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Fluorescence Spectroscopy of Formaldehyde for Carbon-14 Isotope Separation

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1. Introduction

The radiocarbon (C-14) isotope is generated during the operation and dismantling of heavy water reactors. It disposed as medium-level radiocarbon waste due to the lack of effective treatment technology.

On the other hands, C-14 isotope is used as a high value-added material, such as application in the synthesis of medical radiolabeled compounds and being proposed as a raw material for nuclear batteries.

In contrast to the growing amount of radiocarbon waste, global industrial supplies of C-14 isotope remains limited. Consequently, the extraction of high purity C-14 from radiocarbon waste, not only alleviate the burden of radioactive waste disposal, but also foster economic value generation.

Various separation and enrichment technologies for recycling C-14 in resin in heavy water reactor and radioactive medical waste have been proposed, such as low-temperature distillation carbon monoxide [1] or thermal diffusion of methane [2], however, these have yet to be practically implemented.

Over the past decade, our research team has proposed and demonstrated the separation of carbon, oxygen, and hydrogen isotopes using the selective photo-dissociation of formaldehyde through a fiber laser system [3]. By applying this technique to C-14 isotope separation, we expect that we secure the cost-effective C-14 separation technology.

In this paper, we describes the experimental setup and preliminary results for spectroscopy of C-14 formaldehyde, which is important step towards realizing C-14 separation using selective photo-dissociation of formaldehyde.

2. Methods and Results

In this section, the brief introduction for isotope separation technique based on the selective photo-dissociation, experimental setup, and preliminary results for formaldehyde spectra are described.

2.1 C-14 Separation by Selective Photo-dissociation

The formaldehyde (CH_2O) molecule consists of carbon, hydrogen, and oxygen. And, this molecule is dissociated to carbon monoxide and hydrogen molecules when the 352 nm ultraviolet photon is exposed.

The high resolution spectra of formaldehyde with different isotope configurations show different absorption lines by an isotope shift. Therefore, by tuning the wavelength of narrow linewidth laser to the absorption lines which can dissociate the only the formaldehyde molecules with target isotope, we can selectively dissociate the formaldehyde molecules which contain specific isotope of carbon, hydrogen and oxygen using this chemical reaction

This technique was initially proposed in the 1980s [4]. However, practical application has been impeded over time due to the limitation in high power laser technologies. As we successfully developed the fiber based high-power ultraviolet laser [5], we demonstrated the cost-effective of the carbon and oxygen isotope separation.

To apply this technique to C-14 separation, we first obtained the high resolution spectra of C-14 formaldehyde. Then we identified the optimal absorption line of C-14 formaldehyde showing maximum selectivity by analyzing these spectra with the spectra of formaldehyde featuring other isotope configurations.

2.2 Experimental Setup

In general, absorption spectroscopy is advantageous to obtain the high resolution spectrum. For example, we obtained spectra of formaldehyde with the non-radioactive isotopes using an absorption spectroscopy technique with a beam path length of ~8 m and a cell pressure about 10 torr.

However, since C-14 formaldehyde is radioactive chemical, there are usage restrictions. To minimize the radioactive waste during experiment, both the sample amount and instrument dimension must be as minimal as possible. Thus, we applied fluorescence spectroscopy technique which has very high sensitive, although calibrating the absolute values of absorption cross-section is hard. In this experiment, we focused on the exact positions of the proper absorption peaks of C-14 formaldehyde, therefore the precise values of absorption cross-section are less important.

The experimental setup consists of a laser system and fluorescence cell for measurement. The laser system requires wavelength tuning around the 352 nm range. Ti achieve this, we designed an ytterbium (Yb)-fiber based master oscillator power amplifier (MOPA) system and a non-linear frequency conversion system. The fluorescence cell is 5 cm long and made of stainless steel. And photomultiplier tube (PMT) is used for detecting the weak fluorescence signal. The picture of the experimental setup is shown in Fig. 1.

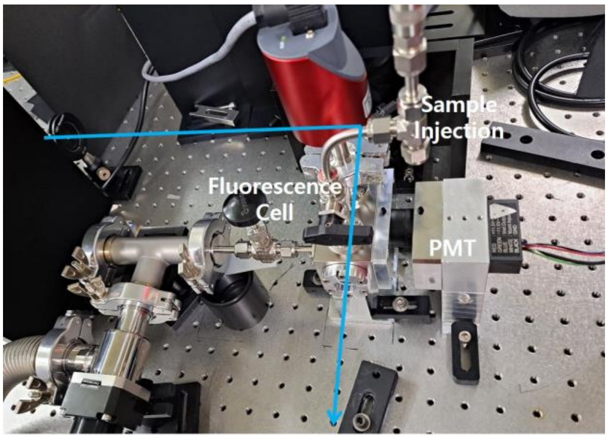

Fig. 1. The picture of experimental setup. The setup consists of the laser system, florescence cell, and PMT. (The laser system are not shown in this picture.)

2.3 Results and Discussion

In order to check the performance of the experimental apparatus, we measured the spectra for various concentration of aqueous solution of formaldehyde.

For 1% formaldehyde solution, we could easily measure the spectrum. And the results showed that we can measure the absorption lines with absorption cross-section above 10^{-20} cm^2. It is noted that the fluorescence signal is few hundred times smaller than the expected values from theoretical calculation. Thus, we cannot measure the spectrum for 0.01 % formaldehyde solution which is similar concentration to available C-14 sample. This may be originated from either the vapor pressure difference between water and formaldehyde or unexpected chemical reaction between water and formaldehyde.

To overcome this problem, we develop the method to increase the concentration of formaldehyde inside the fluorescence cell. First, we injected formaldehyde solution into the sample inlet about 10 times of the required amount for single measurement. Then, we injected the sample into the fluorescence cell by carefully adjusting the valve and pumped out. When repeating this process, a relatively large amount of water is injected initially driven by the vapor pressure difference, consequently, with successive iteration of the process, the concentration of formaldehyde is augmented.

The spectra of first and last sample injection for 0.01 % formaldehyde solution were shown in Fig. 2. We observed the fluorescence signal is significantly improved, and confirmed that the C-14 formaldehyde signal can be measured in these conditions.

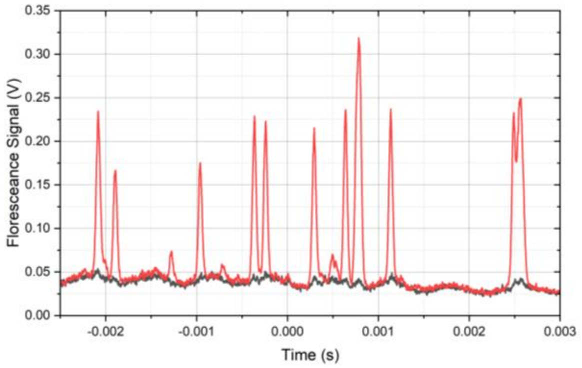

Fig. 2. The spectra of 0.01 % formaldehyde solution for the first (black line) and the last (red line) injection processes.

3. Conclusions

We built the experimental setup of fluorescence spectroscopy for C-14 formaldehyde. Then, we verified the system performance by measuring the non-radioactive formaldehyde sample with a concentration similar to that of the available C-14 sample.

We are working on the preparation of the experiment in the radiation control area. We expect that we will be able to obtain the high resolution spectra of C-14 formaldehyde in the near future.

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