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Separation of absorption spectra and determination of absorption cross sections of iodine oxides relevant in photolysis experiments of I2+O3 and in the atmosphere

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Fast time resolved recordings of UV-Vis absorption following the photolysis of mixtures of I_2 and O_3 in bath gases N_2 and O_2 were analysed using multivariate analysis techniques. For the first time the overlapped absorption spectra of IO(ν'$\leftarrow$0), IO(ν'$\leftarrow$ ν") with ν">0, and OIO(ν_1','ν_2',0$\leftarrow$0,0,0) could be separated from each other and from other underlying absorptions of I_2 and higher iodine oxides. The separated spectra presented here could be shown to be free of other absorptions to better than $\pm$3%. Based on this separation the absorption cross sections of all detected absorptions were determined. Used was the principle of iodine conservation, which reduces the necessary a-priori knowledge. The absorption cross section of I_2, which is the only required parameter was also checked in a separate determination. The cross sections, which by this method are independent of previously determined rate coefficients, mechanistic assumptions or cross sections are presented and discussed. The cross section results are $\sigma_{IO(\nu'\leftarrow 0)}$=(3.5$\pm$0.3)$\cdot 10^{-17}$cm^2/molec at (427.16$\pm$0.05)nm and 0.12nm FWHM, $\sigma_{IO(\nu'\leftarrow 1)}$=(2.0$\pm$1.1)$\cdot 10^{-17}$cm^2/molec at (449.1$\pm$0.1)nm and 0.35nm FWHM, σ_{OIO}=(1.1$\pm$0.3)$\cdot 10^{-17}$cm^2/molec at (549.33$\pm$0.1nm) at 0.35nm FWHM. Spectra of two higher oxides were separated. One is tentatively identified as I_2O_3 with a cross section of (2.0$\pm$0.4)$\cdot 10^{-18}$cm^2/molecule at (340.1$\pm$0.1)nm and at 0.13nm FWHM. The other – also tentatively – as I_2O_2 with a cross section of (1 to 3)$\cdot 10^{-18}$cm^2/molecule at (322.1$\pm$0.1)nm and at 0.13nm FWHM. All wavelength are vacuum wavelength.