Collision- and photon-induced dynamics of complex molecular ions in the gas phase

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Abstract

In this thesis, I report experiments probing collision- and photon-induced molecular dynamics in the gas phase. Excited molecules formed in such interactions may relax by emitting electrons or photons, isomerization or fragmentation. For complex molecular systems, these processes typically occur on timescales exceeding picoseconds following statistical redistribution of the excitation energy across the internal degrees of freedom. However, energy transfer to molecules through ion/atom impact may in some cases lead to prompt atom knockout in Rutherford-type scattering processes on much faster timescales. Another example of such a non-statistical process is photon-induced excited-state proton transfer, a structural rearrangement occurring on the femtosecond timescale.

In this work, I investigate the competition between statistical and non-statistical fragmentation processes for a range of molecules colliding with He at center-of-mass energies in the sub-keV range. I show that heavy atom knockout is an important process for systems containing aromatic rings such as Polycyclic Aromatic Hydrocarbons (PAHs) or porphyrins, while statistical fragmentation processes dominate for less stable and/or smaller systems such as adenine or hydrogenated PAHs. Furthermore, I present the first measurements of the threshold energies for prompt single atom knockout from isolated molecules. The experimental results are interpreted with the aid of Molecular Dynamics (MD) simulations which allow us to extract the energy deposited into the system during a collision, knockout cross sections, fragmentation pathways and the structures of the fragments. The results presented in this work may be important for understanding the response of complex molecules to energetic processes in e.g. astrophysical environments.

Furthermore, I present the results of photodissociation and luminescence experiments probing flavin mono-anions in the gas phase. These are compared against calculations and previously measured spectra in solution. The discrepancies between the present results and the theoretical values suggest that more consideration of the vibronic structure is needed to model the photoabsorption and emission in flavins. Finally, I present the results of photoisomerisation experiments of flavin di-anions where two different isomers have been found and I discuss the proton transfer mechanisms which govern the structural changes.

Keywords: *PAHs, Porphyrins, Adenine, Flavins, Biomolecules, Collisions, Experiments, Reactions, Non-Statistical Fragmentation, Molecular Dynamics, Photon-Induced Fragmentation, Luminescence, Photoisomerization, Proton Transfer.*

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