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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 para-formaldehyde 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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