Terahertz Dynamics of Ionic Liquids from a Combined Dielectric Relaxation, Terahertz, and Optical Kerr Effect Study: Evidence for Mesoscopic Aggregation

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ABSTRACT

To exploit the great potential of room-temperature ionic liquids (RTILs) as solvents that offer both low environmental impact and product selectivity, an understanding of the liquid structure, the microscopic dynamics, and the way in which the pertinent macroscopic properties, such as viscosity, thermal conductivity, ionic diffusion, and solvation dynamics depend on these properties, is essential. We have measured the intermolecular dynamics of the 1,3-dialkylimidazolium-based RTILs [emim][BF_4], [emim][DCA], and [bmim][DCA], at 25 °C from below 1 GHz to 10 THz by ultrafast optical Kerr effect (OKE) spectroscopy and dielectric relaxation spectroscopy (DRS) augmented by time-domain terahertz and far-infrared FTIR spectroscopy. This concerted approach allows a more detailed analysis to be made of the relatively featureless terahertz region, where the higher frequency diffusional modes are strongly overlapped with librations and intermolecular vibrations. In the terahertz region, the signal-to-noise ratio of the OKE spectra is particularly high and the data show that there is a greater number of librational and intermolecular vibrational modes than previously detected. Of greatest interest though, is an intense low frequency (sub-alpha) relaxation that we show is in strong accordance with recent simulations that observe mesoscopic structure arising from aggregates or clusters; structure that explains the anomalous and inconveniently-high viscosities of these liquids.

Terahertz spectroscopy, dielectric relaxation spectroscopy, Kerr spectroscopy, room-temperature ionic liquids

1   INTRODUCTION

To exploit the potential of room-temperature ionic liquids (RTILs) an understanding of the liquid structure, the microscopic dynamics, and the way in which the macroscopic properties depend on these properties, is essential [1, 2]. For the widely studied RTILs based on the imidazolium cation, these properties can be optimized by functionalizing the imidazolium ring as well as by choice of anion [3-5]. The high viscosity of most RTILs would be a drawback in many applications and an understanding of the interactions and structure of these liquids is therefore of paramount interest. The structure of a neat RTIL is largely determined by a combination of long-range Coulombic forces, hydrogen-bonding interactions, and packing factors. Computer simulations have long predicted the emergence of mesoscopic structure in RTILs [6-13] but this has been difficult to verify experimentally [14]. Recent small-angle x-ray scattering experiments and light scattering experiments have indicated the presence of structure in RTILs [15]. Here we discuss the application of MHz to THz dielectric and Raman spectroscopies that demonstrate the presence of mesoscopic clusters in RTILs. This

work demonstrates the power of combining multiple spectroscopies to disentangle broad and relatively featureless spectra in the terahertz frequency domain,

There are many spectroscopic techniques to study the structure and dynamics of liquids including Brillouin light and X-ray scattering, inelastic neutron scattering (INS), dielectric relaxation, Raman spectroscopy, *etc*. Most of these techniques measure a two-point correlation function of some kind, such as that of the dipole moment, polarisability, or position [16]. A typical spectrum in the terahertz range is shown in Fig. 1 and consists of many overlapping bands. In molecular liquids, there are vibrations and librations at the highest frequencies (a few THz), diffusional rotational motions at the lowest frequencies (MHz–GHz), and incoherent cage rattling motions at intermediate frequencies [17-19]. This makes meaningful analysis very difficult.
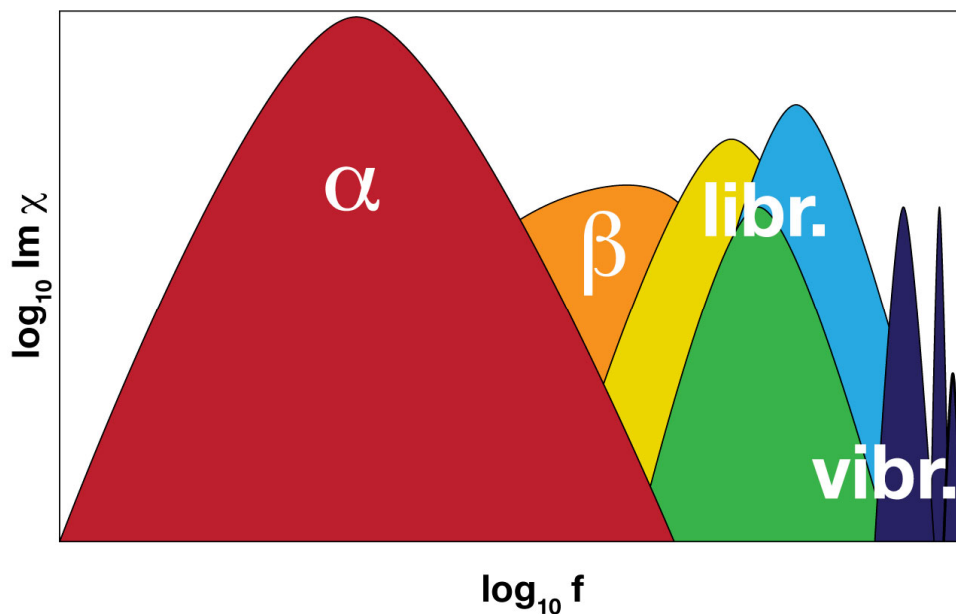
Fig. 1. *A typical terahertz-frequency spectrum of a molecular liquid consists of several overlapping broad bands. The fundamental structural α relaxation at low frequency is accompanied by an unresolved β relaxation. At higher frequencies, additional processes including librations and low-frequency intramolecular vibrational modes occur. In this study, an intense band below the α relaxation (the sub-α mode) is also observed in the optical Kerr-effect spectrum.*

In this work, two complementary spectroscopic techniques that measure a two-point correlation function are used: dielectric relaxation (DR) and the optical Kerr effect (OKE). **DR** measures the $<\mu\mu(t)>$ correlation function of the (collective) dipole moment. Through our collaboration, we have been able to measure DR spectra over an extended frequency range: Regensburg & Murdoch (0.2 - 89 GHz), Freiburg (0.1 - 3 THz), and Strathclyde (1 - 20 THz). This uses classic dielectric relaxation spectroscopy, terahertz time-domain spectroscopy (THz-TDS), and Fourier-transform infrared (FTIR) spectroscopy [19, 20]. The full DR spectrum is reconstructed by patching using the Kramers-Kronig transform. **OKE** measures the $<\alpha_{xy}\alpha_{xy}(t)>$ correlation function of the anisotropic part of the polarisability tensor directly in the time domain [17, 21-24]. In our set-up using a laser producing 20-fs pulses, delays from 10 fs to 4 ns can be achieved corresponding to the effective frequency range 250 MHz to ~50 THz.

Both OKE and DR spectroscopies are mostly sensitive to rotational motions and only weakly sensitive to translations through the collision-induced response [19, 25]. The two techniques are complementary for intramolecular modes (as Raman- or IR-active vibrations) but this is not the case at lower frequencies where the modes are typically delocalized and arise from the cooperative motions of multiple molecules. Therefore, the measured dynamics will be in many respects similar, with the two techniques generally measuring the same modes with different intensities [16]. Consequently, comparison of the DR and OKE spectra allows one to analyze the broad overlapping modes in a meaningful way. A specific difference between the two techniques arises for the special case of isotropic single molecule

diffusional rotations for which the OKE relaxation time constant is typically three times smaller than the DR relaxation time constant.

RTILs have been widely studied experimentally by spectroscopic techniques. Raman and optical Kerr-effect (OKE) spectroscopy have been able to access the relatively high frequency region from ~0.1 to 10 THz. [26-28] The sub-THz region, corresponding to intermolecular modes, has been investigated by terahertz time-domain spectroscopy [29, 30], dielectric relaxation spectroscopy (DRS) [31-37], and OKE spectroscopy [3, 5, 26, 38-45]. In general, DRS is limited to a maximum frequency of about 100 GHz whereas the spectra of most RTILs are continuous up to several THz. Time-domain terahertz spectroscopy is generally limited to the range 0.1-3 THz where the spectra tend to be extremely featureless [30]. Coverage of the entire spectral region is therefore crucial for an accurate analysis of even the low frequency relaxational modes. Here we have supplemented DRS by both time-domain terahertz spectroscopy and Fourier transform far-infrared spectroscopy to give an overall coverage from about 400 MHz to more than 10 THz. We have then combined these measurements with OKE spectra, which cover this frequency range in a single measurement and provide excellent signal-to-noise ratios in the terahertz region. Therefore, where previous spectroscopic studies of RTILs in the gigahertz to terahertz region have concentrated on either the low frequency structural relaxation modes or the higher frequency region where librational modes appear, we can fit the entire intermolecular spectrum with good precision.

We have applied this approach to a small cross-section of RTILs based on the 1,3-dialkylimidazolium ion: 1-*N*-ethyl-3-*N*-methylimidazolium dicyanamide ([emim][DCA]), 1-*N*-butyl-3-*N*-methylimidazolium dicyanamide ([bmim][DCA]), and 1-*N*-ethyl-3-*N*-methylimidazolium tetrafluoroborate ([emim][BF$_4$]). A common model can describe the measured dynamics while the comparison of the DR and OKE spectra allows the identification of motions due to the presence of the mesoscopic structure that has been predicted for some RTILs by molecular dynamics computer simulations.

2   INTERPRETATION OF THE INTERMOLECULAR SPECTRUM

It has been shown previously that a simple model of relaxation can be applied to the low-frequency spectra of *molecular* liquids [46]. In this model, the α relaxation – the fundamental structural relaxation representing the decay of correlation over the greatest spatial and temporal scales – is described, as a function of angular frequency, by the Debye function, $S_D(\omega) = (1 + i\omega\tau)^{-1}$, corresponding to an exponential decay with time constant τ in the time domain. Typically, the α relaxation is accompanied by a higher frequency β relaxation associated with molecular "rattling-in-a-cage" or diffusional cage-constrained motions [25, 47]. The β relaxation is generally inhomogeneously broadened by the large-scale fluctuations associated with the α relaxation and can be modeled by the Cole-Cole function

$$S_{CC}(\omega) = \frac{1}{1 + (i\omega\tau)^\beta}, (0 < \beta < 1),\qquad(1)$$

where the exponent β acts as a broadening parameter. Because the α relaxation imposes an upper limit on the lifetime of the inhomogeneity of the β relaxation (*i.e.*, the components of the β relaxation cannot be slower than the structural α relaxation), the β relaxation is terminated such that it evolves into a Debye relaxation at times $t \geq \tau_\alpha$ where τ_α is the time constant of the α relaxation [46]. To take into account the inertial response of the system to an impulse, the Debye-like functions can also be terminated at high frequency, enabling the relaxational modes to rise at a rate consistent with librational motions. The modified Debye function can then be written as [46, 47]

$$S_D'(\omega) = \frac{1}{1 + i\omega\tau} - \frac{1}{1 + (i\omega + \gamma_{\text{LIB}})\tau},\qquad(2)$$

where γ_{LIB} is the inertial rise rate. Similarly, the Cole-Cole function modified by both the inertial rise and α termination becomes [46, 47]

$$S_{CC}'(\omega) = \frac{1}{1 + ((i\omega + 1/\tau_\alpha)\tau)^\beta} - \frac{1}{1 + ((i\omega + \gamma_{\text{LIB}} + 1/\tau_\alpha)\tau)^\beta}.\qquad(3)$$

The Cole-Cole function is often described as a distribution of Debye functions. These two modifications then simply impose physically reasonable upper and lower limits on the distribution without changing its fundamental character.

At higher frequencies, typically up to a few terahertz, modes appear that include librations and low-frequency intramolecular modes. Generally it is found that these modes can be satisfactorily fit by the Brownian (damped-harmonic) oscillator function [16, 23]

$$S_B(\omega) = \frac{\omega_0^2}{\omega_0^2 - \omega(\omega + i\gamma_B)},$$
(4)

where ω_0 is the resonant (undamped) angular frequency and γ_B the damping rate. In some cases, the Gaussian oscillator, which is generally defined as

$$\text{Im}\left[S_G(\omega)\right] = \exp\left[-\frac{(\omega - \omega_0)^2}{\gamma_G^2}\right] - \exp\left[-\frac{(\omega + \omega_0)^2}{\gamma_G^2}\right]$$
(5)

provides a better fit. The Gaussian lineshape is generally interpreted as inhomogeneity of the mode although linear spectroscopies such as OKE and DR cannot explicitly distinguish homogeneous and inhomogeneous line-broadening mechanisms. For less-simple molecular liquids, supramolecular structure or domains may give rise to one or more additional relaxation modes that are slower than, and consequently broaden, the single-molecule relaxations. We refer to such a process as a sub-α mode.

3   MATERIALS AND METHODS

[bmim][DCA] was prepared from purified reactants as described in previously while [emim][BF$_4$] and [emim][DCA] were obtained from Iolitec [45]. All samples were dried under vacuum and stored in a nitrogen-filled glove box while all measurements were conducted under a dry atmosphere.

Broadband dielectric spectra were obtained by a combination of data from a frequency-domain reflectometer using a Hewlett-Packard 85070M dielectric probe system based on a vector network analyzer (VNA) at 0.2 to 20 GHz, two waveguide interferometers (IFMs) at 27 to 89 GHz, and a transmission/reflection terahertz time-domain spectrometer (THz-TDS) at 0.3 to 3 THz [19]. Raw VNA data were corrected for calibration errors with a Padé approximation. For selected samples, two further IFMs at 8.5 to 17.5 GHz were used to crosscheck the reliability of the VNA results and showed excellent agreement, within the precision of the instruments. The far-IR data were recorded from 0.9 to 12 THz on a Bruker Vertex 70 FTIR spectrometer with the liquids held between a pair of polymethylpentene (TPX) windows with a path length of 20 μm. An average of about 4000 scans was taken for each sample and a background spectrum taken from the windows alone was subtracted. Complex permittivity spectra were then derived by Kramers-Kronig transformation.

The quantity measured in DRS is the total complex dielectric response $\ddot{\eta}(\omega)$ which is related to the permittivity $\ddot{\varepsilon}(\omega)$ by $\ddot{\eta}(\omega) = \ddot{\varepsilon}(\omega) - i\kappa/(\omega\varepsilon_0)$, where κ is the dc conductivity, and ε_0 the permittivity of free space. At low frequencies, $\ddot{\eta}/\ddot{\varepsilon}$ is the limiting factor and determines the minimum accessible frequency [19]. At the high frequency limit of this work, the value of ε' has become almost constant, and ε'' has declined almost to zero, so that all intermolecular terahertz modes are well defined within the spectral range. The composite DR spectra were resampled to evenly-spaced logarithmic frequencies before fitting in order to give an equal weighting across the whole spectrum. This ensures that the two wings of a symmetrical function, such as a Debye or Cole-Cole, are weighted equally. As a measure of fit quality, the reduced error function χ^2 was simultaneously summed for ε' and ε''.

The OKE technique is well established and our experiment has been described previously [45-47]. A Coherent Mira-SEED Ti:sapphire oscillator provided 8 nJ ~20 fs pulses at a repetition rate of 76 MHz. After pre-compensation for group-velocity dispersion in a *homosil* prism pair, the beam was split into (90%) pump and (10%) probe beams. A high-speed optical delay line (Newport IMS600LM) in the pump beam path controlled the pump-probe relative delay with sub-fs resolution. The two beams were then co-focused by a 10-cm-focal-length achromatic lens into the sample. The

transmitted probe beam was recollimated and then analysed by the combination of an achromatic quarter-wave retarder, Wollaston prism, and balanced photodiode detector which measure the ellipticity of the polarisation of the beam induced by the transient birefringence of the sample (optical-heterodyne detection). The optical material in each beam was equalised in order to match the optical dispersion.

In this setup, where, with balanced detection, the probe intensity is nulled, the principal sources of noise are due to fluctuations that cause transient unbalancing of the detector. Fluctuations in the path of the probe beam are minimised by using beam tubes, but a second stronger noise source was found to be small wavelength fluctuations from the laser, which unbalance the analyser via chromaticity in the quarter-wave plate. These were removed by employing a Fresnel "rhomb" as the quarter-wave retarder. This optic inconveniently introduces a beam displacement, but it is inherently achromatic. In addition, fluctuations and drift in the signal intensity can be significantly reduced by ensuring that the pump and probe beams undergo an equivalent set of reflections before the sample, thus stabilising the overlap of the two beams. To this end, the corner-cube retroreflector employed on the delay stage is matched by a similar optic in the probe beam. To minimise spurious signals from scattered pump light, both pump and probe beams were mechanically chopped at rates of *ca*. 3 kHz in the ratio of 5:7 with lock-in demodulation at the difference frequency. Chopping the probe beam normally introduces transient out-of-balance signals and to minimise these, and to allow high modulation rates, each chopper was placed at the focus of a 1:1 (f = 16 cm) telescope.

The OKE data are fit in the time domain on linear scales where the noise in the data is normally distributed. However, to allow the use of the Cole-Cole function, which has no time-domain analytical form, and reconvolution of the fit, the fit function was generated in the frequency domain and fit through a Fourier transform. All measurements were conducted at 25.0° C.

4   RESULTS AND ANALYSIS

Fig. 2 shows the imaginary part of the DR spectrum and the deconvoluted frequency-domain OKE signal for [emim][DCA] while the data for the other RTILs are shown elsewhere [36, 45]. The apparently featureless region extending from *ca*. 30 GHz up to *ca*. 4 THz is shown by simulations to be comprised of cage-rattling motions consisting of librational modes. The high signal-to-noise ratio of the OKE data and the comparison of the OKE and DR spectra provide very critical tests. The Gaussian oscillator, Eq. (5), is found to describe best the highly asymmetric high-frequency onset at *ca*. 3 THz. At higher frequencies multiple underdamped intramolecular modes occur.
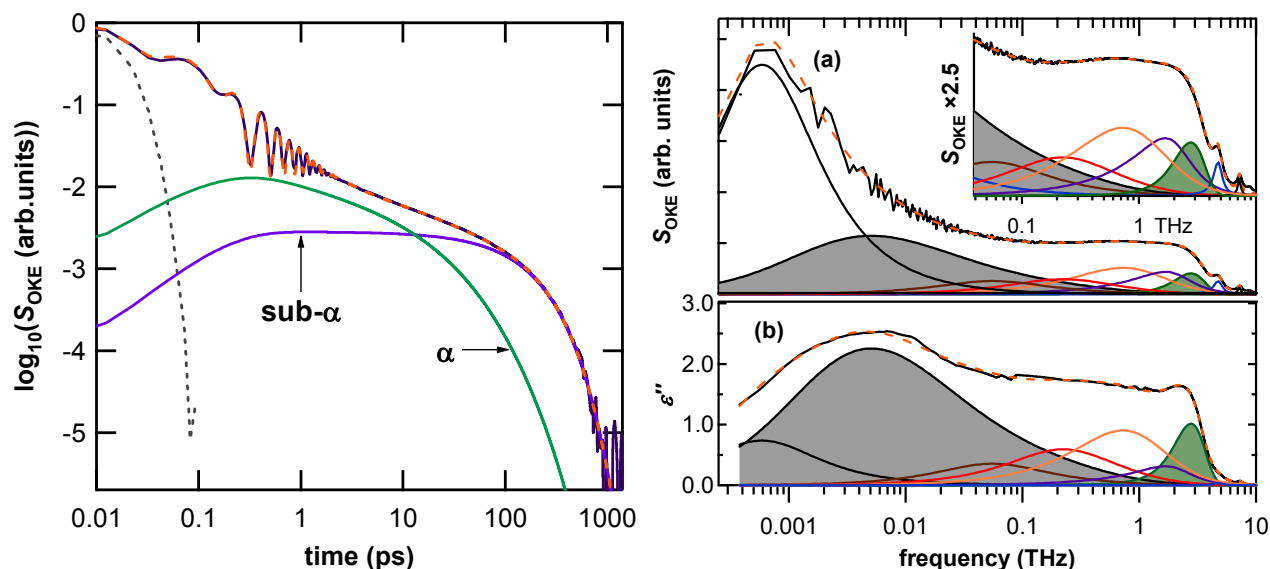

Fig. 2. *(left) OKE data in the time domain for [emim][DCA] at 25 °C showing the overall fit (dashed) as described in the text and the two lowest frequency components. The sub-α Debye relaxation shows the characteristic logarithmic scale curvature. Both the sub-α and α function are modified with the inertial rise functions, while the Cole-Cole α relaxation is additionally terminated by the sub-α relaxation. The instrument cross-correlation (dotted) is also shown. (right) Spectra for [emim][BF₄] showing the total fit (dashed)*

and its component parts with the α relaxation (modified Cole-Cole function) and Gaussian oscillator shaded, to distinguish them from the Brownian oscillators and the sub-α relaxation: (a) OKE (imaginary part), with, inset, a vertical expansion; (b) dielectric loss, ε''. The fit parameters are shown in Table 1 of Ref. [45].

For each RTIL spectrum six Brownian oscillators, Eq. (4), were employed in addition to the α relaxation, Eq. (3), the sub-α relaxation, Eq. (2) and the Gaussian oscillator, Eq. (5). The same model then fits very closely both the OKE and DR spectra, including the stronger intramolecular modes up to 10 THz [45]. We have shown previously that a multi-Brownian oscillator model can be applied to both OKE and IR absorption spectra with a simple transformation in amplitudes [16]. Here again, a single model can be seen to fit both OKE and DR spectra with just a change in amplitudes. Although the broad nature of the spectra in the terahertz region means that the choice of modes required for describing the intermolecular cage-rattling motions is still somewhat uncertain, the combination of the two techniques allows many inappropriate models to be eliminated. In most respects the model for each liquid is very similar, suggesting that, in agreement with simulations, the terahertz dynamics are dominated by the strong, many particle, interactions, rather than by the specific nature of, the ions.

At higher frequencies, (underdamped) intramolecular modes appear. However, the most surprising feature of these data occurs at low frequency where, at *ca*. 1 GHz, a mode appears that is intense in the OKE spectra but so weak in the DR spectra that it would normally not be detected. This mode is best modeled by a Debye function. Normally, in both OKE and DR spectra the lowest-frequency modes reflect rotational relaxation. For single molecule rotational diffusion, the macroscopic shear viscosity η can be related to the diffusivity $D_{\rm rot}$ through Stokes-Einstein-Debye theory, by $D_{\rm rot} = k_B T / 8\pi\eta R^3$, where R is the effective molecular radius [48]. In the simplest cases of diffusional relaxation in which the dipole moment is coincident with the principal axis of the molecular polarizability ellipsoid, the OKE signal relaxes three times faster than the DR signal [25, 49]. Here, however, a simple qualitative comparison of the peak positions would suggest that the OKE relaxation is approximately five times *slower* than when measured by DR.

The Cole-Cole mode in the OKE spectrum occurs at a very similar frequency to that in the DR spectrum. Since the slow components of the Cole-Cole mode cannot be slower than the sub-α relaxation we now terminate the Cole-Cole function by the time constant of the sub-α relaxation, in contrast to the approach employed previously for DRS data alone. A Debye function then accounts well for the OKE sub-α mode if the DR τ_α is used as the basis of the fit. The fit to the OKE signal measured in the time domain for [emim][DCA] (the least viscous of the present RTILs) is plotted on logarithmic axes in Fig. 2, where it can be seen that the final decay ($t > 100$ ps) corresponds closely to a Debye function over almost three orders of magnitude in the OKE intensity. The DR spectrum can also be fit closely by the same model, albeit with a small amplitude for the *sub*-α relaxation.
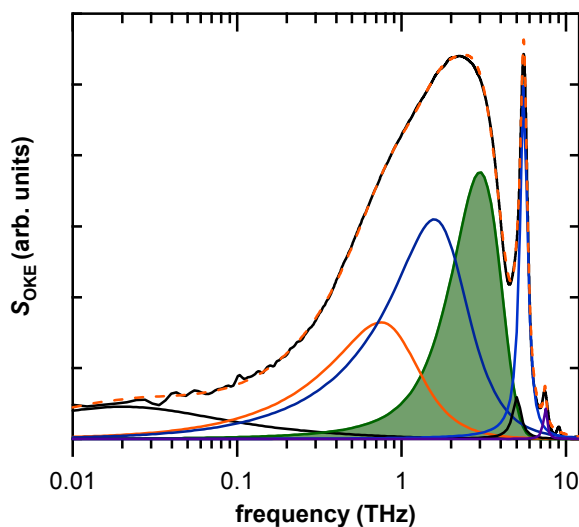
Fig. 3. *OKE spectrum for deeply supercooled [emim][DCA] at 180 K showing the overall fit (dashed) and its components: a Cole-Cole mode, two Brownian oscillators, a Gaussian oscillator (shaded) at the high-frequency onset of the librational band, and a further three Brownian oscillators. The fit parameters are shown in Table 2 of Ref. [45].*

At lower temperatures the diffusional modes slow down and we cannot study them with the current experimental bandwidth. However, consistent with other liquids exhibiting structure, RTILs are generally good glass-formers; Fig. 3 shows the OKE spectrum measured for deeply-supercooled [emim][DCA] at 180 K (T_g = 169 K). As the diffusional modes freeze out, the librational band becomes better defined. Compared with the room-temperature fit, the Gaussian mode shifts to slightly higher frequency, but maintains the same damping rate, while the higher frequency Brownian librational modes broaden slightly. The lower frequency Brownian modes essentially freeze out suggesting their diffusional nature. A broad weak band remains below 0.1 THz that might be residual diffusional cage motions as implied by studies of ionic conductivity that report enhanced diffusivity in the glassy state. Here the mode is fit by a Cole-Cole function, although this is quite approximate.

5   DISCUSSION

The outstanding feature of the present measurements is undoubtedly the large signals in the OKE spectra that appear at considerably lower frequencies than the α relaxations measured by DR. It is reasonable to conclude that OKE is sensitive to a sub-α mode that is only very weakly DR-active. The vast difference in the intensities observed for the sub-α contribution in the OKE and DR spectra strongly implies that this process must correspond to a motion that causes a substantial change in the polarizability tensor without a simultaneous change in the macroscopic dipole moment. The sub-α mode implies a motion in a large scale aggregation introducing a major change in the polarizability with negligible influence on the macroscopic dipole moment. This suggests a mode with high symmetry such as a simple breathing mode of a cation-stacked or micelle-like cluster [50]. Recent X-ray scattering studies reported structure (nanoscale domains) in RTILs due to tail aggregation that increases with length of the alkyl substituents [15, 44, 51-55]. We cannot presently study these larger cations due to bandwidth limitations, but in line with MD simulations, the present spectra suggest that structure exists even in RTILs with smaller (ethyl-substituted) cations. The OKE signal is not quantitative, but the magnitude of the sub-α mode implies that the clustering is extensive, in agreement with the simulations.

Insight into structure can often be gained from a comparison of the measured α relaxation time constants with macroscopic viscosities. Although there are uncertainties in the available literature values for viscosity, we showed recently that the effective volumes calculated through Stokes-Einstein-Debye theory for these liquids are extraordinarily small. This would suggest that single-molecule rotation is essentially decoupled from bulk viscosity and shear viscosity is more dependent on the rearrangements of the stacked clusters.

In the terahertz region, the signal-to-noise ratio of the OKE spectra is particularly high and the data show that there is a greater number of librational/intermolecular vibrational modes than previously detected. If simple functions (Eqs. (4) & (5)) are employed, five modes are required to fit this region, although the degree of overlap still prevents an entirely unambiguous analysis. In fact, although there are distinct differences between the three liquids, this region of the spectrum is relatively flat and featureless.

The observation of an intense low frequency mode in the OKE spectra is explained by the presence of mesoscale structure, while our finding of similar time constants for the OKE and DRS α relaxations supports recent claims from computer simulations suggesting that imidazolium cations re-orient through large-angle jumps. The fact that a Cole-Cole function was required to fit the α relaxation band in the dielectric spectrum can now also be understood. Normally, if not accounted for by a simple Debye function, α relaxation can be modeled by a Cole-Davidson or stretched exponential function, as these tend to exponential relaxation at long times (*i.e.*, they approach Debye behavior at low frequency). In the RTILs studied here, the lowest frequency motions are sub-α, which we have suggested correspond to mesoscopic clusters and hence inhomogeneity, which is reflected by the non-Debye nature of the α-relaxation.

6   ACKNOWLEDGEMENTS

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