Available online at www.sciencedirect.com

ScienceDirect

Proceedings of the Combustion Institute 35 (2015) 779–786

Proceedings of the Combustion Institute

www.elsevier.com/locate/proci

Electron ionization, photoionization and photoelectron/photoion coincidence spectroscopy in mass-spectrometric investigations of a low-pressure ethylene/oxygen flame

Daniel Felsmann[a], Kai Moshammer[a,*], Julia Krüger[a],
Alexander Lackner[a], Andreas Brockhinke[a], Tina Kasper[b],
Thomas Bierkandt[b], Erdal Akyildiz[b], Nils Hansen[c],
Arnas Lucassen[c], Patrick Oßwald[d], Markus Köhler[d],
Gustavo A. Garcia[e], Laurent Nahon[e], Patrick Hemberger[f],
Andras Bodi[f], Thomas Gerber[f], Katharina Kohse-Höinghaus[a]

[a] *Department of Chemistry, Bielefeld University, Universitätsstraße 25, D-33615 Bielefeld, Germany*
[b] *Mass Spectrometry in Reactive Flows – Thermodynamics (IVG), University of Duisburg-Essen, Duisburg, Germany*
[c] *Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94551, USA*
[d] *Institute of Combustion Technology, German Aerospace Center (DLR), Pfaffenwaldring 38-40, D-70569 Stuttgart, Germany*
[e] *Synchrotron SOLEIL, L'Orme des Merisiers, St. Aubin BP 48, 91192 Gif sur Yvette, France*
[f] *Molecular Dynamics Group, Swiss Light Source, Paul Scherrer Institut, Villigen CH 5232, Switzerland*

Abstract

Quantitative species data for the development and critical examination of combustion mechanisms are in high demand regarding the need for predictive combustion models that may assess the emission potential of current and emerging fuels. Mass spectrometric investigation is one of the often-used techniques to provide mole fractions of stable and reactive intermediates including radicals from specifically designed laboratory experiments. Molecular-beam mass spectrometry (MBMS) has been coupled with electron ionization (EI) and photoionization (PI) to determine the species compositions, and combinations of these techniques have been successful in the investigation of the combustion pathways in flames of numerous hydrocarbon, oxygenated and nitrogenated fuels. Photoelectron/photoion coincidence spectroscopy (PEPICO) has recently emerged as a novel diagnostics to be combined with flame-sampling mass spectrometry, and its potential as a complement of existing techniques is just about being explored. In a

---

* Corresponding author. Address: Physical Chemistry I, Department of Chemistry, Bielefeld University, 33615 Bielefeld, Germany. Fax: +49 521 106 6027.
E-mail address: kmoshammer@uni-bielefeld.de (K. Moshammer).

http://dx.doi.org/10.1016/j.proci.2014.05.151

multi-laboratory investigation, the present study has thus combined four different MBMS spectrometers (in Bielefeld, Germany, the Advanced Light Source in Berkeley, USA, the Swiss Light Source in Villigen, Switzerland, and the SOLEIL synchrotron in St. Aubin, France) to study a rich premixed argon-diluted low-pressure (40 mbar) ethylene–oxygen flame under comparable conditions. This was done with the aim of illustrating the respective properties and capabilities of the methods under these conditions, with an emphasis on the power offered by the synchrotron-based techniques, including PEPICO, for combustion chemistry studies. Examples include comparisons of selected species quantification as well as PEPICO spectra measured at different instruments.

Keywords: Molecular-beam mass spectrometry; Combustion chemistry; Electron ionization; Photoionization; PEPICO

1. Introduction

The world's demand for energy is still predominantly covered by combustion and, in spite of efforts to substitute fossil with renewable fuels, this situation will not drastically change in the foreseeable future. Detailed insight into the combustion chemistry of a wide range of different bio-fuels is thus needed [1] to develop new and optimized strategies for efficient and low-emission combustion processes. To this end, widely-used model systems are investigated combining theoretical and experimental methods to understand the complex chemical reaction networks in these systems. Typically, simplified systems such as low-pressure flames are used to provide experimental data with full speciation for the development of predictive models. A major challenge is the quantitative and structural identification of characteristic intermediate species, including isomers, for each fuel. Molecular-beam mass spectrometry (MBMS) is well established for quantitative combustion chemistry analysis.

Different ionization and detection methods provide a powerful instrumentarium for probing flame chemistry. Specifically, electron-ionization (EI) and photoionization (PI) MBMS, often in combination, have proven invaluable in numerous studies [2–7].

A newly explored technique in flame diagnostics, synchrotron-based photoelectron/photoion coincidence (PEPICO) spectroscopy, may add another dimension to the detection of combustion intermediates [8] with the potential to explore the simultaneous detection of the photoelectrons to reveal additional information about the detected species.

The aim of this study is to provide a first assessment of the combined power of these methods, choosing a fuel-rich low-pressure ethylene/oxygen flame as a model target.

2. Experiments

2.1. Experimental procedures

Molecular-beam mass spectrometry (MBMS) is a well-established technique for the investigation of laminar premixed low-pressure flames and has been accurately described before [2–4,7,9]. In brief, a gas probe is sampled out of the flame at ~40 mbar by a quartz nozzle and expanded into high vacuum to form a molecular beam and inhibit further reactions. The molecular beam passes through a skimmer into the ionization volume where the species are ionized by electrons (EI-MBMS) or photons (PI-MBMS). These ions are then separated by their mass with time-of-flight mass spectrometers that offer simultaneous species detection. Mass resolutions up to 4000 allow determination of the elemental composition of C/H/O species in the flames by their exact mass.

EI-MBMS has been applied successfully in many flame-sampling experiments [2], including ethylene flames [10–13]. The broad energy distribution of the electron beam does not permit isomer-selective species detection, and fragmentation reactions may occur that must then be considered. The power of EI-MBMS laboratory instruments lies in their facile use to provide a detailed and fast overview of nearly all species in the combustion process with only one single scan along the height above the burner at one fixed electron energy.

Isomer-selective combustion analysis has been realized with PI-MBMS, using synchrotron-generated tunable vacuum-ultraviolet (VUV) light [2,3,14–16]. With its high energy resolution, isomer identification and quantification of species is possible by their different ionization thresholds (IE), avoiding fragmentation problems by evaluating scans with the lowest photon energy above the IE. Thus, PI-MBMS requires a series of scans for a detailed analysis of the flame chemistry. Also, isomer-selective species identification relies on the energy resolution and comparison data such as photoionization efficiency (PIE) curves and ionization cross sections. Typically, isomers can be identified by their ionization energies and the form of the PIE curve. Although there is no principal limit in the number of isomers which can be separated with this technique, identification becomes difficult when three or more isomers are present as well as when two have very similar ionization energies. Both, EI-MBMS and