

D.E. VOGLER
M.W. SIGRIST 

Near-infrared laser based cavity ringdown spectroscopy for applications in petrochemical industry

Institute of Quantum Electronics, ETH Zurich, Schafmattstr. 16, 8093 Zurich, Switzerland

Received: 24 March 2006/Revised version: 4 May 2006
Published online: 27 June 2006 • © Springer-Verlag 2006

ABSTRACT A simple, economic diode laser based cavity ringdown system for trace-gas applications in the petrochemical industry is presented. As acetylene (C_2H_2) is sometimes present as an interfering contaminant in the gas flow of ethylene (ethene, C_2H_4) in a polyethylene production process, an on-line monitoring of such traces is essential. We investigated C_2H_2 – C_2H_4 mixtures in a gas-flow configuration in real time. The experimental setup consists of a near-infrared external cavity diode laser with an output power of a few mW, standard telecommunication fibers and a home-made gas cell providing a user-friendly cavity alignment. A noise-equivalent detection sensitivity of $4.5 \times 10^{-8} \text{ cm}^{-1} \text{ Hz}^{-1/2}$ was achieved, corresponding to a detection limit of 20 ppbV C_2H_2 in synthetic air at 100 mbar. In an actual C_2H_2 – C_2H_4 gas-flow measurement the minimum detectable concentration of C_2H_2 added to the C_2H_4 gas stream (which may already contain an unknown C_2H_2 contamination) increased to 160 ppbV. Moreover, stepwise C_2H_2 concentration increments of 500 ppbV were resolved with a 1-min time resolution and an excellent linear relationship between the absorption coefficient and the concentration was found.

PACS 07.07.Df; 42.62.Fi; 82.80.Gk

1 Introduction

The large volume and variety of polyethylene products like plastic bags, polyethylene terephthalate (PET) bottles, car interiors, etc. emphasizes the significance and importance of plastic products nowadays. The basis for the largest single class of plastics is formed by ethylene or ethene (C_2H_4). It is one of the most important raw materials of the organic chemical industry and occurs in both petroleum and natural gas. Since the production of plastics demands pure C_2H_4 , impurities and their monitoring during the production process play a crucial role. Currently, measurements of contaminants like acetylene (C_2H_2), CO and CO_2 , ethane (C_2H_6) and methane (CH_4) – to mention only a few of them – are carried out by gas chromatography (GC). This well-established technique is, however, operating at its limit of detection and furthermore the preferred temporal resolution for true on-line

measurements is not met by GC. Petrochemical industries are therefore seeking alternative sensing schemes to monitor impurities at the ppbV (10^{-9} parts per volume) concentration level in order to prevent problems occurring downstream in polymer-production plants. Alternatives to gas chromatography would also be attractive if they offered ways of multiplexing that could enable several measurements with one spectrometer [1]. Here we propose cavity ringdown (CRD) spectroscopy as a new and valuable scheme for this challenging task.

2 Cavity ringdown spectroscopy


Cavity ringdown (CRD) is a sensitive optical spectroscopic technique which was introduced almost 20 years ago and which has been employed in numerous studies in various configurations and applications [2–18]. In contrast to conventional optical absorption and transmission techniques, CRD is based on the time measurement of the exponential decay of the light intensity within a cavity formed by highly reflective dielectric mirrors. Hence the CRD method is insensitive to power fluctuations of the laser incident on the cavity. The cavity ringdown time τ depends on the reflectivity of the mirrors (we consider two identical mirrors, each with reflectivity R , forming the cavity) and the absorption coefficient α of a medium present between the mirrors. The cavity ringdown time is given by [2]

$$\tau = \frac{L}{c[(1-R) + \alpha L]}, \quad (1)$$

where L is the length of the cavity and c denotes the speed of light. Equation (1) implies that the absorption coefficient α of a sample can directly be derived from a measurement with empty cavity (yielding a decay time τ_0) and a measurement with the sample present (yielding τ):

$$\alpha = \frac{1}{c} \left(\frac{1}{\tau} - \frac{1}{\tau_0} \right). \quad (2)$$

Thus, no calibration is required. The minimum detectable absorption coefficient α_{\min} depends on the deviation of the acquired ringdown time. The more accurately the ringdown time can be measured, the better the detection limit of the absorption measurement. The detection limit of the CRD method is

 Fax: +41-44-6331230, E-mail: sigrist@iqe.phys.ethz.ch

given as [6]

$$\alpha_{\min} = \frac{1}{c} \left(\frac{1}{\tau_0 - \Delta\tau} - \frac{1}{\tau_0} \right) = \frac{(1-R)\Delta\tau}{L(\tau_0 - \Delta\tau)}$$

$$= \left(\frac{1-R}{L} \right) \left(\frac{\Delta\tau}{\tau} \right)_{\min}, \quad (3)$$

where $\Delta\tau$ denotes the minimum change in ringdown time that can be accurately measured. For a signal-to-noise ratio SNR = 3, $\Delta\tau$ is equal to six times the standard deviation of the measured ringdown time without an absorbing sample present between the mirrors. Hence, α_{\min} measured with the CRD technique is limited by the available mirror reflectivity R and $\Delta\tau$.

3 Experimental setup

The experimental design is based on a continuous-wave (cw) CRD spectroscopic setup. This ensures a high detection selectivity in a multi-component gas mixture as encountered in an industrial environment, owing to the narrow line width of the laser. In addition, a high sensitivity is enabled by the excitation of only one fundamental longitudinal cavity mode [16].

The CRD arrangement to be applied to gas streams was designed for the near-infrared (NIR) range. Although molecular absorption cross sections are typically 10 to 100 times lower in the NIR than in the mid-IR range, the NIR is preferred here as it allows the implementation of robust and economic optical devices (diode lasers and detectors, etc.) as well as the use of silica-based single-mode fibers for easy light handling at still appreciable detection sensitivity. The schematic CRD spectroscopic setup is depicted in Fig. 1. As monochromatic tunable light sources, fiber-coupled external cavity diode lasers (ECDLs) are employed: either an ECDL with a tuning range from 1520 nm to 1550 nm and maximum cw output power of 1.5 mW (Newport, EOSI 2010) or an ECDL tunable between 1520 nm and 1600 nm and 9-mW maximum power (Santec, TSL-210). Each laser is directly coupled to a silica-based single-mode fiber. After the laser output, an optical isolator prevents back reflections of light into the laser cavity and thus a distortion of the lasing process. The laser light is then guided to an acousto-optical modulator (AOM; IntraAction, FCM-401E5C) enabling a fast amplitude modulation in case of a mode match between the laser and a resonance frequency of the CRD cavity. After the AOM, a fiber collimator (FC) and a lens (L₁) focus the light into the middle of the hermetically sealable cell, made out of stainless steel. The cavity in the cell is formed by two mirrors (Los Gatos Research, Inc.) with a reflectivity R of > 99.99% at around 1550 nm and a curvature radius of 1 m. The cell body is built in a modular design with one, two or three 150-mm-long stainless steel tube elements with an inner diameter of 35 mm. Three connections offer the possibility of inserting a pressure sensor and tubes to flow gases into and out of the cell. The length of the entire cavity is given by the cell body and a cell end part screwed onto it. In this home-made mount, a highly reflective mirror is fixed on a high-voltage piezo-electric ring transducer (PZT; Piezomechanik HPSt 1000/25-15/15 VS35). The PZT serves to sweep the length of the cavity to ensure the excitation of a single fundamental longitudinal cavity mode, while the AOM switches off the laser beam immediately after the incident laser frequency has matched a cavity mode frequency. The PZT ring transducer is screwed onto a plate whose orientation can be adjusted by three micrometer screws, making the alignment of the mirror possible from outside the cell. This special feature allows an easy realignment of the cavity without opening the cell. An O-ring between the cell body and the PZT plate ensures that the cell is well sealed. Pressure changes of less than 1 mbar/h were observed. In addition, the mount features an electric input for the PZT drive. The other end of the cavity cell consists of a commercial mirror mount (Los Gatos Research, Inc.), also allowing mirror alignment by three screws from outside the cell. Thus, the total gas-cell length amounts to 57 cm, of which the distance between the mirrors (with three tube elements) comprises 52 cm. This configuration has a cell volume of 540 cm³.

After the PZT, the plate-embedded AR-coated lens (L₂) focuses the light exiting the cavity onto an InGaAs photodiode (PD; New Focus, model 1811) placed 25 cm after the cell (see Fig. 1). The 3-dB bandwidth of the photodetector amounts to 125 MHz, ensuring accurate detection of ringdown events with a characteristic ringdown time of about 20 μ s. The photon-induced diode current is internally amplified with a gain factor of 4×10^4 by a transimpedance amplifier and acquired by an oscilloscope (Tektronix, TDS 620). A trigger level, which can be set on the oscilloscope, controls the fast amplitude modulation (with ~ 120 ns rise and fall times) in the AOM in case of a coincidence between the laser and cavity mode frequencies. The digitized ringdown event is finally sent from the oscilloscope to a computer for analysis. Two fitting procedures have been evaluated, namely a fast fitting algorithm for a single-exponential function [19, 20] and the nonlinear Levenberg–Marquardt procedure provided by LabView. Both fits yielded identical results. Since the former algorithm proved to be much faster it was used for the analysis of all the measurements.

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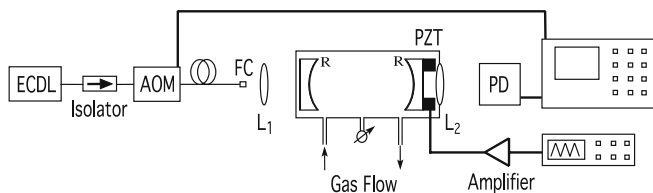


FIGURE 1 Schematic setup of the cavity ringdown spectroscopy system. ECDL: external cavity cw diode laser, AOM: acousto-optical modulator, FC: fiber collimator, L: lens, PZT: piezo-electric transducer, PD: photodiode

4 Results and discussion

Although about 20 times less strong than at the fundamental absorption range around 7.4 μ m, acetylene (C₂H₂) still features a reasonable absorption in the wavelength range near 1530 nm of our ECDLs. The determination of the minimum detectable C₂H₂ concentration with our near-infrared cw CRD setup was accomplished by recording the P(10) absorption line at 1530.977 nm [21] of the ($\nu_1 + \nu_3$)-

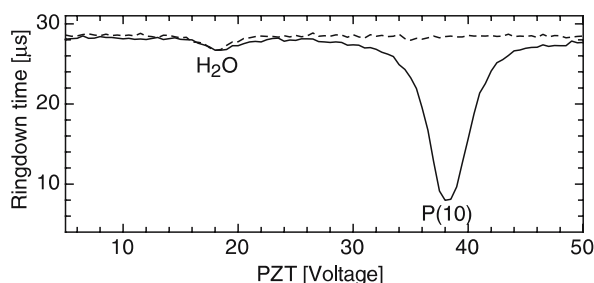


FIGURE 2 Synthetic air (equivalent baseline) (*broken curve*), 10 ppmV C_2H_2 diluted in synthetic air (*solid curve*) at a total pressure of 100 mbar

combination band. Spectra around 1530.977 nm at a total pressure of 100 mbar were recorded for pure synthetic air (20.5% O_2 , 79.5% N_2 , $H_2O < 5$ ppm, total hydrocarbons < 0.1 ppm, $NO_x < 0.1$ ppm, CO and $CO_2 < 0.5$ ppm) as well as for 10 ppmV C_2H_2 diluted in synthetic air by fine tuning the ECDL (EOSI) with a PZT. First, the cavity gas cell was filled with synthetic air and the baseline of the ringdown times was measured around the P(10) line of C_2H_2 with a laser output power of 1.4 mW. The average ringdown time of the stable baseline in this range was determined to be 28.3 μs with a standard deviation of the mean of 236 ns. By taking a signal-to-noise ratio of 1, i.e. twice the standard deviation, the minimum accurate deviation $\Delta\tau$ in the ringdown time τ (see (1)) of the baseline is 472 ns. According to (3), this results in a minimum detectable absorption coefficient $\alpha_{min} = 2 \times 10^{-8} \text{ cm}^{-1}$ (or $\alpha_{min} = 6.2 \times 10^{-8} \text{ cm}^{-1}$ for $SNR = 3$). After the measurement with synthetic air, the cell was filled with the mixture of 10 ppmV C_2H_2 diluted in synthetic air and the measurement was repeated. Figure 2 shows the results of the two measurements. Since the cavity was swept at a frequency of 10 Hz during the scan, the ringdown events were collected at a maximum rate of 20 Hz. We averaged 100 ringdown events for the evaluation of one ringdown time at one position of the laser PZT, yielding an acquisition time T of 5 s. This results in a minimum detectable absorption coefficient $\alpha_{min} = 4.5 \times 10^{-8} \text{ cm}^{-1} \text{ Hz}^{-1/2}$ for $SNR = 1$. If the low laser power of only 1.4 mW is taken into account, a noise-equivalent limit $\alpha_{min} = 6.3 \times 10^{-11} \text{ cm}^{-1} \text{ W Hz}^{-1/2}$ results. This limit is independent of the absorption line selected because it is determined only by the ringdown time τ_0 and its deviation $\Delta\tau$ as indicated in (3). Apparently, the sensitivity can be increased by choosing higher PZT modulation frequencies to sweep the CRD cavity, i.e. to average the same number of ringdown times within a shorter integration time. If we drove the PZT at its maximum frequency of 300 Hz we could achieve a noise-limited sensitivity of $\alpha_{min} = 8 \times 10^{-9} \text{ cm}^{-1} \text{ Hz}^{-1/2}$. However, as the PZT mirror mount in our CRD arrangement was not designed for sweeping rates at such frequencies, we normally did not operate the system above 10 Hz.

A comparison of detection limits with other laser-based detection systems employed for monitoring C_2H_2 or other trace gases is not straightforward, in view of rather different experimental configurations and definitions of sensitivity and sometimes lack of specific information. However, a comparison is made here with some recently reported systems employing CRD or photoacoustic (PA) detection

schemes at near-IR wavelengths around 1.5 μm . He and Orr [13] reported a noise-limited absorption sensitivity of $2.5 \times 10^{-9} \text{ cm}^{-1} \text{ Hz}^{-1/2}$ with a single-ended, rapidly swept cw CRD scheme with optical heterodyne detection and 500-Hz collection rate of the ringdown events. Hornberger et al. [22] achieved a minimum detectable absorption coefficient $\alpha_{min} = 2.6 \times 10^{-9} \text{ cm}^{-1}$ with a multi-pass PA system employing a color-center laser of 250-mW power, an integration time of 1 s, an (optimum) pressure of 130 mbar and $SNR = 1$. A detection limit of $\alpha_{min} = 3 \times 10^{-9} \text{ cm}^{-1}$ for $SNR = 3$ was reported by Awtry and Miller [23], realized with a cw ECDL at 1.55 μm with a typical output power of 5 mW combined with a CRD spectroscopic detection scheme. Without specifying the integration time, this value resulted in a calculated detection limit of 4 ppbV for C_2H_2 . A limit of $\alpha_{min} = 1.4 \times 10^{-9} \text{ cm}^{-1}$ corresponding to a bandwidth-normalized noise level of $5 \times 10^{-10} \text{ cm}^{-1} \text{ Hz}^{-1/2}$ was reported by Morville et al. [24] for a cw NIR diode laser CRD system. Webber et al. [25] used fiber-amplifier-enhanced PA spectroscopy and reported a limit of $\alpha_{min} = 9.5 \times 10^{-10} \text{ cm}^{-1}$ or $3 \times 10^{-9} \text{ cm}^{-1} \text{ Hz}^{-1/2}$ for a laser power of 500 mW and $SNR = 1$. Kosterev et al. [26] claimed a detection limit $\alpha_{min} = 5.4 \times 10^{-9} \text{ cm}^{-1} \text{ W Hz}^{-1/2}$ for a technique named quartz-enhanced PA spectroscopy (QEPAS) for $SNR = 1$, a laser power of 38 mW and an optimized gas pressure of 80 mbar. Most recently, Scotoni et al. [27] reported the simultaneous detection of ammonia, methane and ethylene with a near-IR diode laser PA system resulting in ppm detection limits. Finally, Laurila et al. [28, 29] introduced the novel concept of a cantilever-based PA scheme and reported a normalized detection sensitivity of $2.2 \times 10^{-9} \text{ cm}^{-1} \text{ W Hz}^{-1/2}$ realized with a distributed feedback (DFB) diode laser at 1572 nm with 34-mW power, resulting in a noise-equivalent detection limit for CO_2 in Ar of 4.6 ppm and of sub-ppm employing a fiber amplifier. Hence, our detection limit is competitive with that of other established near-IR diode-laser-based schemes. However, it falls short of state-of-the-art measurements. As an example, Baer et al. [30] claimed a noise-equivalent absorption sensitivity of $3.1 \times 10^{-11} \text{ cm}^{-1} \text{ Hz}^{-1/2}$ for off-axis integrated cavity output (ICOS) measurements with a 88-cm-long cavity, a 10^4 -sweep average and a detection bandwidth of 1.1 Hz. Those authors achieved a detection limit of 0.2 ppbv for C_2H_2 in N_2 ($SNR = 3$) at 1532 nm for a 500-Hz laser tuning rate and a 1-s integration time. They emphasized that for measurements in industrial process flows, absorption features of other hydrocarbons present in the probed flow like C_2H_4 would have to be accounted for. A similar sensitivity of $3.2 \times 10^{-11} \text{ cm}^{-1} \text{ Hz}^{-1/2}$ was reported by Crosson et al. [31] for near-IR isotope-ratio measurements of CO_2 in human breath with an ECDL CRD setup. An effort was put into increasing the data-acquisition rate by a special tracking circuit that enabled the generation of ringdown decay waveforms at a rate of 1 kHz. Ye et al. [32] even claimed a sensitivity of $1 \times 10^{-14} \text{ cm}^{-1}$ over 1-s averaging time in a scheme that combines the external cavity enhancement approach with frequency-modulation spectroscopy, named NICE-OHMS (noise-immune cavity-enhanced optical heterodyne molecular spectroscopy). These high sensitivities, however, involve rather sophisticated and costly instrumental refinements whereas our main objective has been to develop

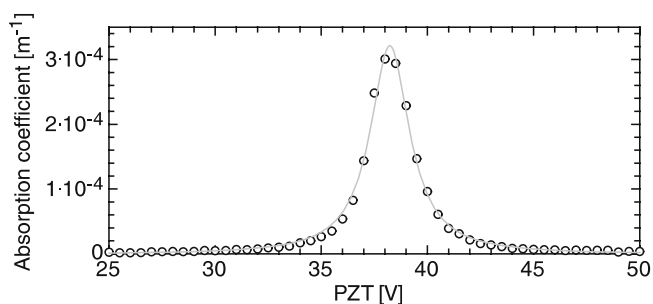


FIGURE 3 10 ppmV C_2H_2 diluted in synthetic air at a total pressure of 100 mbar. Measured P(10) absorption peak (\circ), Lorentzian fit (solid curve)

a relatively simple, robust and economic measurement system for an industrial application rather than to further enhance the sensitivity.

Figure 3 depicts the measured absorption peak of the P(10) line of C_2H_2 fitted by a Lorentzian curve. The maximum absorption coefficient $\alpha_{\max} = 3.21 \times 10^{-4} \text{ m}^{-1}$ of this fit corresponds to 10 ppmV of C_2H_2 . The HITRAN 2004 database [33] provides line intensity and frequency data about C_2H_2 in the NIR range based on data by El Hachtouki and Vander Auwera [34]. In order to evaluate the detection limit, we divide α_{\max} by our noise-equivalent $\alpha_{\min} = 2 \times 10^{-8} \text{ cm}^{-1}$ and obtain a minimum detectable concentration for C_2H_2 diluted in synthetic air of 62 ppbV at the P(10) line and at a total pressure of 100 mbar. Since the absorption cross section of the stronger line P(9) at 1530.3718 nm [21] is about three times larger than of the P(10) line [33, 34], it results in a C_2H_2 detection limit of 20 ppbV for the P(9) line at 100 mbar.

Similar to the measurements depicted in Fig. 2, a baseline of the ringdown time of synthetic air was also recorded in the range of the C_2H_2 P(9) line at 1530.3718 nm [21]. After evacuation, the cell was then filled with 99.95% pure C_2H_4 in order to determine a spectrum of C_2H_4 with a degree of purity typically encountered in petrochemical production lines. The wavelength range around the C_2H_2 P(9) absorption line was scanned with the EOSIECDL. The total cell pressure was 20 mbar. After this scan, the measurement was repeated under the same conditions except that 10 ppmV of C_2H_2 diluted in

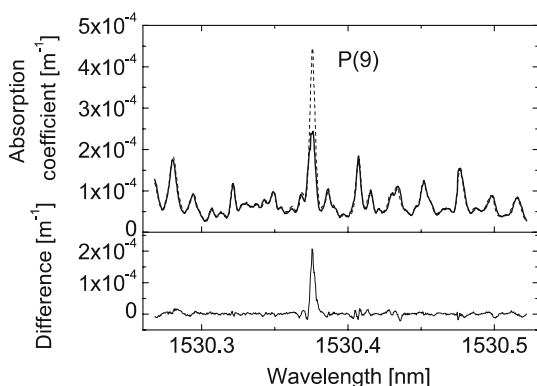


FIGURE 4 Recorded spectra of 99.95% pure C_2H_4 (solid curve) and of 99.95% pure C_2H_4 plus 10 ppmV C_2H_2 diluted in synthetic air (broken curve). Both spectra are recorded around the C_2H_2 P(9) line at 20-mbar total gas pressure. The lower trace shows the difference between the two spectra. Apart from the additional C_2H_2 absorption, evident at the P(9) line, the two spectra exhibit excellent agreement

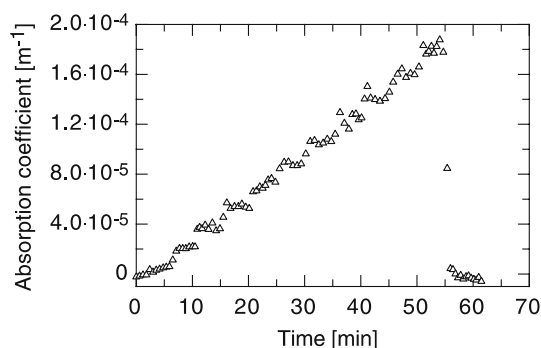


FIGURE 5 Gas-flow measurement of different C_2H_2 concentrations in C_2H_4 . The flow rate amounts to $200 \text{ cm}^3/\text{min}$ at 20-mbar cell pressure. The stepwise increase of the absorption coefficient is caused by the addition of 500 ppbV C_2H_2 to the C_2H_2 - C_2H_4 mixture every 5 min. After 55 min the cell was flushed with a pure C_2H_4 -synthetic air mixture

C_2H_4 were added. We waited for several minutes to allow adequate mixing of the gases. Both spectra as well as their difference are depicted in Fig. 4. We find an excellent congruence between the two spectra beside the C_2H_2 P(9) line. The additional absorption at 1530.3718 nm caused by the added C_2H_2 is clearly detectable. The total difference in the absorption coefficients is $2.0 \times 10^{-4} \text{ m}^{-1}$, corresponding to $2.0 \times 10^{-5} \text{ m}^{-1}$ per ppmV of C_2H_2 added. However, since the reproducibility of the laser tuning was not perfect, the two recorded spectra had to be slightly shifted in wavelength with respect to each other so that the positions of the absorption peaks overlapped exactly. Since a small concentration of synthetic air is also introduced into the gas cell with the addition of C_2H_2 , the absorptions of the mixed spectrum are slightly below those of pure C_2H_4 as seen in Fig. 4. In addition, the spectra indicate that the laser absorption by 99.95% pure C_2H_4 never equals zero, i.e. the recorded ringdown times are always shorter than the ringdown times acquired in the cell filled with synthetic air. This implies that it is not possible to determine the absolute C_2H_2 concentration but the additional concentration only. The superposition of different absorption lines of different gas components within the mixture, which are not completely known in advance, prevents the determination of the absolute concentration.

Instead of stationary gas fillings as described above, measurements of different C_2H_2 concentrations were performed in a constant flow of C_2H_4 with the second ECDL (Santec) at an output power of 7 mW (see Fig. 5). The gas-flow rate was $200 \text{ cm}^3/\text{min}$ at a total cell pressure of 20 mbar. 100 ringdown events were again averaged for each data point before the computer analyzed the ringdown times. The flow started with $180 \text{ cm}^3/\text{min}$ 99.95% pure C_2H_4 and $20 \text{ cm}^3/\text{min}$ synthetic air. Every 5 min, 500 ppbV C_2H_2 were added to the C_2H_4 -synthetic air mixture controlled by a mass-flow controller (Sierra Instruments Inc.). The steps in the absorption coefficient are clearly visible in Fig. 5, indicating that the mixing of the gases is adequate and that adsorption/desorption processes at the cell walls are negligible. After 55 min, corresponding to a total addition of 5 ppmV of C_2H_2 , the cell was flushed again with the pure C_2H_4 -synthetic air mixture. This yields a system response time of about 1 min as seen by the sudden drop of the signal after 55 min in Fig. 5. The evaluated absorption coefficients at the P(9) line during the

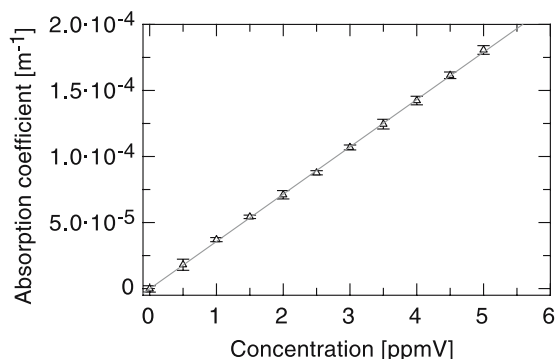


FIGURE 6 Measured absorption coefficient vs. C_2H_2 concentration present in C_2H_4 . The absorption recorded at the P(9) line of C_2H_2 shows a linear dependence on the C_2H_2 concentration, with a slope of $3.58 \times 10^{-5} \text{ m}^{-1}$ per ppmV of C_2H_2

1-h measurement are depicted in Fig. 5. At the beginning, the measured ringdown time in the C_2H_4 –synthetic air mixture is only about $11.72 \mu\text{s}$ due to strong initial C_2H_4 absorption at this particular wavelength (see Fig. 4). The standard deviation of the ringdown time is 107 ns. According to (3) this implies a minimum detectable absorption coefficient $\alpha_{\text{min}} = 5.3 \times 10^{-8} \text{ cm}^{-1}$ (SNR = 1) at the P(9) line and at a total pressure of 20 mbar. This value is higher than the limit of $\alpha_{\text{min}} = 2 \times 10^{-8} \text{ cm}^{-1}$ obtained for C_2H_2 in synthetic air. The difference can be explained by the additional absorption in C_2H_4 , i.e. on the short ringdown time and on the resulting small ratio of $\Delta\tau/\tau$ in (3).

In Fig. 6, the measured absorption coefficient is plotted vs. the C_2H_2 concentration. An excellent linear relationship is found and the fit procedure yields a slope of $3.58 \times 10^{-5} \text{ m}^{-1}$ per ppmV. This results in a detection limit of 160 ppbV (for SNR = 1) for additional C_2H_2 present in a C_2H_4 stream.

5 Conclusions

A near-infrared-based cavity ringdown system was designed and built for potential use in petrochemical industries. The design included a reliable and cost-effective near-IR laser with a power of only a few mW, standard telecommunication fibers and a home-made gas cell to provide a user-friendly cavity alignment. A noise-equivalent minimum detectable absorption coefficient of $4.5 \times 10^{-8} \text{ cm}^{-1} \text{ Hz}^{-1/2}$ was achieved in a hermetically sealed gas cell. As discussed in Sect. 3, this sensitivity is comparable to or lower than sensitivities reported previously. However, the special design offering easy external cavity alignment from outside the closed gas cell limited the sensitivity of our near-IR system.

Emphasis of this development was on an important practical application of trace-gas sensing for the petrochemical industry, namely the on-line recording of the contamination of technical grade (99.95% purity) ethylene (C_2H_4) by acetylene (C_2H_2) in a gas-flow configuration. This entailed the evaluation of the most suitable laser wavelengths and the determination of detection limits. We achieved a limit of 160 ppbV (at SNR = 1) for an additional C_2H_2 concentration, i.e. in addition to that possibly already present in the C_2H_4 background gas at 20-mbar total pressure. This limit is appreciably higher than the 20 ppbV derived for C_2H_2 traces in synthetic air at

100 mbar. The discrepancy is mainly explained by interfering absorption in the case of a C_2H_4 gas flow. Although the CRD detection scheme in combination with a tunable near-IR diode laser appears promising, further improvements are necessary to offer a valid alternative to existing gas-chromatography devices in petrochemical facilities. Notably, sensitivity requirements with detection limits in the low-ppbV concentration range need to be satisfied. Since molecular absorption cross sections in the mid-IR region are higher, an alternative to the near-IR lasers used could be a mid-IR laser system, e.g. based on difference-frequency generation (DFG) around $3 \mu\text{m}$, as employed by Rusciano et al. [35] who achieved a detection limit of 4 ppbV for C_2H_2 diluted in N_2 in a multi-pass arrangement. Although comparable to the C_2H_2 detection limit reported earlier by Awtry and Miller [23] and even worse than that claimed by Baer et al. [30] or by He and Orr [36] for a near-IR CRD system, mid-IR lasers could prove more favorable in avoiding potential absorption interferences between actual contaminants and background gas components than near-IR sources thanks to their broad tunability. However, they involve more sophisticated complex instrumental architecture and thus appear less appropriate for practical applications in harsh industrial environments. In order to still better meet sensitivity and stability requirements for industrial applications, the performance of our simple and economic approach with near-IR diode lasers and CRD detection could be further improved by a better ringdown cavity design with higher mechanical stability, by higher-reflectivity mirrors, more stable lasers, higher laser power and higher-resolution electronics. Based on this feasibility study, the (tunable) ECDL could be replaced in a future instrumental setup by DFB diode lasers emitting specified ‘on’ and ‘off’ wavelengths with respect to absorption lines of the species of interest.

ACKNOWLEDGEMENTS The authors thank H. Brändle (ABB Corporate Research) for many fruitful discussions. This work was supported by ABB Corporate Research, Switzerland.

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