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Atmospheric Chemistry and Physics Discussions

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.

Anonymous Referee #1

Received and published: 26 April 2007

The manuscript by Brauers et al. describes formaldehyde measurements by low and high-resolution differential optical absorption spectroscopy instruments in the SAPHIR smog chamber. Formaldehyde was introduced into the chamber by thermolysis of para-formaldehyde and through the ozone-ethene reaction. The measurements with para-formaldehyde as a source were used to validate literature HCHO absorption cross sections, as well as to determine the absorption strength of HCHO at a 2.7pm spectral resolution. The ozone + ethene experiments, which were performed at low and high CO concentrations, were compared to simulations with the master chemical mechanisms. While the results of the low-CO experiment compared favorably, a marked difference was found for the high-CO experiment. The authors interpret this discrepancy with a

240 times slower reaction of the Criegee intermediate with CO.

The manuscript presents some interesting data on the spectroscopy of HCHO as well as one of the most basic chemical reactions pathways in the atmosphere, the O_3 + ethene reaction. I recommend the manuscript for publication in ACP after some major revisions, which I describe below.

- The usage of a differential absorption cross section is somewhat arbitrary since this value strongly depends on the high-pass filter, or in the case reported in the manuscript, the MCST setup [Brauers et al., 1995]. It would be helpful to the non-specialist reader to provide an explanation of the nature of the differential absorption cross section compared to a normal absorption cross section.

- To fully assess the high-resolution HCHO absorptions reported in the manuscript more information has to be given on the spectroscopy. While details about the HR-DOAS instrument have been published, the dependence of the differential cross section on the instrument function and the MCST setup should be discussed in more detail. Perhaps showing a known atomic emission or absorption line in comparison with literature data could provide this information. In addition, a differential cross section should be given between two wavelengths, or three wavelengths if an interpolation over the band edges is used.

- Page 2998, lines 6 - 20 and Figure 3: Is N = 1172 the number of all data point, including those from February 2005? If so, how would the results change if this data was excluded? The change in slope between summer 2004 and February 2005 deserves more consideration. If this change is indeed caused by a temperature dependence of the absorption cross-section, this observation would have important implications for atmospheric HCHO DOAS observations, which often do not consider a temperature dependence of the HCHO absorption cross section. If it is not caused by a temperature dependence, another explanation has to be found to ensure the accuracy of the presented measurements.

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- Please provide an uncertainty to the rate constant of the Criegee intermediate - CO reaction. (page 3000, line 10). It would help the impact of the manuscript if the discrepancies with the results from Su et al. [1980] would be discussed in more detail.

- Figure 1: Are the values for the HR-DOAS differential optical density correct, or is a factor of 10^{-3} missing? If they are indeed correct, why can the authors not provide an absolute high-resolution absorption cross section for HCHO?

- Figure 2 middle panel: Please provide an explanation why the BB-DOAS HCHO data seems to increase with time at 12:00 and 13:00.

Minor Comments:

Abstract, line 19, delete “to” at end of line

Figures 3 and 5: Please present the fit results differently, for example by writing HCHO(BB) = 0.280 + 0.987 * HCHO(Calc). The results can only be understood after reading the text.

Figure 6. Please provide a legend for the figure or assign the two curves to their axis in the caption.

References

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

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

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Interactive Comment