

## ***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.***

**A. Orr-Ewing (Referee)**

a.orr-ewing@bris.ac.uk

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Brauers et al. report interesting studies of the absorption of UV light by atmospheric formaldehyde conducted in the SAPHIR atmospheric simulation chamber using two differential optical absorption spectroscopy (DOAS) instruments. The spectrometers differ in their wavelength resolution and are specified as 0.2 nm (broad-band, BB) and 2.7 pm (high-resolution, HR) at 308.1 nm, equivalent to bandwidths of 21 and 0.28 cm<sup>-1</sup> respectively. The BB-DOAS measurements can be compared with absorption data of Meller and Moortgat [1] obtained with a spectrometer with 0.028 nm resolution. Experiments are conducted at very low mixing ratios of HCHO, thus avoiding the com-

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plicating issues of dimerisation and further polymerisation. Samples are prepared by thermolysis of paraformaldehyde, with the assumption of complete conversion to HCHO, and no decomposition to other compounds, which appears to be supported under the conditions used. Further comparisons are drawn with the HCHO produced by ozonolysis of ethene, and a side issue for the paper is then whether the mechanism of reaction of the Criegee intermediate with CO (introduced to inhibit other OH reactions) is correctly quantitatively described by the Master Chemical Mechanism [2]. The primary conclusion of the paper, however, is calibration of a DOAS instrument for retrieval of atmospheric HCHO concentrations, although temperature dependence effects of the absorption cross section are still not fully quantified.

The manuscript is generally clearly written, although some parts that merit clarification are listed below. The prior literature on HCHO absorption cross section data and on DOAS measurements is appropriately referenced.

The focus of this work is on a small region of the HCHO absorption spectrum at wavelengths near to 308 nm because this region of the UV is used for DOAS retrieval of OH radical mixing ratios. The simultaneous retrieval of HCHO concentrations thus becomes possible if a sharp line can be identified that is attributed to this molecule, and that lies in this UV region. The authors concentrate on a relatively weak line in the HCHO spectrum that lies between the main regions of two vibrational bands of the A - X band system. There are not, therefore, significant implications of this work for the wider importance of the UV absorption of HCHO in the atmosphere. 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.

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 (the absorption cross section is not yet established at this

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wavelength resolution) but this issue is addressed later in the paper. 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.

The comment on page 3001, lines 10 and 11 is potentially misleading and merits some clarification. The data of Smith et al.[3] deliberately focused on the stronger regions of vibronic absorption bands of HCHO with the intention of establishing absorption cross sections for all the main spectral features, with less emphasis on the weak inter-band regions such as at the wavelengths studied here. The experiments were carried out at partial pressures of HCHO below 1 Torr to avoid deviations from Beer-Lambert behaviour characteristic of HCHO at higher partial pressures [4], and were not optimized for sensitivity to weaker features. There may thus be uncertainties with the Smith et al. data for weaker absorption regions, but there is no reason to suppose these translate to the stronger absorption lines. 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 HCHO or elsewhere in the extensive UV band system of this molecule.

The data presented in figure 6 (previously published in Faraday Discussion 130, page 128, 2005) are puzzling and require more explanation. In particular, absorption cross sections for molecules cannot be negative yet the HR-DOAS data consistently go negative at several points in the spectrum which may be a consequence of the choice of baseline in differential spectrum analysis. Should the positive absorption cross sections then be shifted upwards to correct for this baseline choice? The analysis is somehow introducing negative going spikes to the low wavelength side of the stronger spectral features, and some of the oscillations in the DOAS spectrum may thus also be artefacts of the spectral methodology. Where is the true background level (zero of absorption cross section) in figure 6? This level should be established for a fairer

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comparison with the Smith et al. data, and may influence the peak cross section of the HCHO line used in the measurements of Brauers et al. If the data are obtained at higher resolution than the spectra of Smith et al., it is reasonable to suppose that the peak cross sections will reach much higher (positive) values as discussed in detail, and supported by spectral simulations, by Smith et al. For those of us who are not practitioners of differential optical absorption spectroscopy, some further discussion of the method used to analyse and interpret experimental data would be apposite. In particular, for a highly structured spectrum such as that of HCHO, with overlapping spectral features at all the wavelengths considered here, how is a baseline value selected for the differential optical density plot shown in figure 1? What is the meaning of a positive going differential optical density?

Some parts of the text are not very clear. For example, on page 2999 the authors discuss MCM yields of 1.00, compared to a value of  $0.91 \pm 0.29$  that do not directly compare with the scales plotted on the vertical axes in figure 4. On page 3000, line 19, what is meant by occurring within one HR-DOAS interval?

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

[1] Meller, R.; Moortgat, G.K. *J. Geophys. Res.*, 105, 7089-7101, 2000. [2] Saunders, S.M., Jenkin, M.E., Derwent, R.G., and Pilling, M.J., *Atmos. Chem. Phys.*, 3, 161 - 180, 03. [3] Smith, C.A., Pope, F.D., Cronin, B., Parkes, C.B. and Orr-Ewing, A.J., *J. Phys. Chem. A* 110, 11645 - 11653, 2006. [4] Pope F.D., Smith, C.A. Davis, P.R., Shallcross, D.E., Ashfold, M.N.R. and Orr-Ewing, A.J., *Faraday Discuss.* 130, 59 - 72,

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