

Interactive comment on “Investigation of the formaldehyde differential absorption cross section at high and low spectral resolution in the simulation chamber SAPHIR” by T. Brauers et al.

T. Brauers et al.

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We would like to thank Dr. Andrew Orr-Ewing for the detailed review of our manuscript which gives us the opportunity to clarify some points. In the following we *quoted his review* and added our response after each paragraph.

1. *The focus of this work is on a small region of the HCHO absorption spectrum at wavelengths near to 308 nm Although there are hints that the measurements support cross section data of Meller and Moortgat, it must be remembered that only a very small wavelength range is studied, and I have some questions concerning the absorption data that are included below.*

The support of the cross section data of Meller and Moortgat is solely based

upon the BB-DOAS data, which uses a broad interval (312 nm to 348 nm) in the UV covering the major absorption bands of HCHO. In combination with the two methods to prepare HCHO in the chamber the result of the BB-DOAS measurements allows to assess the different absorption cross sections of the UV absorption of HCHO and is therefore significant for atmospheric implications and spectroscopic applications. To clarify this issue we will add the information about the BB-DOAS evaluation interval in a revised version to the text and the caption of Figure 1. We also would like to add a reference to a recent paper by Gratien et al., J.Geophys.Res., 2007, doi:10.1029/2006JD007201. Their findings do also support the use of Meller and Mortgaat cross section data.

- In figure 2, data are plotted for time-dependent profiles of HCHO, put on an absolute scale of ppb mixing ratios derived from BB and HR-DOAS measurements. At this stage of the manuscript it is not apparent how the HR absorption measurements are converted to mixing ratios*

In order to avoid misinterpretations we will emphasize in the caption of Figure 2 that the HR-DOAS data is plotted in units of optical density (right axis). Indeed the conversion to the absorption cross section is done later and does not apply to this figure.

- There are some discrepancies between the BB and HR results (see for example panel (iii) of figure 2) that are not fully explained, but may stem from the temperature effects described briefly on page 2998.*

Our chamber experiment were carried out at only two different temperatures. This set of experiments was not foreseen to study the temperature effect on the HCHO cross section. Therefore we discuss the temperature dependencies of the Cantrell et al. (1990) and Meller and Mortgaat (1990) papers.

- The comment on page 3001, lines 10 and 11 is potentially misleading and merits some clarification. ...There may thus be uncertainties with the Smith et al. data*

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for weaker absorption regions, but there is no reason to suppose these translate to the stronger absorption lines.

Obviously the weaker absorption lines around 308 nm are not reproduced by the Smith et al. data. The measurements of the HR-DOAS extended to the adjacent spectral region of stronger HCHO absorption (approximately 50% of the strongest spectral features of HCHO in the UV) should allow to calculate a reference spectrum for HR-DOAS, however as shown in Figure 6 some of the highly resolved spectral features of the HR-DOAS are not reproduced by the Smith et al. data. The latter appear to be measured with slightly lower spectral resolution and superimposed with a weakly variable background. For an instrument using a broader spectral region and which has a lower spectral resolution this may not be an issue, because differences may be insignificant or scatter. Our work simply states that the uncertainties with the Smith et al. data when using a small spectral interval are too large for the calibrations of the HR-DOAS. This will be clearly stated in a revised version.

- 5. The further comment on page 3001 lines 22 – 23 about 20% deviations in other literature absorption cross sections thus should to be interpreted with caution, and not taken to imply such disagreements in the stronger absorption regions of of HCHO or elsewhere in the extensive UV band system of this molecule.*

The BB-DOAS instrument with low spectral resolution measures a relatively broad spectral interval of ≈ 40 nm. Independent from the discussion of the spectral features in comparison with the HR-DOAS, up to 20% deviation was calculated when using the different absorption cross sections for analysis of the BB-DOAS data. This is of interest for many other instruments with similar spectral resolution that are using the same spectral range.

- 6. The data presented in figure 6 (previously published in Faraday Discussion 130, page 128, 2005) are puzzling and require more explanation. In particular, ab-*

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sorption cross sections for molecules cannot be negative yet the HR-DOAS data consistently go negative ...

During the preparation of the document we considered the conversion of the original absorption cross section data of Smith et al. to differential absorption cross section data. However, the differences are large enough without such a conversion and we preferred to cite the data as published. Thus the Smith et al. data are scaled by the left axis and the HR-DOAS data are scaled by the right axis as indicated by the color and the text. Absorption cross sections and differential absorbance do not scale directly, but the position and resolution of the spectral features are comparable. The baseline for the DOAS technique is the broadband filtered (=highpass) component of the optical density, the offset can be arbitrarily chosen. The HR-DOAS spectrum in Figure 6 is constructed by the combination of multiple wavelength frames of our instruments. We applied the high-pass filter procedure to the Smith et al. data as well. An updated Figure 6 is available from our web site at <http://saphir.fz-juelich.de/public/acpd-2006-0449>.

7. *on page 2999 the authors discuss MCM yields of 1.00, compared to a value of 0.91 ± 0.29 that do not directly compare with the scales plotted on the vertical axes in figure 4.*

The differences of the fit to the BB-DOAS data and the MCM model run amount to such a difference in the HCHO yield. As indicated by the error there is some uncertainty.

8. *On page 3000, line 19, what is meant by occurring within one HR-DOAS interval?*

The HR-DOAS measurement has a lower time resolution than the BB-DOAS data. In order to synchronize the data sets, the longer HR-DOAS time interval was used. Within this interval several BB-DOAS data points may be available which are consequently averaged. This will be explained in a revised version.

9. *Is the yield of reaction R2c really known precisely as claimed on page 3000, line 9? As far as I am aware, the Criegee intermediate product has never been directly observed, let alone measured, so evidence must be indirect. Perhaps the authors mean that quenching will occur with unit efficiency, but is this quenching then implicitly assumed to occur in a single collision?*

The reaction CH_2OO^* to CH_2OO has been well studied (see table of the experimentally derived stabilization yields of the Criegee intermediate below).

Reference	Yield
Hasson et al., J.Geophys.Res., 2001, 106, 34131	0.39 ± 0.11
Neeb et al., J.Phys.Chem., 1998, 102, 6778	0.50
Horie and Moortgat, Atmos.Env., 1991, 25, 1881	0.47
Hatakeyama et al., J.Phys.Chem., 1984, 88, 4736	0.39 ± 0.05
Niki et al., J.Phys.Chem., 1981, 85, 1024	0.35 ± 0.05
Kan et al., J.Phys.Chem., 1981, 85, 2359	0.37 ± 0.02
Su et al., J.Phys.Chem., 1980, 84, 239	0.38 ± 0.05

Of course the Criegee intermediate is difficult to measure directly, but the observed differences can not be explained within the given errors. The MCM in its current version uses 0.37.

10. *The experimental data shown in Figure 2 would benefit from a more complete description of procedure and outcomes in the text on page 2997.*

The chamber air is well mixed and therefore we can use Eq. 1 for the calculation of concentration of a tracer. This has been studied several times with different trace gases and instruments. More examples of these experiments were included in the thesis of S. Rodriguez-Bares and the thesis of J. Bossmeyer.

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