Measurement of CO$_2$ by Wavelength Modulated Reinjection Off-Axis Integrated Cavity Output Spectroscopy at 2 µm

Zhihao Yuan$^{1,2,3}$, Yinbo Huang$^{1,3}$, Xingji Lu$^{1,3}$, Jun Huang$^{1,2,3}$, Qiang Liu$^{1,3}$, Gang Qi$^{1,2,3}$ and Zhensong Cao$^{1,3,*}$

Abstract: A high sensitivity wavelength modulated reinjection off-axis integrated cavity output spectroscopy (WM-RE-OA-ICOS) experimental setup was built at a 2 µm band. On the basis of an off-axis integrated output spectroscopy (OA-ICOS), combined with an optical reinjection (RE) approach to improve signal intensity, and wavelength modulation spectroscopy (WMS) to improve the signal-to-noise ratio (SNR) of the system, the experimental study of trace CO$_2$ with high sensitivity was carried out using the setup. The performance was compared and evaluated, and the results show that: Compared with the OA-ICOS, the wavelength modulated reinjection OA-ICOS enhanced the signal intensity by 6.3 times, and the SNR increased 7.2 times from 179 to 1288. The Allan variance results showed that the detection limit of the system is 0.35 ppm when the average system time is 230 s. The setup was used to measure the indoor CO$_2$ concentration for a long time (22 h), and the measured results were in line with the actual concentration change. The proposed method shows good performance enhancement for the OA-ICOS system in trace gas measurements.

Keywords: off-axis integrated cavity output spectroscopy; reinjection; wavelength modulation spectroscopy; CO$_2$ detection

1. Introduction

Laser absorption spectroscopy in the aspect of trace gases measurement, with high sensitivity and high selectivity, has caught the attention of relevant researchers [1–3], especially cavity-enhanced absorption spectroscopy (CEAS), and cavity ring-down spectroscopy (CRDS). By establishing a high-finesse cavity and coupling the narrow-band laser into the cavity with mode matching, the effective absorption path length can be increased to thousands of meters and the detection sensitivity can be greatly improved. This has been successfully applied to the detection of various trace gases [4–6]. In 2001, Paul [7] et al. proposed the off-axis integrated cavity output spectroscopy (OA-ICOS), which effectively suppresses the cavity-mode noise because it is able to excite more high-order transverse modes. At the same time, it has the advantages of easy operation, high robustness, and low requirement on the linewidth of the laser, which has been recognized by more researchers [8–10]. However, in the experiment, researchers found that, in the case of off-axis incidents, the energy of the original single fundamental mode was distributed to many higher-order transverse modes, which resulted in very weak output power detected by the detector. Due to the limitations of laser power and detector sensitivity, the signal-to-noise ratio (SNR) of the device was difficult to further improve [11]. To solve the problem, J. B. Leen and A. O’Keefe [11] used ZEMAX software to track and simulate the optical...
The light reflected from the front mirror of the off-axis cavity was reused to enter the cavity based on the proposed optical reinjection method, which improved the detectable power by 22.5 times. In the same year, R. Centeno et al. [12,13] improved the structure of reinjection off-axis integrated cavity output spectroscopy (RE-OA-ICOS). They optimized the distance between the reinjection mirror and the front cavity mirror and the SNR increased up to 10 times. On the basis of that, the continuous real-time measurement of ethylene was realized, and the measurement accuracy reached 18 ppb in 32 s. In 2018, F. Nadeem et al. [14,15] obtained the maximum enhancement through a grid search and the genetic algorithm optimization of the reinjection method. It achieved a gain of 1000 times the signal intensity on a short cavity (only 3 cm long), which further developed the miniaturization and integration of the optical gas sensor. It opened up a new opportunity for the field of ultra-sensitive absorption spectroscopy. Given the research on the reinjection method, our group [16,17] built a reinjection off-axis integrated cavity setup that achieved a 4.6 times improvement in the SNR, while the signal intensity increased by eight times. However, while the reinjection technique enhances the signal, the noise also increases, which results in the limited improvement of the SNR.

To further improve the SNR of the system, in our recent work, wavelength modulation spectroscopy (WMS) was added to a RE-OA-ICOS system. A high sensitivity wavelength modulated reinjection off-axis integrated cavity output spectroscopy (WM-RE-OA-ICOS) experimental setup was designed and built. A series of comparative experiments was carried out by measuring the absorption spectrum of CO$_2$ gas at 4993.7431 cm$^{-1}$. Then, the optimum parameters of the experimental setup were obtained, and the change of CO$_2$ concentration in the room air was measured. Based on OA-ICOS, the device combines the reinjection method and wavelength modulation spectroscopy and, thus, provides a new solution for high sensitivity spectral measurement.

2. Materials and Methods

2.1. Theory

In an OA-ICOS experiment, the concentration of the measured gas can be obtained by measuring the intensity of light passing through the cavity. When a laser with an intensity of $I_{in}$ passes through a resonator cavity of length $d$, the reflectivity of the cavity mirror is $R_c$ and there is an absorbing medium in the cavity. The transmitted light intensity is given by

$$I = I_{in} \frac{(1 - R_c)^2 \exp(-ad)}{1 - R_c^2 \exp(-2ad)}$$

where $\alpha$ is the absorption coefficient. When there is no absorbing medium in the cavity, the transmitted light intensity is given by

$$I_0 = I_{in} \frac{1 - R_c}{1 + R_c}$$

According to Equations (1) and (2), the absorption coefficient can be expressed as

$$\alpha(\nu) = \frac{1}{d} \ln \left\{ \frac{1}{2R_c^2} \left[ \sqrt{4R_c^2 + \frac{I_{0}^2}{I_{in}^2} (1 - R_c)^2} - \frac{I_0}{I_{in}} (1 - R_c) \right] \right\}$$

When a cavity mirror with high reflectivity is used, $R_c$ tends to 1. Therefore, the absorption coefficient can be simplified as [18]

$$\alpha \approx \frac{1}{d} \left( \frac{I_0}{I_{in}} - 1 \right) (1 - R_c)$$
The effective absorption path can be approximated as

$$L_{\text{eff}} \approx \frac{d}{1 - R_c}$$  \hspace{1cm} (5)$$

Integrate both sides of Equation (4)

$$\int_{-\infty}^{+\infty} \alpha dv = \int_{-\infty}^{+\infty} \frac{1}{d} \left( \frac{I_0}{I} - 1 \right) (1 - R_c) dv = A(1 - R_c)$$  \hspace{1cm} (6)$$

The relationship between absorption coefficient $\alpha$ and the concentration of absorbed gas in the cavity is

$$\alpha(v) = \sigma(v)c = S\Phi(v)c$$  \hspace{1cm} (7)$$

where $\sigma(v)$ is the absorption cross-section, $c$ is the molecular number density, $S$ is the line strength of the absorption spectrum line, and $\Phi(v)$ is the line profile. The Voigt profile was selected for the linear fitting of the obtained absorption lines [19].

Since the integral of the $\Phi(v)$ is equal to 1, the integral of both sides of Equation (7) can be written:

$$\int_{-\infty}^{+\infty} \alpha dv = \int_{-\infty}^{+\infty} \sigma(v)cdv = Sc$$  \hspace{1cm} (8)$$

Then it can be obtained from Equations (6) and (8):

$$Sc = A(1 - R_c)$$  \hspace{1cm} (9)$$

Then, the integral area of the absorption spectrum $A$ can be calculated according to the absorption spectrum lines of the known gas concentration, and the reflectance of the cavity mirror $R_c$ can be obtained. Under the same experimental conditions, the molecular number density can be known according to the reflectivity of the cavity mirror and the parameters of the molecular absorption line to obtain the concentration of the measured gas.

In the RE-OA-ICOS device, the radius of the curvature of the reinjection mirror $M_{re}$ and the cavity mirror $M_{in}$, are $R_{re}$ and $R_{in}$, respectively, and the spacing between $M_{re}$ and $M_{in}$ is $L$. The stability formula of a class multi-pass pool structure composed of $M_{re}$ and $M_{in}$ is written as follows:

$$0 < \left( 1 - \frac{L}{R_{in}} \right) \left( 1 - \frac{L}{R_{re}} \right) < 1$$  \hspace{1cm} (10)$$

Wavelength modulated spectroscopy (WMS) is based on the original low-frequency triangular wave scanning signal loaded with a high-frequency sine wave modulation signal to regulate and control the laser current to improve the signal-to-noise ratio [20]. At this point, the laser driving current can be expressed as

$$i(t) = i_0 + a \cdot \sin(2\pi f_m t + \theta)$$  \hspace{1cm} (11)$$

where $i_0$ is the initial current, $a$ is the modulated signal amplitude, $f_m$ is the modulated frequency, and $\theta$ is the modulated phase. The working frequency of the laser can be known as

$$v(t) = v_0(t) + a \cdot \sin(2\pi f_m t + \theta)$$  \hspace{1cm} (12)$$

The second harmonic signal can be deduced as

$$H2 = \frac{1}{4} \eta I_0 L_{\text{eff}} SNa^2 \left. \frac{d^2 \varphi}{dv} \right|_{v=v_0}$$  \hspace{1cm} (13)$$

where $\eta$ is the photoelectric conversion coefficient, $\varphi$ is the peak normalized line function in the absorption spectrum, and $N$ is the molecular concentration. It can be seen that the amplitude of the second harmonic signal is proportional to the gas concentration, so the gas concentration detection can be realized through the expression of the gas calibration relation of the measured standard gas.
2.2. Experimental Equipment

The experimental setup of the wavelength modulated reinjection OA-ICOS (WM-RE-OA-ICOS) is shown in Figure 1. The temperature and current of a distributed feedback diode (DFB) laser were controlled by a laser diode controller (Lightwave-LDC3724, ILX, Irvine, CA, USA). The DFB laser (Nanoplus-2004) with an output power of 3 mW emitted at a wavelength of 2004 nm. The 40 Hz (800 mV) triangle signal generated by the function signal generator, and the 5 kHz (0.172 V) sine wave signal output by the phase-locked amplifier, scanned and modulated the DFB laser at the same time. The laser passed through the optical isolator and the plano-convex lens and was then divided into two beams by the beam splitter (2:8). One beam of light entered the wavemeter (Bristol 621A, USA) for wavelength monitoring, and the other beam was reflected by the mirror and coupled into the cavity through the reinjection mirror. The length of the cavity was 50 cm, and a pair of highly reflective mirrors with 99.94% reflectivity was placed at both ends. The transmitted light reflected back and forth in the cavity many times was received by the photodetector and demodulated by the phase-locked amplifier to obtain a 2f signal, which was captured by a high-speed data acquisition card (USB-6353, National Instruments, Austin, TX, USA) and recorded by a computer for further processing. In the gas passage part, the standard CO₂ gas (400 ± 1 ppm, Nanjing Special Gas, Nanjing, China) and the pure N₂ were passed though the mass flow controller (D07-7B, Sevenstar, Beijing, China) to get the required concentration of CO₂ gas, which was entered into the cavity by the gas inlet. The gas outlet was connected to the pressure controller (Type 640B, MKS, Andover, MA, USA) and the suction pump, controlling the pressure inside the cavity. The He-Ne red light was used as the indicator light, adjusting the common path with the detecting laser by the reflector mirror.

![Experimental setup of WM-RE-OA-ICOS set-up. DFB: distributed feedback laser; BS: beam splitter; MFC: mass flow controller; PD: photodetector; DAQ: data acquisition card.](image)

**Figure 1.** Experimental setup of WM-RE-OA-ICOS set-up. DFB: distributed feedback laser; BS: beam splitter; MFC: mass flow controller; PD: photodetector; DAQ: data acquisition card.

2.3. Spectral Line Selection

In the experiment, an isolated CO₂ absorption line was selected to avoid the interference of other gas molecules and, at the same time, the laser range of use was considered, and the gas absorption spectra near 2 µm was simulated according the HITRAN database [21]. The simulation conditions were set as follows: temperature 296 K, pressure 90 Torr, absorption path length 407.4 m. The gas molecular concentration was set as: CH₄ 2 ppm, CO₂ 400 ppm, H₂O 1.8%, N₂O 320 ppb, and NH₃ 20 ppb, and the remaining gas in the mixture was N₂. The simulation results are shown in Figure 2. It can be seen from the figure that the absorption near the 2 µm band is mainly CO₂ and H₂O, while the absorption of the other molecules is very weak. Therefore, the absorption spectrum line at 4993.7431 cm⁻¹
In the experiment, an isolated CO$_2$ absorption line was selected to measure the CO$_2$ concentration. During the measurement, the temperature of the laser was set at 17 °C and the current was 136.83 mA.

Figure 2. HITRAN simulation of the real atmosphere spectrum near 2 μm. Simulation conditions: temperature 296 K; pressure 90 Torr; absorption light path 407.4 m. (CH$_4$ 2 ppm, CO$_2$ 400 ppm, H$_2$O 1.8%, N$_2$O 320 ppb, NH$_3$ 20 ppb). The black arrow indicates the CO$_2$ absorption line at 4993.7431 cm$^{-1}$ selected during the measurement.

3. Results and Discussion

3.1. Reinjection Mirror Design and Wavelength Modulation Parameters Determination

LIGHTTOOLS (Optical Research Associates, LIGHTTOOLS 8.4) software was used to simulate the structural parameters of the reinjection OA-ICOS setup [16]. As shown in Figure 3: (a) is the light simulation of the overall reinjection off-axis setup, consisting of a reinjection mirror and a pair of cavity mirrors with a 1 m radius of curvature, while the diameter is 25.4 mm, and the cavity length is 50 cm; (b) is the reinjection mirror, with light passing through the hole on the reinjection at a certain tilt angle coupling into the cavity, the tilt angle is X: 0.5°, Y: 0.3°; (c) is the reflectional arrangement of the light spot on the surface of the reinjection mirror, the spot was closely distributed in a circular shape, greatly improving the light utilization. According to the simulation results, the optimal experimental parameters were obtained. The reinjection mirror was designed and processed with a diameter of 25.4 mm, a radius of curvature of 683 mm, and an average reflectivity greater than 98%. The placement of the reinjection mirror was 11 cm from the front cavity mirror. The light was directed to the front cavity mirror through the reinjection mirror, and the cavity mirror reflectivity was higher than 99.9%. According to Equation (2), the light intensity transmitted into the cavity is very weak. In order to increase the light intensity into the cavity, the light reflected from the front cavity mirror was received by the reinjection mirror and coupled into the cavity again. By adjusting the reinjection mirror, the signal strength can be enhanced to the maximum extent on the premise of ensuring the signal quality. Figure 4 shows experimentally recorded data. The reinjection mirror improves the signal strength by 6.3 times.

The reinjection mirror enhances the signal strength but also brings amplification of the interference signal. To further improve the SNR, wavelength modulation spectroscopy (WMS) was added to the RE-OA-ICOS system. In WMS, the laser wavelength is modulated by a sinewave (kHz to MHz) to suppress laser noise and photodetector electronic noise, and then demodulated by a lock-in amplifier to obtain a harmonic signal proportional to the measured gas concentration. The WMS effectively suppressed 1/f noise in the system, thus improving the sensitivity of the measurement system.
ensuring the signal quality. Figure 4 shows experimentally recorded data. The reinjection mirror improves the signal strength by 6.3 times.

Figure 3. Reinjection structural parameter simulation: (a) light simulation of integral reinjection off-axis device; (b) reinjection mirror; (c) reflectional arrangement of light spots on the surface of the reinjection mirror.

Figure 4. Absorption spectra were compared with or without reinjection systems. The red line is the RE-OA-ICOS absorption signal, the blue line is the OA-ICOS absorption signal; the RE-OA-ICOS signal strength is 6.3 times that of OA-ICOS.

In order to obtain the best harmonic signal, an appropriate modulation coefficient needs to be obtained. The modulation coefficient is defined as the ratio of modulation amplitude to the absorption line half width at half maximum (HWHM), and the theoretical value is 2.2 [22]. At room temperature (~23 °C), and a gas pressure of 90 Torr, the function generator generated a triangular wave signal with a frequency of 40 Hz and an amplitude of 800 mV to scan the current of the laser controller, and a concentration of 400 ppm CO₂ was introduced into the cavity. The lock-in amplifier output a high-frequency sine wave signal loaded onto the laser that was used, together with the triangle wave, to vary the laser current and adjust the sine wave signal frequency, with the maximum 2f signal amplitude obtained when it was 5 kHz. After obtaining the best modulation frequency, we continued to adjust the modulation amplitude and phase, and the 2f signal got the maximum value when the phase was 50° and the amplitude was 0.172 V. Figure 5 shows the experimentally observed waveforms of the 1f, 2f, 3f, and 4f harmonic components under the above conditions, with 1000 times average.
Figure 5. The harmonic component signal was obtained by demodulation of the lock-in amplifier. (a) 1f signal; (b) 2f signal; (c) 3f signal; (d) 4f signal.

The 400 ppm CO₂ and pure N₂ were mixed into the CO₂ sample gas with different concentrations of 100 ppm, 200 ppm, 300 ppm, and 400 ppm, respectively, by the mass flow controller (Sevenstar D07-7B). At the same room temperature of 23 °C and gas pressure of 90 Torr, the prepared sample gas was passed into the cavity, and a 2f signal was collected with the acquisition card for an average of 1000 times, as shown in Figure 6. The higher the concentration of sample gas, the greater the amplitude of the 2f signal.

Figure 6. 2f signal in different concentrations of CO₂. The sample gas (100 ppm, 200 ppm, 300 ppm, 400 ppm) prepared was successfully passed into the cavity to obtain a 2f signal at a room temperature of 23 °C and a gas pressure of 90 Torr.

According to Equation (13), there is a linear relationship between gas concentration and 2f signal amplitude, and the fitting results are shown in Figure 7. The fitting results
verified the theoretical linear relationship and prove the effectiveness of the system. The fitting curve is

\[ y = 754.3885x - 709.51683 \]  \hspace{1cm} (14)

The goodness of fit was 0.9992.

3.2. Comparative Analysis of Systems Performance

In order to compare and evaluate the performance of OA-ICOS, RE-OA-ICOS, and WM-RE-OA-ICOS, the 400 ppm CO\(_2\) was passed into the three measuring devices, respectively. The experimental environment and data acquisition methods were kept the same. The laser current was scanned by a triangle wave signal with a frequency of 40 Hz and an amplitude of 800 mV. In wavelength modulation, the modulated signal was a sine wave with a frequency of 5 kHz, an amplitude of 0.172 V, and a phase of 50°. The CO\(_2\) absorption signals of the three devices were measured and processed at 4993.7431 cm\(^{-1}\), and the experimental results are shown in Figure 8. Figure 8a was the signal obtained from the OA-ICOS measurement, Figure 8b was the signal from the RE-OA-ICOS, and Figure 8c was the 2f signal from WM-RE-OA-ICOS. According to the absorption signal measured by RE-OA-ICOS (Figure 8b), the sensitivity of the detecting device is obtained, the actual reflectivity of the cavity mirror is 99.94%, the cavity finesse is 2600, and the theoretical absorption optical path is 941 m.

The experimental results showed that the RE-OA-ICOS (Figure 8b) improved the system sensitivity compared with the OA-ICOS (Figure 8a), and the SNR increased from 179 to 573. After adding the WMS, the SNR of the WM-RE-OA-ICOS (Figure 8c) was 1288, which was obtained by calculating the ratio of the peak-to-peak value and the standard deviation of the 2f signal, which is 7.2 times higher than that of the OA-ICOS and further improves the detection sensitivity of the system. Therefore, the WM-RE-OA-ICOS system possesses better performance.
3.3. Measurement of Room Atmospheric CO$_2$

The WM-RE-OA-ICOS device was built to measure CO$_2$ in the room environment for a long time. Before the measurement, the system stability time and detection limit were tested. Pure N$_2$ was injected into the cavity, the flow rate was controlled to 80 SCCM/min, the pressure inside the cavity was 90 Torr, and the temperature was kept at 23 °C. The continuous measurement was performed for 30 min, with 50 times of average times for each dataset, and the average time was 4 s, as shown in Figure 9a. The total variation range of the measured concentration was from ~10 ppm to 20 ppm for a 30 min measurement time. The $2f$ signal amplitude was extracted and substituted into Equation (14) to get the measured gas concentration, and the Allan variance of the system was calculated, as shown in Figure 9b. The detection limit of the system was 4.5 ppm when the averaging time was 4 s, and the minimum detectable concentration (MDC) was 0.35 ppm at an integration time of 230 s.

The CO$_2$ concentration in the room was continuously measured from 9:00 on March 31 to 7:00 on April 1. The room area is about 100 square meters, and the number of people was up to seven indoors. Windows and air conditioning were on when people were around. The measurement results are shown in Figure 10. Indoor CO$_2$ concentration varies between 450 ppm and 750 ppm, which is greatly affected by indoor personnel. A few representative time points are selected here to illustrate. On the first day, from 9:00 to 11:30, the indoor CO$_2$ concentration showed an increasing trend due to the increased number of people indoors, from 600 ppm at the time of measurement to 700 ppm. At 11:30, the indoor personnel left the room and the CO$_2$ concentration dropped rapidly to around 520 ppm. From 13:30 to 17:00, the personnel started to enter the room and the CO$_2$ concentration increased to around 725 ppm, reaching the maximum concentration during...

![Figure 8](image-url)
the measurement period. From 17:00 to 23:00, the personnel came out of the room one after another and the CO\textsubscript{2} concentration showed a fluctuating downward trend. After 23:00, all indoor personnel left and the CO\textsubscript{2} concentration rapidly dropped to around 500 ppm, which was maintained until 7:00 the next morning. When leaving the room at night, the windows were closed and the air conditioning was turned off. During this period, CO\textsubscript{2} concentration increased slightly from 2:00 to 4:00. The reasons are speculated as follows: the air conditioner was turned off at night, so the temperature difference between day and night was large, resulting in a change in the environment of the experimental setup and drift in the system. The problem can be solved by adding a temperature controller to obtain a stable performance.

Figure 9. Stability performance of the WM-RE-OA-ICOS system: (a) CO\textsubscript{2} concentration measurements of the sample with zero concentration for a time of 30 min; (b) Allan deviation as a function of averaging time, based on the data. Each black dot represents a group of data. The average number of each group of data is 50, the average time is 4 s, and the test time is 30 min. When the average time is 4 s, the detection limit of the system is 4.5 ppm, and the average time is 230 s. The lowest detection limit of the system is 0.35 ppm.
The variation of indoor CO$_2$ concentration is measured by the device over time. Continuous measurement for 22 h. The red vertical line marks several representative time nodes. There is a large turnover of people nearby, and CO$_2$ changes significantly.

![Figure 10](image)

**Figure 10.** The variation of indoor CO$_2$ concentration is measured by the device over time. Continuous measurement for 22 h. The red vertical line marks several representative time nodes. There is a large turnover of people nearby, and CO$_2$ changes significantly.

4. Conclusions

In this paper, a set of WM-RE-OA-ICOS setups, based on the reinjection method, WMS, and OA-ICOS, was proposed in order to realize the signal enhancement and the improvement of SNRs. CO$_2$ standard gas with a concentration of 400 ppm was selected as the gas to be measured. Comparative experiments and results analysis were carried out to compare and evaluate the performances of the three approaches and whether to add the reinjection method and WMS. The optimal parameters were obtained through a simulation of the design and process of the reinjection mirror. The results show that, compared with the OA-ICOS approach, the signal intensity of the system was enhanced by 6.3 times with the addition of the reinjection mirror. After adding wavelength modulation, the absorption signal measured by the 2$f$ signal improved the SNR from 179 to 1288, and an increase of 7.2 times was obtained. The Allan variance of the system shows that when the average time is 230 s, the lowest detection limit is 0.35 ppm. The experimental setup was used to continuously measure indoor CO$_2$ gas at 4993.7431 cm$^{-1}$ for 22 h, and the measured results accurately reflected the changing trend of gas concentration. The method provides a new solution for OA-ICOS to detect trace gases.

**Author Contributions:** Conceptualization, Z.Y.; methodology, Z.C. and Z.Y.; software, Z.Y. and X.L.; validation, Z.Y. and J.H.; formal analysis, Z.Y. and G.Q.; investigation, Z.Y., J.H. and G.Q.; resources, Z.C., Q.L. and Y.H.; data curation, Z.Y.; writing—original draft preparation, Z.Y.; writing—review and editing, Z.Y. and Z.C.; visualization, Z.Y.; supervision, Z.C., X.L., and Y.H.; project administration, Z.C. and Y.H.; funding acquisition, Z.C. and Y.H. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by Technology and Industry for National Defence of China (JCKY2019130D021).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data presented in this study are available on request from the corresponding author.
Acknowledgments: The authors gratefully acknowledge the support of Technology and Industry for National Defence of China (JCKY2019130D021).

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Liu, W.Q.; Chen, Z.Y.; Liu, J.G.; Xie, P.H.; Zhang, T.S.; Zhao, N.J.; Si, F.Q.; Hu, R.Z.; Yin, G.F. Advances with Respect to the Environment Spectroscopy Monitoring Technology. Acta Opt. Sin. 2020, 40, 7–14.
2. Bogomolov, A.; Zbabarylo, U.; Kirshonov, D.; Belikova, V.; Ageev, V.; Usenov, I.; Galyanin, V.; Mitne, O.; Sakharova, T.; Danielyan, G.; et al. Development and Testing of an LED-Based Near-Infrared Sensor for Human Kidney Tumor Diagnostics. Sensors 2017, 17, 0914–0930. [CrossRef]
3. Harilal, S.S.; Brumfield, B.E.; Lahaye, N.L. Optical spectroscopy of laser-produced plasmas for standoff isotopic analysis. Appl. Phys. Rev. 2018, 5, 021301. [CrossRef]
4. Cygan, A.; Wcisło, P.; Wójciewicz, S.; Maskowski, P.; Domysławska, J.; Trawiński, R.S.; Ciuryło, R.; Lisak, D. Precise cavity enhanced absorption spectroscopy. J. Phys. Conf. Ser. 2014, 548, 012015. [CrossRef]
5. Matiñan, S.; Pradhan, M. Cavity ring-down spectroscopy and its applications to environmental, chemical and biomedical systems. J. Chem. Sci. 2020, 132, 114. [CrossRef]
6. Kiseleva, M.; Mandon, J.; Persijn, S.; Harren, F.J.M. Accurate measurements of line strengths and air-broadening coefficients in methane around 1.66 μm using cavity ring down spectroscopy. J. Quant. Spectrosc. Radiat. Transf. 2019, 224, 9–17. [CrossRef]
7. Paul, J.B.; Lapson, L.; Anderson, J.G. Ultrasensitive absorption spectroscopy with a high-finesse optical cavity and off-axis alignment. Appl. Opt. 2001, 40, 4904–4910. [CrossRef] [PubMed]
8. Zheng, K.Y.; Zheng, C.T.; He, Q.X.; Yao, D.; Hu, L.; Zhang, Y.; Wang, Y.D.; Tittel, F.K. Near-infrared acetylene sensor system using off-axis integrated-cavity output spectroscopy and two measurement schemes. Opt. Express 2018, 26, 26205–26216. [CrossRef]
9. Sprenger, M.; Tetzlaff, D.; Soulsby, C. No influence of CO₂ on stable isotope analyses of soil waters with off-axis integrated cavity output spectroscopy (OA-ICOS). Rapid Commun. Mass Spectrom. 2017, 31, 430–436. [CrossRef]
10. Chandran, S.; Ruth, A.A.; Martin, E.P.; Alexander, J.K.; Peters, F.H.; Anandarajah, P.M. Off-Axis Cavity-Enhanced Absorption Spectroscopy of 14NH₃ in Air Using a Gain-Switched Frequency Comb at 1.514μm. Sensors 2019, 19, 5217. [CrossRef]
11. Leen, J.B.; O’Keeffe, A. Optical re-injection in cavity-enhanced absorption spectroscopy. Rev. Sci. Instrum. 2014, 85, 093101. [CrossRef]
12. Centeno, R.; Mandon, J.; Cristescu, S.M.; Harren, F.J.M. Three mirror off axis integrated cavity output spectroscopy for the detection of ethylene using a quantum cascade laser. Sens. Actuators 2014, 203, 311–319. [CrossRef]
13. Centeno, R.; Mandon, J.; Cristescu, S.M.; Harren, F.J.M. Sensitivity enhancement in off-axis integrated cavity output spectroscopy. Opt. Express 2014, 22, 27985–27991. [CrossRef] [PubMed]
14. Nadeem, F.; Postma, B.R.; Postma, G.; Cristescu, S.M.; Mandon, J.; Harren, F.J.M. Comprehensive three-dimensional ray tracing model for three-mirror cavity-enhanced spectroscopy. Appl. Opt. 2018, 57, 154–163. [CrossRef] [PubMed]
15. Nadeem, F.; Mandon, J.; Cristescu, S.M.; Harren, F.J.M. Intensity enhancement in off-axis integrated cavity output spectroscopy. Appl. Opt. 2018, 57, 8536–8542. [CrossRef] [PubMed]
16. Zhou, Z.X.; Huang, Y.B.; Lu, X.J.; Yuan, Z.H.; Cao, Z.S. Design and experiment of re-injection off-axis integrated cavity output spectroscopy technology in 2 μm band. Acta Phys. Sin. 2019, 68, 339–349.
17. Zhou, Z.X.; Huang, Y.B.; Lu, X.J.; Yuan, Z.H.; Cao, Z.S. Method of suppressing interference noise for re-injection off-axis integrated cavity output spectroscopy. Chin. J. Quantum Electron. 2019, 36, 651–657.
18. Fiedler, S.E.; Hese, A.; Ruth, A.A. Incoherent broad-band cavity-enhanced absorption spectroscopy. Chem. Phys. Lett. 2003, 371, 284–294. [CrossRef]
19. Zhao, W.X. Integrated Cavity Output Spectroscopy and Its Application; Chinese Academy of Sciences: Hefei, China, 2008.
20. Zhao, W.X.; Gao, X.; Chen, W.; Zhang, W.; Huang, T.; Wu, T.; Cha, H. Wavelength modulated off-axis integrated cavity output spectroscopy in the near infrared. Appl. Phys. B 2007, 86, 353–359. [CrossRef]
21. Gordon, I.E.; Rothman, L.S.; Hall, C.; Kochanov, R.V.; Tan, Y.; Bernath, P.F.; Birk, M.; Boudon, V. The HITRAN2016 molecular spectroscopic database. J. Quant. Spectrosc. Radiat. Transf. 2017, 203, 3–69. [CrossRef]
22. Reid, J.; Labrie, D. Second-harmonic detection with tunable diode lasers—Comparison of experiment and theory. Appl. Phys. B Photophysics Laser Chem. 1981, 26, 203–210. [CrossRef]