# radiochimie et chimie sous rayonnement
## industrie nucléaire

## Radiolysis of ionic liquids and molten salts

### Challenges and successes in the energy domain

**Abstract**  Ionic liquids have important potential applications in the recycling of used nuclear fuel, and as battery electrolytes, lubricants and ion thruster fuel in spacecraft. Being comprised entirely of charged species, ionic liquids and molten salts have dramatically different properties than those of conventional molecular liquids. They provide new and unusual environments to test our understanding of physical chemistry phenomena. These unusual properties influence physical and dynamical processes that determine the stability and lifetimes of reactive intermediates and thereby affect the courses of reactions and product distributions that have consequences in multiple areas of primary and applied radiation chemistry. In addition, molten salts are proposed as liquid fuel in a new generation of molten salt nuclear reactors with operational and safety advantages over present systems. In both cases, understanding the effects of radiation exposure (radiolysis) is essential to reliable use in sustainable energy applications.

**Keywords**  **Ionic liquids, molten salts, radiolysis, radiation chemistry.**

**Résumé**  **La radiolyse des liquides ioniques et des sels fondus : défis et réussites dans le domaine de l'énergie**
Les liquides ioniques sont des sels qui fondent en-dessous de 100 °C. Comme les sels fondus (qui fondent à haute température), ils sont composés d'anions et de cations. Ils ont d'importantes applications potentielles dans le recyclage du combustible nucléaire, comme électrolytes de batterie, lubrifiants et carburants pour propulseurs d'ions dans les engins spatiaux. Leurs propriétés sont radicalement différentes de celles des liquides moléculaires conventionnels et ils fournissent des environnements nouveaux et inhabituels pour tester notre compréhension des phénomènes de physico-chimiques. Ces propriétés inhabituelles influencent les processus physiques et dynamiques qui déterminent la stabilité et la durée de vie des intermédiaires réactifs et affectent ainsi le cours des réactions et la distribution des produits. Ceci a des conséquences dans de multiples domaines allant des processus fondamentaux de la chimie sous rayonnement aux applications. En effet, les sels fondus pourraient être des combustibles liquides dans une nouvelle génération de réacteurs nucléaires. Ainsi, la compréhension des effets des rayonnements sur ces sels (la radiolyse) est essentielle pour une utilisation contrôlée dans des applications énergétiques toujours plus durables.

**Mots-clés**  **Liquides ioniques, sels fondus, radiolyse, chimie sous rayonnements.**

### Ionic liquids and their significance in the energy domain

The last two decades have seen an enormous growth in interest and research in ionic liquids (ILs), which are generally defined as salts that melt below 100 °C. The materials we call ionic liquids usually consist of organic cations and inorganic or organic anions (a variety of representative cations and anions is depicted in *figure 1*), while molten salts are less complex and typically made from inorganic cations and monoatomic (halide, oxide, sulfide) or complex (nitrate, carbonate, sulfate) anions. Nevertheless, they are overlapping parts of the same continuum and they share some common properties and behaviors.

Recently, molten salts have had their own resurgence in the areas of concentrating solar thermal power systems [1] and molten salt nuclear reactors, where molten salt is both the heat transfer fluid and the medium containing the nuclear fuel [2]. In both the solar and nuclear applications, molten salts are attractive because of their high volumetric heat capacities and high boiling points, which allow very high operating temperatures (550-750 °C) that lead to higher thermodynamic efficiency (compared to water-cooled nuclear reactors, for example) while maintaining the significant safety advantage of operating near atmospheric pressure.
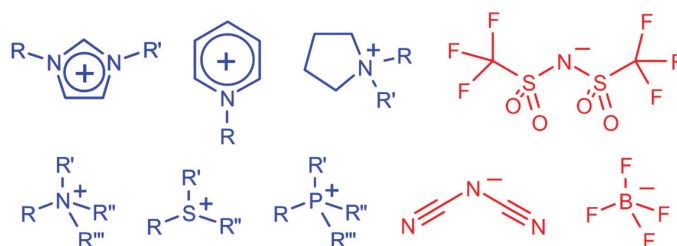


Figure 1 - Representative ionic liquid cations (blue) and anions (red). Top from left: imidazolium ($C_nC_mim^+$), pyridinium ($C_npy^+$), pyrrolidinium ($C_nC_mpyrr^+$), bis(trifluoromethylsulfonyl)amide ($NTf_2^-$). Bottom from left: quaternary ammonium ($N_{nopq}^+$), tertiary sulfonium ($S_{nop}^+$), quaternary phosphonium ($P_{nopq}^+$), dicyanamide ($DCA^-$), tetrafluoroborate ($BF_4^-$). Subscripts m, n, o, p, and q represent the lengths of hydrocarbon side chains. Adapted from [35] with permission from The Royal Society of Chemistry.

In this article, we examine the behavior of ionic liquids and molten salts exposed to ionizing radiation in some of their important applications. Ionic liquids are subjected to irradiation when they are used in separations systems for recycling spent nuclear fuel and in spacecraft where they are used as battery electrolytes, lubricants and ionic thruster propellants. Molten salts are irradiated in molten salt reactors and in pyroprocessing baths. Radiolysis is also a good way to mimic material degradation from aging and overstressing

electrochemical systems such as ionic liquid batteries and supercapacitors because degradation and ageing are due mostly to oxidation and involve similar mechanisms to radiolysis [3].

## Distinguishing characteristics of ILs and their radiation chemistry

Ionic liquids derive their interesting and useful properties from their composition, starting with the fact that even in "pure" form they are binary mixtures of cations and anions. Since they are Coulombic fluids, electrostatic attractions keep their vapor pressures low and their boiling points high. Combined with their low melting points, and the tendency of many ILs to deeply supercool, their generally high boiling points mean that ILs are liquid over very wide temperature ranges, which is an advantage for their use as electrolytes, lubricants and functional fluids for example.

Over almost two decades, molecular dynamics (MD) simulations [4-7], in conjunction with experimental probes of IL structure (X-ray and neutron scattering, multidimensional NMR, Raman spectroscopy and atomic force microscopy) have enabled us to understand how the structures of anions, cations and their functional groups contribute to the observable macroscopic physical properties of ILs (viscosity, conductivity, phase behavior) and how they interact with solutes, cosolvents and air, liquid and solid interfaces [8]. *Figure 2* presents snapshots from MD simulations showing how minor changes in the structure of quaternary ammonium cations, combined with the same anion, result in ILs with significantly different structure and behavior. In the center, the simulation of 1-butyl-1-methylpyrrolidinium $NTf_2$ is dominated by alternating cationic head groups (blue) and $NTf_2^-$ anions, with the nonpolar butyl side chains interspersed randomly among them. On the right, increasing the side chain by six carbons makes them long enough to aggregate, resulting in molecular-scale rearrangement into domains of polar (blue-red clusters of ions) and nonpolar phases (white hydrocarbon clusters). Since the polar and nonpolar components are covalently linked, the domains are forced to intertwine. Because of the Coulombic interactions, it is energetically unfavorable for ions to enter the nonpolar phase or for hydrocarbon tails to enter the polar phase. This lowers the diffusion rate of the ions because the dimensionality of the polar network is decreased, restricting the directions available for the ions to move along. Consequently, the viscosity of $C_{10}C_1pyrr$ $NTf_2$ at 20 °C is over double that of $C_4C_1pyrr$ $NTf_2$. $N_{1444}$ $NTf_2$ contains almost the same number of $CH_2$ groups as $C_{10}C_1pyrr$ $NTf_2$, but they are arranged differently around the quaternary ammonium center. As a result, the polar domains are extended into narrow channels, and the viscosity is increased again fourfold.

The remarkable and tunable molecular-scale structure of ILs has consequences for the behavior of solutes, whether they are stable molecules or radical transient species produced by radiolysis. While the diffusion behavior of large molecules is controlled by the viscosity of the IL, the diffusion of molecules that are small compared to the ions of the IL is fast if they are uncharged but slow if they are charged [12]. MD simulations have shown that the local mobility in nonpolar regions is higher than in adjacent polar regions with higher friction, leading to dynamical heterogeneity within ILs on the molecular scale [13-15]. These unique and intriguing
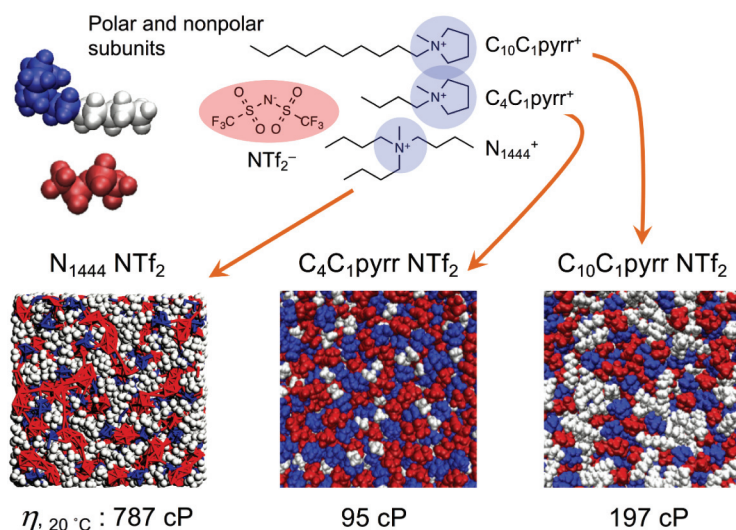


Figure 2 - Structures of three ionic liquids obtained from molecular dynamics simulations, with their viscosities at 20 °C. Cationic head groups are depicted in blue and nonpolar hydrocarbon side chains in white. $NTf_2^-$ anions are depicted in red. $N_{1444}$ $NTf_2$ simulation adapted with permission from [9]. © 2010 American Chemical Society. Space filling ion depictions adapted with permission from [10]. © 2013 American Chemical Society. $C_4C_1pyrr$ $NTf_2$ and $C_{10}C_1pyrr$ $NTf_2$ simulations courtesy of Jeevapani Hettige and Claudio Margulis, generated from simulations reported in [11].

dynamical properties of ILs have consequences for chemical reactivity that can be applied to control reaction chemistry and the performance of ILs in practical applications. In particular, the slow and heterogeneous dynamics of ILs, due to their higher viscosities and complex structure, can provide insights into fundamental processes of radiolysis that are very difficult to obtain from conventional molecular liquids.

## Early processes in ionic liquid radiolysis

The radiation chemistry of water has been studied for over a century, but important details about it continue to be revealed. Compared to water's simple elemental and structural composition ($H_2O$), ionic liquids are much more complex. Therefore, it helps to divide the radiolysis process and subsequent physics and chemistry into steps, and to treat the IL generically until specifics need to be addressed. *Figure 3* (p. 108) depicts the physical step of the radiolysis mechanism in ILs, while *figures 4* and *5* (p. 108-109) depict the early chemical steps (up to 10 ns).

At the beginning, ionizing radiation produces three species (*figure 3*). The incident radiation transfers enough energy to eject an electron from a component of the IL. The electron thus liberated is "excess" with respect to the solvent, in that it is in addition to the local solvent's normal complement of electrons. When it comes to kinetic rest it is called a "pre-solvated" electron ($e_{ps}^-$), because the solvent still has to reorganize in multiple dynamical steps in response to the sudden appearance of the electron, eventually reaching a "solvated" state, ($e_s^-$). The solvation process localizes the excess electron and reduces its potential energy. This has consequences for its reactivity that will be described below.

The electron vacancy left behind during the ionization event is called a "hole". The question of whether holes also begin in pre-solvated states and become stabilized by solvation/localization (depicted in *figure 3* as a red hole going to brown) is a matter of active debate and research. In addition to electrons and holes, exited states are generated by direct energy transfer from the radiation. Excited states can
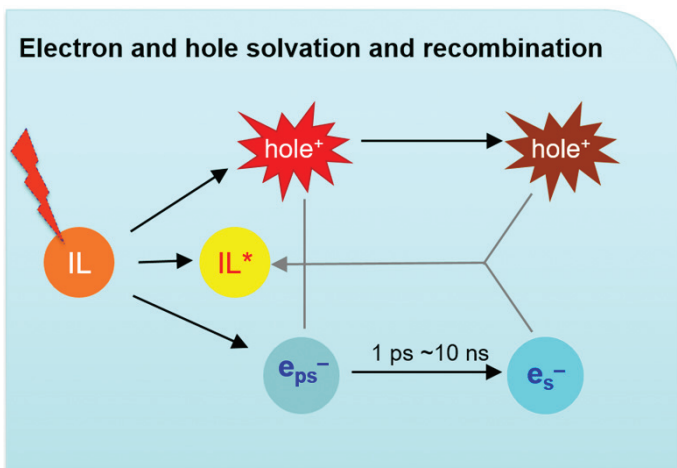
**Figure 3 - Early radiolysis processes in ionic liquids. In *figures 3-5*, "IL" can represent the ionic liquid as a whole.**
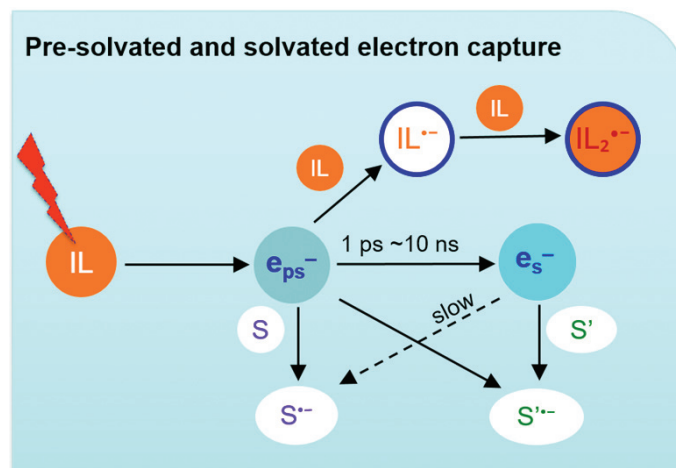


**Figure 4 - Reactions of excess electrons in ionic liquids. Electron solvation and scavenging processes compete and produce distributions of products. In some ILs, the excess electron reacts with one of the ions to produce radicals that induce further chemistry.**

also be generated by electron-hole recombination. In the radiolysis of neutral molecular solvents, coulombic attraction (attenuated by the dielectric response of the medium) promotes recombination of the ions formed by radiolysis. In ILs, the high density of charges screens the electron and hole (which could be neutral radical or a dication), and recombination occurs by random diffusion. Consequently, a significant fraction of initially-formed electrons and holes avoid recombination and participate in chemical reactivity (below).

**Excess electron reactivity in ILs**

The reactivity patterns of excess electrons in ILs are given in *figure 4*. They depart significantly from those of molecular solvents in two important respects. The first is that pre-solvated electron reactivity plays a larger role in ILs than in conventional solvents, and the second is that diffusive solvated electron reactions are generally slower than one would expect at first glance. *Figure 4* shows the competition between the solvation process and pre-solvated electron scavenging. At room temperature, the solvation dynamics of molecular solvents is very fast, leaving only a narrow time window for scavenging before the electrons convert to the less reactive solvated form. In water, solvation occurs in less than a picosecond, while in alcohols it takes only a few picoseconds, e.g., 5.4 ps in methanol and 6.9 ps in ethanol [16]. On the other hand, solvation times in ILs can be 100 to 1 000 times longer, because of the slow dynamics described above [17-19]. When the electrons remain in the pre-solvated state for that long, their higher mobility and chemical potential provides greater opportunity for them to react with scavengers (S or S') to give product distributions and yields that are different from solvated electrons. It is important to consider pre-solvated reactivity when accounting for electron products, otherwise the reaction mechanisms inferred from product distributions could be invalid [20].

Detailed investigations of the electron solvation process in $C_4C_1pyrr$ $NTf_2$ revealed two discrete steps: a sub-15 ps component that may be related to a quasi-free electron [21], and a slower, final step (~ 270 ns average) corresponding to localized but not fully solvated electrons [22]. Direct comparison of the electron solvation dynamics and scavenging kinetics showed that electron scavenging is gated by the solvation process and that each step is associated

with a reaction radius. The apparent rate of a given step was equivalent to the rate of that solvation process and did not change with scavenger concentration, but the amplitude of the scavenging increased as the probability of finding a scavenger within the reaction radius increased. The higher viscosity and slower dynamics of this IL revealed aspects of pre-solvated (often called "dry" in the literature) electron scavenging that were not apparent from many years of studying dry electron reactions in conventional solvents, in particular the important fact that multiple steps can be involved. Actually, using recently-installed near infrared optical fiber single-shot capabilities at the BNL Laser-Electron Accelerator Facility, we are currently able to explore these processes in much more viscous ILs than it was possible before [23].

Once the electron becomes solvated in an IL, the nature of its reactivity changes dramatically. Solvated electrons are strongly reducing chemical species, and their reactions with common molecular scavengers in conventional solvents are generally very fast, with second-order rate constants on the order of ~5 x $10^{10}$ $M^{-1}$ $s^{-1}$. When they were first measured [24], it was a surprise to learn that diffusion-controlled electron scavenging rate constants in ILs are only on the order of (1-5) x $10^8$ $M^{-1}$ $s^{-1}$ (depending on the IL), about 100 times slower. As quantum particles, excess electrons diffuse very rapidly in conventional solvents, but in ILs the fact that they are charged means that their motion is coupled to the constituent ions of the IL. In effect, their diffusional properties in ILs are similar to molecular anions, which have similar rate constants for bimolecular electron transfer reactions with the same substrates (~$10^8$ $M^{-1}$ $s^{-1}$). Knowing that this is the case is important for predicting and controlling radiolysis product yields in ILs.

In some ILs, the electron reacts quickly with one of the constituent ions, resulting in radical chemistry as depicted in the top part of *figure 4*. This is a dominant feature of the radiation chemistry of ILs with aromatic cations such as the imidazolium and pyridinium ions. In the imidazolium case, the electron induces a pyramidal distortion of the ring localized at the C-2 carbon between the two nitrogens. This rearrangement induces such radical character at C-2 that it attacks an adjacent imidazolium cation to form a covalent $(C_nC_mim)_2^{•+}$ dimer [25]. Continued irradiation of imidazolium

ILs leads to polymerization and degradation of the IL. Since imidazolium ILs have been proposed as microsatellite propellants [26], one wonders if this susceptibility to radiation-induced polymerization limits their tolerance to radiation exposure in space. Radiation stability can be increased by substituting a methyl group for the hydrogen at the C-2 position. On the other hand, pyridinium ions form relatively stable neutral radicals when they capture an electron because the electron is well delocalized, sometimes over two pyridinium rings in a charge-resonance state [27].

## Hole reactivity in ILs

The reactivity of radiolytically-produced holes in ILs is shown in *figure 5*. The transition from the instantaneously-formed hole depicted in red and the "relaxed" hole depicted in brown can represent two different processes. First, in analogy to the excess electron, the hole may become solvated as the surrounding medium reorganizes to the new distribution of charge. In the hole solvation process, bond lengths may change but bonds do not break. The second form of hole relaxation is fragmentation, where bonds are broken and new radical species are formed. Hole fragmentation is very common in liquid radiolysis. The most famous example is the fragmentation of the water cation by proton transfer to form hydroxyl radical and hydronium ion (eq. 1):

$$H_2O^{\bullet+} + H_2O \rightarrow {}^{\bullet}OH + H_3O^+ \qquad (1)$$
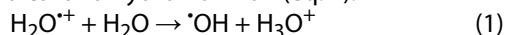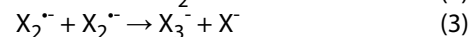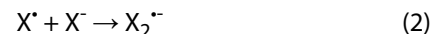
Because hydrogen bonding in water makes proton transfer so facile, the lifetime of the elusive water cation is very short and profiling its reactivity is thus very difficult. Progress has been made in recent years using indirect means that involve high concentrations of solutes (halides, mineral acids, DNA) to detect products produced through reactions with the water cation by measuring their excess yield over that produced by direct radiolysis of the solute [28].

Detecting holes and their fragmentation products in ILs by transient absorption spectroscopy is generally more difficult than for electrons and their products, because holes and their products seldom have distinctive absorption features in the UV-Vis-NIR region. Holes or oxidizing radiolysis products have been indirectly detected by the addition of aromatic hydrocarbons, such as pyrene, that have distinctive radical cation absorption features and form dimer radical cations

with characteristic charge-resonance absorption features (e.g., $(Pyrene)_2^{\bullet+}$) at higher aromatic concentrations [20]. Hole-induced fragmentation is a major source of IL radiation damage, leading to a wide array of radical species that depends on the composition of the IL.

Electron paramagnetic resonance (EPR) spectroscopy, combined with $^1H$-$^2H$ isotopic substitution, is ideally suited for identifying many types of radicals. The hole-driven radiation damage mechanisms of many families of ILs have been elucidated using EPR [29]. This wealth of mechanistic information has been useful in developing strategies to limit IL radiation damage. As with electron-driven IL damage, delocalization can stabilize excess charges so that they do not induce radical chemistry. For example, substitution of benzyl groups onto pyridinium, imidazolium and pyrrolidinium cations produced ILs that show strong aromatic dimer radical cation ($Bz_2^{\bullet+}$) charge resonance absorption bands when irradiated [27]. Benzylpyridinium cations are thus capable of stabilizing both holes and electrons. They could have future uses as stable redox intermediates for the study of electron transfer processes in ILs.

IL anions also play important roles in radiolytic hole chemistry. Halide anions tend to form high-melting salts, but pseudohalides such as thiocyanate ($SCN^-$) and dicyanamide ($N(CN)_2^-$) are the basis of many common and useful ILs due to their low melting points, low viscosities and high conductivities. When oxidized, halides and pseudohalides ($X^-$) produce radicals ($X^{\bullet}$) that react with another halide or pseudohalide ion to form dimer radical anions ($X_2^{\bullet-}$) that delocalize the hole (eq. 2). Reactive halide dimer radical anions can disproportionate to produce trihalide anions (eq. 3), which are in equilibrium with the diatomic halogen and halide anion (eq. 4):

$$X^{\bullet} + X^- \rightarrow X_2^{\bullet-} \qquad (2)$$
$$X_2^{\bullet-} + X_2^{\bullet-} \rightarrow X_3^- + X^- \qquad (3)$$
$$X_3^- \rightarrow X_2 + X^- \qquad (4)$$

The hole chemistry of halide salts plays a critical role in the operation of dye-sensitized solar cells (DSSCs, also called Grätzel cells) [30]. These cells contain large concentrations of iodide anions, which are used to re-reduce the sensitizer dye molecules that were oxidized by excited-state electron transfer to the $TiO_2$ photoanode. Once the dye has transferred the hole to $I^-$, reactions 2 and 3 occur, and the triodide anion $I_3^-$ diffuses to the cathode, where it is reduced to $3I^-$ to complete the electrical circuit. Ionic liquids are popular electrolytes for use in DSSCs because their volatility is low and their boiling points are high. Optimized electrolyte formulations typically contain a high proportion of iodide and triodide ions, with the addition of other anions ($SCN^-$, $B(CN)_4^-$, $NTf_2^-$) to improve transport properties and a mixture of short-chain imidazolium cations to frustrate crystallization and increase the liquid range of the IL.
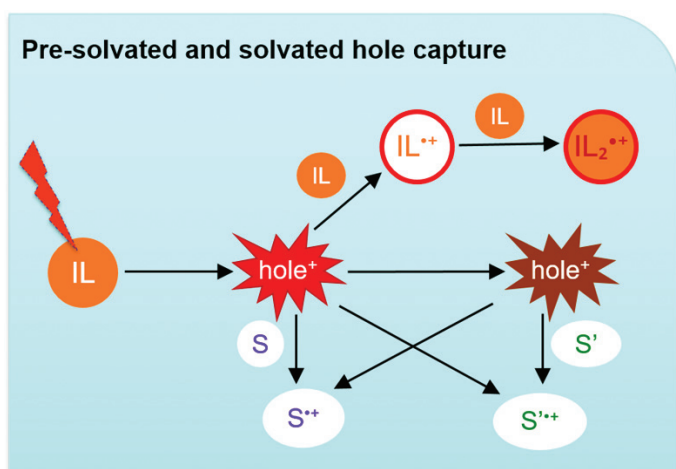


Figure 5 - Reactions of holes in ionic liquids. There is increasing evidence that holes undergo a solvation process similar to electrons, which would have mechanistic consequences for their reactions with scavengers. In some ILs, the hole localizes on one of the ions to produce a radical that induces further chemistry, or in some cases the hole is stabilized by excess charge delocalization via dimer formation.

## Renewed interest in molten salt radiation chemistry

The radiation chemistry of halide salts has been receiving much more attention recently because of the development of molten salt nuclear reactor (MSR) concepts [2], which use molten salts as the reactor coolant fluid for high thermal efficiency and safety advantages. Several companies are actively developing MSR technologies that are based on fluoride or chloride salt systems, and in most of those cases the fissile nuclear fuel will be dissolved directly in the molten salt
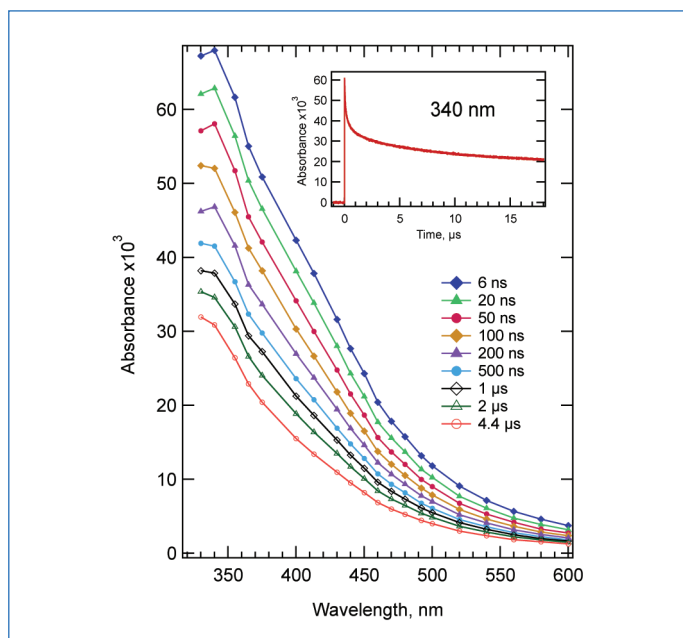
Figure 6 - Transient absorption spectra at indicated delays after pulse radiolysis of pure molten $ZnCl_2$ at 340 °C. Inset: transient absorption kinetics at 340 nm.

coolant fluid rather than being used in a solid form. The molten salt in MSRs will be subjected to high levels of radiation, thus it is necessary to understand not only the radiation chemistry of the salt itself but also the reactivity of salt radiolysis products with the dissolved actinide fuel, as well as with the many elements generated by fission and the transition metals that enter the salt from corrosion of reactor components.

Pioneering experiments in molten salt pulse radiolysis at elevated temperature (≤ 800 °C) were performed by Russian and Japanese groups in the 1970s-1980s [31-32]. Most of the experiments were on alkali chlorides, which are much easier to handle than fluorides. Both groups detected broad solvated electron spectra in the visible-NIR region in molten pure or mixed alkali halide salts and observed that the electron reacts with dissolved metal ions, but due to the limitations of the experiments, reliable rate constants were not obtained. They also observed an absorption peaking at 340 nm that they attributed to $Cl_2^{\bullet-}$, which decayed by a second-order process (eq. 3).

In preparation for a large project on the radiation chemistry of molten salts to support the development of MSRs, we constructed a high-temperature sample holder for the LEAF accelerator [23]. *Figure 6* shows the results of a preliminary experiment on the pulse radiolysis of molten $ZnCl_2$ at 340 °C, showing the transient spectra at different delays after the electron pulse. The solvated electron spectrum is not observed because electrons are very rapidly captured by the $Zn^{2+}$ ions to produce a product that absorbs weakly in the UV region. This permits the $Cl_2^{\bullet-}$ absorption signal to be observed clearly as it decays via eq. 3 to produce $Cl_3^-$, which absorbs further towards the UV. The kinetics of the decay are shown in the inset.

A much larger effort to understand the radiation chemistry of molten salts is now underway as part of the Molten Salts in Extreme Environments Energy Frontier Research Center [33], a U.S. Department of Energy-funded collaboration of 18 principal investigators who are studying molten salt structure, dynamics and reactivity in the bulk molten salt,

including the effects of solutes and radiation, and at liquid-solid interfaces representative of reactor materials. As part of that effort, our team is investigating the yields and reactivity of primary molten salt radiolysis products and their reactions with metal ions, in order to understand the effects of radiation on the salt matrix as it evolves over time.

## Ionic liquids for a more sustainable society

The substantial attention that ionic liquids have enjoyed in recent years has overshadowed the large body of earlier work on higher-temperature molten salts. This article presents just a brief glimpse into the diverse and fascinating behavior of ionic liquids, and how that behavior affects their radiation chemistry. Because there are so many possibilities to make ionic liquids from widely different components, it is not possible to make generalizations without an infinite number of exceptions. Early ionic liquid science was loaded with empirical observations, which developed into rules of thumb that seldom endured. Fortunately, a tremendous amount of insight into the workings of ILs has been obtained through increasingly sophisticated molecular dynamics simulations over the past 15 years. This has enabled a growing mechanistic framework for rational design and predictive capability of ionic liquid properties and radiation chemistry. The experience that has been gained from ionic liquids is now being applied to the domain of molten salts.

Their low melting points (compared to mineral salts) result from purposefully combining anions and cations with various kinds of asymmetry, side groups and charge delocalization that reduce their coulombic interactions and thereby destabilize their solid crystalline forms. While the early expectations that ILs could replace volatile organic solvents in many widespread applications have not been fulfilled, the particular and distinct properties of ILs have enabled numerous innovations with technological impact [34-38].

Ionic liquids contribute to making our society more sustainable through advancements in the production, storage and utilization of energy. In the domain of production this includes the removal of sulfur and mercury from fuels, $CO_2$ capture, photoelectrochemical cells, conversion of biomass and biopolymers to fuel and valuable materials, and the collection, transport and storage of solar thermal energy. Ionic liquids contribute to more efficient energy utilization through their uses in supercapacitors and batteries, fuel cells, catalysis, chemical separations (e.g., gases and hydrocarbons), metallurgical extraction and nuclear separations, and their high performance as non-volatile lubricants, functional fluids, performance additives, and even as propellants for microsatellite thrusters (for review see [26, 34-38]).

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