Isomer selective combustion analysis by double-imaging fixed-photon-energy photoelectron/photoion coincidence (i²PEPICO) spectroscopy

Julia Pieper(1,*), Steffen Schmitt(1), Julia Krüger(2), Gustavo A. Garcia(2), Laurent Nahon(2), Wolfgang Eisfeld(3), Andreas Brockhinke(1), Katharina Kohse-Höinghaus(1)

(1) Physical Chemistry I, Bielefeld University, Germany
(2) Synchrotron SOLEIL, Gif-sur-Yvette, France
(3) Theoretical Chemistry, Bielefeld University, Germany
* Corresponding author; email address: julia.pieper@uni-bielefeld.de

Alternative fuels are being advocated to reduce combustion-induced emissions, especially in view of globally increasing transportation. Their combustion mechanisms are, however, often not known in sufficient detail to predict pollutant formation. Low-pressure premixed flame experiments, typically coupled with species diagnostics via molecular-beam mass spectrometry (MBMS), offer critical test cases to analyze fuel-specific reaction pathways and to develop and examine kinetic reaction models. Such investigations conventionally use electron ionization (EI) or photoionization (PI) with synchrotron-based tunable vacuum ultraviolet radiation. While EI-MBMS does not usually offer isomer separation, even PI-MBMS isomer identification capabilities are limited, especially in cases where multiple molecular structures with similar ionization energies must be detected at the same mass.

Photoelectron/photoion coincidence (PEPICO) spectroscopy, recently demonstrated for flame analysis [1-3], provides not only photoion detection, but offers simultaneous mass-selected characteristic photoelectron spectra (PES) as a new discriminative dimension for species identification and quantification. Fixed-photon-energy double-imaging i²PEPICO measurements lead to competitive measurement times and can prove particularly useful to reveal isomer contributions in chemically complex combustion situations.

Results will be presented from premixed laminar low-pressure flames of C₅ hydrocarbon fuels, including isomer identification, separation and mole fraction ratios for crucial combustion intermediates. This approach must rely on reference PES of each of the considered isomers, preferably recorded at the same apparatus and under identical conditions as the flame measurements. Reference spectra are therefore provided from the same experiment and in addition, theoretical calculations have been performed to obtain the photoelectron spectra of further species, including radicals. Results are promising for the extension of combustion models beyond C₄ and show useful perspectives for further applications.