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-\(\nu\) Rydberg states of aliphatic amines seeded in a molecular beam. Time-resolved mass spectra, obtained by [1+1"] multiphoton ionization, show that the \(\alpha\) 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 3\(p\) level, which rapidly decays into a bath of vibrationally excited states of 3\(g\). As a result of this process, a large amount of energy is inserted into vibrational coordinates, opening the path to cleavage of the \(\alpha\) bond.