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Accurate measurements of ozone absorption cross-sections in the Hartley band provide evidence for a revision of the conventional value for tropospheric ozone measurements

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Tropospheric levels of ozone are monitored by networks using mostly Ultra Violet absorption instruments, with traceability to Standard Reference Photometers (SRP), relying on the UV absorption of ozone at the 253.65 nm line of mercury. We have recently re-determined the ozone cross-section at this wavelength by two independent methods, with reduced uncertainties. First, a system to generate pure ozone in the gas phase was setup, together with an optical system based on a UV laser with lines in the Hartley band, including accurate path length measurement of the absorption cell and a careful evaluation of possible impurities in the ozone sample by mass spectrometry and Fourier Transform Infrared spectroscopy. This resulted in new measurements of absolute values of ozone absorption cross-sections with relative expanded uncertainties better than 0.7 %, for the wavelengths (in vacuum) of 244.06, 248.32, and 257.34 nm respectively. The cross-section at the 253.65 nm line of mercury was determined by comparison with an SRP. In parallel, a gas phase titration (GPT) experiment was conducted, using the reaction of ozone (O_3) at the nmol/mol level with nitrogen monoxide (NO) resulting in nitrogen dioxide (NO_2) and oxygen (O_2). NO and NO_2 reactants/calibrants were diluted down from standards with nominal mole fractions at the μmol/mol level with state-of-the art flow measurement devices. Accurate measurements of NO, NO_2 and O_3 mole fractions variations allowed the calculation of two values of the ozone absorption cross section with an expanded relative uncertainty better than 0.9 %, one based on reacted NO values, the other on the NO_2 gain. In conclusion, a very good agreement was demonstrated between these three values, providing strong evidence for revising the conventionally accepted value of ozone cross section at 253.65 nm, measured by Hearn in 1961.
Those new results, together with published papers on ozone cross section measurements at 253.65 nm, will be reviewed by a Task Group recently established by the Gas Analysis Working Group of the CCQM (Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology). This group is in charge of recommending a value and uncertainty for the ozone cross section at 253.65 nm to be used in ozone reference photometers and for comparisons of these standards in the on-going international comparison BIPM.QM-K1.