Solvent effects on electron- and photon-triggered reactions in clusters

M Fárník¹, J Fedor¹, J Kočišek¹, A Pysanenko¹ and J Lengyel²

¹J. Heyrovský Institute of Physical Chemistry, CAS, Dolejškova 3, 18223 Prague 8, Czech Republic

²Lehrstuhl für Physikalische Chemie, Fakultät für Chemie und Zentralinstitut für Katalyseforschung, Technische Universität München; Lichtenbergstraße 4, 85748 Garching, Germany

Here we focus on interactions of fast and slow electrons, and UV and IR photons with molecules in clusters. Fast electrons (10–100 eV) cause positive ionization, while slow electrons with energies below 10 eV produce negative ions via dissociative electron attachment (DEA) [1]. Interactions with UV photons leads to photodissociation, or photoionization via multiphoton processes. Adding an IR vibrational excitation yields vibrationally mediated predissociation. These – and some other – processes can be investigated with our versatile CLUster Beam apparatus (CLUB) in Prague encompassing velocity map imaging and several mass spectrometric techniques [2-4].

The above processes change significantly when molecules are surrounded by an environment. To investigate the influence of solvent, we study these processes in clusters complex enough to reveal the solvent effects, yet simple enough to allow a detailed molecular level insight. In addition, controlling the cluster size allows us to investigate the evolution of the processes in systems of increasing complexity. The unique advantage of the CLUB apparatus is that different experiments are performed with one cluster beam allowing a direct comparison and complementarity of the results.

We demonstrate the above experimental approach on several examples, e.g. mixed nitric acid—water clusters. These clusters can be used in laboratory studies to mimic polar stratospheric cloud particles which play a key role in atmospheric chemistry, e.g. in ozone depletion. We have studied $(HNO_3)_m \cdot (H_2O)_n$ clusters by mass spectrometry with electron ionization. A special method of doping the clusters with Na atoms revealed a solvated electron reactivity in them [5]. Attachment of free electrons to these clusters points to DEA and subsequent negative ion-molecule reactions in them [6,7]. In addition, photodissociation and photoionization experiments are currently under way to investigate their excited state dynamics. Thus we present a complex picture of a nitric acid molecule undergoing different processes triggered by electrons and photons in water environment.

- [1] Fabrikant I et al 2017 Advances in Atomic, Molecular, and Optical Physics 66 545
- [2] Svrčková et al 2015 Phys. Chem. Chem. Phys. 17 25734
- [3] Grygoryeva K et al 2018 J. Chem. Phys. 149 094303
- [4] Fárník M and Lengyel J 2018 Mass Spec. Rev. 37 630
- [5] Lengyel J et al 2012 J. Phys. Chem. Lett. 3 3096
- [6] Lengyel J et al 2017 Phys. Chem. Chem. Phys. 19 11753
- [7] Lengyel J, Fedor J and Fárník M 2019 Phys. Chem. Chem. Phys., submitted