Final Technical Report

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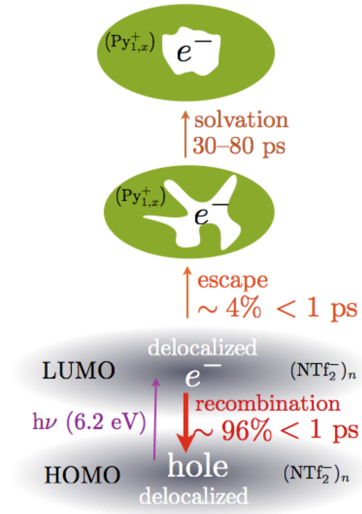
Abstract / Executive Summary
Room temperature ionic liquids (RTILs) are liquids made up of atomic and molecular ions. This is in contrast with more common liquids, such as water, that are made up of neutral molecules. The additional charges on the atoms and molecules can alter the properties of these liquids, for example they tend to have a very high vapor pressure and the ability to shield charge in electronic devices. For these and other reasons RTILs have recently been deployed in a number of applications that involve production of free electrons in the liquid, such as batteries, capacitors, nuclear power plants, and solar cells. Electrons tend to be very reactive, and understanding their behaviour in these liquids is important for the future design of ionic liquids to be employed in these environments. This study investigated the behavior of electrons generated in RTILs by pulses of ultraviolet light, including how long they survive, and how reactive they are with the both the surrounding liquid and impurities in the liquid. The ionic liquid studied was one of the most commonly used, called N-alkyl-N-methyl-pyrrolidinium bistriflimide. What the study revealed was that the majority of the electrons initially created, about 96%, had a very short lifetime of less than one picosecond (10^{-12} second) due to a process called geminate recombination. The study also demonstrated that the electrons are very reactive at the moment they are detached from the molecules in the liquid by light, but that they relax very quickly and lose almost all of their reactivity in much less than one picosecond. The short lifetime and rapid loss of reactivity both serve as important mechanisms that protect the liquid from radiolytic damage.

Project Summary
The use of room temperature ionic liquids (RTILs) in a wide range of radiolytic environments, such as solar cells and nuclear power plants, has been expanding rapidly. The strong intermolecular Coulombic interactions in RTILs have the potential to alter their influence on the behavior, such as lifetime, stability, cooling, and reactivity, of species generated through radiolysis such as electrons. While the stability and reactivity of electrons in common liquids consisting of neutral atoms and molecules has received considerable attention, much less is known about the analogous dynamics in RTILs.

The project used ultrafast spectroscopy to investigate photodetachment of electrons in a series of N-alkyl-N-methyl-pyrrolidinium bistriflimide, $[Py_{1x}^+][NTf_2^-]$, room temperature ionic liquids. The series varied the length of the alkyl tail on the pyrrolidinium cation (*x* represents the number of carbons), which altered the structure of the liquid on a nanometer length scale and changed the dynamics with the liquid becoming more viscous with an increase in *x*.



One of the the larger challenges with the RTILs is purification. This study developed a method to clean the RTILs, demonstrated that prior studies had incorrectly interpreted photodetachment from impurities as photodetachment from the neat liquid, and by minimizing the impurities measured the ultrafast dynamics following photodetachment of the neat liquid with ultraviolet light at 200 nm. The dynamics are summarized in the illustration at the right and were shown to be dominated by the first picosecond following detachments. The initially detached electron was delocalized on the length scale of a nanometer and highly reactive. The majority of these hot electrons rapidly undergo geminate recombination. However, a minority of the hot electrons escaped their geminate hole, and these evolve to become localized, free solvated electrons evolving over a series of time scales from hundreds of femtoseconds to hundreds of picoseconds, The reactivity of these electrons with simple species such as protons declines rapidly as the electrons cool, and once solvated the electrons are quite stable with lifetimes that appear to be limited by impurities in the liquid. The cooling dynamics of the electron were strongly dependent on the length of the alkyl chain on the cation and correlated well with the viscosity of the RTIL.

After studying the clean, neat liquids, an impurity was added to be a source of free electrons as a first step to better understanding the ultraviolet exposure in real world applications. Detachment from iodide demonstrated very different initial dynamics than the neat liquid. The detachment process proceeded through an initial charge transfer to solvent intermediate state with subsequent dissociation to a separated electron and neutral iodine atom in 300 to 500 femtoseconds. Subsequent solvation and localization of free electrons mirrored the free electrons detached from the neat liquid, with a higher asymptotic yield of free solvated electrons from iodide solute than from the liquid.

References

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