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# INVESTIGATION ON INTERMOLECULAR INTERACTIONS LIQUIDS IN IONIC USING ACCELERATOR-BASED THz TRANSITION RADIATION

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*Abstract*

Ionic liquids (ILs) are interesting material that can be used in many applications. Spectroscopic measurement using accelerator-based terahertz transition radiation (THz TR) is one of potential techniques to investigate their intermolecular interactions by observing the vibrational bands in the terahertz region due to TR's exceptional properties: coherent, broadband, and high intensity. This work aims to study intermolecular interactions of ILs using the THz TR produced from an electron beam at the PBP-CMU Electron Linac Laboratory. The THz TR with the frequency range of 0.3-2.5 THz can be produced from electron beam of energy 10-25 MeV. This radiation is produced and transported to the experimental area, where it is used as the coherent and polarization selective light source for the Fourier transform infrared (FTIR) spectrometer. The absorption spectrum in the THz region of the ILs is then measured. In addition, to explain the experimental results deeply, theoretical calculations using the density functional theory are performed. In this contribution, we present the results from experiment and computational calculation that can be used together to describe the intermolecular interactions in ILs.

## INTRODUCTION

Ionic liquids (ILs) are room temperature liquids comprised entirely of cations and anions [1-2]. Originated from their molecular structures and strong Coulombic interactions, ILs possess a collection of properties that are of technological interest, e.g., extremely low vapor pressure, modest intrinsic ionic conductivity, high thermal and chemical stability, and can dissolve a wide range of chemical species [3-4]. These properties can be tuned by changing the choice of cation and anion, whose variety is large and can form countless combinations. As a consequence of this unusual range of properties, ILs are significantly promising for several applications, such as electrochemical energy storage devices, materials for nano-lubrication, high temperature and/or vacuum phase materials synthesis, semiconductor and superconductor gating applications, and novel self-assembly media [5].

To apply ILs in each application effectively, insight knowledge about their properties, structures, dynamics, and reactions is greatly important. Special intermolecular interactions such as hydrogen bonds can somehow strongly affect these properties [6]. The vibration of this hydrogen bonding is in the terahertz (THz) region and can be studied with the spectroscopic techniques such as terahertz Fourier transform infrared (THz FTIR) spectroscopy and terahertz time-domain spectroscopy (THz TDS) with the high intensity accelerator-based coherent terahertz transition radiation (THz TR) produced at the PBP-CMU Electron Linac Laboratory (PCELL). We expect to be able to study properties of ILs with better signal to noise ratio and lower sample volume compared with the conventional THz source.

## ACCELERATOR-BASED THZ TRANSITION RADIATION

The THz TR can be generated from the accelerator system at PCELL. Schematic diagrams of the system for generation of THz TR are shown in Fig. 1-2. From these figures, the electron bunches with energy in the range of 2-2.5 MeV are obtained from a thermionic cathode radio frequency (RF) electron gun. These electron bunches are compressed to have a bunch length in the order of femtosecond using an alpha magnet. After that, they travel through the travelling-wave linear accelerator (linac) and are accelerated to have the beam energy in the range of 10-25 MeV [7-8]. In the THz TR station, an aluminium foil is used as a radiator. It is tilted by 45° with respect to the electron beam direction. When the electron bunches from the linac travel from vacuum to conductor, the backward TR is emitted perpendicular to the electron beam path. This radiation is collimated using a first-surface gold coated parabolic mirror to obtain a parallel ray. Finally, this collimated THz radiation is transported through a high-density

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polyethylene (HDPE) window to the THz spectroscopic instruments.

Unlike the black body radiation sources, the accelerator-based THz TR can produce a coherent broadband light with radial polarization. Therefore, the intensity of THz TR is much higher than the conventional black body radiation sources. The THz-TR from our accelerator system has the frequency range about 0.3-2.5 THz, equivalent to the wavenumber range about 10-85 $cm^{-1}$ in far-IR region [9]. The absorption bands in this region are related to the molecular vibrations due to the intermolecular forces in which we are interested and can be obtained from FTIR technique.

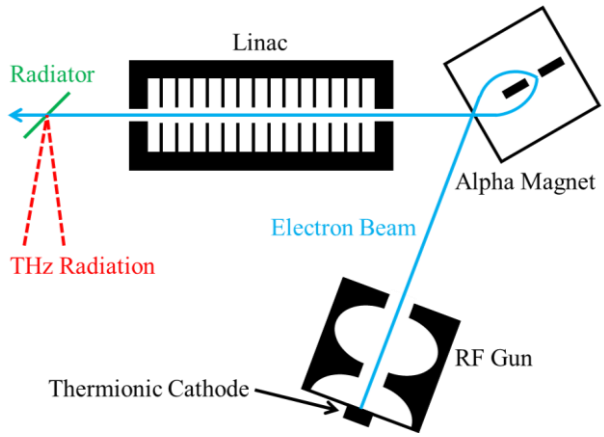


Figure 1: Schematic diagram (top view) of an accelerator system from RF gun to radiator for generation of THz TR.

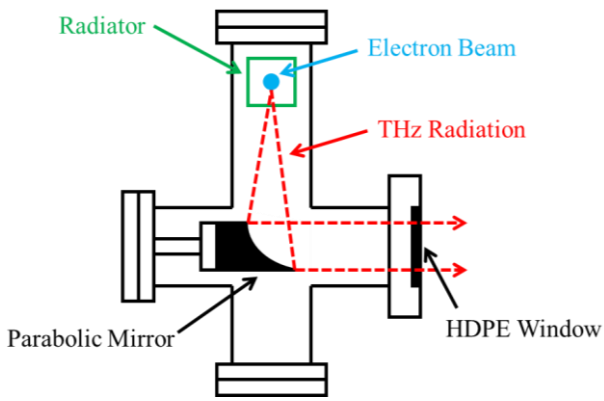


Figure 2: Schematic diagram (side view) of an experimental setup from radiator to HDPE window for generation of THz TR.

Besides, changing and shifting of the vibrational bands of the IL molecules can be used to explain interactions between cation and anion in different ILs and mixtures [10]. Furthermore, TDS technique is also possible since the THz TR pulse length generated from our system is in the order of femtosecond. This will allow the possibility to study some additional properties of ILs such as complex permittivity and absorption coefficient [11-12].

## EXPERIMENTAL INVESTIGATION

The PCELL has planned to measure ILs using the accelerator-based THz TR in the future. Thus, for the preliminary experimental study, the VERTEX 80v FTIR spectrometer with black body radiation sources were used to investigate the spectrum in THz region (30-300 $cm^{-1}$). A mercury lamp was used as thermal light source for the wavenumber range of 30-100 $cm^{-1}$, and a Globar source was used as thermal light source for the wavenumber range of 100-300 $cm^{-1}$. In this research, the 1-Ethyl-3-methylimidazolium Bis(Trifluoromethylsulfonyl)imide ($[Emim]^+$-$[NTf2]^-$) (Sigma-Aldrich, Switzerland), whose molecular structure is shown in Fig. 3, was used. The far-IR spectrum of $[Emim]^+[NTf2]^-$ from FTIR spectroscopy is shown in Fig. 4.

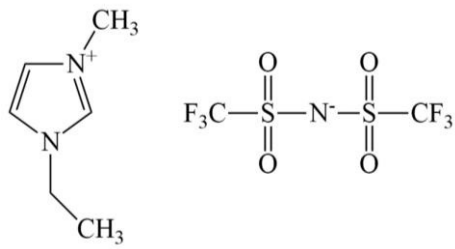

Figure 3: Molecular structures of $[Emim]^+[NTf_2]^-$.

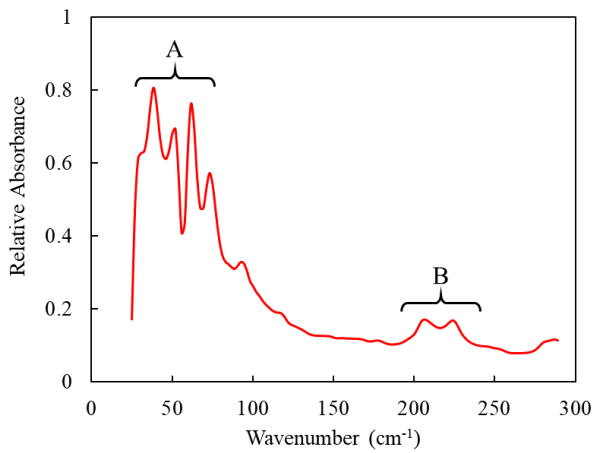


Figure 4: Experimental THz absorbance spectrum of $[Emim]^+[NTf_2]^-$.

From the experimental result, there are two separated absorption bands. The first band (A) has the wavenumber range about 40-80 $cm^{-1}$, which is in the wavenumber range of our THz-TR. The other band (B) has the wavenumber range about 200-230 $cm^{-1}$, which is outside the wavenumber range of our THz-TR. Thus, for the FTIR spectroscopy technique using accelerator-based THz-TR, only the band A is expected to be observed. This result is in line with the results done by Fumino *et al.* in 2008 [13]. However, the experimental result cannot explain the vibrational modes of the IL molecule. Consequently, computational calculation is necessary to investigate these modes from the experiment.

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## COMPUTATIONTAL INVESTIGATION

Cation, anion, and ion pair of $[Emim]^+[NTf2]^-$ were calculated computationally to investigate the IR spectra. First of all, optimization of the molecular structures of IL in ground state energy was done with the density functional theory (DFT) methods of the ORCA 4.2.0 program [14]. Since including the dispersion corrections is important for this IL, the cc-pVTZ basis set with BLYP-D3 functional were used in this calculation [15]. Furthermore, the vibrational modes, and the IR spectra of these optimized structures were investigated. The optimized molecular structure of $[Emim]^+[NTf2]^-$ is presented in Fig. 5. In addition, the calculated THz spectra of cation, anion, and ion pair of this IL are shown in Fig. 6.

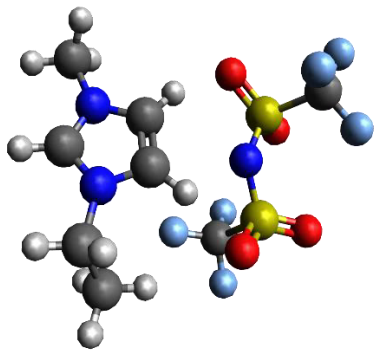

Figure 5: Molecular structures of $[Emim]^+[NTf_2]^-$ optimized computationally.

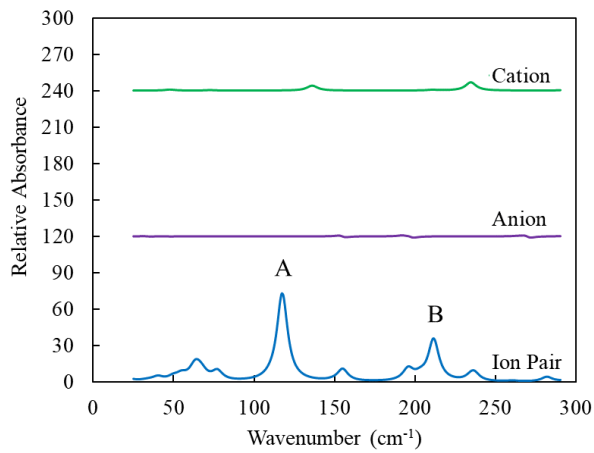


Figure 6: Calculated THz absorbance spectra of cation, anion, and ion pair of $[Emim]^+[NTf_2]^-$.

From the computational results, the vibrational bands in THz region appears only on ion pair spectrum and only weak absorption is seen on the spectra of the isolated cation and anion, indicating the relation of this absorption band and the interaction between these two ions. The first calculated band A with the wavenumber range about 100-130 $cm^{-1}$ is attributed to stretching modes of the intermolecular interaction between cation and anion, while the second band B with the wavenumber range about 200-220 $cm^{-1}$ refers to the bending and wagging modes of the anion. These vibrational modes from the computational results also agree with the results by Fumino *et al.* [13]. When this calculated spectrum is compared with the experimental spectrum in Fig. 4, these spectra are quite different because IL in the experiment is composed of several ion pairs of $[Emim]^+[NTf_2]^-$. Nevertheless, the two main absorption bands A and B can still be captured. This implies that the calculation of this IL using only single ion pair can be used as a preliminary investigation of this IL having more ion pairs in the future work.

## CONCLUSION

The PCELL has developed the accelerator-based THz light source that can generate the coherent THz TR to study the intermolecular interaction in ILs. The FTIR spectroscopy technique with black body radiation sources and computational calculation with the DFT method of $[Emim]^+[NTf2]^-$ were done as a preliminary study. The results show that the vibrational modes of intermolecular interaction between cation and anion with the wavenumber of 40-80 $cm^{-1}$ was in the frequency range of THz TR. In addition, these results can be used as the guideline information for the experimental study of IL with FTIR spectroscopy or TDS techniques using THz TR light source in the future.

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