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Raman Wavelength Conversions in Ionic Liquids

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Abstract: We explored the use of room-temperature ionic liquids (ILs) as Raman wavelength converters. ILs provide an engineerable framework to design suitable liquids for wavelength conversions over a broad spectral range, through careful selection of the molecular structures of the IL anions and cations so that specific characteristics can be obtained, such as a desirable Raman shift, low Brillouin scattering and good optical transmission in the pump and Stokes wavelengths. Applying such criteria, we demonstrated that 1-ethyl-3-methylimidazolium dicyanamide (EMIM DCA) is an effective medium for conversion of 532 nm pulses from a Q-switched Nd:YAG laser to 603 nm. This corresponds to a ~2200 cm^{-1} shift, which can be used to generate mid-infrared (MIR) radiation through subsequent difference frequency generation (DFG) for optical pumping of CO_2 lasers. Threefold-higher Raman conversion efficiency was obtained in EMIM DCA compared to water under identical conditions in a proof-of-principle, single-pass conversion setup, resulting in an efficient generation of multi-mJ, <6 ns duration, high-quality orange laser pulses, in a wavelength region that is difficult to access at high energies. Consequently, we examined ILs representing two other classes of Raman-active functional groups and obtained conversion up to the fifth-order Stokes shift and first anti-Stokes shift. Through the tunable selection of their components and their useful dynamical properties, ILs provide a platform for efficient, simple, and alignment-tolerant high-energy Raman shifting with numerous industrial and technological applications.

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I. Introduction

Efficient, high energy (> few mJ), short pulse (~ few ns, ps or fs scale) laser sources only exist in a limited number of wavelengths. If an application requires a wavelength that cannot be produced directly from a laser, a wavelength conversion method is needed, typically in the form of a nonlinear optical process [1], and even then, some spectral regions are not easily accessible. One example of such a region is the yellow-orange spectral range (570-625 nm) that is of particular interest for medical applications [2] in dermatology [3,4], ophthalmology [5], and flow cytometry [6], among others. In addition, if one could obtain an efficient pulsed orange laser source, coherent MIR radiation for optical pumping of CO_2 lasers could be generated through difference frequency generation (DFG) from green light. For these reasons, finding new techniques to convert light from existing laser sources into this spectral range is appealing.

Stimulated Raman Scattering (SRS) [1,7] is an efficient method of obtaining high-energy laser pulses at wavelengths that are otherwise hard to generate, by wavelength shifting of an available pump source in a Raman-active media. SRS is stimulated inelastic scattering of photons from a coherently excited state of the system, and it can be achieved in any state of matter, including solids, liquids, and gases [8]. In molecular SRS, the pump wavelength is converted into Stokes and anti-Stokes wavelengths that are shifted by the dominant bond vibration frequency, $\omega_R = \omega_L \pm N_R \omega_v$, where $\omega_p, \omega_L, \omega_v$ are the pump, Raman and vibration frequencies, respectively and N_R is the shift order in case of a cascade process. In other words, the shifts are defined by the molecular normal vibration modes, which are determined by the chemical and isotopic structure of the molecule.

While it may appear simple at first, the process of SRS in molecules is rather complex and different models and assumptions can capture different aspects of it. A comprehensive review can be found in ref [9], the essentials will be discussed next. By considering the effective Hamiltonian of an ensemble of molecules with a vibrational degree of freedom interacting with a non-resonant laser electric field and performing a steady state second-quantized analysis considering only the first mode ($N_R = 1, \omega_R = \omega_S = \omega_P - \omega_v$), we can derive the Stokes photons generation rate:

$$\frac{dn_s}{dt} = N \frac{\partial \alpha}{\partial q} \frac{4\pi^3}{\mu_L \mu_S^2 mc} I_L \sum_{\mathrm{k_S}} \frac{\omega_S}{\omega_v} (\overrightarrow{\boldsymbol{e_L}} \cdot \overrightarrow{\boldsymbol{e_S}})^2 (1 + n_S + n_v) \delta(\omega_S - \omega_L + \omega_v) \quad (1)$$

Where N is the number density of molecules in volume V, $\partial \alpha / \partial q$ is the normal-mode derivative of the molecular polarizability tensor with q being the normal mode amplitude and m the reduced mass, μ_L and μ_S are the permeabilities at the pump and Stokes wavelength, respectively, $I_L = (\hbar \omega_L c / \mu_L V) \Sigma_{\mathrm{k_L}} n_L$ is the pump laser intensity, $\overrightarrow{\boldsymbol{e_L}}, \overrightarrow{\boldsymbol{e_S}}$ are the linear polarization vectors of the pump and Stokes, respectively, n_L, n_S, n_v are the occupation numbers of the pump, Stokes and molecular vibration modes, the summations are over all the laser ($\mathrm{k_L}$) and Stokes (k_S) modes, c is the speed of light and δ is Kronker's delta. From the middle parentheses we can see the contributions of spontaneous emission, stimulated emission, and parametric coupling of the Stokes light and material excitation, respectively. However, for moderate pumping, the contribution of n_v is generally negligible and its population is on the order of its thermal equilibrium value $n_v \sim (\exp(\hbar\omega_v/kT) - 1)^{-1}$. This is also the reason for the typical lower intensity of the anti-Stokes emission compared to Stokes, as most of the molecules are in the vibrationally ground state at room temperature. The vector product in eq. 1 is responsible for the polarization of the Stokes being generally the same as the pump. Furthermore, we can define the differential cross section for the spontaneous Raman ($n_S, n_v \approx 0$, assuming $\overrightarrow{\boldsymbol{e_L}} \cdot \overrightarrow{\boldsymbol{e_S}} = 1$):

$$\frac{\partial\sigma}{\partial\Omega} = \left(\frac{\partial\alpha}{\partial q}\right)^2 \frac{\omega_S^4 \mu_S}{c^4 \mu_L} \frac{\hbar}{2m\omega_v} \tag{2}$$

And by assuming a narrow laser line and homogeneous broadening of the molecular transition, we can derive the Raman gain for the stimulated case:

$$g(\omega_S) = N \left(\frac{\partial\alpha}{\partial q}\right)^2 \frac{4\pi^2 \omega_S}{\mu_L \mu_S c^2 m \omega_v} \frac{\Gamma}{(\omega_S - \omega_L + \omega_v)^2 + \Gamma^2} \tag{3}$$

Where $\Gamma = 1/\mathrm{T}_2$ is the linewidth associated with the dephasing time (T_2, not to be mistaken with the excited state lifetime T_1) of the system. It should be noted that in most cases the driving laser field frequency is far from resonance with the electronic states of the molecule so, $\partial\alpha / \partial q$ can be treated as a constant. Another notable feature is the asymmetry between backward and forward SRS, favoring the latter, and that is mainly because of asymmetry in the Doppler line broadening [10]. While the full quantum mechanical approach shows the origin of SRS and its buildup from spontaneous noise, it is only valid in steady state and the occupation number formalism does not provide any information on the phases. Phase information can be obtained from semiclassical analysis of the density matrix evolution by solving the Liouville equation. We also note that for the 3-dimensional case, spatiotemporal effects play a major role, and current models did not fully reproduce the Stokes buildup profile that was observed in experiments (see, for example, the supplementary material of ref [11]).

In the short-pulse regime, high conversion efficiency can be achieved with a pump-pulse duration that is longer than the vibration dephasing time (typically on the order of a few picoseconds) and a multi-pass [12] or cavity [13,14] configuration can be used to increase the interaction length. Of particular interest is the fact that any chirp in the pump pulse is maintained in the Raman-shifted pulses [15,16], so broadband, temporally-stretched pump pulses can be used and the output pulses can be compressed later to ultrafast durations. In this application, chirped pump pulses from a conventional chirped pulse amplification system can be wavelength shifted and subsequently recompressed in a standard compressor to provide temporally synchronized, spectrally distinct source that can be used as a probe, seed, or beatwave generator for two color laser-plasma experiments. For example, a detuned probe can be useful for example for high energy density physics experiments with solid targets that produce significant high/sub harmonics of the pump light.

Notable practical challenges in SRS conversion include forward and backward SRS, high-order Stokes and anti-Stokes generation, self-focusing/de-focusing, transient effects, stimulated Brillouin scattering (SBS), optical breakdown, and self-phase modulation so the physical and thermal properties of the medium play a crucial role in the overall achievable conversion efficiency in addition to the inherent Raman gain.

Solids offer high densities of Raman active centers, high damage thresholds and allow shorter interaction lengths, while the shift frequency is determined by the characteristic phonon frequencies and may depend on crystal orientation [8,14–19]. Typical shift frequencies are in the range of ~700-1300 cm^{-1} and conversion efficiencies of >70% have been observed. However, design and fabrication of large crystals for particular shift frequencies is complex and expensive. In comparison, SRS in gases can provide higher-frequency shifts [17], for example 4155 cm^{-1} in H_2, due to scattering from higher-frequency single molecule vibrations, but the lower densities reduce the conversion efficiency, even at high pressure. Gas-filled hollow core fibers [18–22] have been used to extend the interaction length to achieve high power in continuous wave operation, lower the SRS energy threshold at pulsed operation, and to achieve overall higher efficiency. Gases also present higher thresholds for self-focusing and lower scattering losses compared to solids or liquids.

Liquids offer somewhat of a mid-way regime, with higher density of Raman scattering centers compared to gases while still maintaining the single-molecule Raman shift. Ganot *et. al.* [11] reported up to 35% conversion efficiency from 532 nm to 649 nm (~3400 cm^{-1}) in liquid water, limited mostly due to thermal effects, absorption and competing Brillouin scattering [11,23,24]. Self-guiding in filaments was shown to increase efficiency to ~60% [25] while even higher efficiency, 80%, was obtained in liquid molecular nitrogen [26]. By using aqueous sodium nitrate solution, Raman shifts to 564 nm and 599 nm were observed due to first- and second-order Stokes shifts from the nitrate ions [31]. In this case, the higher Raman cross-section of the nitrate ion outcompeted the solvent water. Welch *et. al.* [27], described a two-step scheme, Raman followed by DFG, that was used to generate long-wave infrared (LWIR) pulses. Deuterated benzene was used as a Raman medium to convert 1064 nm pulses from a mode-locked Nd:YAG laser to 1180 nm. The residual pump and the generated Stokes were then frequency-differentiated in a nonlinear GaSe crystal to generate 10.6 µm pulses, which correspond to the Raman shift of 944 cm^{-1}.

However, efficiency was low because the pump laser duration was on the order of the Raman dephasing time.

Here, we propose the use of room-temperature ionic liquids (ILs), synthetic salts that are liquid at ambient temperature, as Raman wavelength converters. These liquids can be "designed" to have a given set of properties because they can be prepared in an infinite variety of combinations. While the use of ILs as solvents [28,29], electrolytes [30,31], lubricants [32–34], and many other applications [35–37] have been extensively explored for years, there is no substantial prior work about their applicability as nonlinear optical materials. Many ILs have wide optical transmission windows and they are typically chemically stable. The viscosities of ILs are higher than most molecular liquids, which help suppress the buildup of competing Brillouin scattering since the Brillouin gain [38–40], $g_B = \gamma^2/(n_P^3 c\eta)$ scales inversely with viscosity, η, and γ is the electrostrictive coefficient. In particular, the specific structure of the liquid can be chosen in a way to provide a desired Raman shift with transparency at the pump and Stokes wavelengths.

II. Results and discussion

A. Tailoring an Ionic Liquid for a Specific Raman Wavelength Shift. In this work, we focused on finding a suitable liquid for spectral shifting of the second harmonic (532 nm) of a Q-switched Nd:YAG laser by ~2200 cm^{-1}. This shift corresponds roughly to a 4.5 µm photon that can be generated down the line by DFG of the Stokes and residual pump and can be used for optical pumping of high-pressure mixed isotope CO_2 lasers [41–43] by directly exciting the upper laser level via broadband vibrational transition $00^00 \rightarrow 00^10$ transition centered at 4.3 µm. Optical pumping is expected to enable the operation of CO2 laser amplifiers at very high pressures (>10 bar) and high CO2 concentrations (>10%). Such operation regime not achievable with gas-discharge pumping is beneficial for (sub)picosecond long-wave infrared laser systems [41,44,45]. Some detuning from this frequency (~2325 cm^{-1}) is needed to better manage the absorption in the CO_2, so either lower or higher shifts within the bandwidth of this transition are preferable. For that goal, the selection process was as follows: (1) the liquid needs to have a dominant peak in the Raman spectrum around ~2200 cm^{-1}. (2) the liquid should have good transmission in the pump and Stokes wavelengths, i.e., 532 nm and ~600 nm for Nd:YAG second-harmonic pumping, or 1064 nm and ~1390 nm for Nd:YAG fundamental pumping. In addition, the liquid should be chemically stable, have high enough viscosity to suppress Brillouin scattering, and have a low thermo-optical coefficient to minimize thermal effects.

We began by seeking ILs with the desired Raman shift of ~2200 cm^{-1}. Raman spectra were acquired with a confocal Raman microscope (Witec Alpha) equipped with a 532 nm excitation laser. A single drop of a sample liquid was placed on a microscope slide and covered with a slip. Selected Raman spectra are presented in Fig. 1(a). The desired Raman characteristics can be designed into the IL by using anions containing nitrile groups (C-N triple bonds) that have intense Raman bands in the region of 2190-2230 cm^{-1}. Examples include the dicyanamide (DCA, $[N(CN)_2]^-$), tricyanomethanide (TCM, $[C(CN)_3]^-$), and tetracyanoborate (TCB, $[B(CN)_4]^-$) anions.

The next important criterion is high optical transmission at the pump and shift wavelengths, in this case based on the Nd:YAG fundamental and second harmonic, 1064 and 532 nm. Transmission spectra of representative ILs, measured using a PerkinElmer Lambda 950 UV/Vis/NIR spectrophotometer, are shown in Fig. 1(b). While the ILs generally have clear transmission windows at 532 nm and its Stokes-shift region, shifts derived from 1064 nm may fall into a region where the IL absorbs. Absorption in the ~1400 nm region is primarily due to overtones of C-H stretching bands in the aliphatic regions of the cations. To minimize that absorption, the best IL cations for shifting 1064 nm would be those with the smallest numbers of aliphatic C-H bonds. Examples are aromatic (imidazolium or pyridinium) cations with the shortest aliphatic side chains that still form room-temperature ILs (e.g. 1-ethyl-3-methylimidazolium, or EMIM) or have aromatic side chains (e.g., 1-benzylpyridinium, or BzPy) since aromatic C-H bond overtones absorb in another, less important region. Based on the optical transmission and Raman spectra, we picked EMIM DCA as the first candidate for the wavelength conversion studies.

For complete description of the relevant optical properties, we also measured the refractive index of EMIM DCA, both as a function of wavelength and temperature, as presented in Figs. 1(c) and 1(d), respectively. Refractive indices were measured using an Atago DR-M2 1550 refractometer equipped with an infrared viewer, a thermo-electrically-driven liquid chiller/heater for sample temperature control, and a set of bandpass filters. The refractive index exhibits an inflection point around 1200 nm, consistent with the absorption peak at that region. This can be understood directly from the Kramers–Kronig relations that relate the real and imaginary components of the refractive index. In particular, this variation is important when operating with pump and Stokes wavelengths that are close to, and on opposing sides of an absorption peak, a situation that is unusual in nonlinear optics but possible with ILs. It is worthwhile to note that the extended optical transmission windows of ILs could be used for refractive-index-matched cooling of laser gain media [46] in the near infrared, in particular, when considering their good thermal conductivity and heat capacity [47–49]. From the temperature dependence of the refractive index, we deduced the thermo-optical coefficient to be $\sim -3.5 \times 10^{-4}\, K^{-1}$, which is conveniently negative for our purposes and comparable in magnitude to liquid water.

B. High-Energy Wavelength Conversion. To evaluate the applicability of ILs as Raman converters at high energies, we assembled a simple convertor setup and compared the performance of EMIM DCA vs. liquid water under identical conditions. The setup is depicted in Fig. 2. 532 nm, 9.8 ns laser pulses, with energies up to 115mJ, from a frequency-doubled Nd:YAG laser at 12 Hz repetition rate were used. We adjusted the input energy using a λ/2 waveplate and a thin-film polarizer to keep other laser parameters such as beam profile and pulse duration identical during energy scans. The p-polarized pump beam was focused using a 50 cm lens and sent for a single pass through a 63 cm-long cell filled with liquid (water or EMIM DCA) and capped with 5 mm-thick sapphire windows. Our experimental conditions were below the threshold for optical breakdown in both liquids. Back-reflection and Brillouin scattering were monitored by a wedged fused-silica pickoff window and an energy meter. After recollimation using a second 50 cm lens, we imaged the reflection off a second wedge pickoff using a CCD camera and a removable notch filter to observe the pump and Stokes beam profiles. An equilateral prism was used to separate the pump and Stokes beams, and each beam was measured using a dedicated energy meter. The pump and Stokes temporal profiles were recorded using two fast photodiodes (2 GHz bandwidth) and an oscilloscope (500 MHz bandwidth), and the spectra were obtained using a fiber-coupled spectrometer (Ocean Insight FLAME-S-XR1-ES).

The conversion efficiencies from pump to first Stokes as a function of pump pulse energy for water and EMIM DCA are presented in Fig. 3(a). This efficiency is defined as $E_{Stokes}/(\beta E_{pump})$, where E_{pump}, E_{Stokes} and β are the pump pulse input energy, Stokes pulse energy, and the optical transmission of the setup without a liquid as was measured with an empty cell. The energies were recorded after thermal stabilization, which occurred after ~10 sec from the moment of turning the pump on, and averaged over 120 shots. It should be noted that Raman output actually dropped during this thermal stabilization from an initially ~30% higher value. EMIM DCA showed a lower pump threshold for the initiation of Raman conversion and noticeably higher efficiency, up to ~38%. It also proved to be resistant and pure enough to avoid electrical breakdown and plasma generation, and no discoloration or deterioration was observed after the experiment. Brillouin back-scattering efficiencies, defined as the excess back-reflected signal on top of reflection from the optics, are shown in Fig. 3(b). As expected, the higher viscosity of EMIM DCA, 14.5 mPa•s at 25 °C [50], resulted in a negligible Brillouin signal.

We observed the spectrum of the emitted light after the IL converter by pointing the tip of the spectrometer's collection fiber at a screen that was placed in the path of the beams. The measured spectra are shown if Fig. 3(c). Note that the relative intensities of the peaks depend on the orientation of the collection tip and do not represent the actual relative intensities, which have been accurately measured with energy meters. For water, we observed the expected first Stokes peak at 652 nm, corresponding to a Raman shift of 3460 cm^{-1}, while EMIM DCA showed both first- and second-order Stokes peaks at 603 nm and 695 nm, corresponding to a Raman shift of 2200 cm^{-1}. This implies a higher Raman cross-section for EMIM DCA compared to water. Nevertheless, the actual energy at the second Stokes peak was lower than the measurement threshold of our energy meters. In addition, if conversion to the next order becomes a limiting factor, one could conceivably mix in a small concentration of a solute having absorption around the second Stokes frequency to prevent its buildup.

The oscilloscope traces of the pump and Stokes pulses are presented in Fig 3(d). As expected, due to the nonlinear process, the Stokes pulse was shortened by 40% compared to the pump, 5.9 ns compared to 9.8 ns, respectively. Similarly, the beam profile of the Stokes beam also showed improvement over the pump as can be seen in Figs. 3(e) and 3(f). It appears that the nonlinear process effectively conditioned the multimode structure of the pump, resulting in a noticeably narrower beam that is closer to a single-mode profile.

Finally, to evaluate the durability of EMIM DCA in this application, we compared a post-experiment sample of the liquid with an unused one. We were looking for evidence of any breakdown- or heat-induced decomposition products [51–53]. However, the before-and-after UV/Vis (taken with Agilent Cary 60 spectrometer) and fluorescence spectra (measured with Horiba Fluorlog-QM fluorometer), compared in Figs. 3(g) and 3(h), respectively, show no measurable degradation of the liquid over the duration of the experiment, approximately 4 hours at a 12 Hz repetition rate. Additional operation of more than 16 hours showed no decrease in conversion efficiency.

It should be noted that our experimental setup was not optimized for maximal efficiency in any way: the cell length and diameter were chosen arbitrarily based on experience with water. None of the optics were coated, resulting in significant losses that can be easily reduced with properly anti-reflective parts, and proper wavelength separation can better be done with a dichroic mirror rather a prism. For MIR generation through DFG, pumping with the 1064 nm Nd:YAG fundamental would be preferable to reduce the quantum defect. However, under our experimental conditions we did not observe Raman shifting of the Nd:YAG fundamental because the absorption of EMIM DCA at the Stokes wavelength of 1390 nm was found to be too high. The fact that the liquid did not damage even at high pumping energies suggest that the absorption at 1064 nm is low, since any significant absorption would have resulted in optical damage.

While dye lasers can also operate in the yellow-orange range, IL based Raman converter has several advantages [54–56]: comparable efficiency can be achieved in a single pass configuration without the need for a cavity for wavelength selection and linewidth narrowing. ILs do not exhibit triplet state absorption at the signal wavelength and are easier to handle compared to laser dyes which are often toxic, carcinogenic or corrosive. More generally, the non-resonant nature of SRS is insensitive to the wavelength pump source compared to in-band pumping of dye lasers which can be useful for conversion from and to the NIR or when only fine detuning from the pump is needed. Like laser dyes, the liquid in an IL converter can be circulated for heat management. One drawback of SRS is that it cannot provide the on-the-fly tunability of dye lasers as the generated signal is set by the pump and the specific IL that are being used.

C. Tunability Considerations. The above demonstration is only one example of the wide variety of Raman shifting options possible with ionic liquids. While we had a specific application in mind for targeting ILs that would provide a Stokes shift of ~2200 cm^{-1}, the tunability of ionic liquids allows for a variety of possible Stokes shifts by selection of anions and cations with specific intense Raman bands. Fig. 1(a) suggests that there are several non-nitrile ILs with strong Raman bands that could be used for shifting to other wavelengths. (It is important to remember that the spectra in Fig. 1(a) are arbitrarily scaled, so we are focusing on Raman bands that are more intense than the C-H stretching manifold between 2800 – 3200 cm^{-1}, which can be used as a rough reference for relative scaling.) For example, aryl groups generally have strong Raman bands in the region of 1000-1100 nm. In Fig. 1(a), 1-butylpyridinium bis(trifluoromethylsulfonyl)amide (BuPy NTf$_2$) shows a strong Raman band at 1029 cm^{-1} for the pyridinium ring, and aryl-functionalized 1-benzylpyridinium bis(trifluoromethylsulfonyl)amide (BzPy NTf$_2$) and 1-benzylpyridinium bis(fluorosulfonyl)amide (BzPy FSA) show strong Raman bands at 1020 and 1036 cm^{-1}, for the benzyl and pyridinium rings, respectively. Thus, pyridinium ILs or ILs containing benzyl functionalities could be used to shift a 532 nm laser beam to ~563 nm for the first Stokes shift and ~597 nm for the second one. Likewise, the NTf$_2$ anion that is used in a large number of ionic liquids has a strong Raman signal for the anion breathing mode [57] in the 740 – 750 cm^{-1} range, depending on the IL, that could shift 532 nm to ~554 and ~578 nm, respectively, for the first and second Stokes shifts.

To assess the Raman-shifting potential of ionic liquids containing NTf$_2$ anions or aryl groups, we performed Raman shifting experiments on 1-butyl-1-methylpyrrolidinium NTf$_2$ (P$_{1,4}$ NTf$_2$) and 1-butylpyridinium NTf$_2$ (BuPy NTf$_2$) in the same optical configuration used for EMIM DCA. The resulting spectra are shown in Fig. 4. Both ILs show a strong response, with P$_{1,4}$ NTf$_2$ displaying Stokes shifts up to fifth order and one anti-Stokes shift, with intervals of ~740 cm^{-1}. BuPy NTf$_2$ produced Stokes shifts up to fourth order and one anti-Stokes shift, with intervals of ~1033 cm^{-1}. Despite the presence of the NTf$_2$ anion in BuPy NTf$_2$, which contributes a strong Raman band at 740 cm^{-1}, the stronger pyridinium ring vibration at ~1033 cm^{-1} determines the observed Raman shifting. This has excellent implications for practical use since the NTf$_2$ anion is very commonly used in ILs for its inertness and its tendency to form ILs with desirable physical properties. This experiment shows that the NTf$_2$ anion can serve as a “silent partner” to provide desirable liquid properties when paired with an IL cation selected specifically for its Raman shifting qualities.

Other ILs that we did not test could also be effective for Raman shifting. For example, the thiocyanate anion (SCN$^-$) in 1-butyl-3-methylimidazolium SCN has a nitrile-centered Raman band [58] at

2040 cm^{-1} that could shift 532 nm laser light to ~597 and ~680 nm for the first and second Stokes signals, respectively. Given that nitrate ions proved effective in aqueous solution, nitrate ILs might work well. However, nitrate ILs with aprotic cations like EMIM tend to be solid at room temperature, and protic ILs with cations such as ethylammonium ($CH_3CH_2NH_3^+$) are relatively volatile because they can dissociate to the free amine (RNH_2) and nitric acid when heated. In addition, the nitrate anion is a strong oxidant and IL cations contain fuel-like hydrocarbon groups, which is not a good combination in high-power laser applications. Since we have demonstrated that aryl groups such as pyridinium cations effectively produce the same Raman shifts, the multiple complications of nitrate ILs would seem to render them unnecessary for Raman shifting applications.

Physically, shift tunability can be thought of as an adjustment of the oscillator frequency $\omega_v = \sqrt{k/m}$ in a simple oscillator model by either adjusting the reduced mass (m, ions involved or isotopic substitution) or the effective force constant (k, type of chemical bond). Compared to solids, ILs allow greater freedom since they operate via molecular vibrational modes rather than collective phonons, and the desired vibrational modes can be designed into the molecules by the inclusion by the inclusion of specific structural motifs. This is readily applicable for generation of high-energy laser radiation at wavelengths of interest where no good direct source is available, such as in our example with orange light, especially with shifts above the typical phonon energy in solids (> ~1300 cm^{-1}) or when a specific shift is needed. Another use is generation of MIR/LWIR by performing an additional step of frequency differentiation of the Raman shifted light with the spent pump, which is our original motivation for this study. This also applies to shifting broadband ultrafast pulses that are stretched to more than a few ps, for example when a detuned, red-shifted probe is needed, a Raman-shifted portion can be generated from the main beam and can be used either in its chirped or fully compressed form. Thinking further ahead, the high refractive indices and low SBS of ILs make them interesting candidates to be incorporated into hollow-core core fibers, where their nonlinear properties could be exploited. Furthermore, if a suitable liquid can be found, it is intriguing to explore the possibility of generating mid-IR light directly in a single Raman shifting step by pumping with one of the emerging, highly efficient short-wave infrared (SWIR) sources such as Thulium-doped Yttrium Lithium Fluoride (Tm: YLF) [59] In the quantum mechanical picture, the Raman process can be understood as an absorption of the pump photon in a virtual state followed by stimulated emission of a Stokes photon. This intermediate short lived virtual state is allowed due to Heisenberg energy-time uncertainty principle. Typically, with a visible or NIR pump, this virtual state gains its short but finite lifetime from the probability tails of the excited electronic states with energies comparable to ~UV photons. When using a longer wavelength pump, the virtual state gets further away from these excited electronic states and its lifetime gets shorter leading to a decrease in cross section that scales like λ^{-4}. However, it would be interesting to test whether this scaling is valid at longer wavelengths or there is rather a change of trend in cross section when the virtual state nears the upper probability tails of molecular vibrational states and overtones, which are typically comparable to mid-IR photon energies.

III. Conclusion

This work has demonstrated that ionic liquids perform well as Raman wavelength converters. Our method allows efficient wavelength conversion of existing laser systems by simply passing the beam through a Raman conversion cell filled with a specifically tailored IL and with no sensitive alignment or phase-matching tuning. We provide examples how to select an appropriate IL for a given conversion application by considering the chemical bonds that are responsible for the dominant Raman shift and optical absorption. As proof of principle, we demonstrated and characterized a high-energy IL-based, single-pass Raman converter from 532 nm to 603 nm, and showed the superior performance compared to liquid water. We have shown that different ILs can be selected to efficiently provide other wavelength conversions, based on their chemical composition. More generally, we demonstrated the concept of using ILs as a nonlinear optical media by showing that they can provide an engineerable framework to allow a wide range of wavelength shifts. We anticipate that this method could allow flexible and convenient generation of high energy laser radiation in spectral regions that are useful for various scientific and medical applications but are challenging to attain with other techniques.

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Competing Interests

The authors declare no competing interests.

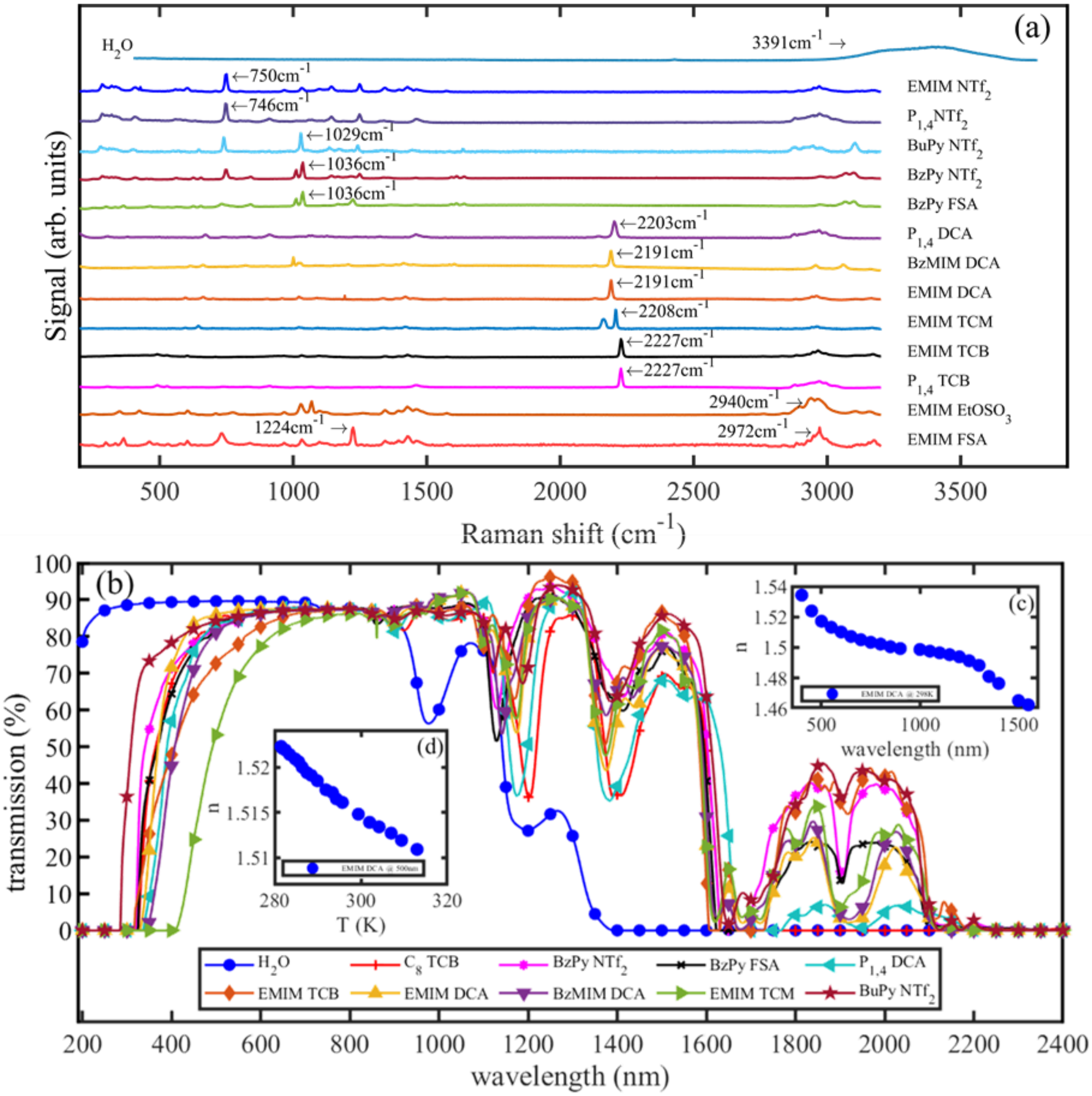

Figure 1. (Color online) Spectroscopic measurements of various ionic liquids. (a) Spontaneous Raman spectra of the surveyed ionic liquids. The dominant Raman peak for each liquid is marked with an arrow. (b) Transmission spectra of various ILs showing extended transmission into the infrared compared to water. Note that the spectra are not corrected for Fresnel losses. (The sample of EMIM TCM used contained a colored contaminant that is responsible for the lower transmittance in the UV, but the focus is on the NIR.) (c) Refractive index of EMIM DCA as a function of wavelength at 298 K (d) refractive index of EMIM DCA at 500 nm as a function of temperature. Abbreviations: 1) Cations: EMIM = 1-ethyl-3-methylimidazolium, $P_{1,4}$ = 1-butyl-1-methylpyrrolidinium, BzMIM = 1-benzyl-3-methylimidazolium, BzPy = 1-benzylpyridinium; 2) Anions: NTf_2 = bis(trifluoromethylsulfonyl)amide, FSA = bis(fluorosulfonyl)amide, DCA = dicyanamide, TCM = tricyanomethanide, TCB = tetracyanoborate,

$EtOSO_3$ = ethylsulfate. The ILs reported here were all used as received or synthesized. $P_{1,4}$ NTf_2, $P_{1,4}$ DCA, BzMIM DCA, EMIM DCA and EMIM TCM were purchased from IoLiTec (Ionic Liquids Technologies GmbH, Heilbronn, Germany). EMIM TCB and $P_{1,4}$ TCB were purchased from EMD Chemicals. EMIM $EtOSO_3$ was a commercial sample from Solvent Innovations. EMIM NTf_2 [60], BzPy FSA, BzPy NTf_2 [61], and EMIM FSA [62] were prepared in our laboratory.

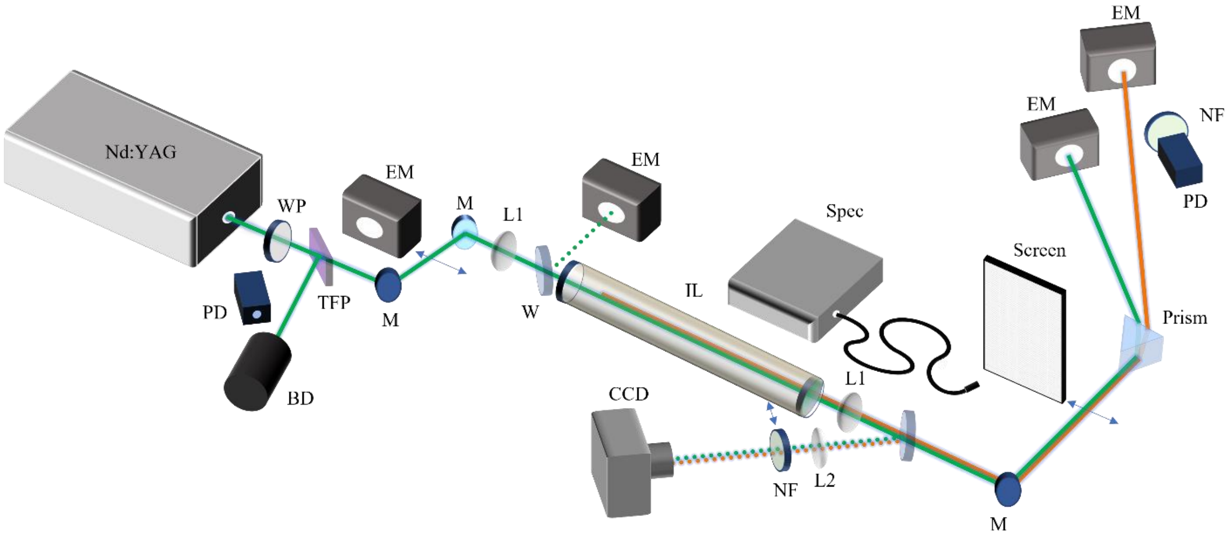

Figure 2. (Color online) Illustration of the experimental setup: The pump source was a frequency doubled Nd:YAG laser at 532 nm. We regulated a p-polarized transmitted pump energy by a λ/2 waveplate (WP) and a thin film polarizer (TFP) while a reflected s-polarized component has been sent to a beam dump (BD). The input pulse shape and energy were monitored with a fast photodiode (PD) and an energy meter (EM). The pump was focused and recollimated using a pair of 50 cm focal length lenses (L1). Back reflection and scattering were monitored using a wedged fused silica window (W) and an energy meter. Within the telescope, the pump passed through a 63 cm-long stainless-steel cell capped with 5 mm thick sapphire windows and filled with EMIM DCA (IL). At the cell's output, we observed the profile of the pump or Stokes beam using the reflection from a wedge (W) that was focused to a CCD camera using a 15 cm focal length lens (L2) through a removable notch filter (NF). The pump and Stokes beams were separated by an equilateral prism and sent to two energy meters. The Stokes temporal profile was monitored by a second fast photodiode equipped with a notch filter. The spectrum after the cell was acquired using a fiber-coupled spectrometer (Spec) with the fiber tip pointing to a screen that was inserted into the beam path.

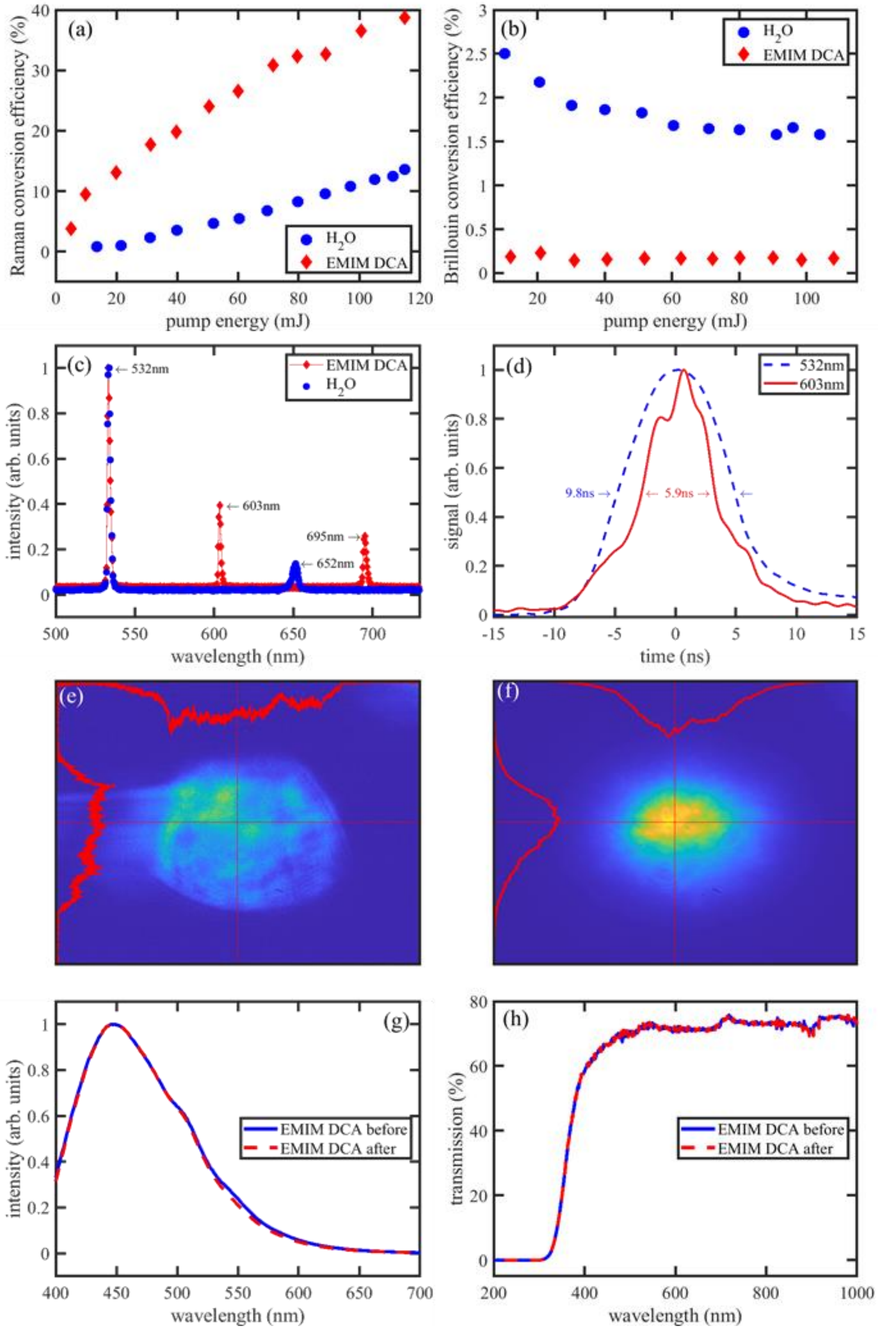

Figure 3. (Color online) Characterization of high-energy water and EMIM DCA Raman converters. (a) Conversion efficiency to the first Stokes order, defined as the ratio of first Stokes energy over pump energy and adjusted for optical losses in the optics except the liquid itself. EMIM DCA showed lower threshold energy and higher conversion efficiency than water (b) Backward Brillouin scattering efficiency, defined as the ratio of excess backward signal (on top of reflection from the optics) over pump energy. The Brillouin scattering from EMIM DCA was negligible due to the high viscosity of the IL. (c) Optical spectrum after the converter. Note that the intensity of each peak depends on the orientation of the collection fiber tip and

does not represent the actual intensity ratios. (d) Pump and Stokes temporal profiles (averaged over 300 shots) showing temporal shortening of the Stokes pulses. (e) and (f) Profiles of the pump and Stokes beams, respectively at the output of the converter at 25 mJ pump energy. The Stokes profile shows significant effective spatial cleaning of the multimode pump profile. Comparison of (g) UV/Vis transmission spectra and (h) fluorescence spectra of a post-experiment EMIM DCA sample with an unused one showed no degradation of the liquid.

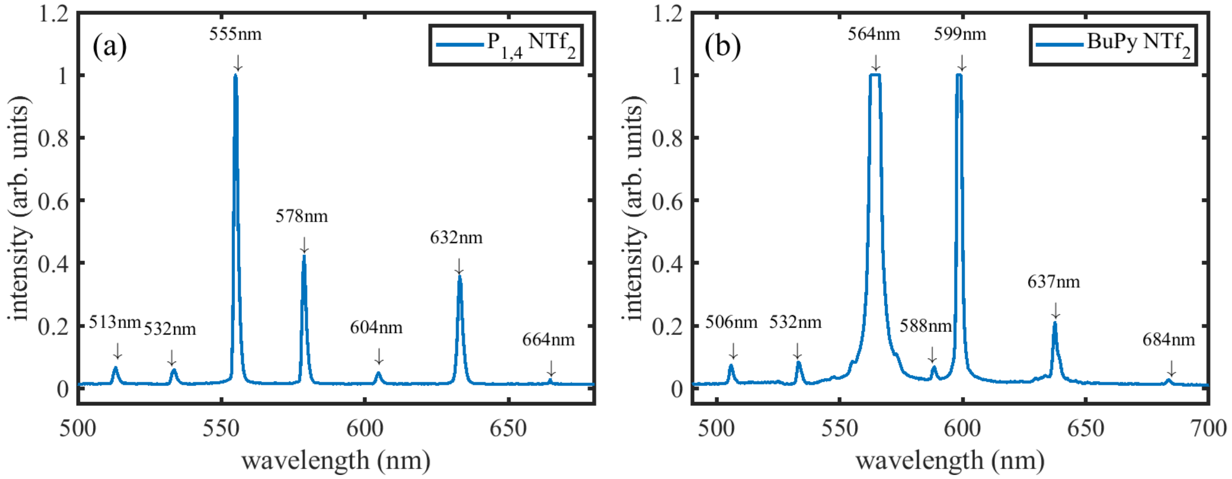

Figure 4. Raman-shifting spectra of (a) $P_{1,4}$ NTf$_2$ and (b) BuPy NTf$_2$ with the pump wavelength attenuated by a 532nm notch filter showing anti-Stokes and high order Stokes conversions. Note that the intensity of each peak depends on the orientation of the collection fiber tip and does not represent the actual intensity ratios.

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