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Developments in laser-induced fluorescence spectroscopy for quantitative in situ measurements of free radicals in the troposphere

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Photo-oxidation in the troposphere is highly complex, being initiated by short lived free radical species, in the daytime dominated by the hydroxyl radical, OH. Chemical oxidation cycles, which also involve peroxy radicals (HO_2 and RO_2), remove natural or anthropogenic emissions (for example methane) and generate a range of secondary products, for example ozone, nitrogen dioxide, acidic and multifunctional organic species, and secondary organic aerosol, which impact on human health and climate. Owing to their short lifetime in the atmosphere, the abundance of radicals is determined solely by their rate of chemical production and loss, and not by transport. Field measurements of the concentrations of radicals and comparison with calculations using a numerical model therefore constitutes one of the very best ways to test whether the chemistry in each of these locations is understood and accurately represented in the model. Validation of the chemistry is important, as the predictions of climate and air quality models containing this chemistry are used to drive the formulation of policy and legislation.

However, *in situ* measurements of radical species, owing to their very low abundance (often sub part per trillion) and short lifetimes ($<$ 1 second for OH), remain extremely challenging. Laser-induced fluorescence spectroscopy (LIF) has enjoyed considerable success worldwide for the quantitative detection of radicals in a range of environments. The radicals are either excited directly by the laser (e.g. OH, IO) or are first chemically converted to OH prior to detection (e.g. HO_2, RO_2). Recent developments in the LIF technique for radical detection, which uses a supersonic expansion with detection at low pressure and multi kHz pulse repetition rate tunable laser systems, will be discussed, together with calibration methods to make signals absolute, and identification of potential interferences. LIF instruments have been operated on ground, ship and aircraft platforms at a number of locations worldwide, and examples from recent fieldwork involving the Leeds instruments will be presented.