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Sensitivity of Electron Transfer Mediated Decay to Ion Pairing

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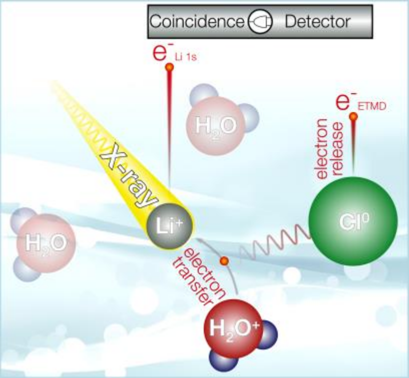
ABSTRACT

Ion pairing in electrolyte solutions remains a topic of discussion despite a long history of research. Very recently, nearest-neighbor mediated electronic deexcitation processes of core hole vacancies (Electron Transfer Mediated Decay, ETMD) were proposed to carry a spectral fingerprint of local solvation structure and in particular of contact ion pairs. Here, for the first time, we apply electron–electron coincidence detection to a liquid microjet, and record ETMD spectra of Li 1s vacancies in aqueous solutions of lithium chloride (LiCl) in direct comparison to lithium acetate (LiOAc). A change in the ETMD spectrum dependent on the electrolyte anion identity is observed for 4.5 M salt concentration. We discuss these findings within the framework of the formation and presence of contact ion pairs and the unique sensitivity of ETMD spectroscopy to ion pairing.

TOC GRAPHICS



KEYWORDS

Contact ion pairs, charge transfer, core-level ionization, lithium chloride, lithium acetate, aqueous solution, autoionization, ETMD, liquid microjet

The formation of temporarily stable complexes of two oppositely charged ions, ‘ion pairs’, in electrolyte solution has been known for a long time.[1–3] Conductivity measurements as well as various spectroscopic methods have been used to detect ion pairs, yet in particular for aqueous solutions unsolved questions remain. Adding to these, in the last decade structural differences of the surface of an ionic solution compared to its bulk have been intensively discussed.[4–6] A suggestion of an unconventional spectroscopic technique that might allow to take a fresh look on ion pairing has been made very recently: using electron spectroscopy from a liquid microjet, the observation of certain types of autoionization decays, such as ‘Electron Transfer Mediated Decay’ (ETMD), was predicted to deliver a spectroscopic fingerprint of the presence of ion pairs.[7]

In this letter, we report ETMD spectra for aqueous solutions of two different Li salts at various concentrations, and discuss their potential on elucidating the local solvation structure of the Li^+ ions in the system. Experimentally, we have recorded these spectra with an electron–electron coincidence technique, which is applied to a liquid microjet for the first time, and allows to record ETMD spectra at much improved signal-to-noise ratio compared to conventional electron spectroscopy. Furthermore, the coincidence technique can shed more light into mechanistic details due to its ability to unequivocally identify the physical origin of the detected electrons, whether they are created by autoionization processes like ETMD or by inelastic electron scattering.[8]

Electron spectroscopy in its arguably most common form detects core-level photoelectrons ejected upon ionization by soft X-rays. But also the subsequent electronic non-radiative relaxation processes are of great importance for revealing information on the electronic structure. In light elements, a core hole is typically refilled by a valence-shell electron within femtoseconds, with another electron being emitted into the continuum (Auger decay).[9] Auger decay involves only the atom which has been initially ionized, although interatomic Auger-like processes have been considered relatively early, e.g. in ionic crystals.[10] In weakly bonded systems, like hydrogen-bond coordinated liquids, other non-radiative decay processes are also possible, and involve atoms or molecules surrounding the site that was originally ionized. These mechanisms, now known as ETMD and Intermolecular Coulombic Decay (ICD), were first predicted by Cederbaum *et al.*,[11,12] and have been broadly investigated in recent years.[13–16]

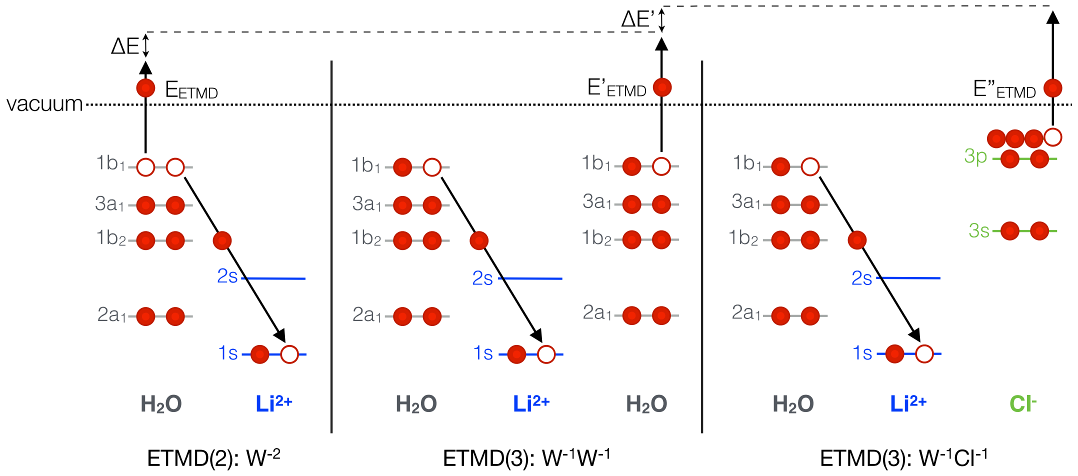


Figure 1: Electron Transfer Mediated Decay of a Li^{2+} (aq) ion after creation of a Li 1s core hole by photoionization. Depending on the final state, different types of ETMD processes may take place. ETMD(2):W^{-2}, ETMD(3):$\mathrm{W}^{-1}\mathrm{W}^{-1}$ and ETMD(3):$\mathrm{W}^{-1}\mathrm{Cl}^{-1}$. W and Cl refer to the species ionized in the final state (water molecules and a chloride anion), and the numerals (2) and (3) refer to the numbers of monomers involved in the ETMD processes, including the initially core-ionized Li^{+}. Superscripts describe the final charge state of the respective molecule (e.g. W^{-1} indicates a singly ionized water monomer). The starting point in each case is the 1s core-level ionization of Li^{+} (aq), forming Li^{2+} (aq). *E*ETMD denotes the kinetic energies of electrons emitted in the ETMD processes. These are measured in the experiment.

ETMD is initiated by core or inner-valence ionization or excitation. The initially created vacancy is refilled by an electron that is transferred from a neighboring molecule. The excess energy is then used to release another electron into the continuum (the 'ETMD electron'), from either the electron-donor molecule itself or from a third, so far uninvolved molecule in the close proximity; see Figure 1. These two variants of the process are termed ETMD(2) and ETMD(3), respectively, referring to the number of molecules involved.[17] Both processes have been experimentally demonstrated in rare gas clusters.[18–20] ICD, in contrast to ETMD, involves a local relaxation and a subsequent transfer of energy to a neighboring molecule from which a secondary electron ('ICD electron') is ejected.

Theoretical work showed that ICD and ETMD are important relaxation channels also in liquids.[16] When sufficient excitation energy is deposited into a solvated metal atom in a liquid, Auger decay, ICD and ETMD may combine into complex relaxation cascades, as recently delineated in extensive simulations.[21] Experimental evidence for ICD in aqueous solutions has also been found, mostly in competition with normal Auger decay.[22–24]

An important motivation for the study of these various non-local relaxation processes in liquids is their potential sensitivity to solvent structure; weak effects have indeed been found for both Auger decay and ICD.[25,26] ETMD is a short-range effect, i.e. *both* electrons involved in the relaxation process reside within the first solvation shell of the atom that was initially ionized. Therefore, it is plausible to expect a stronger influence of the solvation shell in the ETMD channel as compared to the other two processes. A prototypical system to investigate this assertion is the solvated lithium cation. The ground-state electronic configuration of lithium in aqueous solution is Li^+ $1s^2 2s^0$, and hence non-radiative relaxation of a Li 1s vacancy *inevitably* involves an electron transfer. Calculations of the Li 1s ETMD spectrum of microhydrated Li^+, which is expected to exhibit intensity between 25 and 40 eV kinetic energy (KE),[27] have been published very recently, and show that the energies of the ETMD spectrum sensitively depend on the composition of the hydration shell.[7,28] In particular, configurations differing with respect to the type of ion pairing had been considered: contact (CP), solvent shared (SShP), and solvent separated (SSP) ion pairs. As can be surmised from Figure 1, final states involving W^{-2}, $W^{-1}W^{-1}$ and $W^{-1}Cl^{-1}$ configurations each contribute at a characteristic kinetic energy (given by the energy difference between the Li^{2+} state and the two-hole final state) to the ETMD spectrum. Decay into the $W^{-1}Cl^{-1}$ channel will, however, only contribute for sufficiently small distances between Li^{+} and Cl^{-} ions, which is the case for CPs. The intensity of ETMD electron signal at kinetic energies associated with $W^{-1}Cl^{-1}$ final states is therefore considered a straight indicator for the presence of CPs. Note that the timescale of ETMD is short (~fs) compared to the minimum lifetime of an ion pair in solution (~ns).[1,20]

Unger *et al.*[7] have presented experimental evidence for the occurrence of ETMD in a LiCl solution at photon energies sufficient for core-level ionization of the Li^{+} (aq). In their experiment, a conventional hemispherical electron analyzer (HEA) was used to record autoionization electrons emitted after irradiating a liquid microjet of a LiCl aqueous solution by synchrotron radiation. An excess of autoionization electrons in the KE interval expected for ETMD was observed after subtracting a neat water spectrum recorded under identical conditions. Although clearly detectable, the ETMD spectrum however suffered from a poor signal-to-noise ratio.

In order to directly relate the production of Li 1s vacancies in aqueous solution to their decay by ETMD, we employ here a different, more direct detection technique. Using a magnetic bottle time-of-flight (TOF) spectrometer for electron spectroscopy with a large acceptance angle, we have detected Li 1s photoelectrons and the pertaining ETMD electrons from solvated LiCl in coincidence. This allowed us to unequivocally assign the ETMD electron spectrum resulting from Li 1s ionization, and to achieve better signal statistics due to the higher detection efficiency of the spectrometer, with significantly less contribution of background electrons. Motivated by the improved ETMD signal quality, we also explored here the actual sensitivity of ETMD to ion pairing, pursuing two strategies. First, for investigating the effect of different counter ions we performed back-to-back measurements from LiCl and lithium acetate aqueous solution (CH_3COOLi, short: LiOAc). Previous X-ray absorption measurements in combination with *ab initio* and molecular dynamics calculations of LiOAc (aq) showed a strong tendency for close contact ion pairs.[29] This originates from the bidentate ion interaction geometry and the high electronegativity of the acetate group. For LiCl, the contact ion pair has a monodentate geometry and a lower electronegativity of the anion. Secondly, for LiCl we studied different concentrations from 4.5 to 8 molar (M). The expectation is that more CPs form with increasing salt concentration, which should be reflected in the spectra.

The ETMD electron spectra from a LiCl solution were extracted from the electron–electron coincidence signals obtained for 110 eV and 135 eV incident photon energy, provided by the UE56/2-PGM1 beamline at the synchrotron radiation facility BESSY II at the Helmholtz-Zentrum Berlin (HZB). Details of this procedure are described in the Supporting Information (SI). We do not observe any changes dependent on photon energy (as expected for an autoionization process), and therefore present only the spectra measured at 110 eV. Spectra measured at 135 eV can be found in the SI. Figure 2A shows aqueous LiCl (black) and LiOAc (red) ETMD data measured for 4.5 M salt concentration, as well as the data previously measured for LiCl (aq) by Unger *et al.* (dashed line).[7] This comparison unequivocally confirms that the feature measured earlier arises from Li 1s ETMD. Qualitatively, no differences between the two spectra can be seen, but the level of noise in the earlier data had prevented the authors from drawing further conclusions.

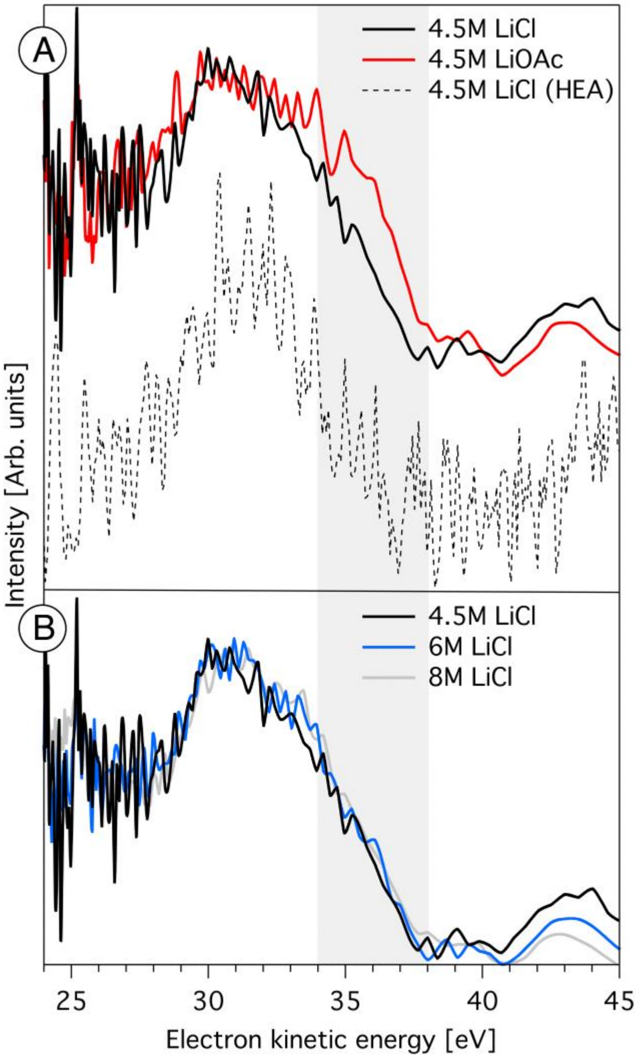


Figure 2: A) ETMD electron spectra after Li 1s photoionization of 4.5 M aqueous LiCl (black) compared with 4.5 M aqueous LiOAc (red), measured by an electron–electron coincidence method at 110 eV photon energy. The bottom spectrum (black dashed) represents data for 4.5 M LiCl (aq) measured with an HEA at 175 eV photon energy, reprinted from Ref. [7]. B) ETMD spectra for LiCl aqueous solutions of 4.5 M (black), 6 M (blue); and 8 M (gray) salt concentration. The transparent gray rectangle indicates the energy region between 34 eV and

38 eV, in which an enhanced ETMD signal is theoretically predicted for strong ion pairing.[7] Kinetic energies from this work are subject to a systematic uncertainty of ±0.25 eV.

In all electron spectra measured in the present work, a peak is visible between 41 and 45 eV KE. This peak is not of importance for our discussion of ETMD; it arises from electron pairs produced by ionization of the water vapor surrounding the liquid jet by electron impact of water valence photoelectrons, as detailed in the SI.

Assuming that for both 4.5 M solutions, LiCl and LiOAc, the lithium ions are well separated from their counter anions (solvent separated), no spectral differences were expected between the two salt solutions since in both cases ETMD would likely occur with the water molecules in the Li^{2+} hydration shell. However, there is a distinct spectral difference between LiCl and LiOAc in the 34 eV to 38 eV KE range (see gray bar in Figure 2A). The spectrum of lithium acetate exhibits a pronounced shoulder, showing considerably higher intensity than LiCl. We refer to Figure 1 for the interpretation of this finding. The high-kinetic energy shoulder in the ETMD spectrum pertains to the states with lowest final state energy which are of $W^{-1}Cl^{-1}$ type (right-most panel). Similar to chloride, also acetate has occupied valence orbitals with lower binding energies than the highest occupied molecular orbital of water.

We now elaborate in some more detail on the ETMD spectral positions. We can approximate the KE of an ETMD if we assume that the repulsion energy between the two final state holes is compensated by solvent induced stabilization of the positively charged final state. The respective KEs can then be estimated from the single hole energies as

$$E_{\mathrm{ETMD}} \doteq E_{\mathrm{Core}} - E_1 - E_2. \quad (1)$$

Here, E_{Core} is the binding energy of Li 1s, which is 60.4 eV; E_1 and E_2 are the vertical ionization energies of the transferred and the outgoing ETMD electron. In Ref. [7] it was shown that the water $3a_1$ channel has the largest contribution to the ETMD signal. We therefore use E_1 = 13.5 eV for a water $3a_1$ electron,[30] and E_2 = 13.5 eV for water $3a_1$, E_2 = 9.50 eV for the chloride anion, or E_2 = 9.76 eV for an acetate anion (with the latter two values from unpublished measurements of our laboratory). The ETMD(3) contribution leading to $W(3a_1)^{-1}W(3a_1)^{-1}$ should thus be seen at 33.4 eV KE, and the one associated with $W(3a_1)^{-1}Cl^{-1}$ at around 37.4 eV KE. As these energies are only approximate, the region highlighted in Figure 2B does not necessarily pertain to $W^{-1}Cl^{-1}$ exclusively, but may contain smaller contributions also from signals to $W^{-1}W^{-1}$ states. The emergence of a high KE shoulder for LiOAc in Figure 2A can be attributed to Li^+-CH_3COO^- CPs, resulting in an estimated KE of 37.14 eV. Since closer ion pairing occurs for LiOAc than for LiCl,[29,31] the observed spectral change is expected. It is safe to conclude that ETMD spectroscopy is indeed sensitive to ion pairing, and apparently also to the nature of the anion (see Figure 2A).

Having confirmed the occurrence of ETMD and its dependence on the nature of the anion in Li^+ solutions, we next discuss ETMD spectra from LiCl (aq) solution measured at different concentrations. The existence of contact ion pairs in highly concentrated LiCl solution is plausible considering that at 8 M LiCl concentration the water-to-LiCl ratio is around 5.875 (47:8; neat water has 55 M concentration), thus one Li^+–Cl^- ion pair shares approximately six water molecules. The full hydration shell for Li^+ contains four, and for Cl^- six water molecules,[32] implying a shortage of water molecules. Hence, a considerable fraction of lithium ions must be in direct contact with chloride ions. When we approximately double the number of water molecules per ion pair by reducing the salt concentration from 8 M to 4.5 M, the ratio increases to ~12. In this case, stoichiometrically each ion can have its own complete hydration shell. Also, several molecular dynamics (MD) simulations showed an increasing abundance of CPs over the range of salt concentrations we have probed,[7,33–37] and the absence of CPs for concentrations below 1 M has been measured.[38] Thus, the contribution of the CP spectral signal should increase for increasing salt concentration. But this is not observed experimentally. As can be seen from Figure 2B the ETMD spectral part assigned to CPs (gray bar) does not change when increasing the LiCl concentration from 4.5 M to 6 M and 8 M. Why are the ETMD spectra in Figure 2B insensitive to the concentration of LiCl in aqueous solution, and why are the spectra in Figure 2A sensitive to the species of lithium salt? In order to discuss possible answers we review some findings on LiCl solutions from the literature.

Several other spectroscopies have been used to access structural properties, and in particular ion pairing, of electrolyte solutions. Here we explicitly mention dielectric relaxation spectroscopy[1,38] (DRS) and neutron diffraction. Isotopic substitution (NDIS) can be used to extract the neutron diffraction signal specific to one type of atoms, e.g. the Cl atoms in a LiCl solution.[37] A large number of studies on LiCl, with an emphasis on NDIS, have been critically compiled by Chialvo and Vlcek,[32] who concluded '*Yet, no clear picture of its hydration behavior emerges*'. For example, a simulation carried out by these authors shows an increase in the fraction of paired Li^+ ions from approximately 0.35 to 0.44 when concentration is increased from 4.5 M to 8 M. This ratio is much smaller than expected from earlier neutron scattering work (0.2 and 0.5-0.6 for concentrations of 3 and 7 M)[34] and from our simple estimate. Therefore, we suggest that signal from CPs is also contained in the spectra of Figure 2B, and experiments with yet better statistics will reveal the concentration dependence.

The observation that the water $3a_1$ orbital gives rise to a much larger ETMD decay signal than for example the water $1b_1$ orbital[7] is an indication that quite generally the ETMD decay amplitude is sensitive to the type and the orientation of the orbitals involved in the decay.[20]

However, the (Coulomb) matrix elements, governing the ETMD decay probabilities, are yet unknown for the systems studied here, and it cannot be excluded that too low decay probabilities inhibit ETMD into a Cl^- final state, or strongly prefer other final states.

Another aspect relevant for the discussion of Figure 2B is the surface sensitivity of electron spectroscopy, and hence the particular solution interfacial structure. For 30 eV KE of the emitted electrons from water the electron mean free path is on the order of 0.6 - 2 nm,[39] the measured signal thus originates from the first few layers (exponentially weighted) of the solution, which usually exhibits an unique structure distinctly different from that in bulk solution.[40,41] In particular, certain atomic anionic solutes (such as I^- and, to a lesser extent, Cl^-) have a larger propensity to exist at the surface,[42] and also the type and probability of ion pairing may differ.[4] Most studies of alkali-halide aqueous solutions, both experimental and theoretical, have focused on sodium and potassium counter ions. We are aware of only one MD simulation performed for LiCl which suggests a quite unique behavior of Li^+ due to its small size.[43] Unlike the larger cations, Li^+ at the solution–vacuum interface is able to maintain a tetrahedral, intact hydration shell which acts as a bridge between the first and second solution layer. This might hinder the formation of contact pairs near the surface. The effect is rather insensitive to concentration variation between 0.25 and 1 M. The calculations, however, do neglect polarization terms in the force field, which were found important in other MD simulations of aqueous surfaces.[37,42] Therefore, a good understanding of the LiCl solution–vacuum interface is currently lacking.

To gain more insight into this particular interfacial structure we have measured the Li 1s and Cl 2p photoemission spectra at fixed kinetic energies: 100 eV to probe rather surface sensitive, and 600 eV for more bulk sensitivity. We found no significant variation of the Li^+/Cl^- signal ratio at any concentration, as shown in the SI. A hypothetical layering of ionic species, if present, seems not to depend on the concentration. Regarding the acetate solutions, unpublished data from our laboratory indicate a considerable surface propensity of the acetate ion (in line with theory),[44] which would explain the strong CP ETMD signal for this solution.

In summary, we have introduced electron–electron coincidence spectroscopy on a liquid microjet as a new method for the investigation of electronic relaxation processes in liquids. Using this technique, we measured the Li 1s ETMD from aqueous LiCl and LiOAc. Li^+ aqueous salt solutions were chosen as a showcase to explore the possibility of ETMD detection in aqueous media without competing autoionization processes. The extracted signal reveals a clear spectral difference between the two solutes probed, thus underlining the sensitivity of ETMD spectroscopy to ion pairing. Contrary to our expectations, different concentrations of LiCl (aq) show no spectral differences within the sensitivity of the experiment. We argue that the abundance of contact ion pairs in this system might differ less than expected from a comparison of the solute concentrations, and might further be influenced by surface effects on the ion solvation structure. Although the latter points have to be clarified in future studies, we have shown the potential of using ETMD electron spectroscopy as a new method for research on electrolytes. We expect that electronic decay spectra (ETMD or ICD) can be used as a sensitive fingerprint for the surroundings of the decaying state, as long as the decay is not in competition with (more effective) local Auger decay. This condition will be met in a broad range of alkaline and halide salt solutions. While existing techniques offer a handle on ion pairing via the related electric dipole moments (DRS) or the geometric positions of the nuclei (NDIS), the mechanism we propose exploits the electronic (orbital) structure of the paired species. Although more theoretical work is needed to come to quantitative predictions of ion pairing by ETMD spectroscopy, it therefore clearly is a promising complement to existing techniques.

Supporting Information

The following files are available free of charge:

A description of the experimental methods, detailing in particular the acquisition of electron-electron coincidence spectra to extract the ETMD signal.

ETMD spectra from 4.5 M LiCl (aq) and 4.5 M LiOAc (aq) acquired at 110 eV and at 135 eV photon energy.

Area ratios of core-level photoelectron spectra of LiCl (aq) at low and high kinetic energies (preferentially sensitive to surface and bulk species), for different solvent concentrations.

Notes

The authors declare no competing financial interests.

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