

Radical reactions in combustion

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Reactive, short-lived intermediate species play a crucial role in combustion. Small radicals are involved at all stages of the combustion reaction network which determines important factors of the process, including the available energy, the amount of greenhouse gases emitted, and the formation of undesired air toxics and aerosols. It is a considerable challenge to quantitatively detect such reactive intermediates which are typically formed in small concentrations, and in-situ techniques are necessary for this analysis.

To investigate the species composition in flames suited to unravel details of the combustion chemistry, we typically combine laser diagnostic and molecular beam mass spectrometry. Especially valuable methods include cavity ring-down spectroscopy (CRDS) and laser-induced fluorescence (LIF) which were used to detect some key di- and tri-atomic radicals. Collisional energy transfer, investigated using picosecond time resolution, has been studied as a prerequisite for quantitative LIF measurements. From the several variants of *in situ* molecular beam mass spectrometry, which can provide a complete analysis of the reactive mixture, photoionization techniques using synchrotron radiation are especially useful to distinguish isomeric species. This combination of techniques has been invaluable in studying important reaction pathways for a variety of fuel families, including hydrocarbons, ethers, alcohols, aldehydes, ketones, esters and amines, as well as fuel mixtures. Many of these investigations have been performed in collaborations, including teams from the USA and China. As a general conclusion, the structure of the fuel molecule is of significance for the formation of some undesired combustion emissions – a fact which must be considered in the discussion of alternative, bio-derived fuels.

Radicals are also at the origin of some of the characteristic luminous emissions of flames. The chemiluminescent signature of a flame depends on the combustion conditions and is proposed as an intrinsic sensor for active control of practical combustion devices. While flame luminescence has been described in the literature for more than hundred years, its spectral structure is not easily predicted since radiative and energy transfer processes are involved. These will depend on the reaction channels producing nascent energy level distributions that may not be known and on the specific collisional environment. Some recent results will be presented to discuss this approach of using chemiluminescence as a flame sensor.