

Analysis of Hydrogen Isotopes in Liquid Water Using Laser Ablation Molecular Isotopic Spectrometry

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1. Introduction

The hydrogen isotope quality control in heavy water is one of the most important concerns of the pressurized heavy water reactor (PHWR). The isotopic purity of deuterated water significantly affects the criticality of uranium fission reaction. Therefore, its purity should be maintained higher than 99.75% in terms of deuterium to hydrogen (D/H ratio). In addition, the production of tritium is the major safety issue in PHWR [1]. In this framework, *in-situ* monitoring of hydrogen isotope in heavy water is needed to enhance the safety as well as the economic feasibility of the operation of PHWR.

Laser ablation molecular isotopic spectrometry (LAMIS) is an analytical technique, which directly measures optical spectra of molecular radicals in laser-induced plasma [2]. Since the energy states are different among the isotopes, the emission light from a transition between energy states are also distinguishable in accordance with isotopes. This phenomenon is called the isotope shift. In case of the molecular emission, its isotopic shift is much greater than the atomic isotopic shift. Therefore, LAMIS has a relatively high resolution for the isotope detection in comparison to other laser-based analytical tools, such as LIBS. For this reason, LAMIS can be one of the promising techniques for *in-situ* detection of hydrogen isotopes.

The advantages of LAMIS in isotope detection have been demonstrated in various studies [3-6]. However, to the best of our knowledge, the utilization of LAMIS for the aquatic system has not yet been studied. In this study, the molecular spectra of hydroxyl radical in liquid water were measured. In addition, the D/H isotopic ratio was analyzed by a partial least squares regression (PLSR) method.

2. Experimental

2.1 Apparatus and samples

The laser pulse was generated by the Q-switched Nd:YAG laser (Quantel, Brilliant, wavelength = 532 nm, pulse width = 5.5 ns, repetition rate = 20 Hz, energy = 50 mJ). The laser was focused onto the surface of the laminar water jet by a fused-silica plano-convex lens (Focal length = 76.0 mm). The laser-induced plasma light was collected by two fused-silica plano-convex lenses (Focal length = 30 mm, 40 mm) onto the optic fiber and delivered to the spectrometer.

An echelle spectrometer (LLA, Model ESA3000), which provides a wide spectral range (200-780 nm) and a high resolution ($\lambda/\Delta\lambda = 40000$), was utilized. Spectral image dispersed by echelle was converted to electrical signal with an intensified charge-coupled device (ICCD). Liquid samples were prepared by mixing light water (H_2O , Milli-Q Synthesis) and heavy water (D_2O , Aldrich Co., 99.9% purity) in varying proportions.

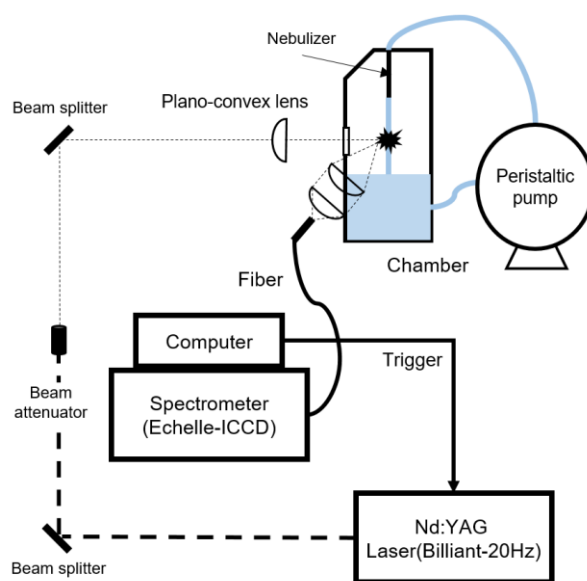


Fig. 1. Schematic diagram of LAMIS system

2.2 Method of quantitative analysis

In case of high-dimensional data set, the multivariate calibration is a more accurate approach for quantitative analysis [7]. Among various multivariate calibration tools, PLSR was applied for the spectrum data processing. PLSR was performed with a commercial template, Matlab (Mathworks Inc.). The spectral range considered in the data processing was limited the range from 306 nm to 318 nm, where the intense molecular emission of OH and OD is observed.

3. Result and discussion

3.1 Isotope shift of hydroxyl radical spectrum

In a laser-induced plasma, the emission of hydroxyl radical in the range of 306 nm to 318 nm was detected. The measured band heads matched well with the reported data [3].

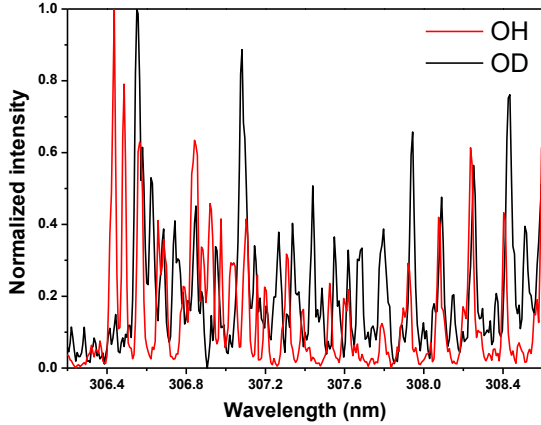


Fig. 2. Molecular OH/OD emission (Accumulation = 500 shots, gate delay = 7 μ s, gate width = 30 μ s)

The molecular spectra of OH and OD are shown in Fig. 2. We could clearly observe some isotope shifts in the $A^2\Sigma(v=0) \rightarrow X^2\Pi(v=0)$ transition spectrum. Each rotational branch head and isotope shift were obtained from the LAMIS spectrum, as represented in Table I.

Table I: Band head of OH/OD

Vibrational band	Rotational branch	Branch head (nm)		
		OH	OD	Δ
0-0	R11	306.352	306.475	0.123
	R22	306.792	307.012	0.22
	Q11	307.845	307.158	-0.687
11	Q11	314.429	311.358	-3.071

3.2 Quantitative analysis of hydrogen isotopes with PLSR

For the PLSR cross validation, eight samples with different concentrations of heavy water were prepared as a calibration set and validation set. From the analysis, the root mean square error of calibration (RMSEC) of the calibration set and the root mean square error of prediction (RMSEP) of the validation set showed the lowest values at a latent value of 3.

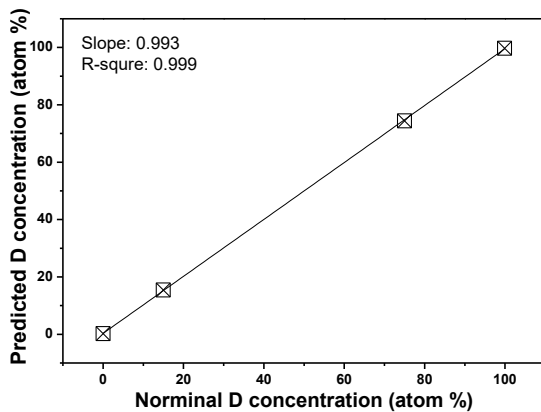


Fig. 3. Predicted D concentration versus nominal D concentration

In this condition, the predicted values were in good agreement with the nominal values, as shown in Fig. 3, and the relative error of prediction (REP) was calculated to be around 1 %.

4. Conclusions

LAMIS was utilized to measure the isotope ratio of hydrogen in deuterated water. The molecular spectra of the hydroxyl radical in the plasma plume were measured. In this system, isotope shifts of the OH/OD spectrum were clearly observed. For the quantitative analysis of the deuterium concentration, PLSR was applied as a multivariate calibration tool. The deuterium concentration prediction tool, developed in this study, showed high accuracy at low REP (~ 1 %).

In this study, we demonstrated the feasibility of *in-situ* monitoring of deuterium concentration in PHWR using LAMIS. For the field application of LAMIS to the water quality control of PHWR, further experiments with tritium isotopes are needed.

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