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Temperature- and pressure-dependent infrared spectroscopy of 1-butyl-3-methylimidazolium trifluoromethanesulfonate: A dipolar coupling theory analysis

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A B S T R A C T

Continued growth and development of ionic liquids requires a thorough understanding of how cation and anion molecular structure defines the liquid structure of the materials as well as the various properties that make them technologically useful. Infrared spectroscopy is frequently used to assess molecular-level interactions among the cations and anions of ionic liquids because the intramolecular vibrational modes of the ions are sensitive to the local potential energy environments in which they reside. Thus, different interaction modes among the ions may lead to different spectroscopic signatures in the vibrational spectra. Charge organization present in ionic liquids, such as 1-butyl-3-methylimidazolium trifluoromethanesulfonate ($[C_4mim]CF_3SO_3$), is frequently modeled in terms of a quasicrystalline structure. Highly structured quasilattices enable the dynamic coupling of vibrationally-induced dipole moments to produce optical dispersion and transverse optical-longitudinal optical (TO-LO) splitting of vibrational modes of the ionic liquid. According to dipolar coupling theory, the degree of TO-LO splitting is predicted to have a linear dependence on the number density of the ionic liquid. Both temperature and pressure will affect the number density of the ionic liquid and, therefore, the amount of TO-LO splitting for this mode. Therefore, we test these relationships through temperature- and pressure-dependent FT-IR spectroscopic studies of $[C_4mim]CF_3SO_3$, focusing on the totally symmetric S—O stretching mode for the anion, $\nu_s(SO_3)$. Increased temperature decreases the amount of TO-LO splitting for $\nu_s(SO_3)$, whereas elevated pressure is found to increase the amount of band splitting. In both cases, the experimental observations follow the general predictions of dipolar coupling theory, thereby supporting the quasilattice model for this ionic liquid.

1. Introduction

Intense research efforts have produced a wide assortment of ionic liquids with diverse properties that may be targeted through sensible choices of cation and anion combinations [1,2]. In many cases, ionic liquids are now poised to move into technological niches that have been traditionally dominated by molecular solvents. A defining characteristic of ionic liquids is the presence of an extensive charge-organized network among the constituent ions that arises from a combination of Coulombic interactions among the ions and short range repulsive forces. The presence of charge organization has led to the emergence of a quasilattice model for the liquid structure of ionic liquids, wherein ions are viewed as being distributed over sites of a disordered solid-like lattice. Furthermore, many cations and, to a lesser extent, anions possess long alkyl side chains. These non-polar moieties may produce mesoscale structural organization through the segregation of the polar and apolar domains of the ions [3]. Ionic liquids, therefore, have a rich liquid structure that is only now beginning to be fully unraveled. The molecular factors that govern ionic liquid structure are not known nor is the relationship between liquid structure and the properties that make ionic liquids interesting as solvents well understood. Elucidating these structure-property maps remains a critical need and is an active area of research.

Vibrational spectroscopy is frequently used to investigate ionic interactions within an ionic liquid, for the intramolecular vibrational mode frequencies and intensities of the ions are sensitive to their local potential energy environments. Consequently, changes in molecular interactions between ions may be detected through variations in band intensities and frequencies in the IR and Raman spectra of the compounds. For instance, Akai and co-workers [4] thermally vaporized $[C_2mim]CF_3SO_3$ to isolate ion pairs within a neon gas matrix. Vibrational spectroscopy of the matrix-isolated ion pair reveals five hydrogen bonds between the oxygen atoms of the $CF_3SO_3^-$ anion and four individual hydrogen atoms belonging to the imidazolium cation. Three of these hydrogen atoms are located on the ethyl and methyl side chains, while

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the fourth hydrogen atom is bonded to the $C_{(2)}$ carbon atom found between the two nitrogen atoms of the imidazolium ring. Singh et al. [5] and Faria and Ribeiro [6] used a combination of density functional theory calculations and vibrational spectroscopy to characterize ion-ion interactions in bulk samples of $[C_2mim]CF_3SO_3$. These experiments also consistently show an interaction between triflate anions and imidazolium cations through $C_{(2)}$-H⋯O interactions as well as hydrogen atoms found along the methyl and alkyl side chains of the cation. Molecular dynamics (MD) simulations provide a powerful set of tools for understanding vibrational spectroscopic signatures of $CF_3SO_3^-$-containing ionic liquids [7–9]. The prevailing result from MD simulations is that local interactions among ions is best described in terms of ionic cages rather than the formation of discrete, long-lived ion pairs between cations and anions; an observation that is in excellent agreement with prior Raman spectroscopic experiments of the ionic liquid [10,11] and the inherently low vapor pressures of these compounds.

From a vibrational spectroscopy point of view, charge organization of ions into a quasilattice will affect the vibrational spectroscopic signatures of the cations and anions. Coupling of vibrationally-induced dipole moments across the quasilattice may produce long-wavelength optical phonons that split vibrational modes into transverse optic (TO) and longitudinal optic (LO) modes [12]. Polarization of the ionic liquid by the optical phonons will influence the local potential energy of the anions, shifting the LO mode frequency higher than the frequency of the TO modes. Such TO-LO splitting of infrared-active vibrational modes has previously been invoked to explain the vibrational spectrum of $[C_nmim]CF_3SO_3$ [12–14] and $[C_nmim](CF_3SO_2)_2N$ [15,16] ionic liquids. More recently, Reichenbach and co-workers [17] argued that the far-IR spectrum of protic ionic liquids must be interpreted in terms of transverse and longitudinal optical phonons.

According to dipolar coupling theory [18], the degree of TO-LO splitting depends on the magnitude of the dipole moment derivative $\partial\mu/\partial q$, the number density N of the ionic liquid, molecular polarizabilities, and the long-range geometric arrangement of the molecules (embodied by the term L). If we ignore the role of molecular polarizabilities in mediating the dipole-dipole interactions, the TO-LO splitting of a vibrational mode (in units of cm^{-1}) is given by the relatively simple formula

$$\tilde{\nu}_{LO}^2 - \tilde{\nu}_{TO}^2 = L\left(\frac{\partial\mu}{\partial q}\right)^2 N \tag{1}$$

The value of L is calculable if the compound is crystalline and the crystal structure is known. For simple cubic crystals containing a single formula unit, $L = \pi^{-1}c^{-2}$ where c is the speed of light in cm s^{-1} [18,19]. An important prediction of this equation is the linear relationship between the amount of TO-LO splitting manifested by a molecular vibration and the number density of the ionic liquid.

Dipolar coupling theory successfully explained the band shapes of select vibrational modes for ionic liquids containing the $CF_3SO_3^-$ and $(CF_3SO_2)_2N^-$ anions [13–15]. In those experiments, however, the number density of the anions was varied by lengthening the alkyl side chain grafted onto the cations. Longer alkyl chains reduce the density of the ionic liquid, and concomitantly, the amount of TO-LO splitting was diminished. Varying the temperature and pressure offers an alternative means to affect the number density of the ionic liquid. Indeed, temperature increases will decrease the number density, while elevated pressures will increase the number density. If the dipolar coupling theory formalism is correct, we anticipate corresponding changes in the infrared spectra of an ionic liquid in keeping with the predictions of dipolar coupling theory.

2. Experimental Methods

Temperature-dependent Fourier transform infrared (FT-IR) spectra were recorded with a Nicolet 6700 infrared spectrometer operating under dry air purge. Spectra were collected at 1 cm^{-1} resolution with a deuterated triglycine sulfate detector. Approximately 0.9 μL of 1-butyl-3-methylimidazolium trifluoromethanesulfonate ($[C_4mim]CF_3SO_3$, Iolitech) was sandwiched between two ZnSe windows. The temperature was varied in 10 K increments from 253 to 353 K (± 0.1 K). The sample thicknesses are estimated to be 8 μm.

Pressure-dependent IR spectra were measured on a Perkin-Elmer IR spectrometer (Spectrum RXI) equipped with a 5× beam condenser. Typically, we chose a resolution of 4 cm^{-1} (data resolution of 2 cm^{-1}). High-pressure technical details are available elsewhere [20]. Briefly speaking, a diamond anvil cell (DAC) of Merrill-Bessett design with two type–IIa diamonds was used to generate pressures of up to ca. 2 GPa. Samples were contained in a 0.3 mm-diameter hole in a 0.25 mm-thick Inconel gasket, and part of the hole was filled with CaF_2 to avoid saturation of the absorption bands. To remove absorption of the diamond anvils, the absorption spectrum of the DAC was measured first and subtracted from those of the samples. The pressure-dependent IR spectra have variable thicknesses as the application of pressure results in some degree of sample compression and a concomitant reduction of the path length.

Spectral processing was performed with Spectragryph v1.1.1. Derivative spectra were calculated after a Savitsky-Golay smoothing algorithm was applied to the infrared spectra. The smoothing routine uses a third order polynomial with 20 points.

3. Results and Discussion

Fig. 1 contains FT-IR spectra of $[C_4mim]CF_3SO_3$ measured at ambient pressure and temperatures ranging from 253 to 353 K. The spectra consist of a single, asymmetric band centered near 1032 cm^{-1}. This band is assigned to symmetric stretching motions of the S—O bonds in the $CF_3SO_3^-$ anion, $\nu_s(SO_3)$ [21]. The frequency of the band maximum decreases slightly from 1032.0 to 1031.5 cm^{-1} as the temperature is increased. Simultaneously, the band undergoes a smooth progression to become more symmetric. Above 333 K, the band has lost all discernable asymmetry.

The asymmetry of $\nu_s(SO_3)$ finds its origin in the long-range coupling of vibrationally-induced dipole moments across the charge-organized quasilattice of $[C_4mim]CF_3SO_3$ [13,14]. While the $\nu_s(SO_3)$ TO modes may be directly measured through the absorption of a photon during an infrared spectroscopic experiment, the corresponding LO mode cannot be probed in the same manner [22]. During an IR transmission experiment, infrared radiation is incident upon the ionic liquid, and the amount of electromagnetic radiation that is transmitted through the sample is detected. In this experimental configuration, absorption and reflection processes both contribute to the total measured band intensity. When a photon enters the ionic liquid, the electromagnetic field of the photon may mix with the mechanical vibrational motions of the ionic liquid to produce a polariton. These entities are neither purely electromagnetic nor purely mechanical in nature, and the relative fraction of electromagnetic and mechanical character of the polariton depends on the frequency of the incident electromagnetic radiation and the resonance frequency of the vibrational mode. Between the TO and LO mode frequencies, the polariton that is formed will have a large amount of phonon-like character, and the ionic liquid will be unable to support the transmission of electromagnetic radiation. This will result in a substantial amount of reflection. Anharmonic forces between the vibrating ions ensure at least partial transmission of electromagnetic radiation between the TO and LO mode frequencies. From an experimental point of view, the combination of absorption at the TO mode frequency and reflection between the TO and LO frequencies lead to the asymmetric band shape observed in Fig. 1. Therefore, it is possible to discern the frequency of the LO mode from an IR transmission experiment by analyzing the shape of the band that is produced.

The TO mode frequency is typically identified as the frequency of the band maximum, while the LO mode frequency is generally located near