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Peroxy radical measurements by photoacoustic spectroscopy coupled to chemical amplification

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Peroxy radicals (HO_2+RO_2) are crucial intermediates in many key atmospheric processes and contribute to the formation of major air pollutants, such as ozone and secondary organic aerosols[1]. Due to their high reactivity and their extremely low concentrations (typically <100 pptv), in-situ real time and interference-free measurements of peroxy radicals remain challenging. In the present work, photoacoustic spectroscopy (PAS)[2] is applied, for the first time to our best knowledge, to the measurements of peroxy radicals with the help of the well established chemical amplification approach. Peroxy radical chemical amplification (PERCA)[3] is based on chemical conversion of peroxy randicals into NO_2 and followed by chemical amplification to achieve the necessary measurement sensitivity for the measurement of atmospheric peroxy radical concentration. The resulting NO_2 concentration is measured by PAS to infer the total concentration of peroxy radicals. The performance of the developed PERCA-PAS approach was demonstrated with a reference ECHAMP chemical amplification system using cavity attenuated phase shift spectroscopy (CAPS) for NO_2 monitoring. The determined amplification gains (referred to as chain length, CL) of the ECHAMP system using PAS are well consistent with the values determined using CAPS. A 1-σ limit of detection of ~12 pptv for peroxy radicals was achieved in an integration time of 90 s at a relative humidity of about 9.8%. The detection limit of the current ECHAMP-PAS system can be further improved by using higher laser power and increasing the number of microphones in the photoacoustic spectrophone, which would allow reaching sub-pptv detection limits for the measurements of peroxy radicals in the atmosphere.

This work provides a promising technique to develop novel compact and very cost-effective (compared to all methods currently used) sensors, which will allow readily developing network measurements and investigation of the spatial distribution of peroxy radicals in the atmosphere.

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