HAL
open science

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

T. Brauers, J. Bossmeyer, H.-P. Dorn, E. Schlosser, R. Tillmann, R. Wegener, A. Wahner

To cite this version:

T. Brauers, J. Bossmeyer, H.-P. Dorn, E. Schlosser, R. Tillmann, et al.. Investigation of the formaldehyde differential absorption cross section at high and low spectral resolution in the simulation chamber SAPHIR. Atmospheric Chemistry and Physics Discussions, 2007, 7 (1), pp.2991-3012. hal-00302621

HAL Id: hal-00302621

https://hal.science/hal-00302621v1

Submitted on 18 Jun 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Atmos. Chem. Phys. Discuss., 7, 2991–3012, 2007
www.atmos-chem-phys-discuss.net/7/2991/2007/
© Author(s) 2007. This work is licensed
under a Creative Commons License.

Atmospheric Chemistry and Physics Discussions

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

T. Brauers, J. Bossmeyer, H.-P. Dorn, E. Schlosser, R. Tillmann, R. Wegener, and A. Wahner

Institut für Chemie und Dynamik der Geosphäre (ICG-II: Troposphäre), Forschungszentrum Jülich, Germany

Received: 12 January 2007 – Accepted: 21 February 2007 – Published: 26 February 2007

Correspondence to: T. Brauers (th.brauers@fz-juelich.de)

Abstract

The results from a simulation chamber study on the formaldehyde (HCHO) absorption cross section in the UV spectral region are presented. We performed 5 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 three experiments HCHO was injected into the clean chamber by thermolysis of well defined amounts of para-formaldehyde reaching mixing rations of 40 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) was 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 to 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.

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 NO_3 to small molecules like NO_2, SO_2, 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. The setup of 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), $S_1 \longleftarrow S_0$, giving rise to the $\tilde{A}^1A_2 - \tilde{X}^1A_1$ 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). A recent analysis of the differences in these spectra by Hak et al. (2005) referenced all spectra to the Meller and Moortgat (2000) data which are recommended by IUPAC (Atkinson et al., 2006) and NASA (Sander et al., 2006). Hak et al. used a spectral resolution of a broad-band DOAS instrument of 0.5 nm. The integrated band intensities of the most recent cross section measurements of Smith et al. (2006) is (depending on the vibrational band) between 0.1% and 14% higher than the measurements of Meller and Moortgat (2000) while older data tend to be lower; i.e. the previous recommendation of NASA based on Cantrell (1990) is 11% lower than the Meller and Moortgat (2000) data.

The spectral resolution of the original HCHO absorption cross sections published range from 3.5 pm (Smith et al., 2006) to 0.11 nm (Bogumil et al., 2003). An effective cross section for broad-band-DOAS can be calculated using any of these cross sec-

tions by convolution with an appropriate instrument function. For the high-resolution DOAS (HR-DOAS) instrument designed to detect tropospheric OH radicals (Hausmann et al., 1997; Brauers et al., 2001; Schlosser et al., 2006) no literature data at sufficiently high spectral resolution (2.7 pm) is available. However, a comparison between the highest resolution literature data of Smith et al. (2006) and the HR-DOAS data is given in the discussion of this paper.

This article presents measurements of HCHO with two DOAS instruments at different spectral resolutions (0.2 nm and 2.7 pm) which were performed at the atmosphere simulation chamber SAPHIR. HCHO mixing ratios were in the lower ppbV range in contrast to the laboratory measurements where mixing ratios in the percent range are applied. 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 para-formaldehyde. 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., 2006). The chamber consists of double-walled FEP foil (DuPont). The space between the two foils is flushed continuously with high purity N_2. 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 m^3) and operated with synthetic air (N_2, O_2, 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 $m^3 h^{-1}$ diluting every trace gas by 2 to 3 % h^{-1}. The replenishment flow can be operated at rates up to 500 $m^3 h^{-1}$ 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. O_3 is measured by an instrument based on absolute UV absorption at 254 nm (Ansyco). Hydrocarbons are detected by a gas chromatograph (Chrompack) which is described in detail by Wegener et al. (2006). 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 10×10^6 cm^{-3}. This is achieved by use of a multiple-reflection cell (MRC) of 20 m base with 112 travels corresponding 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 °C) photo diode array operated by the MFC program (Gomer, 1995). The digitized laser spectrum range of 1024 pixel corresponds to 0.25 nm. The Multichannel Scanning Technique (MCST) is used to reach the required signal to noise

ratio (Brauers et al., 1995). One air spectrum is recorded within 135 s. The deconvolution of the measured spectrum is performed by fitting a trigonometric background consisting 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 optical 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 installed 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 (Osram XBO 75W) 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 spectra 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-σ-precision of the BB-DOAS HCHO measurement is approximately 0.5 ppbV.

2.4 Experiment description

In three 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_2H_4+O_3. The experiments were conducted in the well purged chamber at H_2O levels of less than 10 ppmV. Fan operation in the chamber during the injection periods guaranteed that the reactants were well mixed within minutes. In the first ethene-ozone experiment C_2H_4 and C_3H_8 (purities >99.95 % each) were injected. C_3H_8 was used as an inert tracer to monitor the dilution of chamber air independently from the flow controllers. C_2H_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_2H_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 three days with HCHO injected into the clean chamber are presented in Fig. 2. The experiments (i), (ii), and (iii) 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 40 ppbV.

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

$$C(t)=C(0) \times \exp\left(-\int_0^t k_{\mathrm{Dil}}(t')dt'\right) \quad (1)$$

The dilution rate $k_{\mathrm{Dil}}(t)=F(t)/V$ is calculated from the measured replenishment flow

$F(t)$ and the chamber volume V. The concentrations were calculated in steps of 60 s. The center of the injection period, typically 20 min, was used as injection 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 %) assuming a 100 % conversion to the gas-phase.

The data measured by the BB-DOAS instrument and the model of the three experiments show an excellent correlation (N = 1172, r = 0.9989, see Fig. 3). We calculated a slope of 0.987±0.001 with an intercept of (0.28±0.03) ppbV when using the absorption cross sections of Meller and Moortgat (2000) for the BB-DOAS evaluation. A slope of 1.006±0.036 was calculated for the same data set when we force the regression line through the origin. We can deduce that the addition of HCHO by thermolysis is reproducible and yields constant values within the accuracies of the measurement (5 %) and calculation (6 %) over seven months.

The data of experiment (iii) in February (T = 275 K) show an approximately 6% steeper slope than the summer data (T = 300 K). This may be explained by a temperature dependence of the HCHO absorption cross section. 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.

3.2 Ozonolysis Experiments

The homogeneous production of HCHO from the ozonolysis of ethene provides an alternative way to compare HCHO measurements in the chamber. The reaction is well known because it represents the simplest alkene + ozone reaction which is an important oxidation pathway for atmospheric VOC. The monitored loss of ethene and ozone in combination with the accurate knowledge of the involved reactions and their rate constants allows to model the yield of HCHO and to compare the predicted concentration with the measurements. As shown in Table 1, HCHO is the primary product of

the ozonolysis (R1). However, reactions of the formed stabilised Criegee intermediate (CH_2OO) with H_2O (R3b) or CO (R4) will yield additional HCHO. The degradation of ethene is also initiated by hydroxy radicals leading to the formation of HCHO via 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 (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 one experiment (iv) ethene is consumed both by the added ozone and the produced OH. For the other experiment (v) 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 were used as a constraint instead.

The results of the measurements and the model calculations are presented in Fig. 4. For the first experiment (iv) 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 experiment (v) 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_2OO) with CO (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 (i, ii, and iii) and the low CO experiment (iv) 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 (R2c) is significantly lower than presumed or the reaction of the stabilized Criegee with CO (R4) is much slower. We assume the latter case since the yields of reactions R2a, R2b, and R2c are well known. Reaction R4, however, is not well investigated. A rate constant of 5×10^{-18} cm^3s^{-1} would be needed to explain the observed difference, i.e. 240 times lower than the value stated by Su et al. (1980) that is used in the MCM.

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, but number (iii) (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 (σ') 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 σ' of a HCHO absorption line line at 308.1034 nm as a reference using the high resolution of the HR-DOAS ($\Delta\lambda$=2.7 pm). A value of 6.08×10^{-21} cm^2 for the same line was reported earlier by (Neuroth, 1991; Brandenburger 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 $\sigma' = 8.97\times10^{-21}$ 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 5×10^{-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 5 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 three thermolysis experiments HCHO concentrations were calculated from the sample weight of para-formaldehyde 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 3 experiments were performed at different temperatures ($\Delta T = 25$ 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 $CH_2OO + CO$ reaction in the MCM. This is of minor effect in the atmosphere since the ratio of CO/H_2O normally promotes the $CH_2OO + H_2O$ 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 useful.

Acknowledgements. This work was supported by the EU FP-6 program EUROCHAMP. We thank U. Platt (U. Heidelberg) and B. Bohn for helpful discussions, R. Häseler and F. J. Johnen for assistance with the experiments, and T. Langner and H. Schütze (Foiltec, Bremen) for engineering work when setting up the SAPHIR chamber.

References

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E.,Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II reactions of organic species, Atmos. Chem. Phys., 6, 3625–4055, 2006, http://www.atmos-chem-phys.net/6/3625/2006/. http://www.iupac-kinetic.ch.cam.ac.uk/ 2993

Bass, A. M., Glasgow, L. C., Miller, C., Jesson, J. P., and Filkin, D. L.: Temperature dependent absorption cross sections for formaldehyde (CH_2O): The effect of formaldehyde on stratospheric chlorine chemistry, Planet. Space Sci., 28, 675–679, 1980. 2993

Bogumil, K., Orphal, J., Homann, T., Voigt, S., Spietz, P., Fleischmann, O. C., Vogel, A., Hartmann, M., Bovensmann, H., Frerick, J., and Burrows, J. P.: Measurements of molecular absorption spectra with the SCIAMACHY pre-flight model: Instrument characterization and reference data for atmospheric remote sensing in the 230–2380 nm region, J. Photochem. Photobiol. A, 157, 167–184, 2003. 2993

Bossmeyer, J.: Studies of Aldehydes in an Atmosphere Simulation Chamber, PhD thesis, Universität Heidelberg, Germany, 2006. 2993, 2996

Bossmeyer, J., Brauers, T., Richter, C., Rohrer, F., Wegener, R., and Wahner, A.: Simulation Chamber Studies on the NO_3 Chemistry of Atmospheric Aldehydes, Geophys. Res. Lett., 33, doi:10.1029/2006GL026778, 2006. 2994

Brandenburger, U., Brauers, T., Dorn, H.-P., Hausmann, M., and Ehhalt, D. H.: In-situ measurement of tropospheric hydroxyl radicals by folded long-path laser absorption during the field campaign POPCORN in 1994, J. Atmos. Chem., 31, 181–204, 1998. 3000

Brauers, T., Hausmann, M., Brandenburger, U., and Dorn, H.-P.: Improvement of Differential Optical Absorption Spectroscopy with a multichannel scanning technique, Appl. Optics, 34, 4472–4479, 1995. 2996

Brauers, T., Hausmann, M., Bister, A., Kraus, A., Dorn, H.-P.: OH radicals in the boundary layer of the Atlantic Ocean 1. Measurements by long-path laser absorption spectroscopy, J. Geophys. Res., 106, 7399–7414, 2001. 2994

Cantrell, C. A., Davidson, J. A., McDaniel, A. H., Shetter, R. E., and Calvert, J. G.: Temperature-dependent formaldehyde cross sections in the near-ultraviolet spectral region, J. Phys. Chem., 94, 3902-3908, 1990. 2993, 2998, 3001, 3007

Carlier, P., Hannachi, H., and Mouvier, G. : The Chemistry of Carbonyl Compounds in the Atmosphere – a review, Atmos. Environ., 20, 2079-2099, 1986. 2993

De Haan, D. O., Brauers, T., Oum, K., Stutz, J., Nordmeyer, T., and Finlayson-Pitts, B.J.: Heterogeneous chemistry in the troposphere: experimental approaches and applications to the chemistry of sea salt particles, International Reviews in Physical Chemistry, 18 (3), 343–385, 1999. 2993

Finlayson-Pitts, B. J. and Pitts, J. N. : Chemistry of the Upper and Lower Atmosphere – Theory, Experiments and Applications, Academic Press, San Diego, 2000. 2993

Gomer, T., Brauers, T., Heintz, F., Stutz, J., and Platt, U.: MFC User Manual, Version 1.98, Institut für Umweltphysik, Universität Heidelberg, 1995. 2995

Hak, C., Pundt, I., Trick, S., et al.: Intercomparison of four different in-situ techniques for ambient formaldehyde measurements in urban air, Atmos. Chem. Phys., 5, 2881–2900, 2005, http://www.atmos-chem-phys.net/5/2881/2005/. 2993

Hausmann, M., Brandenburger, U., Brauers, T., and Dorn, H.-P. : Detection of tropospheric OH radicals by long-path differential-optical-absorption spectroscopy: Experimental setup, accuracy, and precision, J. Geophys. Res. 102, 16 011–16 022, 1997. 2994, 2995

Kleffmann, J., Lörzer, J.C., Wiesen, P. Kern, C., Trick, S., Volkamer, R., Rodenas, M., Wirtz, K.: Intercomparison of the DOAS and LOPAP techniques for the detection of nitrous acid (HONO), Atmos. Environ. 40, 3640–3652, 2006. 2993

Kraus, S. and Geyer, A.: DOASIS Jscript programming description, Institut für Umweltphysik, University of Heidelberg, 2001. 2996

Meller, R. and Moortgat, G. K.: Temperature dependence of the absorption cross sections of formaldehyde between 223 and 323 K in the wavelength range 225–375 nm, J. Geophys. Res., 201(D6), 7089-7101, 2000. 2992, 2993, 2996, 2998, 3000, 3001, 3007

Neuroth, R., Dorn, H.-P., and Platt, U.: High resolution spectral features of a series of aromatic hydrocarbons and BrO: Potential interferences in the atmospheric OH-measurements, J. Atmos. Chem., 12, 287–298, 1991. 3000

Platt, U.: Differential Optical Absorption Spectroscopy, Air Monitoring by, In: R. A. Meyers (Ed.), Encyclopedia of Analytical Chemistry, John Wiley & Sons Ltd (Chichester), 1936, 2000. 2992

Platt, U., Perner, D., and Pätz, H. W.: Simulataneous measurements of atmospheric CH_2O, O_3, and NO_2 by differential optical absorption, J. Geophys. Res, 84, 6329–6335 . 3000

Pope, F. D., Smith, C. A., Ashfold, M. N. R., and Orr-Ewing, J.: High-resolution absorption cross sections of formaldehyde at wavelengths from 313 to 320 nm, Phys. Chem. Chem. Phys., 7, 79–84, 2005. 2993

Rogers, J. D.: Ultraviolet absorption cross sections and atmospheric photodissociation rate constants of formaldehyde, J. Phys. Chem., 94, 4011–4015, 1990. 2993

Rohrer, F., Bohn, B., Brauers, T., Brüning, D., Johnen, F.-J., Wahner, A., and Kleffmann, J.: Characterisation of the photolytic HONO-source in the atmosphere simulation chamber SAPHIR, Atmos. Chem. Phys., 5, 2189-2201, 2005, http://www.atmos-chem-phys.net/5/2189/2005/. 2994

Sander, S. P., Finlayson-Pitts, B. J. Friedl, R. R., et al.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, NASA Panel for Data Evaluation Number 15, JPL Publication 06-2, Pasadena, 2006. 2993

Saunders, S. M., Jenkin, M. E., Derwent, R. G., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds, Atmos. Chem. Phys., 3, 161–180, 2003. 2999

Schlosser, E., Bohn, B., Brauers, T., Dorn, H.-P., Fuchs, H., Häseler, R., Hofzumahaus, A., Holland, F., Rohrer, F., Rupp, L. O., Siese, M., Tillmann, R., and Wahner, A.: Intercomparison of two hydroxyl radical Measurement Techniques at the Atmosphere Simulation Chamber

SAPHIR, J. Atmos. Chem., doi:10.1007/s10874-006-9049-3, 2006. 2993, 2994, 2995, 2996

Smith, C. A., Pope, F. D., Cronin, B., Parkes, C. B., and Orr-Ewing, A. J.: Absorption Cross Sections of Formaldehyde at Wavelengths from 300 to 340 nm at 294 and 245 K. J. Phys. Chem. A 110, 11 645–11 653, doi:10.1021/jp063713y, 2006. 2993, 2994, 3001, 3012

Su, F., Calvert, J. G., and Shaw, H.: A FTIR Spectroscopic Study of the Ozone-Ethene Reaction Mechanism in O_2-Rich Mixtures. J. Phys. Chem., 84(3), 239–246, 1980. 3000

Wegener, R., Brauers, T., Koppmann, R.Rodríguez Bares, S., Rohrer, F., Tillmann, R., Wahner, A., Hansel, A., Wisthaler, A.: Investigation of the ozonolysis of short chained alkenes in the atmosphere simulation chamber SAPHIR, J. Geophys. Res., doi:10.1029/2006JD007531, 2007. 2994, 2995

Table 1. The ozone + ethene reaction and the production of HCHO.

(R1)	$C_2H_4 + O_3$	$\longrightarrow$	$CH_2OO^* + \mathbf{HCHO}$
(R2a)	$CH_2OO^* + M$	$\longrightarrow$	$CO + H_2O + M$
(R2b)	$CH_2OO^* + O_2$	$\longrightarrow$	$CO + OH + HO_2$
(R2c)	$CH_2OO^* + M$	$\longrightarrow$	$CH_2OO + M$
(R3a)	$CH_2OO + H_2O$	$\longrightarrow$	$HCOOH + H_2O$
(R3b)	$CH_2OO + H_2O$	$\longrightarrow$	$HCHO + H_2O_2$
(R4)	$CH_2OO + CO$	$\longrightarrow$	$HCHO + CO_2$

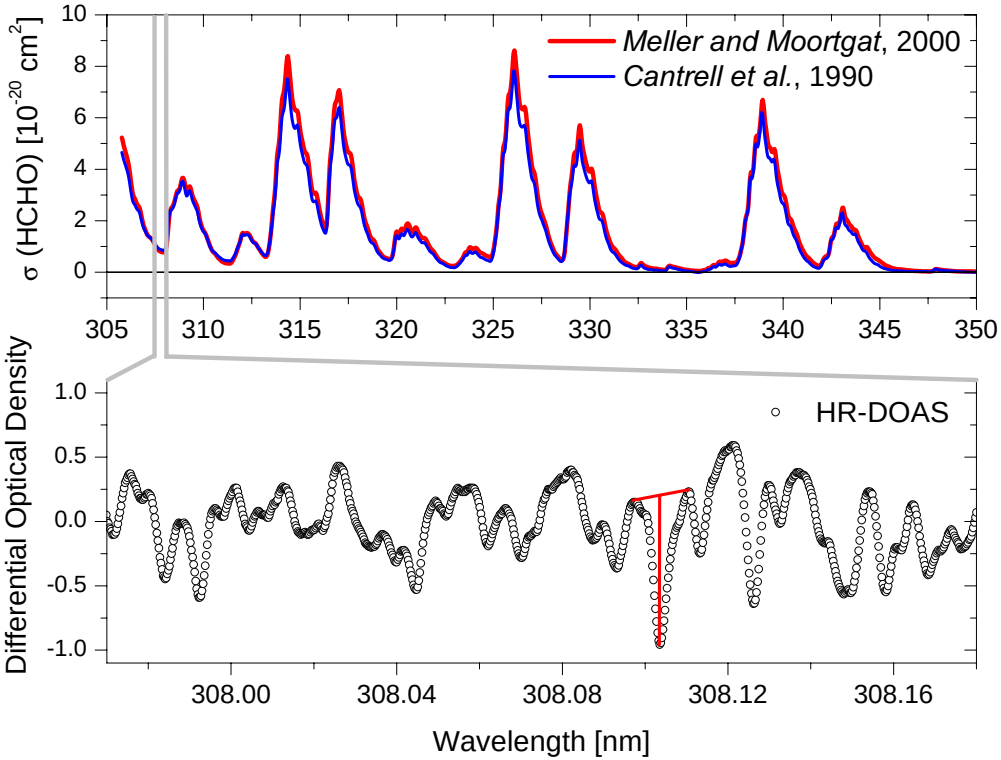

Fig. 1. Upper panel: HCHO cross sections (Meller and Moortgat, 2000; Cantrell, 1990) convolved to a resolution of 0.2 nm and interpolated to a wavelength grid of 0.04 nm. Lower panel: HCHO absorbance measured by the HR-DOAS at a resolution of 2.7 pm in the narrow range extending over 0.21 nm. The differential optical density of the absorption line used to scale the data is marked in red.

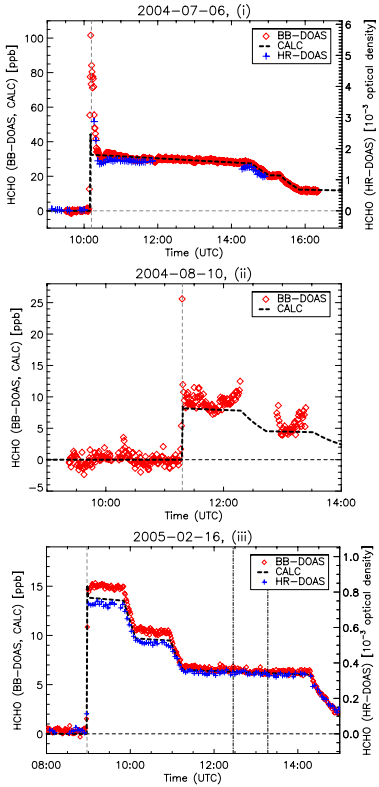

Fig. 2. HCHO profiles of the first three experiments measured by BB-DOAS and HR-DOAS, and the calculated values. Grey vertical line: HCHO injection. Top: Experiment (i), Since the fan was not operated during injection of HCHO concentration fluctuations were observed at the start of the experiment. Center: Experiment (ii), HR-DOAS data is not available on that day. Bottom: Experiment (iii), The vertical lines (– · –·) after 12:00 mark the two injections of ozone (60 ppbV each) as a check for interferences with the measurements.

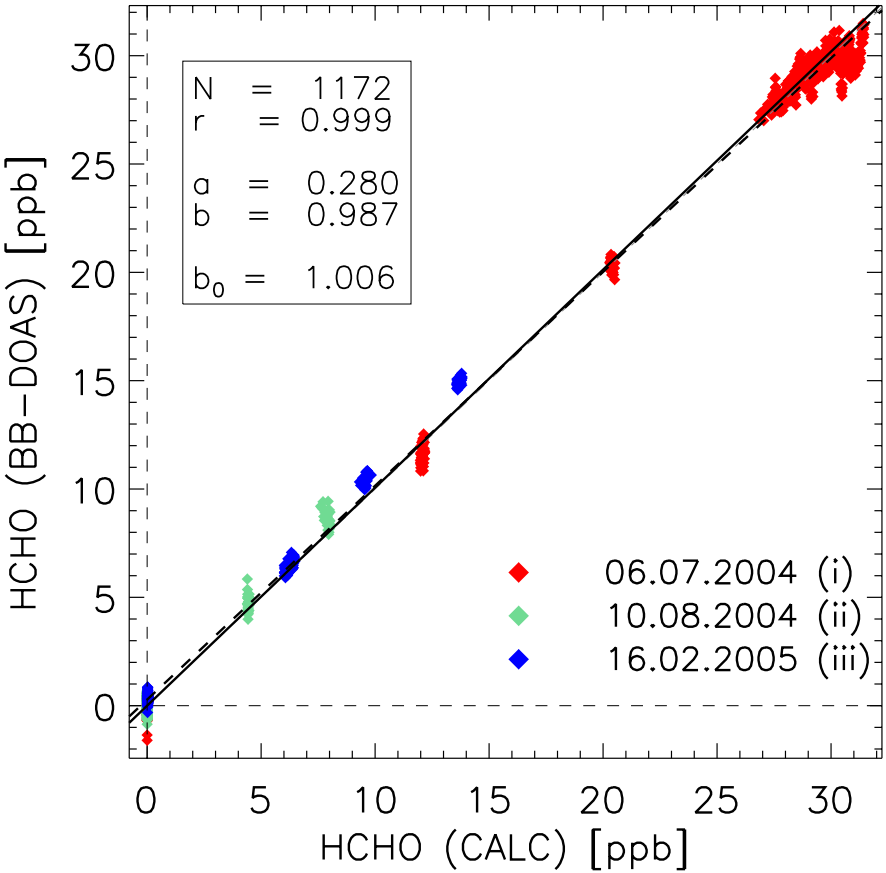

Fig. 3. Correlation of all BB-DOAS data with calculated concentrations in the thermolysis experiments. Different colors denote the different experiments (see Fig. 2). The dashed and solid lines indicate linear fits with intercept and forced through the origin, respectively.

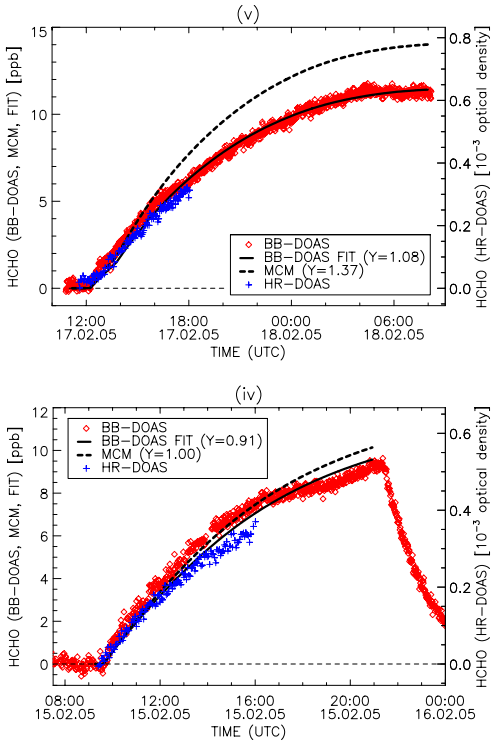

Fig. 4. HCHO time profiles in the ethene-ozone experiments (iv, low CO) and (v, high CO) performed in Feb 2005. Dotted line: best fit of modelled HCHO data to the measurement of the BB-DOAS (hollow diamonds) applying the yield based on C_2H_4 consumption as fit parameter. Dashed line: yield predicted by the MCM. Agreement between the BB-DOAS measurement and the MCM model is found for experiment (iv), whereas in experiment (v) the model overestimates the HCHO yield. The HR-DOAS measurement (red) is also shown, but in units of the optical density (right axis). It can be compared on a relative scale.

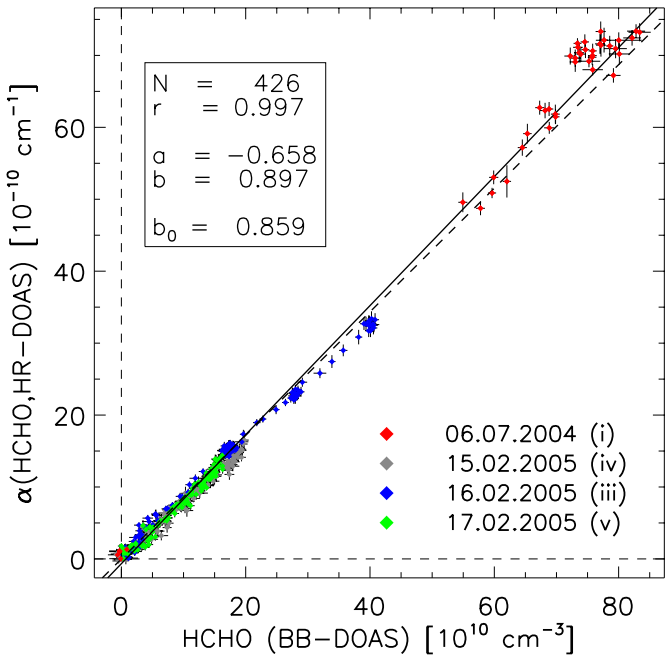

Fig. 5. Correlation of all simultaneously measured HR-DOAS and BB-DOAS data. The data were recorded during 2 thermolysis (i and iii) and 2 ozonolysis (iv and v) experiments. The slopes b and b_0 (in units of 10^{-20}cm^2) equal to the differential absorption cross section of a line at 308.1034 nm (see Fig. 1) as the differential absorption coefficient $\alpha = \sigma' \times$ [HCHO]. α was calculated from the measured differential optical density divided by path length (2240 m).

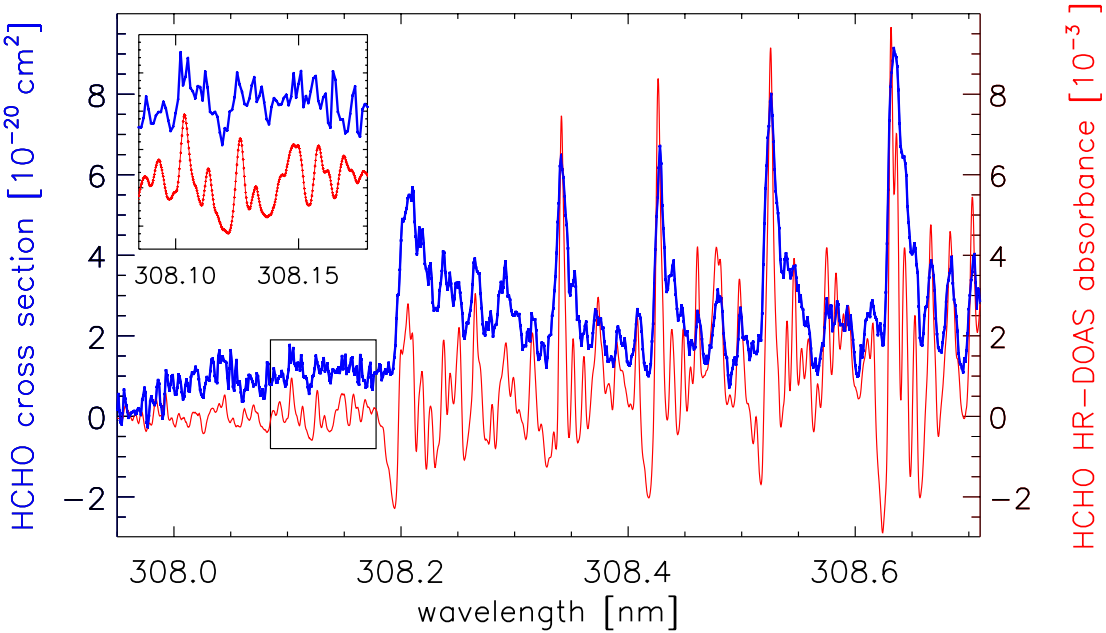

Fig. 6. Comparison of the high resolution HCHO absorption cross section of Smith et al. (2006) and the HR-DOAS absorbance. The extended spectral range of the HR-DOAS was recorded in 7 overlapping frames of 0.21 nm. The inset expands the spectral range which contains the main HCHO features recorded by the HR-DOAS instrument when used for OH measurements.