Development of time-domain interferometry for the study of glass formers

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Abstract. We developed time-domain interferometry (TDI) using \textsuperscript{57}Fe nuclear resonant scattering and applied to the study of the dynamics of ionic liquid 1-butyl-3-methylimidazolium iodide (BmimI). By using a multi-element avalanche photo diode as a detector, four TDI time spectra reflecting different momentum transfers were obtained at 250 K. By considering additional Gaussian broadening of resonant energy in stainless steel foils, the relaxation times of the density correlation in super-cooled BmimI were successfully obtained. The momentum transfer dependence of those relaxation times was confirmed to follow the Gaussian behaviour. Moreover, we discussed the trends of the TDI development in the future.

1. Introduction

Slow dynamics of atoms, molecules and ions of the order of 1 ~ 100 nanoseconds has attracted much interest. Exploring the slow dynamics of super-cooled liquids and polymers are, in particular, important challenges. Rayleigh scattering of Mössbauer radiation (RSMR) has been employed to reveal the slow dynamics of soft matters [1]. In this method, a gamma ray with a narrow line-width (of the order of neV) from a Mössbauer radioactive isotope is scattered by a sample, and the energy of the scattered gamma ray is analyzed with the neV-order energy resolution. However, available photons are severely limited because Mössbauer radioactive isotopes emit gamma rays in $4\pi$ radians. Therefore, studying slow dynamics using RSMR is a tedious task. On the other hand, neV-resolution spectroscopy by using synchrotron radiation (SR) as an incident source has been reported recently [2] and clarified to be much quicker measurements than RSMR, because of the directivity and high brilliance of SR. As a time-domain analog of this quasi-elastic scattering experiment, a time-domain interferometry (TDI) method is also available. TDI was applied to the study of the dynamics of glycerol using \textsuperscript{57}Fe nuclear resonant scattering (NRS) [3,4]. These studies clarified that TDI provides information on slow dynamics correctly and reduces the measurement time. Then TDI using NRS of
Figure 1. Experimental setup for (a) nuclear resonant forward scattering measurement corresponding to TDI measurement without a sample and (b) TDI quasi-elastic scattering measurement using a multi-element APD.

$^{151}$Eu has been developed by authors and nuclide selectivity of TDI has been demonstrated [5].

At this experiment the slow dynamics in ionic liquid was focused on, therefore TDI using NRS of $^{57}$Fe was developed. Ionic liquid was discovered recently as a salt which exists as liquid at around room temperature. Among ionic liquid, 1-butyl-3-methylimidazolium iodide (BmimI) was selected as a sample, because BmimI does not crystallize easily in the super-cooled phase. The glass transition temperature of BmimI is 200 K.

2. Experimental

BmimI produced by Tokyo Chemical Industry Co., Ltd. was used without purification. The sample was packed in argon atmosphere and kept in a polyethylene bag to avoid moisture from air. The measurement was performed at the NRS beam line (BL09XU) of SPring-8 in Japan. The storage ring was operated in a several-bunch timing mode (1/14-filling +12-bunch mode, with a bunch interval of 342.1 ns) during our experiment. Incident radiation with 3.5-meV bandwidth at the nuclear resonant energy of $^{57}$Fe’s first excited state was obtained using a high-resolution monochromator consisting of Si (5 1 1) and Si (9 7 5 ) single crystals. The experimental set up is shown in figure 1. A multi-element avalanche photo diode (APD) was used as a detector. Two stainless steel (SS) foils in which isotope enrichment of $^{57}$Fe is 90% were used as nuclear resonant absorbers. The SS foil on the upstream was driven with a constant velocity through our experiment.

Firstly, nuclear resonant forward scattering (NRFS) was measured to calibrate the effective thickness ($T_e$) of SS foils and the velocity of the driven foil. The set up is shown in figure 1(a). After that, the static structure factor $S(q)$ of BmimI was measured by scanning the angle dependence of the scattered intensity from the sample at 250 K. Then APD, whose elements cover four different angles each other, was placed 43 mm downstream of the sample’s centre through the measurements by TDI. Finally, time spectra of TDI were obtained at 250K. Measurements were performed during about 6 hours. The experimental set up of TDI is shown in figure 1(b).

3. Results and discussion

If the velocity is sufficiently large ($\Delta E >> \Gamma_0$, where $\Delta E$ is the energy shift of NRS generated by movement of the SS foil, $\Gamma_0$ is the natural width of the $^{57}$Fe first nuclear excited state), the radiation coupling of the two SS foils can be neglected. The time spectrum of NRFS follows

$$ I(t) = A[g(t)]^2 [1 + F_D(t) \cos(\omega_D t)]. $$

where $A$ is the coefficient, $\omega_D$ is the angular frequency of the quantum beat owing to the difference of the nuclear resonant energy between two SS foils, $F_D(t)$ expresses the additional Gaussian
broadenings of resonant energy in SS foils. \(g(t)\) is the time response function of the radiation in a forward direction from the SS foils and is expressed as

\[
g(t) \propto \frac{T_e}{t_0} \exp \left( -i \omega t - \frac{t}{2t_0} \right) J_1 \left( \sqrt{\frac{T_e}{t_0}} \right),
\]

where \(J_1\) is the first-order Bessel function, \(\omega\) is the angular frequency of the NRS, \(t_0\) is the lifetime of the \(^{57}\)Fe first nuclear excited state. By considering the response function \(P(t')\) of the detector and background \(B\), experimental time spectrum \(\tilde{I}(t)\) is expressed as \(\tilde{I}(t) = \int dt' I(t - t') P(t') + B\). By fitting of NRSF time spectrum (shown in figure 2), \(\omega_D\) was found to be 1.13 GHz. This \(\omega_D\) corresponds to the constant velocity \(-15.6\) mm/s of the SS foil and \(\Delta E\) is evaluated as \(\Delta E \sim 160T_0\). Therefore, the validity of the assumption at (1) is justified. \(T_0\) is found to be 19.75. The line with of the additional Gaussian broadenings is estimated to be 1.3\(T_0\), which is consistent with the line with of the Mössbauer spectra of SS foils.

Generally, intermediate scattering function (ISF) of \(\alpha\) relaxation follows the Kohlrausch-Williams-Watt (KWW) law [6], therefore, the observed TDI time spectra as a function of the momentum transfer \(q\) and time \(t\) are expressed as

\[
I(q,t) = \int dt' I(q,t - t') P(t') + B,
\]

where \(f_{DW}(q)\) is the Debye-Waller factor, \(\beta(q)\) is the stretching parameter, \(\tau(q)\) is the relaxation time of the density correlation. The relaxation times of density correlations in BmimI could be successfully extracted from the details of the spectra. Incidentally, \(\tau\) is the relaxation time analytically obtained by the fitting and usually does not correspond to the relaxation times on average in the system. If ISF of considering relaxation follows KWW function, the new defined relaxation time is expressed as

\[
\left\langle \tau \right\rangle = \tau \Gamma(1/\beta)/\beta,
\]

where \(\Gamma(x)\) is the Gamma function. Least-squares fittings were applied to the spectra assuming \(\beta\) as 0.6, 0.8, and 1.0, respectively, because of the relatively large uncertainty. Finally, each time spectrum was fitted well. The fits assuming \(\beta = 0.8\) are shown in figure 2. The momentum transfer dependences of these relaxation times at \(\beta = 0.6, 0.8,\) and 1.0 are shown in figure 3 with \(S(q)\).

4. Conclusion

TDI using \(^{57}\)Fe NRS was developed to study the microscopic dynamics of super-cooled BmimI at 250 K. Four quasi-elastic time spectra with different momentum transfer were successfully obtained by considering the additional Gaussian broadening of resonant energy in SS foils, and relaxation times of the density correlations were extracted. From the momentum transfer dependence of the relaxation
Figure 2. Observed nuclear resonant forward scattering spectra and quasi-elastic scattering time spectrum observed at four angles respectively at 250 K, and their respective fitted spectra with $\beta = 0.8$.

Figure 3. The momentum transfer dependences of the relaxation time of BmimI for $\beta = 0.6$ (triangle), 0.8 (square), and 1.0 (circle), the static structure factor (open circle) and fitting curves of each $\langle \tau \rangle$ (solid line). The momentum transfer ranges covered by each element of APD (shadow ranges).

times, the Gaussian dynamic behaviour of BmimI was confirmed. Moreover, the trends of the TDI development in the future were discussed.

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