Infrared Spectroscopy of Ionic Liquids: Quantitative Aspects and Determination of Optical Constants

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The infrared (IR) spectra of ionic liquids involving 1-butyl-3-methylimidazolium (BMI) and the $(CF_3SO_2)_2N$, BF_4, or PF_6 anions, recorded in the **transmission and attenuated total reflection (ATR) modes, exhibit strong differences in the most intense anion absorption profiles**. These distortions come from optical effects and make difficult any quantitative analysis of, for example, the antisymmetric stretching vibrations of the BF_4 and PF_6 anions. **A method is proposed to determine the optical constants, from which any type of experimental spectrum can be simulated**. It is then possible to use the anion vibrational bands as spectroscopic probes of the local interactions occurring in the neat ionic liquids and in solutions. This is illustrated by a direct identification of ion pairs and separated ions in the IR spectra of BMI–PF6 solutions.

2011.08.03.

Seoncheol Cha

Introduction

IR Spectroscopy for Ionic Liquids

conformational state of cations & anions
(with Raman spectroscopy & *ab initio* calculations)

interactions within ion pairs & larger clusters

Introduction

IR spectra of ionic liquids exhibit intense anion absorption bands (high concentration)

<0.5 µm thickness are required in the FT-IR

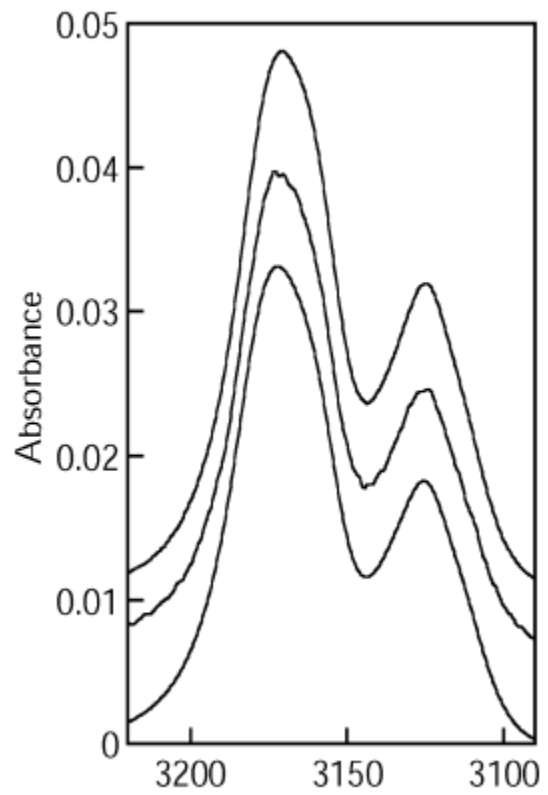# Comparison of the Infrared Spectra of Ionic Liquids Obtained Under Different Conditions

[BMIM][PF6]

Imidazolium CH stretching   Antisymmetric stretching PF6   Symmetric stretching PF6

Comparison of the Infrared Spectra of Ionic Liquids Obtained Under Different Conditions
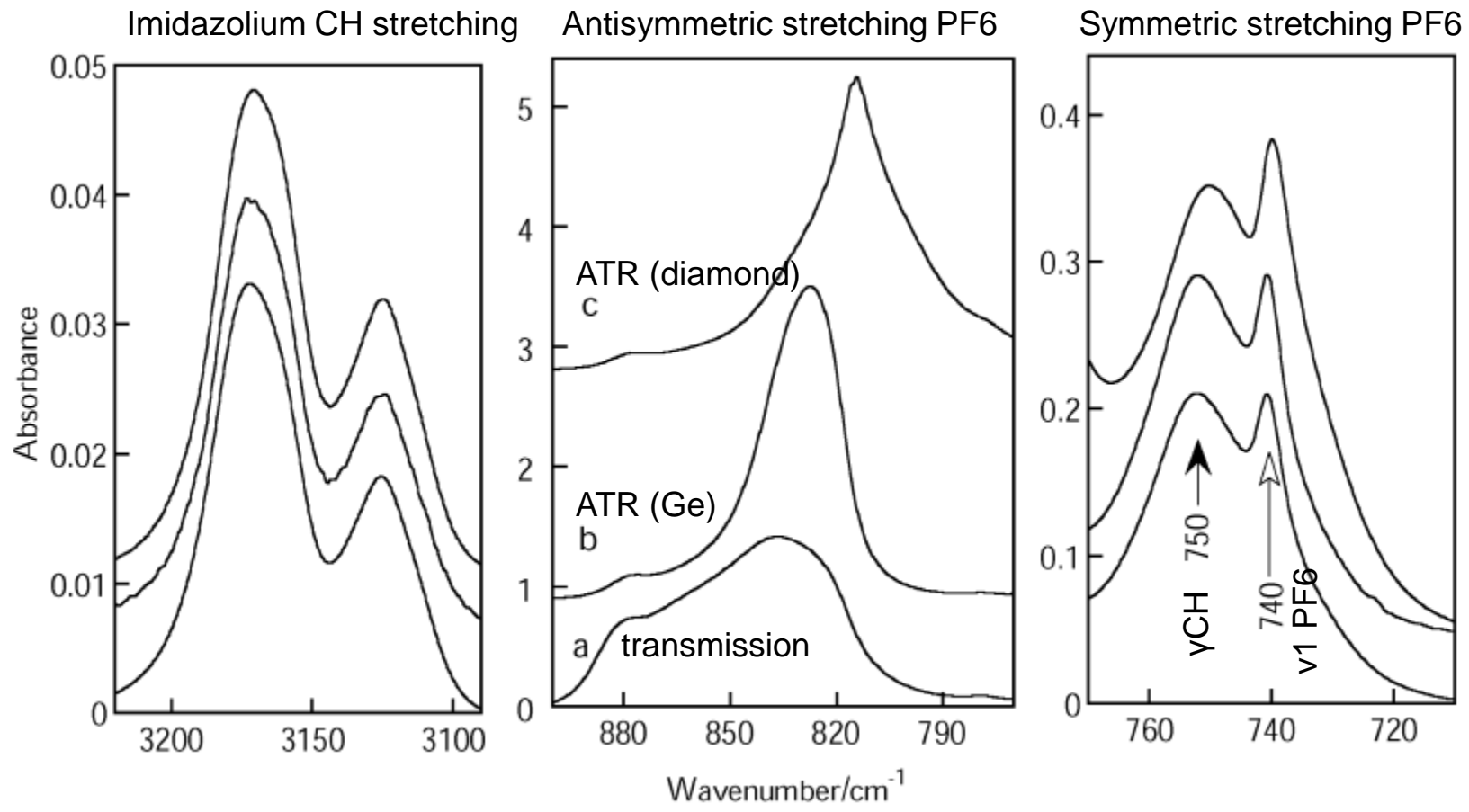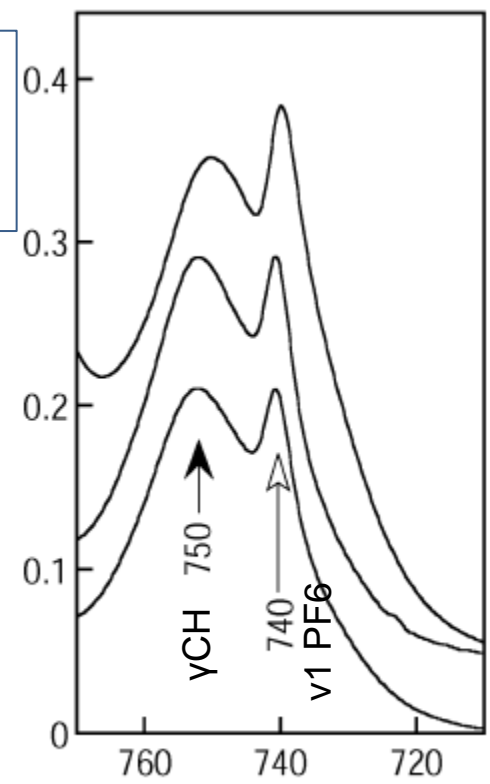
[BMIM][PF6]

Imidazolium CH stretching

Symmetric stretching PF6

For absorptions of weak to medium intensities, the ATR and transmission spectra are little different
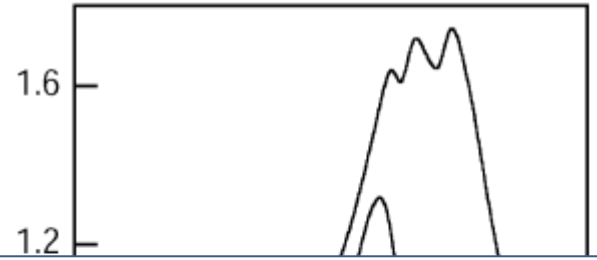
Comparison of the Infrared Spectra of Ionic Liquids Obtained Under Different Conditions
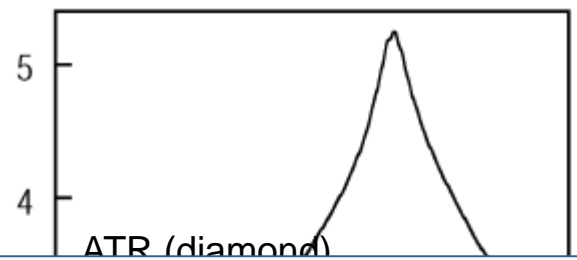
[BMIM][BF4]
Antisymmetric stretching BF4

[BMIM][PF6]
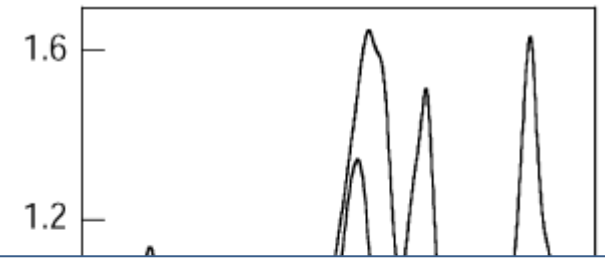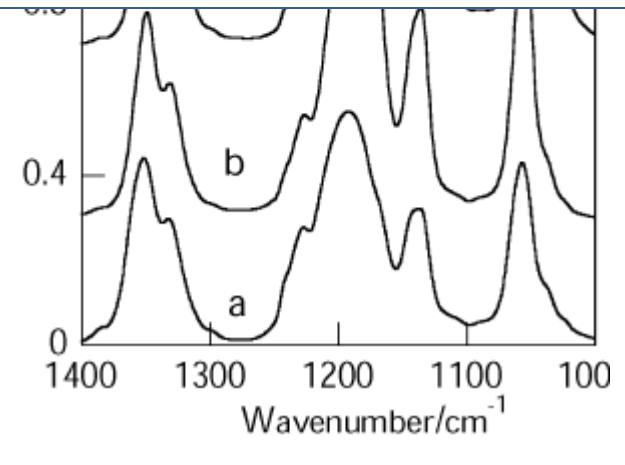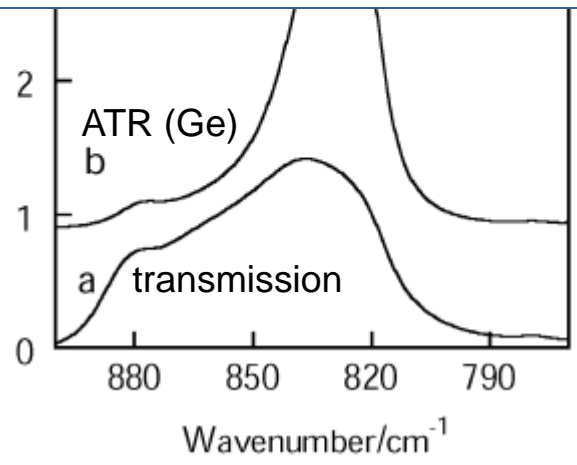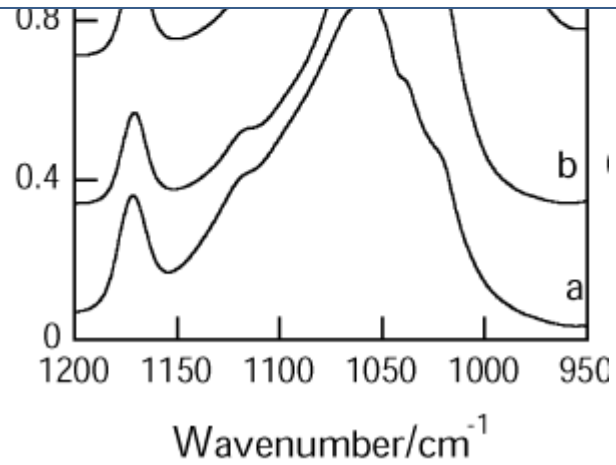Antisymmetric stretching PF6

[BMIM][TFSI]
$v_a CF_3$ stretching TFSI

PF6 antisymmetric stretcing mode is considerbly distorted as a strong absorption.
And less intense absorptions of BF4 and TFSI bands are less distorted

ATR (diamond)

ATR (Ge)
b

a   transmission

b

a

Wavenumber/cm^{-1}

Comparison of the Infrared Spectra of Ionic Liquids Obtained Under Different Conditions

[BMIM][PF6]

Symmetric stretching PF6

γCH 750 →
740 →
v1 PF6
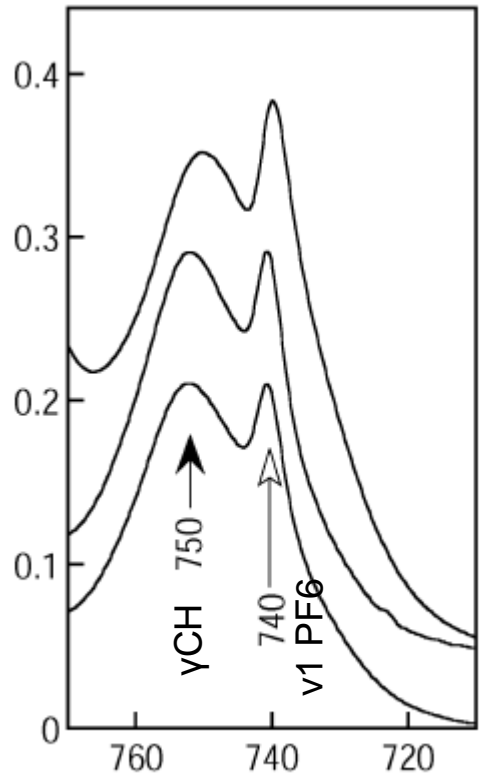
[BMIM][BF4]

Symmetric stretching BF4

850 →
v1 BF4
763 →
753
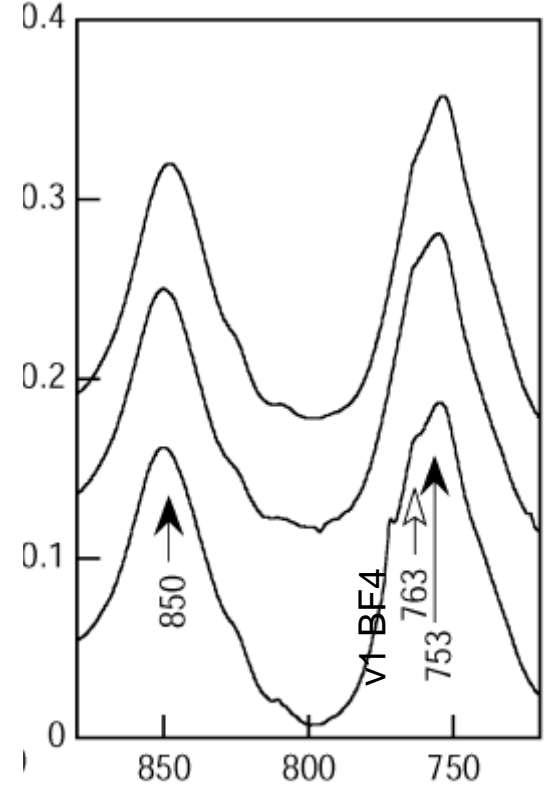
Symmetric stretching of PF6 (octahedral) and BF4 (tetrahedral) is observed

The symmetry of the octahedral and tetrahedral symmetric stretching is IR inactive

Symmetry has been lowered

Anions have the anisotropic interaction

Determination of the Optical Constants

Fresnel Reflection coefficients

$$\hat{r}_v = R_v^{\pm} \exp(i\theta_v),$$

$$\hat{r}_s = \frac{n_0 \cos \alpha_0 - \hat{n}_t \cos \alpha_s}{n_0 \cos \alpha_0 + \hat{n}_t \cos \alpha_s}$$

$$\hat{r}_p = \frac{\hat{n}_t \cos \alpha_0 - n_0 \cos \alpha_p}{\hat{n}_t \cos \alpha_0 + n_0 \cos \alpha_p}$$

$$\hat{\varepsilon} = \hat{n}^2$$

$$\hat{\varepsilon}_t / \varepsilon_0 = \sin^2 \alpha_0 + [(1 - \hat{r}_s)/(1 + \hat{r}_s)]^2 \cos^2 \alpha_0$$

$$\hat{\varepsilon}_n / \varepsilon_0 = \sin^2 \alpha_0 / [1 - (\hat{\varepsilon}_t / \varepsilon_0)\{(1 - \hat{r}_p)/(1 + \hat{r}_p)\}^2 \cos^2 \alpha_0]$$

Snell's law

$$n_0 \sin \alpha_0 = \hat{n}_t \sin \alpha_s = \hat{n}_n \sin \alpha_p$$

$$\theta'_s + \Delta \theta_s \simeq \theta_s$$

Determination of the Optical Constants

Fresnel Reflection coefficients

$$\hat{r}_v = R_v^{\frac{1}{2}} \exp(i\theta_v),$$

$$\hat{r}_s = \frac{n_0 \cos \alpha_0 - \hat{n}_t \cos \alpha_s}{n_0 \cos \alpha_0 + \hat{n}_t \cos \alpha_s}$$

$$\hat{r}_p = \frac{\hat{n}_t \cos \alpha_0 - n_0 \cos \alpha_p}{\hat{n}_t \cos \alpha_0 + n_0 \cos \alpha_p}$$

Snell's law

$$n_0 \sin \alpha_0 = \hat{n}_t \sin \alpha_s = \hat{n}_n \sin \alpha_p$$

Kramers –Kronig relation with F.T.

$$\theta'_v(\bar{v}) = -4 \int_0^\infty d\delta \sin(2\pi\bar{v}\delta)$$

$$\times \int_0^\infty d\bar{v}_0 \ln[R_v(\bar{v}_0)]^{\frac{1}{2}} \cos(2\pi\bar{v}_0\delta)$$

Phase correction

$$\Delta\theta_s = \theta_s - \theta'_s = 2 \arctan[(n_0^2 \sin^2 \alpha_0 - n_t^2)^{\frac{1}{2}}/n_0 \cos \alpha_0] - \theta'_s,$$

$$\Delta\theta_p = \theta_p - \theta'_p = 2 \arctan[(n_0^2 \sin^2 \alpha_0 - n_n^2)^{\frac{1}{2}} n_0/n_n n_t \cos \alpha_0] - \theta'_p,$$

Determination of the Optical Constants

$$\delta(\nu_a) = I + \frac{2}{\pi} P \int_0^\infty \frac{\nu . \ln \sqrt{R_s(\nu)}}{\nu^2 - \nu_a^2} d\nu$$

$$I = 2 \arctan \frac{\sqrt{n_0^2 \sin^2 \theta_0 - n^2(\nu_u)}}{n_0 \cos \theta_0}$$
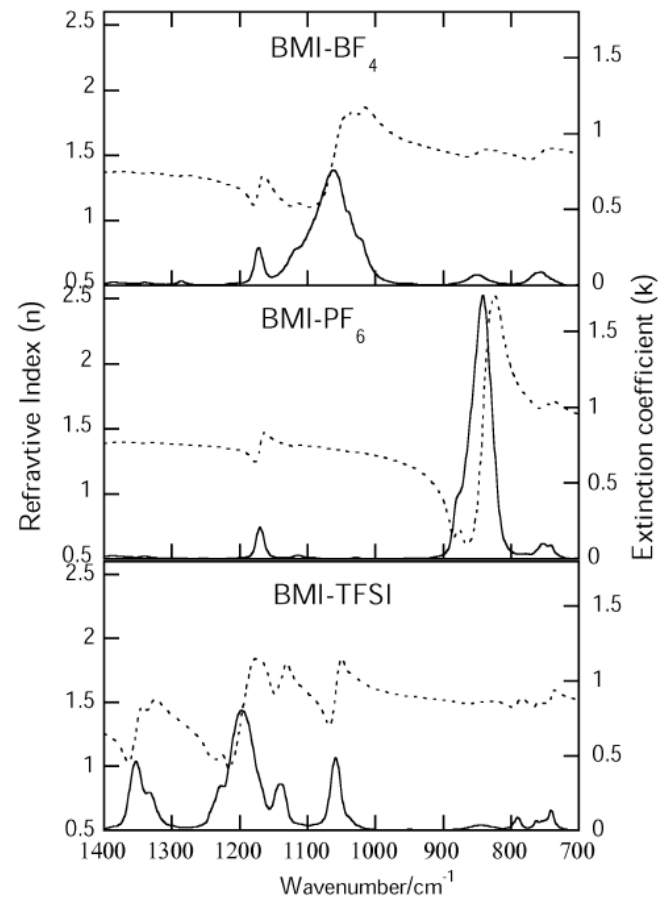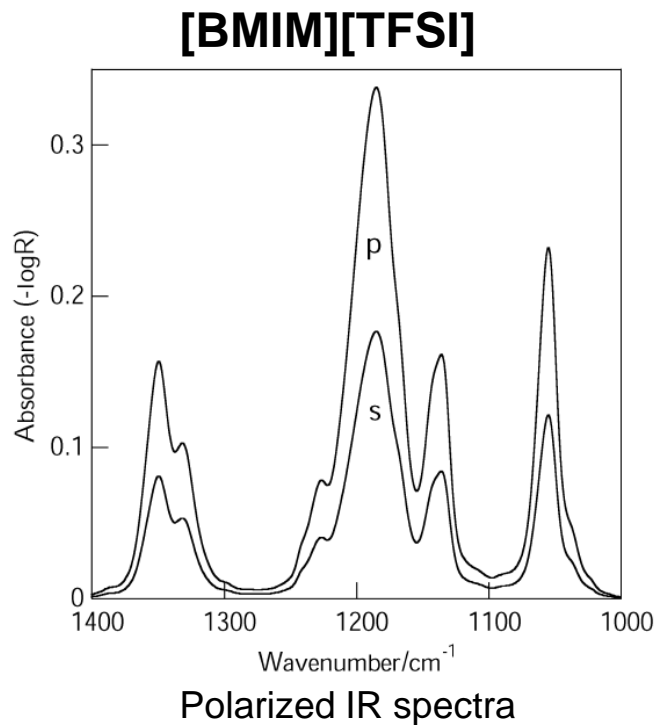
$$n(\nu) = n_0 \mathrm{Re} \left[\sin^2 \theta_0 + \left[\frac{1 - \hat{r}_s(\nu)}{1 + \hat{r}_s(\nu)} \right]^2 \cos^2 \theta_0 \right]^{1/2}$$

$$k(\nu) = -n_0 \mathrm{Im} \left[\sin^2 \theta_0 + \left[\frac{1 - \hat{r}_s(\nu)}{1 + \hat{r}_s(\nu)} \right]^2 \cos^2 \theta_0 \right]^{1/2}$$
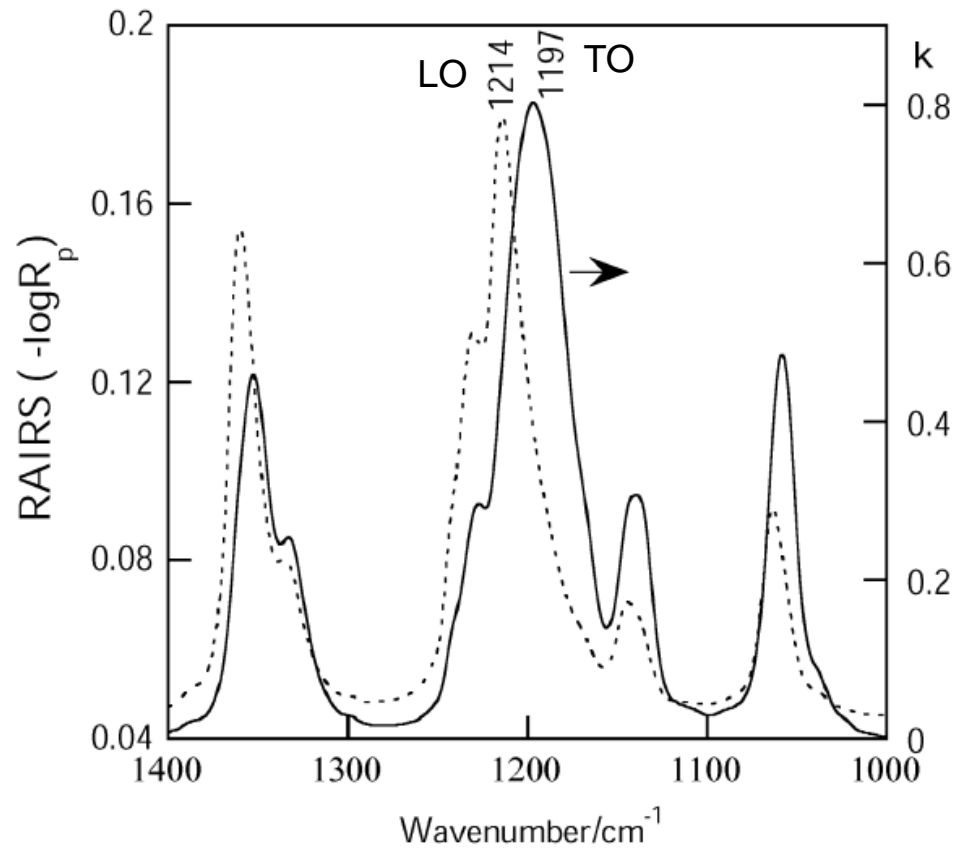
For K-K relation,
n(v, large) ~ constant
k(v, large) ~ small

n(v, small) ~ neglect
k(v, small) ~ neglect

Determination of the Optical Constants of Ionic Liquids from the ATR Spectra

[BMIM][TFSI]

Polarized IR spectra

Simulation of Various Infrared Spectra from the Optical Constants

RAIRS
p-pol
83.5 deg

Pure Ionic Liquids

	BMIM[PF6]		BMIM[BF4]		
	v_1	v_3	v_1	v_3	
Octahedral	Raman only	IR only	Raman only	IR, Raman	tetrahedral
C4v	IR (741cm^{-1}) Raman (741cm-1)	IR (841cm-1) Raman (864cm-1)	IR (763cm-1) Raman (764cm-1)	IR (1061, 1039 cm-1) Raman (1056 cm-1)	C3v

TABLE I. Observed anion vibrations for BMI-PF$_6$ at room temperature.

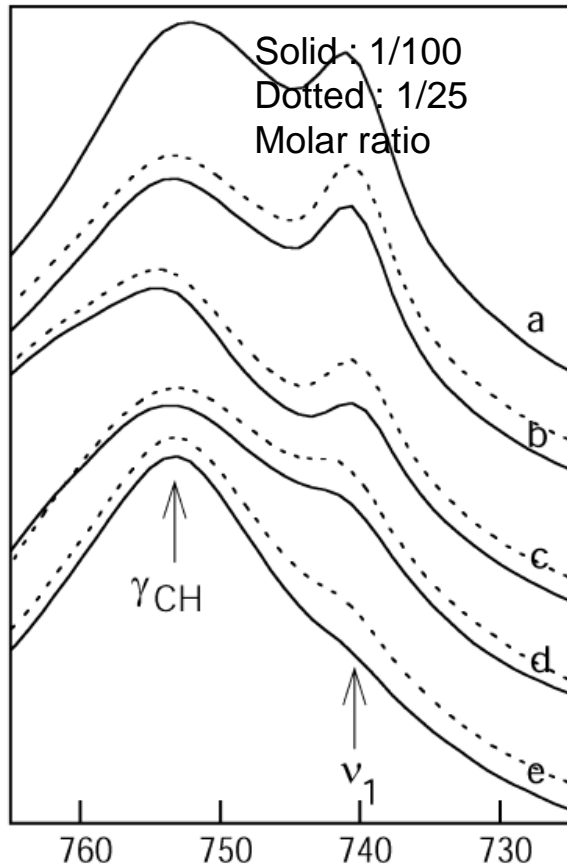| BMI-PF$_6$	v_1	v_2	v_3
O_h	A_{1g}, R	E_g, R	F_{1u}, IR
C_{4v}	A_1, IR, R	A_1, IR, R, B_1, R	A_1, IR, R, E, IR, R
IR, exp cm^{-1}	741[a]		841
Raman, exp cm^{-1}	741	567	864[a]

[a] Vibrations normally IR or Raman inactive in the O_h symmetry.

TABLE II. Observed anion vibrations for BMI-BF$_4$ at room temperature.

BMI-BF$_4$	v_1	v_2	v_3
T_d	A_1, R	E, R	T_2, IR, R
C_{3v}	A_1, IR, R	E, IR, R	E, IR, R, A_1, IR, R
IR, exp cm^{-1}	763[a]		1061, 1039
Raman, exp cm^{-1}	764.6	353	1056

[a] Vibrations normally IR inactive in the T_d symmetry.

From Pure Ionic Liquids to Dilute Solutions

Solid : 1/100
Dotted : 1/25
Molar ratio

TABLE I. Observed anion vibrations for BMI-PF$_6$ at room temperature.

BMI-PF$_6$	v_1	v_2	v_3
O$_h$	A$_{1g}$, R	E$_g$, R	F$_{1u}$, IR
C$_{4v}$	A$_1$, IR, R	A$_1$, IR, R, B$_1$, R	A$_1$, IR, R, E, IR, R
IR, exp cm^{-1}	741[a]		841
Raman, exp cm^{-1}	741	567	864[a]

[a] Vibrations normally IR or Raman inactive in the O$_h$ symmetry.

High dielectric constant

Small v1 IR signal
Oh > C4v

A : pure
B : DMC, dymethyl carbonate (ε=3.1)
C : Ac, acetone (ε=20.7)
D : PC, propylene carbonate (ε=64.4)
E : CAN-d$_3$, deuterated acetonitrile (ε=35)

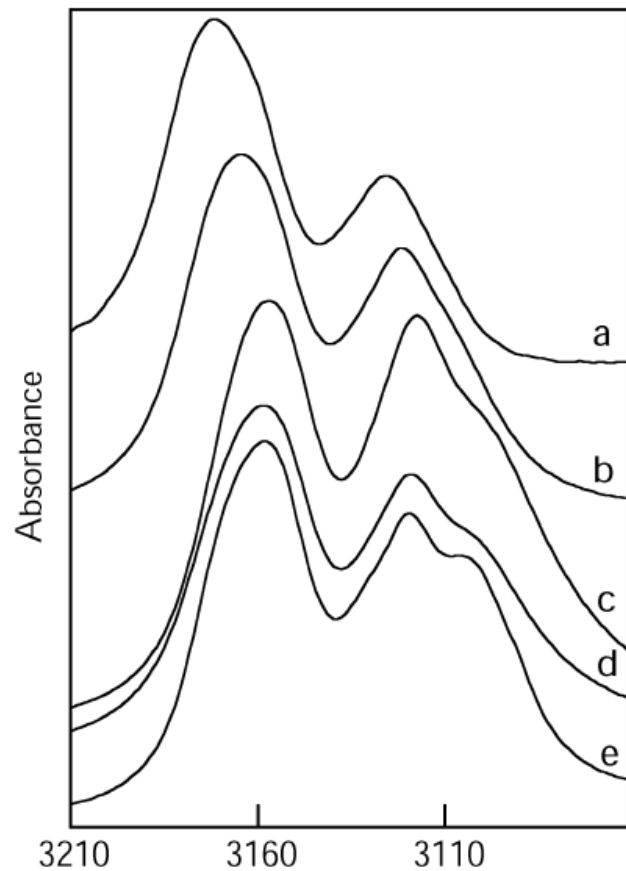# From Pure Ionic Liquids to Dilute Solutions

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Conclusion

Careful analysis is required in ATR measurement
(especially, low refractive index crystal and strong absorption)

Optical constants could be obtained by IR measurement.
-> ultimate quantitative information
-> oscillator strength effects, anisotropic orientations, simulating IR spectra

Anion vibrations constitute a good spectroscopic probe

Imidazolium-Based Ionic Liquids: Quantitative Aspects in the Far-Infrared Region

Thierry Buffeteau,* Joseph Grondin, Yann Danten, and Jean-Claude Lassègues

Institut des Sciences Moléculaires, UMR 5255, CNRS, Université Bordeaux I, 351 Cours de la Libération, 33405 Talence Cedex, France

The optical constants of some imidazolium-based ionic liquids (ILs) are determined in the mid- and far-infrared regions by combining polarized attenuated total reflection (ATR) and transmittance spectra. The internal vibrations of the cations and anions and the interionic vibrations can thus be quantitatively evaluated. A comparison of the far-IR spectral response of several imidazolium derivatives associated with the $(CF_3SO_2)_2N^-$ anion shows that methylation of the more acidic $C_{(2)}H$ imidazolium group does not change the far-IR intensity and hence that the $CH\cdots$anion hydrogen bonds play a negligible role compared with electrostatic interactions. The calculated spectra of ion-pair dimers reproduce the far-IR density of states better than those of simple ion pairs.
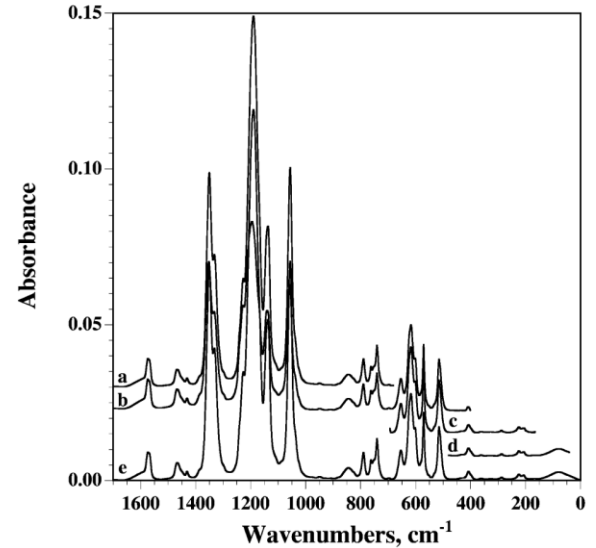
T.Buffeteau, J.Grondin,Y.Danten,J.C.Lassegues, JPCB (2010)

Determination of the Optical Constants

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$$I = 2\arctan\frac{\sqrt{n_0^2\sin^2\theta_0 - n^2(\nu_u)}}{n_0\cos\theta_0}$$

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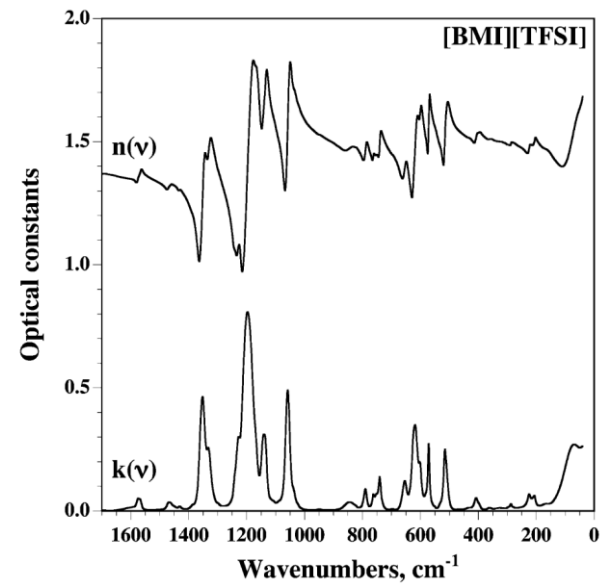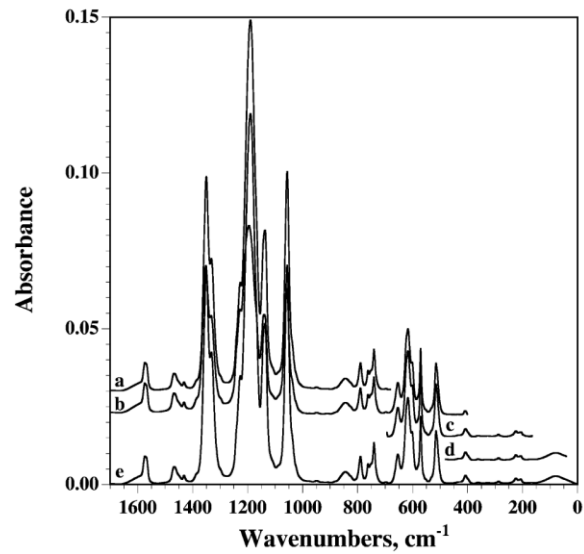
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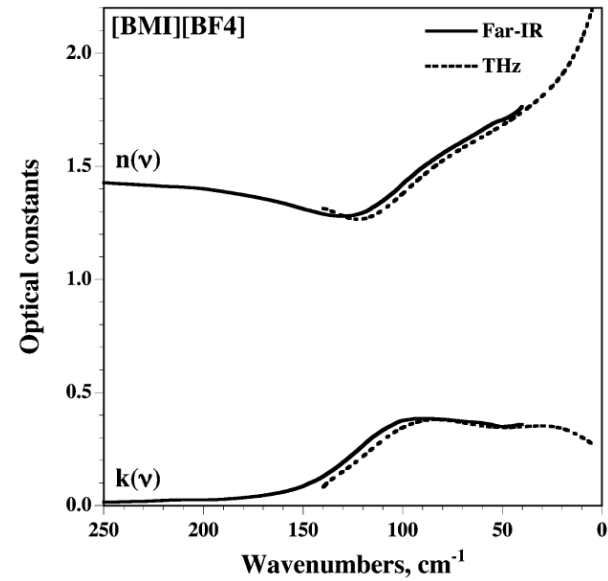
n(v, small) ~ neglect
k(v, small) ~ neglect
a

Determination of the Optical Constants

Comparison of the optical constants

Well-agreed with result from THz measurement

Determination of the Optical Constants