

First Observation of Electron Transfer Mediated Decay (ETMD) in Aqueous Solutions - A Novel Probe of Ion Pairing

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Electronic (non-radiative) relaxation processes following photoionization, most prominently Auger-electron decay, have been widely used to probe chemical composition, electronic structure, and correlation in the valence-electron region. For several years experimental and theoretical works have demonstrated that also non-local electronic relaxation processes occur, and efficiently compete with the local Auger decay. Utilizing non-local processes as a spectroscopic tool promises to provide additional important insight on the local chemical environment, since nearby atomic / molecular units are actively involved in the decay through electron and energy transfers.

In the present study we address a largely unexplored non-local electronic relaxation process involving up to three units, Electron transfer mediated decay (ETMD)[1]. Here, the first step is the refilling of a created vacancy by an electron from a *neighboring* atomic or molecular monomer. The subsequent energy released is used to ionize either the same electron-donating monomer (ETMD(2) process) or yet a third monomer in the vicinity (ETMD(3) process). This is illustrated in Figure 1. ETMD is a sensitive probe of the environment due to its active involvement through electron and energy transfer steps. ETMD has been predicted theoretically to occur in various environments, and is regarded as a rather general phenomenon. So far, valence-ionized rare-gas clusters were the only systems where ETMD was observed experimentally [2]. In the current study, we report the first experimental observation of ETMD in the liquid phase. Furthermore, this marks the first unequivocal observation of ETMD following core ionization based on experiment.

We chose LiCl aqueous solution because the ionized Li²⁺ (aq) cannot provide an electron to refill the 1s core hole, and ETMD is the only possible (non-radiative) decay. Photoelectron (PE) spectroscopic experiments were conducted at the U41-PGM beamline of BESSY II. PE spectra from 3 and 4.5 M LiCl aq. solution were measured from a 15- μ m liquid-jet. Solutions were prepared by dissolving commercial LiCl salt in de-ionized water. A further description can be found in [3].

The experimental results are interpreted with the help of classical molecular dynamics and high-level ab initio calculations. We simulated ETMD spectra for three cluster models, representative of the different ion pairing situations occurring in aqueous solutions: contact (CP), solvent-shared (SShP) and solvent-separated (SSP) ion

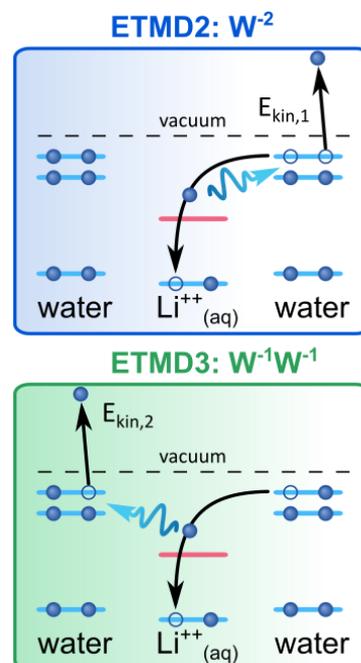


Fig.1: Sketch of ETMD(2) and ETMD(3) processes occurring in LiCl aq. solution. Starting point is the 1s core-level ionization of Li+(aq) forming Li²⁺(aq).

pairs. By considering various solvation structures we show that both water molecules and Cl anions can participate in ETMD, with each process having its characteristic spectral fingerprint. For comparison with experiment, each spectral line has been Gaussian-broadened.

The ETMD spectrum from 3 LiCl aq. solution, which is a result of subtracting a neat water spectrum, is shown in Figure 2. The spectra are photon-energy independent which shows that the signal indeed arises from electronic decay. Only a very small concentration dependence of the spectra between 3-4.5 M was found, which leads us to conclude that the hydration structure and ion pairing are similar in this range. We observe a broad structure in the 20-40 eV energy range, with a dominant peak at 31.5 eV. This peak is attributed to the ETMD(3)W,W processes producing two outer-valence ionized water molecules H_2O^+ . Analysis of the radial distribution function for $\text{Li}^+\text{-Cl}^-$ and $\text{Li}^+\text{-O}$ reveals that a solvent-shared arrangement prevails in the concentration range studied here. Thus, the calculated data of the SShP model is expected to fit best to the experimental spectrum, which is indeed the case.

Decomposition of different spectral contributions reveals that only a small fraction of the created water cations is found to be in the cationic ground state (1b1 electron removed). According to our calculations, the main peak mostly comprises the ETMD(3)3a1,3a1 states where two 3a1 vacancies on two different water molecules are produced. The high probability of the 3a1 electrons to participate in ETMD results from favorable orientations of the water monomers in the first solvation shell of Li^+ . Their oxygen atoms point toward the cation which maximizes the overlap of the 3a1 orbitals with the 1s orbital of Li^+ . ETMD(2)W processes mainly contribute to the 20-25 eV region, also mostly involving water 3a1 electrons. The difference in intensity for these two channels arises because the total ETMD(2)W efficiency is approximately proportional to the number of water monomers in the first solvation shell, whereas the total ETMD(3)W,W efficiency correlates with a much larger number of water pairs.

Our theoretical computations have reveal that ETMD spectra are sensitive to the structure of the first solvation shell around the initially ionized lithium ion, reflecting orientations of solvent water molecules, ion-water distances, and ion pairing. Different features are clearly visible in the theoretical ETMD spectra obtained for different cluster models which are representative of the distinctive ion pairing situations. This study on $\text{Li}^+(\text{aq})$ is a first step into a new research field, and the unequivocal demonstration of ETMD in more complex systems is experimentally challenging. Further experiments and theoretical calculations are needed to firmly establish ETMD spectroscopy.

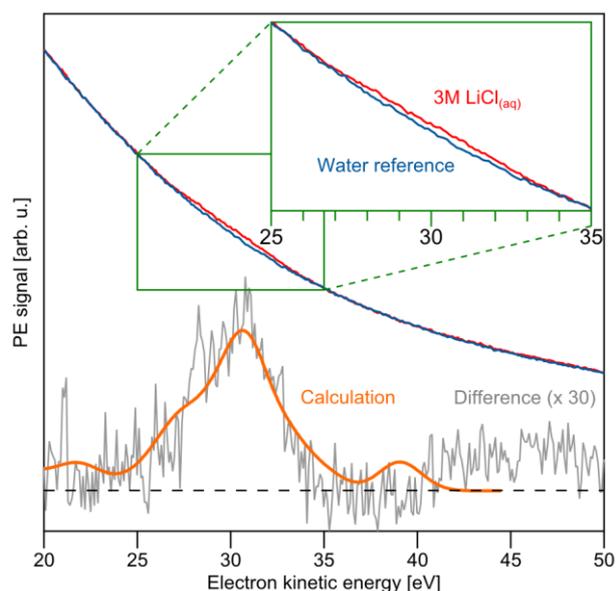


Fig.2: Experimental ETMD spectrum of 3.0M LiCl aq. solution (in red). The reference spectrum of neat water (in blue) is subtracted, yielding the difference spectrum (pure ETMD contribution) in grey. The calculated spectrum of the SShP cluster model is overlaid in orange.