Geophysical Research Abstracts
Vol. 17, EGU2015-7742, 2015
EGU General Assembly 2015

Resonant cavity spectroscopy of radical species

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Photo-oxidation in the troposphere is highly complex, being initiated by short lived radical species, in the daytime dominated by the hydroxyl radical, OH, with contributions from Cl atoms, and at night by either NO_3 radicals or ozone. Chemical oxidation cycles, which couple OH, HO_2 and peroxy (RO_2) radical species, remove primary emitted trace species which are harmful to humans or to the wider environment. However, many of the secondary products produced by atmospheric photo-oxidation are also directly harmful, for example O_3, NO_2, acidic and multifunctional species, many of which are of low volatility and are able to partition effectively to the condensed phase, creating secondary organic aerosol (SOA), which contributes a significant fraction of tropospheric aerosol, with associated impacts on climate and human health. The accuracy of atmospheric models to predict these impacts necessarily requires accurate knowledge of the chemical oxidative cycling.

Two of the simplest intermediates are the hydroperoxy radical, HO_2, and the smallest and dominant organic peroxy radical, CH_3O_2, formed directly by the reactions of OH with CO/O_2 and CH_4/O_2, respectively, and indirectly following the oxidation of larger VOCs. OH, HO_2 and RO_2 (collectively known as RO_x) are rapidly cycled, being at the centre of tropospheric oxidation, and hence are some of the best targets for models to compare with field data. The reaction of HO_2 and RO_2 with NO constitutes the only tropospheric *in-situ* source of O_3. Despite their importance, neither HO_2 nor CH_3O_2 is measured *directly* in the atmosphere. HO_2 is only measured indirectly following its conversion to OH and CH_3O_2 is not measured at all. Typically only the sum of RO_2 radicals is measured, making no distinction between different organic peroxy radicals. This contribution will detail recent studies using (i) optical feedback cavity enhanced absorption spectroscopy with both quantum and inter-band cascade lasers in the mid-IR, and (ii) near-IR diode laser based noise immune cavity enhanced heterodyne molecular spectroscopy as potential methods for the direct detection of HO_2 and CH_3O_2 at atmospheric levels.