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Dynamics of iodine anions in KI and LiI aqueous solutions studied by ^{127}I nuclear resonant quasi-elastic scattering

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Abstract The dynamics of iodine ions in potassium iodide (KI) and lithium iodide (LiI) aqueous solutions have been studied through ^{127}I nuclear resonant quasi-elastic scattering (NRQES). A newly developed Si (12 2 2) double crystal monochromator for ^{127}I 57.6 keV excitation is used. Broadening due to a diffusive motion is measured in the energy spectra of the NRQES from the solutions.

Keywords Nuclear resonant quasi-elastic scattering · Diffusion · Aqueous solution

1 Introduction

Iodine is one of the essential elements for human beings, which is strongly related to metabolism as a thyroid hormone. During metabolism, iodine acts as iodide in an aqueous solution. Thus the research related to the iodide is important. One of the effective

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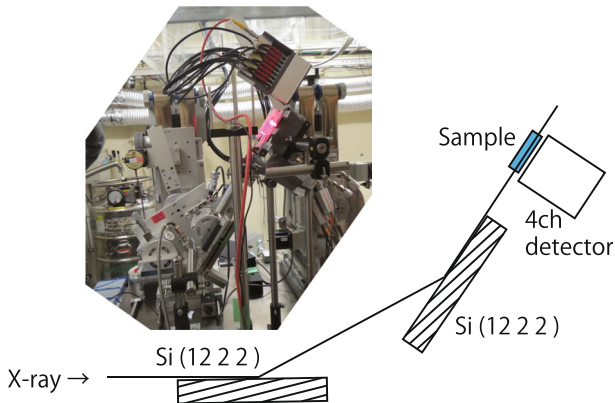
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Fig. 1 Experimental setup. Si(12 2 2) double crystal monochromator and a 4-channel scintillation detector

methods to study iodide is Mössbauer spectroscopy. There are two isotopes, ^{127}I and ^{129}I, used in Mössbauer spectroscopy. But, both of them require short lifetime radio-isotope (RI) sources made at a research reactor. Moreover, ^{129}I is an RI itself, so sample preparation is restricted in a special area with exhaust system. Compared to ^{129}I, ^{127}I has 100 % natural abundance, and is not radioactive, so that sample preparation has no restriction for RI. Developing nuclear resonant scattering (NRS), Mössbauer spectroscopy using synchrotron radiation, with iodine suggests an extension of the field of application. Although the nuclear resonant scattering of ^{127}I was first measured by Yoda [1], the nuclear resonant inelastic scattering of ^{127}I has not been reported up to this time, because of its high excitation energy (57.6 keV) and short lifetime (2.81 ns), which both make measurement difficult. Imai *et al.* has developed a high resolution monochromator using backscattering from a sapphire crystal and measured nuclear resonant inelastic scattering [2]. In this study, we developed a Si (12 2 2) double crystal monochromator and obtained much higher throughput counts than before.

Our group has studied iron in an HCl solution [3], Fe(II) ion in cation exchange membrane, Nafion [4, 5], and Fe(III) ion in an H_2SO_4 solution [6] by NRQES. The center peak in all spectra showed a broadening compared with the resolution function. In the analysis, the shape of the spectra was reproduced using self-correlation function obtained from the normal diffusion equation assuming that the iron ions diffuse in a solution [4]. But in the higher energy part, the calculated spectrum deviated from the experimental data. This is because dynamics of the particle in a short time is not correctly described in the diffusion equation. Therefore we used the Langevin equation instead of the diffusion equation to make the fitting better [5]. And we have obtained better fit in the part with the energy higher than the excitation energy. It imposes a limit on parameters, mass and diffusive coefficient, to avoid convergence in the polynomial type solution of γ ray absorption equation from the Langevin equation. When the diffusing particle is a single atom of ^{57}Fe, the mass is light and the limit does not apply. But when assuming the total mass of a large molecule, the limit of the parameter occurs during least square fitting. In the case of ^{127}I, even the mass of a single atom is heavy enough to account for the limit. Therefore we introduce the inverse Fourier transformation form which is a previous form of the polynomial type solution and has no limit in the mass of the particle.
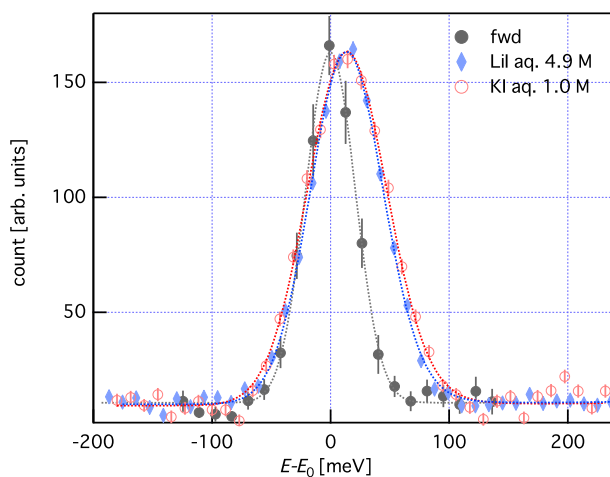
Fig. 2 Nuclear resonant quasi-elastic scattering spectra from 4.9 M LiI and 1.0 M KI aqueous solutions and resolution function

2 Experimental

The experiment was performed at the Nuclear Resonant Scattering beamline (BL09XU) of the SPring-8, Japan. The storage ring was operated in a 203 bunch mode, which provided 23.6 ns intervals between bunches, and the electron current of The produced beam was monochromatized to 57.6 keV, the first excitation energy of an ^{127}I nucleus. The bandwidth of the incident beam was obtained by nuclear forward scattering using a $Na_3H_2IO_6$ pellet, which was set in a cryostat at a temperature of 20 K in order to increase the recoilless fraction. Two Si (12 2 2) crystals asymmetry reflections shown in Fig. 1 were used to monochromatize 57.6 keV X-ray to 49±1 meV in full width at half maximum.

The NRQES signals from 1.0 M KI and 4.9 M LiI solutions were detected using a four-channel scintillation detector, consisting of Pb 5 wt % included in plastic scintillators (NE142) and photo-multiplier tubes (Hamamatsu R7400P) [7]. The air temperature in the experimental hutch was precisely controlled at 298.0 K during the measurement and the solution samples were kept at room temperature. The X-ray signals were 150 kilo counts per second (kcps) (for NFS), and 100 kcps (for NRQES).

3 Results and discussion

The NFS data from $Na_3H_2IO_6$ are shown in Fig. 2, represented by black open circles and error bars. The NRQES spectra from iodine ions in LiI and KI aqueous solutions are represented in Fig. 2 by blue and red open circles with error bars respectively. The center of gravity of the data is decided to be 14.0 meV, which is the recoil energy for ^{127}I with 57.6 keV. This value was proved by sapphire monochromator which gives certain energy difference between forward scattering peak and quasi-elastic scattering peak [8]. Both spectra shows broadenings from the resolution function.

Table 1 The results and used parameters to fit the NRQES data

Sample	4.9 M LiI aq.	1.0 M KI aq.
D [10^{-5} cm^2/s]	1.1 [10]	1.92 [10]
M [amu]	338.01$\pm$15.4	251.64$\pm$12.5

In order to analyze these spectra, we introduce the form obtained by our group. The γ-ray absorption cross section for diffusing particle governed by the Langevin equation is obtained as [5, 8, 9]

$$\sigma(E) = \frac{\sigma_0 \Gamma}{4\hbar} \exp\left(\frac{E - E_0}{2kT} - 2W\right) \int dt$$

$$\times \exp\left[-i\frac{(E - E_0)t}{\hbar}\right] \cdot \exp\left(-\frac{\Gamma|t|}{2}\right) \cdot \exp\left(-\frac{Q^2}{2}\gamma(t)\right). \tag{1}$$

$$\gamma(t) = \frac{2D}{\beta}\left(\beta t - 1 + e^{-\beta t}\right), \tag{2}$$

where σ_0 is the resonance absorption cross-section, Γ is the natural width of the excited state, $\hbar$ is the reduced Planck constant, E_0 is the excitation energy for the nucleus, k is the Boltzmann constant, T is the temperature, Q is the wave number, D is the diffusion coefficient, β represents the dynamical friction constant, M is the mass of the particle, and $2W = (\hbar^2 Q^2)/(8kM_n T)$ is the so-called Debye-Waller factor, with M_n being the mass of the nucleus. In order to handle the parameter β, we adopt the Einstein relation $\beta = kT/MD$. Thus we can use M as a parameter instead of β. This final form can be treated as an inverse time Fourier transformation.

Equation 1 is applied to analyze the broadenings of the spectra. The fitting parameters are the diffusion coefficient, D, and the mass of the diffusing particle, M. The diffusion coefficients D of the iodine ion in the solutions were reported in ref. [10]. We substitute these values for D in (1), so M becomes a fitting parameter, and the least square fitted line is represented in Fig. 2 by broken lines. The calculated M values were shown in Table 1.

The X-ray diffraction (XRD) result from a 4.6 M LiI solution indicates that there are 9.6 water molecules around the iodine ion within a sphere of radius 3.7 Å [11]. The XRD result from a 0.5 M KI solution indicates that there are 4.2 water molecules around the iodine ion. Our results show that the iodine ion in a 4.9 M LiI solution has the mass of 211 amu. A simple interpretation to the obtained mass indicates that 12 water molecules move with the iodine ion. The iodine ion in a 1.0 M KI solution moves with 7 water molecules. The number is larger than the number shown by XRD. These results show that iodine ions in these solutions move with water molecules not only in the first shell but also in the second shell.

References

1. Yoda, Y., Kishimoto, S., Zhang, X.W., Seto, M., Kikuta, S.: Hyperfine Interact C **5**, 17 (2002)

2. Imai, Y. et al.: in preparation
3. Zhang, X.W. et al.: Jpn. J. Appl. Phys **34**, L330 (1995)
4. Haruki, R., Seto, M., Kitao, S., Yoda, Y., Maeda, Yu.: J. Phys. Soc. Jpn **69**, 4049 (2000)
5. Haruki, R. et al.: J. Phys. Soc. Jpn **70**, 445 (2001)
6. Haruki, R. et al.: Hyperfine Interact C **5**, 139 (2002)
7. Kishimoto, S., Nishikido, F., Haruki, R., Shibuya, K., Koshimizu, M.: Hyperfine Interact. **204**, 101 (2012)
8. Haruki, R.: in preparation
9. Bhide, V.G., Sundaram, R., Bhasin, C., Bonchev, T.: Phys. Rev. B **3**, 673 (1971)
10. Hertz, H.G., Holz, M., Klute, R., Stalidis, G., Versmold, H.: Ber. Bunsenges. Phys. Chem **78**, 24 (1974)
11. Fishkis, M.Ya., Soboleva, T.E.: J. Struct. Chem **15**, 175 (1974)