

Intermolecular Decay and Ultrafast Energy Transfer in Clusters and Weakly Bound Systems

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Recent theoretical investigations accompanied by large-scale ab initio computations [1-5] were devoted to the question how molecular clusters relax that have been excited by inner-valence ionization. For water clusters, for instance, electron emission dominates the overall relaxation behavior, taking place on the femtosecond time scale. The occurrence of this newly discovered process in such a relatively low-excitation regime may be surprising, particularly in view of the fact that isolated, inner-valence excited cations, for instance H_2O^+ , can dissipate their excess energy only by vibrational motion and photon emission. Hence, the nature of the electronic decay process taking place in cationic clusters is intermolecular.

The following, simplified picture has emerged. Ionization out of an inner-valence orbital leads to the formation of a hole which is localized at one of the monomers constituting the cluster. An outer-valence electron at this cationic monomer can drop into the inner-valence vacancy. Due to an extremely efficient Coulomb mechanism, which will be discussed in the presentation, the released energy is transferred to neighboring monomers. In this way, an outer-valence electron is ejected in the molecular environment of the initial cation. The resulting final states are characterized by two positive charges distributed over two or more monomers. Thus, Coulomb repulsion of the two holes is reduced, which explains the energetic accessibility of electronic decay channels. We would like to emphasize that for the systems we studied, inner-valence excited cation monomers without a cluster environment are electronically stable. Particularly interesting nuclear dynamics arise as a consequence of the weak chemical bond in the clusters considered here and the Coulomb repulsion pattern originating from electron emission.

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