



## Intermolecular dynamics of room temperature ionic liquids having imidazolium cations

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### ABSTRACT

Room temperature ionic liquids having 1-butyl-3-methylimidazolium ([BMIM]) cations and three different anions ([BMIM][PF<sub>6</sub>], [BMIM][BF<sub>4</sub>], [BMIM]Br) were studied by using Optical Heterodyne Detected-Optical Kerr Effect (OHD-OKE) spectroscopy to find out the effect of the anion size on the intermolecular dynamics. Fourier transformation of the time-domain OHD-OKE signals yielded a broad band in the spectra below 150 cm<sup>-1</sup>. The modes with frequencies around 15, 80 and 100 cm<sup>-1</sup> used to fit the spectra all shifted to higher frequencies with the decrease in the anion size due to changes in the intermolecular force and the reduced mass.

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### 1. Introduction

Room temperature ionic liquids (RTILs) consist only of cation and anion, and stay in liquid form at room temperature. Generally, ILs are nonvolatile and inflammable at wide temperature ranges, and have high solvation ability for different chemicals. With these favorable material properties, they have potential to replace conventional toxic solvents (thus termed as 'green solvents') in bioscience [1], solar cells [2] and batteries [3]. They are also called 'designer solvents' because virtually unlimited number of materials can be made by the combination of numerous kinds of anions and cations [4]. As the representative cations, 1-alkyl-3-methylimidazolium ([C<sub>n</sub>MIM]) cations such as 1-butyl-3-methylimidazolium [BMIM] and 1-ethyl-3-methylimidazolium [EMIM] are most common, and [PF<sub>6</sub>]<sup>-</sup>, [BF<sub>4</sub>]<sup>-</sup> and [NTf<sub>2</sub>]<sup>-</sup> are commonly used as prototypical anions. Compared to the advances in synthesis and chemical applications, general understanding on their physical properties is still lagging behind.

The interionic Coulomb force is usually stronger than the van der Waals force between the molecules of ordinary liquids. Thus, typical inorganic salts melt at much higher temperatures compared to usual molecular crystals. In contrast, ILs exist in liquid state at room temperatures, as the bulkier ions increase the interionic distance to reduce Coulomb interaction and asymmetric shape of consisting ions hinders crystallization [5]. The strong electrical interactions between molecules at room temperature still have an effect on the ionic liquids to have extremely low vapor pressures and strong solvation ability favorable for

green chemistry [6]. In spite of these unique properties, the intermolecular forces and dynamics in ILs have not been well understood yet.

Optical Heterodyne Detected-Optical Kerr Effect (OHD-OKE) has been known as one of the most ideal methods to investigate intermolecular interactions in complex fluids, and inter- and intramolecular vibrational dynamics [7,8]. Change in the relative optical phase of the probe beam due to pump-induced nuclear motion of the molecule in the sample reflecting intermolecular forces and dynamics occurs on time scales ranging from ~50 fs to 10 ps. The time domain data in this range (called 'Kerr signal') is measured, and is converted to the low-frequency spectrum up to several hundreds cm<sup>-1</sup> to give quantitative information on intermolecular dynamics and interactions between anions and cations in ILs. This OHD-OKE using femtosecond laser systems has been used for simple molecular liquids [9,10], and for more complex condensed phases such as polymer solutions [11], liquid crystal [12], and supercooled liquid [13].

By using IL samples in which the cations and the anions are changed systematically, Giraud and Wynne et al. reported that the librational modes (pseudooscillatory orientational motion of the molecules within local potential minima defined by their nearest neighbors) associated with the imidazolium rings have characteristic frequencies at around 30 cm<sup>-1</sup>, 65 cm<sup>-1</sup> and 100 cm<sup>-1</sup>, which originate from certain local configuration of the anions with respect to the cations [14]. Quitevis and co-workers found that in a homolog series of alkyl methyl imidazolium ionic liquids [C<sub>n</sub>mim][NTf<sub>2</sub>] (n=2, 4, 5, 6, 8), frequencies of intermolecular modes below 200 cm<sup>-1</sup> did not change much with the chain length of imidazolium cations [15]. Recently they also found an evidence of the nanostructures in bulk ionic liquids from low-frequency Kerr spectra of some imidazolium-based ILs [16]. By comparing silyl- and siloxy-substituted imidazolium ionic liquids, it was suggested that the

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substitution by a heavy atom in the anion leads to the weaker force constant, causing the redshift of the peak frequency associated with ion–ion interactions [17].

In this report, OHD-OKE measurement was performed and the reduced spectral density (RSD) is deduced for the following IL samples as shown in Fig. 1; 1-butyl-3-methylimidazolium bromide ([BMIM]Br), [BMIM][BF<sub>4</sub>], and [BMIM][PF<sub>6</sub>]. These [BMIM]-based ILs having different anions were used to find out how the anion size affects the low-frequency modes arising from the intermolecular interactions, by relating the volume change to the force constant and the effective reduced mass changes in the interactions.

## 2. Experimental

All ILs used in the experiment had the purities over 99% and used without further purifications (Futurechem). [BMIM][PF<sub>6</sub>] and [BMIM][BF<sub>4</sub>] are in liquid phase at room temperature while [BMIM]Br is in solid phase. Therefore, [BMIM]Br was first melted at ~350 K on a hot plate, afterwards it remained stable in liquid phase at room temperature. Molecular masses (Mm), reduced mass ( $\mu$ ), Viscosities ( $\eta$ ), densities (d), and van der Waals Volumes ( $V_{vdW}$ ) are listed in Table 1. Notable among them is the van der Waals volume for the anions; Br<sup>-</sup> (31.5 Å<sup>3</sup>) < [BF<sub>4</sub>]<sup>-</sup> (53 Å<sup>3</sup>) < [PF<sub>6</sub>]<sup>-</sup> (72.1 Å<sup>3</sup>). The ILs were contained in a sealed 2 mm path length, quartz suprasil cell for OHD-OKE measurement.

Fig. 2 shows the schematic of the experimental set-up. Ti:sapphire laser (800 nm, 100 fs, 82 MHz) with an energy of 10 nJ/pulse was used for the experiment. The light source after passing through the beamsplitter was separated into two beams. The vertically polarized pump beam had 90% of the power after the beamsplitter. The weaker probe beam passed through the stage of which the time delay was controlled with the stage resolution of 0.1  $\mu$ m. After passing through the half-wave plate and the Glan laser polarizer (POL), probe beam had 45°-polarization. Fast axis of the quartz quarter-wave ( $\lambda/4$ ) plate was first set parallel to the axis of POL. The input polarizer, POL, was then rotated by about  $\pm 3^\circ$  away from the initial angle, to introduce 90° out-of-phase local oscillator field with respect to the probe field. The pump beam was focused on the sample to an intensity of <1 GW/cm<sup>2</sup>. The measured signal from the Si photodiode was fed into the lock-in amplifier (Stanford Research System SR850), which was referenced to 1.2 kHz corresponding to the sum of the frequencies of the mechanical chopper modulating the probe and pump beams (500 Hz and 700 Hz, respectively). The laser pulsewidth measured with a 500  $\mu$ m BBO crystal was 104 fs FWHM. The time resolution of the Kerr signal was 6.6 fs

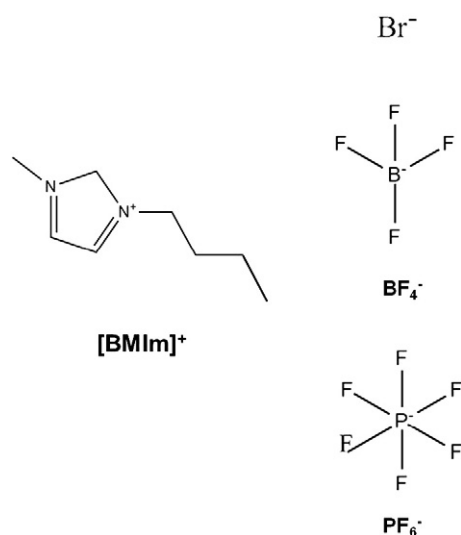


Fig. 1. Chemical structures for the cation and the anions of the ILs.

Table 1

Selected physical properties of ILs at 298 K. Molecular mass Mm, Reduced Masses  $\mu$ , Viscosity  $\eta$ , Densities d, van der Waals Volume  $V_{vdW}$ .

| Ionic liquid             | Mm (g/mol)          | $\mu$ (g/mol) | $\eta$ (cp)          | d (g/mL) | $V_{vdW}$ (Å <sup>3</sup> )             |
|--------------------------|---------------------|---------------|----------------------|----------|---|
| [BMIM]Br                 | 219.12              | 50.77         | 1486.49 <sup>b</sup> | 1.30     | 182.0 <sup>d</sup><br>(C:150.5; A:31.5) |
| [BMIM][BF <sub>4</sub> ] | 226.02              | 53.47         | 279.86 <sup>b</sup>  | 1.21     | 203.5 <sup>d</sup><br>(C:150.5; A:53)   |
| [BMIM][PF <sub>6</sub> ] | 284.18 <sup>a</sup> | 71.02         | 395.00 <sup>c</sup>  | 1.37     | 222.6 <sup>d</sup><br>(C:150.5; A:72.1) |

C: cation, A: anion.

<sup>a</sup> Ref. [21].

<sup>b</sup> Ref. [31].

<sup>c</sup> Ref. [32].

<sup>d</sup> Ref. [33].

throughout the scan range (–1–10 ps). To reduce the shot noise and time delay-related noise, each Kerr signal was averaged more than five times. The typical scan took 15 min.

## 3. Result and discussion

### 3.1. Time domain response and tail matching

As is well known from the Kerr signal of CS<sub>2</sub> and other liquids [18,19], the Kerr signal from simple liquid can be sorted as follows; (1) electronic response at  $\tau \approx 0$  ( $\tau$ : the interval between pump and probe beam), (2) intermolecular motion at  $0 < \tau < \sim$  few hundred fs, (3) polarizability distortion which originates from the dipole moment induced by the pump should be seen to decay exponentially at approximately few hundred fs  $< \tau < 1$  ps, and (4) the aligned molecules lose their directionality reduced exponentially at  $\tau > 1$  ps, this behavior is called orientational anisotropic motion [18,20].

Fig. 3 shows OHD-OKE signals for [BMIM]Br, [BMIM][BF<sub>4</sub>] and [BMIM][PF<sub>6</sub>] in the scan range of –1–10 ps. The main portion of the measured Kerr signal is related to the intermolecular dynamics. If the laser pulse shorter than 50 fs was used, the beating pattern strongly associated with intramolecular motion could be observed at around 1 ps [21]; this feature cannot be seen with the laser used in this experiment.

OHD-OKE signal ( $S(\tau)$ ,  $\tau$ : time delay of probe with respect to the pump beam) is the convolution of the autocorrelation function  $G_0^{(2)}(t)$  and the impulse response function  $R(t)$ .

$$S(\tau) = \int_{-\infty}^{\infty} G_0^{(2)}(t) R(t-\tau) dt. \quad (1)$$

The response function is the sum of the electronic and the nuclear response as follows [9]:

$$R(t) = R_e(t) + R_{nuc}(t). \quad (2)$$

Here  $R_e(t) = A_e \delta(t)$  if the electronic response is instantaneous on the time scale of the laser pulse. The second term in Eq. (2) is called

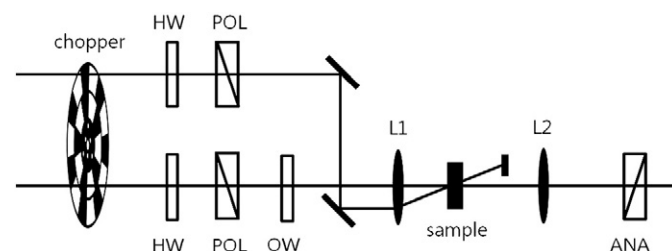


Fig. 2. The schematic setup for OHD-OKE experiment. HW: half waveplate, POL, ANA: Glan Laser Polarizers, QW: quarter waveplate, L1, L2: lenses.

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