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The effects of anion and cation substitution on the ultrafast solvent dynamics of ionic liquids: A time-resolved optical Kerr-effect spectroscopic study

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Ultrafast solvent dynamics of room-temperature ionic liquids have been investigated by optical heterodyne-detected Raman-induced Kerr-effect spectroscopy (OHD-RIKES) by studying the effects of cation and anion substitution on the low frequency librational modes. The spectra of two series of imidazolium salts are presented. The first series is based on the 1-butyl-3-methylimidazolium salts $[bmim]^+$ containing the anions trifluoromethanesulfate $[TfO]^-$, *bis*(trifluoromethanesulfonyl)imide $[Tf_2N]^-$, and hexafluorophosphate $[PF_6]^-$. The second series is based on $[Tf_2N]^-$ salts containing the three cations 1-butyl-2,3-dimethylimidazolium $[bmmim]^+$, 1-methyl-3-octylimidazolium $[omim]^+$, and $[bmim]^+$. It is found in all five samples that the signal is due to libration of the imidazolium ring at three frequencies around 30, 65, and 100 cm^{-1} corresponding to three local configurations of the anion with respect to the cation. [DOI: 10.1063/1.1578056]

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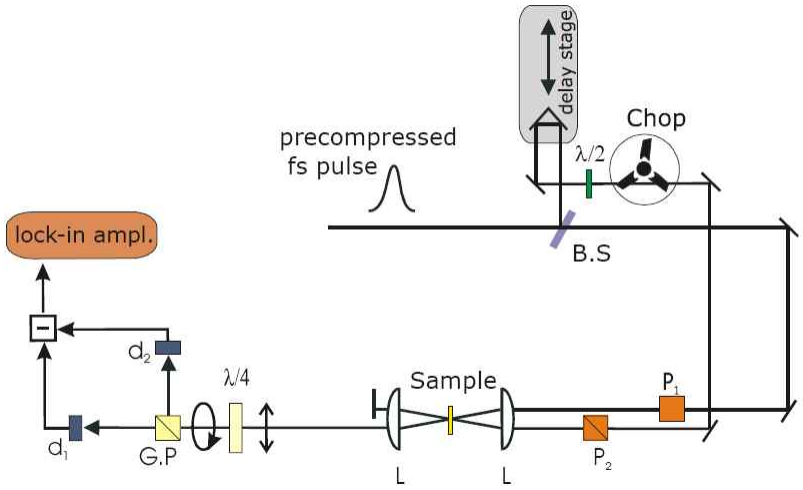
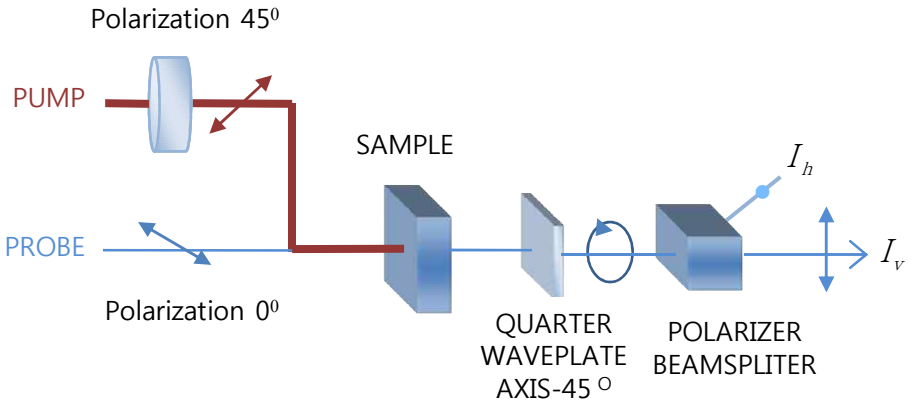
Schematic diagram of OHD-RIKES

P1 and P2 : polarizers,
BS : beamsplitter,
Chop : 1-kHz light chopper,
L : a pair of lenses.
l/2 : a zero-order half-wave retardation plate,
l/4 : quarter-wave retardation plate,
GP : Glan–Thompson polarizer,
d1 and d2 : photodiodes wired up for balanced detection.



※ Balanced detection



$$\begin{bmatrix} E_h \\ E_v \end{bmatrix} = \underbrace{\frac{1}{\sqrt{2}}\begin{bmatrix} 1 & i \\ i & 1 \end{bmatrix}}_{\frac{\lambda}{4}} \underbrace{\begin{bmatrix} \cos 45^\circ & -\sin 45^\circ \\ \sin 45^\circ & \cos 45^\circ \end{bmatrix}\begin{bmatrix} e^{i\phi_x} & 0 \\ 0 & e^{i\phi_y} \end{bmatrix}\begin{bmatrix} \cos 45^\circ & \sin 45^\circ \\ -\sin 45^\circ & \cos 45^\circ \end{bmatrix}}_{\text{SAMPLE (pump 45°)}} \underbrace{\begin{bmatrix} 1 \\ 0 \end{bmatrix}}_{\text{probe beam}}$$

$$I_h - I_v \propto (E_h E_h^*) - (E_v E_v^*)$$

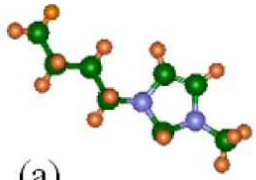
$$\therefore \; I_h - I_v \propto \Delta\phi$$

※ OHD-OKE

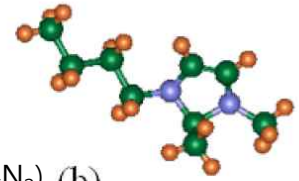
$$I = \varphi^2 + \varphi\Delta\phi + \frac{\Delta\phi^2}{4}$$

(φ : local oscillator)

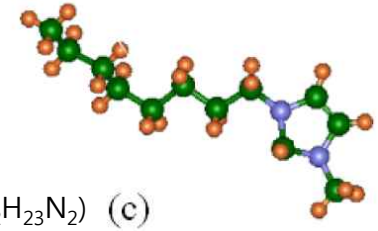
Structure of anions and cations constituting the room-temperature ionic liquids



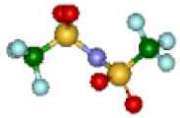
$[bmim]^+$ $(C_8H_{15}N_2)$ (a)



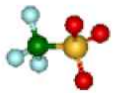
$[bmmim]^+$ $(C_9H_{17}N_2)$ (b)



$[omim]^+$ $(C_{12}H_{23}N_2)$ (c)



(d) $[Tf_2N]^-$ $([(CF_3SO_2)_2N]^-$



(e) $[TfO]^-$ $[(CF_3SO_3)]$

(f) $[PF_6]^-$

Samples :

$[bmim][PF_6]$

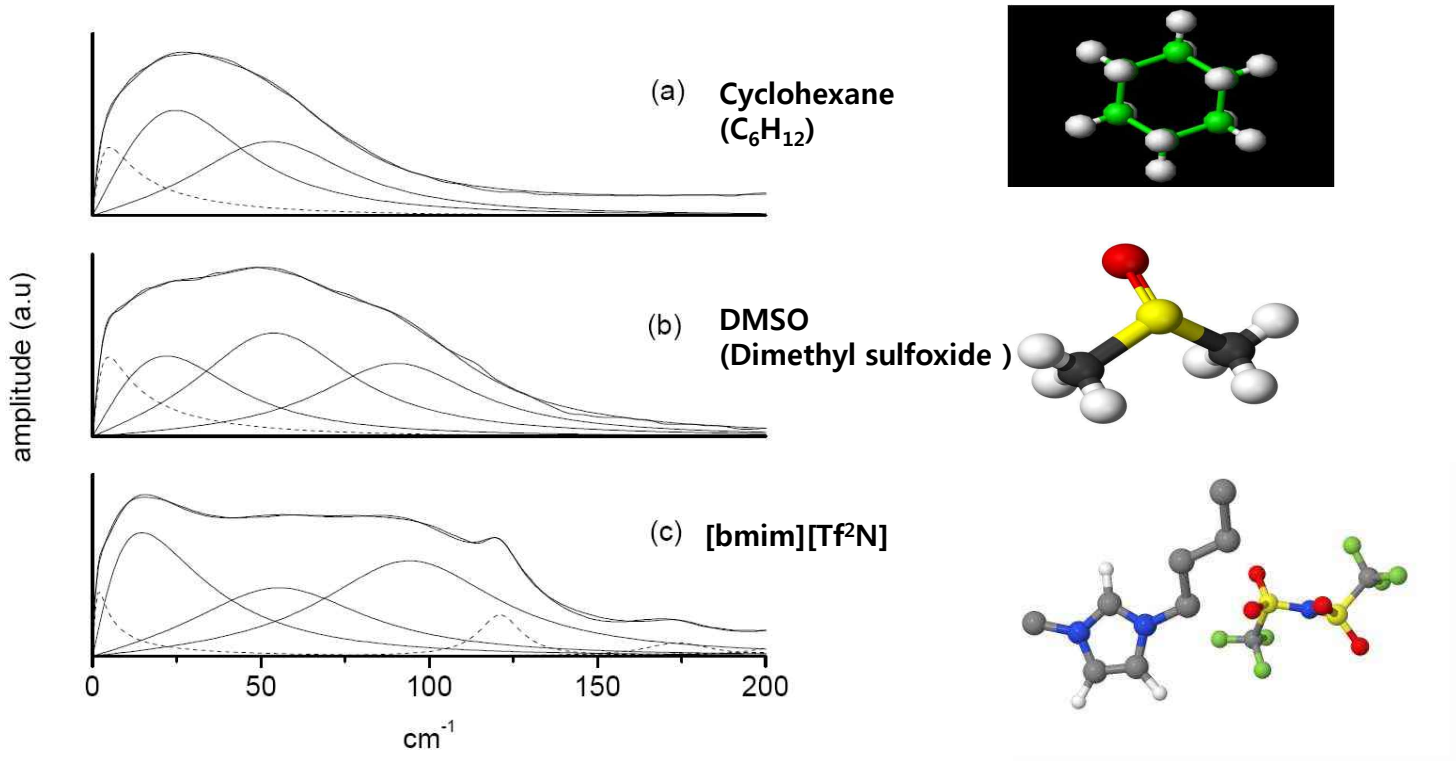
$[bmim][Tf_2N]$

[bmim][TfO]

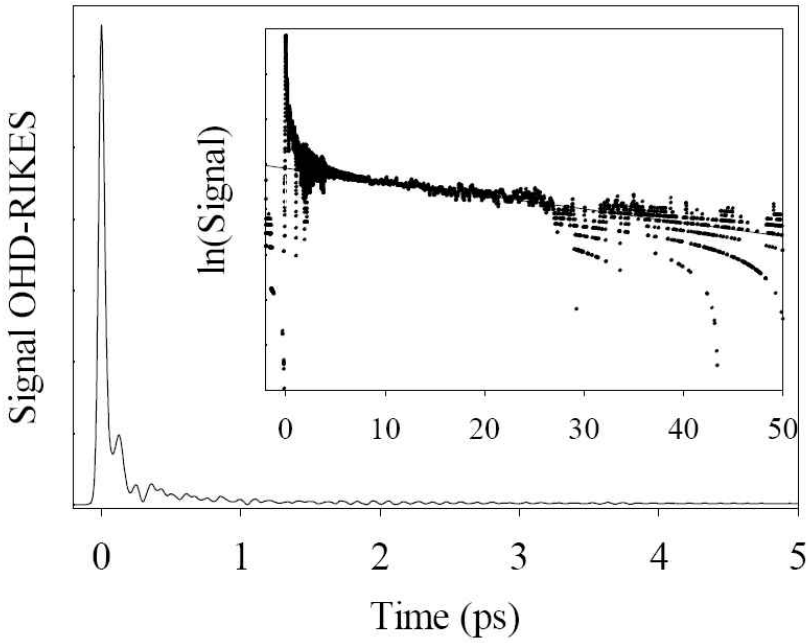
$[bmmim][Tf_2N]$

$[omim][Tf_2N]$

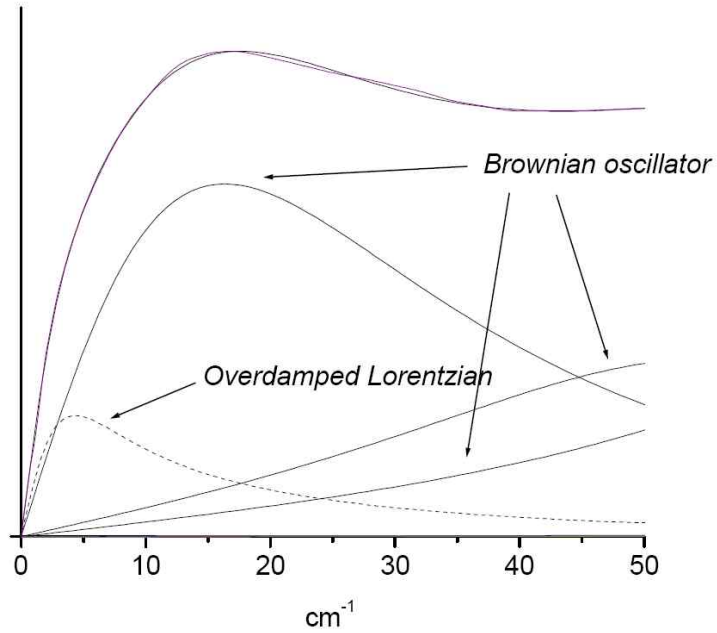
Imaginary part of the Fourier transform of the ultrafast optical heterodyne-detected Raman-induced Kerr-effect spectroscopy (OHD-RIKES) signal



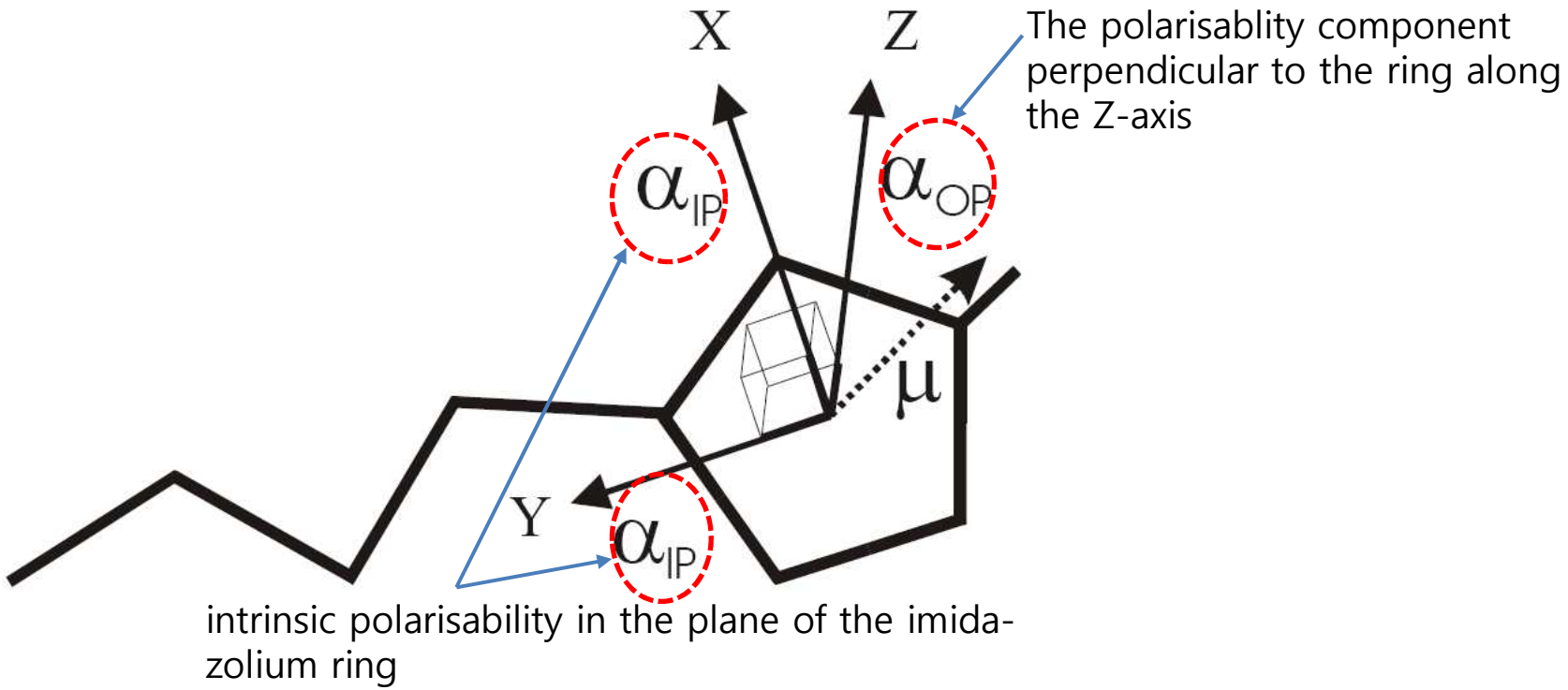
Unprocessed **OHD-RIKES time-domain data of [bmmim][Tf^{2}N].**



Close up of the first 50 cm^{-1} of **OHD-RIKES spectrum of [bmmim][Tf^{2}N]**



Schematic of the imidazolium for understanding libration.



OHD-RIKES spectra of ionic liquids classified according to the composition