

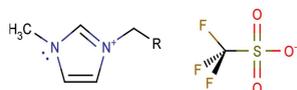


Introduction

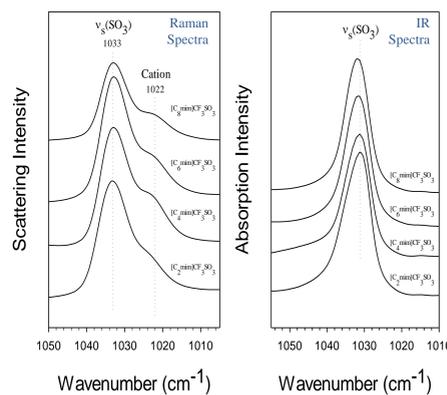
- The long-range structure of room-temperature ionic liquids (RTILs) is believed to exhibit some degree of charge organization that extends over several solvation shells.
- According to a quasilattice model of charge organization, the local environment about the constituent ions of a RTIL may be viewed in terms of a perturbed crystal lattice with some degree of disorder introduced over the ion sites.
- The resulting uniform distribution of charge has important implications on the properties of ionic liquids, for these properties are rooted in the ion-ion interactions that give rise to the quasilattice structure of the materials.
- Ionic liquid charge organization is usually measured through neutron scattering experiments. These methods are not practical for routine measurements, which are needed to enable the rational, targeted synthesis of RTILs towards specific technological applications.
- We present a new approach for quantifying charge organization in ionic liquids using relatively simple infrared spectroscopic measurements.

Compounds Investigated

1-alkyl-3-methylimidazolium trifluoromethanesulfonate $[C_n\text{mim}]CF_3SO_3$ ($n = 2, 4, 6, \text{ and } 8$)



Vibrational Spectroscopy



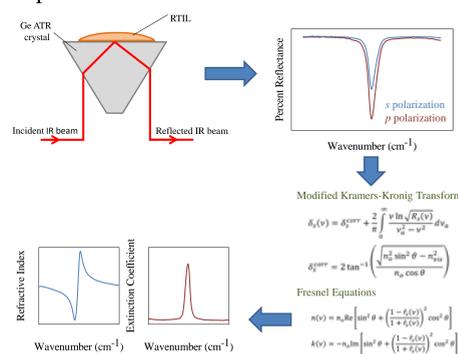
- Minor changes in $v_s(SO_3)$ bands as alkyl side chain is lengthened
- There is a slight asymmetry in the IR bands

Theoretical Background

A quantitative measure of charge organization is achieved by comparing two independent measurements of the dipole moment derivative of select vibrational modes. The first is derived from the Kramers-Kronig transform of ATR IR spectra, while the second comes from transmission IR spectra and applying dipolar coupling theory.

ATR FT-IR Spectroscopy

- Bardwell and Dignam developed methods for calculating optical constants from s-polarized ATR FT-IR spectra

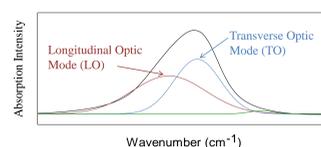


- Calculate the dipole moment derivative from the extinction coefficient: $\left(\frac{\partial\mu}{\partial q}\right)_{ATR}^2 = \frac{12cv_0}{N} \int_{band} k(\tilde{\nu}) d\tilde{\nu}$

Transmission FT-IR Spectroscopy

- Transverse optic and longitudinal optic (TO/LO) mode splitting is observed in molten alkali metal salts.
- Magnitude of splitting correlates to the degree of quasilattice structure in the molten phase.
- Dipolar coupling theory (DCT) relates the degree of TO/LO splitting to the dipole moment derivative:

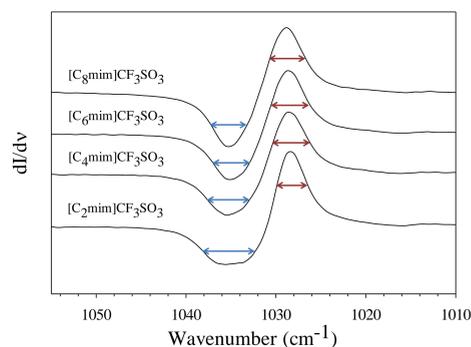
$$\left(\frac{\partial\mu}{\partial q}\right)_{Trans}^2 = \frac{1}{4\pi N} (v_{LO}^2 - v_{TO}^2)$$



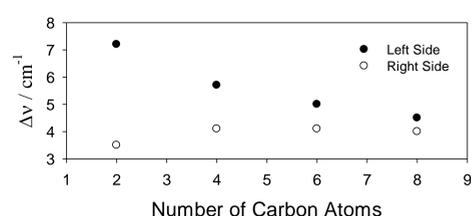
- Disparities between the dipole moment derivatives calculated from dipolar coupling theory (transmission spectra) and the Kramers-Kronig transform (ATR spectra) is likely due to a violation of dipolar coupling theory, specifically the assumption of perfect crystalline lattice.

First Derivative Plots

- First derivatives of the transmission FT-IR spectra are plotted to better depict the asymmetry in the $v_s(SO_3)$ band:



- The degree of asymmetry decreases as the alkyl side chain length increases:



Dipole Moment Derivative Ratios

- Dipole moment derivative ratios are calculated from ATR and transmission FT-IR spectra using the methods outlined in the theoretical background.

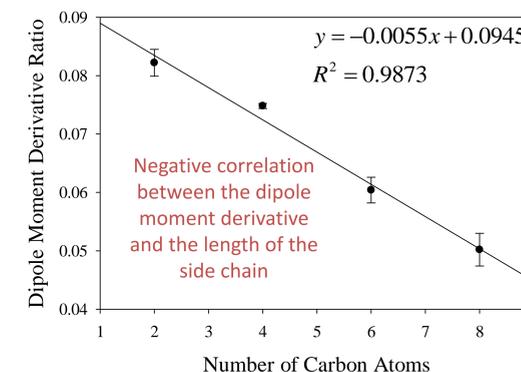
Compound	$\left(\frac{\partial\mu}{\partial q}\right)_{ATR}$ ($cm^{3/2}\cdot s$)	$\left(\frac{\partial\mu}{\partial q}\right)_{Trans}$ ($cm^{3/2}\cdot s$)	Dipole Moment Derivative Ratio
$[C_2\text{mim}]CF_3SO_3$	172.3	14.16 ± 0.40	0.0822 ± 0.0023
$[C_4\text{mim}]CF_3SO_3$	170.0	12.71 ± 0.07	0.0748 ± 0.0004
$[C_6\text{mim}]CF_3SO_3$	174.7	10.56 ± 0.38	0.0604 ± 0.0022
$[C_8\text{mim}]CF_3SO_3$	177.0	8.88 ± 0.49	0.0502 ± 0.0028

$$\text{Dipole Moment Derivative Ratio} = \frac{\left(\frac{\partial\mu}{\partial q}\right)_{Trans}}{\left(\frac{\partial\mu}{\partial q}\right)_{ATR}}$$

- The dipole moment derivative determined from ATR FT-IR spectra is virtually unchanged as the alkyl chain length increases ($173.5 \pm 3.0 \text{ cm}^{3/2}\cdot s$)
- The dipole moment derivative calculated from dipolar coupling theory is much smaller than that calculated from the Kramers-Kronig transform and decreases with increasing alkyl chain length

Assessing Charge Organization

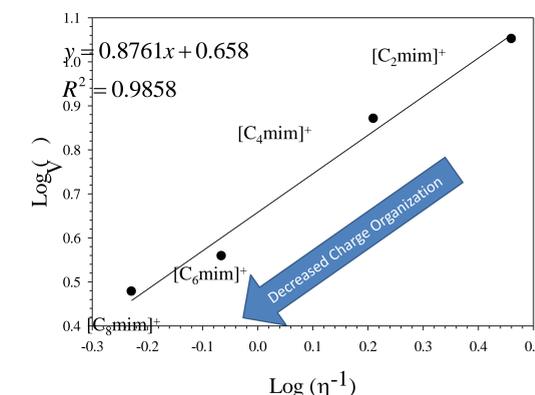
- Dipole moment derivative ratios (transmission to ATR) decrease with increasing alkyl chain length.
- Charge organization in ionic liquids can be assessed from dipole moment derivative ratios because theory giving $\left(\frac{\partial\mu}{\partial q}\right)_{Trans}$ sensitive to quasilattice structure whereas that giving $\left(\frac{\partial\mu}{\partial q}\right)_{ATR}$ is not.



- The ionic liquids studied are all disorganized and those with longer side chains are more disorganized than short side-chain analogs.

Transport Properties

- Molar conductivities (L) and fluidities (h^{-1}) of the four ionic liquids are reported for $T = 30^\circ C$:



- Increasing the length of the alkyl side chain on the imidazolium ring decreases both the fluidity and conductivity of the ionic liquid
- Decreased values in these transport properties may be due to decreased amounts of charge organization for these ionic liquids.

Conclusions

- We propose that charge organization in ionic liquids can be effectively measured with simple ATR and transmission FT-IR spectroscopic methods.
- The ionic liquids investigated are all somewhat disorganized at room temperature, with longer alkyl side chains producing a higher amount of disorder.
- Long alkyl side chains may inhibit charge organization by frustrating ion-ion interactions
- Conductivity and fluidity trends for the four ionic liquids decrease as the length of the alkyl side chain increases.
- It is possible that trends in the transport properties of ionic liquids may be explained, in part, by variations in the degree of charge organization and our methods provide a simple, cheap way to obtain such information.

Acknowledgments

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