ULTRAFAST STRUCTURAL DYNAMICS OF TERTIARY AMINES UPON ELECTRONIC EXCITATION

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The structural response of several tertiary amines to electronic excitation has been investigated using Rydberg Fingerprint Spectroscopy. The 3p Rydberg states are reached by excitation with a 5.93 eV photon while 3s states are populated by electronic relaxation from 3p state. We observe binding energy shifts on ultrafast time scales in all peaks that reflect the structural change of the molecular ion cores. The shifts are in the range of 15 meV to 30 meV, within time scales of less than 500 fs, depending on the specific molecular systems and the nature of the electronic state. In cases where the p states are spectrally separate, the trends of the energy shifts are different for the p_z and p_{xy} Rydberg states whereas the p_z and s states are similar. This suggests that the response of the Rydberg states to structural displacements depends on the symmetry. Very fast binding energy shifts, observed on sub-picosecond time scales, are attributed to the structural adjustment from a pyramidal to a planar structure upon Rydberg excitation. The quantitative values of the binding energy shifts can also be affected by laser chirp, which we model using simulations.