

# Sensitive detection of acetylene by second derivative spectra with tunable diode laser absorption spectroscopy

HAO DENG, JUAN SUN, PENGFEI LI, YU LIU, BENLI YU, JINGSONG LI\*

Key Laboratory of Opto-Electronic Information Acquisition and Manipulation of Ministry of Education, Anhui University, 230601 Hefei, China.

\*Corresponding author: [jingsong\\_li@ahu.edu.cn](mailto:jingsong_li@ahu.edu.cn)

A tunable diode laser absorption spectrometer was developed for trace acetylene gas analysis, the system performance was evaluated by combing an appropriate digital signal processing methods, *i.e.*, Savitzky–Golay smoothing and differentiation algorithm. The calculation of the derivative spectra by this method is accompanied by simultaneous data smoothing. Based on the 2nd derivative spectra detection method, the Allan variance technique indicates a C<sub>2</sub>H<sub>2</sub> detection limit of 1.7 ppm for 1-s averaging time, and a minimum noise level of 62 ppb (parts per billion), at the optimum integration time of ~60 s. The calculated 2nd derivative spectra with better resolution, lower detection limits, save signal processing time, and improve the ability to distinguish unresolved spectral signals.

Keywords: tunable diode laser absorption spectroscopy (TDLAS), signal processing, Savitzky–Golay filter, trace gas detection.

## 1. Introduction

Industrial gas measurements are usually performed using gas chromatographs (GCs) which have time constants of minute level. Being high sensitive and selective, rapid (typical second level), non-contacting and nondestructive, and environmentally friendly (*i.e.*, no use of chemicals and no harmful by-products to the environment), tunable diode laser absorption spectroscopy (TDLAS) is a versatile tool for the analysis of concentration, temperature, pressure, velocity, and eddy flux of molecules and radicals under observation. Recent advances in diode laser sources and spectroscopic analysis techniques generally have triggered an increase in infrared spectrometric trace gas detection for quantitative assessments of a wide spectrum of gas species in atmospheric pollution monitoring, chemical analysis, industrial process control, and monitoring of agricultural emissions, medical breath analysis, and combustion diagnostics, as well as atmospheric chemistry [1].

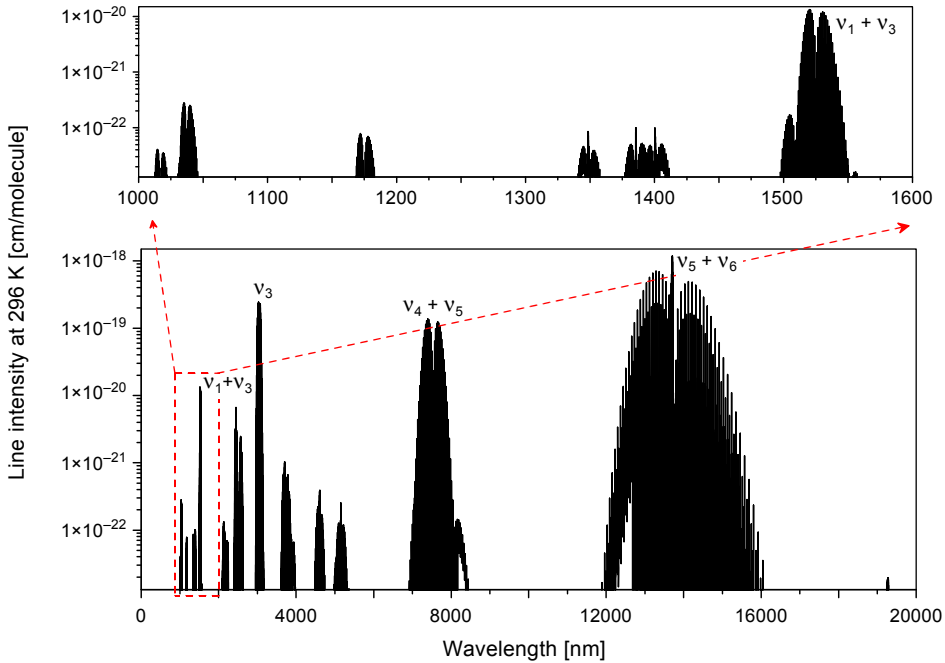


Fig. 1. Absorption line-strengths of acetylene in the infrared spectral range.

Acetylene ( $C_2H_2$ ,  $H-C\equiv C-H$ ) is one of the feature gases in transformer fault diagnosis [2], and is also considered as a tracer of air mass age [3]. As shown in Fig. 1,  $C_2H_2$  shows several strong absorption bands in the infrared spectral range [4], for example, at  $1.5\ \mu m$  corresponding to  $\nu_1 + \nu_3$  band of acetylene, at  $3\ \mu m$  corresponding to  $\nu_3$  band of acetylene, at  $7.5\ \mu m$  corresponding to  $\nu_4 + \nu_5$  band of acetylene, and at  $14\ \mu m$  corresponding to  $\nu_5 + \nu_6$  band of acetylene. Generally, the  $3\ \mu m$  infrared spectral range is only accessible via cryogenically cooled lead salt diode lasers [5] or fairly complicated difference frequency generation (DFG) light sources [6], which represent a serious drawback especially for *in situ* measurements. In 1994, a new class of diode lasers, *i.e.*, quantum cascade lasers (QCLs) [7], have opened new horizons to access the spectral region of the mid-infrared. Recently, QCL-based acetylene sensor operating near  $8\ \mu m$  [8] and  $14\ \mu m$  [9, 10] have been successfully reported for providing access to  $\nu_4 + \nu_5$  and  $\nu_5 + \nu_6$  bands of acetylene, respectively. QCLs are very promising for fast and sensitive detection of  $C_2H_2$ . However, they still suffer from some drawbacks like extreme costs and limited available wavelengths without cryogenic temperature operation for continuous wave (CW) mode. In contrast, detection of  $C_2H_2$  via the  $\nu_1 + \nu_3$  vibrational combination band near  $1.5\ \mu m$  is much easier since telecommunication-type diode lasers are available with low cost, high spectral quality and room-temperature operation capability [11, 12]. Although line intensities of  $C_2H_2$  at

the  $\nu_1 + \nu_3$  band are weaker at least by one order of magnitude than those at other three fundamental bands. Taking advantage of multi-pass absorption cells [13] and high-finesse optical cavities [14], which typically can provide an enhanced interaction length of up to  $\sim 2$  orders of magnitude, and modulation techniques [15] as well as signal processing methods [16], near-infrared TDLAS can also achieve very low detection limits of the order of parts per billion (ppb) [17].

In present work, we report on the development of a laser spectrometer based on a compact Herriott-type absorption cell for trace  $C_2H_2$  gas detection. In addition, an adaptive Savitzky–Golay filter algorithm was integrated for signal processing, *i.e.*, data smoothing and calculating second derivative spectra for signal-to-noise ratio (SNR) and resolution enhancement, respectively.

## 2. Experimental details

### 2.1. Sensor design

The experimental setup is shown schematically in Fig. 2. The tunable diode laser source is purchased from Agilent Technologies with an average output power of  $\sim 5$  mW, the laser linewidth  $< 10$  MHz and there are no mode-hops in the tunable range between  $6523$  and  $6587$   $cm^{-1}$  [18]. The room-temperature single mode diode laser is fiber-coupled and the optical fiber ends with a beam collimator, and the laser beam is focused to the center of an astigmatic multi-pass gas absorption cell (AMAC-76, Aerodyne Research, Inc.). A visible diode laser ( $\lambda = 640$  nm) was injected into the system via a reflector mirror and co-aligned with the infrared beam to facilitate the beam alignment with the multi-pass cell, which has a base length of 32 cm, a volume of 0.5 litre and provides a maximum optical path length of 76 m at 238 passes. The laser beam exiting from the multi-pass cell was monitored by an InGaAs photodetector (New

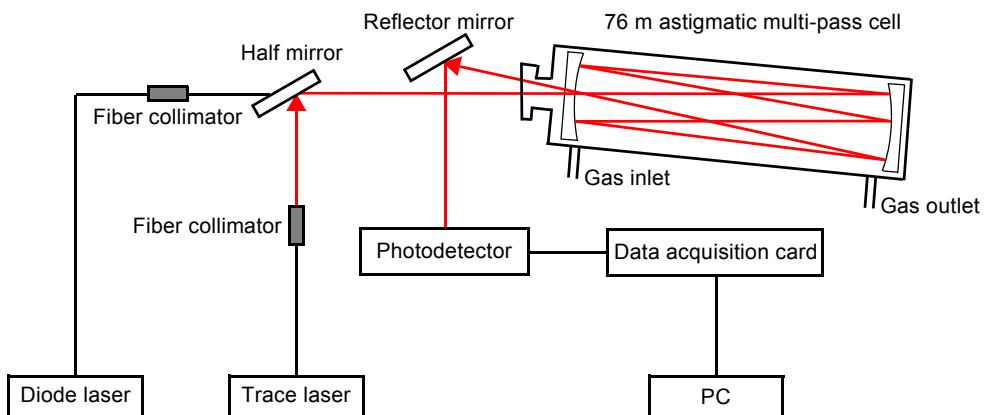


Fig. 2. Schematic diagram of the near-infrared diode laser absorption spectrometer.

Focus 2053), and then sent to a data acquisition (DAQ) system implemented with a DAQ card NI-6212 (National Instruments, USA) and a LabView-based graphical user interface software program run on a laptop.

## 2.2. Selection of spectral line and sampling pressure

It is well-known that the detection sensitivity of TDLAS is, to a large extent, dependent on the inherent absorption line strength of the target gas under study. In addition, spectral interference from the target gas or other species is common issue for TDLAS-based gas sensors and can adversely affect detection specificity, precision, and accuracy. In this study, the  $C_2H_2$  line transition R9e of  $\nu_1 + \nu_3$  band ( $\nu = 6578.5761 \text{ cm}^{-1}$ ) with a line intensity factor of  $1.340 \times 10^{-20} \text{ cm}^{-1}/(\text{molecule} \cdot \text{cm}^{-2})$ , as reported on the HITRAN2012 database [4], was selected for evaluating the sensitivity of the TDLAS system. This line is found to be free of interference from other atmospheric gases (such as CO,  $H_2O$ ,  $CH_4$ , *etc.*). By reducing sample gas pressure, the neighbor absorption interferences from other bands of  $C_2H_2$  near  $6578.53 \text{ cm}^{-1}$  will be greatly reduced, as shown in Fig. 3. Therefore, enhanced specificity, improved accuracy, faster response, and lower cost of ownership all become achievable. As can be seen from this figure and the inset, at low pressures, the absorption depth increases linearly with pressure, whereas at high pressures, the absorption signal intensity becomes almost constant due

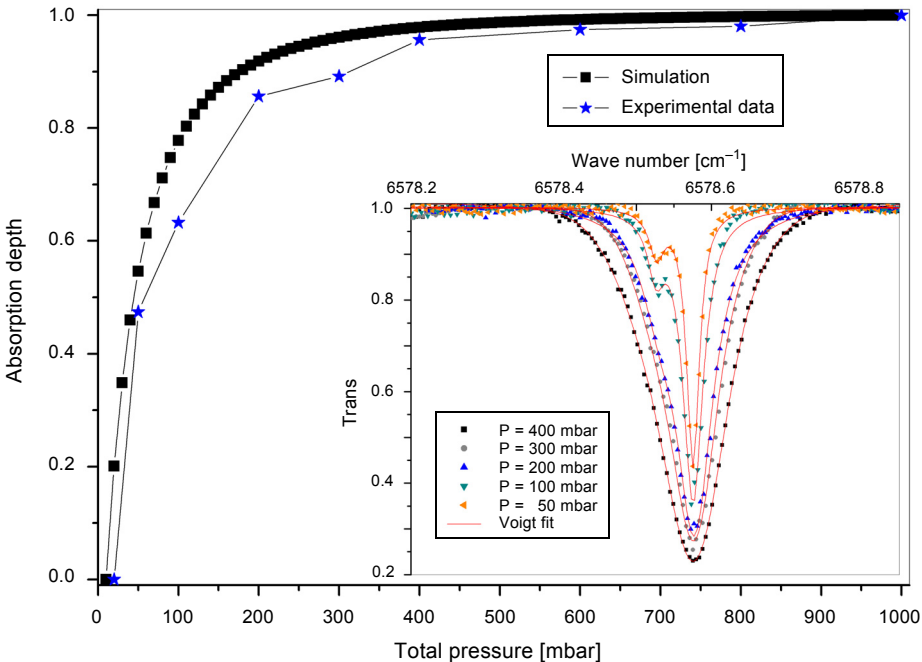


Fig. 3. Dependence of absorption depth of the R9e transition line of  $C_2H_2$  on total sample gas pressure. The inset shows the absorption spectra recorded under different pressure and the corresponding Voigt fit.

to the canceling of two opposing terms with pressure. Therefore, a compromise between sensitivity and selectivity is desirable. Finally, the optimum sampling pressure of about 100 mbar is selected for evaluating our TDLAS system.

### 2.3. Signal processing

Apart from decreasing sampling pressure, derivative spectroscopy is also an effective method for resolution enhancement in various spectroscopic applications [19, 20]. Digital signal processing (DSP) is particularly attractive due to its flexibility. The Savitzky–Golay filter is one of the most popular filtering techniques first described in 1964 by SAVITZKY and GOLAY [21]. The main advantage of this filter is that it tends to preserve the original shape and features of the signal better than other types of filtering approaches, such as a moving average technique. Instead of just averaging the adjacent sampling points, it performs a least-square-fit with a polynomial of high order over an odd-sized window centered at the point. A wavelet transform is a powerful technique for digital signal processing, however, this method largely depends on too many filter parameters, for example, wavelet type, thresholding policy, threshold estimation and decomposition level, *etc.* Comparing to a wavelet denoising technique, the Savitzky–Golay smoothing filter has been shown to be especially attractive since both the smoothed signal and the derivatives can be calculated in a single step, and only two filtering parameters need to be set, *i.e.*, the width of the smoothing window and the degree of the smoothing polynomial.

Analogous to most filter methods, the choice of inappropriate filter parameters will lead to failure to optimally remove noise and accurately reproduce the signal, thereby introducing a systematic error for concentration retrieval in TDLAS. In our previous work [22], an adaptive Savitzky–Golay smoothing algorithm was developed to optimally select the input filter parameters for noise reduction and signal fidelity. Here, we recapitulate the main points. A varying window Savitzky–Golay filtering integrated with two additional criteria for TDLAS signal processing was proposed. The first criterion is to introduce a real signal or noise-free signal referred to PolyFit which is generated by fitting a polynomial function to a small segment near the absorption peak of the raw signal. The multiple linear regression analysis method is used to calculate the correlation coefficient between the PolyFit and the same segment in the Savitzky–Golay filter smoothed data, instead of using SNR for assessing the optimal filtering parameters. The second criterion is to employ a threshold defined as the difference of peak heights between PolyFit and the Savitzky–Golay filtering smoothed data, in order to optimize filtering parameters without excessive signal distortion.

Moreover, in order to resolve the spectral interference effect mentioned above, herein, the algorithm has been improved with both function of smoothing filter and differential calculation for noise removal and resolution enhancement, respectively. The calculation of the derivative spectra by this method is accompanied by simultaneous data smoothing [23]. The formula of Savitzky–Golay filter for calculating the

smoothed data ( $s = 0$ ) or the desired  $s$ -th derivative ( $s > 0$ ) using a polynomial of degree  $n$  on  $(2m + 1)$  data points can be written as [24]

$$f_t^{n,s} = \sum_{i=-m}^m h_i^{n,s,t} y_i \quad (1)$$

where  $h_i^{n,s,t}$  is the convolution weight of the  $i$ -th point to evaluate the  $s$ -th derivative at the point  $t$ . It can be calculated as

$$h_i^{n,s,t} = \sum_{k=0}^n \frac{(2k+1)(2m)^{(k)}}{(2m+k+1)^{(k+1)}} P_k^m(i) P_k^{m,s}(t) \quad (2)$$

where  $(a)^{(b)}$  is a generalized factorial function  $(a)(a-1)\dots(a-b+1)$ , and  $(a)^{(0)} = 0$ ;  $P_k^m(i)$  is the Gram polynomials defined as

$$P_k^m(i) = \sum_{j=0}^k \frac{(-1)^{j+k} (j+k)^{(2j)} (m+t)^{(j)}}{(j!)^2 (2m)^{(j)}} \quad (3)$$

Unlike the fixed-degree Savitzky–Golay filter, the developed adaptive polynomial regression analysis is based on changes in the sum of squares of residuals ( $\chi^2$ ) by using the selection rule of Stein's unbiased estimate of risk (SURE) for optimizing filter coefficients [25], which can be expressed as

$$\chi_n^2 = \sum_{t=-m}^m (y_t - f_t^{n,s})^2 = \sum_{t=-m}^m \left( y_t - \sum_{i=-m}^m h_i^{n,s,t} y_i \right)^2 \quad (4)$$

### 3. Sensor performance evaluation

For purposes of evaluation the sensor performance and the developed algorithm, a series of mixture of  $C_2H_2$  and laboratory air were prepared for recording TDLAS absorption signal. The effective optical path length was firstly calibrated with pure  $C_2H_2$  sample with several weaker absorption lines. According to the Lambert–Beer law, an effective path length of approximate 40 m was obtained under the non-optimal coupling case. As we mentioned above, all the sample pressures are set to 100 mbar in order to reduce the influence of pressure broadening effect. We restricted the data records to a single laser scan (1 Hz) without any averaging. Figure 4 shows the experimentally observed  $C_2H_2$  absorption spectra between 6578.4 and 6578.8  $cm^{-1}$  with concentrations between 19 and 100 ppm, and the smoothed data by the Savitzky–Golay filter (upper panel), as well as the corresponding residual (lower panel). From this figure, one can see that the Savitzky–Golay filter leads to a better spectral SNR, in particular, when the  $C_2H_2$  sample concentration decreased to 19.01 ppm, a  $C_2H_2$  weak absorption line approaching the transition R9e at 6578.5761  $cm^{-1}$  can still be clearly observed after the application of the Savitzky–Golay smoothing filter. However, the spectral resolution becomes in-

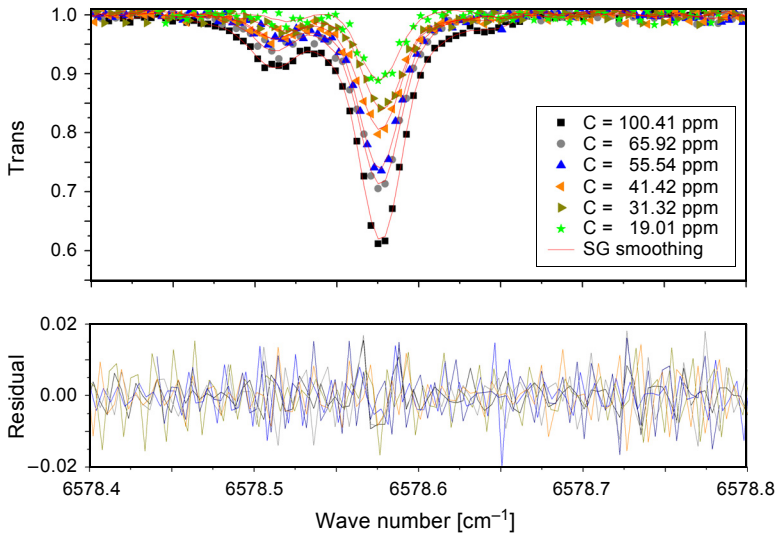


Fig. 4. Experimentally observed absorption spectra between 6578.4 and 6578.8 cm<sup>-1</sup> with different C<sub>2</sub>H<sub>2</sub> concentrations and the corresponding Savitzky–Golay (SG) smoothed data.

sufficient due to the limitations of pressure broadening effect and the influence of noises. For these issues, the corresponding second derivative spectra are calculated, as presented in Fig. 5, which is accompanied by simultaneous data smoothing. As discussed [22, 23], the selection of suitable parameters plays an important role in the Savitzky–Golay smoothing and differentiation algorithm. In order to achieve a trade-off

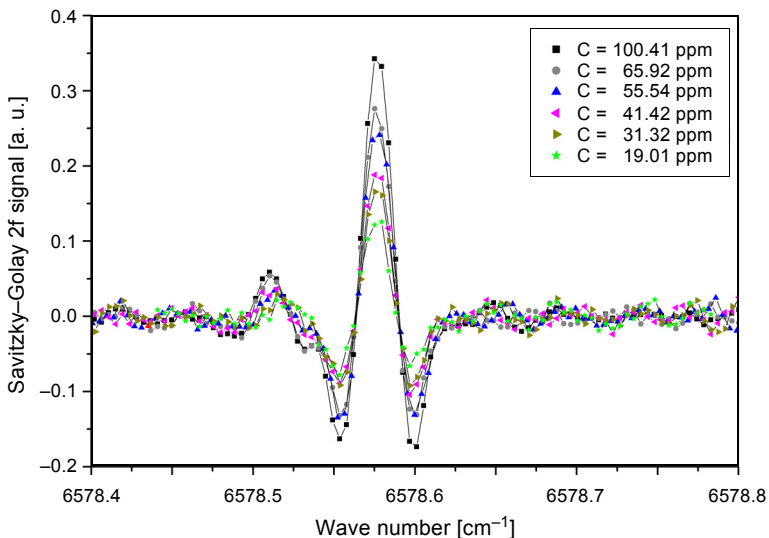


Fig. 5. The calculated second derivative spectra using the developed Savitzky–Golay differentiation algorithm for data presented in Fig. 4.

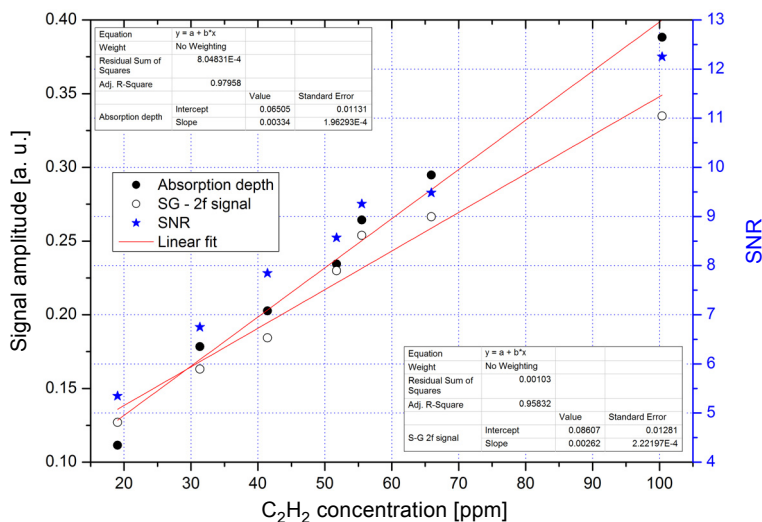


Fig. 6. Plot of absorption depth, the signal amplitude of 2nd derivative spectra and SNR *versus* C<sub>2</sub>H<sub>2</sub> concentrations for C<sub>2</sub>H<sub>2</sub> transition R9e at 6578.5761 cm<sup>-1</sup>. The straight lines are the best linear fit of the data points.

between noise reduction and resolution enhancement, the window size and polynomial degree of 23 and 8, respectively, were selected in this study.

Analogous to a wavelength modulation spectroscopy technique [26], we check the relationship between 2nd derivative signal amplitude and sample concentration. Linear regression leads to equations of  $y_{\text{absorption depth}} = 0.00334 C_{\text{C}_2\text{H}_2} + 0.06505$  and  $y_{\text{Savitzky-Golay 2f signal}} = 0.00262 C_{\text{C}_2\text{H}_2} + 0.08607$  with regression coefficients of  $R^2 = 0.97958$  and  $0.95832$  for  $n = 7$  sampling points, respectively, as inserted tables in Fig. 6. As expected in theory, the absorption depths of direct absorption spectra show linear dependence on sample concentration under an optically thin case. Noted that the calculated signal amplitude of 2nd derivative spectra also shows a good linear response. This linear expression determined from the 2nd derivative signals can be used for unknown trace gas concentration measurement [27]. It offers advantages (*i.e.*, time and cost) over traditional direct absorption spectroscopy and wavelength modulation spectroscopy, which must utilize a complicated fitting algorithm model (such as Voigt model) and a digital lock-in amplifier technique, respectively.

Finally, the system performance was evaluated using the Allan variance technique [28] (as shown in Fig. 7), based on a time series of 2nd derivative measurements of a certified C<sub>2</sub>H<sub>2</sub> sample. The Allan deviation is plotted in a log-log scale *versus* the averaging time, indicating a detection limit of 1.7 ppm with 1-s averaging time, and a minimum noise level of 62 ppb, at the optimum integration time of ~60 s. The performance of our TDLAS sensing system is satisfying for industrial application. However, the sensitivity needs to be further improved for atmospheric observations, which could be realized by optimizing the effective optical path (*i.e.*, a maximum optical path



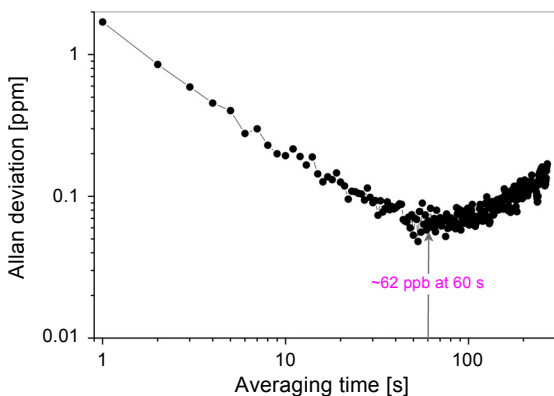


Fig. 7. Allan deviation plot of the 2nd derivative signal as a function of the signal averaging time.

length of 76 m) and improving the Savitzky–Golay smoothing and differentiation algorithm.

## 4. Conclusion

In summary, a TDLAS spectrometer with 2nd derivative detection was developed for trace acetylene gas analysis, the system performance was evaluated by combining appropriate digital signal processing methods, *i.e.*, Savitzky–Golay filtering and differentiation algorithm. The calculation of the derivative spectra by this method is accompanied by simultaneous data smoothing. The Savitzky–Golay smoothing and differentiation algorithm produces 2nd derivative spectra with better resolution, lowering detection limits, saving signal processing time, and improving the ability to distinguish unresolved spectral signals. This method is potentially well-suited to real-time automated spectral analysis of chemical species and volatile organic compounds, where spectral interference from the target gas or foreign species seriously affects measurement precision and accuracy in optical spectroscopy based sensors.

*Acknowledgments* – This work was supported in part by Anhui University Personnel Recruiting Project of Academic and Technical Leaders under Grant 10117700014, the Natural Science Fund of Anhui Province under Grant 1508085MF118, the National Natural Science Foundation of China under Grant 61440010 and 61675005, the National Program on Key Research and Development Project under Grant 2016YFC0302202, and the Key Science and Technology Development Program of Anhui Province under Grant 1501041136.

## References

- [1] LIZHU ZHANG, GUANG TIAN, JINGSONG LI, BENLI YU, *Applications of absorption spectroscopy using quantum cascade lasers*, *Applied Spectroscopy* **68**(10), 2014, pp. 1095–1107.
- [2] ZHIQUN DING, HONGXIA ZHAO, XIAOHUI FANG, JILONG BAO, *Trace detection of C<sub>2</sub>H<sub>2</sub> using tunable diode laser absorption spectroscopy*, *Proceedings of SPIE* **8192**, 2011, article 81923B.

- [3] YAPING XIAO, JACOB D.J., TURQUETY S., *Atmospheric acetylene and its relationship with CO as an indicator of air mass age*, Journal of Geophysical Research: Atmospheres **112**(D12), 2007, article D12305.
- [4] ROTHMAN L.S., GORDON I.E., BABIKOV Y., BARBE A., BENNER D.C., BERNATH P.F., BIRK, L., BIZZOCCHI M., BOUDON V., BROWN L.R., CAMPARGUE A., CHANCE K., COUDERT L.H., DEVI V.M., DROUIN B.J., FAYT A., FLAUD J.M., GAMACHE R.R., HARRISON J., HARTMANN, C., HILL J.M., HODGES J.T., JACQUEMART D., JOLLY A., LAMOUROUX J., LE ROY R.J., LI G., LONG D., MACKIE C.J., MASSIE S.T., MIKHAILENKO S., MÜLLER H.S.P., NAUMENKO O.V., NIKITIN A.V., ORPHAL J., PEREVALOV V.I., PERRIN A., POLOVTSEVA E.R., RICHARD C., SMITH M.A.H., STARIKOVA E., SUNG K., TASHKUN S.A., TENNYSON J., TOON G.C., TYUTEREV V.G., WAGNER G., *The HITRAN2012 molecular spectroscopic database*, Journal of Quantitative Spectroscopy and Radiative Transfer **130**, 2013, pp. 4–50.
- [5] WERLE P., *A review of recent advances in semiconductor laser based gas monitors*, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy **54**(2), 1998, pp. 197–236.
- [6] RUSCIANO G., PESCE G., PIGNATIELLO F., SASSO A., *Difference-frequency-generator-based spectrometer at 3  $\mu\text{m}$  for high-sensitivity  $\text{C}_2\text{H}_2$  and  $\text{H}_2\text{O}$  detection*, Optics Express **11**(23), 2003, pp. 3010–3021.
- [7] FAIST J., CAPASSO F., SIVCO D.L., SIRTORI C., HUTCHINSON A.L., CHO A.Y., *Quantum cascade laser*, Science **264**(5158), 1994, pp. 553–556.
- [8] SAJID M.B., JAVED T., FAROOQ A., *High-temperature measurements of methane and acetylene using quantum cascade laser absorption near 8  $\mu\text{m}$* , Journal of Quantitative Spectroscopy and Radiative Transfer **155**, 2015, pp. 66–74.
- [9] HERBST J., SCHERER B., SINGER F., ERB J., LAMBRECHT A., RATHKE C., FILIP S., KAPPLER J., FUCHS P., KOETH J., FRIEDL J., SCHLERETH T.W., SEMMEL J., HÖFLING S., WORSCHER L., FORCHEL A., *Acetylene measurement using quantum cascade lasers at 14  $\mu\text{m}$* , Proceedings of SPIE **7945**, 2011, article 79450J.
- [10] JINGSONG LI, XIAOMING GAO, WEIZHENG LI, ZHENSONG CAO, LUNHUA DENG, WEIXIONG ZHAO, MINGQIANG HUANG, WEIJUN ZHANG, *Near-infrared diode laser wavelength modulation-based photo-acoustic spectrometer*, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy **64**(2), 2006, pp. 338–342.
- [11] UTSAV K.C., NASIR E.F., FAROOQ A., *A mid-infrared absorption diagnostic for acetylene detection*, Applied Physics B **120**(2), 2015, pp. 223–232.
- [12] WAGNER S., FISHER B.T., FLEMING J.W., EBERT V., *TDLAS-based in situ measurement of absolute acetylene concentrations in laminar 2D diffusion flames*, Proceedings of the Combustion Institute **32**(1), 2009, pp. 839–846.
- [13] GAGLIARDI G., GIANFRANI L., *Trace-gas analysis using diode lasers in the near-IR and long-path techniques*, Optics and Lasers in Engineering **37**(5), 2002, pp. 509–520.
- [14] PRADHAN M., LINDLEY R.E., GRILLI R., WHITE I.R., MARTIN D., ORR-EWING A.J., *Trace detection of  $\text{C}_2\text{H}_2$  in ambient air using continuous wave cavity ring-down spectroscopy combined with sample pre-concentration*, Applied Physics B **90**(1), 2008, pp. 1–9.
- [15] RICHARD E.C., KELLY K.K., WINKLER R.H., WILSON R., THOMPSON T.L., MCLAUGHLIN R.J., SCHMELTEKOPF A.L., TUCK A.F., *A fast-response near-infrared tunable diode laser absorption spectrometer for in situ measurements of  $\text{CH}_4$  in the upper troposphere and lower stratosphere*, Applied Physics B **75**(2–3), 2002, pp. 183–194.
- [16] JINGSONG LI, BENLI YU, WEIXIONG ZHAO, WEIDONG CHEN, *A review of signal enhancement and noise reduction techniques for tunable diode laser absorption spectroscopy*, Applied Spectroscopy Reviews **49**(8), 2014, pp. 666–691.
- [17] MARCHENKO D., NEERINCX A.H., MANDON J., ZHANG J., BOERKAMP M., MINK J., CRISTESCU S.M., TE LINTEL HEKKERT S., HARREN F.J.M., *A compact laser-based spectrometer for detection of  $\text{C}_2\text{H}_2$  in exhaled breath and HCN in vitro*, Applied Physics B **118**(2), 2015, pp. 275–280.
- [18] HAO DENG, JUAN SUN, BENLI YU, JINGSONG LI, *Near infrared diode laser absorption spectroscopy of acetylene between 6523 and 6587  $\text{cm}^{-1}$* , Journal of Molecular Spectroscopy **314**, 2015, pp. 1–5.

- [19] ZIMMERMANN B., KOHLER A., *Optimizing Savitzky–Golay parameters for improving spectral resolution and quantification in infrared spectroscopy*, *Applied Spectroscopy* **67**(8), 2013, pp. 892–902.
- [20] CZARNECKI M.A., *Resolution enhancement in second-derivative spectra*, *Applied Spectroscopy* **69**(1), 2015, pp. 67–74.
- [21] SAVITZKY A., GOLAY M.J.E., *Smoothing and differentiation of data by simplified least squares procedures*, *Analytical Chemistry* **36**(8), 1964, pp. 1627–1639.
- [22] JINGSONG LI, HAO DENG, PENGFEI LI, BENLI YU, *Real time infrared gas detection based on an adaptive Savitzky–Golay algorithm*, *Applied Physics B* **120**(2), 2015, pp. 207–216.
- [23] BARAK P., *Smoothing and differentiation by an adaptive-degree polynomial filter*, *Analytical Chemistry* **67**(17), 1995, pp. 2758–2762.
- [24] CHAO ZUO, QIAN CHEN, YINGJIE YU, ASUNDI A., *Transport-of-intensity phase imaging using Savitzky–Golay differentiation filter – theory and applications*, *Optics Express* **21**(5), 2013, pp. 5346–5362.
- [25] JINGSONG LI, PARCHATKA U., FISCHER H., *Applications of wavelet transform to quantum cascade laser spectrometer for atmospheric trace gas measurements*, *Applied Physics B* **108**(4), 2012, pp. 951–963.
- [26] JINGSONG LI, PARCHATKA U., FISCHER H., *Development of field-deployable QCL sensor for simultaneous detection of ambient N<sub>2</sub>O and CO*, *Sensors and Actuators B: Chemical* **182**, 2013, pp. 659–667.
- [27] FAROOQ A., JEFFRIES J.B., HANSON R.K., *Sensitive detection of temperature behind reflected shock waves using wavelength modulation spectroscopy of CO<sub>2</sub> near 2.7 μm*, *Applied Physics B* **96**(1), 2009, pp. 161–173.
- [28] WERLE P., MÜCKE R., SLEMR F., *The limits of signal averaging in atmospheric trace gas monitoring by tunable diode-laser absorption spectroscopy (TDLAS)*, *Applied Physics B* **57**(2), 1993, pp. 131–139.

*Received October 25, 2015  
in revised form March 30, 2016*