Investigation of the formaldehyde differential absorption cross section at high and low spectral resolution in the simulation chamber SAPHIR

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Abstract. The results from a simulation chamber study on the formaldehyde (HCHO) absorption cross section in the UV spectral region are presented. We performed 4 experiments at ambient HCHO concentrations with simultaneous measurements of two DOAS instruments in the atmosphere simulation chamber SAPHIR in Jülich. The two instruments differ in their spectral resolution, one working at 0.2 nm (broad-band, BB-DOAS), the other at 2.7 pm (high-resolution, HR-DOAS). Both instruments use dedicated multi reflection cells to achieve long light path lengths of 960 m and 2240 m, respectively, inside the chamber. During two experiments HCHO was injected into the clean chamber by thermolysis of well defined amounts of paraformaldehyde reaching mixing ratios of 30 ppbV at maximum. The HCHO concentration calculated from the injection and the chamber volume agrees with the BB-DOAS measured value when the absorption cross section of Meller and Moortgat (2000) and the temperature coefficient of Cantrell (1990) were used for data evaluation. In two further experiments we produced HCHO in-situ from the ozone + ethene reaction which was intended to provide an independent way of HCHO calibration through the measurements of ozone and ethene. However, we found an unexpected deviation from the current understanding of the ozone + ethene reaction when CO was added to suppress possible oxidation of ethene by OH radicals. The reaction of the Criegee intermediate with CO could be 240 times slower than currently assumed. Based on the BB-DOAS measurements we could deduce a high-resolution cross section for HCHO which was not measured directly so far.

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1 Introduction

Differential Optical Absorption Spectroscopy (DOAS) is widely used in atmospheric research to measure the concentration of trace gases by their absorption in the visible and near UV spectral regions. The review of Platt (2000) provides an overview on the technique and possible applications. The trace gases which can be measured by DOAS range from radicals like OH, BrO, and NO3 to small molecules like NO2, SO2, and HCHO to larger molecules like toluene and benzaldehyde. DOAS applications split into passive DOAS instruments which use scattered sun light (cf. MAX-DOAS) and active DOAS instruments having a distinct light source (lamps or lasers). The latter have been used in open long path and folded path setups. Multiple reflection cells, however, allow the setup of DOAS measurements with long light paths inside simulation chambers of different sizes (e.g. De Haan et al., 1999; Kleffmann et al., 2006; Schlosser et al., 2006; Bossmeyer, 2006).

In this study we focus on DOAS measurements of formaldehyde, HCHO. It is a key compound in the tropospheric photo-chemistry (e.g. Carlier et al., 1986; Finlayson-Pitts and Pitts, 2000). HCHO exhibits a strong electronic transition from the ground state to the first excited singlet state (260–360 nm), S1 ↔ S0, giving rise to the A1 A2 – X A1 band system, which consists of an extended progression of vibronic bands. The formaldehyde absorption spectrum in the near UV between 300 nm and 350 nm (Fig. 1) was measured many times at different spectral resolutions (Bass et al., 1980; Cantrell, 1990; Rogers, 1990; Meller and Moortgat, 2000; Bogumil et al., 2003; Pope et al., 2005; Smith et al., 2006; Gratien et al., 2007). A recent analysis of the differences in the HCHO spectra by Hak et al. (2005) referenced all spectra to the Meller and Moortgat...
Therefore any recombination or polymerisation of HCHO vapour can be excluded in this study. In one set of experiments HCHO was injected by means of thermolysis of paraformaldehyde. In the other set HCHO was generated in-situ by the ethene + ozone reaction. The time profiles of HCHO at SAPHIR were modelled taking into account the chamber properties in both sets and the chemical mechanism in the second set of experiments to predict the expected concentration of HCHO.

2 Experimental

2.1 Atmosphere simulation chamber SAPHIR

The atmosphere simulation chamber SAPHIR is designed for the investigation of chemical systems at atmospheric concentrations and under controlled conditions (e.g. Rohrer et al., 2005; Bossmeyer et al., 2006; Wegener et al., 2007). The chamber consists of double-walled FEP foil (DuPont). The space between the two foils is flushed continuously with high purity N2. The inner part of the chamber is kept at 40 to 60 Pa above ambient pressure in order to prevent the contamination with outside air. The chamber is of cylindrical shape (diameter: 5 m, length: 18 m, volume: 270 m³) and operated with synthetic air (N₂, O₂, purity >99.9999%). A flow controller regulates the replenishment of chamber air lost due to sampling air probes and wall leakage at rates of 6 to 8 m³ h⁻¹ diluting every trace gas by 2 to 3% h⁻¹. The replenishment flow can be operated at rates up to 500 m³ h⁻¹ to purge trace gas levels in the chamber below the limit of detection. A shutter system keeps the chamber volume in darkness if required, but can also be opened for daylight exposure. All experiments described here were performed in the dark.

The chamber set-up comprises standard instruments for temperature, pressure, humidity, and gas replenishment flow. O₃ is measured by an instrument based on absolute UV absorption at 254 nm (Ansysco). Hydrocarbons are detected by a gas chromatograph (Chrompack) which is described in detail by Wegener et al. (2007). The system is equipped with a flame ionisation detector (FID). Due to sampling (20 min) and sample processing (30 min) the repetition rate is one data point per 50 min. The system is calibrated on a commercially available certified standard mixture of 30 VOC compounds in synthetic air (NPL). The accuracy of the calibration is better than 8%.

2.2 High-resolution DOAS Instrument

The HR-DOAS instrument has been described in detail before (Hausmann et al., 1997; Schlosser et al., 2006), therefore, only a brief summary is given here. The instrument is designed to detect OH radicals by a number of absorption lines at 308.00 nm and 308.16 nm. A long path is required to obtain sufficient signal to noise ratio as the ambient daytime concentration of OH is extremely low, usually
below $10 \times 10^6 \text{ cm}^{-3}$. This is achieved by use of a multiple-
reflection cell (MRC) of 20 m base with 112 travels corre-
sponding to 2240 m light path length. A ps-laser is used as a
light source emitting broad-band UV-light with a full width
at half maximum of 0.42 nm around 308.1 nm. The power of
the UV laser beam is about 1 mW. The light leaving the MRC
is transferred to the high resolution spectrograph (SOPRA
F1500, $\Delta \lambda=2.7$ pm) and the spectrum is detected by a cooled
($-45^\circ \text{C}$) photo diode array operated by the MFC program
(Gomer et al., 1995). The digitized laser spectrum range of
1024 pixel corresponds to 0.25 nm. The Multichannel Scan-
ning Technique (MCST) is used to reach the required sig-
nal to noise ratio (Brauers et al., 1995). One air spectrum is
recorded within 135 s. A comparison of measured and mod-
celled MCST spectra is given by Haussmann et al. (1997) who
found a maximum 1.7% error contribution to the accuracy of
the measurement. The deconvolution of the measured spec-
trum is performed by fitting a trigonometric background con-
sisting of 16 terms and three reference spectra, namely OH,
HCHO, and an so far unidentified absorber X (Schlosser et al.,
2006). We present the HCHO data in units of the opti-
cal density (absorbance) at 308.1034 nm (see Fig. 1, lower
panel).

2.3 Broad-band DOAS instrument

The setup of the BB-DOAS instrument is described in detail
in the thesis of Bossmeyer (2006). It is constructed and in-
 stalled at the chamber alongside the HR-DOAS instrument
for the detection of a large number of species (e.g. HONO,
NO$_2$, NO$_3$, O$_3$, and HCHO). It uses a Xenon arc lamp (Os-
ram XBO 75 W) as light source and a modified version of a
multiple reflection cell that allows 48 travels along the axis
of the chamber’s cylindrical volume, corresponding to 960 m
light path length. The outgoing light is guided via transfer
optics into a Czerny-Turner type spectrograph (Jobin-Yvon,
HR460) equipped with a blazed holographic grating offering
a spectral resolution of 0.2 nm. A photo diode array (PDA,
Hamamatsu, S3904) with 1024 pixels detects a wavelength
range of 44 nm. Spectra are acquired through a controller
(Hoffmann Messtechnik) at a rate of 1 min$^{-1}$. The spec-
trum recording, handling and fitting is operated using a script
mode of the software DOASIS (Kraus and Geyer, 2001). The
HCHO cross section of Meller and Moortgat (2000) at 298 K
is used for the evaluation (Fig. 1, upper panel). The 1-$\sigma$
-precision of the BB-DOAS HCHO measurement is approxi-
mately 0.5 ppbV.

2.4 Experiment description

In two experiments HCHO was generated by thermolysis
of para-formaldehyde. A weighted amount of solid para-
formaldehyde was heated until it was thermolysed at 383 K
completely into a stream of high purity N$_2$ (>99.999%),
which flushed the gaseous HCHO into the chamber. In the
first experiments in 2004 a homogeneous mixing ratio level
in the chamber was reached after a characteristic dark mixing
time of 30 min. In 2005 a fan was operated, which distributed
the injection in the chamber within 2 min.

In two experiments the HCHO was generated in-situ from
the gas-phase reaction of C$_2$H$_4$ + O$_3$. The experiments
were conducted in the well purged chamber at H$_2$O levels of less
than 10 ppmV. Fan operation in the chamber during the injec-
tion periods guaranteed that the reactants were well mixed
within minutes. In the first ethene-ozone experiment C$_2$H$_4$
and C$_3$H$_8$ (purities >99.95% each) were injected. C$_3$H$_8$ was
used as an inert tracer to monitor the dilution of chamber air
independently from the flow controllers. C$_2$H$_4$ degradation
was initiated by the addition of O$_3$. In the second experiment
additional 500 ppmV CO was injected in order to suppress
possible reactions of ethene with OH radicals formed during
ozonolysis. During this experiment C$_2$H$_4$ was added to the
chamber again 2 h after the start of the experiment to enhance
HCHO production.

3 Results and discussion

3.1 Thermolysis experiments

The profiles of the two days with HCHO injected into the
clean chamber are presented in Fig. 2. Both experiments
were performed in a similar way. After measuring at a small
dilution rate of about 3%/h we increased the replenishment
flow in order to clearly reduce the HCHO concentration by
30% within 30 min. The range of HCHO mixing ratios in these
chamber experiments was from 0 to $\approx$30 ppbV.

The only loss process of HCHO added to the dark chamber
is the dilution by clean synthetic air. Therefore, the concen-
tration C as function of time can be written as

$$C(t) = C(0) \times \exp\left( -\int_{0}^{t} k_{\text{Dil}}(t') dt' \right)$$

(1)

The dilution rate $k_{\text{Dil}}(t)=F(t)/V$ is calculated from the mea-
sured replenishment flow $F(t)$ and the chamber volume $V$.
The concentrations were calculated in steps of 60 s. The cen-
ter of the injection period, typically 20 min, was used as injec-
tion time for the calculated values to generate comparable
data sets. The initial mixing ratio $C_0$ was deduced from the
weighted para-formaldehyde (Merck, purity >95%) assum-
ing a 100% conversion to the gas-phase.

Figure 3 presents the scatter plot of the HCHO mixing ra-
tios measured by the BB-DOAS instrument and the calcu-
lated HCHO (Eq. 1). Data points close to the injection of
HCHO were excluded. The whole dataset of N=1152 clearly
separates into two groups belonging to the two different days.
Both groups highly correlate, however, the regression param-
eters are different (Table 1). A weighted regression yields
small offsets of different sign and slopes of 1.01 and 1.06,
respectively. Since only a minority of the data in both cases
is at zero HCHO mixing ratios a regression through the origin was also included in the analysis. The difference of the slopes is even larger (Fig. 3). The data from 10:05 to 11:00 were excluded from the correlation (Fig. 3). Bottom: 16 February: The vertical lines (---) after 12:00 mark the two injections of ozone (60 ppbV each) as a check for interferences with the measurements. According to the data of Meller and Moortgat (2000) an increase by 1% is expected whereas applying the temperature dependence reported by Cantrell (1990) a change of 7% is predicted which is closer to our observation. However, the temperature range of the experiments here is not sufficient to deduce a new value for the temperature coefficient.

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Table 2. The ozone + ethene reaction and the production of HCHO.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
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<tbody>
<tr>
<td>(R1)</td>
<td>CH$_2$H$_4$ + O$_3$ → CH$_2$OO$^*$ + HCHO</td>
</tr>
<tr>
<td>(R2a)</td>
<td>CH$_2$OO$^*$ + M → CO + H$_2$O + M</td>
</tr>
<tr>
<td>(R2b)</td>
<td>CH$_2$OO$^*$ + O$_2$ → CO + OH + HO$_2$</td>
</tr>
<tr>
<td>(R2c)</td>
<td>CH$_2$OO$^*$ + M → CH$_2$O + M</td>
</tr>
<tr>
<td>(R3a)</td>
<td>CH$_2$O + H$_2$O → HCOOH + H$_2$O</td>
</tr>
<tr>
<td>(R3b)</td>
<td>CH$_2$O + H$_2$O → HCHO + H$_2$O</td>
</tr>
<tr>
<td>(R4)</td>
<td>CH$_2$O + CO → HCHO + CO$_2$</td>
</tr>
</tbody>
</table>

secondary pathways. The HCHO + OH reaction is a sink of the product. Even in the dark chamber, there is a significant yield of OH via the reaction of the energy rich Criegee intermediate and molecular oxygen (Reaction R2b). To model the HCHO formation in the chamber we used the master chemical mechanism MCM (Saunders et al., 2003) in its current version 3.1, where we also included the dilution of all compounds by the replenishment flow. The MCM is the reference mechanism for the gas phase reaction of atmospheric species.

Therefore, two different ozonolysis experiments in the dark chamber were planned to investigate the HCHO yield: During the first experiment (15 February 2005) ethene is consumed both by the added ozone and the produced OH. For the second experiment (17 February 2005) an excess of 500 ppmV of CO was added to scavenge the OH radicals in order to reduce the number of reactions important to the production or loss of HCHO. Boundary conditions of the detailed model are the measured time profiles of ethene, ozone, humidity, temperature, pressure, and dilution of all species by the replenishment flow. Since the OH concentration was expected to be well below the detection limit of the HR-DOAS instrument in both experiments, the OH concentration was used as a free parameter and predicted by the model. In a second model run the HCHO yield was used as a free parameter and the BB-DOAS measurement of HCHO was used as a constraint instead.

The results of the measurements and the model calculations are presented in Fig. 4. For the first experiment the MCM predicts a HCHO yield of 1.00 while 0.91±0.29 is found by the fit to the whole data set of BB-DOAS measurements. However, if we restricted the fit to the first 6 h of the experiment the experimental yield would even more closely match the MCM calculation. For the second, high CO, experiment both the model and the measurement find a higher HCHO yield. This can be attributed to the very high CO concentration that was used to scavenge OH at low humidity. There is no loss of HCHO through OH, but the reaction of the stabilized Criegee intermediate (CH$_2$OO) with CO (Reaction R4) becomes important leading to an increase of the HCHO yield. However, a significant difference between the HCHO yield predicted by the MCM (1.37) and the BB-DOAS measurement (1.08±0.19) is observed. The good agreement of the thermolysis experiments and the low CO experiment suggests an error in the model. Only two reactions leading to the production of HCHO may be responsible since OH is scavenged. Either the stabilization yield of the excited Criegee (Reaction R2c) is significantly lower than presumed or the reaction of the stabilized Criegee with CO (Reaction R4) is much slower. We assume the latter case since the yields of Reactions (R2a), (R2b), and (R2c) are well known. Reaction (R4) is not well investigated. In order to fit our observations we had to divide the rate constant by a factor β of 250 (k$_4$=5×10$^{-18}$ cm$^3$ s$^{-1}$). Since the sensitivity of this experiment to the rate is small, a range of 100 to 500 for β is compatible with a ±3% calibration error of the HCHO measurement. Therefore, an independent determination of this rate constant would be useful.
Fig. 5. Correlation of all simultaneously measured HR-DOAS and BB-DOAS data. The data were recorded during 2 thermolysis and 2 ozonolysis experiments. We fitted a line with errors in both coordinates. The slope (in units of $10^{-20}$ cm$^2$) corresponds to the differential absorption cross section of a line at 308.1034 nm (marked in Fig. 1). The differential absorption coefficient $\alpha = \sigma' \times [\text{HCHO}]$ was calculated from the measured differential optical density divided by path length (2240 m).

3.3 High resolution HCHO cross section at 308 nm

Simultaneous DOAS measurements of both the BB-DOAS instrument and the HR-DOAS instrument were recorded for all experiments (Figs. 2 and 4). BB-DOAS measurements that are linked to absorption cross section measurements (Meller and Moortgat, 2000) can be used to determine the unknown highly resolved differential absorption cross section ($\sigma'$) needed for the HR-DOAS instrument (Fig. 5). Several concentration values measured by the BB-DOAS instrument were averaged if they occurred within one HR-DOAS interval. An excellent correlation coefficient $r=0.997$ was found for the two data sets. The slope of the linear regression is used to calculate $\sigma'$ of a HCHO absorption line at 308.1034 nm as a reference using the high resolution of the HR-DOAS ($\Delta \lambda=2.7$ pm). A value of $6.08 \times 10^{-21}$ cm$^2$ for the same line was reported earlier by (Neuroth, 1991; Brandenburg et al., 1998) who also used a BB-DOAS instrument for calibration, but it was based on a different absorption cross section (Platt et al., 1979) and they had a lower resolution. Including the down-scaling effect (factor = 0.729) of the MCST detection method we found an effective differential absorption cross section for the HCHO absorption line marked in Fig. 1 of $\sigma'=8.97 \times 10^{-21}$ cm$^2$ with an accuracy of 6% accounting for the uncertainty of the dilution and the purity of para-formaldehyde.

The recent publication of Smith et al. (2006) provides a HCHO spectrum at a resolution (3.5 pm) which is close to that of our HR-DOAS instrument (2.7 pm). This spectrum could, in principle, provide an independent way of calibrating the HR-DOAS instrument. We compared the absorbance recorded over an extended wavelength range of 0.75 nm (Fig. 6). For the major absorption features both instruments show clearly the same line positions and relative line strengths. However, the weaker lines in the HR-DOAS spectrum are not reproduced by the Smith et al. (2006) data (e.g. see inset of Fig. 6). All features seen in the HR-DOAS spectrum are well above the detection limit of $5 \times 10^{-5}$. We assume that also the stronger absorption lines might be influenced by the effect observed at the weaker lines. Therefore, we refrained from using Smith et al. (2006) data for the calibration of our instrument.
4 Conclusions

We performed 4 experiments on formaldehyde in the SAPHIR chamber. The experiments were designed to improve the knowledge on the absorption cross sections used for DOAS in the atmosphere.

In the two thermolysis experiments HCHO concentrations were calculated from the sample weight of paraformaldehyde and the gas replenishment flows at the chamber. The calculated concentrations are qualitatively and quantitatively reproduced by the BB-DOAS evaluation using the current absorption cross section recommendation (Meller and Moortgat, 2000). When other literature cross sections were used deviations of up to 20% from the good agreement would appear. Since the experiments were performed at different temperatures ($\Delta T=20$ K) the Cantrell (1990) temperature dependence is supported. Since the cross section changes significantly over the temperature range observed in the atmosphere, the temperature dependence of the HCHO absorption cross section remains an important issue to be resolved.

In this study we present an approach to calibrate the differential optical density of HCHO at a resolution of 2.7 pm between 307.97 nm and 308.18 nm. This is an important step to make use of the HCHO data simultaneously measured with OH by a DOAS instrument.

Finally, an ethene-ozone experiment conducted under high CO conditions showed that measured HCHO yields underestimated predictions of the MCM 3.1. The most likely explanation is an overestimation of the rate coefficient of the CH$_2$OO + CO reaction in the MCM. This is of minor effect in the atmosphere since the ratio of CO/H$_2$O normally promotes the CH$_2$OO+H$_2$O reaction. However, this finding is important for experiments at low humidities and high CO levels in chamber experiments. Therefore, a re-determination of this rate and similar reactions would be worthwhile.

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