Differential Measurement for Cavity Ring-Down Spectroscopy with Dynamic Allan Variance

1. Introduction

As one of the widely accepted absorption spectroscopic technologies, cavity ring-down spectroscopy (CRDS) shows a rapid progress in company with the development of high-quality mirrors and cavities. Two significant advantages bring CRDS with distinctive features different from other absorptive spectroscopic methods [1]. First, CRDS has ultrahigh spectral resolution due to its very narrow line width, which enables it to accurately distinguish the similar absorption wavelength of two different substances or the similar absorption wavelength of the same substance. Second, the usage of ultrahighly reflecting mirrors in constructing ring-down cavity enables an effective absorption path up to tens of kilometers and thus guarantees an extremely sensitive operation. CRDS was originally introduced to calibrate the reflectivity of ultrahighly reflecting mirrors. Since the pioneering works of O’Keefe and Deacon [2], this technique has been incorporated and thus played an important role in the detection of trace gas by virtue of its high detection sensitivity. Crosson used a CRDS-based analytical instrument to measure the concentration of greenhouse gases (i.e., CH₄/CO₂/H₂O) in the air, in an outfield environment, and conducted an evaluation on the long-term operational performance along with the U.S. National Oceanic and Atmospheric Administration (NOAA) [3]. Their work verifies the feasibility to use a CRDS-based apparatus for atmospheric monitoring. Chen et al. used the CRDS technology to measure methane and its isotopes. The CRDS spectrum analyzer of their work will be used for future Mars surface missions, since it is capable of meeting the detecting requirements of the Mars atmosphere relying on its extremely high sensitivity [4]. Chen et al. used the CRDS technology to detect HCN in oral exhalation, of which the sample concentration ranged from 0.9 to 10.9 ppb [5]. HCN is considered as a potential marker for Pseudomonas aeruginosa lung infection. In addition to its application in the field of trace gas detection, the CRDS
technology is also widely used in various fields, such as aerosol detection [6], combustion chemical analysis [7], and liquid chromatogram [8].

Error analysis plays an important role in determining CRDS measurement sensitivities. Huang and Lehmann studied the mode noises which arise from high-order modes and suggested to insert spatial filtering apertures to suppress the formation of these high-order modes [9]. The authors also studied the beat-frequency noises from residual strains caused by linear birefringence and proposed suitable polarizing filtering means to improve the detection accuracy. Wang et al. studied the influences of white-noise amplitude on the fast Fourier transformation (FFT), discrete Fourier transformation, linear regression summation, Lev- enberg–Marquart algorithm, and the least square method, respectively [10]. The authors carried out not only comparative analysis in terms of influences of noises, the accuracy and precision of fitting, and the fitting rate but also experimental studies as the verification of their discussion. Tan et al. studied the noises from mode mismatching, proposed an evaluation criterion based on the quality factor Q, and performed an analysis on the errors aroused from the inefficient intracavity build-up process [11]. It can be noted that these previous studies concern mainly on the error analysis in a single ring-down curve and discuss the time-domain characteristics of noises with standard Allan variance. For example, Stowasser et al. used Allan variance to perform a comparative analysis on the CRDS measurement accuracy, linearity, and drifts under different air pressures [12]. Huang and Lehmann used Allan variance to analyze the long-term stability of a CRDS apparatus and studied the relationship between mechanical deformations and the detection accuracy [13].

Although the standard Allan variance can easily fulfill the task of different error source identification and overall noise statistics derivation [14, 15], it is not able to characterize nonstationary, time-varying stochastic processes [16–18]. However, since the actual ring-down process is inevitably affected by the variations in the temperature, pressure, and even the performance change of different components, one can find that the standard Allan variance is no longer valid in the separation and characterization of these complex situations. Karhu et al. suggested that these time-varying errors were originated by the fluctuations in the cavity ring-down rate which were usually believed to be constant [19]. Another issue which needs to be noticed is that these time-varying drift noises in the ring-down rate present an ultimate limit for the sensitivity of CRDS, especially when long time averaging fitting is included. One possible solution is to record simultaneously the ring-down times at or away from the absorption, owing to the fact that the difference between them can be used directly to calculate the attenuation coefficient.

In this paper, the dynamic Allan variance (DAVAR) is used to simulate the feature of time-dependent noise and to analyze their influences on the CRDS measurement accuracy. In order to eliminate the influence of time-varying noise caused by environmental factors and instrument drift, this paper proposes a practical approach for differential measurement. By virtue of the detection of ring-down times with or without gas absorption, the error caused by time-varying noise is corrected. The validity of the above method was verified in the experiment by changing the temperature of the CRDS device.

2. DAVAR and Simulation

2.1. Allan Variance. It is supposed that the output signal of the cavity ring-down process is collected at a sampling period of $T_0$, and totally N sets of curves are recorded in this paper. The ring-down time for the $i_{th}$ set $\tau_i$ (where $0 < i \leq N$) is obtained by the CRDS formula [20] and fast fourier transform analysis method [21]. Separate $\tau_i$ into $K = N/M$ groups with $M \leq (N - 1)/2$ representing the number of data within each group. Then, the average of each group can be given by

$$\bar{\tau}_k(M) = \frac{1}{M} \sum_{j=1}^{M} \tau_{(k-1)M+j} \quad k = 1, 2, \ldots, K,$$  \hspace{1cm} (1)

where $\sigma$ is a parameter in connection with the Allan variance.

According to the definition of the Allan variance,

$$\sigma^2(T) = \frac{1}{2} \left\langle \left( \bar{\tau}_{k+1}(T) - \bar{\tau}_k(T) \right)^2 \right\rangle = \frac{1}{2(K\sigma - 1)} \sum_{k=1}^{K\sigma-1} \left( \bar{\tau}_{k+1}(T) - \bar{\tau}_k(T) \right)^2,$$ \hspace{1cm} (2)

where $T = T_0/M$ is the correlation time of each group, the triangular bracket denotes an overall average, and $\tau_i(M)$ is a discrete sequence. The curve showing the dependence of $\sigma^2(T)$ on $T$ can be obtained by adjusting the quantity of the correlation time $T$. A further double logarithmic treatment of the curve $\sigma^2(T) \sim T$ gives then the Allan variance.

2.2. DAVAR. As a method proposed by Galleani et al., the DAVAR was originally used in the time-varying stability measurement of an atomic clock [16–18]. DAVAR characterizes a time-varying signal $\tau(t)$ and obtains its Allan variance through sliding estimation of the signal sequence with different time periods. DAVAR thus introduces the temporal information into the standard Allan variance, which may be expressed in the form of a three-dimensional graph characterizing the statistical evaluation tendency of the noises over time.

Assume that $\tau(t)$ is the discrete CRDS signal sampled and recorded with a length of $N$. A sliding interception on $\tau(t)$ with a window function $P_w(t)$ centered at the point $T_c$ of the length $L_w(t)$ gives the intercepted signal as follows:

$$\tau(t, T_c) = \tau(t)P_w(t),$$

$$t - \frac{L_w}{2} \leq T_c \leq t + \frac{L_w}{2}.$$ \hspace{1cm} (3)

There are $L_w$ continuous data $\tau(t, T_c)$ intercepted at the sampling period of $T_0$. Follow the definition of Allan
variation and separate $\tau(t, T_0)$ into groups with $M$ continuous data. $T = T_0, M$ gives the correlation time within
the group. Let $T$ takes the values of $T_0, 2T_0, \ldots, MT_0$, and
the average within each correlation time can be expressed as

$$\tau_k(t, T) = \frac{1}{M} \sum_{j=1}^{M} r_{(k-1)M+j}, \quad k = 1, 2, \ldots, L_w - M + 1,$$

(4)

where $\tau_k(t, T)$ is the average of the array within the
correlation time starting from the $k$th data of the inter-
cepted $L_w$ continuous data. Totally, $L_w - M + 1$ arrays can
be obtained with a step length of $M$ within the data length of
$L_w$. The average difference between the two neighboring
arrays is

$$\Delta \tau_{k,k-1} = \overline{\tau_{k+1}}(t, T) - \overline{\tau_k}(t, T).$$

(5)

Group all the average difference values between every
two neighboring arrays within $L_w$ and thus form a set in-
cluding $L_w - M + 1$ elements. According to the definition of
Allan variance, one has

$$\sigma^2(t, T) = \frac{1}{2} \left\langle \left( \overline{\tau_{k+1}}(t, T) - \overline{\tau_k}(t, T) \right)^2 \right\rangle$$

$$= \frac{1}{2(L_w - M - 1)} \sum_{k=1}^{L_w-M-1} \left( \overline{\tau_{k+1}}(t, T) - \overline{\tau_k}(t, T) \right)^2.$$

(6)

2.3. Simulation. In case that the CRDS apparatus works in
an unsatisfactory environments, the changing temperature,
pressure, or vibration situation lead to the misalignment of
the cavity or to the variation of the absorption cross section
of the trace gas. This results in the deterioration in the
measurement accuracy. In order to simulate the actual
situation of unstable environments such as periodic varia-
tion, sudden change, and slow evolution, additional noises
are imposed on the ring-down time sequence in the present
paper, and the influences on the measurement accuracy are
analyzed with standard Allan variance and DAVAR.

Gaussian noise as an additive noise exists in the decaying
time series. In this paper, the amplitude of Gaussian noise is
modulated sinusoidally to simulate the influence of environ-
ment. $r(t)$ is a ring-down time sequences with a length of 8000
data. The mean of $r(t)$ is $36 \mu$s. The Gaussian noise intensity is
40 dB. A sinusoidally modulated Gaussian noise of 10 dB is
then added to $r(t)$, as shown in Figure 1(a). Allan variance is
caused as the difference between the average value of the
sampled data in the previous correlation time and the next
correlation time. If the average value of the data in the cor-
relation time does not change, the effect of change cannot be
exhibited. Since the mean value of the Gaussian noise of the
sinusoidal modulation tends to 0, the analysis using Allan
variance cannot reflect the influence of the sinusoidal mod-
ulation noise. The trends of the two curves are basically the
same. The noise equivalent absorption coefficient has changed
from $9.8 \times 10^{-8} \text{cm}^{-1} \text{Hz}^{-1/2}$ to $1.5 \times 10^{-8} \text{cm}^{-1} \text{Hz}^{-1/2}$. The
difference in absorption coefficient is due to the short cor-
relation time setting. In order to increase the time resolution,
the correlation time in the Allan variance is set relatively small. This
will cause the mean value of noise loaded during the relevant
time may not be zero, which will increase the equivalent noise
figure. Using DAVAR to analyze the loaded sinusoidal modulation
noise, as shown in Figure 1(c), in the time period unaf-
fected by noise, such as from 0 s to 2000 s and 6000 s to
8000 s, the noise equivalent absorption coefficient is about
$4.4 \times 10^{-9} \text{cm}^{-1} \text{Hz}^{-1/2}$. In the period of 2000 s-6000 s affected
by noise, the noise equivalent absorption coefficient changes
from $4.4 \times 10^{-9} \text{cm}^{-1} \text{Hz}^{-1/2}$ to $2.2 \times 10^{-8} \text{cm}^{-1} \text{Hz}^{-1/2}$, and the
change shows a sine wave trend, which is consistent with the
loaded noise.

Changes in gas pressure and environmental vibrations
may cause sudden changes in the ring-down time. The
sudden-changed signal is a discontinuous change, which
usually indicates the change of the operating state of the
instrument, which may be caused by gas pressure shock or
vibration to cause the resonance cavity to detune, or it may
be a circuit failure. A 2 $\mu$s mutation signal was added to the
decay time series, in which ring-down time is 36 $\mu$s and the
Gaussian noise intensity is 40 dB. Allan variance was used to
analyze the change of the stagnation time series before and
after the sudden-changed signal was added, as shown in
Figure 2(b). The noise equivalent absorption coefficient is
$9.1 \times 10^{-7} \text{cm}^{-1} \text{Hz}^{-1/2}$. It can be known that the large var-
ciance caused by the sudden-changed signal makes the cal-
ulation divergent, and subsequent sampling cannot be
analyzed. Allan variance can reflect the change of the signal,
and it is impossible to obtain the moment when the abrupt
signal occurs and the impact on the entire process.

Figure 2(c) uses DAVAR to analyze the time series con-
taining sudden-changed signals. The noise equivalent co-
efficient before the sudden change is $4.6 \times 10^{-8} \text{cm}^{-1} \text{Hz}^{-1/2}$,
and the NEA within the duration of the sudden change
signal is $1.4 \times 10^{-8} \text{cm}^{-1} \text{Hz}^{-1/2}$. DAVAR has the resolution
capability in the time domain, which can track the dynamic
change process of the abrupt signal in time. It is also noticed
that the ability of real-time tracking and reliability of per-
formance estimation is strongly related with the type and
length of the configured calculation window [22–24]. The
window type in this article is a rectangular window with
a length of 100 samples.

Drift noise is to simulate the temperature drift of a device
in CRDS for a short time or the degradation of device
performance for a long time. Add drift noise to the 40 dB
Gaussian noise decay time series. Noise drift is twice the
standard deviation of Gaussian noise, as shown in
Figure 3(a). It can be known from formula (2) that when the
average value of the signal changes during the cor-
relation time, the Allan variance can reflect this change, as shown in
Figure 3(b). Drift noise prevents repeated sampling from
improving detection accuracy, and the minimum equivalent
noise absorption coefficient is $1.3 \times 10^{-7} \text{cm}^{-1}$. DAVAR can
show the change of drift noise in the time domain, as shown in
Figure 3(c), the noise equivalent absorption coefficient changed
from $4.5 \times 10^{-9} \text{cm}^{-1} \text{Hz}^{-1/2}$ to
$8.4 \times 10^{-9} \text{cm}^{-1} \text{Hz}^{-1/2}$. 

Journal of Spectroscopy
During the detection process, the CRDS device is affected by the environment and its own factors, and the ring-down time will change in the time domain, such as sudden changes, drifts, and periodic changes. According to the above simulation and analysis, Allan variance cannot analyze non-stationary time-varying signals. However, DAVAR is able to clearly and intuitively reveal the temporal evolution of the signal variance by tracking the error changes via a sliding window. DAVAR gives thus an effective approach to evaluate the time-varying characteristics of random errors in CRDS.

3. Experiment and Analysis

3.1. Experiment and Analysis of Temperature Variation in a Ring-Down Cavity. A continuous wave CRDS (CW-CRDS) experiment is constructed to detect the concentration of methane (CH$_4$), as sketched in Figure 4. A fiber-coupled output distributed feedback diode laser (DFB-LD, NLK1U5FAAA, NEL) with the center wavelength of ∼1654 nm is used as the light source. After passing through a set of mode-matching optics, the infrared laser beam is coupled into the 360 mm-long linear ring-down cavity which is composed of two identical concave high reflectivity mirrors. Each mirror has a radius of curvature of 500 mm and a reflectance higher than 0.9999 around the ring-down wavelength. An optical isolator (IO-4-1650-VLP, Thorlabs) is inserted before the coupling optics in order to suppress the optical feedback caused by the optics. A laser controller (LDC-3724C, Lightwave) is used to set the operation temperature and modulating current of the DFB laser so as to adjust the output wavelength of the laser. The output wavelength of the DFB laser is then adjusted to 1653.722 nm, i.e., the 2v3 absorption band of methane. With a periodic triangular wave signal at the frequency of 10 Hz from the signal generator (33600A, Aglient), the DFB laser achieves a spectral scanning region slightly larger than the free spectral range (FSR) of the ring-down cavity and thus guarantees the happening of laser-cavity spectral matching. The transmission from the ring-down cavity is then collected by a photodetector (PDA10CS-ES, Thorlabs) with a focusing lens.

Figure 1: Allan variance and DAVAR analysis of modulated signals. (a) Add sinusoidally modulated Gaussian noise to the ring-down time series. (b) Using Allan variance to analyze the effect of noise on detection accuracy. (c) DAVAR analysis detection accuracy changes over time.
When the output of the photodetector reaches the preset threshold, an oscilloscope (MSO 4104C, Tektronix) is triggered on and sends out an order to sharply turn off the modulation from the signal generator. Thus, it enables a laser-cavity mismatching shutoff and completes the whole ring-down process. In the experiment, the sample gas enters the cavity through a mass flow controller, and gas pressure in the cavity is 0.996 bar. Additional desiccant and particle filter are introduced on both ends of the cavity to stop the entrance of water vapor and fine particles.

A thermistor placed within the cavity housing measures the temperature. A thermal controller (TCM-X107, Chengdu Yexian Technology) functions to receive the information from the thermistor and precisely control the temperature of the ring-down cavity with a thermo-electric cooler (TEC) fixed at the center of the aluminum alloy plate. The first step of the experiment is to set the temperature of the ring-down cavity at 25°C and measure the cavity ring-down time of high-purity nitrogen gas (N₂ with a purity of 99.99%). Repeat the measurement and achieve 8000 ring-down events. The ring-down times for different events are extracted with fast fourier transform analysis method as shown in Figure 5. The result is then analyzed with Allan variance which gives the noise equivalent absorption coefficient of $2.4 \times 10^{-10}$ cm$^{-1}$.

The experiment goes on by continuously introducing the high-purity nitrogen gas into the cavity but slowly raises the temperature of the ring-down cavity to 28°C at a rate of 0.001°C/s. The rate is selected as the experiment tells that only a slow variation in the thermal situation guarantees no violent sudden change to the cavity, and thus no failure in ring-down signal collection happens. A thermal controller used in the experiment recorded the temperature change process of the bottom plate, as shown in Figure 6(a). Temperature stability at 25°C is 0.0036°C, and temperature stability at 28°C is 0.013°C. The decay time during the temperature change collected using the CRDS experimental device is shown in Figure 6(b). When the cavity temperature

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2}
\caption{Allan variance and DAVAR analysis of sudden-changed signals. (a) Add sudden noise to ring-down time series. (b) Using Allan variance to analyze the effect of noise on detection accuracy. (c) DAVAR analysis detection accuracy changes over time.}
\end{figure}
is 25°C, the mean of ring-down time is about 35.7 μs, and when the temperature changes to 28°C, the mean of ring-down time decays to 30.6 μs.

The above experiment was divided into three stages according to the temperature, 25°C, temperature change process, and 28°C. Allan variance and DAVAR were used to analyze the experimental data. According to the analysis of Allan variance, the minimum noise equivalent absorption coefficient is $1.6 \times 10^{-8}$ cm$^{-1}$, and the time normalized noise equivalent absorption coefficient is $1.1 \times 10^{-8}$ cm$^{-1}$ Hz$^{-1/2}$. Due to the temperature change process, the mean of the samples in the adjacent correlation time changes, making the Allan variance unable to evaluate the entire acquisition process. The DAVAR is used to analyze the experimental data, as shown in Figure 7(b). The noise equivalent absorption coefficient is $1.5 \times 10^{-9}$ cm$^{-1}$ Hz$^{-1/2}$ at a temperature of 25°C, and it is basically consistent with Allan analysis of variance. Due to the temperature change process, the noise equivalent absorption coefficient increased to $7.9 \times 10^{-9}$ cm$^{-1}$ Hz$^{-1/2}$. After the temperature stabilized at 28°C, the noise equivalent absorption coefficient is $3.4 \times 10^{-9}$ cm$^{-1}$ Hz$^{-1/2}$. The reason for noise equivalent absorption coefficient enlargement is that the stability of cavity temperature becomes worse. The DAVAR analysis clearly shows the three stages of temperature change and reflects the effect of temperature control accuracy on the stability of the decay time.

In the experiment, the ring-down cavity is fixed on a plate made of aluminum alloy with a thermal expansion coefficient of 23.6 μm/m·K. As compared with the material of invar steel with a thermal expansion coefficient of 1.6 μm/m·K, aluminum alloy shows a larger deformation under thermal changing environment. With a conventional finite element analysis, as shown in Figure 8, one can notice that when the temperature of the aluminum alloy base plate changes by 3°C, the base plate for fixing the ring-down cavity of mirror is deformed in 87.2 nm. This deformation due to temperature produces an off-axis angle of 1.3 arc-second with the optical axis. The generation of the off-axis angle will increase the loss in the cavity and shorten the ring-down time. The off-axis angle increases the loss in the cavity and
shortens the ring-down time. The aluminum alloy base plate used in the experiment amplifies this phenomenon due to its large thermal expansion coefficient. Repeating the above finite element analysis process, replacing the aluminum alloy material with invar steel, the base plate has a deformation of about 5.7 nm, and the off-axis angle is about 0.17 arc seconds. The influence of temperature changes cannot be eliminated by using the invar steel base plate.

3.2. Differential Measurement Method and Experiment. Both the temperature of the ring-down cavity and the pressure of the input gas are always strictly controlled in CRDS devices, to the level of a few hundredths of a K(1σ) and pressure accuracy of 0.05 Torr, respectively, as in the product fabricated by the Picarro Inc. [3]. This point is quite similar to the fact that always a very accurate reference of GROUND is defined in electronics. The existence of this reference helps to perform the measurement by merely the detection of the relative values of a single-ended signal with respect to GROUND. Therefore, the accuracy of the measured signal depends on the consistency of this “GROUND” in the system during the whole measurement. When this reference fluctuates due to influences of the external environment, the error caused by such fluctuations is also superimposed on the results. In CRDS, the ring-down time $\tau_0$ can be regarded corresponding to the abovementioned “GROUND” in the electrical measurements.

Using the differential method for suppressing common mode interferences in electrical measurements for reference, researchers have implemented differential measurements by measuring the “GROUND.” Courtois et al. [25] and Ye and Hall [26] use acousto-optic modulators as a frequency shifter to fine-tune the laser frequency and measure the ring-down time of the absorption peak and the nonabsorption peak in a time-sharing manner to realize differential measurement. In their experiments, the output frequency of the laser is fixed, and two serial or parallel acousto-optic modulators are used to modulate the output frequency. The differential measurement may also be implemented using two lasers [13]. One of the two lasers has a wavelength corresponding to an absorption peak of the gas to measure absorption loss, and the other is used to measure the drift of the instrument, which is to be corrected by the differential measurement method.

Based on the analysis of existing methods and drawing on the principle of differential measurement in electrical measurement, this paper proposes a practical differential measurement method. By modulating the output frequency of a laser quickly, the ring-down times at the absorption and nonabsorption peaks are measured in a time-sharing.
The ring-down time at the nonabsorption peak is used to record the influence of the instrument on the environment and its drift. At the absorption peak, the ring-down time becomes shorter due to gas absorption loss. The gas concentration is calculated by the change of the ring-down time. The measurement at the absorption peak is also affected by environmental factors and instrument drift.

In this paper, a self-developed laser driving circuit is used instead of the LDTC in the experimental device of Figure 4. The steps for differential detection are as follows:

1. Set the base voltage \( V_{\text{OFF}} \) so that the laser output wavelength is at the nonabsorption peak
2. Load the modulating waveform on the MODULATE terminal, and the wavelength can be matched with the cavity mode by laser current scanning
(3) When the amplitude of the signal received by the detector reaches the threshold, SHUTOFF realizes the laser shutdown process by detuning.

(4) Set the base voltage $V_{ON}$ so that the laser output wavelength is at the absorption peak; repeat steps 2 and 3 and acquire the ring-down time at the absorption peak.

A laser spectrum analyzer (771B-NIR, Bristol instruments Inc.) was used to test the laser output wavelength stability, and the output stability within 1 hour was ±1.2 pm, which was consistent with the performance of LDTC in Figure 4. The large current modulation will affect the thermal stability of the laser. The difference between the voltage settings of $V_{ON}$ and $V_{OFF}$ should be as small as possible.

By setting the parameters of $V_{ON}$ and $V_{OFF}$, the wavelength variation is about 0.4 nm, which can be seen from Figure 9. MODULATE is loaded with a 20 Hz triangle wave. Due to the symmetry of the triangle wave signal, it can achieve 40 Hz detection. The free spectral range of the cavity is 441 MHz, and the wavelength modulation range is set to 4 pm.

Then, methane standard gas (1 ppm, uncertainty is 2%) is injected into the cavity. When the temperature of the ring-down cavity changes from 25°C to 28°C, the differential measurement method detects the ring-down time at the absorption peak and the nonabsorption peak, as shown in Figure 10. In order to ensure the stability of the wavelength during the switching process, the detection frequency is also set to 1 Hz. Due to the influence of temperature change, the decay time at the absorption peak has changed from 21.1 µs to 19.0 µs. The Pearson correlation coefficient is introduced to evaluate the relationship between the ring-down time at the absorption peak and the nonabsorption peak [27]. The Pearson correlation coefficient between the ring-down time at the absorption peak and the nonabsorption peak detected by the differential method is 0.95. Due to the effects of temperature changes, two independent detections show a very high correlation. The ring-down time series $\tau$ at the absorption peak is affected by the gas absorption attenuation, and it is also affected by the drift of instrument detection baseline due to temperature change.

The theory of CRDS gives that the concentration of trace gas can be expressed as [28]

$$N = \frac{1}{c \sigma(v)} \left( \frac{1}{\tau} - \frac{1}{\tau_0} \right),$$

where $c$ is the light speed, $\sigma(v)$ the absorption cross section, $\tau$ the ring-down time when the input laser wavelength coincides with the strongest absorption in the absorption spectrum, and $\tau_0$ the ring-down time of the empty cavity when no absorption exists. According to the database of HITRAN, the gas absorption cross section is related to parameters such as temperature and pressure [29]. In this paper, the absorption cross sections at different temperatures are calculated using the Voigt linear [30] and the HIRAN database. The absorption cross section at 25°C is $1.479 \times 10^{-20}$ cm$^2$ molecule$^{-1}$, and the absorption cross section at 28°C is $1.471 \times 10^{-20}$ cm$^2$ molecule$^{-1}$. The detailed calculation process is explained in the Appendix. Therefore, during the experiment from 25°C to 28°C, the differences in absorption cross sections were ignored.

According to formula (7), cavity decay spectroscopy is self-calibrated. By substituting $\tau$ and $\tau_0$ obtained by differential measurement into formula (7), the effect on temperature change can be corrected. In this paper, the concentration of standard methane gas was calculated using the experimental device shown in Figure 4. The ring-down time shown in Figure 5 was used as the ring-down time at the nonabsorption peak. The calculated result is shown in Figure 11(a) with the standard deviation of 0.181 ppm. The test results using the differential measurement are shown in Figure 11(b), and the standard deviation is 0.00914 ppm. The effect of temperature change is corrected in real time by differential measurement, and the detection accuracy is improved about 19 times.
4. Discussion

DAVAR is an extension of the classical Allan variance, which can not only meticulously characterize and identify the statistical characteristics of various error sources in CRDS detection but also analyze the dynamic characteristics of signals over time. The DAVAR is helpful to analyze the time-varying characteristics of nonstationary signals in the application of cavity ring-down spectroscopy in vehicle, airborne, and other harsh environments, so as to more intuitively characterize the correlation between environmental changes and detection accuracy.

The time-varying error characteristics reflected by DAVAR can be corrected by applying a differential measurement method. In this paper, a differential measurement method is used to correct the influence of temperature change on the detection accuracy. The differential measurement method herein improves the detection accuracy by detecting the “GROUND” of the CRDS device in real time and performing online calibration.
A stable “GROUND” is easy to obtain in a laboratory environment, but it is difficult to guarantee a stable detection environment in some practical CRDS technical solutions and applications. For example, it is a good detection solution for aerosols and corrosive gases using an open cavity, but the open cavity structure makes the detection device susceptible to the ambient. Moreover, in CRDS detection devices based on ball-borne platforms and UAV platforms, strict control of pressure and temperature requires additional power consumption and precise mechanical design, which will limit the application of CRDS. As mentioned above, in the CRDS equipment of Crosson [3], the temperature control accuracy is required to a few hundredths of a K. It can be seen that, from the experiments described herein, the practical differential measurement method can reduce the requirement on temperature control accuracy. The improved differential measurement method can reduce the requirements on the operating environment and thus improve the environmental adaptability of the instrument.

This method is not applicable in all cases. The differential measurement method requires detect the ring-down time at the absorption peak and the nonabsorption peak, respectively, which reduces the detection rate. Secondly, for the gas to be measured with a wide absorption peak, the current of DFB laser needs to be adjusted in a wide range to make the wavelength deviate from the absorption peak. This process will affect the thermal stability of the laser and may lead to the deterioration of the stability of the wavelength. Due to the above characteristics, the application of differential correction method in fast detection and the detection accuracy of gas with wide absorption cross section are limited.

5. Conclusions

In this paper, the DAVAR method is used to simulate the time-domain error in CRDS, and a differential detection method is proposed to correct the baseline drift in real time. With the numerical simulation of the influence of instabilities of sudden, slow, or periodic changes on the measurement accuracy in the ring-down process, DAVAR is proved to be an effective way to evaluate random error characteristics in an interfering environment. In this paper, a practical differential measurement method is proposed to correct the time-varying error by detecting ring-down times at the absorption peak and nonabsorption peak. A CRDS experimental device was constructed, and DAVAR was used to analyze the influence of cavity temperature change on detection accuracy. The effect of temperature change is corrected in real time by differential measurement, and the detection accuracy is improved about 19 times. The differential measurement method can be used to correct the time-varying error in real time and is helpful to improve the environmental adaptability of the CRDS instrument.

6. Future Work

Dynamic Allan variance analysis method and differential measurement method based on cavity decay spectrum will
be used in open-path CRDS. The open cavity has great advantages in rapid detection of ambient gas and detection of extinction coefficient of aerosol [31, 32]. However, due to the open structure, the cavity is more susceptible to the interference of the external environment. DAVAR can be used to analyze the impact of environmental changes on the detection accuracy, and the differential measurement method improves the environmental adaptability of CRDS instruments.

Appendix

The premise of the differential measurement calculation using equation (7) in the experiment of this paper is that the effect of temperature change on the gas absorption cross section is negligible. The Voigt linear combination with the HIRAN database was used to calculate the methane absorption cross sections at different temperatures [30]. The specific calculation process is as follows.

Voigt line is the convolution of Gaussian line and Lorentz line and can be expressed as follows:

\[
f_v(y - y_0) = A \frac{2 \ln 2}{\pi^{3/2}} \frac{\gamma_L}{\gamma_G} \int_{-\infty}^{\infty} \left( \sqrt{\ln 2} \left( \frac{y_L}{\gamma_G} \right) - t \right) e^{-t^2} \, dt,
\]

where \( \gamma_L \) is the FWHM (the full width half maximum) of the Lorentz line, \( \gamma_G \) is the FWHM of the Gaussian line, and \( A \) is the amplitude parameter. However, the function is not inferable, and it is processed here using the discrete method.

\[
f_v(y - y_0) = \frac{2}{\gamma_G} \sqrt{\ln 2} V(X, Y),
\]

\[
\gamma_G = 2 \sqrt{\frac{\ln 2 N_A kT}{M}},
\]

\[
\gamma_L = 2 \left( \frac{T_c}{T} \right)^{1/2} \left[ \gamma_{\text{air}} \cdot (p - p_s) + \gamma_{\text{self}} \cdot p_s \right],
\]

where \( M \) is the relative molecular mass of the gas; \( n_{\text{air}} \) is the temperature dependence coefficient; \( \gamma_{\text{air}} \) is the air-broadened width; \( \gamma_{\text{self}} \) is the self-broadened width; \( p \) is the pressure, and \( p_s \) is the partial pressure of the gas. The pressure in the HITRAN database is a standard atmospheric pressure, so the actual pressure is calculated as a ratio to the standard atmospheric pressure.

\[
V(X, Y) = \frac{Y}{\pi} \int_{-\infty}^{\infty} e^{-z^2} \, dz - \frac{\ln 2}{\gamma_G} (y - y_0),
\]

Since \( V(X, Y) \) has no analytical solution, approximate calculations are used. The maximum deviation of the approximate calculation results is less than \( 5 \times 10^{-4} \).

\[
V(X, Y) = \sum_{i=1}^{4} \left( C_i (Y - A_i) + D_i (X - B_i) \right). \tag{A.4}
\]

The parameters \( A_i, B_i, C_i, \) and \( D_i \) are shown in Table 1. Through MATLAB simulation, the absorption cross section of \( R(3) \) at 1653.722\( \mu \)m with temperature was obtained, as shown in Figure 12. Figure 12(a) is a methane absorption cross section at 25\(^\circ\)C; the absorption cross section is \( 1.479 \times 10^{-20} \) cm\(^2\)-molecule\(^{-1}\) at the absorption peak of 1653.722 nm, and Figure 12(b) is a methane absorption cross section at the temperature of 28\(^\circ\)C, and the absorption cross section is \( 1.471 \times 10^{-20} \) cm\(^2\)-molecule\(^{-1}\) at the absorption peak of 1653.722 nm.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare no conflicts of interest.

Authors’ Contributions

Z.M. and J.Y. conceptualized the study; Z.M. and J.H. were responsible for methodology; Z.M., J.Y., J.W., and J.H. prepared the original draft; Z.M., J.W., and S.D. were responsible for formal analysis; Z.M. and J.W. investigated the study, J.Y. acquired funding; Z.M. and Y.L. reviewed and edited the study.

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