Revisited vibrational assignments of imidazolium-based ionic liquids

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Journal of Raman Spectroscopy **42**, 733 (2011)

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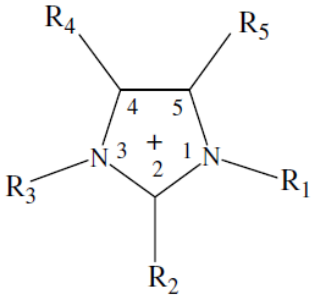
2012.2.18.Sat.

Introduction

Understanding ion-ion interaction

IR/Raman Spectroscopy & DFT calculation



	Cations	
	1,3-dimethyl imidazolium	MMI
	1-ethyl-3-methyl imidazolium	EMI-d_0
	1-ethyl-2d_1-3-methyl imidazolium	EMI-d_1
	1-ethyl-3-methyl-4,5-d_2- imidazolium	EMI-d_2
	1-ethyl-3-methyl-2,4,5-d_3- imidazolium	EMI-d_3
	1-butyl-3-methyl imidazolium	BMI
	1-butyl-2,3-dimethyl imidazolium	BMMI
	N-trimethyl-N-butylammonium	Me_3BuN
	1-butyl-1-methylpyrrolidinium	BuMePyr
	Anions	
$N(FSO_2)_2^-$	Bis(fluorosulfonyl)imide	FSI
$N(CF_3SO_2)_2^-$	Bis(trifluoromethanesulfonyl)imide	TFSI

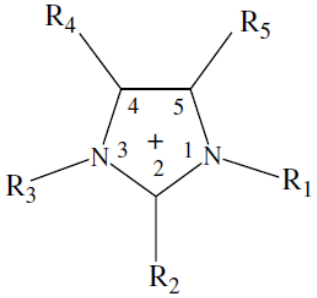
Materials

99.9% purchased from Solvionic

Three CH bonds of [EMI][Br] & [EMI][TFSI] were deutrated
$C_{(2)}$-H only for other Ils

[EMI][Br] / D_2O – molar ratio 1/5 to 1/100
$C_{(2)}H$ only
EMI-d_3 : 1/100 373K few weeks
EMI-d_2 : EMI-d_3 and H_2O

[EMI][TFSI] – CD_3OD -> EMI-d_1
EMI-d_3 : D_2O 423K 2 weeks (~90 %)
EMI-d_2 : EMI-d_3 and CH_3OH



IR and Raman Experiments / Calculation Methods

Raman : Labram HR800 Jobin-Yvon spectrometer (ANDOR CCD, 600 grooves / mm 2cm^{-1})
Krypton laser (752.42 nm)
IR : Thermo-Nicolet 6700 Nexus spectrometer (2cm^{-1} resolution)
with SPECAC ATR (diamond & germanium)

Gaussian 03
B3LYP / 6-31G**

The anion vibrations

PF_6^- octahedral symmetry IR Inactive for ν_1
($B(CN)_4^-$ tetraherdal : Raman inactive) ->perturbed

But, no symmetry lowering O_h to C_{4v}

DMC : low dielectric constant -> ion pair
Acetonitrile -> separated ion apris -> octahedral

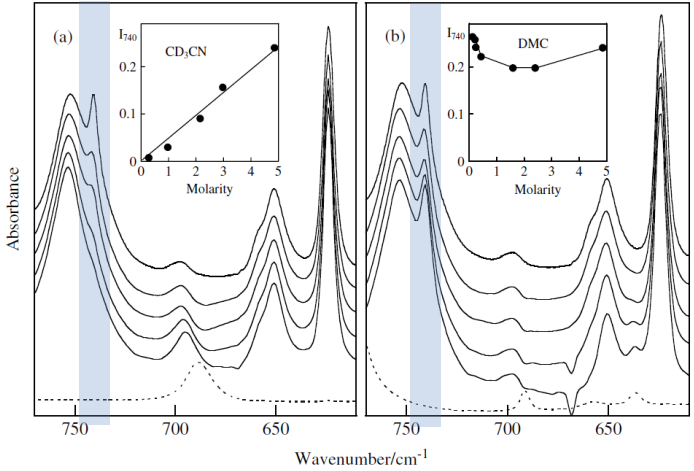


Table 1. Observed anion vibrations for [BMI][PF_6] at room temperature

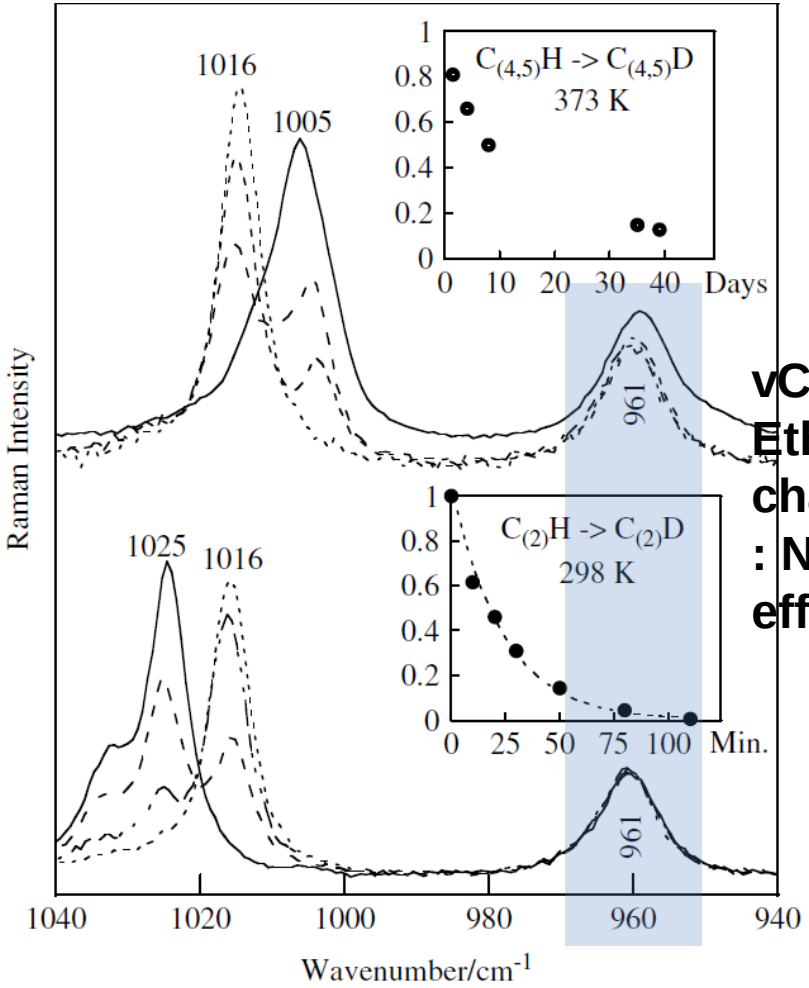
Symmetry	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
O_h	A_{1g}(R)	E_g(R)	F_{1u}(IR)	F_{1u}(IR)	F_{2g}(R)	F_{2u}
C_{4v}	A_1(IR, R)	A_1(IR, R); B_1(R)	A_1(IR, R); E(IR, R)	A_1(IR, R); E(IR, R)	B_2(R); E(IR, R)	B_1(R); E(IR, R)
IR (cm^{-1})	741[a]		841	557.5	470[a]	–
Raman (cm^{-1})	741	567	864[a]	560[a]	470	

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

The cation vibrations

Selective deuteration
of 1,3-dialkylimidazolium cations

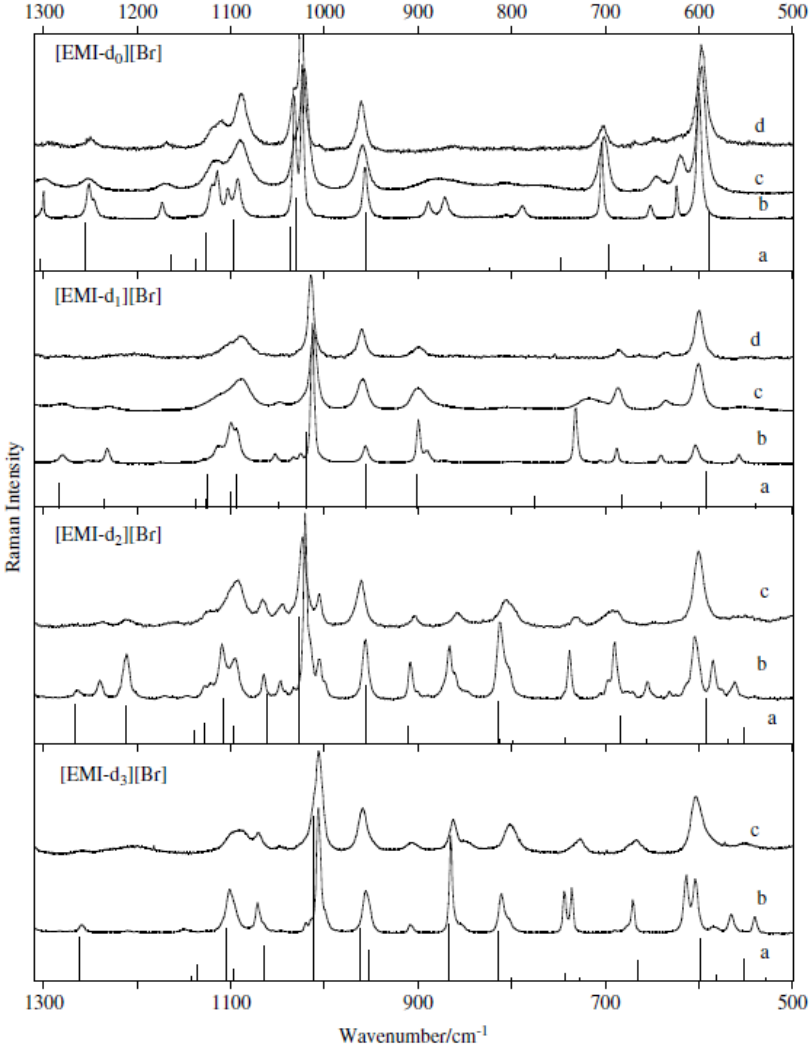
PF_6^- octahedral symmetry IR Inactive for ν_1



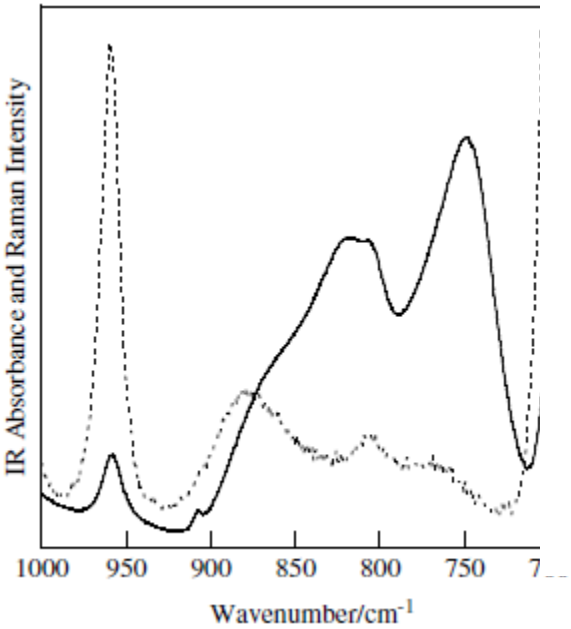
vC-C Ethyl chain : No effect

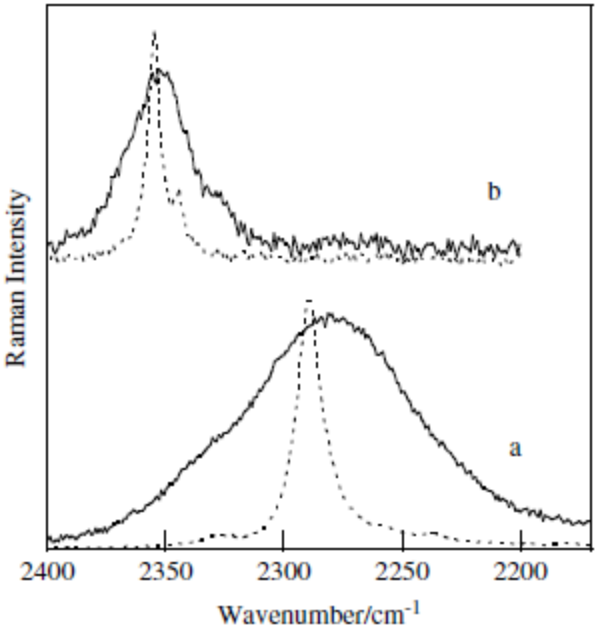
Below 1600cm^{-1}

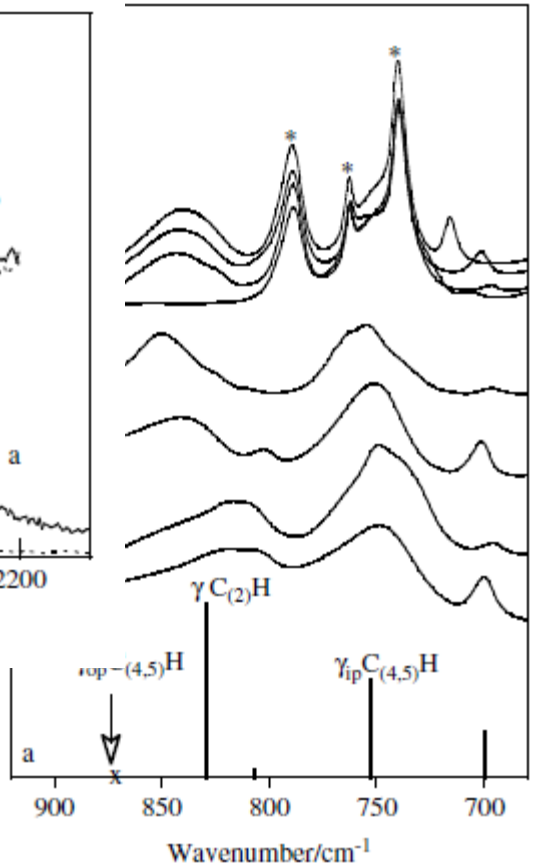
a calculation
b solid at 298K
c liquid at 353K
d 1/30 [EMI][Br]/H2O



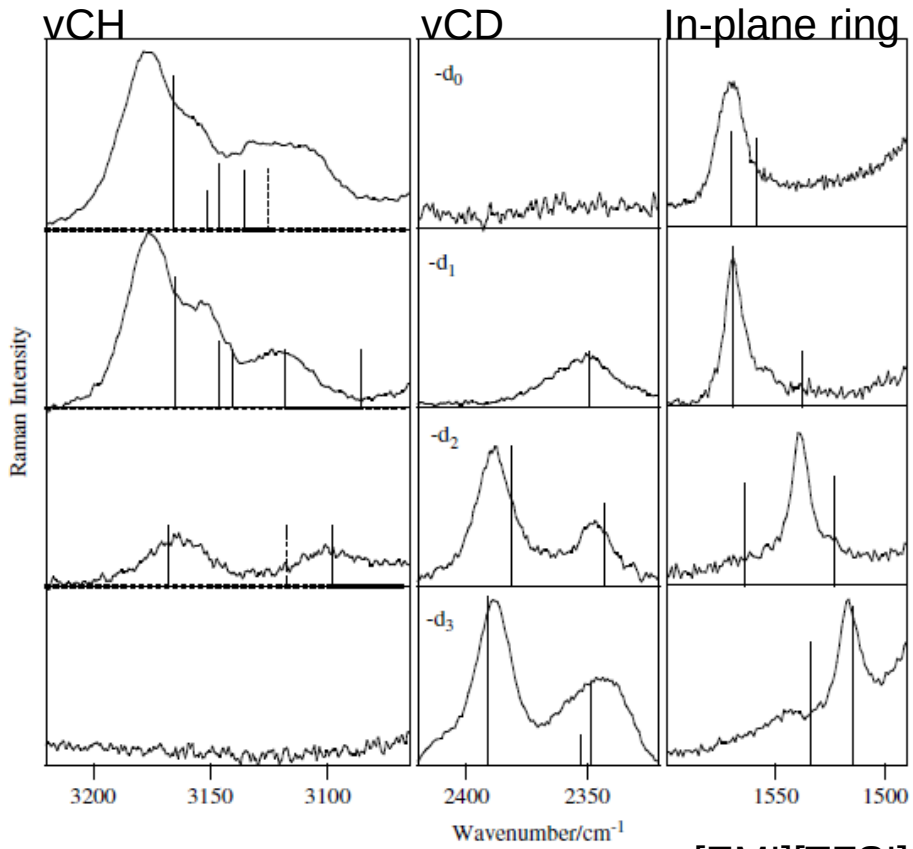
The cation vibrations







Above 2800 cm^{-1}



[EMI][TFSI]

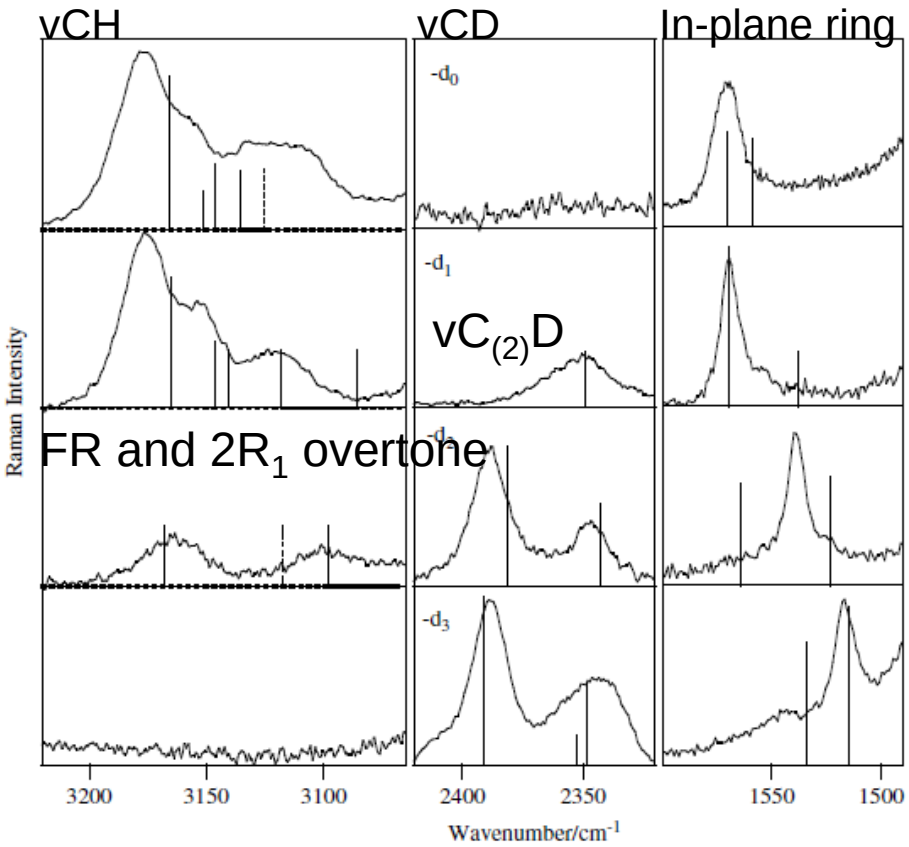
[EMI][TFSI]

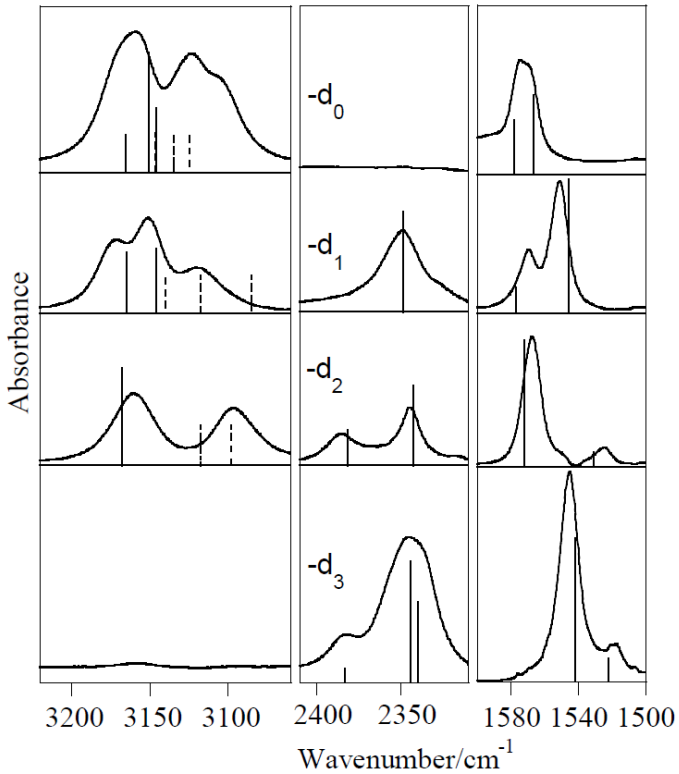
vCH : 3160cm^{-1} – $v_{ip}C_{(4,5)}H$ $v_{op}C_{(4,5)}H$
3120cm^{-1} – $vC_{(2)}H$ shifted by $C_{(2)}H$ by anion hydrogen bond interaction

Ludwig *et al*
3125cm^{-1} – aggregate
3105cm^{-1} – Ion pairs

Umebayashi *et al*
3102cm^{-1} corresponds to isolated (aggregated 3125)

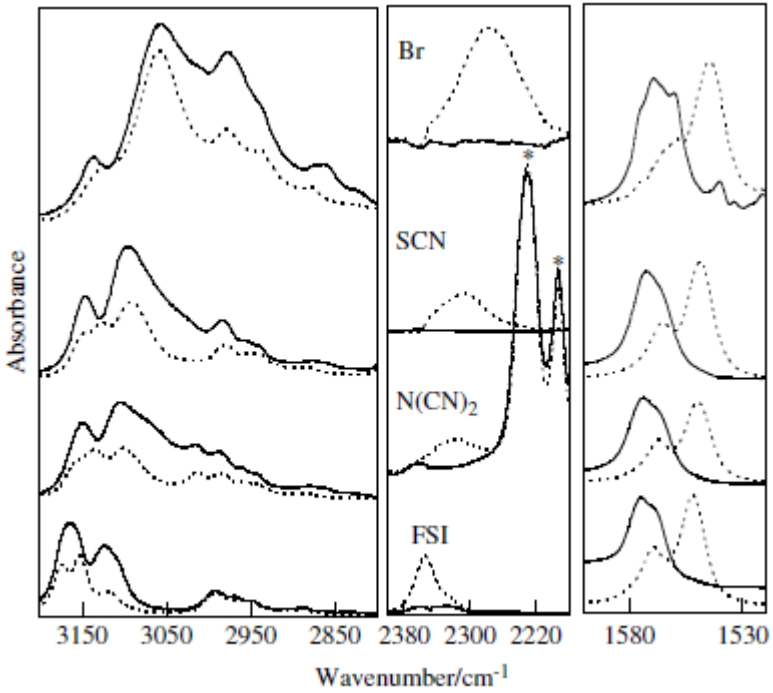
Above 2800 cm^{-1}



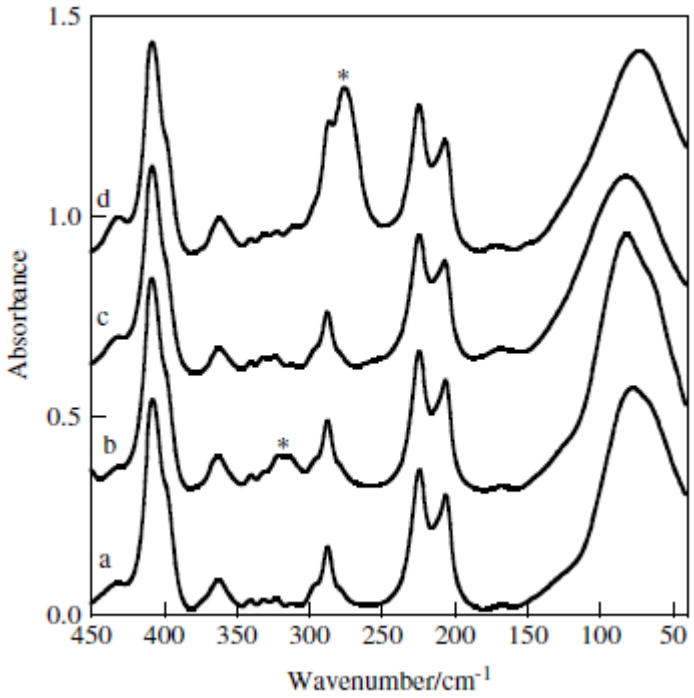


[EMI][TFSI] Raman IR

Above 2800 cm^{-1}



Intermolecular cation-anion vibrations



a [BuMePyr][TFSI]
b [Me_3BuN][TFSI]
c [BMI][TFSI]
d [BMMI][TFSI]

* : due to the cation absorption

Basis set

A basis set is the mathematical description of the orbitals within a system used to perform the theoretical calculation. Standard basis sets for electronic calculations use linear combinations of gaussian functions to form the orbital.

Slater type orbital
Gaussian type orbital

STO-3G
H : 1s
C : 1s, 2s, $2p_x$, $2p_y$, $2p_z$