Existence of optical phonons in the room temperature ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate

Christopher M. Burba^{1,a)} and Roger Frech²

¹Department of Natural Sciences, Northeastern State University, Tahlequah, Oklahoma 74464-2302, USA

²Department of Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma 73019-3051, USA

(Received 21 December 2010; accepted 8 March 2011; published online 4 April 2011)

The technologically important properties of room temperature ionic liquids (RTILs) are fundamentally linked to the ion–ion interactions present among the constituent ions. These ion–ion interactions in one RTIL (1-ethyl-3-methylimidazolium trifluoromethanesulfonate, $[\text{C}_2\text{mim}]\text{CF}_3\text{SO}_3$) are characterized with transmission FTIR spectroscopy and polarized attenuated total reflection (ATR) FTIR spectroscopy. A quasilattice model is determined to be the best framework for understanding the ionic interactions. A novel spectroscopic approach is proposed to characterize the degree of order that is present in the quasilattice by comparing the dipole moment derivative calculated from two independent spectroscopic measurements: (1) the TO–LO splitting of a vibrational mode using dipolar coupling theory and (2) the optical constants of the material derived from polarized ATR experiments. In principle, dipole moment derivatives calculated from dipolar coupling theory should be similar to those calculated from the optical constants if the quasilattice of the RTIL is highly structured. However, a significant disparity for the two calculations is noted for $[\text{C}_2\text{mim}]\text{CF}_3\text{SO}_3$, indicating that the quasilattice of $[\text{C}_2\text{mim}]\text{CF}_3\text{SO}_3$ is somewhat disorganized. The potential ability to spectroscopically characterize the structure of the quasilattice, which governs the long-range ion–ion interactions in a RTIL, is a major step forward in understanding the interrelationship between the molecular-level interactions among the constituent ions of an ionic liquid and the important physical properties of the RTIL. © 2011 American Institute of Physics. [doi:10.1063/1.3571458]

I. INTRODUCTION

Fundamental and applied research on room temperature ionic liquids (RTILs) has increased substantially over the past decade, due in large part to the extraordinary properties these materials offer in comparison with traditional solvents (e.g., organic, aqueous, or fluorocarbon systems). The tremendous synthetic versatility available in designing constituent ions that compose a RTIL allows researchers to tailor important properties of an ionic liquid to meet the specific needs of a particular application (e.g., degree of hydrophobicity or hydrophilicity, reactivity, viscosity, conductivity, and electrochemical window). Perhaps the most important properties of ionic liquids are their inherently low vapor pressures, high conductivities, and high fluidities. Indeed, most applications of RTILs hinge on the very low vapor pressures and low flammabilities afforded by RTILs, making them ideal replacements for more hazardous volatile solvents.

The central thrust of most synthetic work in this field is to design highly conductive and highly fluid ionic liquids. However, there are certain situations where compounds exhibiting different properties (e.g., high conductivity and high viscosity) have viable applications. The favorable properties typically targeted in designing an ionic liquid are fundamentally linked to the strong cohesive forces that exist between the constituent ions composing the material. In this regard, the

conductivity and viscosity of an ionic liquid are intimately connected to the correlated motion between the cations and anions. For example, highly correlated ionic motions can lead to the formation of discrete ion pairs, thereby reducing the conductivity of the material by lowering the number of effective charge carriers present in the liquid. Furthermore, RTILs containing a large fraction of ion pairs typically exhibit higher vapor pressures. Thus, in the case of strong interionic interactions, the important phenomenological properties of an ionic liquid begin to approach values typical of molecular liquids.

Xu *et al.*¹ provided a useful method for cataloging RTILs according to their position on a Walden-like graph of molar conductivity versus fluidity (i.e., a $\log \Lambda$ – $\log \eta^{-1}$ plot). Most ionic liquids lie slightly below an ideal Walden line, which is defined by the position of an aqueous KCl solution. Molecular liquids occur in regions with high fluidity and low conductivities, while highly conductive glasses and superionic conductors are found in regions of very low fluidity and high conductivity. Under this formalism, highly ion-paired ionic liquids lie between “true” ionic liquids and “true” molecular liquids. The tetraalkylphosphonium-based ionic liquids described by Fraser *et al.*² provide an example of this class of materials. In contrast, Bourlinos *et al.*³ describe a family of polyoxometalates that lie above the ideal KCl line. The possibility of tuning the ionicity of the RTILs holds tremendous promise in understanding the molecular-level interactions responsible for controlling the behavior of these materials.

In this article, infrared spectroscopy is used to investigate the ion–ion interactions present in one RTIL:

^{a)} Author to whom correspondence should be addressed. Electronic mail: burba@nsuok.edu.

1-ethyl-3-methylimidazolium trifluoromethanesulfonate (hereafter, the cation will be abbreviated as $[\text{C}_2\text{mim}]^+$ and the anion as “triflate” or CF_3SO_3^-). This RTIL was chosen because the vibrational modes of the $[\text{C}_2\text{mim}]^+$ cation^{4–8} and CF_3SO_3^- anion^{7–14} are well characterized in the literature. Thus, the $[\text{C}_2\text{mim}]\text{CF}_3\text{SO}_3$ ionic liquid provides an excellent starting point for future spectroscopic studies on lesser known analogues.

II. EXPERIMENTAL METHODS

The room temperature ionic liquid $[\text{C}_2\text{mim}]\text{CF}_3\text{SO}_3$ was purchased from Aldrich and used without further purification. All sample preparation and manipulation of the ionic liquid was performed under an argon atmosphere (VAC glovebox, <1 ppm H_2O , <1 ppm O_2). Transmission FTIR spectra were recorded with a Nicolet 6700 infrared spectrometer (DTGS detector operating with 1 cm^{-1} resolution) under dry air purge. IR spectra were collected by placing the compound between two ZnSe windows, and each spectrum consists of eight individual scans averaged together. Spectral deconvolution of the transmission FTIR spectrum was performed with Galactic Grams AI®. Polarized attenuated total reflection (ATR) FTIR spectroscopy was performed with variable-angle ATR FTIR equipment purchased from Pike Technologies. A holographic wire-grid polarizer was used for the polarized FTIR spectroscopy. ATR spectra were collected by placing the sample on a single crystal of germanium with a 45° angle of incidence. The ATR FTIR spectra consist of 16 averaged scans recorded at 1 cm^{-1} resolution at room temperature.

III. RESULTS AND DISCUSSION

A. Transmission FTIR spectroscopy

Figure 1 depicts transmission FTIR spectra of $[\text{C}_2\text{mim}]\text{CF}_3\text{SO}_3$ recorded at room temperature between

FIG. 1. Room temperature infrared absorption spectrum of $[\text{C}_2\text{mim}]\text{CF}_3\text{SO}_3$. The inset shows the curve fit analysis described in the text. The red dashed lines correspond to the two $\nu_s(\text{SO}_3)$ bands, while the green dotted line is a $[\text{C}_2\text{mim}]^+$ vibration. The baseline is represented as a solid blue line. Abs. = Absorbance.

1075 and 980 cm^{-1} . Spectral curve fitting of this region is presented in the inset to Fig. 1. The analysis reveals two overlapped, intense bands at 1036 and 1029 cm^{-1} along with a weaker broad band centered near 1031 cm^{-1} . The two dominant bands in Fig. 1 may be assigned to symmetric stretching motions of the SO_3 portion of the CF_3SO_3^- anion [i.e., $\nu_s(\text{SO}_3)$].¹² The third band at 1031 cm^{-1} is assigned to the $[\text{C}_2\text{mim}]^+$ cation. *Ab initio* calculations by Talaty *et al.*⁴ indicate this band consists of a mixture of imidazolium ring symmetric stretching and C–N stretching motions. There are two possible explanations for the appearance of multiple $\nu_s(\text{SO}_3)$ bands in the IR spectrum of $[\text{C}_2\text{mim}]\text{CF}_3\text{SO}_3$: (1) the associated-ion model and (2) the quasicrystal model. Each of these models is discussed separately below.

B. The associated-ion model

It is well known that changing the coordination environment about the triflate ion has a significant impact on the electronic distribution within the ion and consequently results in measurable changes in the band frequencies and intensities of the vibrational modes of the anion. In the case of degenerate vibrational modes, cation coordination may alter the symmetry of the triflate anion, thereby removing the degeneracy and producing multiple bands in the IR spectrum. For nondegenerate vibrational modes, such as $\nu_s(\text{SO}_3)$, the associated-ion model posits that multiple bands in an IR or Raman spectrum originate from distinctly different populations of the ions, each having a different local coordination environment.

Previous spectroscopic,^{7,12,15–18} computational,^{12,13} and crystallographic^{7,15–18} studies have clearly established the existence of ion pairs and higher-order aggregate species in liquid and polymer electrolyte systems containing dissolved inorganic triflate salts. In those systems, triflate ions become coordinated with one or more counter ions to form discrete entities in the solutions, with lifetimes that at least exceed the time to complete a few oscillatory vibrations of the aggregate species. The exact frequency of the $\nu_s(\text{SO}_3)$ mode is slightly dependent on the choice of counter ion and solvent system. In the context of the associated-ion model, the 1029 cm^{-1} band is consistent with the presence of “free” triflate anions in a system where the oxygen atoms undergo hydrogen bonding interactions,^{19,20} whereas the 1036 cm^{-1} band may be attributed to either ion-paired or more highly aggregated moieties in the ionic liquid. However, the strong monopole–monopole interactions that exist among the constituent ions composing the molten salt make it difficult to unambiguously assign the bands to specific entities.

Assigning the two $\nu_s(\text{SO}_3)$ bands in the IR spectrum to two separate populations of triflate-containing species is inconsistent with the observation of a single $\delta_s(\text{CF}_3)$ band at 757 cm^{-1} in the Raman and IR spectra of $[\text{C}_2\text{mim}]\text{CF}_3\text{SO}_3$ (e.g., see Ref. 8). The nondegenerate $\delta_s(\text{CF}_3)$ vibrational mode primarily consists of symmetric deformations of the CF_3 portion of the triflate anion, and the mode is frequently used as a spectroscopic probe of ionic association for systems containing triflate anions. Although, the coordinative interactions occur through the oxygen atoms of the triflate ion, the

resulting redistribution of electron density throughout the anion affects the frequencies and intensities of several CF₃ modes.¹² Under the associated-ion model, the frequency of the $\delta_s(\text{CF}_3)$ mode is more consistent with a single coordination environment for the triflate anion. As with the $\nu_s(\text{SO}_3)$ bands, it is difficult to assign the 757 cm⁻¹ band to a specific coordination geometry. Nonetheless, the frequency of the 757 cm⁻¹ band does decrease to 754 cm⁻¹ when the ionic liquid is dissolved in poly(ethylene oxide) (PEO) at an ether oxygen atom to [C₂mim]⁺ ion mole ratio of 20:1, and the frequency of the 754 cm⁻¹ band in P(EO)₂₀[C₂mim]CF₃SO₃ is consistent with “free” triflate anions.²¹ This assignment is supported by numerous spectroscopic studies of inorganic triflate salts dissolved in PEO where the $\delta_s(\text{CF}_3)$ mode occurs near 754 cm⁻¹. The absence of the 754 cm⁻¹ band in the spectra of pure [C₂mim]CF₃SO₃ argues that the pure ionic liquid lacks a significant number of “free” triflate anions. In this regard, the associated-ion model results in conflicting interpretations of the transmission FTIR spectrum of [C₂mim]CF₃SO₃. For this reason, we turn now to a second model to explain the spectroscopic features of $\nu_s(\text{SO}_3)$ in Fig. 1.

C. The quasilattice model

The quasilattice model has a rich history in the field of high-temperature molten salts, with most applications centered on explaining the vibrational spectra of molten alkali metal nitrates and alkali metal halides.^{22–30} According to the model, the local environment about the [C₂mim]⁺ and CF₃SO₃⁻ ions may be viewed in terms of a perturbed crystal lattice with some degree of disorder introduced over the available ion sites. Xu *et al.*¹ argue that this uniform distribution of charge results in the ionic liquid acquiring a Madelung energy (E_{Mad}) that is comparable to what would be present in the crystalline state. Thus, ionic motion is correlated in the quasilattice but not in a way that produces discrete ionic entities—such as ion pairs—that lower the ionic conductivity of the system. Furthermore, Xu *et al.*¹ argue that the value of the quasilattice Madelung energy for the RTIL has an impact on the vapor pressure of the ionic liquid, for it is the Madelung energy that must be overcome to extract an ion pair from the liquid phase to the vapor phase. That is, the vapor pressure of an ionic liquid is proportional to the Boltzmann factor $\exp(-\Delta H_{\text{vap}}/RT) \approx \exp(-E_{\text{Mad}}/RT)$ at a given temperature.

According to the quasilattice model, the molten state retains some properties of the crystalline state, and the infrared spectrum would be expected to have some spectral features that resemble ionic, solid-state materials. Collective lattice-like coupling of the [C₂mim]⁺ and CF₃SO₃⁻ ion motions in a quasilattice could produce long-wavelength vibrational modes and result in optical dispersion for the RTIL. During a typical IR transmission experiment, incident electromagnetic radiation will be partly reflected and partly absorbed by the sample, with the remaining light being transmitted. The intensity of light transmitted (T), absorbed (A), and reflected (R) by a sample at a frequency ν is related to the intensity of

the incident radiation $I(\nu)$ by Kirchoff’s law:

$$T(\nu) = I(\nu) - A(\nu) - R(\nu) \quad (1)$$

Under the quasi-lattice model, the electromagnetic field of the vibrating charges in a normal mode may couple with the mechanical vibrational motion of the mode, resulting in a polariton that is neither purely electromagnetic nor purely mechanical in nature. Such a polariton does not support the propagation of a photon through the lattice. Consequently for relatively intense bands with large dipole moment derivatives, such as $\nu_s(\text{SO}_3)$, a substantial amount of reflection may be expected between frequencies corresponding to transverse optic (TO) and longitudinal optic (LO) modes.³¹ However, anharmonic forces between the constituent ions composing the ionic liquid will ensure at least partial transmission of the incident electromagnetic radiation. Further reduction in the polariton energy flux propagating across the sample could occur through absorption mechanisms, such as coupling between different phonon vibrations of the quasilattice.

TO–LO splitting of a vibrational mode is distinct from site group and factor group splitting, which is commonly observed in crystalline substances. Site group splitting occurs when the symmetry of an individual ion is higher than the symmetry of the potential energy environment of the site that the ion occupies within the unit cell. The lower symmetry of the potential energy environment may lift the degeneracy of some vibrational modes, producing multiple bands in a vibrational spectrum. In factor group splitting, multiple bands appear for a vibrational mode due to correlation effects of crystallographically equivalent ions within the unit cell. The relative magnitude of site group and factor group splitting depends on the strength of the intermolecular forces coupling individual ions together as well as the potential energy environment of the ions. Disorder among the ions in the lattice or sublattice of a crystalline compound collapses the vibrational multiplet structure generated by factor group splitting into an inhomogeneously broadened band centered near the frequency of the vibrational mode for the isolated ion.³² Plastic crystalline phases, such as LiNaSO₄,³³ provide an excellent example of how orientational disorder among constituent ions that possess translational symmetry can disrupt factor group correlation effects well below the melting point of the solid. In contrast, TO–LO splitting of a vibrational mode does not depend on the periodicity of a crystalline lattice.³⁴ For instance, it is common for TO–LO splitting to be observed in glasses (e.g., see the review article by Mayerhöfer *et al.*³⁵). In the context of the quasilattice model, however, long-range coupling of vibrationally induced dipole moments is needed to sustain optical phonons in an ionic liquid. This will require some degree of translational and orientational registry in the “disordered” liquid state, ranging over a few quasiunit cells in the ionic liquid.

Under the quasilattice model, the appearance of the two bands in the $\nu_s(\text{SO}_3)$ region is explained as originating from long-wavelength motions of the constituent ions across a quasilattice. The overall line shape of the $\nu_s(\text{SO}_3)$ bands depicted in Fig. 1 is very similar to that observed in an IR reflection measurement of the antisymmetric stretching motion of nitrate anions, $\nu_3(\text{NO}_3^-)$, for several molten alkali

FIG. 2. The (a) first derivative and (b) second derivative of the infrared absorption spectrum of $[\text{C}_2\text{mim}]\text{CF}_3\text{SO}_3$ shown in Fig. 1 Abs. = Absorbance.

nitrate systems.^{26,29,30} In those systems, the intense $\nu_3(\text{NO}_3^-)$ reflection band appears as two overlapped bands that occur at frequencies near the TO and LO bands of the $\nu_3(\text{NO}_3^-)$ phonons in the crystalline compounds.³⁰ The frequency of the TO mode in the alkali nitrates is set equal to the frequency of the band maximum in the spectrum of the melt, while the LO mode frequency is approximated by the frequency of the inflection point on the high frequency side of the $\nu_3(\text{NO}_3^-)$ band. When a similar analysis is applied to the $\nu_s(\text{SO}_3)$ band in Fig. 2, the frequency of the TO mode may be estimated as 1029 cm^{-1} from the frequency at which the first derivative of the $\nu_s(\text{SO}_3)$ band is zero (see Fig. 2). Likewise, the frequency of the LO mode is 1038 cm^{-1} based on the second derivative curve provided in Fig. 2. The frequencies of these two bands closely correspond to the two $\nu_s(\text{SO}_3)$ bands used to generate the curve fit in Fig. 1. Infrared spectroscopic experiments probe molecular processes that occur over a relatively fast time scale (subpicoseconds). This places a lower limit on the time scale of long-range ion-ion interactions that produce the TO-LO splitting of the $\nu_s(\text{SO}_3)$ mode. Other spectroscopic investigations, which probe longer time scales, are needed to assess whether these interactions persist for longer periods of time. Although important, such studies are not the focus of this article.

D. Calculating the dipole moment derivative for $\nu_s(\text{SO}_3)$

Dipolar coupling theory³⁶ has been previously used to relate the magnitude of the TO-LO splitting to the dipole moment derivatives of vibrational modes in a variety of isotropic and anisotropic crystals.³⁷⁻³⁹ In its general form,

this method calculates the coupling of vibrationally induced dipoles, mediated by electronic polarizability tensor components of the individual anions and cations (“background polarization model”). A simplified form of dipolar coupling theory that neglects the role of electronic polarizabilities (“resonant mode model”) results in an expression for the TO-LO splitting of a normal mode in a unimolecular unit cell,

$$\nu_{\text{LO}}^2 - \nu_{\text{TO}}^2 = \frac{4\pi}{V} \left(\frac{\partial \mu}{\partial q} \right)_o^2. \quad (2)$$

Here ν_{LO} and ν_{TO} are the frequencies of the longitudinal and transverse optic modes, respectively, V is the unit cell volume, and $(\partial \mu / \partial q)_o$ is the dipole moment derivative of the vibrational mode.

This model has been applied to the nitrate ion $\nu_3(\text{NO}_3^-)$ mode in disordered $\text{NaNO}_3(\text{I})$ and $\text{KNO}_3(\text{I})$.^{40,41} Values of ν_{LO} and ν_{TO} were deduced from TE- and TM-polarized ATR IR spectra of the disordered phases. These values did not appreciably change between the ordered and the disordered phases, which led to very similar values of the dipole moment derivatives in the two phases as well as between the two alkali metal nitrates. A number of earlier studies of high temperature molten salts suggest the quasilattice of a molten salt results in collective vibrational motions that can be described in terms of the optical phonons present in the corresponding solid crystalline phase. Examples of the application of this concept include AgNO_3 and the alkali metal nitrates LiNO_3 , NaNO_3 , KNO_3 , and RbNO_3 , where the TO-LO splitting is proportional to the particle density as implied in Eq. (2).³⁰ The most striking example is LiNO_3 , where two very distinct components in the Raman spectrum of ν_3 occur at 1350 and 1470 cm^{-1} and are assigned to ν_{TO} and ν_{LO} , respectively.³⁰ These frequencies are remarkably close to the values measured in the crystalline phase at 1360 and 1480 cm^{-1} .³⁷

Because a RTIL is merely an ionic salt whose melting point is near or below room temperature, we now apply Eq. (2) to the $\nu_s(\text{SO}_3)$ mode of $[\text{C}_2\text{mim}]\text{CF}_3\text{SO}_3$, estimating the magnitude of the dipole moment derivative of the $\nu_s(\text{SO}_3)$ mode from the experimentally measured TO and LO mode frequencies. The volume per formula unit for $[\text{C}_2\text{mim}]\text{CF}_3\text{SO}_3$ is estimated at $312\text{ \AA}^3$ from the known density of the ionic liquid, assuming cubic symmetry for the unit cells of the quasilattice. This value is in reasonable agreement with the available crystallographic data. Crystalline $[\text{C}_2\text{mim}]\text{CF}_3\text{SO}_3$ occupies an orthorhombic unit cell ($a = 10.183\text{ \AA}$, $b = 12.384\text{ \AA}$, and $c = 18.294\text{ \AA}$) in the $Pbca$ space group.⁴² Each unit cell contains eight $[\text{C}_2\text{mim}]\text{CF}_3\text{SO}_3$ formula units, resulting in a volume of $288\text{ \AA}^3$ for each formula unit. The slightly larger volume estimated in the ionic liquid at room temperature is probably due to increased amounts of free volume in the liquid phase compared to the crystalline compound.

In general, the symmetry of the unit cell for the quasilattice approaches cubic symmetry as the temperature of the molten salt is increased. For example, James and Leong²⁶ described a progressive change in the quasicrystal structure of RbNO_3 as it is heated. Furthermore, they propose that the quasilattice of molten LiNO_3 , NaNO_3 , and AgNO_3

adopt a cubic symmetry 50 °C above the melting point. The melting point of [C₂mim] is approximately −25 °C. Thus, the orthorhombic symmetry of the [C₂mim]CF₃SO₃ may not be retained in the quasilattice of the ionic liquid at room temperature. Based on an estimated volume of 312 Å³ for each [C₂mim]CF₃SO₃ formula unit at room temperature, the value of $|d\mu/dq|$ is approximated as 20.4 cm^{3/2} s^{−1} using Eq. (2). It should be noted that the Raman frequency of the $\nu_s(\text{SO}_3)$ mode is approximately 3 cm^{−1} higher (1032 cm^{−1}) than the corresponding IR mode.⁷ This g - u splitting of the nondegenerate $\nu_s(\text{SO}_3)$ is a result of dynamic coupling between symmetrically inequivalent triflate anions.³⁷ Thus, it is possible that more than one triflate anion occupies each unit cell of the quasilattice.

If the quasilattice model is imperfect in describing the ion–ion interactions in the ionic liquid, then some degree of error will be associated with the dipole moment derivative calculated from dipolar coupling theory. Specifically, there is no temperature-dependent factor in equation (2) that reflects the random thermal motion of ions that is inherently present in the ionic liquid. This thermal motion will decrease dipole–dipole correlation across multiple quasiunit cells, thus reducing the TO–LO frequency split in the transmission IR spectrum. Smaller values of TO–LO splitting will decrease the magnitude of the dipole moment derivative calculated from Eq. (2). In addition, dipolar coupling theory assumes a perfect crystalline lattice, which is certainly violated to some extent for an ionic liquid above the melting point. Fortunately, an independent method for calculating the dipole moment derivative is available that relies on neither a quasilattice model for the ion–ion interactions nor dipolar coupling theory. Bardwell and Dignam^{43–45} developed a routine method for determining the optical constants from single-reflection polarized ATR IR spectroscopy. The algorithm proposed by Bardwell and Dignam is based on the Kramers–Kronig transform between $\ln(\sqrt{R_s(\nu)})$, where $R_s(\nu)$ is the reflectance in an s -polarized ATR experiment at a particular frequency ν , and the phase angle, $\delta_s(\nu)$, of the complex Fresnel reflection coefficient, $\hat{r}_s(\nu)$:

$$\delta_s(\nu) = \delta_s^{\text{corr}} + \frac{2}{\pi} \int_0^\infty \frac{\nu_a \ln(\sqrt{R_s(\nu)})}{\nu_a^2 - \nu^2} d\nu_a. \quad (3)$$

Here, P represents the Cauchy principle value of the integral. The phase angle must be corrected when the Kramers–Kronig relation is applied to an ATR IR experiment, and the corresponding correction term is given as

$$\delta_s^{\text{corr}} = 2 \arctan \left(\sqrt{\frac{n_o^2 \sin^2 \theta_o - n_{\text{vis}}^2}{n_o \cos \theta_o}} \right), \quad (4)$$

where n_o is the refractive index for the ATR crystal ($n_o = 4$ for Ge), θ_o is the angle of incidence (45°), and n_{vis} is the refractive index of the ionic liquid recorded in the visible region of the electromagnetic spectrum (1.433 for [C₂mim]CF₃SO₃ at room temperature). In practice, the integration range in Eq. (3) is reduced to the available data.

The complex Fresnel coefficient is calculated from Eqs. (3) and (4) using appropriate ATR IR spectra,

$$\hat{r}_s(\nu) = \sqrt{R_s(\nu)} \exp(i\delta_s(\nu)). \quad (5)$$

From the complex Fresnel coefficient, the refractive indices and extinction coefficients of the ionic liquid may then be directly calculated from the following two equations:

$$n(\nu) = n_o \text{Re} \left[\sin^2 \theta_o + \left(\frac{1 - \hat{r}_s(\nu)}{1 + \hat{r}_s(\nu)} \right)^2 \cos^2 \theta_o \right], \quad (6)$$

$$k(\nu) = -n_o \text{Im} \left[\sin^2 \theta_o + \left(\frac{1 - \hat{r}_s(\nu)}{1 + \hat{r}_s(\nu)} \right)^2 \cos^2 \theta_o \right]. \quad (7)$$

Dignam and Mamiche-Afara⁴⁶ later extended the analysis to include p -polarized ATR IR spectroscopic studies. The methodology accurately reproduced the optical constants for weak and medium strength bands of benzene, chloroform, and carbon tetrachloride. However, strong bands (i.e., spectral regions with $R < 6\%$) typically gave values of k that were approximately 20% too low.⁴⁵ Buffeteau and co-workers^{47,48} successfully applied this methodology to calculate the optical constants for several ionic liquid materials in the mid- and far-IR region. Limitations of calculating optical constants from polarized ATR IR experiments have been addressed by Yamamoto *et al.*⁴⁹

The ability to compare dipole moment derivatives derived from two independent methods (polarized ATR FTIR spectra and dipolar coupling theory) provides a unique opportunity to assess the degree to which the ion–ion interactions may be described by a quasilattice. For example, if the two calculations of the dipole moment derivative are very similar, then it is likely that the quasilattice is highly structured and might be similar to a slightly disorganized form of the crystalline phase for a particular ionic liquid. In contrast, significant disparities in the two assessments would argue that the quasilattice is poorly structured and long-range correlated motion among the constituent ions is hindered.

Polarized ATR IR spectra of [C₂mim]CF₃SO₃ are depicted in Fig. 3. A single band centered at 1030 cm^{−1} is present in both spectra. As expected for isotropic solutions, the p -polarized spectrum is approximately twice as intense as the s -polarized spectrum. Optical constants derived from the polarized spectra for this region are presented in Fig. 4. Again, as expected, large values of the extinction coefficient are associated with dispersion of the refractive index for the $\nu_s(\text{SO}_3)$ mode. Integrated values of the extinction coefficient over a band may be related to the transition dipole moment, $\langle \psi_{n'} | \mu | \psi_{n''} \rangle$, of the corresponding vibration through the appropriate Einstein coefficient,⁵⁰

$$\int_{\text{band}} k(\nu) d\nu = \frac{2\pi^2 N}{3h} \langle \psi_{n'} | \mu | \psi_{n''} \rangle. \quad (8)$$

The quantity N represents the particle density of the ionic liquid (i.e., the number of [C₂mim]CF₃SO₃ formula units within a volume of the RTIL). Using the relationship between the transition dipole moment and the dipole moment derivative found in Ref. 31, an equation relating the dipole moment

FIG. 3. Polarized ATR FTIR spectroscopy of $[\text{C}_2\text{mim}]\text{CF}_3\text{SO}_3$ recorded with a Ge ATR crystal (45° angle of incidence).

derivative to the extinction coefficient for a particular band with frequency ν_o may be written:

$$\left(\frac{\partial\mu}{\partial q}\right)^2 = \frac{12c\nu_o}{N} \int_{\text{band}} k(\nu)d\nu. \quad (9)$$

This relationship requires the application of the harmonic oscillator approximation for the wave functions in the transition dipole moment expression.^{31,50}

The dipole moment derivative calculated from the optical constants of $[\text{C}_2\text{mim}]\text{CF}_3\text{SO}_3$ is $164.2 \text{ cm}^{3/2} \text{ s}^{-1}$. The $\nu_s(\text{SO}_3)$ mode is relatively intense in the IR spectrum, leading to reflectance values near 60% for s-polarized light. As noted above, extinction coefficients calculated from intense bands under estimate the actual values of the extinction coefficients. Based on the work of Bardwell and Dignam,⁴⁵ a 20% under estimate is a conservative approximation to the maximum error introduced in calculating the extinction coefficient of $\nu_s(\text{SO}_3)$ from the ATR infrared spectrum. Therefore, a maximum dipole moment derivative of the $\nu_s(\text{SO}_3)$ mode is $183.6 \text{ cm}^{3/2} \text{ s}^{-1}$. These values are approximately 8–9 times larger than that calculated from Eq. (2), which suggests that

FIG. 4. Optical constants for $[\text{C}_2\text{mim}]\text{CF}_3\text{SO}_3$ for the $\nu_s(\text{SO}_3)$ mode.

the quasilattice for $[\text{C}_2\text{mim}]\text{CF}_3\text{SO}_3$ at room temperature is most likely significantly perturbed by the thermal motion of the $[\text{C}_2\text{mim}]^+$ and CF_3SO_3^- ions at room temperature.

There is a general consensus that substantial charge ordering among the constituent ions of a RTIL exists in the liquid state. Neutron scattering experiments on 1,3-dimethylimidazolium-based ionic liquids reveal long-range structuring of the ions that extends over several distinct solvation shells.^{51–53} Moreover, oscillations in the cation–anion and cation–cation pair distribution functions derived from the neutron scattering data are out of phase, suggesting that charge ordering extends over the first few solvation shells about the 1,3-dimethylimidazolium cations. Charge ordering is clearly defined in the scattering data for the 1,3-dimethylimidazolium ionic liquids possessing chloride anions⁵¹ and, to lesser extent, PF_6^- anions.⁵² In both examples, ion–ion interactions in the liquid state mimic those of the corresponding solid state, with larger distances separating ions in the liquid state than the solid state. Larger anions, such as $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, also exhibit charge ordering in the liquid state, but the features are less pronounced compared to the smaller anion analogs.⁵³ In addition, the structure of the liquid state bears few similarities to the corresponding solid state. Charge-ordered structures have also been reported for ionic liquids possessing asymmetrical cations ($[\text{C}_n\text{mim}]\text{PF}_6$, where $n = 2, 4, 6$, and 8).^{54–56}

A number of researchers in this field have also proposed that 1-alkyl-3-methylimidazolium-based ionic liquids possess extended nanostructural organization in which the hydrocarbon side chains of the 1-alkyl-3-methylimidazolium ion aggregate into nonpolar moieties embedded within charge-ordered domains. This model is largely derived from x-ray scattering experiments,^{57–59} molecular dynamics simulations,⁶⁰ and optical Kerr effect spectroscopy.^{59,61,62} Observing mesoscopic organization in ionic liquids with long alkyl chains is not surprising, for the properties of ionic liquids should approach those of surfactants when the alkyl chain length is large.^{63,64} However, x-ray scattering data reported by Triolo *et al.*^{57,58} suggests that these domains may exist in asymmetrical imidazolium ions with relatively short alkyl chains ($4 \leq n \leq 10$). Triolo *et al.*⁵⁸ further proposed a pseudomicellar motif with a low amount of interdigitation among the alkyl side chains as a potential model for the mesoscopic domains in these ionic liquids. The existence of mesoscopic ordering is more controversial for ionic liquids possessing short alkyl chains. Indeed, neutron scattering data for $[\text{C}_n\text{mim}]\text{PF}_6$ ($n = 4, 6$, and 8) do not support alkyl-chain-dominated nanostructural aggregation in the liquid state but are more consistent with a local aggregation similar to $[\text{C}_1\text{mim}]\text{PF}_6$ with the extended side chains frustrating the close packing of the ions.⁵⁴ It should be emphasized, however, that the neutron scattering data could neither confirm nor refute “the existence of a loosely organized spongelike microphase defined by ribbons or strings of alternating anions and cations.”⁵⁴

Taken together, the neutron and x-ray scattering experiments strongly suggest that imidazolium-based ionic liquids possess substantial long-range structuring in the liquid state, with the degree of the structure dependent on

the type of anion and the length of the alkyl chain. The quasilattice model used to explain the FTIR spectroscopic data for [C₂mim]CF₃SO₃ is consistent with the long-range, charge-ordered structures observed from neutron and x-ray scattering experiments on related ionic liquid systems. The size of the CF₃SO₃[−] anion is intermediate to the PF₆[−] and (CF₃SO₂)₂N[−] anions. Thus, charge ordering is expected to be intermediate to those two systems. Even if short chain [C_{*n*}mim]-based ionic liquids possess mesoscopic organization driven by the aggregation of nonpolar side chains attached on the imidazolium ring, it is very unlikely that the ethyl side chain could support any significant ordering in this system. However, the addition of the ethyl group on the imidazolium ring may play an important role in disrupting the charge order of the [C₂mim]CF₃SO₃ ionic liquid, leading to the poorly organized quasilattice detected in the infrared spectroscopic experiments described above.

IV. CONCLUSIONS

The important phenomenological properties of RTILs, which make them attractive as potential solvent systems for a wide range of applications, are fundamentally linked to the ion–ion interactions that are present among the constituent ions. Therefore, it is critical to develop an excellent understanding of those interactions. Two distinct models for the ion–ion interactions are examined to explain the spectral features, specifically the $\nu_s(\text{SO}_3)$ mode for [C₂mim]CF₃SO₃, present in the transmission FTIR spectrum of one RTIL: the associated-ion model and the quasilattice model. The associated-ion model results in conflicting interpretations for coordinative environments of the triflate anions. Thus, this model is rejected in favor of a quasilattice model for the ion–ion interactions of [C₂mim]CF₃SO₃, similar to what has been proposed for molten alkali nitrate and alkali halide salt systems. Furthermore, there is an increasing number of ionic liquid systems^{1,47} that are best understood in the context of the quasilattice model. Even though the associated-ion model is rejected for this particular ionic liquid, there are reports of a few ionic liquids that might be best explained by an associated-ion model, especially those systems that lie far below the ideal KCl line in a log Λ –log η^{-1} plot. In those instances, we might expect the associated-ion model to not result in conflicting interpretations for the transmission IR spectra as observed for the [C₂mim]CF₃SO₃ system.

In order to effectively determine the degree to which the quasilattice model describes the long-range ion–ion interactions of an ionic liquid, the dipole moment derivative of the $\nu_s(\text{SO}_3)$ mode is calculated using two independent methods: (1) the TO–LO split in conjunction with dipolar coupling theory and (2) the optical constants of the RTIL derived from polarized ATR FTIR spectroscopy. Dipolar coupling theory neglects any temperature dependence of the correlated motion originating in the ion–ion interactions and necessarily assumes a highly organized quasilattice, similar to what is found in crystalline compounds. Polarized ATR FTIR spectroscopy affords an independent assessment of the dipole moment derivative by first calculating the optical constants of

the material. Thus, it is possible to assess the degree to which the ionic liquid violates the core assumptions of dipolar coupling theory and provide some measure of the structure of the quasilattice. In the context of the [C₂mim]CF₃SO₃ ionic liquid, the dipole moment derivative for the $\nu_s(\text{SO}_3)$ mode is approximately eight times smaller when calculated from dipolar coupling theory than from the optical constants derived from the ATR IR spectrum. Thus, it appears that the quasilattice of [C₂mim]CF₃SO₃ is somewhat disordered. Comparing the two measurements demonstrates the power of combining transmission and ATR FTIR spectroscopy to assess fundamental ion–ion interactions in RTILs.

ACKNOWLEDGMENTS

C.M.B. is indebted to Northeastern State University for partial support of this project. Acknowledgment is made to the Donors of the American Chemical Society Petroleum Research Fund for partial support of this research. This publication was also made possible by Grant No. P20RR016478 from the National Center for Research Resources (NCRR), a component of the National Institutes of Health (NIH). Its contents are solely the responsibility of the authors and do not necessarily represent the official views of NCRR or NIH. This work was also partially funded by the (U.S.) Department of Defense (DOD), Army Research Office under Project No. W911NF-04-1-0322.

- ¹W. Xu, E. I. Cooper, and C. A. Angell, *J. Phys. Chem. B* **107**, 6170 (2003).
- ²K. J. Fraser, E. I. Izgorodina, M. Forysth, J. L. Scott, and D. R. MacFarlane, *Chem. Commun. (Cambridge)* 3817 (2007).
- ³A. B. Bourlinos, K. Raman, R. Herrera, Q. Zhang, L. A. Archer, and E. P. Giannelis, *J. Am. Chem. Soc.* **126**, 15358 (2004).
- ⁴E. R. Talaty, S. Raja, V. J. Storhaug, A. Dölle, and W. R. Carper, *J. Phys. Chem. B* **108**, 13177 (2004).
- ⁵Y. Umebayashi, T. Fujimori, T. Sukizaki, M. Asada, K. Fujii, R. Kanzaki, and S.-I. Ishiguro, *J. Phys. Chem. A* **109**, 8976 (2005).
- ⁶J. C. Lassègues, J. Grondin, R. Holomb, and P. Johansson, *J. Raman Spectrosc.* **38**, 551 (2007).
- ⁷C. M. Burba, N. M. Rocher, R. Frech, and D. R. Powell, *J. Phys. Chem. B* **112**(10), 2991 (2008).
- ⁸C. M. Burba, N. M. Rocher, and R. Frech, *J. Phys. Chem. B* **113**, 11453 (2009).
- ⁹S. Schantz, J. Sandahl, L. Börjesson, L. M. Torell, and J. R. Stevens, *Solid State Ionics* **28–30**, 1047 (1988).
- ¹⁰S. Schantz, L. M. Torell, and J. R. Stevens, *J. Chem. Phys.* **94**(10), 6862 (1991).
- ¹¹W. Huang, R. Frech, P. Johansson, and J. Lindgren, *Electrochim. Acta* **40**(13–14), 2147 (1995).
- ¹²W. Huang, R. Frech, and R. A. Wheeler, *J. Phys. Chem.* **98**(1), 100 (1994).
- ¹³W. Huang, R. A. Wheeler, and R. Frech, *Spectrochim. Acta* **50A**(5), 985 (1994).
- ¹⁴S. Chintapalli, C. Quinton, R. Frech, and C. A. Vincent, *Macromolecules* **30**, 7472 (1997).
- ¹⁵C. P. Rhodes and R. Frech, *Macromolecules* **34**(8), 2660 (2001).
- ¹⁶R. Sanders, R. Frech, and M. A. Khan, *J. Phys. Chem. B* **108**(34), 12729 (2004).
- ¹⁷R. A. Sanders, R. Frech, and M. A. Khan, *J. Phys. Chem. B* **107**(33), 8310 (2003).
- ¹⁸R. A. Sanders, R. Frech, and M. A. Khan, *J. Phys. Chem. B* **108**(7), 2186 (2004).
- ¹⁹S. S. York, S. E. Boesch, R. A. Wheeler, and R. Frech, *PhysChemComm* **5**, 99 (2002).
- ²⁰L. Hu, R. Frech, D. T. Glatzhofer, R. Mason, and S. S. York, *Solid State Ionics* **179**, 401 (2008).
- ²¹C. M. Burba, *ECS Trans.* **13**(17), 3 (2008).

- ²²C. A. Angell, J. Wong, and W. F. Edgell, *J. Chem. Phys.* **51**(10), 4519 (1969).
- ²³J. H. R. Clarke, *Chem. Phys. Lett.* **4**(1), 39 (1969).
- ²⁴J. P. Devlin, P. C. Li, and G. Pollard, *J. Chem. Phys.* **52**(3), 2267 (1970).
- ²⁵G. H. Wegdam, R. Bonn, and J. Van Der Esken, *Chem. Phys. Lett.* **2**(3), 182 (1968).
- ²⁶D. W. James and W. H. Leong, *J. Chem. Phys.* **51**(2), 640 (1969).
- ²⁷J. K. Wilmshurst, *J. Chem. Phys.* **39**(7), 1779 (1963).
- ²⁸J. K. Wilmshurst, *J. Chem. Phys.* **36**(9), 2415 (1962).
- ²⁹J. K. Wilmshurst and S. Senderoff, *J. Chem. Phys.* **35**(3), 1078 (1961).
- ³⁰J. P. Devlin, D. W. James, and R. Frech, *J. Chem. Phys.* **53**(11), 4394 (1970).
- ³¹P. M. A. Sherwood, *Vibrational Spectroscopy of Solids* (Cambridge University Press, Cambridge, 1972).
- ³²G. Dharmasena and R. Frech, *J. Chem. Phys.* **102**(17), 6941 (1995).
- ³³R. Frech and D. Teeters, *J. Phys. Chem.* **88**(3), 417 (1984).
- ³⁴C. Kittel, *Introduction to Solid State Physics*, 3rd ed. (Wiley New York, 1968).
- ³⁵T. G. Mayerhöfer, H. H. Dunken, R. Keding, and C. Rüssel, *J. Non-cryst. Solids* **333**, 172 (2004).
- ³⁶J. C. Decius, *J. Chem. Phys.* **49**(3), 1387 (1968).
- ³⁷R. Frech and J. C. Decius, *J. Chem. Phys.* **54**(6), 2374 (1971).
- ³⁸R. Frech, *J. Chem. Phys.* **60**(4), 1678 (1974).
- ³⁹G. J. Wu and R. Frech, *J. Phys. Chem.* **66**(3), 1352 (1977).
- ⁴⁰J. P. Devlin, D. W. James, and R. Frech, *Chem. Phys. Lett.* **12**(4), 602 (1972).
- ⁴¹J. P. Devlin, G. Pollard, and R. Frech, *J. Chem. Phys.* **53**(11), 4147 (1970).
- ⁴²A. R. Choudhury, N. Winterton, A. Steiner, A. I. Cooper, and K. A. Johnson, *Cryst. Eng. Comm.* **8**, 742 (2006).
- ⁴³J. A. Bardwell and M. J. Dignam, *Anal. Chim. Acta* **172**, 101 (1985).
- ⁴⁴J. A. Bardwell and M. J. Dignam, *J. Chem. Phys.* **83**(11), 5468 (1985).
- ⁴⁵J. A. Bardwell and M. J. Dignam, *Anal. Chim. Acta* **181**, 253 (1986).
- ⁴⁶M. J. Dignam and S. Mamiche-Afara, *Spectrochim. Acta* **44A**(12), 1435 (1988).
- ⁴⁷T. Buffeteau, J. Grondin, and J.-C. Lasségues, *Appl. Spectrosc.* **64**(1), 112 (2010).
- ⁴⁸T. Buffeteau, J. Grondin, Y. Danten, and J.-C. Lasségues, *J. Phys. Chem. B* **114**(22), 7587 (2010).
- ⁴⁹K. Yamamoto, A. Masui, and H. Ishida, *Appl. Opt.* **33**(27), 6285 (1994).
- ⁵⁰E. Bright Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra* (Dover, New York, 1955).
- ⁵¹C. Hardacer, J. D. Holbrey, S. E. J. McMath, D. T. Bowron, and A. K. Soper, *J. Chem. Phys.* **118**(1), 273 (2003).
- ⁵²C. Hardacer, S. E. J. McMath, M. Nieuwenhuyzen, D. T. Bowron, and A. K. Soper, *J. Phys.: Condens. Matter* **15**, S159 (2003).
- ⁵³M. Deetlefs, C. Hardacer, M. Nieuwenhuyzen, A. A. H. Padua, O. Sheppard, and A. K. Soper, *J. Phys. Chem.* **110**, 12055 (2006).
- ⁵⁴C. Hardacer, J. D. Holbrey, C. L. Mullan, T. G. A. Youngs, and D. T. Bowron, *J. Chem. Phys.* **133**, 074510 (2010).
- ⁵⁵K. Fujii, Y. Soejima, Y. Kyoshoin, S. Fukuda, R. Kanzaki, Y. Umebayashi, T. Yamaguchi, S.-I. Ishiguro, and T. Takamuku, *J. Phys. Chem. B* **112**, 4329 (2008).
- ⁵⁶A. Triolo, A. Mandanici, O. Russina, V. Rodriguez-Mora, M. Cutroni, C. Hardacer, M. Nieuwenhuyzen, H.-J. Bleif, L. Keller, and M. A. Ramos, *J. Phys. Chem. B* **110**, 21357 (2006).
- ⁵⁷A. Triolo, O. Russina, H.-J. Bleif, and E. Di Cola, *J. Phys. Chem. B* **111**, 4641 (2007).
- ⁵⁸A. Triolo, O. Russina, B. Fazio, R. Triolo, and E. Di Cola, *Chem. Phys. Lett.* **457**, 362 (2008).
- ⁵⁹D. Xiao, L. G. Hines Jr., S. Li, R. A. Bartsch, and E. L. Quitevis, *J. Phys. Chem. B* **113**, 6426 (2009).
- ⁶⁰J. N. A. Canongia Lopes and A. A. H. Pádua, *J. Phys. Chem. B* **110**, 3330 (2006).
- ⁶¹D. Xiao, J. R. Rajian, L. G. Hines Jr., S. Li, R. A. Bartsch, and E. L. Quitevis, *J. Phys. Chem. B* **112**, 13316 (2008).
- ⁶²D. Xiao, J. R. Rajian, A. Cady, S. Li, R. A. Bartsch, and E. L. Quitevis, *J. Phys. Chem. B* **111**, 4669 (2007).
- ⁶³C. J. Bowles, D. W. Bruce, and K. R. Seddon, *Chem. Commun. (Cambridge)* 1625 (1996).
- ⁶⁴J. D. Holbrey and K. R. Seddon, *J. Chem. Soc. Dalton Trans.* 2133 (1999).