Sensitive measurements of trace gas of formaldehyde using a mid-infrared laser spectrometer with a compact multi-pass cell

Kotaro Tanaka^{1,*}, Kai Miyamura², Kazushi Akishima², Kenichi Tonokura³, Mitsuru Konno¹

1. *Department of Mechanical Engineering, Ibaraki University, 4-12-1 Nakanarusawa, Hitachi 316-8511, Ibaraki, Japan*

2. *Graduate School of Science and Engineering, Ibaraki University, 4-12-1 Nakanarusawa, Hitachi 316-8511, Ibaraki, Japan*

3. *Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa 277-8563, Chiba, Japan*

*Corresponding author: E-mail address: kotaro.tanaka.comb@vc.ibaraki.ac.jp;

Tel/Fax +81-294-38-5080

Abstract

A compact multi-pass cell with a pair of cylindrical mirrors for sensitive detection of trace gases in emission from combustion was constructed. The cell path-length was 9.8 m and its volume was 0.13 L. Each mirror shape was a square with a side length of 25.4 mm and the mirrors were placed 100 mm apart. The cell was applied to detection of formaldehyde (HCHO), which is formed during fuel combustion and is harmful to the environment. The direct absorption spectrum in the range 2979.06–2981.2 cm⁻¹ was recorded with a mid-infrared distributed feedback (DFB) interband cascade laser. The recorded spectrum of HCHO was in good agreement with a spectrum simulated using the HITRAN 2012 database. An absorption line at 2979.663 cm⁻¹ (4.26×10^{-21} cm²molecule⁻¹cm⁻¹, ν_5 , 11₈₄–10₇₃), which showed the strongest absorption in the emission frequency range of the DFB

27 interband cascade laser, was selected for HCHO detection. We also confirmed that there were no
28 interferences of absorption peaks of major combustion products in the selected HCHO absorption
29 peaks. At a signal-to-noise ratio of two and 3 kPa using $2f$ wavelength modulation spectroscopy at
30 less than 1 MHz bandwidth, the limit of detection for HCHO was 73 parts per billion by volume.

31

32

33 1. Introduction

34 Real time measurements of trace gases using laser absorption spectrometry (LAS) provide
35 important information for reducing emissions of gases from fossil fuel combustion. The
36 measurement sensitivity for LAS is dominated by the concentration of the measured gas, the
37 absorption cross section of absorbing species, and the total light path length, based on the
38 Beer-Lambert law. For high-sensitivity measurements, it is desirable to combine advanced
39 spectroscopy techniques, such as wavelength modulation spectroscopy (WMS) [1] and cavity
40 ring-down spectroscopy [2], with strong ro-vibrational molecular transitions.

41 Optical cells with long path lengths can be used for high-sensitivity measurements of trace gases.
42 Studies using long path cells have been performed in a number of areas, including atmospheric
43 measurements, combustion processes, and portable emission measurement systems (PEMS) for
44 on-board real-time measurements of automobile exhaust. Many fields require compact measuring
45 devices, and the compact multi-pass cell has become important. Especially, for PEMS for measuring
46 automobile exhaust, the compact cell with a long path length is required, because a small size pump
47 can be set for the small size cell, which leads to saving electricity consumption used in the total
48 system. The most frequently used multi-pass cells are the White cell [3] and the Herriott cell [4].
49 Cells with denser spot patterns and smaller size than the White and the Herriott cells have been
50 produced with two cylindrical mirrors [5–8]. Hao et al. developed a model for a cell with two
51 cylindrical mirrors [5]. Silver investigated the behavior of a multi-pass cell, including light patterns
52 and beam density, when one cylindrical mirror was rotated with respect to the other mirror [6]. Based
53 on the model of Hao et al., Kasyutich et al. constructed a cell with a path length of 15.18 m using
54 cylindrical mirrors ($\varnothing$ 76 mm) spaced 110 mm apart [7]. More recently, Das et al. developed a cell
55 with a path length of 50.31 m using 40 mm diameter mirrors spaced 88.9 mm apart [8]. A compact
56 dense-pattern multi-pass cell has been constructed using two concave spherical mirrors to give an
57 effective optical path length of 26.4 m [9].

58 For trace gas measurements, the selection of a measurement wavelength that coincides with the

ro-vibrational molecular transitions for fundamental vibrational modes in the mid-infrared region is essential because these transitions show strong absorptions. Advances in semiconductor laser technology, including development of high-quality narrow bandwidths, have contributed to the success of trace gas measurements in the mid-IR region [10–12]. The 3 μm wavelength region is particularly important as it contains the C–H and O–H vibrational modes, which show strong absorptions. There are few light sources that are suitable for the 3 μm region, and quasi-phase-matched difference-frequency generation systems have been widely used [13]. Recently, distributed feedback (DFB) interband cascade lasers, which directly emit light in the 3 μm region with narrow line width of less than 1 MHz and good stability, have been used for high sensitivity measurements of trace gases. The 3 μm region is important for high sensitivity measurements of hydrocarbons in combustion emission, because there are many hydrocarbon absorption bands in the 3 μm region [14]. For example, formaldehyde (HCHO) is one of the important intermediate species in the oxidation of the hydrocarbons [15], and is present in industrial exhaust gas [16]. Because HCHO is harmful to the environment, measurements of HCHO are very important for environmental monitoring. Several studies have conducted measurement of HCHO using LAS in the mid-infrared region [17–21]. Lundqvist et al. measured HCHO at 3493 nm and their detection limit was 1 ppm [17]. Wang et al. observed HCHO at high temperatures in shock tube kinetic study at 3453 nm [21]. HCHO measurements with WMS and the multi-pass cell were also performed at 3.6 μm [18, 19] and 5.68 μm [20]. Detection limit was achieved to be 6 ppb [19] at 2778.5 cm^{-1} ($3.1 \times 10^{-20}\text{ cm}^2\text{ molecule}^{-1}\text{ cm}^{-1}$, ν_1 , $5_{50}-5_{51}$).

In this study, a compact multi-pass cell was developed using two cylindrical mirrors separated by a distance of 100 mm, which gave an effective path-length of 9.8 ± 0.1 m. This cell was coupled with a mid-IR DFB interband cascade laser in the 3.3 μm range and applied to measurements of trace gaseous HCHO. A second derivative (2f) WMS technique was used to detect HCHO. To utilize the spectroscopic measurements system for the PEMS for measuring HCHO in combustion exhaust, the compact optics system (45 cm $\times$ 45 cm square) was constructed with keeping the high-sensitive level

to detect HCHO in combustion exhaust (~ ppm level) [16].

2. Development of the multi-pass cell

The theory behind a multi-pass cell with two cylindrical mirrors has been described by Kasyutich and Martin [7]. A schematic diagram of the multi-pass cell is shown in Fig. 1. A cell such as this uses a cylindrical mirror M_1 with a focal length f_1 and a central input/output hole. An xy -plane is set at the central hole of M_1 , and a horizontal axis against the xy -plane is defined as the z -axis. The position $z = 0$ is at the center of the hole in M_1 , and a cylindrical mirror M_2 with a focal length f_2 is set at $z = d$ and placed parallel to M_1 at a rotational angle $\beta \neq 0$. An input beam is introduced into the cell through the hole in M_1 at an angle α in the xz -plane. When the radii of the curvatures of the two cylindrical mirrors, the distance between the mirrors, and β are adjusted adequately, the N th reflected beam exits the cell at an angle $-\alpha$ on the xz -axis through the hole in M_1 . The parameters for determining the beam patterns (e.g. radii of the curvatures, mirror placement distance, and β) can be obtained by calculating the ray matrix formalism [22].

Using this theory, we constructed a compact multi-pass cell equipped with two 25.4 mm square cylindrical mirrors that gave a path length of 9.8 ± 0.1 m. Calculated spot patterns expected for 106 passes (total path length = 10.6 m) with cylindrical curvatures of $f_1 = f_2 = 100$ mm, $\alpha = 4^\circ$ and $\beta = 53.8^\circ$ are shown in Fig. 2(a) for M_1 and 2(b) for M_2 at $d = 100$ mm. The diameter of the central hole of M_1 was 4 mm, and light passed through this. Both M_1 and M_2 were coated with gold and had reflectivity of 97%. Because the light intensity of the output reduces exponentially with the number of reflections, high-reflectivity mirrors are required to achieve very long optical path lengths with sufficient light intensity. Although it is necessary to count the number of spots to determine the path length, this is difficult in practice. In this case, the laser intensity was modulated, and the phase shift induced by the path in the cell was measured as described previously [8]. The same procedure was performed and the path length was determined by the phase difference between the input and output beams, which gave a path length of 9.8 ± 0.1 m. There was a discrepancy between the measured and

the calculated path lengths, which arose from the precision of the curvatures of the cylindrical mirrors or the parallelism of the two mirrors. Mirror mounts made of stainless steel were used. M_2 was set in a rotating mirror holder in the cell so that β (Fig. 1) could be adjusted. The cell body was made of quartz glass so that spots on the mirrors could be visualized.

3. Experiments

The experimental apparatus is shown in Fig. 3. A 3.356 μm DFB interband cascade laser (Nanoplus, Gerbrunn, Germany) with a maximum output power of 1.2 mW was used as the light source. The injection current and the laser-chip temperature of the interband cascade laser were maintained using a laser control unit (ILX LDC3724C, ILX Lightwave, Bozeman, MT, USA). The beam was collimated with an anti-reflection coated aspheric lens ($f = 11$ mm) and introduced into the multi-pass cell. The cell had a path length of 9.8 ± 0.1 m and a volume of 0.13 L. Before introducing into the cell, the beam was focused onto the center of the multi-pass cell using a CaF_2 lens with a focal length of 150 mm. The beam passed through the multi-pass cell and was focused on an InSb photodiode detector (HAMAMATSU P4631-03, Hamamatsu, Japan). The optics was set up within a $45 \text{ cm} \times 45 \text{ cm}$ square.

HCHO was detected using $2f$ WMS. The wavelength of the DFB interband cascade laser was modulated sinusoidally at 13.5 kHz using the output of a digital lock-in amplifier (Stanford Research Systems, SR810, Sunnyvale, CA, USA). The laser was scanned at 1 Hz by changing the injection current, which was controlled by a triangle voltage wave supplied by a function generator (Wavestation 2012, Teledyne Lecroy, Chestnut Ridge, NY, USA). The signal obtained from the photodetector was received by a lock-in amplifier with a 10 ms time constant and 24 db/oct digital filtering, which corresponded to an equivalent noise bandwidth of 7.8125 Hz. The modulation condition was adjusted to obtain the highest signal-to-noise ratio for the $2f$ WMS of HCHO. The data were acquired using a laptop computer with a 16 bit AD PCMA card (AD16-8/2(CB)L, CONTEC, Osaka, Japan).

The multi-pass cell was evacuated using a rotary pump, and the pressure in the cell was monitored

using a capacitance manometer (Model 730, Setra, Boxborough, MA, USA). The pressure was kept at 3 ± 0.01 kPa. A PID controller (E5CN-RQ2BT, Omron, Kyoto, Japan) was used to control the gas and cell temperature at 393 ± 0.01 K. HCHO gas was generated by evaporation of paraformaldehyde at 443 K in a glass bottle and diluted by a pure nitrogen (Taiyo Nissan, >99.99995%). The concentration of HCHO was determined from the partial pressure in the cell.

4. Results and discussion

4.1 Measurements of HCHO spectrum in the $3.3 \mu\text{m}$ region

A direct absorption spectrum of 6% HCHO diluted by with nitrogen (99.999%) was obtained using the new multi-pass cell at a total pressure of 1 kPa in the $2979.5\text{--}2981.2 \text{ cm}^{-1}$ region, as shown in Fig. 4(a). A simulated spectrum shown in Fig. 4(b) was calculated with parameters in the HITRAN 2012 database [23] at 393 K. The measured spectrum agreed with the simulated one. Two absorption peaks, labeled with asterisks in Fig. 4(a), are not listed as HCHO in the HITRAN 2012 database. These peaks may be from contaminants in paraformaldehyde, for instance, H_2O , which has absorption peaks at 2980.240 cm^{-1} and 2980.388 cm^{-1} . The absorption line with the largest cross section, which was detected at 2979.663 cm^{-1} ($4.26 \times 10^{-21} \text{ cm}^2 \text{ molecule}^{-1} \text{ cm}^{-1}$, ν_5 , $11_{84}\text{--}10_{73}$), was selected for the HCHO measurements. When HCHO in combustion emission is measured, absorption interference that derives from combustion products is required to be accounted for. The simulated spectra of HCHO, ethylene, methane, ethane, and water at around 2979.663 cm^{-1} at 3 kPa are shown in Fig. 5. Although ethylene and water have absorption peaks in this wavelength region, there are no interference of their absorption peaks in the selected HCHO absorption peak. Methane and ethane also have absorption peaks at around 2979.663 cm^{-1} , whose cross sections are two orders lower than that of HCHO. For example, in the case of typical combustion condition where equivalence ratio is 1.0 or less than 1.0, HCHO concentration has been approximately same or larger than those of methane or ethane [24], which indicate that methane and ethane is insignificant for HCHO measurement. It has also been reported that various kinds of hydrocarbons are included in

combustion emission [25, 26, 27] and main species are small sized hydrocarbons such as methane, ethane and HCHO, whose concentrations are at least a factor of two larger than those of other hydrocarbons [26]. Therefore, if other hydrocarbons have the absorption peaks at around 2979.663 cm^{-1} , it is considered that their peaks have little influence on HCHO measurements in combustion emission. Although carbon dioxide, carbon monoxide, and nitrogen oxide are major combustion products, they have no absorption peaks in this wavelength region.

4.2 Limit of detection

The $2f$ WMS spectrum for 50 ppm HCHO at 3 kPa and 393 K is shown in Fig. 6. Signals were averaged over 40 consecutive scans at 1 Hz. The modulation amplitude, v_m/v_{HCHO} , was optimized to 2.13 to obtain the best signal-to-noise ratio for the $2f$ WMS signal. This modulation amplitude was consistent with the theoretical value of 2.2 [28]. To assess the signal stability with the measurement system using the developed compact multi-pass cell, continuous measurements of 100 ppm HCHO at 3 kPa and 393 K were performed by $2f$ WMS over 1800 s. The signal was obtained with 1 Hz resolution. The time series of HCHO signals and the associated Allan variance (σ_A^2) were plotted, as shown in Fig. 7. From the Allan variance plot, an optimum integration time of 40 s with $\sigma_A^2 = 1.04 \times 10^{-9}$ was derived.

The limit of detection was obtained using a plot of the WMS signals for concentrations between 6 and 36 ppm shown in Fig. 8. The WMS signal intensities, which are the difference between the peak intensity and the base line, were proportional to the HCHO concentrations. The slope and the noise level, which was determined from the average baseline deviation, were used to calculate the limit of detection for a signal-to-noise ratio of two. The limit of detection was 73 ± 6 ppb. The WMS spectrum with 50 ppm HCHO shown in Fig. 6 had an approximate signal-to-noise ratio of 1324, and the limit of detection for a signal-to-noise ratio of two was 75 ppb. This value was consistent with that obtained from the slope and the baseline. From these results, the minimum detectable absorbance is obtained to be approximately 1.0×10^{-7} . The limit of detection obtained at $5.68\text{ }\mu\text{m}$ and 5 kPa with $2f$ WMS

using multi-pass cell, which had 36 m optical path length, was reported to be ~ 2.5 ppb [20]. As the integrated cross sections at around $3.3\ \mu\text{m}$ is approximately 20 times smaller than those at around $5.68\ \mu\text{m}$ [23], the present limit of detection obtained using our developed spectrometer is consistent with that reported in the previous study [20]. Although the limit of detection was reasonable, the maximum detectable absorbance has reported to be approximately 3.0×10^{-8} [19]. Reducing the signal noise derived from the optics, such as the non-AR coated window of the cell, would improve the detection limit for HCHO measurements using the cell. Dense beam spots on the cylindrical mirrors can interfere with the laser beam spot on the mirrors, and this affects the noise level. Therefore, a narrow diameter laser beam is beneficial for improving the limit of detection. Even though the limit of detection could be improved, the present system will still allow for measurement of HCHO at the levels it is typically found at in emissions from combustion, which are usually on the order of parts per million [29, 30].

Conclusions

We constructed a compact and sensitive spectrometer for measurements of trace gases using WMS coupled with a new developed multi-pass cell. The multi-pass cell (volume 0.13 L) consists of two cylindrical mirrors placed 100 mm apart giving a path length of 9.8 ± 0.1 m. HCHO was selected as a representative trace gas in emissions from combustion. HCHO was measured at $2979.663\ \text{cm}^{-1}$ ($4.26 \times 10^{-21}\ \text{cm}^2\text{molecule}^{-1}\text{cm}^{-1}$, ν_5 , $11_{84}-10_{73}$) using a mid-IR DFB interband cascade laser. The estimated limit of detection was 73 ± 6 ppb at 393 K and 3 kPa with averaging over 40 consecutive scans. This portable measurements system with the compact multi-pass cell can be a powerful tool for measurements of trace gases in emissions from combustion, such as in automobile exhaust.

Acknowledgements

The authors thank Mr. Masahiro Sekita and Mr. Syunsuke Fukagawa for helping with the experiments. This study was partly supported by JSPS KAKENHI (Grant Numbers 2682005 and

215 26288086), and by Council for Science, Technology and Innovation (CSTI), Cross-ministerial
216 Strategic Innovation Promotion Program (SIP), “Innovative Combustion Technology” (Funding
217 agency: JST).

218

219

220 **Figure captions**

221 Figure 1

222 Geometry of the cell with two cylindrical mirrors.

223

224 Figure 2

225 Calculated spot pattern of 106 passes on (a) mirror M_1 and (b) mirror M_2 at $d = 100$ mm, $f_1 = f_2 = 100$
226 mm, $\beta = 53.8^\circ$ and $\alpha = 4^\circ$.

227

228 Figure 3

229 Schematic diagram of the experimental setup.

230

231 Figure 4

232 (a) Experimental direct absorption spectrum of 6% HCHO with 1 kPa of N₂ at 393 K; and (b)
233 simulated spectrum at a total pressure of 1 kPa at 393 K using spectroscopic parameters in the
234 HITRAN 2012 database [23]. The absorption peaks labeled by asterisks are not listed as HCHO in
235 the HITRAN 2012 database, and the species are unknown.

236

237 Figure 5

238 Simulated spectra of HCHO, ethylene, methane, ethane and water at 3 kPa using parameters in
239 HITRAN 2012 database [23].

240

241 Figure 6

242 Second-harmonic WMS signals for 50 ppm HCHO at 2979.663 cm^{-1} at 3 kPa and 393 K.

243

244

245

246 Figure 7

247 Top: Time profiles of the 100 ppm HCHO signals. Bottom: Allan variance plot. The broken line
248 shows the white noise.

249

250 Figure 8

251 Signal intensity of HCHO as a function of concentration. A least squares fitting line is also shown in
252 the graph.

253

References

1. J. A. Silver, Frequency-modulation spectroscopy for trace species detection: theory and comparison among experimental methods, *Appl. Opt.* **31**, 707 (1992).
2. G. Berden, R. Engeln: *Cavity Ring-Down Spectroscopy Techniques and Applications*(Blackwell, Oxford, UK 2009).
3. J. U. White, Long optical paths of large aperture, *J. Opt. Soc. Am.* **32**, 285 (1942).
4. D. Herriott, H. Kogelnik, R. Kompfner, Off-axis paths in spherical mirror interferometers, *Appl. Opt.* **3**, 523 (1964).
5. L. Hao, S. Qiang, G. Wu, L. Qi, D. Feng, Q. Zhu, Cylindrical mirror multipass Lissajous system for laser photoacoustic spectroscopy, *Rev. Sci. Instrum.* **73**, 2079 (2002).
6. J. A. Silver, Simple dense-pattern optical multipass cells, *Appl. Opt.* **44**, 6545 (2005).
7. V. L. Kasyutich, P. A. Martin, Multipass optical cell based upon two cylindrical mirrors for tunable diode laser absorption spectroscopy, *Appl. Phys. B* **88**, 125 (2007).
8. D. Das, A. C. Wilson, Very long optical path-length from a compact multi-pass cell, *Appl. Phys. B* **103**, 749 (2011).
9. K. Liu, L. Wang, T. Tan, G. Wang, W. Zhang, W. Chen, X. Gao, Highly sensitive detection of methane by near-infrared laser absorption spectroscopy using a compact dense-pattern multipass cell, *Sens. Actuators, B* **220**, 1000 (2015).
10. A. Kosterev, G. Wysocki, Y. Bakhirkin, S. So, R. Lewicki, M. Fraser, F. Tittel, R. F. Curl, Application of quantum cascade lasers to trace gas analysis, *Appl. Phys. B* **90**, 165 (2008).
11. W. Chen, J. Cousin, E. Pouillet, J. Burie, D. Boucher, X. Gao, M. W. Sigrist, F. K. Tittel, Continuous-wave mid-infrared laser sources based on difference frequency generation, *C. R. Phys.* **8**, 1129 (2007).
12. L. Naehle, S. Belahsene, M. Edlinger, M. Fischer, G. Boissier, P. Grech, G. Narcy, A. Vicet, Y. Rouillard, J. Koeth, L. Worschech, Continuous-wave operation of type-I quantum well DFB laser diodes emitting in 3.4 μm wavelength range around room temperature, *Electron. Lett.* **47**,

- 280 46 (2011).
- 281 13. F. K. Tittel, D. Richter, A. Fried, Mid-infrared laser applications in spectroscopy, *Appl. Phys.* **89**,
282 458 (2003).
- 283 14. R. K. Hanson, D. F. Davidson, Recent advances in laser absorption and shock tube methods for
284 studies of combustion chemistry, *Prog. Energy Combust. Sci.* **44**, 103 (2014).
- 285 15. M. J. Pilling: Low-temperature combustion and autoignition: Comprehensive chemical kinetics
286 (Elsevier, Netherland, 1997).
- 287 16. J. K. E. Johansson, J. Mellqvist, J. Samuelsson, B. Offerle, J. Moldanova, B. Rappengluck, B.
288 Lefer, J. Flynn, Quantitative measurements and modeling of industrial formaldehyde emissions
289 in the Greater Houston area during campaigns in 2009 and 2011, *J. Geophys. Res.: Atmos.* **119**,
290 7 4303 (2014).
- 291 17. S. Lundqvist, P. Kluczynski, R. Weih, M. V. Edlinger, L. Nahle, M. Fischer, A. Bauer, S. Hofling,
292 J. Koeth, Sensing of formaldehyde using a distributed feedback interband cascade laser emitting
293 around 3493 nm, *Appl. Opt.* **51**, 6009 (2012).
- 294 18. L. Dong, Y. Yu, C. Li, S. So, F. K. Tittel, Ppb-level formaldehyde detection using a CW
295 room-temperature interband cascade laser and a miniature dense pattern multipass gas cell, *Opt.*
296 *Express* **23**, 19821 (2015).
- 297 19. W. Ren, L. Luo, F. K. Tittel, Sensitive detection of formaldehyde using an interband cascade
298 laser near 3.6 μm , *Sens. Actuators, B* **221**, 1062 (2015).
- 299 20. J. Li, U. Parchatka, H. Fischer, A formaldehyde trace gas sensor based on a thermoelectrically
300 cooled CW-DFB quantum cascade laser, *Anal. Methods* **6** 5483 (2014).
- 301 21. S. Wang, D. F. Davidson, R. K. Hanson, High-temperature laser absorption diagnostics for CH₂
302 O and CH₃ CHO and their application to shock tube kinetic studies, *Combust. Flame* **160**, 1930
303 (2013).
- 304 22. H. Kogelnik, T. Li, Laser beams and resonators, *Proc. IEEE* **54**, 1312 (1966).
- 305 23. L. S., Rothman, I. E., Gordon, Y., Babikov, A., Barbe, D., Chris Benner, P. F., Bernath, M., Birk,

- 306 L., Bizzocchi, V., Boudon, L. R., Brown, A., Campargue, K., Chance, E. A., Cohen, L. H.,
307 Coudert, V. M., Devi, B. J., Drouin, A., Fayt, J. M., Flaud, R. R., Gamache, J. J., Harrison, J. M.,
308 Hartmann, C., Hill, J. T., Hodges, D., Jacquemart, A., Jolly, J., Lamouroux, R. J., Le Roy, G., Li,
309 D. A., Long, O. M., Lyulin, C. J., Mackie, S. T., Massie, S. N., Mikhailenko, H. S. P., Muller, O.
310 V., Naumenko, A. V., Nikitin, J., Orphal, V., Perevalov, A., Perrin, E. R., Polovtseva, C., Richard,
311 M. A. H., Smith, E., Starikova, K., Sung, S., Tashkun, J., Tennyson, G. C., Toon, V. I. G.,
312 Tyuterev, G., Wagner, The HITRAN2012 molecular spectroscopic database, *J. Quant. Spectrosc.*
313 *Radiat. Transf.* **130**, 4 (2013).
- 314 24. O. Herbinet, B. Husson, Z. Serinyel, M. Cord, V. Warth, R. Fournet, P. Glaude, B. Sirjean, F.
315 Battin-Leclerc, Z. Wang, M. Xie, Z. Cheng, F. Qi, Experimental and modeling investigation of
316 the low-temperature oxidation of n-heptane, *Combust. Flame*, **159**, 3455 (2012).
- 317 25. Ho, K. F., Ho, S. S. H., Lee, S. C., Louie, P. K. K., Cao, J., Deng, W., Volatile organic
318 compounds in roadside environment of Hong Kong, *Aerosol. Air. Qual. Res.*, **13**, 1331 (2013).
- 319 26. Chin, J. Y., Batterman, S. A., Northrop, W. F., Bohac, S. V., Assanis, D. N., Gaseous and
320 particulate emissions from diesel engines at idle and under load: Comparison of biodiesel blend
321 and ultralow sulfur diesel fuels, *Energy Fuels*, **26**, 6737 (2012).
- 322 27. Guo, H., Zou, S. C., Tsai, W. Y., Chan, L. Y., Blake, D. R., Emission characteristics of
323 nonmethane hydrocarbons from private cars and taxis at different driving speeds in Hong Kong,
324 *Atmos. Environ.*, **45**, 2711 (2011).
- 325 28. J. Reid, D. Labrie, Second-harmonic detection with tunable diode lasers—comparison of
326 experiment and theory, *Appl. Phys. B*, **26**, 203 (1981).
- 327 29. R. Holzinger, C. Waeneke, A. Hansel, A. Jordan, W. Lindinger, Biomass burning as a source of
328 formaldehyde, acetaldehyde, methanol, acetone, acetonitrile, and hydrogen cyanide, *Geophys.*
329 *Res. Lett.* **26**, 1161 (1999).
- 330 30. S. M. Correa, G. Arbilla, Formaldehyde and acetaldehyde associated with the use of natural gas
331 as a fuel for light vehicles, *Atmos. Environ.* **39**, 4513 (2005).

Figure 1

Figure 2

32

Figure 3

Figure 4

Figure 5

62

63

64

65

66

67

68

69

70

71

72

Figure 6

Figure 7

Figure 8