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Understanding the Photoexcitation of Room Temperature Ionic Liquids

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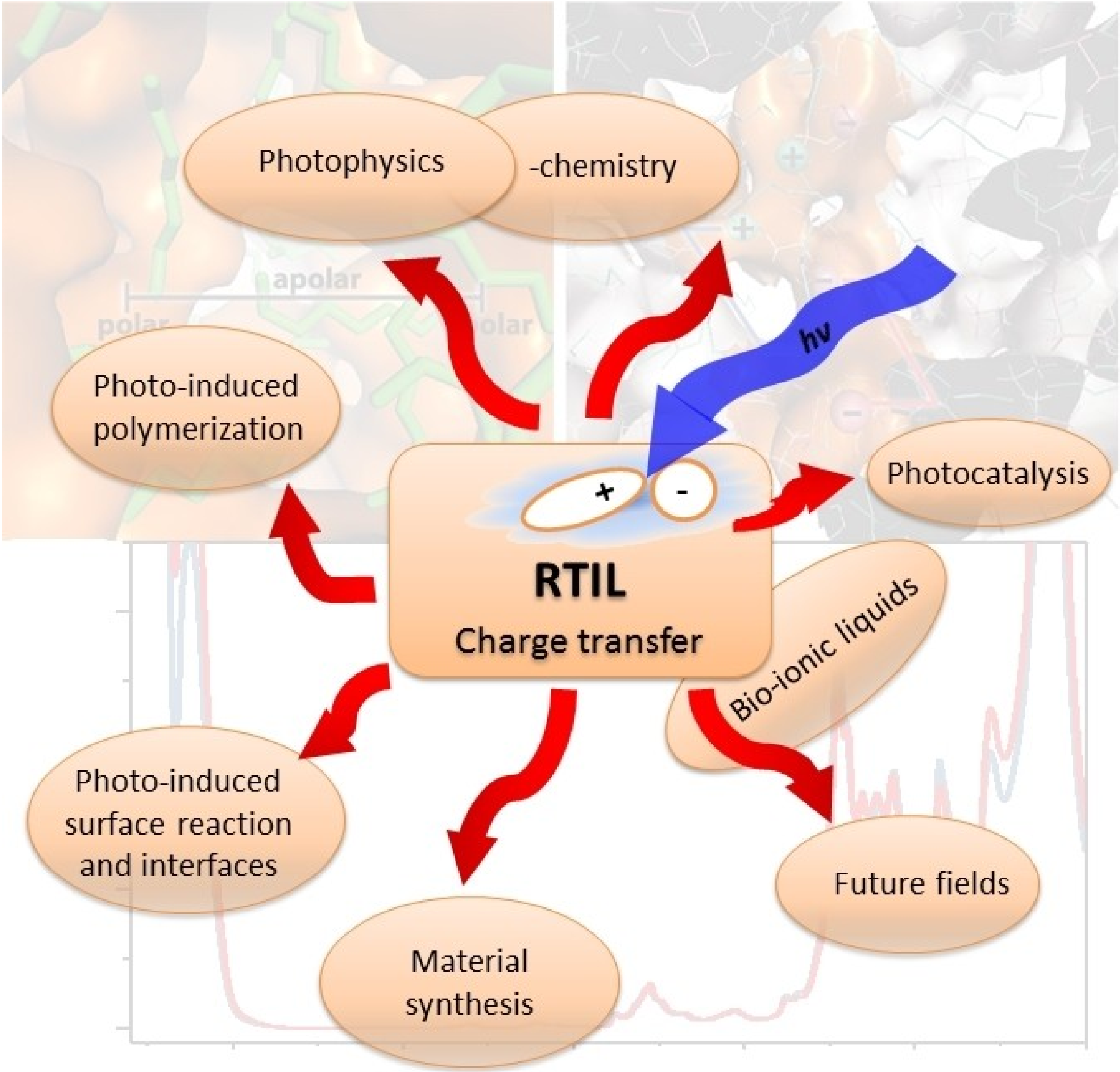

Photoexcitation of (neat) room temperature ionic liquids (RTILs) leads to the observation of transient species that are reminiscent of the composition of the RTILs themselves. In this minireview, we summarize state-of-the-art in the understanding of the underlying elementary processes. By varying the anion or cation, one aim is to generally predict radiation-induced chemistry and physics of RTILs. One major task is to address the fate of excess electrons (and holes) after photoexcitation, which implies an overview of various formation mechanisms considering structural and dynamical aspects. Therefore, transient studies on time scales from femtoseconds to microseconds can greatly help to elucidate the most relevant steps after photoexcitation. Sometimes, radiation may eventually result in destruction of the RTILs making photostability another important issue to be discussed. Finally, characteristic heterogeneities can be associated with specific physicochemical properties. Influencing these properties by adding conventional solvents, like water, can open a wide field of application, which is briefly summarized.

1. Introduction

Ionic liquids exist at high and low temperatures. During the past two to three decades, especially low temperatures ionic liquids have been subject to many investigations. Typically, this group of liquids is described by consisting of ions only and prevail in their liquid state below temperatures of 100 °C.[1] As such they are often called room temperature ionic liquid (RTILs) or simply ionic liquids (ILs). The latter term in a sense neglects the existence of high temperatures ionic liquids, such as alkali halide melts, whose properties – e.g. electron localization – have already been studied and described in detail some time ago.[2]

In contrast, this minireview deals with RTILs that fascinate researchers due to typical properties such as low vapor pressure, good thermal stability, high conductivity and wide electrochemical window.[3–7] But what about stability after photoexcitation?

Photoexcitation of neat RTILs can lead to the formation of transient species that has been observed from the femtosecond (fs) to the microsecond (µs) regime. For example, it has been reported for alkyl and aromatic cations with varying anions, most often halides and amides. Since their first description of air and water stable ionic liquid based on imidazolium,[8] RTILs have often been used. Before we start our overview, it is worth mentioning that this minireview is about the observation of transient species in neat RTILs after photoexcitation. Thus, it is not about photochemistry of dissolved compounds in ionic liquids, applications or photocatalysis – although some work will also be useful in this review – where other reviews exist.[9–12]

This minireview is divided into five major parts, one dealing with photophysical and -chemical properties of RTILs, while the second part – though not exclusively – focuses on findings after photoexcitation. The third part deals with the behaviors of RTILs within mixtures, whereas in the fourth RTILs as solvent are shown. These chapters are followed by RTILs applications. In addition, there were some reviews published around 2010[13–15] – all with different foci, which motivates a further summary on advances in understanding elementary processes in ionic liquids after photoexcitation.

2. Experimental Approaches

Many experimental and theoretical approaches show high potential to unravel properties of ionic liquids after photoexcitation. Here, it seems inappropriate to discuss all the different techniques, but highlight the techniques that have been used most in recent years. Details of the setups and procedures are part of the corresponding publications and the readers are referred to the list at the end. Experimental techniques can be categorized in stationary (absorption and fluorescence) and time-resolved methods. Also, Fourier-transform infrared (FTIR) spectroscopy, photoelectron spectroscopy (PES), atomic force microscopy (AFM) and x-ray diffraction are important tools for characterizing RTILs, because it can be conveniently compared to results from theoretical methods. Time-resolved studies can be further divided at which nanosecond (ns) and fs photoexcitations are the most dominant excitation sources. The subsequent probing of photo-induced events are performed by various techniques, e.g. broadband absorption spectroscopy or in general, nonlinear optical spectroscopy such as optical heterodyne detected optical Kerr effect (OHD-OKE) measurements, fluorescence up-conversion, two-dimensional IR detection and fs coherent anti-Raman scattering (fs-CARS), electron paramagnetic resonance (EPR), dielectric spectroscopy and some more that are mentioned in the due course of this review. The following data analysis plays also a major role and is therefore worth mentioning.[16] Theoretical calculations are often based on density functional theory (DFT)[17] and molecular-dynamics (MD) simulations.[18]

3. Results

A major field of interest of the early investigations of RTILs was the radiation chemistry within these molecules.[19–21] UV-radiation can form solvated electrons in RTILs, detectable by a broad

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absorption spectrum peaking in the near-infrared (NIR) spectral region.[22,23] A subsequent detrapping can lead to an inhomogeneous bleaching in the spectral region revealing heterogeneity in RTILs.[23]

An aspect of radiation stability was published by Huang et al.[24] Although RTILs can be damaged by radiation emission, addition of $FeCl_3$ to an imidazolium chloride scavenges solvated electrons and makes RTILs more stable against radiation interaction. In general, formation of molecular hydrogen in RTILs is a good indicator to judge solvent stability after γ-ray and heavy ion irradiations.[25] Comparable studies after photoexcitation would be nice to have, but have not yet been reported.

3.1. Photophysical and -Chemical Properties

In analogy to their high temperature equivalent, molten salts, photoexcitation of RTILs can lead to the solvation of excess electrons in ionic liquids. In early photo-induced investigations, two main issues have been addressed: i) where do the transient species absorb and ii) where does the excess charge come from – the cation or the anion?

3.1.1. Stationary Properties

RTILs are often colorless or light yellow. The respective absorption spectra usually show no significant bands in the visible (Vis) spectral region or, at best, a tail starting around 400 nm and extending towards the ultraviolet (UV) region (see Figure 1). The absorbance (A) is obtained through Beer-Lambert's law via $A = \log \frac{I_0}{I}$.

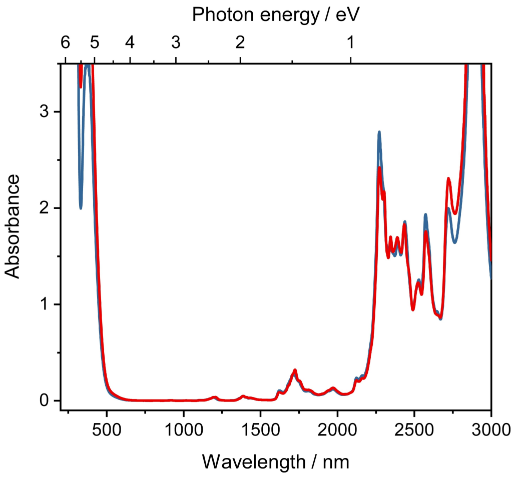


Figure 1. Absorption spectra of 1-butyl-3-methylimidazolium iodide (blue) and 1-hexyl-3-methylimidazolium iodide (red) from 200 to 3000 nm measured in 1 mm quartz glass cuvettes (Starna). The RTILs were used as received (Sigma Aldrich, grades: 99 % and $\geq$ 98 % (HPLC), respectively).

Structural aspects on a more general level were studied by FTIR spectroscopy with special emphasis on contact ion pairs, solvent-separated ion pairs[26] and hydrogen bonding[27] in imidazolium-based RTILs. As a spectral signature, they observed low vibrational frequency modes indicating intra- and intermolecular interactions.[27] By changing the anion in RTILs with imidazolium cations, the Ludwig group could show a change of interaction of ion pairs.[26] The strength of the anion-cation interaction can directly be read off from the red-shift of the OH stretching in the region between 3200 and 3600 cm^{-1} (Figure 2). This property is well-known for ethylphosphate and acetate anions in cellulose.[28] Although not that pronounced, it is interesting to note that RTILs also show such capabilities.

Applying total internal reflection IR spectroscopy and DFT calculations revealed a red-shift upon increasing alkyl chain length.[29] This is indicative of conformational isomerism and

Biographical Sketch. Julia Leier finished her studies in higher education of chemistry and mathematics in 2018 before she started her PhD work within the GRK 2039 at Karlsruhe Institute of Technology (KIT). Her research is devoted to the elucidation of competing relaxation channels of fluorescence especially in organic compounds, which are important for bio-imaging techniques using broadband femtosecond UV and visible transient absorption spectroscopy.

Biographical Sketch. Nadine Michenfelder studied chemistry on the bachelor and later on the master level at the Karlsruhe Institute of Technology (KIT) and started her PhD project under the supervision of Dr. A.-N. Unterreiner in October 2017. Her research field primarily addresses charge (de-) localization of inorganic cluster compounds in solution environments applying femtosecond broadband spectroscopy from the UV to the NIR spectral region.

Biographical Sketch. Dr. Andreas-Neil Unterreiner. After studying chemistry (diploma 1995) he graduated with a Dr. rer. nat. degree from the University of Karlsruhe (TH) in 1998 on constructing two table-top femtosecond laser systems from scratch and experimental work on ammoniated and hydrated electrons. He continued to couple femtosecond laser spectroscopy with confocal microscopy during his postdoc stay at the University of Chicago. Since 2001, he has been an independent group leader at the University of Karlsruhe (TH, "habilitation" in 2006) and later at the Karlsruhe Institute of Technology (KIT). In all his research projects, priority has been given to elucidate fundamental and elementary steps of molecular systems after photoexcitation mostly in the liquid phase and in collaboration with many other research groups.

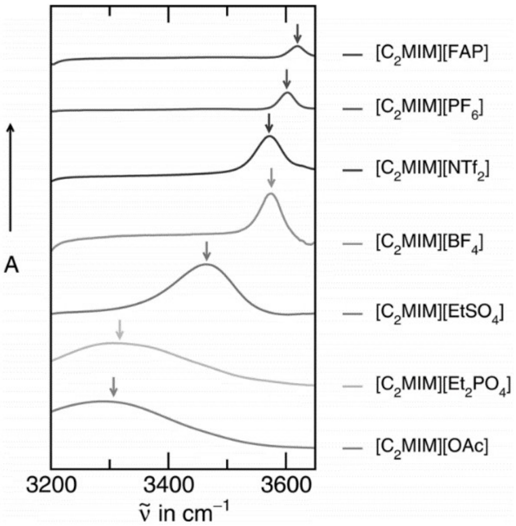


Figure 2. Absorption spectra of imidazolium-based ILs. Changing the anion demonstrates the interaction strengths observable in the OH stretching region. Hereby, 1-ethyl-2-methylimizadolium (C_2MIM) serves as cation, whereas the anions are tris(pentafluoroethyl)trifluorophosphate (FAP^-), hexaflurophosphate (PF_6^-), bis[(trifluoromethyl) sulfonyl]imide (NTf_2^-), tetrafluoroborate (BF_4^-), ethylsulfate ($EtSO_4^-$), diethylphosphate ($Et_2PO_4^-$) and acetate (OAc^-). The absorption (A) is in arbitrary units. Reproduced (slightly adapted) from Ref. 26 with permission. Copyright 2014 by Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

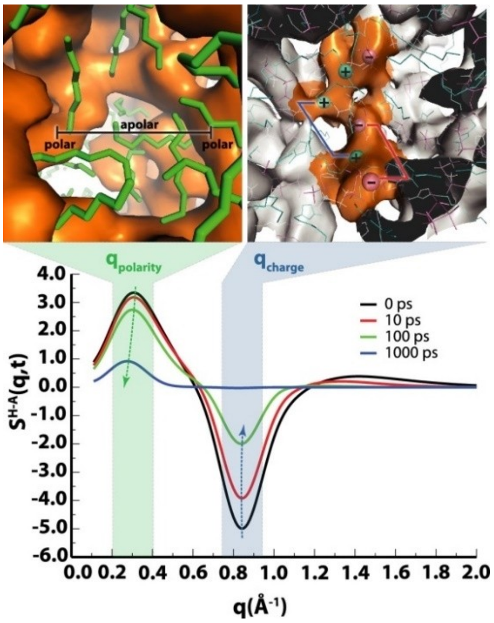


Figure 3. Structural characterization of the heterogeneity within RTILs, highlighting the behaviour of the cation and anion. Also, the liquid structural pattern – positive-negative charge and polar-apolar alternations – with voids between the ion pairs is being portrayed. Reproduced from Ref. 41 with permission. Copyright 2020 by American Chemical Society (ACS). Further permissions related to the material excerpted should be directed to the ACS.

also for the interaction between the alkyl chain with the anion, in this case chloride. Interestingly, the dynamic after photoexcitation does not dependent on the length of the alkyl chain in imidazolium-based ILs.[30]

Apparently, fluorescence spectroscopy – in terms of spectral shape and quantum yield – is very sensitive to structure of RTILs while stationary absorption spectroscopy is rather unaltered.[31]

3.1.2. Structural Peculiarities

Many studies showed that preformed cavities in RTILs are much less favored by the excess electrons and therefore less existent than in conventional solvents, like water.[15,32–36] It was also found that these excess electrons exhibited different structures and dynamics within both solvent classes.[32] Margulis et al.[36] found via simulations that the distribution of such cavities was similar within the studied RTILs. Those could be long-living and large,[36] with a size of 0.1–1 nm.[37]

Furthermore, not only does the interaction of different charged ions affect the properties of ILs. Interactions due to hydrogen bonds between ions of the same charge can control the boundary laver friction at an RTIL-mica interface. Therefore, it can have an impact on various applications, electrochemistry[7,38,39] and physical properties like enthalpies. Especially the enthalpy of vaporization is influenced by hydrogen bonds in hydroxyl-functionalized RTILs.[40]

The heterogeneity within RTILs can be further categorized into polar-apolar and positive-negative charged parts, whereas both parts are alternating through the RTIL (see Figure 3). Voids are detectable between the ion pairs.[41] This cavity seems to have an influence in charge transfer reactions by the ability to transport ions, especially protons, into this void.[42]

Diffusion of radical ions in short and long alkyl chains studied by magnetic field effects combined with ns laser flash photolysis showed no effect of the alkyl chains on the dynamics.[43] In contrast, the authors observed an influence of viscosity that favors a different value for microviscosity compared to macroviscosity. Such magnetic field investigations can be quite successful in revealing properties of RTILs as the same group demonstrated before, by elucidating nanoscale heterogeneous structures in a propylammonium-based RTIL.[44]

Time-resolved EPR studies[45] and MD simulations[46] addressed heterogeneities in RTILs, which is another important topic of this class of solvents. As excitation wavelengths are usually available from higher harmonics from ns Nd:YAG lasers, additional chromophores such as fullerenes have to be added to RTILs such as imidazolium tetrafluoroborates. To circumvent the low solubility issue of C_{60}, phenyl-C_{61} butyric acid methyl ester (PCBM) or alternatively, ZnTPP,[47] were used as probes. In frozen RTILs, this resulted in the detection of two microenvironments between temperatures from 100 to 200 K. Segregation of polar and non-polar in RTILs can be traced back to the existence of internal pressure and cohesive density energy, which are comparable to molten salts.[48]

Another aspect of elucidating structural details of RTILs on a molecular level comes from dielectric spectroscopy in the MHz and GHz frequency range.[49] Alkyl chain length dependent studies demonstrated the existence of polar but also non-polar domains, which lead to additional intramolecular reorientation in alkylammonium formates.[50] The large influence of symmetry of anions on the dielectric constant in protic RTILs has also been measured leading to permittivities from 10 to 85.[51]

The Cola group could show that this heterogeneity has a size dependency, which is proportional to the length of the alkyl chain. Furthermore the temperature has also a significant influence of the heterogeneity of RTILs.[52] It can have an impact on various physical properties, like the red-edge effect within the fluorescence, which is a wavelength dependent shift of the emission by red-shifting the excitation.[53]

As expected, several theoretical studies highlight the importance of electrostatistics. Interestingly, there are other aspects like electron exchange, delocalization and dispersion that needs to be considered in calculating macroscopic properties of RTILs with theoretical methods.[54] In another study,[55] dipole moment distributions showed a great sensitivity to specific ion environments. Thus, it is important to characterize locality and fluctuations defining the interaction length for each RTILs or at least for groups of similar RTILs in order to understand the underlying physics (here: static electrostatic properties/dielectric properties[56]) in order to predict properties of new RTILs by theoretical methods. Systematic screening of the cation-anion distances can be best done with scaled-charge MD simulations, which revealed significant aggregation, e.g. of alkyl chains indicating microheterogeneities, but also solvation shell determination, which is not an easily describable process in RTILs.[57] More of these studies are urgently needed for a better rational design of ionic liquid, which, on the other hand, is not the main topic of this minireview, but underlines the importance of combining theoretical and spectroscopic efforts.

3.2. Transient Species Formation with Time Dependent Detection

3.2.1. EPR Studies

Combining photoexcitation with EPR allows also the elucidation of the influence of concentration, viscosity and local structural transformation on photoinduced electron transfer (PET) between an anthraquinone derivative and trimethylamine in 1-butyl-3-methylimidazolium hexafluorophosphate.[58] Using chemically induced dynamic electron polarization (CIDEP), the authors found evidence for radical formation in PET with radical lifetimes to be longer in the RTIL compared to acetonitrile. Transient absorption spectra in the Vis spectral region up to 1 μs after photoexcitation has been interpreted as triplet state population in imidazolium-based RTILs,[59] while the longer lifetimes of these states allows new possibilities to study energy reactions from the RTIL with β-carotene.[59–61]

EPR studies in combination with absorption spectroscopy and photolysis can also be used to obtain information on hole species in pyrrolidinium- and piperidinium-based RTILs at glassy temperatures (77 K).[62] However, it is questionable whether excess species behave as in liquids under glassy conditions. Certainly, more studies would be helpful.

3.2.2. Fluorescence Studies

The description of diffusion-limited processes has been further investigated in imidazolium and phosphonium amides.[63] In this combined experimental (steady-state and time-resolved fluorescence quenching) and theoretical (MD simulations) approach it is shown that spherical diffusion-reaction models are not perfectly suited for reactions in RTILs, but that contact pairs serve to gate the electron transfer. These findings have been intensified in a subsequent study where it is shown that depending on the imidazolium cation the size of the anion led to percolation aggregation influencing physicochemical properties such as conductivity.[64]

3.2.3. Absorption Studies

3.2.3.1. Non-Linear Detection Schemes

Studying charge transfer vs. electron transfer, to be explored in chapter 3.2.3, revealed that charge transfer seemed to be too fast even when applying 3PEPS (three pulse photon echo peak-shift) to monitor ultrafast solvation dynamics on a few tens of fs time scale.[65] The authors found experimental evidence for heterogeneities of RTILs by x-ray diffraction. The influence of heterogeneous solvation on reaction rates is yet to be explored. On the other hand, vibrational energy transfer of neat imidazolium-based RTILs can be followed by fs-CARS, where typically vibrational dynamics are monitored.[66] Another powerful experimental tool, two-dimensional fs IR spectroscopy, can be used to observe dramatic viscosity increase after methylation of the strongest hydrogen bond of the thiocyanate ion within the same sort of RTILs.[67] Using this technique, one can directly "see" an activation of molecular diffusion after breaking the ion cage on a tens of ps time scale.

3.2.3.2. Linear Detection Schemes

Coming back to photoexcitation of neat RTILs, there are many more studies with linear detection schemes compared to non-linear ones that deepened our understanding of transient visible and near-infrared absorption spectra after UV excitation.[68]

The ejection of an electron from an RTIL originates from cations or anions, which is different from conventional liquids where a positive radical species remains after photodetachment. Also different from polar liquid is the fact that the excess electron in RTILs can localize on ions or in cavities resulting in different spectral signatures.[69] Calculations of the corresponding UV-Vis-NIR absorption spectrum succeeded for a pyrrolidinium dicyanamide IL (Figure 4) where photoexcitation leaves a neutral radical behind implying hole localization on the anionic nitrogen atom.[33,70]

Thus, two main mechanisms on the formation of excess electrons after photoexcitation were proposed – the excitation of the anion or the cation. Excitation of the anion (halides) in

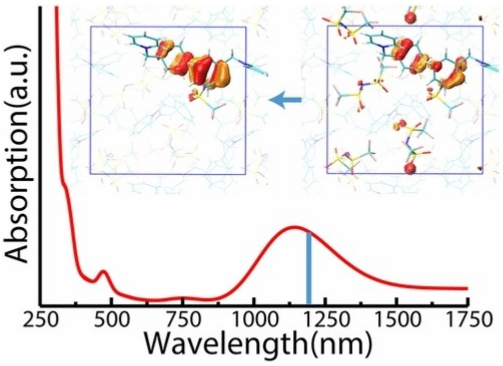


Figure 4. Calculated absorption spectrum of an excess electron in a benzylpyridinium-based IL at 7.5 ps simulation time. The NIR absorption is due to the excess electron localized in a cavity. The inset depicts a unit cell (blue box) for the periodic system with an RTIL occupied by an excess hole. Reproduced from Ref. 71 with permission. Copyright 2017 by the American Chemical Society (ACS). Further permissions related to the material excerpted should be directed to the ACS.

imidazolium-based RTILs led to generation of a halogen-electron contact pair, dissociating into solvated electrons and a halogen atom – usually iodine. This mechanism is supported by the fact that the dynamics are not affected significantly by the alkyl chain length or temperature. This proposed mechanism is contrary to the second one – the excitation of the cation. Here, a dimer-radical is formed, which is rapidly reduced by an anion nearby or an excess electron. This electron can be generated through photoexcitation, where electrons are detached, while forming dication radicals.[15]

Another important conclusion and one step further in understanding of RTILs comes from Ref. 36 where MD simulations and DFT calculations showed that the binding of an excess electron in a RTIL is similar – independent whether the cation is based on pyridinium or imidazolium – but is considerably different from other molecular solvents. One reason for this behavior is that the excess electron in an RTIL resides in the π^* orbital of the cation from where switches between localized – excess electron over one or two cations – and delocalized states occur – many more than over just two cations. Such findings can be important for a better understanding of electron solvation processes in RTILs if analogies exist to polar liquids. For example, it has been shown that the librational motions of surrounding water molecules directly interact with hydrated electrons.[72]

Interestingly, imidazolium-based RTILs with hydrophobic anions revealed that the electron localization yields a dimer radial cation with absorption bands from the Vis to the NIR region. RTILs tend to primarily localize charges as radical ions as contrary to neutral radicals. Secondary chemistry in ionized RTILs dominated in radical ion reactions.[73] Significant work on the formation of intermediate species has been performed by Wishart et al.[74] They studied photoreactions, where bromine atoms are being formed after photoexcitation that abstract hydrogen from alkyl chains of the cation. Therefore, no solvated bromine radicals in RTILs could be formed.[74]

In contrast, photodetachment of RTILs with iodide as anions leads to the formation of solvated electrons.[75,76] In subsequent reactions, iodine atoms react with iodide to form diiodide anion radicals, which is well-known for conventional liquids.[77] The corresponding reaction rate points towards a Coulomb shielding that weakens the electrostatic repulsion and is close to the diffusion-limited rate for neutral molecules.[78] The rate of the disproportionation of diiodide anions depends on the cation of the salt and increases in RTILs.[79]

A so far undiscussed issue may arise if Coulomb interaction is not the only prevailing driving force in RTILs. As pointed out by Shkrob,[80] it is impossible to accurately describe geminate recombination processes for arbitrary potentials except Coulomb interactions.

To further demonstrate the complexity of these liquids, Musat et al.[81] reported the formation of photo-products such as Br_2^-, Br_3^- and imidazolium radicals highlighting charge transfer induced reactions in an imidazolium bromide. This is in contrast to imidazolium iodides where solvated electrons have been postulated,[76,77] which can also be found in phosphonium- and imide-based RTILs.[82] Consequently, there is a difference between charge-transfer-to-solvent excitation (iodide) and charge transfer reaction (bromide).

Significant work has been devoted to early-time dynamics of RTILs after UV-photoexcitation. At very early times, i.e. before the time scale of solvent reorganization, a so-called "dry" electron (hole) can occur.[33] In more general, this is the topic of excess electron solvation in an ionic liquid[33,70] such as 1,3-dimethyl-imidazolium[34] or in 1-methylpyridinium chlorides.[35]

Studies with photons and ultrafast temporal resolution still focus on elementary processes such as electron solvation observed with fs broadband absorption spectroscopy in a propylammonium amide.[83] The time resolution of 80 fs did not allow the detection of dry electrons, but spectral shifts reflecting solvation time are unraveled from 100 fs to 1 ns delay time after 5.17 eV photoexcitation (cf. Figure 5).

Experimentally, the simultaneous observation of absorption spectra of pyrrolidinium-based RTILs in the UV and NIR region were interpreted as hole (UV) and solvated electron (NIR) to occur on a ns time scale.[84] The relatively long lifetime of the solvated electron prompted them to hypothesize the excess electron to be localized on the anion as there is no immediate reaction with the parent cation. Further studies from the same group[85] showed a decrease of solvated electron yield with decreasing temperature implying a side reaction of the initially "dry" electron prior to being fully solvated.

On the other hand, photoexcitation at 200 nm (6.2 eV) of methyl-alkyl-pyrrolidinium bis(trifluoromethylsulfonyl)amides led to the observation of solvated electrons in the NIR region.[86] The onset of the HOMO-LUMO transition is around 215 nm (5.8 eV) whereas calculations from generalized gradient approximation predict the onset of this transition red-shifted around 250 nm (5 eV; Figure 1 in Ref. [87]), which can still be considered as a satisfactory agreement. The latter work, which is a theoretical study, deserves some more concern because it differs between radiolytic and photodetached excitation schemes. This can especially be seen by the recombination rate

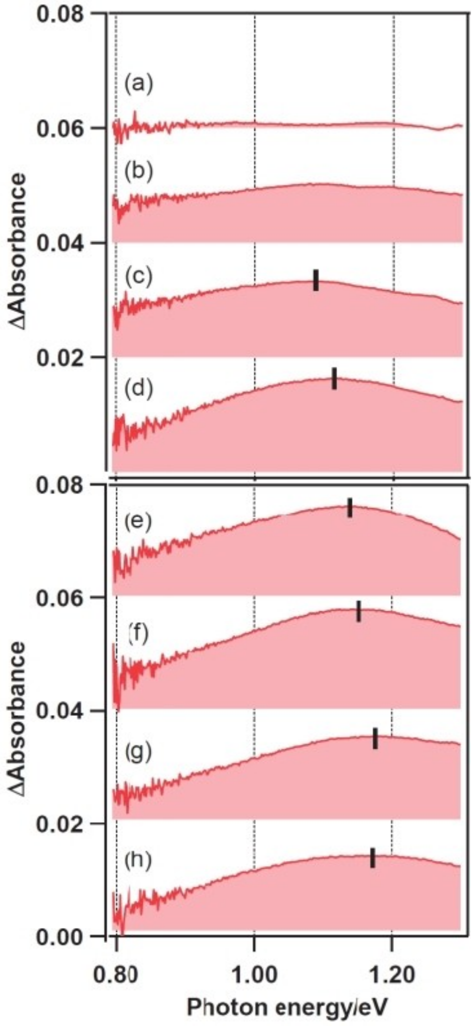


Figure 5. Transient absorption spectra of a propylammonium amide after 5.17 eV excitation. Delay times: a) −400 fs, b) 160 fs, c) 800 fs, d) 1.5 ps, e) −8.6 ps, f) 120 ps, g) 380 ps, h) 1.1 ns. Reproduced (and slightly adapted) from Ref. 83 with permission. Copyright 2019 by the Chemical Society of Japan.

because in radiolysis experiments the excess electron and the hole are usually well separated with little recombination while in photodetached systems this is clearly different where the electron and the hole can form a kind of an excitonic state that is going to relax with increasing time after photoexcitation.

Low-frequency components of RTILs, i.e. in the THz regime, can be unravelled by femtosecond Raman-induced Kerr effect spectroscopy (fs-RIKES), which has been proven to be a versatile tool to discriminate between subtle differences of pyrrolidinium- and imidazolium-based ionic liquids.[88,89] This is especially due to a larger polarizability anisotropy of imidazolium cations, which can be recorded as a considerably larger spectral density. In fs-RIKES, low-frequency spectra are obtained that reveal both translational motions (below 50 cm^{-1}). Above 50 cm^{-1}, Raman-active librational motions, which are temperature-insensitive, occur.[89]

Accompanied by additional steady-state absorption and fluorescence measurements plus time-resolved methods such as transient anisotropy and pump-probe fs- and picosecond absorption spectroscopy, they concluded that the RTILs used can be quantitatively described by diffusion-controlled processes. This is especially interesting because it brings RTILs to a more common level of understanding liquid state dynamics. For their studies, they used different imidazolium-based RTILs with water contents of several hundreds of ppm after high-temperature (80–100 °C) treatment for several hours. Whether the remaining water traces play a (catalytic) role has not yet been subject of further investigations. It should be added that this does not exclude special effects of RTILs per se, but they are difficult to unravel. In contrast, fs absorption studies of various imidazolium-based RTILs showed an influence on the formation of donor-acceptor complexes although these liquids possess a vide electrochemical windows, which implies more or less inert behavior. It remains an open question whether such results will influence the understanding of microscopic structural organization that is essential in many resonance energy transfer studies.[90–92]

If the photophysical mechanisms after photoexcitation are elucidated properly, RTILs reveal promising areas of application and properties in many research fields, like polynitrile-based RTILs as a replacement for molecular diluents.[93]

3.3. RTILs in Mixtures

3.3.1. RTILs Mixed with Water

The importance of the effect of water in RTILs has been analyzed in various studies,[29,94–97] especially for so called "bio ionic liquids".[98] This interaction hints at an ion pair separation, observable through an equal wavenumber position of the asymmetric alkyl vibration mode. Furthermore, the intensity decreases and blue-shifts with addition of water.[29] This effect can be seen in Figure 6, where the absorption band at 375 nm blue-shifts to 360 nm with the addition of water (green).

The importance of understanding the microstructure of RTILs was also the topic of a combined study using Raman spectroscopy and DFT calculations on a mixture of an imidazolium-based RTIL with water.[99] Due to red-shifts of some Raman peaks while increasing the amount of water, the authors proposed some kind of self-encapsulation of the RTIL as further supported by DFT calculations, i.e. formation of clusters of ion pair dimers that proved to be more geometrically stable compared to hydrated single ion pairs.

A series of studies combining optical heterodyne detected optical Kerr effect (OHD-OKE) measurements and fluorescence depolarization proved the distinction of RTILs from simple organic liquids especially after addition of even small amounts of water.[100–103]

Finally, various studies revealed that addition of water to RTILs can alter the properties for their application. Even small amounts of water could reduce the electrochemical properties of electrolytes, also if they are used as solvents for electrocatalysis.[104]

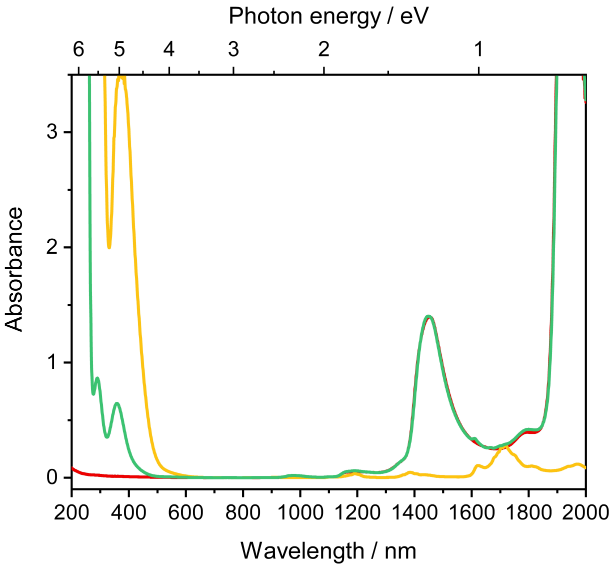


Figure 6. Absorption spectra of 1-butyl-3-methylimidazolium iodide (yellow), diluted with water (green) and pure water (red) measured in 1 mm quartz glass cuvettes (Starna). The RTILs were used as received (Sigma Aldrich, grade 99 %).

3.3.2. RTILs Mixed with Other Solvents

Studying the influence of cosolvents in RTILs revealed that the solvation and rotational relaxation time of coumarin 153 in those cosolvents decreased gradually in contrast to neat RTILs. The latter decreased more with addition of water compared to the same amount of alcohol.[105] Furthermore, it could be shown that the addition of methanol or isopropanol to this dissolved coumarin dye in a RTIL does not influence the photophysical properties, namely absorption and emission profiles. In contrast, the addition of water resulted in a red shift of both spectra. Hence, the mixture of RTILs with conventional solvents can tune the physicochemical properties, leading to a wider field of application.[106]

Further studies analyzed the dynamics in microemulsions of RTIL/triton/benzene after photoexcitation.[107,108] These studies unraveled an increase of FRET contribution (~1 ps) with the addition of water in a rhodamine dye.[107] Dissolved pyranine undergoes an ultrafast excited state proton transfer. With addition of water, an additional slow rise could be observed suggesting trapped water around the palisade layer of the RTIL microemulsion, which influences the relaxation dynamic.[108]

3.4. RTILs as Solvents in Photochemical Reactions

Further studies on charge transport showed the difference of RTILs to conventional electrolyte solutions.[109] Slower diffusion of smaller anions compared with large cations, were reported over a wide range of temperatures, i.e. formation of a strongly repulsive glass by the anions – termed arrested states.[110]

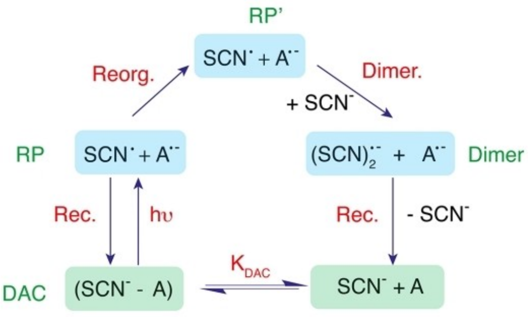
To reveal the effect of the environment of RTILs in contrast to other solvents, dynamics of dissolved compounds in RTILs need to be analyzed. To characterize the dynamics and the frontier molecular orbitals involved in electron reactions, a dissolved transition metal complex $[Ru(bpy)_3]^{2+}$ was investigated by Aziz et al.,[111] where a charge transfer from the S_1 to the ^{1}MLCT occurs. Other groups also used dissolved dyes in RTILs to characterize rotational diffusion.[112,113] A donor-donor excitation transfer of 9-phenylanthracene in octylimidazolium chloride can be best described by a nanostructure RTIL, i.e. by a distribution of spheres to represent the nanostructured hydrophobic regions.[114] The importance of nanostructuring in RTILs has also been highlighted by Pereiro et al.[115]

Nevertheless, the influence of solvents in general remains an issue because it is often neglected or not well understood in chemical processes. In three studies, the Vauthey group investigated the influence of RTILs on bimolecular reactions and electron transfer processes.[116–118] For example, one studied bimolecular reaction comprised the reaction of 3-cyanoperylene whose fluorescence was quenched upon electron transfer from N,N-dimethylaniline. To follow the fluorescence over several orders from the fs to the μs regime they used fluorescence up-conversion and time-correlated single-photon counting (TCSPC).

The influence of RTILs on bimolecular reactions after photoexcitation is displayed in Scheme 1 in terms of a simplified photocycle of SCN^--A. The addition of organic electron acceptors to RTILs leads to a charge transfer due to a donor-acceptor-complex-formation between the anion of the RTIL and the electron acceptor. This is (one of) the reason(s) why RTILs can actively participate in photochemical reactions.[117]

Studies of RTILs can also help to improve our understanding of concentrated electrolytes, which is a challenging and complex topic.[119]

Dynamics at metal/RTIL interfaces have been studied via two-photon photoemission spectroscopy (TPPE). The electron solvation seemed to be interface-specific with a time range of 350 fs on an Ag-surface, where the injected excess electrons are lingering.[120] The influence of anions in RTILs[121] was analysed by Endres et al.[122] via AFM and PES. They detected a strong influence on the metal/RTIL interface due the interactions of cation and anion, which alter the structure of the RTIL.



Scheme 1. Simplified representation of a photocyle of a donor-acceptor complex upon charge transfer excitation at 400 nm in thiocyanate (SCN^-)-based RTILs and electron acceptors (A). Reproduced from Ref. 117. Copyright 2018 by the American Chemical Society (ACS). Further permissions related to the material excerpted should be directed to the ACS.

Table 1. A selection of formed species after photoexcitation of RTILs. The excitation of the cation or anion resulted in different species, inter alia a dication C^{2+}, dimer-cation radicals $C_2^{+\bullet}$, excess electron e^-_{excess}, solvated electron e^-_{solv}, halogenid-electron contact pair ($X{:}e^-$) or imidazolium radical Im^- could occur. Furthermore, diimidazolium radical cation $Im_2^{+\bullet}$ or species after not specified excitation can originate from an electron transfer ET, a charge transfer CT or a charge transfer to solvent CTTS.

Excitation	Formed species
Cation	C^{2+}, $C_2^{+\bullet}$,($X{:}e^-$), $e^-_{solv,}$ e^-_{excess}
Anion	($X{:}e^-$), e^-_{solv}, X^-, Br_2^-, Br_3^-, I_2^-, I, I_2, $SCN^\bullet$, $SCN^{-\bullet}$, $(SCN)_2^{-\bullet}$, $Im^\bullet$, dry e^- (holes)
Not specified	$Im_2^{+\bullet}$, pyrrolidinium dicyanamide neutral radical, ion dimer pairs, donor-acceptor-complex, ET, CT, CTTS, excitonic state

3.5. RTILs Towards Applications

At this point, it is time to underline the importance of such fundamental studies in terms of application. For example, charge transfer in battery devices will inevitably lead to transient species where a careful characterization can contribute to higher efficiency. Recent advances in developing batteries beyond lithium-containing systems highlight reversible, i.e. rechargeable, conversion mechanisms of aluminum-chalcogenide batteries with a thiourea-$AlCl_3$ electrolyte. While this is not an ionic liquid, it is inspired by the large electrochemical window of the reference compound, an imidazolium chloride-based RTIL, but with less side effects, e.g. the reaction of the RTIL cation with chalcogenides under electrochemical conditions.[123]

As a brief summary one can conclude that the electronic properties are nowadays understood on a quantitative level, but small influences of the ligand sphere are still difficult to be elucidated.

In this minireview, we showed that various species can be formed after photoexciting RTILs. A brief selection is given in Table 1. The formed species depend on cation or anion excitation of the RTILs, but its quantitative understanding is yet to be explored.

4. Outlook

All these studies demonstrate that it is of utmost importance to synthesize well-defined and clean RTILs. Nevertheless, even under very clean conditions, influences of the RTILs on reaction partners and/or the formation of transient species are possible – especially when working with light-induced conditions. Consequently, purity of RTILs in photo-induced studies should always be checked carefully, before and after reactions. Shallow yellowish coloring can be indicative of side reactions that may influence the desired reactions.

Independent from this issue, it remains an open question how the number of excitation photons influences the appearance of transient species. Results from thoroughly studied solvated electrons in polar liquids like ammonia[124,125] or water[126,127] indicate such dependencies. Thus, charge localization in RTILs is not as equally well understood as, for example, in water.[128] The overall understanding of photo-excited RTILs would greatly benefit from such studies under well-defined conditions.

Another aspect of future challenges concerns the initiation of photo-induced chemical reactions in ionic liquids. In this respect, it will be necessary to quantify the formed species after photoexcitation, their role in photochemical reactions as well as the influence of heterogeneities on photophysical properties and quantum yields of transient species. At the current stage of knowledge, this is far away from what is usually possible in thermally initiated chemistry, most contributions in this special issue will report on. In contrast, there exist some studies concentrating on interactions of molecules in RTILs,[129] more specifically of photo-induced reactions, e.g. the photolytic behavior of naphthoquinone in a pyridinium-based RTIL[130] or the photo-induced reduction of methylene blue in BMIMCl.[131] As methylene blue shows distinct absorption spectra depending on the oxidation state, this reaction could be nicely followed by absorption spectroscopy at 280–370 nm excitation wavelengths where the oxidized form shows pronounced absorption. Especially excitation at 350 nm suggests electron transfer from the solvent to the reagent, but there is still a long way to go for elucidating the reaction mechanism in detail. Another example of interest for new synthetic strategies could be particle aggregation in water/RTIL mixtures on a sub-micron length scale, in one known case of polystyrene latex particles.[132]

The next years should bring together the different experimental results outlined in this minireview. While one must admit that certain aspects have already been combined like the interplay between theory and spectroscopy, this is a rather conventional approach long known for many other systems. What is needed for a quantitative understanding are new combinations. Maybe more systematic studies of photoexcited RTILs with varying ligands would also be helpful – e.g. in terms of careful selection of anions and cations with respect to ion pair interaction and hydrogen bridging capabilities. This would also further challenge advanced pictures of solvent cavities of simple species like the excess electron.

To explore the important question how radiolysis and photoexcitation with UV light leads to different excited state population and relaxation pathways, studies with varying excitation wavelengths and intensities (including higher photo-excited processes) are necessary. This could also advance the knowledge of (geminate) recombination in RTILs by investigating transient absorption spectra obtained on largely extended time scales (e.g. from fs to µs) in greater detail.

In summary, RTILs remain what they were from the very beginning: a fascinating class of solvent with many variation potentials introducing new and often unknown properties. Photo-induced processes of and in these liquids will certainly continue to play an important role in current and future developments in different areas such as photocatalysis,[11,133] photo-induced polymerization[134] or water capturing from air by RTILs for photocatalytic H_2 generation.[135]

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: ionic liquids · photoexcitation · photochemical intermediates · solvated electrons · time-resolved investigations

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