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Threshold photoelectron spectroscopy to trace chemistry in molecular beams and flames

Thomas Gerber, Patrick Hemberger
Molecular Dynamics Group, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland
thomas.gerber @psi.ch

The Molecular Dynamics Group investigates chemical reaction mechanisms using spectroscopic techniques. We apply non-linear laser spectroscopies in the frequency domain and time domain, time-of-flight mass spectrometry and tunable synchrotron radiation to characterize short-lived intermediates relevant in combustion. Our efforts aim at establishing thermochemical data and dissociation patterns of radicals. To achieve this objectives three fundamental tasks have to be solved:

- Preparation of radicals in reactors and molecular beam – sources with a sufficient density.
- Adaptation of reactors and sources in the test rigs at the Swiss Light Source, Vacuum Ultraviolet Beamline (SLS / VUV) and the laser laboratory.
- Development of linear and nonlinear spectroscopic techniques in combination with photoionization and photoelectron spectroscopy.

For a correct modelling of combustion processes that goes beyond a purely random phenomenological description, detailed knowledge of the involved short-lived intermediates are necessary. It is not sufficient to describe molecules with the same function, e.g., Alkyl radicals together as one class of reagents. Rather, each radical must be broken down to its individual isomers, since each isomer can have its own reaction channels and reaction rates. Such isomer specific dependency show, for example, the xylene isomers, we investigated intensively in the past two years.
The enormous number of issues that arise in the context of assessing individual species and their behaviour in flames appears at first sight, as a task without end. A strategy to rank the individual questions in terms of their urgency, cannot be clearly defined despite many studies. Interest in a particular species must be weighed against the feasibility of a corresponding experiment and the associated costs. Furthermore, the success of many experiments is still uncertain and requires a steady development of experimental methods.

An approach according to the following criteria proved useful:

- Development of measurement techniques with groups of molecules already often studied, e.g., substituted benzenes.
- Characterization of species that have been identified with other methods as important intermediates in flames and whose accurate thermochemical quantities must be determined for their kinetic modelling.
- Direct measurements in flames and reactors with the now available isomer-specific methods to break down to individual intermediates what so far has been described by summarily lumped reaction mechanisms.

It is clear that this extensive work can only be addressed in association with several research groups. In fact, increased efforts are underway to organize elaborate experiments across groups. Many of these joint efforts centre around the SLS / VUV and other similarly equipped beamlines.

The demand for beam time is currently very high, since worldwide essentially only four beamlines provide relevant equipment for combustion research:
ALS, (USA), Soleil (France), LVD, (China), SLS / VUV (Switzerland).

According to the strategy outlined above, our recent work comprised the following parts:

- Development of the isomer-specific mass spectrometry based on well-known species such as C_4H_6-, C_5H_8- isomers and xylenes. Although the xylenes were often studied in other contexts we succeeded with the isomer-specific detection to unveil some new aspects of their role in combustion. In particular, it was shown that the para- and ortho-xylyl radicals after loss of a hydrogen atom form as expected para- and ortho-xylylene but that the meta-xylyl isomerizes to para-xylylene in the same reaction. This rearrangement changes the burning behaviour of meta-xylyl compared to the other isomers.
- We responded on questions emerging in other groups with our own and with cooperative investigations. Furans, currently raise much interest as oxygenated fuels that can be produced from biomass. Measurements at the SLS/VUV beamlines were carried out in cooperation with the DLR Stuttgart. More measurements are in preparation together with Barney Ellison, University of Colorado, as well as fs-pump-probe experiments in our laser laboratory on the unimolecular dissociation dynamics.
- Researchers from other groups use our experimental facilities. Since SLS/VUV experiments cannot be run without our expertise, we are usually also involved with the scientific background of these experiments. With a flat flame burner attached to the PEPICO (Photo-Electron, Photo-Ion Coincidence) endstation we measured concentrations profiles of individual, isomerically resolved, intermediates. Isomer-resolved species detection offers a significant improvement over conventional methods. The profiles can be compared with detailed kinetic models.

An ARPES-PIMS experimental setup (Angle Resolved Photo-Electron Ionization Mass Spectrometry Spectroscopy- Photo-) was made available in the laser laboratory to study inter-molecular dynamics across their bound and dissociative states. The ARPES-PIMS apparatus is similar to the imaging-PEPICO set up. However, the electrostatic optics were designed for highest possible temporal and spatial resolution. In combination with available fs-pump probe techniques, molecular dynamics can be followed on the femtosecond time scale. Earlier measurements of ethylbenzene and o-xylene were extended to the ionic system. Though the ionized species find less interest with combustion researchers, ionic states and the temporal evolution of their population is essential for the evaluation and interpretation of mass spectrometric measurements. Since these data are often not available, models must be used, which cannot be trusted a priori. An investment in the dynamics of ions and their dissociation is thus quite important for the reliable interpretation of experimental data.

Recent publications

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