Quasi-elastic neutron scattering of dense molecular liquid selenium bromide

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Abstract. Quasi-elastic neutron scattering spectra of liquid Se2Br2 at 298 K, 373 K and 473 K were measured by utilizing the cold-neutron disk-chopper spectrometer AMATERAS in J-PARC. The obtained dynamic structure factors are reproduced well by a two-Lorentzian model consisting of slow and fast modes. With increasing temperature, the maxima in the \( Q \)-dependence of the magnitude for both modes shift to a low \( Q \) direction, while the temperature dependence of the magnitude is opposite between slow and fast modes. The temperature dependence of the magnitude and the analysis of the energy width for these modes reveal that the fast mode is originated from dynamics in strongly interacted neighbouring molecules, while the slow mode is derived from inter-molecular dynamics without the strong interaction.

1. Introduction

Chalcogen-halogen equi-atomic liquids consist of chain molecule with X-A-A-X (A: S, Se, X: Cl, Br) form, where the bond angle and the dihedral angle between X-A-A and A-A-X planes are about 100° and 85°, respectively [1,2]. For Se2Cl2 and Se2Br2, the static structure factors obtained from neutron diffraction measurements were analyzed by Misawa’s method [3] where total structure factor, \( S(Q) \), as a function of momentum transfer \( Q \) were dissolved into intra-molecular correlation with molecular form factor, inter-molecular correlation by hard-sphere (HS) packing of the molecules and orientational correlation among neighbouring molecules. It is found in this paper that \( S(Q) \) can be reproduced by intra-molecular correlation in the \( Q \)-region beyond 5 Å\(^{-1}\), while \( S(Q) \) in relatively low \( Q \) region is strongly affected by inter-molecular correlations. The HS packing of molecules creates a relatively sharp peak in \( S(Q) \) at a specific low \( Q \) corresponding to an averaged number density of molecules. The orientational correlation introduced among neighbouring molecules is dominant in a middle \( Q \) range beyond the sharp peak by HS packing and below a prominent peak of the intra-
molecular correlation (molecular form factor) at around 4 Å⁻¹, so that the adjacent molecules lie with the Se-Se bond parallel with each other ([1] and Fig.5 in [4]).

Recently ab initio molecular-dynamics (MD) simulations of liquid Se₂Cl₂ [5] suggested that the interaction energy between Se₂Cl₂ molecules has local minimum at around 3.2 Å, when the adjacent molecules arrange with the Se-Se bond parallel to each other and that an attractive interaction of this molecular arrangement is derived from p-p hybridization between the occupied lone-pair orbital of Se atom and the unoccupied anti-bonding σ⁺ orbital of Cl-Se bond on the neighbouring molecule and also p-d hybridization.

Quasi-elastic neutron scattering (QENS) measurements of liquid A₂X₂ performed at room temperature by Yao et al. [4] revealed that there are two kinds of dynamical modes with fast and slow relaxation times and that the former depends on the kind of halogen species while the latter depends on the molecular mass. However, detailed Q-dependence of QENS was not discussed in this study because of shortage of scattering angles where good statistics was achieved. The temperature dependence of QENS of liquid Se₂Br₂, was studied [6], suggesting that there are two terms of non-correlating inter-molecular contribution and the orientational correlation between strongly coupled neighbouring molecules. The precise profile analysis including fitting with model functions was not performed because of limited instrumental energy resolution.

To obtain dynamic structure factors, S(Q,E), over a wide Q-E ranges with sufficient energy resolution at various temperatures and to discuss inter-molecular dynamics associating with static structure information, new QENS measurements of liquid Se₂Br₂ has been performed.

2. Experimental procedure

The QENS experiments of liquid Se₂Br₂ were performed with time-of-flight technique using the cold-neutron disk-chopper spectrometer AMATERAS installed in Materials and Life Science Experimental Facility (MLF), Japan Proton Accelerator Research Complex (J-PARC), Tokai, Japan. AMATERAS covers the scattering angles of 4.7° ~ 111.7° in horizontal and -16° ~ 22° in vertical [7]. To access dynamics in different time scales easily, multiple-E₁ technique [8] was applied, where the monochromating chopper operating at 150 Hz, 6 times faster than neutron pulse emerging at 25Hz, and the band chopper at 25Hz yielded incident energies (E₁’s) of 41.8, 7.7 and 3.1 meV simultaneously with energy resolutions of 4.0, 0.2 and 0.04 meV for elastic scattering, respectively. The accessible Q- and E-ranges were 0.37 < Q < 7.4 Å⁻¹ and -20.0 < E < 20.0 meV for E₁ = 41.8 meV, 0.18 < Q < 3.1 Å⁻¹ and -6.0 < E < 6.0 meV for E₁ = 7.7 meV, and 0.13 < Q < 2.0 Å⁻¹ and -2.0 < E < 2.0 meV for E₁ = 3.1 meV, respectively.

The liquid sample of Se₂Br₂ was sealed in a cylindrical silica cell with an inner diameter of 10mm and a wall thickness of 0.3 mm. The sample cell was put into an aluminium container to obtain good thermal contact and to gain temperature uniformity. The measurements were carried out at 298, 373 and 473 K by utilizing a cryo-furnace. The Q-E maps of the scattering intensity were calculated by the software suite Utusemi [9] from the scattering event data of the time-of-flight. To deduce S(Q,E) from the obtained TOF spectra, subtraction and absorption corrections were made by applying the following formula,

\[
S(Q,E) = \frac{1}{C} \left( I_{S+C}(Q,E) - I_S(Q,E) \right) \frac{A_{S+C}^c}{A_c^c} \times \left( I_c(Q,E) - I_S(Q,E) \right),
\]

where \(I_{S+C}(Q,E)\), \(I_c(Q,E)\) and \(I_S(Q,E)\) are the measured scattering intensity for the sample containing in the cell, that for the empty cell and that for the instrumental back ground with crio-furnace, respectively. \(A_{S+C}^c\) presents a coefficient for absorption of neutrons with a scattering event at the sample position (the subscription of S) due to the sample and the cell (the superscription of S+C), and \(A_c^c\) and \(A_c^c\) are absorption coefficients of neutrons with a scattering event at the cell position. Those coefficients are calculated from the integration over scattering positions with the geometry of the sample and the cell at each scattering angle and energy transfer. Therefore, those have also Q- and E-
dependences. $C$ is a normalized factor depending on number of atoms, scattering cross sections and total number of incident neutrons. We evaluated $C$ from comparison between the energy integration of QENS at several $Q$ values and the known structure factor, $S(Q)$ from the earlier neutron diffraction experiment [1], since Se$_2$Br$_2$ is almost coherent scatterer of neutrons.

3. Results of QENS measurements

Figure 1 shows the intensity map of $I_{S+C}(Q,E)$ for liquid Se$_2$Br$_2$ in the silica tube and the Al container at 298 K with $E_i = 41.8$ meV. The overall profile of $I_{S+C}(Q,E)$ consists of three hallow components at around $Q = 2, 3.5$ and 5.5 Å$^{-1}$ contributed by the scattering from the liquid sample in the silica glass tube and Bragg peaks from the aluminium container observed at $Q = 2.7, 3.1, 4.4, 5.2, 5.4, 6.2, 6.8, 6.9$ Å$^{-1}$. Quasi-elastic scattering is clearly observed over an energy transfer range from -10 to 10 meV. These hallow components accompanied by QENS are consistent with the former experiments [6]. Since we are interested in inter-molecular dynamics of Se$_2$Br$_2$ molecules dominant in a relatively low $Q$ region, the result of $E_i = 7.7$ meV which focuses on $Q$-range from 0.3 to 3.3 Å$^{-1}$ is mainly discussed in this paper.

Figure 2 shows QENS spectra of $E_i = 7.7$ meV accumulated over a $Q$-range of $1.9 < Q < 2.1$ Å$^{-1}$ for the measurement of the liquid sample in the silica cell and the aluminium container at 473 K, the measurement of the empty cell, the instrumental back ground and the deduced $S(Q,E)$ of liquid Se$_2$Br$_2$ at 473 K by subtraction of the cell contribution with taking into account the absorption correction. The overall $S(Q,E)$ at 298K corrected by detailed valance factor is shown in Figure 3. Each spectrum was obtained by accumulating scattering events over a Q width of $\pm 0.1$ Å$^{-1}$ at around a representative Q value. The elastic envelope exhibits a maximum at around 1.7 Å$^{-1}$ and the energy width is broader with increasing $Q$ value.
4. profile analysis of QENS and discussion

The profile of the resultant $S(Q,E)$ appears a relatively-sharp peak at $E = 0$ meV and wide tails toward large energy gain and loss, which can be reproduced well by a sum of two Lorentz functions as earlier study demonstrated [4]. Figure 4 shows a fitting result of $S(Q = 2.0$ Å$^{-1},E)$ at 473 K. The model function is a sum of two Lorentz functions, $L(Q,E)$, convoluted by the instrumental resolution function, $R(Q,E)$ as follows;

$$S_{\text{model}}(Q) = \left[ \sum_{n=1}^{2} L_n(Q,E) \right] \otimes R(Q,E),$$

where $n = 2$ and the convolution is performed on $E$ axis. The experimental $S(Q,E)$ is quite well reproduced by the two-Lorentzian model so that liquid Se$_2$Br$_2$ involves two quasi-elastic modes with slow and fast relaxation times corresponding to narrow and broad Lorentzians, respectively. These results are consistent with the earlier work [4]. Hereafter we denote these slow and fast modes as $L_s(Q,E)$ and $L_f(Q,E)$.

Figure 5 shows Q-dependences of the magnitudes of both (a) $L_s(Q,E)$ and (b) $L_f(Q,E)$, which describe as $A_s(Q)$ and $A_f(Q)$, respectively. With increasing temperature, the maxima of the $Q$-dependence of the magnitude for both components shift to a low $Q$ direction, while the temperature dependence of the magnitude is opposite between narrow and broad components. Taking into account that energy integral of $S(Q,E)$ gives $S(Q)$ for coherent scatter, we confirm that the sum of $A_f(Q)$ and $A_s(Q)$ at 298 K is consistent with the profile of the total $S(Q)$ obtained by neutron diffraction [1]. Moreover we observe reasonable temperature dependence of $S(Q)$ by x-ray diffraction [10] which is consistent with the temperature dependence. Figure 6 shows the half widths at the half maxima (HWHM) for $L_s(Q,E)$ and $L_f(Q,E)$ which describe as $\Gamma_s(Q)$ and $\Gamma_f(Q)$, respectively. $\Gamma_f(Q)$ has a minimum at the $Q$ value where the maximum of $A_f(Q)$ locates, while $\Gamma_f(Q)$ does not show clearly a minimum associated with the peak of $A_s(Q)$. The former is so called de Gennes narrowing. $S(Q,E)$ shows narrowing in energy transfer at the $Q$ value where $S(Q)$ has a peak by strong correlation.

The $Q$ positions at the maximum intensity of $A_t$ recall us that the HS packing of molecules creates a sharp peak at a low $Q$ region of the first peak in $S(Q)$, corresponding to an averaged number density. The temperature dependence of $A_t$ can be reasonably interpreted as thermal expansion with...
Increasing temperature, because the \( Q \) position where the maximum in \( A_s \) locates shifts to a lower \( Q \) direction and the intensity of \( A_s \) become weaker. Moreover, it is natural that the relaxation time of the slow mode becomes shorter at a higher temperature due to thermal agitation, which explains the temperature dependence of \( \Gamma_s \). This interpretation on the slow mode is consistent with the suggestion by Yao et al. that the slow mode depends on molecular weight.

The fast mode may be assigned as inter-molecular correlation with strong coupling. Since the \( Q \) position where the maximum in \( A_f \) locates also shifts to lower \( Q \) direction with increasing temperature, the fast mode may depend on density. Yao et al. observed the dependency on halogen species for the fast mode [4]. Although they interpreted from this dependency the fast mode as rotational motion of single molecule, we interpret it as the rotational motion of an orientationally-ordered pair of molecules, i.e., a dimmer. The interesting behavior of the \( Q \) dependence of \( \Gamma_f \) that, with increasing temperature, it decreases in a relatively low \( Q \) region below 1.8 Å\(^{-1}\) while it does not show temperature dependence in a higher \( Q \) region is comprehensible. Dimmer has a relatively short intermolecular distance which makes an effect on structure factor in a relatively high \( Q \) region beyond 1.8 Å\(^{-1}\). When the coupling force is stronger than thermal agitation at the measuring temperatures, the relaxation time may exhibit no temperature dependence. The increase in \( A_f \) with increasing temperature is explained as increase of number of isolated dimmers by thermal expansion. In contrast, when coupled molecules start dissolving, the intermolecular correlation length increases, which relates to dynamic structure factor in a lower \( Q \) region below 1.8 Å\(^{-1}\). The dimmers during dissolving process may have a short relaxation time, which makes \( \Gamma_f \) increase up toward low \( Q \) direction in a low \( Q \) region. The dimmer isolation at higher temperatures may cause slowing down in relaxation, and decreasing \( \Gamma_b \).
5. Summary
The results of QENS experiments for liquid Se$_2$Br$_2$ have been reported. The dynamic structure factor in $Q$ region, where the first peak of $S(Q)$ lies, can separate into the fast mode and the slow mode. The temperature dependence of the maximum intensity of $A_s$ and $\Gamma_s(Q)$ reveals that the slow mode depends on inter-molecular dynamics without orientational correlation. On the other hand, the fast mode depends on rotation of the dimmer because $\gamma_f$ has two aspects, which the relaxation time at high-$Q$ shows similar value and the relaxation time at low-$Q$ becomes longer with increasing temperature. These interpretations are consistent with the earlier works [1, 4, 5, 6].

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