A tunable diode laser absorption spectrometer for formaldehyde atmospheric measurements validated by simulation chamber instrumentation

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Abstract

A tunable diode laser absorption spectrometer (TDLAS) for formaldehyde atmospheric measurements has been set up and validated through comparison experiments with a Fourier transform infrared spectrometer (FT-IR) in a simulation chamber. Formaldehyde was generated in situ in the chamber from reaction of ethene with ozone. Three HCHO ro-vibrational line intensities (at 2909.71, 2912.09 and 2914.46 cm⁻¹) possibly used by TDLAS were calibrated by FT-IR spectra simultaneously recorded in the 1600–3200 cm⁻¹ domain during ethene ozonolysis, enabling the on-line deduction of the varying concentration for HCHO in formation. The experimental line intensities values inferred confirmed the calculated ones from the updated HITRAN database. In addition, the feasibility of stratospheric in situ HCHO measurements using the 2912.09 cm⁻¹ line was demonstrated. The TDLAS performances were also assessed, leading to a 2σ detection limit of 88 ppt in volume mixing ratio with a response time of 60 sec at 30 Torr and 294 K for 112 m optical path. As part of this work, the room-temperature rate constant of this reaction and the HCHO formation yield were found to be in excellent agreement with the compiled literature data.

Key words: formaldehyde; ethene ozonolysis; in situ measurements; stratosphere; simulation chamber; TDLAS; FT-IR

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Introduction

Formaldehyde plays a key role in the odd hydrogen family (HOx = OH + HO₂) chemistry, with its subsequent involvement in HO₂ production (Seinfeld and Pandis, 2006). The largest sources of tropospheric HCHO come from the oxidation of methane (CH₄) and other non-methane volatile organic compounds (VOCs), which have both natural and anthropogenic origins (Anderson et al., 1996). Biomass burning, incomplete combustion, emissions from industries and vegetation represent the main direct emission sources (Carlier et al., 1986; Lee et al., 1998). The main loss processes include photolysis by ultraviolet (UV) radiation and oxidation by OH radicals. Formaldehyde removal can also take place through dry deposition, heterogeneous loss on aerosol particles (Tie et al., 2001), cloud chemistry and precipitation scavenging (e.g., Lelieveld and Crutzen, 1990; Heikes, 1992). HCHO has its greatest mixing ratio in the boundary layer, near its emission sources. Its abundance decreases with altitude up to the upper troposphere, where it can reach values as low as a few tens of ppt in volume mixing ratios (Dufour et al., 2009). The lifetime of formaldehyde regarding the major chemical and physical removal pathways is of the order of a few hours in the troposphere (Possanzini et al., 2002).

In the upper troposphere, HCHO is found to be a relevant indicator for testing the presence of additional HOx precursor species possibly moved upward by convective transport (Crawford et al., 1999). In the stratosphere, the abundance of HCHO increases with altitude, mainly as a result of the oxidation of methane by OH and O(1D), resulting in a “C-shaped” vertical profile from the troposphere to the stratosphere (Barth et al., 2007).

Formaldehyde concentrations have never been measured in situ in the stratosphere. Up to now, only three remote vertically resolved satellite measurements of HCHO have been reported, one by SMR (Sub-Millimeter Radiometer) aboard Odin satellite (Ricaud et al., 2007) in the upper stratosphere (> 35 km altitude), and the other ones by MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) aboard Envisat (Steck et al., 2008) and by FTS (Fourier Transform Spectrometer) aboard ACE-SCISAT (Coheur et al., 2007; Dufour et al., 2009). Whereas the MIPAS measurements are performed using several spectral micro-windows in the 5.7 μm region (i.e., the v₂ band centred at 1746 cm⁻¹), the FTS measurements use the 3.6 μm region (i.e., around 2600–3100 cm⁻¹). Formaldehyde indeed shows strong v₁ and v₅ fundamental vibration bands centred at 2782 and 2844 cm⁻¹, respectively.

TDLAS (Tunable Diode Laser Absorption Spectrometry) measurements of HCHO in the upper troposphere.
no Chamber of ICARE-Orléans. The conventional methods implementing TDLAS instrumentation in the simulation second goal of the study is to evaluate the interest of polymerization and wall adsorption was expected. The was thus produced (2007; Perrin et al., 2009). In the present study, HCHO is rather challenging (Gratien et al., 2007; Brauers et al., sticky and polymerizable, its concentration determination with consistent values between both bands. The well- recorded in an atmospheric simulation chamber, and hence −ing the whole region (1600–3200 cm−1) bands, based on some FT-IR (Fourier transform infra red) −ing a consistent values, which needs confirmation, all the more so as two −ing the three line intensities in the range 2909–2915 cm−1, which opens possibility for field measurements. Several spectroscopic studies have reported line param- eters for the v5 band, but with intensities in disagreement with each other by up to a factor of three (Rothman et al., 2005, Herndon et al., 2006, Perrin et al., 2006, 2009). The study of Perrin et al. (2009) recently identified the reasons of the discrepancies and has been included into the new HITRAN database (Rothman et al., 2009). The existence of numerous overtones and combination bands has sometimes led to inconsistencies in blended or degenerate doublet lines. This study derived a consistent set of line intensity parameters for both the 3.6 and 5.7 µm bands, based on some FT-IR (Fourier transform infra red) lines measurements covering the whole domain (1600–3200 cm−1) and on theoretical spectroscopy calculations. However, this study is the first one delivering consistent values, which needs confirmation, all the more so as two −ing the three line intensities in the range 2909–2915 cm−1 were not directly measured. The first goal of the present study is to determine the ab- solute intensity of these specific lines to allow for deriving reliable stratospheric HCHO concentrations using airborne or balloon-borne instruments such as SPIRALE. Our line calibrations were performed using FT-IR spectra covering the whole region (1600–3200 cm−1) simultaneously recorded in an atmospheric simulation chamber, and hence with consistent values between both bands. The well- known chemical reaction system of ethene ozonolysis was used as source of formaldehyde. Given this compound is sticky and polymerizable, its concentration determination is rather challenging (Gratien et al., 2007; Brauers et al., 2007; Perrin et al., 2009). In the present study, HCHO was thus produced in situ, which has the great advantage to lead to low and so, accurate concentrations, since no polymerization and wall adsorption was expected. The second goal of the study is to evaluate the interest of implementing TDLAS instrumentation in the simulation chamber of ICARE-Orléans. The conventional methods currently used for laboratory measurements of formalde- hyde are limited in detection limit (> 50 ppt in volume mixing ratio units) and/or in measurement frequency (> 1 min) (Hak et al., 2005; Wisthaler et al., 2008; Hotte et al., 2009; Jobson and McCoskey, 2010). TDLAS method is expected to be at least as sensitive, and is known to perform rapid on-line measurements (in a few seconds), which is the main reason for its use aboard mobile instruments such as airborne or balloon-borne spectrometers. In the case of static measurements performed in laboratory simulation chambers, the very short response time should allow for lowering the detection limit and improving the accuracy of the kinetics and mechanistic studies. The well-established reaction of ethene with ozone has been used in the present work to test the TDLAS potentiality with respect to the already existing chamber instrumentation.

1 Experimental

1.1 Atmospheric simulation chamber

Experiments were carried out in the 7300 L ICARE indoor atmospheric simulation made of Fluorene-Ethene-Propene (FEP) foil (DuPont) with a parallellepiped shape. The experiments were performed at (294 ± 1) K in dry purified air (relative humidity, RH < 2%). The chamber was operated at 0.08 Torr above the atmospheric pressure to avoid external contamination and to compensate the sampling flows of the various instruments connected to the chamber. This was achieved during the experiments by continuously adding 5 to 20 L/min of purified air. Between experiments, the chamber was cleaned by flushing it with purified air at a flow rate of 100 L/min for at least 12 hr. A fan made of Teflon insured homogeneous mixing of the reactant within 1 min.

Temperature and relative humidity were monitored by a combined sensor (T870-Series T800, Dostmann elec- tronic, Germany) and the differential pressure was measured using an MKS gauge (0–10 Torr range). The chamber is equipped with an in situ FT-IR spectrometer (Nicolet 5700 Magna) coupled to a White-type multipass cell resulting in an optical path length of 166 m. HgCdTe/B semiconductor was used as detector and cooled with liquid nitrogen at a temperature close to 77 K. The instrument was operated in the mid-IR region, from 4000 to 600 cm−1. The IR spectra were recorded every 4 min 15 sec by co-adding 110 interferograms with a resolution of 1 cm−1, using Happ-Genzel apodization. IR spectra acquisition was operated using OMNIC software (OMNIC, Thermo Electron Corporation, version 6.2). Reactants (ethene and ozone) and products were monitored during the course of the reaction and their concentrations were determined using calibrated reference spectra. The chamber is also equipped with gas monitors for ozone (Horiba, APOA-360) and NO, NO2, and NOx (Horiba, APNA-360), which enabled to measure the O3 concentration and any NOx background during the experiments. Ozone was generated from an electric discharge in an oxygen flow of 2 L/min capable of fast introduction into the chamber, which enables to reach the
desired concentration in few minutes. Known amounts of the C$_2$H$_4$ and SF$_6$ were introduced into the chamber using a calibrated 0.9 L cylinder equipped with two pressure gauges (0–10 Torr and 0–1000 Torr, MKS Baratron). All experiments presented here were conducted in the dark.

Dilution and leak rates were determined before the start of each experiment by monitoring the decay of added amount of SF$_6$ (190 ppb volume mixing ratio) using the IR band (948 cm$^{-1}$). This decay rate was found to be in the range 1×10$^{-5}$–4×10$^{-5}$ sec$^{-1}$ depending on the experimental conditions (added flow during the runs). Ozone was injected before adding ethene, to estimate its total loss rate. This one was found to be slightly higher than that of SF$_6$ (2.6×10$^{-5}$–7.9×10$^{-5}$ sec$^{-1}$). Ethene loss rate, determined in independent runs, was found to be similar to that of SF$_6$. Before each experiment, background concentrations in the chamber were checked systematically and found to be lower than the detection limits (e.g., [NOx] < 1 ppb, [O$_3$] < 1 ppb).

1.2 Tunable diode laser absorption spectrometer (TDLAS)

Gas mixture samples from the simulation chamber were continuously collected via a PFA Teflon tube (6 mm o.d.) and passed through the TDLAS multipass absorption cell, with a controlled flow of 3.0 L min$^{-1}$, using a scroll pump (XDS10 Boc Edwards). It is known that loss of HCHO in the sampling line made of Teflon is not significant (Wert et al., 2002; Herndon et al., 2007). This has been verified by observing no concentration change in the TDLAS cell when the tube length was varied by a factor of two. The pressure cell was around 30 Torr, precisely known (±1 Torr) using a 0–100 Torr range gauge (MKS Baratron), and maintained constant by tuning a simple valve located at the micro-window (0.4–0.7 cm$^2$) swept by the laser. The laser beam was directed through the multipass cell where it was selectively absorbed by the HCHO spectral features. The output beam was directed onto a liquid-N$_2$ cooled HgCdTe detector.

2 Results and discussion

Formaldehyde has been generated in the chamber under two types of experimental conditions, corresponding to two different concentration levels of C$_2$H$_4$ and O$_3$: one at higher concentration to calibrate the TDLAS instrument using FT-IR spectroscopy measurement, and another one at lower concentration to intercompare TDLAS and FTIR performances. This formaldehyde production mean has been earlier used by different groups for the calibration of instruments working at atmospheric concentration levels of formaldehyde (e.g., Brauers et al., 2007). Both sets of experiments were conducted without adding OH radicals scavenger to the reactants mixture (that could be generated during the ozonolysis of ethene), which implies that formaldehyde could also be produced through the reaction of OH with ethene (Paulson et al., 1999; Rickard et al., 1999; Mihelcic et al., 1999; Fenske et al., 2000; Kroll et al., 2001).

2.1 Rate constant of the reaction of ozone with ethene

Prior to TDLAS calibration, a check of the chemical
system used to generate formaldehyde was performed by deriving the rate constant value for the ethene ozonolysis reaction under pseudo first-order conditions. The measurements were conducted at (760 ± 1) Torr and (294 ± 1) K. One typical initial set of C₂H₄ and O₃ volume mixing ratios was (4.5 ± 0.3) ppm and (465.0 ± 0.1) ppb, respectively. Figure 1 shows the plot of ozone consumption versus reaction time in the absence and presence of C₂H₄ for these initial conditions. The reaction rate constant derived from this run is \( k = (1.55 ± 0.11) \times 10^{-18} \text{ cm}^3/(\text{molecule} \cdot \text{sec}) \), which is in excellent agreement with the recommended value \( 1.11 \times 10^{-14} \text{ mol/cm}^3 \) (Atkinson et al., 2006), indicating that the consumption of O₃ in our experimental system was not affected by any noticeable side reactions.

2.2 Validation of the formaldehyde FT-IR spectrum recorded in the Euphore atmospheric simulation chamber

The reaction of ozone with ethene is known to produce formaldehyde with a yield near unity (Horie and Moortgat, 1998; Neeb et al., 1998; Brauers et al., 2007; Wegener et al., 2007). In addition, OH radicals are also produced, with a yield of 0.16 (Atkinson et al., 2006). The OH radicals formed could react with both ethene and formaldehyde. However, considering the concentrations of O₃ formed could react with both ethene and formaldehyde.

During the experiments, HCHO concentrations were derived using a scaled reference spectrum recorded between 4000 and 400 cm⁻¹ at the Euphore facilities (http://euphore.es/FTIRReferences/index.htm). This spectrum, displayed in Fig. 2, has been recorded for a HCHO mixing ratio of 892.4 ppb at 296.5 K and 1004.5 mbar, i.e. \( 2.21 \times 10^{13} \text{ molecule/cm}^3 \), obtained with 553.4 m path length and a resolution of 1 cm⁻¹. 1σ-precision has been attributed to the FT-IR HCHO measurement, resulting in 6% uncertainty on the measured concentration.

The calibration of the Euphore IR spectrum has been obtained with only one injection of paraformaldehyde. Therefore, Integrated Band Intensities (IBIs) have been calculated to ensure the reliability of this spectrum. The IBIs have been defined in the ranges 1660–1820 and 2600–3100 cm⁻¹ and compared to the existing literature data. In a given spectral region, an IBI is determined using Beer-Lambert law, as follows:

\[
A = \sigma \times L \times C
\]  

(1)

where, \( A \) is the IR absorbance (base e) for a given wavenumber \( \tilde{v} \), \( \sigma \) (cm²/molecule) is the absorption cross section, \( L \) (m) is the absorption path length and \( C \) (molecule/cm³) is the HCHO concentration. By integration on the spectral region,

\[
\int A \times d\tilde{v} = \int \sigma \times L \times C \times d\tilde{v}
\]  

(2)

The IBI can be deduced as

\[
\text{IBI} = \int \sigma \times d\tilde{v}
\]  

(3)

The values obtained using the Euphore pure HCHO reference spectrum are in excellent agreement with those reported in the literature, as shown in Table 1. The Euphore values, \( (1.265 ± 0.063) \times 10^{-17} \text{ cm/molecule at 1660–1820 cm}^{-1} \) and \( (2.830 ± 0.141) \times 10^{-17} \text{ cm/molecule at 2600–3100 cm}^{-1} \), match within 1% the average of the previous values, \( (1.263 ± 0.030) \times 10^{-17} \text{ cm/molecule and (2.805 ± 0.087) \times 10^{-17} cm/molecule, respectively. Moreover, the ratio 2.24 between the 2600–3100 and 1660–1820 cm}^{-1} \) Euphore IBIs is in excellent agreement with the previous determined ratios 2.21–2.25 (Perrin et al., 2009). Therefore, we used this Euphore IR spectrum to derive the absolute concentrations of formaldehyde [HCHO]ICARE (molecule/cm³) obtained at the ICARE chamber using the Eq. (4):

![Fig. 1](image1)

**Fig. 1** Ozone loss in the absence and presence of 4.5 ppm C₂H₄.

![Fig. 2](image2)

**Fig. 2** Reference spectrum of 892.4 ppb formaldehyde at 296.5 K and 1004.5 mbar recorded at Euphore at a resolution of 1 cm⁻¹.
2.3 Formaldehyde formation yield deduced from FT-IR spectrometry

Both FT-IR bands have been used to quantify the formation yield of formaldehyde from the runs conducted in the first experimental conditions (e.g., with initial volume mixing ratios: \([\text{C}_2\text{H}_4]_0 = 4.5 \text{ ppm and } [\text{O}_3]_0 = 465 \text{ ppb}\)). Figure 4 shows a linear regression of the plot of HCHO concentration with respect to ozone consumption at the first stage of the reaction, which leads to a formation yield of \((0.96 \pm 0.04; r^2 = 0.9884)\) and \((0.90 \pm 0.03; r^2 = 0.9961)\) using the 1746 and 2800 cm\(^{-1}\) centred bands, respectively, and so, to a mean value of 0.93 ± 0.05. This result is in good agreement with the previous published data, i.e. 0.77–1.00 (Horie and Moortgat, 1998; Neeb et al., 1998; Brauers et al., 2007; Wegener et al., 2007) and thus gives great confidence in the reliability of the HCHO concentration measured by the FT-IR apparatus. Moreover, the absence of formaldehyde polymerization due to the \textit{in situ} generation of HCHO at very low partial pressure (<0.001 hPa) is validated, in agreement with Gratien et al. (2007).

2.4 Calibration of the ro-vibrational line intensities measured by TDLAS by FT-IR spectrometry

The absorption cross section at a given wavenumber \(\tilde{\nu}_0\) can be expressed as:

\[
\sigma(\tilde{\nu}_0) = S(\tilde{\nu}_0)g(\tilde{\nu} - \tilde{\nu}_0)
\]

\[(5)\]

Table 1 Comparison of the calculated Integrated Band Intensities (IBIs) in the regions 1660–1820 cm\(^{-1}\) and 2600–3100 cm\(^{-1}\) using different IR spectra (\(T = 296 \pm 2 \text{ K}\))

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>IBI\times10^{-17} (cm/molecule)</th>
<th>Resolution (cm(^{-1}))</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1660–1820</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.229 ± 0.040</td>
<td>0.25</td>
<td>FT-IR</td>
<td>Nakanaga et al., 1982</td>
<td></td>
</tr>
<tr>
<td>1.248 ± 0.126</td>
<td>1</td>
<td>FT-IR</td>
<td>Klotz et al., 2004</td>
<td></td>
</tr>
<tr>
<td>1.262 ± 0.083</td>
<td>10(^{-3})</td>
<td>TDLAS</td>
<td>Herndon et al., 2005</td>
<td></td>
</tr>
<tr>
<td>1.284 ± 0.064</td>
<td>0.11</td>
<td>FT-IR</td>
<td>Sharpe et al., 2004</td>
<td></td>
</tr>
<tr>
<td>1.31 ± 0.04</td>
<td>0.08</td>
<td>FT-IR/UV</td>
<td>Gratien et al., 2007</td>
<td></td>
</tr>
<tr>
<td>1.242 ± 0.087</td>
<td>0.0035</td>
<td>FT-IR</td>
<td>Perrin et al., 2009</td>
<td></td>
</tr>
<tr>
<td>1.265 ± 0.063</td>
<td>1</td>
<td>FT-IR</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>1.270 ± 0.099</td>
<td>0.25</td>
<td>FT-IR</td>
<td>Nakanaga et al., 1982</td>
<td></td>
</tr>
<tr>
<td>2.800 ± 0.140</td>
<td>0.1</td>
<td>FT-IR</td>
<td>Perrin et al., 2009</td>
<td></td>
</tr>
<tr>
<td>2.92 ± 0.10</td>
<td>0.08</td>
<td>FT-IR/UV</td>
<td>Gratien et al., 2007</td>
<td></td>
</tr>
<tr>
<td>2.79 ± 0.25</td>
<td>0.0035</td>
<td>FT-IR</td>
<td>Perrin et al., 2009</td>
<td></td>
</tr>
<tr>
<td>2.830 ± 0.141</td>
<td>1</td>
<td>FT-IR</td>
<td>This work</td>
<td></td>
</tr>
</tbody>
</table>

Where, \([\text{HCHO}]_{\text{Euphore}} \text{ (molecule/cm}^3\)) is the HCHO concentration of the calibrated spectra, \(L \text{ (m)}\) the optical path lengths, \(T \text{ (K)}\) the temperatures and \(P \text{ (Torr)}\) the pressures of the considered chambers. These results led to consistency between the concentrations of HCHO derived from the bands centred at 1746 cm\(^{-1}\) (i.e., the 1660–1820 cm\(^{-1}\) region) and at 2800 cm\(^{-1}\) (i.e., the 2600–3100 cm\(^{-1}\) region), which are found equal within uncertainties (1%) and very well correlated \((R^2 = 0.9937)\), as shown in Fig. 3.

![Fig. 3](image)

**Fig. 3** Correlation between measurements performed with the 1660–1820 cm\(^{-1}\) band (centred at 1746 cm\(^{-1}\)) and the 2600–3100 cm\(^{-1}\) band (centred at 2800 cm\(^{-1}\)).

![Fig. 4](image)

**Fig. 4** HCHO formation yield from ozonolysis of ethene obtained from the 1746 and 2800 cm\(^{-1}\) centred bands at early stage of the reaction.

\[ [\text{HCHO}]_{\text{ICARE}} = [\text{HCHO}]_{\text{Euphore}} \times \frac{L_{\text{Euphore}}}{L_{\text{ICARE}}} \times \frac{T_{\text{ICARE}}}{T_{\text{Euphore}}} \times \frac{P_{\text{Euphore}}}{P_{\text{ICARE}}} \]  \[(4)\]
where, $S(\tilde{v}_0)$ (cm/molecule) is the ro-vibrational line intensity and $g(\tilde{v} - \tilde{v}_0)$ (cm) is the normalized absorption profile. The calibration of the line intensities is based on the Beer-Lambert law:

$$S(\tilde{v}_0) = \frac{A}{C \cdot g(\tilde{v} - \tilde{v}_0) \cdot L} \quad (6)$$

where, $C$ (molecule/cm$^3$) is the HCHO concentration, $A$ is the absorbance (in base e) and $L$ (cm) is the path length. The principle of the retrieval is to fit the experimental absorbance $A$ to the synthetic one, $S(\tilde{v}_0) \cdot C \cdot g(\tilde{v} - \tilde{v}_0) \cdot L$, by adjusting the line intensity $S(\tilde{v}_0)$. A linear least-square algorithm (of Levenberg-Marquardt) was used for minimizing the difference between these experimental and synthetic absorbances. The HCHO concentration $C$ is known from the FT-IR simultaneous measurements. This calibration was performed at high HCHO concentrations, corresponding to volume mixing ratios above 250 ppb, to maximise the signal-to-noise ratio and therefore the precision. The profile $g(\tilde{v} - \tilde{v}_0)$ is the convolution of the HCHO molecular Voigt profile, including the air-collisional broadening and the Doppler broadening half-widths, with the laser linewidth determined at lower pressure (6 hPa) where its magnitude is not negligible compared to the air-collisional broadening. The air-broadening half-widths and the line positions (the central wavenumber $\tilde{v}_0$) were taken by Perrin et al. (2009), in order to realize direct comparisons with this study and because there was no means to measure these parameters in our present experiments. Moreover, since our experiments were all performed at constant temperature, $(294 \pm 1) \text{ K}$, the temperature dependencies of the air-broadening coefficients and of the line intensities were not taken into account. Figure 5 shows an example of experimental and simulated transmission ($I(I')$) spectra from which the absorbance ($A = \ln(I/I')$) can be deduced, and the associated residual, i.e. the difference between the experimental and the synthetic spectra.

All the results are gathered in Table 2 and compared to the previous studies. Given our experimental pressure conditions (leading to line broadening) and the TDLAS resolution, ro-vibrational lines positioned closer than $10^{-2} \text{ cm}^{-1}$ are undistinguished in our experiments. Therefore, the comparison is made with the sum of the individual line intensities of the other studies within this limit. The overall uncertainties have been evaluated. The main systematic error originates from the laser linewidth determination (9%). The precision includes the experimental scatter (1.3% at 1σ level for seven determinations) and the precision on the fit (2%, 1σ).

![Figure 5](image)

**Fig. 5** Example of a spectral micro-window used to retrieve the HCHO line intensity $S$ at 2914.46 cm$^{-1}$ by TDLAS. (a) Black line represents the experimental transmission spectrum and the red line the synthetic transmission spectrum; (b) represents the residual of the signal, i.e. the subtraction between the experimental and synthetic signals. Statistical precision on this fit is 1.5% (1σ).

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Global line intensity $S$ (10$^{-20}$) cm/molecule</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2909.71</td>
<td>6.6 ± 0.7</td>
<td>This work</td>
</tr>
<tr>
<td>2912.09</td>
<td>6.0 ± 0.6</td>
<td>This work</td>
</tr>
<tr>
<td>2914.46</td>
<td>6.1 ± 0.6</td>
<td>This work</td>
</tr>
<tr>
<td>2909.71</td>
<td>5.78 ± 0.41</td>
<td>Perrin et al., 2009$^a$</td>
</tr>
<tr>
<td>2912.09</td>
<td>6.22 ± 0.44</td>
<td>Rothmann et al., 2005$^b$</td>
</tr>
<tr>
<td>2914.46</td>
<td>5.9 ± 0.3</td>
<td>Jacquiermart, 2009$^c$</td>
</tr>
<tr>
<td>2909.71</td>
<td>5.57 ± 0.39</td>
<td>Perrin et al., 2009$^d$</td>
</tr>
<tr>
<td>2914.46</td>
<td>9.20$^{10}$</td>
<td>Rothman et al., 2005$^1$</td>
</tr>
</tbody>
</table>

$^a$ Reported uncertainties are overall, including precision (1σ) and estimated systematic errors.

$^b$ Sum of two equal intensity lines at 2909.71338 and 2909.71353 cm$^{-1}$.

$^c$ Unknown uncertainty according to the author.

$^d$ Sum of two equal intensity lines at 2909.71300 cm$^{-1}$.

$^e$ Sum of four intensity lines: two of equal intensities (2.84) at 2912.09179 and 2912.09198 cm$^{-1}$, and two of equal intensities (0.27) at 2912.10063 and 2912.10132 cm$^{-1}$.

$^f$ Sum of three equal intensity lines at 2912.09180 cm$^{-1}$.

$^g$ Experimental value obtained by Jacquemart (2009, personal communication) in the study of Perrin et al. (2009).

$^h$ Sum of two equal intensity (2.771) lines at 2914.45917 and 2914.46110 cm$^{-1}$ and one intensity line (0.031) at 2914.46962 cm$^{-1}$.

$^i$ Sum of two equal intensity lines at 2914.45980 cm$^{-1}$.
propagation method (i.e. the square root of the quadratic sum of all errors) leads to an estimated overall uncertainty of about 10%. The agreement is good with the calculated values by Perrin et al. (2009) for the lines at 2909.71 cm\(^{-1}\) (within 13%) and 2914.46 cm\(^{-1}\) (within 9%), and very good (within 4%) for the 2912.09 cm\(^{-1}\) line, taking into account the 7% uncertainty of the later. The agreement is also very good at 2914.46 cm\(^{-1}\) (within 3.4%) if the experimental value obtained in this study is taken (5.91 \(\pm\) 0.3) \(\times\) 10\(^{-20}\) cm/molecule; Jacquemart, 2009, personal communication). In contrast, this is clearly not the case for the previous HITRAN 2004 database (Rothman et al., 2005), with over evaluations ranging from about 50% to 150%. We then confirm the validity of the line intensities calculated by Perrin et al. (2009) included in the new HITRAN database (Rothman et al., 2009). Thus, the use of FT-IR bands, consistent each other between both spectral domains (1660–1820 and 2600–3100 cm\(^{-1}\)) and in agreement with the study by Perrin et al. (2009), leads to sensible and reliable results for the particular lines studied here. The interest of using one of these lines for in situ stratospheric measurements is developed in Section 2.6, compared with the other lines in the 3.6 \(\mu\)m (2600–3100 cm\(^{-1}\)) spectral region.

### 2.5 Performances of the TDLAS instrument

The other goal of the study was to assess the performances of the TDLAS instrument, with a view of completing the atmospheric simulation chamber instrumentation. A second set of experiments of ethene ozonolysis at (760 \(\pm\) 1) Torr and (294 \(\pm\) 1) K has been performed to this end, with initial much lower \(O_3\) and \(C_2H_4\) volume mixing ratios (e.g., (219.0 \(\pm\) 0.1) ppb and (681 \(\pm\) 30) ppb, respectively) giving rise to lower production levels of formaldehyde (< 25 ppb in 1.5 hr reaction time). Only the 2800 cm\(^{-1}\) centred band was used for HCHO quantification by FT-IR due to a better sensitivity than the 1746 cm\(^{-1}\) centred band. Using one of the TDLAS lines reported in the above section, we could simultaneously follow the HCHO formation with a high frequency (each 1.1 sec; Section 1.2), giving rise to lower production levels of formaldehyde (< 25 ppb in 1.5 hr reaction time). Only the 2800 cm\(^{-1}\) centred band was used for HCHO quantification by FT-IR due to a better sensitivity than the 1746 cm\(^{-1}\) centred band. Using one of the TDLAS lines reported in the above section, we could simultaneously follow the HCHO formation with a high frequency (each 1.1 sec; Section 1.2), as illustrated in Fig. 6 for the above quoted initial mixing ratios. Of course, due to the calibration of the TDLAS by the FT-IR spectrometer, the results of both techniques are in agreement. However, what is particularly noticeable is the greater data number with less experimental scatter for TDLAS than for FT-IR, as shown with 1\(\sigma\) precision bars labeled on each measurement point for both setups in Fig. 6. The 1\(\sigma\) precision for TDLAS with 4 sec averaging (the time for cell replenishment by the gases) for 112.3 m path length is 170 ppt HCHO at 40 hPa (30 Torr), whereas the 1\(\sigma\) precision for FT-IR is 2.4 ppb (166 m path length) in 255 sec response time. This TDLAS precision leads to a 2\(\sigma\) detection limit of 88 ppt in 60 sec acquisition time (the sensitivity of the technique increased as the square root of the collection time). Therefore, the TDLAS short response time allows for lowering the detection limit of the reaction products, e.g. HCHO in the present study, and thus improves the accuracy of reaction mechanism studies (e.g., the branching ratios of multichannel reactions).

These performances are similar as those from another TDLAS (Fried et al., 2008), as shown in Table 3, and should even be improved to a detection limit of 35 ppt in 60 sec if the path length would be increased to 280 m, which seems possible with mirrors of better quality (reflectivity > 99%) than the current ones. In contrast, Fried et al. (2008) used a multipass absorption cell that does not allow for reaching a so long optical path, and the sensitivity and accuracy of their HCHO measurements are primarily due to the removing of \(H_2O\) (which generates spectroscopic interferences) and to the calibration of HCHO concentration, obtained by recording cyclically the background signal (without HCHO) and a signal from a HCHO standard. Table 3 summarizes the performances of the different current on-line measurement techniques, only from the detection limit and response time points of view. A more extensive comparison is out of the scope of the present article. This has been already done recently by Hak et al. (2005), Wisthaler et al. (2008) and Hottle et al. (2009), also including off-line techniques. Here we have considered the most recently developed techniques, so with on-line measurements, namely FT-IR, Differential Optical Absorption Spectroscopy (DOAS), Laser Induced Fluorescence (LIF), fluorimetric Hantzsch reaction, and Proton-Transfer Reaction Mass Spectrometry. It is seen that the TDLAS technique offers the best compromise between sensitivity and time resolution, being only in real competition with LIF.

#### 2.6 Selection of spectral lines in the 2600–3100 cm\(^{-1}\) band for HCHO stratospheric TDLAS measurements

The three TDLAS lines (2909.71, 2912.09 and 2914.46 cm\(^{-1}\)) studied in the present work may be used for in situ
stratospheric measurements. These are among the most intense R-branch lines of the HCHO ν1 band, compared to other lines in the 3.6 μm (2600–3100 cm⁻¹) spectral region. The feasibility of the measurements depends on the spectral interferences by other atmospheric species and on the detection limit of the instrument. Applied to the stratosphere, the detection limit derived in the laboratory measurements (in the Section 2.5), that is 35 ppt HCHO for 280 m path length at 40 hPa and 294 K, reduces for instance to 6 ppt at about 16 km altitude and to 27 ppt at 25 km, corresponding to typical pressures and temperatures of 110 hPa and 200 K and 25 hPa and 220 K, respectively, for the 431 m path length of SPIRALE balloon-borne instrument. These limits are well below the typical HCHO volume mixing ratios of 20 ppt and 50 ppt existing at the corresponding altitudes.

The selection of a suitable absorption line is critical for a species such as formaldehyde, which is a relatively weak absorber in the mid-infrared region and not very abundant in the stratosphere. In order to facilitate the HCHO retrievals from high-resolution measurements, it is necessary to select a strong and well-isolated absorption line to minimize as much as possible the impact of interfering species absorbing in the same spectral region. For this purpose, a simulation approach has been adopted to represent simultaneously the absorption lines corresponding to most of stratospheric molecular species. Hence, a home-made program has been developed and was used to simulate interactively the transmission spectra of all the species included in the HITRAN 2008 database (Rothman et al., 2005) and the new one (Rothman et al., 2009) under a standard atmospheric condition defined by mid-latitude (45°) and time of the day (McClatchey et al., 1972; ESSA, NASA and U.S. Air Force, 1976). The operator has flexibility to change these parameters and other ones, such as the selected molecular species considered at a given altitude, the optical path length, and the spectral micro-window width. Line-by-line simulations have been performed over the whole 2600–3100 cm⁻¹ domain, under a typical stratospheric condition, i.e., for 50 ppt HCHO at 25 km altitude. Figure 7 presents detailed parts of this band, with focus on the absorption lines of formaldehyde studied in this work. At 2909.71 and 2914.46 cm⁻¹ (Fig. 7a and c, the HCHO lines are strongly hindered by those of O₃ and CH₃, respectively. It is clear that these lines cannot be used for the quantitative detection of this molecule in the stratosphere. At 2912.09 cm⁻¹ (Fig. 7b), the formaldehyde line is partly perturbed by that of OCS located at 2912.106 cm⁻¹, but can be used taking into account this OCS line during the retrieval process.

Among all the HCHO lines in the 2600–3100 cm⁻¹ region, we found that those located at 2809.83 and 2831.64 cm⁻¹ are the most suited for the detection of this molecule, as illustrated in Fig. 8a and c, respectively. The latter has been used for long time by Fried et al. (2008, and references therein). These lines present the advantage to be relatively strong and are sufficiently isolated from those of other trace gases. Between the previous HITRAN database (Rothman et al., 2005) and the new one (Rothman et al., Perrin et al., 2009), the 2831.64-cm⁻¹ line intensity value has been slightly corrected by an increase whereas the 2912.09-cm⁻¹ line intensity has been decreased by a factor of 2.5, which leads to about the same value for both lines (6.0 × 10⁻²⁰ ± 0.2 × 10⁻²⁰) cm/molecule, and therefore decrease the interest of using the later one studied for atmospheric measurements. Finally, it is to be noted that the HCHO absorption lines located at 2814.48 and 2856.17 cm⁻¹ are also clear of interfering species but about 20%–30% lower than the most interesting ones quoted above, as shown in Fig. 8.

### 3 Discussion and conclusions

This study presents a validation of a tunable diode laser absorption spectrometer (TDLAS) for formaldehyde measurement by a FT-IR spectrometer in an atmospheric simulation chamber. As a first step, the FT-IR HCHO spectrum, recorded in Euphore chamber and used as a reference in the present work, has been compared to most of other ones published. The both absorption integrated line intensities (1660–1820 and 2600–3100 cm⁻¹) have

<table>
<thead>
<tr>
<th>Instrumentation</th>
<th>Detection limit (ppt)</th>
<th>Optical path length (m)</th>
<th>Accuracy (%)</th>
<th>Typical time resolution (sec)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDLAS</td>
<td>340</td>
<td>112.3</td>
<td>10</td>
<td>4</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>88</td>
<td>112.3</td>
<td>13</td>
<td>1</td>
<td>Fried et al., 2008</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>280 (estimated)</td>
<td></td>
<td>60</td>
<td>Fried et al., 2008</td>
</tr>
<tr>
<td>TDLAS</td>
<td>360</td>
<td>100</td>
<td></td>
<td>13</td>
<td>Fried et al., 2008</td>
</tr>
<tr>
<td></td>
<td>66</td>
<td>100</td>
<td></td>
<td>6</td>
<td>Fried et al., 2008</td>
</tr>
<tr>
<td>FT-IR</td>
<td>400</td>
<td>1000</td>
<td>6–27</td>
<td>30</td>
<td>Hak et al., 2005</td>
</tr>
<tr>
<td></td>
<td>4800</td>
<td>166</td>
<td></td>
<td>240</td>
<td>Fried et al., 2008</td>
</tr>
<tr>
<td>DOAS b</td>
<td>400</td>
<td>6</td>
<td>100 s</td>
<td>6</td>
<td>Wisthaler et al., 2008</td>
</tr>
<tr>
<td>LIF c</td>
<td>34</td>
<td>25</td>
<td>1</td>
<td>30</td>
<td>Hostle, et al., 2009</td>
</tr>
<tr>
<td>Fufluorimetric Hantzsch reaction</td>
<td>50–80</td>
<td>6–27</td>
<td>100 s</td>
<td>6–27</td>
<td>Wisthaler et al., 2008</td>
</tr>
<tr>
<td>PTR-MS d</td>
<td>80–200</td>
<td>5–8</td>
<td>60–120</td>
<td>20</td>
<td>Wisthaler et al., 2008; Jobson and McCoskey, 2010</td>
</tr>
</tbody>
</table>

a The 1σ precision can be derived as the half of this detection limit.
b Differential Optical Absorption Spectroscopy.
c Laser Induced Fluorescence.
d Proton-Transfer Reaction Mass Spectrometry.
been revealed to be in agreement within 1% with the average of these previous ones, including the most recent study of Perrin et al. (2009), and also consistent each other as in the latter. Formaldehyde was generated in situ from the reaction of ethene with ozone. This well-documented reaction has been then investigated by FT-IR and ozone UV-monitor, leading to a rate constant and a formaldehyde formation yield at 294 K that are in excellent agreement with the compiled literature data. The three ro-vibrational line intensities (at 2909.71, 2912.09 and 2914.46 cm$^{-1}$) used in the very high resolution TDLAS method were calibrated by FT-IR spectra simultaneously recorded during ethene ozonolysis. The inferred values (Table 2) confirm those from the updated HITRAN database (Rothman et al., 2009), based on the study of Perrin et al. (2009) within 4%–13%.

In addition, the TDLAS performances at low concentration of formaldehyde were assessed. A 2σ detection limit of 88 ppt volume mixing ratio with a response time of 60 sec (or 340 ppt in 4 sec) was obtained at 30 Torr and 294 K, for 112 m optical path, potentially leading to 35 ppt for 280 m. In comparison with the widespread conventional methods used in atmospheric simulation chamber studies, our TDLAS has been shown to be more sensitive than the on-line techniques (FT-IR, DOAS, Hantzsch method, PTR-MS), and as much as sensitive as the dinitrophenyl-hydrazine (DNPH) derivatization followed by off-line high pressure liquid chromatography ultraviolet (HPLC-UV) analysis, but this one needing more than one hour sampling (Whistaler et al., 2008). Therefore, the TDLAS technical performances in terms of response time and detection limit are of great added value for laboratory applications, including mechanism and kinetics of chemical reactions. However, one should keep in mind that the number of species to be monitored and the accuracy of the monitoring are limited by the advances in the very high-resolution spectroscopic databases. The TDLAS implementation can thus be seen as a complementary analysis tool of chamber studies.

Concerning atmospheric embarked in situ measurements, formaldehyde quantification appears to be feasible in the stratosphere with TDLAS instrumentation such as SPIRALE balloon-borne spectrometer, using the 2912.09 cm$^{-1}$ line with detection limits above few tens of ppt for 431 m optical path length. In the upper troposphere, the 2831.64 cm$^{-1}$ line is a better choice since the OCS species is abundant and would hinder the 2912.09 cm$^{-1}$ line. Another interesting line, of similar intensity (> 5 × 10$^{-20}$ cm/molecule) and clear of known spectroscopic interferences, is at 2809.83 cm$^{-1}$. Moreover, the 1660–
1820 cm$^{-1}$ band has to be considered as an alternative, with line intensities of the same order of magnitude. The use of the 1764.9 cm$^{-1}$ line as in the work of Herndon et al. (2007) is an example for stratospheric measurements, but less convenient in the upper troposphere where H$_2$O lines interfere.

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References


