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Investigating ion pairing in a liquid by electron-electron coincidence spectroscopy

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The formation of ion pairs in an electrolyte solution has been investigated by numerous methods, arguably neutron scattering being one of the most powerful. Nevertheless, obtaining unambiguous results has been elusive for a lot of systems. We argue that non-local autoionization processes, in particular the so-called Electron Transfer Mediated Decay (ETMD), have the potential to become a probe for ion pairing that is based on a clearly different mechanism than existing techniques. In ETMD, an inner-valence or shallow core-level vacancy, typically created via photoionization with synchrotron radiation, is filled by an electron from the first solvation shell of the excited site. Using the excess energy of that process, another solvation shell electron is released into the continuum. The kinetic energy spectrum of that second electron, the 'ETMD electron', carries a fingerprint of the surroundings of the excited site. We have developed a set-up to record these ETMD spectra by electron-electron coincidence spectroscopy on a liquid jet. The coincidence technique removes the substantial background of inelastically scattered secondary electrons. Results are presented for solutions of Li and Mg-salts.

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