STRUCTURAL MOTIONS AND CHARGE DELOCALIZATION IN ELECTRONICALLY EXCITED N, N'-DIMETHYLPIPERAZINE

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Time-resolved pump-probe photoelectron spectroscopy was used to study the structural motions associated with a partial charge transfer from one nitrogen atom to the other in electronically excited N, N'-Dimethylpiperazine (DMP). Excitation with a 207 nm pump photon prepares the molecule in the 3p Rydberg state with a localized charge. Internal conversion from 3p to two 3s states, with 230 fs and 480 fs time constants, forms the molecule in a multitude of conformeric structures that retain the charge localized on one nitrogen atom and a rigid conformeric structure that has the charge delocalized over the two nitrogen atoms. The localized and delocalized 3s states can transform into each other and reach an equilibrium within picoseconds. The time-dependent photoelectron spectra show that the charge delocalization and its reverse reaction, i.e. charge re-localization, have time constants of 3.4 ps and 12.0 ps, respectively. The time constants were found to depend on the excitation energy.