# MIR Spectroscopic Method for Detection of $^{14}CO_2$

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## 1. Introduction

$^{14}C$ is an important element in nuclear industry, especially nuclear decommissioning and nuclear power plant. For example, in heavy water reactor, $^{14}C$ is dominantly produced from the nuclear reaction of $^{17}O$ contained in heavy water. The amount reaches up to approximately 20 TBq/yr. And 1% of $^{14}C$ is released to the air in the form of carbon dioxide [1]. Since the carbon is the base material for the living organics, strengthening the monitoring of $^{14}C$ radioisotope becomes a worldwide trend.

$^{14}CO_2$ in nuclear industry is typically detected by the radiation detection method due to the easiness. The carbon dioxide in gaseous effluents is generally captured by the chemical process and the radiation from $^{14}C$ is detected by a liquid scintillation counter [2]. This measurement process requires long detection time and complex procedure. These features make it difficult to detect $^{14}CO_2$ gas in real time.

The laser based detection technique is one possible method for real-time detection. But, it is typically available in the visible and NIR(near infrared) regions where the molecular absorption cross sections are too small. In the case of $^{14}CO_2$, the abundance is too low, and therefore, it is hard to detect it in visible and NIR regions even by using the sensitive detection techniques. For this reason, the laser based technique has been recently developed in mid-infrared region, 3 ~ 12 μm, where the absorption cross sections become $10^3$ ~$10^6$ times bigger than those of the near-IR region. I. Galli et al. demonstrated the $^{14}C$ detection below parts per trillion and G. Genoud et al. did $^{14}C$ detection as low as 50 parts per trillion by using laser based technique in mid-infrared region [3-4]. They showed the feasibility for $^{14}CO_2$ detection by using the cavity ring down spectroscopy which requires complicate electronics and fine adjustment. Therefore, we'd like to develop 14C sensor with better robustness and sensitivity for the future field applications.

In this paper, we introduce mid-infrared spectroscopy and the OA-ICOS for $^{14}CO_2$ measurement and present current status of the experiments.

## 2. MIR Spectroscopy of Carbon Dioxide

Carbon dioxide has 18 stable isotopologues including most abundant $^{16}O^{12}C^{16}O$(98.43%). Isotope abundance of $^{16}O^{14}C^{16}O$ in nature is approximately $10^{-12}$, and the abundance in the stack is ~ thousand times higher. Therefore, any sensitive detection method in NIR/VIS region cannot monitor $^{16}O^{14}C^{16}O$. $^{16}O^{12}C^{16}O$ has various ro-vibrational levels, as shown in Fig. 1. The fundamental mode of $CO_2$ in MIR region has very high absorption strength ( ~ $10^5$ times compared to that of the NIR region). And therefore, we expect that MIR spectroscopy combining with a cavity enhancement technique makes it possible to detect $^{14}CO_2$ in gaseous effluents.

Figure 1 shows the absorption strength of $CO_2$ from NIR to MIR regions [5].

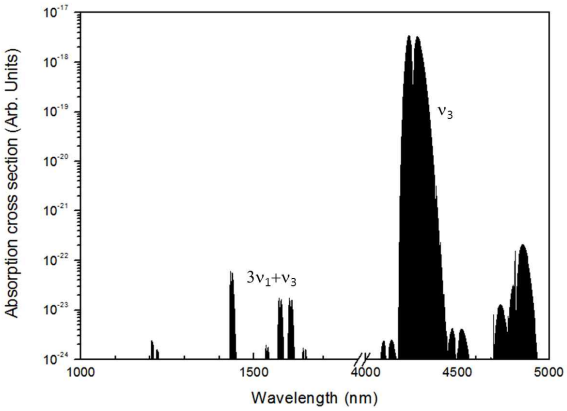


Fig.1. Absorption cross section for $^{12}CO_2$ molecule [5].

## 3. Basic Characteristics of OA-ICOS

We used OA-ICOS (Off-Axis Integrated Cavity Output Spectroscopy) in this experiment. Figure 2 shows the basic linear absorption spectroscopy and the cavity enhanced technique. In the first case, the incident beam experiences small absorption in the gaseous sample, while the incident light in the second case experiences repeated absorption during propagating back and forth inside the cavity. In results, the absorption signal can be enhanced in the cavity. OA-ICOS is one of the most important CEAS(Cavity Enhanced Absorption Spectroscopy) technique.

OA-ICOS which the light is coupled with higher order cavity modes, has the features of less-sensitive for the adjustment maintaining the cavity enhanced properties.

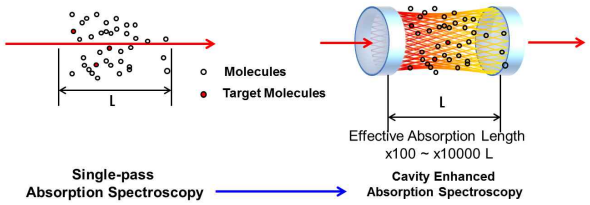


Fig. 2. Linear absorption spectroscopy and cavity enhanced absorption spectroscopy.

## 4. Preliminary Results

### *4.1 Mid-IR generation by using difference frequency generation*

OA-ICOS for improving sensitivity, needs both easy frequency control and good beam quality of the mid-infrared source, and thus we consider the difference frequency generation (DFG) for the probe beam at 4.0 μm - 4.5 μm [6].

This technique requires two co-propagating laser beams at 855 nm and 1056 nm, and a frequency conversion crystal. After phase matching, we obtained the mid-infrared beam with the power up to 1 mW at the range between 4.0 μm to 4.5 μm. Figure 3 shows the beam shape of the mid-infrared beam measured by a mid-infrared camera.

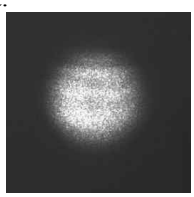

Fig. 3 mid-infrared beam shape at 4.5 μm.

### *4.2 Current Status and Future Improvement.*

The isotopologues of $CO_2$ have many ro-vibrational lines at around 4.5 μm, and we chose several weak lines for the feasibility study of our spectroscopic method. Figure 4 shows the experimental results of the ro-vibrational lines of $CO_2$ isotopologues at 10 Torr of $CO_2$ gas. The signal in Mark A is the absorption signal corresponding to the target isotopologue with the abundance of 10 ppb in $CO_2$ gas. According to the results, we believe that the system can detect $^{14}CO_2$, in $CO_2$ gas less than 10 ppb.

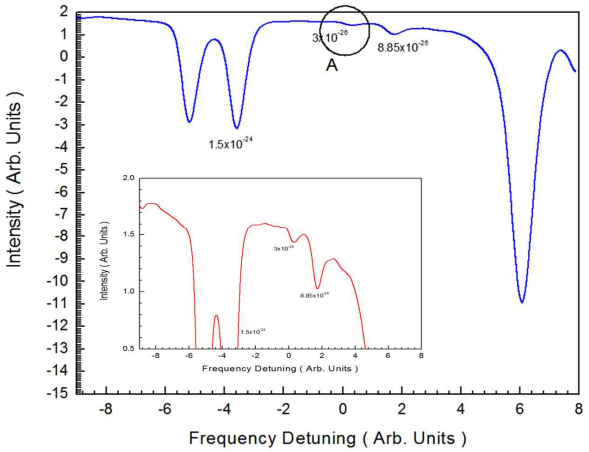


Fig. 4. The absorption signals and their strengths at around 4.5 μm. The sample is $CO_2$ gas at 10 Torr.

## 5. Conclusions

We introduced the laser-based technique for the detection of $^{14}CO_2$ in gaseous effluent in nuclear industry. We demonstrated the OA-ICOS in MIR region, and observed the small absorption signal equivalent to the 10 ppb abundance of target isotopologue. But the system requires higher reliability and sensitivity for the real application. We hope that it can be an alternative for the $^{14}CO_2$ in the nuclear industry.

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