Proc. 2nd Int. Symp. on Radiation Detectors and Their Uses (ISRD2018)
JPS Conf. Proc. **24**, 011024 (2019)
https://doi.org/10.7566/JPSCP.24.011024

Background Noise Reduction in Mid-Infrared Cavity Ring-Down Spectroscopy for Radiocarbon Analysis

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(Received March 14, 2018)

In cavity ring-down spectroscopy (CRDS), background noise caused by spurious reflective surfaces limits the sensitivity. This etaloning effect depends periodically on the laser frequency as well as the distance between the respective surfaces. In this work, Brewster spoiler is proposed as well as cavity temperature modulation. Suppression of baseline fluctuations in the system for ^{14}C analysis based on mid-infrared CRDS has been successfully demonstrated through several measurements of the spectrum baseline.

KEYWORDS: Radiocarbon, Laser Spectroscopy, Trace Isotope Analysis

1. Introduction

As an alternative to radiation detection, mass spectrometry is commonly used for analysis of long lived radionuclides. Accelerator mass spectrometry (AMS) is a specific example and its ultra-high sensitivity leads the radiocarbon (^{14}C) in new applications such as carbon dating [1]. In drug development, so-called microdose studies or human phase-0 trials using ^{14}C have attracted conspicuous attention and are expected to make the drug development process more efficient [2]. The first microdose study demonstration in Japan was reported in 2010 by using AMS [3]. However, complexity and high cost in AMS may prevent these studies from wide applications. In this context, cavity ring-down spectroscopy (CRDS) using a fundamental vibration absorption line of carbon dioxide in 4.5 μm has been proposed as a substitute for AMS [4-8]. ^{14}C analysis based on CRDS especially designed for biomedical samples in microdose study has been developed [9]. In such a system, higher throughput and lower cost are required as well as high sensitivity sufficient for microdose studies (close to natural abundance of ^{14}C/C = 10^{-12}).

CRDS was firstly demonstrated in 1988 [10] and is now known as one of the most sensitive laser absorption spectroscopic techniques. In CRDS, the effective absorption path length is enhanced by using a highly reflective optical resonator. When an optical switch in front of the resonator quickly shuts off the laser light on resonance, the light leaving in the cavity exhibits an exponential decay. The exponential time constant τ

depends on the mirror reflectivity as well as the absorption by molecules inside of the cavity. Here the inverse of τ is defined as a ringdown rate $\beta = \tau^{-1}$.

$$\beta = \beta_0 + \sigma N c = {}^{(1-R)c}/_{L} + \sigma N c, \tag{1}$$

where c is the light speed and β_0 is the inherent ringdown rate of the empty cavity, which depends on the mirror reflectivity R and the cavity length L. The righthand term in Eq. (1) contains the desired information about the number density of absorber N as well as its frequency-dependent absorption cross-section σ. Thus, the molecular density is determined by deducting β_0 from β. Due to the high finesse of the optical cavity, laser frequency stability is one of the key aspects for CRDS along with cavity stability [11]. On the other hand, the ring-down rate is, assuming a non-saturated molecular transition, generally insensitive to laser power fluctuations. However, background fluctuation in β_0 limits the sensitivity. Among the several noise sources, spurious reflections or etalon effects usually cause an uncontrolled baseline drift as well as baseline oscillations on measured spectra [12]. These oscillations are rather large compared to other noise sources and seriously affect trace gas analysis.

The main purpose of this article is presenting techniques to reduce baseline oscillations caused by etalon effects in our present mid-infrared CRDS system for ^{14}C analysis. First results of ^{14}C analysis in biomedical samples with good agreement with the amounts of ^{14}C have been attained already and will be published elsewhere.

2. Experimental Setup

2.1 CRDS setup

An overview of our CRDS setup is shown in Fig. 1. A distributed feedback quantum cascade laser (DFB-QCL) was operated at a center wavelength of 4.53 μm, where a strong $^{14}C^{16}O_2$ absorption line is located. The optical cavity (CRD cavity) consisted of two CRD mirrors, coated for high reflectivity at R = 99.98% with a separation of L = 300 mm. The cavity length was modulated by a piezo actuator. The laser entered the cavity through a pair of mode-matching lenses. An InSb mid-infrared detector monitored the cavity transmission, amplified by a current amplifier. An acoustic optical modulator (AOM) shut off the laser immediately after the signal reached a threshold voltage. Each ringdown event was acquired by a digitizer. For wavelength calibration, a portion of the laser was incident on a low finesse Fabry-Perot interferometer (FPI, finesse: ~4.5).

Carbon in the sample was converted into carbon dioxide in a combustion tube and transported to the cavity via Helium carrier gas. To suppress the interference of absorption from impurities by gas cooling [13], the temperature of the gas cell can be cooled down to 240 K, actively controlled by a peltier element. For effective insulation, the gas cell was placed into a vacuum chamber. Some additional information of our general CRDS setup is given in Refs. [9,11,14].

2.2 Brewster spoiler and cavity temperature modulation

Etalon effects are induced by the spurious reflections from external reflective surfaces, causing deviations from the baseline ring-down rate of the system. Because of

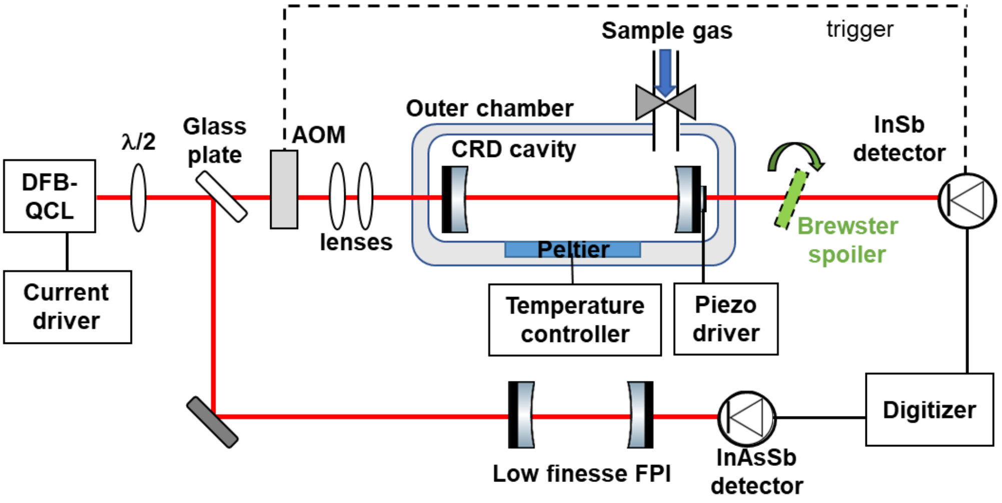

Fig. 1. Overview of experimental setup.

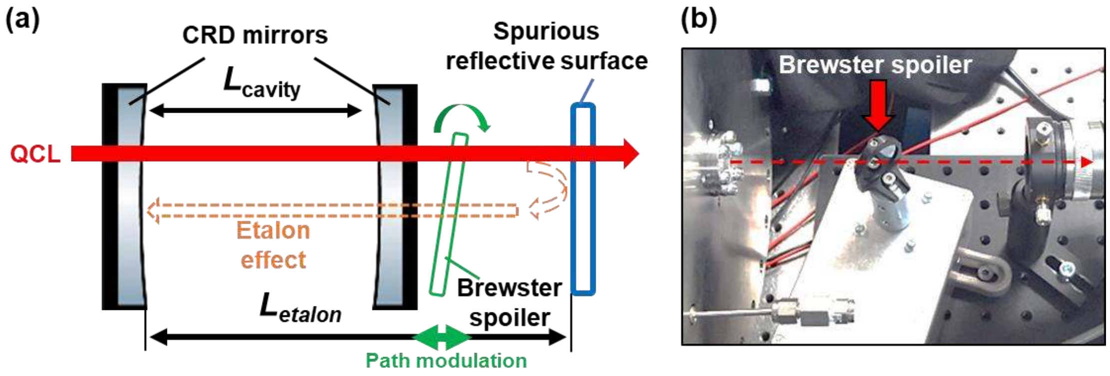

Fig. 2. A simple schematic of the etalon effect and Brewster spoiler operation (a) and installed Brewster spoiler (b). Brewster spoiler was made of a Si window and a stepping motor was controlled via Arduino.

the phase dependent nature of interference, these effects depend periodically on laser frequency as well as the distance between reflecting surfaces, which can vary with temperature or vibration. Thus, these disturbances of the baseline limit the sensitivity and makes it difficult to reliably analyze the spectra. Differential CRDS [15] is one approach to reduce the effects of etalons. Although it successfully cancels the periodic oscillations, some short-period oscillations as compared with the cavity free spectral range (FSR) cannot be suppressed effectively. Saturated absorption cavity ring-down spectroscopy (SCAR) [16] is one of the solutions as well, measuring the absorption loss independently from the cavity loss. With newly acquired higher power QCL, we will be able to saturate the target absorption line. Alternatively, a Brewster spoiler [17,18] consisting of Si window (thickness: 5 mm, refraction index at 4.5 µm: 3.42) with Brewster angle of 74 degrees, angle tuned using a stepping motor was installed to the standard CRDS setup, performing a wide phase/pathlength modulation of etalon effects.

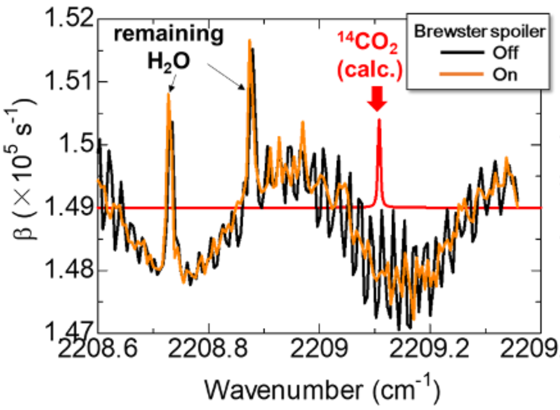

Fig. 3. Direct comparison of background measurements with /without Brewster spoiler (10 scans averaged). Expected $^{14}C^{16}O_2$ peak with β_0 = 1.49 $\times 10^5$ s^{-1} is shown (red line), assuming a gas temperature of 253 K, a pressure of 10 mbar the ^{14}C abundance of 3×10^{-10} in sample.

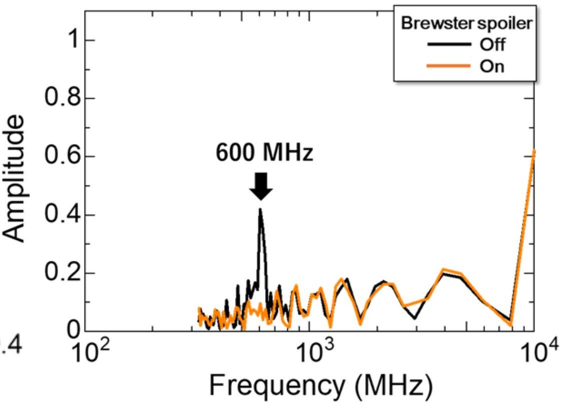

Fig. 4. Fourier transform of backgrounds with clear indication of noise suppression by Brewster spoiler. Although frequency resolution is not so high due to limited sampling intervals, it helps understanding system's noises as well as the estimation of the source of them.

It accomplishes effective smoothing of etalon effect after averaging of measured spectra. Fig. 2 shows a schematic of Brewster spoiler operation (a) and a picture of its setup (b). Furthermore, an active temperature modulation of the CRD cavity was implemented by modulating the setpoint of temperature intermittently. The pressure inside the CRD cavity was kept below 10^{-2} mbar to investigate the level of noise suppression in a spectrum with almost no visible absorption peaks.

3. Results and Discussions

The angle of the Si window was modulated by ± 0.75 degree from Brewster angle. From the thickness and refractive index of Si window, the amplitude of pathlength modulation was approximately 100 μm, many times larger than the laser wavelength. This was sufficient for wide phase modulation. A triangular modulation by stepping motor was performed, with the time period limited by the control board and the torque of the stepping motor, which was evaluated to roughly ~ 100 ms. However, this period was short enough compared to the spectrum acquisition speed of several seconds for a spectrum of wide frequency range shown in Fig. 3. In this figure the effect of the Brewster spoiler on the background comparison is shown, including the region of $^{14}C^{16}O_2$ P20 absorption line (2209.108 cm^{-1}). For the case without Brewster spoiler modulation, stepping motor was stopped, effectively fixing the distance between optical surfaces. A Fourier transform of the spectrum was used to identify the periods of etalon effects as shown in Fig. 4. Around a frequency of 600 MHz a narrow peak was noticeable, equating to a etalon distance of $L = c/2\Delta f = 250$ mm. This corresponded to the distance between one cavity mirror and the InSb detector window. Particularly this etalon effect was effectively reduced by turning on the motor of the Brewster spoiler, positively improving the quality of the spectrum. Similar suppression may be obtained by sufficiently tilting the detector, but at a trade-off on the signal intensity. On the other hand, a wide period oscillation above 10 GHz was not suppressed at all, whose period was not determined by the Fourier transform because of the poor resolution in such high frequencies. It is supposed that the source of this fluctuation was unaffected by the Brewster spoiler; most likely a reflection between the front and back side surfaces of the CRD mirror (L: 6mm, refraction index of ZnSe: 2.4). As the thickness of the CRD mirror is relatively stable due to the temperature stabilization of the gas cell, it should be possible to subtract the slow variation of the background from acquired spectra.

To suppress effects of further possible etalons, an active temperature modulation of the CRD cavity has been tested: the gas cell temperature was at first stabilized at 254.5 K and then actively modulated around ± 1.5 K with a period of 2.5 minutes. Since the physical length of the cavity was slightly changed by temperature, it equally acted as phase modulator of etalon effects. Fig. 5 shows the measured background with the temperature modulation in contrast to fixed temperature. Brewster spoiler motor was turned on in both measurements. The background was smoothed by modulating the temperature of the cavity. By combining these two methods for phase modulation, background oscillations were suppressed by one order of magnitude, to around ± 100 s^{-1} after 500 scans averaged. Based on this, noise equivalent sensitivity of $^{14}C/C = 2.0\times10^{-11}$ was evaluated. Nevertheless, the wide-period fluctuation was still visible (in form of a linear trend due to the narrower frequency region of these spectra). This suggests that the temperature modulation worked as expected but its level was insufficient to suppress this oscillation. To remove the influence of the backside surface of CRD mirrors, off-axis constructions [19] may work effectively. In the same manner, a triangle shaped resonator like the setup in Ref. [7] can reduce these effects, however requiring an additional high reflective mirror. Fig. 6 shows an exemplary spectrum of standard glucose sample (not labeled by ^{14}C) with temperature modulation applied. The experimental data was fit well by Voigt profile based on HITRAN database [20], displaying a good agreement with the gas temperature of 254.5 K and total pressure of 0.02 bar measured by the pressure gauge. Our present ±1.5 K temperature modulation did not significantly affect the spectrum shape; however, larger modulations of the cavity temperature may cause additional uncertainties for analysis of ^{14}C such as variation of Doppler broadening and line intensity of the absorbers.

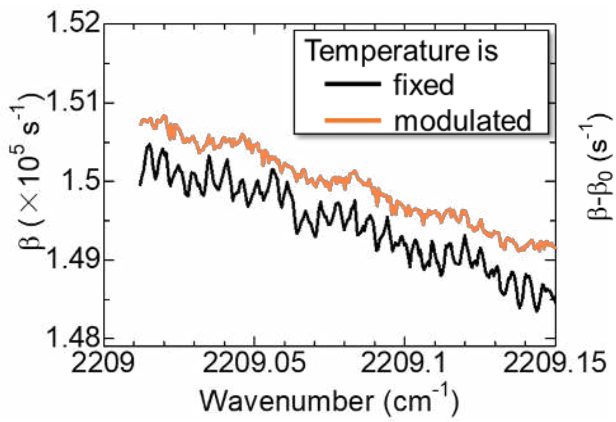

Fig. 5. Comparison of the background with fixed temperature (black trace) and modulated (orange trace, added 500 s^{-1} offset), 500 scans averaged.

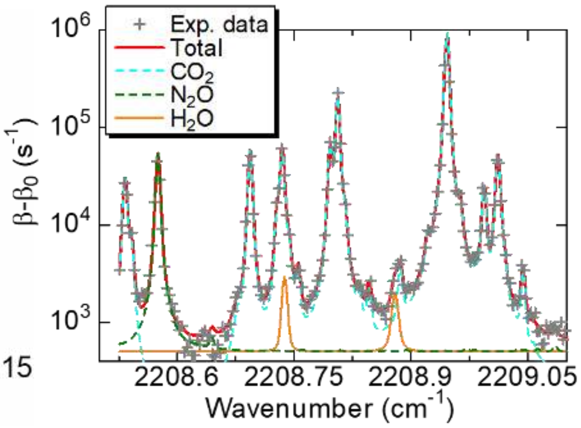

Fig. 6. Measured spectrum of stable CO_2 and impurities. Slow oscillation of background was subtracted.

4. Conclusion

This work demonstrated Brewster spoiler and active temperature modulation for smoothing of baseline oscillations caused by spurious reflections in mid-infrared CRDS system. A successful suppression of etalon effects was obtained and their sources were identified. We are considering further improvement of the signal to noise ratio of our system to achieve our sensitivity goal for ^{14}C analysis. ^{14}C analysis in animal pharmacokinetics study by our CRDS system is planned and first results in the demonstration will be highlighted in an upcoming paper with evaluation of the systems performance in the near future.

Acknowledgement

This research is partially supported by the SENTAN program “Development of Systems and Technology for Advanced Measurement and Analysis” of the Japan Science and Technology Agency (JST), and the Japan Agency for Medical Research and Development (AMED).

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