Probing the electronic structure of the hydration shell of cations through non-local decay pathways

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Inner-shell photoionization and photoexcitation, and the ensuing decay processes, form the basis of many spectroscopic techniques. Understanding these phenomena is also of primary importance to understand the interaction of matter with ionizing radiation. In the condensed phase (e.g. in aqueous media, of prime importance in biological contexts, for instance), in addition to the well-known decay pathways observed in the gas phase (Auger decay and fluorescence, mainly), new ones open[1]. These so-called non-local decay processes involve neighbouring species (e.g. the solvation shell in liquids). Typically, in Intermolecular Coulombic Decay (ICD), the neighbouring species is ionized by energy transfer from the primarily ionized species in the course of its electronic relaxation, making it a two-center analog to Auger decay.

These processes have been extensively studied for model cluster systems. It is however also possible to investigate this kind of process directly in liquids, in large part thanks to the liquid microjet photoemission spectroscopy technique. Pioneering[2,3] and more recent[4] experiments in liquids have been dedicated to ”core” ICD, i.e. ICD from deep inner/core shells, which is in competition with Auger decay. Here we present results on the resonant ICD process in solvated cations ($K^{+,}$ Ca^{2+}, Sc^{3+}). We show how this process can inform on the solvation shell of these cations[5], and in particular how it is possible to access the electronic structure of specifically the water molecules in the hydration shell, which shows differences with the average electronic structure of the bulk solution.

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