHBr_2$-Br) occurs within few hundreds of femtoseconds after photoexcitation and do not correlate with the dynamics of $CHBr_2$ radical. The *iso*- $CHBr_2$-Br isomer species decays single exponentially with a 290-ps time constant in acetonitrile. In methylcyclohexane, however, the intense absorption of the isomer in the visible spectral range dominates the transient spectra up to the longest investigated time delays of 1.2 ns. *Ab initio* and DFT calculations in conjunction with continuum solvation models strongly suggest that acetonitrile opens a pathway for the *iso*-$CHBr_2$-Br to $CHBr_3$ isomerization through a polar, cyclic transition state. This channel is not thermodynamically feasible in the non-polar solvent.