ULTRAFAST DYNAMICS IN RYDBERG STATES OF ALIPHATIC AMINES

J.L. GOSSELIN, M.P. MINITTI and P.M. WEBER, *Department of Chemistry, Brown University, Providence, R.I. 02912*; T.I. SOLLING, *Department of Chemistry, University of Copenhagen, DK-2100, Copenhagen, Denmark.*

We investigated the ultrafast dynamics associated with low-n Rydberg states of aliphatic amines seeded in a molecular beam. Time-resolved mass spectra, obtained by [1+1'] multiphoton ionization, show that the α bonds cleave when the internal energy is large. Time-resolved photoelectron spectra reveal the detailed mechanism for distribution of the excitation energy. The 209 nm photons initially populate the $3p$ level, which rapidly decays into a bath of vibrationally excited states of $3s$. As a result of this process, a large amount of energy is inserted into vibrational coordinates, opening the path to cleavage of the α bond.