Geophysical Research Abstracts
Vol. 13, EGU2011-9038, 2011
EGU General Assembly 2011

Determining the ClOOCl absorption spectrum: Removal of the molecular chlorine spectral impurity using broadband cavity enhanced absorption spectroscopy

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The UV absorption spectrum of chlorine peroxide (ClOOCl) must be known accurately for atmospheric models to predict the rate of seasonal polar ozone depletion. Current measurements of the absorption cross section vary significantly, particularly at wavelengths greater than 300nm which are the most important photolytically. This is largely due to the contamination of ClOOCl laboratory samples.

The main contaminant in ClOOCl samples is molecular chlorine (Cl_2). Cl_2 has a smooth UV absorption feature, with a peak at 330nm, overlapping the ClOOCl spectrum. This means it is difficult to quantify and remove the Cl_2 absorption contribution to reveal the pure ClOOCl spectrum.

This work characterises the visible Cl_2 absorption spectrum using broadband cavity enhanced absorption spectroscopy (BBCEAS) in the 510-570nm wavelength range. Simultaneous measurements in the UV wavelength range (230-370nm) provide a means for accurately calculating Cl_2 concentration, and thus the absolute cross section. The result is the first temperature dependent study of the vibrational structure within the Cl_2 absorption cross section from 520nm to 570nm.

The Cl_2 vibrational structure can now be used to independently determine the concentration of Cl_2 in contaminated ClOOCl samples by use of differential optical absorption spectroscopy (DOAS) processing methods. Accurate subtraction of the calculated Cl_2 contribution in simultaneously measured UV spectra thus reveals the pure ClOOCl spectrum.

The temperature dependent visible absorption cross sections of Cl_2 between 510 and 570nm will be presented together with examples of the deconvolved ClOOCl absorption cross section from 230 to 370nm.