4.076 Towards a complete picture of the atmospheric radical cycles: the speciated detection of gas-phase organic radicals by proton transfer mass spectrometry.

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Abstract:

The understanding of the atmospheric radical cycles and of atmosphere's oxidative capacity is mostly limited today by technical challenges: the inability of current techniques to monitor specific organic radicals in the atmosphere ("speciated detection"), especially organic peroxy radicals ("RO2", where R is an organic group) that are intermediates in the atmospheric oxidation of most organic gases. Past and current techniques employed to monitor these radicals in the atmosphere (PERCA, ROxMax, PerCIMS, ROXLIF...) convert them into a single species (NO2, H2SO4 or HO2/OH) and provide thus overall concentrations or, at best, semi-speciated ones, distinguishing between saturated and unsaturated radicals. While valuable, this information is not sufficient for a full picture of the radical cycles.

Over the last decades, mass spectrometry using chemical ionization has been explored for its ability to detect different organic radical separately (fully speciated detection). Ionization by proton transfer was found to be the most promising approach and instruments based on this principle were built and applied to the detection gas-phase organic radicals. The first applications of this technique will be presented, as well as the many groundbreaking possibilities it offers for the understanding of the radical cycles, such as the investigation of reactions involving several organic peroxy radicals (cross-reactions, radical cycling ...), of their uptake by atmospheric surfaces, of other types of organic radicals and, ultimately, the speciated detection of organic radicals directly in the atmosphere.