Recent theoretical investigations accompanied by large-scale \textit{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$_2$O$^+$ 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 for the process which we call ICD. 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 Coulombic mechanism, which will be discussed in the presentation, the released energy is transferred to neighbouring 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 energetical accessibility of electronic decay channels. We would like to emphasize that for the systems we studied, inner-valence excited cationic monomers without a
cluster environment are electronically stable. The ICD has been recently confirmed by beautiful experiments [6-9]. The underlying process is of a very general nature and its implications reach far beyond clusters and single ionization [10-11].

References

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gez. Prof. Dr. Thomas Koop, Prof. Dr. Uwe Manthe, Prof. Dr. Jochen Mattay