

Non-Destructive Temperature Measurement in Aqueous Solution by Raman Scattering

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1. Introduction

For deep geological disposal of nuclear waste, the transport phenomenon of radioactive elements is important issue. For the evaluation of transport phenomenon, chemical thermodynamic data are needed. Temperature is an impacting variable which can affect chemical behaviors. Many chemical properties such as pH, solubility, redox potential depend on temperature, whose in-situ monitoring is of importance.

The thermometer has been widely used for the temperature measurement. However, the application of thermometers may cause contamination of samples because of a direct contact with samples. In particular, very corrosive samples can damage the contacting probe of thermometers. Therefore, non-invasive methods for temperature measurements are highly desired in case of corrosive environments.

Objective of the present work is to investigate non-destructive temperature measurement using Raman scattering of water molecules. By selecting an appropriate excitation source, temperature of sample is effectively measured by Raman scattering.

2. Experimental

2.1 Sample Preparation

H₂O-D₂O solution: A mixture of H₂O-D₂O solution was prepared by adding D₂O (99.9 wt %, Cambridge Isotope Laboratories Inc.) to H₂O (Millipore Milli-Q, 18.2 M \cdot cm). The ratio of H₂O to D₂O was kept to be 1:1.

Eu(III) solution: Eu(III) stock solutions were made by dissolving 10⁻³ M EuCl₃ (99.9+%, Sigma-Aldrich Co.) in 0.01 M HCl (Merck & Co., Inc), and then added to a mixed solution of H₂O- D₂O.

For maintaining the solution's temperature, the through-flow sample holder was used by circulating tempered water.

2.2 Instruments

Fig. 1 shows experimental apparatus. The H₂O-D₂O solution was excited by 355 nm laser pulses (Continuum, Surelite II-20). The laser energy was used 6 mJ and the pulse width was 6ns. The pulse energy was measured by energy meter (Gentec·eo, XLP12). During the measurements of Raman scattering, the incident laser pulse energy was continuously monitored by reflecting

ca. 5% of laser beam into photodiode detector (Gentec·eo, XLE4). The Raman scattering emission was delivered to spectrometer (ANDOR, SR-303i-A) with optical fiber and recorded by ICCD camera (ANDOR, DH734-18F-C3).

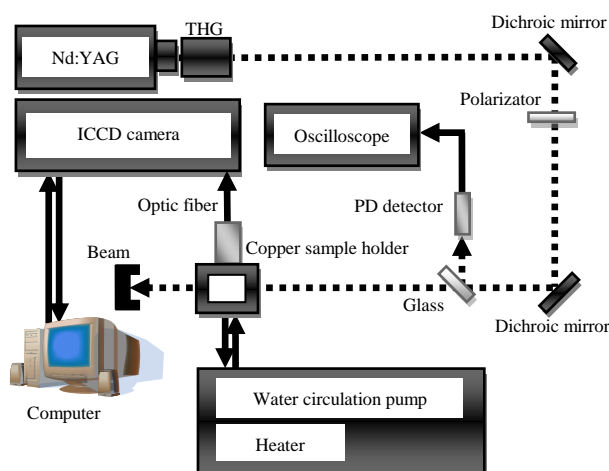


Fig. 1. Schematic illustration of the experimental setup

3. Result & Discussions

The Raman scattering shift of a mixture of H₂O-D₂O solution is shown in Fig. 2. The spectral region of 2200 - 2800 cm⁻¹ represents the OD-stretching modes of water molecules and the region of 3100 - 3700 cm⁻¹ the OH-stretching modes. The various Raman scattering components arise dependent of hydrogen bonding or non-hydrogen bonding in liquid waters [1,2]. Accordingly, the Raman spectrum is deconvoluted into several Gaussian components.

Isosbestic point of OD-stretching was measured at

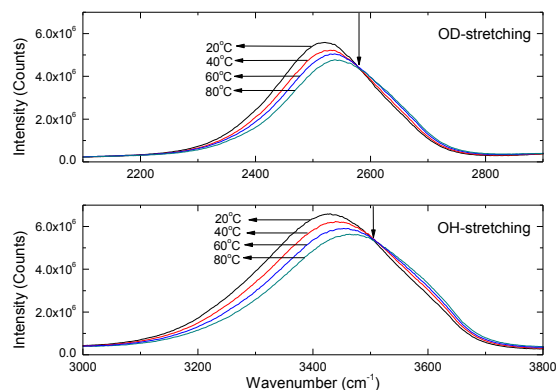


Fig. 2. Raman scattering spectra of 50% H₂O and 50% D₂O solutions

2578 cm⁻¹ and that for OH-stretching at 3506 cm⁻¹. In Fig. 2, isosbestic point bisects total Raman scattering. It is reflected by the presence of at least two substates. Component before isosbestic point represents hydrogen bonded OD- and OH-stretching, called polymers. However, component after isosbestic point represents unbonded OD- and OH-stretching, called monomers. Polymers and monomers are both in rapid equilibrium with each other as a function of temperature [3,4].

A linear relationship between Raman peak position and temperature of H₂O-D₂O sample was found over a temperature range from 20 to 80°C by 3 replicate measurements. Similar experiments were performed in 10⁻³ M Eu(III) in H₂O-D₂O solution. As shown in Fig. 3, slope obtained from a linear fit of OH-stretching is 0.59 cm⁻¹/°C and that of OD-stretching 0.40 cm⁻¹/°C. Slope from Eu(III) solution is similar to that of H₂O-D₂O solution, 0.61 cm⁻¹/°C for OH-stretching and 0.43 cm⁻¹/°C for OD-stretching. Difference in OD- and OH-stretching slopes may depend on hydrogen bonding energy differences. Raman scattering with a shift of OD- and OH-stretching is explained by intensity change of Gaussian components with rising temperature, as the tetrahedral hydrogen bonded structure of water is broken down [1].

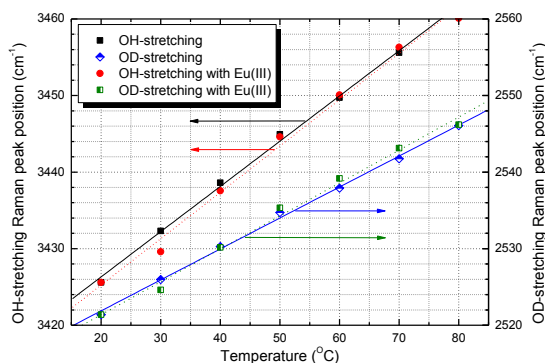


Fig. 3. Temperature and peak position shifting tendency

The van't Hoff behavior is commonly considered an indicator of a two-state system. Temperature dependence of hydrogen bonding can be justified by the van't Hoff expression [4]. Table I shows slopes of the van't Hoff expression [1] which refers to the partial derivative of ln K against the inverse absolute temperature.

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta H}{R}$$

where K is equilibrium constant, ΔH is enthalpy change, T is absolute temperature, and R is gas constant.

Differences between this work and other references may be caused by methods of the ln K calculation. There are two methodologies to calculate ln K: the area ratio on the left and right side at the isosbestic boundary splitting point or by area ratio by peak deconvolution of Raman spectrum. As shown in Table I, ΔH from the van't Hoff expression was calculated in both ways,

however discrepancies between both data are found. Deconvolution method of Raman spectrum is more reliable due to accurate consideration of each bonding state. D. M. Carey [1] applied deconvolution method, whereas G. E. Walrafen [2] and J. D. Smith [4] calculated ΔH with isosbestic boundary splitting method.

Table I: Slopes of the van't Hoff expression, ΔH

	ΔH (kcal/mol)				
	This work ¹⁾	This work ²⁾	[1] ²⁾	[2] ¹⁾	[4] ¹⁾
OH	1.5±0.1	2.8±0.1	2.5±0.1	2.6±0.1	2.00±0.01
OD	1.4±0.1	3.0±0.1	·	·	2.20±0.01

1) Isosbestic boundary splitting method

2) Peak deconvolution method

4. Conclusion

We demonstrated the applicability of Raman scattering of OH and OD-stretching for the temperature measurement. The OH-stretching ($\Delta\nu/\Delta T=0.59$ cm⁻¹/°C) is relatively more sensitive to temperature than the OD-stretching ($\Delta\nu/\Delta T=0.43$ cm⁻¹/°C) due to energy differences of each hydrogen bonding. The shift of Raman spectrum peak position is used to determine sample temperature.

Slopes of Raman scattering shift in metal ion containing aqueous solutions are consistent with those in H₂O-D₂O solutions. The method provides in-situ, non-invasive possibilities for temperature-dependent experiments of radionuclides in aqueous media.

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