

D. Felsmann, K. Moshhammer, J. Krüger, A. Lackner, A. Brockhinke, T. Kasper, T. Bierkandt, E. Akyildiz, N. Hansen, A. Lucassen, P. Oßwald, M. Köhler, G.A. Garcia, L. Nahon, P. Hemberger, A. Bodi, T. Gerber, K. Kohse-Höinghaus, Electron ionization, photoionization and photoelectron/photoion coincidence spectroscopy in mass-spectrometric investigations of a low-pressure ethylene/oxygen flame, Proc. Combust. Inst. 35 (2015) 779-786.

The original publication is available at [www.elsevier.com/](http://www.elsevier.com/)

doi [10.1016/j.proci.2014.05.151](https://doi.org/10.1016/j.proci.2014.05.151)

Elsevier Editorial System(tm) for Proceedings of the Combustion Institute  
Manuscript Draft

Manuscript Number:

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

Article Type: Research Paper

Keywords: molecular-beam mass spectrometry, combustion chemistry, electron ionization, photoionization, PEPICO

Corresponding Author: Dr. Kai Moshhammer,

Corresponding Author's Institution: Bielefeld University

First Author: Daniel Felsmann

Order of Authors: Daniel Felsmann; Kai Moshhammer; Krüger Julia; Lackner Alexander; Brockhinke Andreas, apl. Prof.; Tina Kasper, Prof.; Thomas Bierkandt; Erdal Akyildiz; Nils Hansen, Dr.; Arnas Lucassen, Dr.; Patrick Oßwald, Dr.; Markus Köhler, Dr.; Gustavo A Garcia, Dr.; Laurent Nahon, Dr.; Patrick Hemberger, Dr.; Andras Bodi, Dr.; Thomas Gerber, Dr.; Katharina Kohse-Höinghaus, Prof.

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. As a novel diagnostics to be combined with flame-sampling mass spectrometry, photoelectron/photoion coincidence spectroscopy (PEPICO) has recently emerged, and its potential as a complement of existing techniques is just about being explored. In a 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.

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

Daniel Felsmann<sup>1</sup>, Kai Moshhammer<sup>1\*</sup>, Julia Krüger<sup>1</sup>, Alexander Lackner<sup>1</sup>, Andreas Brockhinke<sup>1</sup>, Tina Kasper<sup>2</sup>, Thomas Bierkandt<sup>2</sup>, Erdal Akyildiz<sup>2</sup>, Nils Hansen<sup>3</sup>, Arnas Lucassen<sup>3</sup>, Patrick Oßwald<sup>4</sup>, Markus Köhler<sup>4</sup>, Gustavo A. Garcia<sup>5</sup>, Laurent Nahon<sup>5</sup>, Patrick Hemberger<sup>6</sup>, Andras Bodi<sup>6</sup>, Thomas Gerber<sup>6</sup>, Katharina Kohse-Höinghaus<sup>1</sup>

<sup>1</sup> Department of Chemistry, Bielefeld University, Universitätsstraße 25, D-33615 Bielefeld, Germany

<sup>2</sup> Mass spectrometry in reactive flows – Thermodynamics (IVG), University of Duisburg-Essen, Duisburg, Germany

<sup>3</sup> Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94551, USA

<sup>4</sup> Institute of Combustion Technology, German Aerospace Center (DLR), Pfaffenwaldring 38-40, D-70569 Stuttgart, Germany

<sup>5</sup> Synchrotron SOLEIL, L'Orme des Merisiers, St. Aubin BP 48, 91192 Gif sur Yvette, France

<sup>6</sup> Molecular Dynamics Group, Swiss Light Source, Paul Scherrer Institut, Villigen CH 5232, Switzerland

Corresponding author: Dr. Kai Moshhammer

Physical Chemistry I, Department of Chemistry

Bielefeld University

33615 Bielefeld, Germany

Phone: +49 521 106 2199

Fax: +49 521 106 6027

Email: [kmoshammer@uni-bielefeld.de](mailto:kmoshammer@uni-bielefeld.de)

Colloquium: **LAMINAR FLAMES**

### Word Count (MS Word)

Abstract:	0242
Introduction:	0244
Experimental Procedures:	1145
Results and Discussion:	0972
Conclusions:	0278
Acknowledgements:	0128
30References:	0560
2 Tables:441+61	0502
7 Figures:478+202+334+186+310+167+281	1958
<b>Total Words (without abstract):</b>	<b>5786</b>

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<sup>1</sup> *Department of Chemistry, Bielefeld University, Universitätsstraße 25, D-33615 Bielefeld, Germany*

<sup>2</sup> *Mass spectrometry in reactive flows – Thermodynamics (IVG), University of Duisburg-Essen, Duisburg, Germany*

<sup>3</sup> *Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94551, USA*

<sup>4</sup> *Institute of Combustion Technology, German Aerospace Center (DLR), Pfaffenwaldring 38-40, D-70569 Stuttgart, Germany*

<sup>5</sup> *Synchrotron SOLEIL, L'Orme des Merisiers, St. Aubin BP 48, 91192 Gif sur Yvette, France*

<sup>6</sup> *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. As a novel diagnostics to be combined with flame-sampling mass spectrometry, photoelectron/photoion coincidence spectroscopy (PEPICO) has recently emerged, and its potential as a complement of existing techniques is just about being explored. In a 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 for each fuel. Molecular-beam mass spectrometry (MBMS) is a well-established technique for quantitative combustion chemistry analysis.

Different ionization and detection methods are available as 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].

As a newly explored technique in flame diagnostics, synchrotron-based photoelectron/photoion coincidence (PEPICO) spectroscopy is about to 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, bright vacuum-ultraviolet (VUV) light from synchrotrons [2,3,14,15]. 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 available photon energy above the IE of the species. Thus, PI-MBMS requires a series of scans for a detailed analysis of the flame chemistry. Also, isomer-selective species identification relies on quality of available 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. However, identification becomes difficult when too many isomers contribute to a flame measured PIE curve because these features overlap. Both techniques, EI-MBMS and PI-MBMS, are based upon the detection of ions. The extraction of the electronic footprint of the cation through electron/ion coincidence techniques, either at fixed photon energies (PEPICO) or fixed electron threshold kinetic energy ((T)PEPICO), has been known for a few decades. Although numerous examples of isomer differentiation using these techniques are available in the literature [16–19], it has not been considered in the context of combustion until very recently [8]. In addition to the electron energy, current setups (see section 2.2.3) incorporate the simultaneous measurement of the ion time-of-flight, so that a mass can be assigned to a direct ionization (parent), or a dissociative ionization (fragment) event. Therefore, PEPICO and (T)PEPICO experiments add another dimension of distinction

capability in the detection of combustion intermediates and will offer a further powerful tool to combustion diagnostics.

In the present study, fuel-rich laminar, low-pressure ethylene/oxygen/argon flames were investigated at four different laboratories (Bielefeld University, Advanced Light Source (ALS), Swiss Light Source (SLS), SOLEIL synchrotron), combining MBMS flame-sampling and different ionization and detection methods to provide a first inspection of some of their important properties.

## **2.2. Experimental setups**

The construction of the burner chamber and flame sampling apparatus of all instruments follows the same concept and is based on earlier designs, e.g. [9]. In brief, flames burn on a flat-flame burner against a quartz probe that is mounted on the cooled end flange of the burner chamber. A gas sample passes through a small orifice in the tip of the conical sampling probe into an intermediate chamber. This chamber is kept at a much lower pressure ( $10^{-3}$  mbar) so that a molecular beam is formed. This preserves flame radicals. The molecular beam passes through a skimmer into the ionization chamber of the detection device that is kept at pressures better than  $10^{-6}$  mbar. Here, the beam intersects with the beam of the ionizing particles and the ions are detected by time-of-flight mass spectrometry. In the instruments at the SLS and SOLEIL the electrons resulting from the ionization event are also detected. In both setups, the detection of an electron triggers the data acquisition on the time-of-flight spectrometer to register the corresponding ion in coincidence with the electron. Photoelectron spectra and mass spectra can be obtained from the raw data. In addition, the photon energy can be scanned. From these scans, mass-selected threshold photoelectron spectra, i.e. ions related to an ionization process without excess energy and PIE curves can be obtained with excellent energy resolution. The main features of the instrument are presented in a comparative table (table1). The technical details of the instrument in Bielefeld, at the ALS, and the SLS are described in [7], [3,20], and [8,21–23], respectively.

Only some details for the setup used at SOLEIL will be given here. A transportable burner and intermediate chamber were designed to fit the geometrical requirements of the SAPHIRS endstation at the DESIRS beamline equipped with the double imaging PEPICO

spectrometer (DELICIOUS III) at SOLEIL [24]. The molecular beam was crossed with the VUV beam and the generated ions and electrons were detected with the DELICIOUS III spectrometer, which couples a Wiley-McLaren TOF analyzer/3D momentum imager on the ion side to a velocity map imaging on the electron side.

Fig. 1 gives an impression how the flame-sampling system couples to the detection system in the four instruments.

### 2.3 Flame conditions

Detailed flame conditions applied at the different locations are summarized in Table 2. Fuel-rich premixed laminar flat ethylene/O<sub>2</sub>/Ar flames were stabilized at 40 mbar on McKenna-type burners.

### 2.4 Data evaluation

The procedure of data evaluation has been described previously [4–6]. In brief, due to the broad energy distribution, the mole fractions can be calculated in the EI-MBMS experiment using a calibration factor  $k_{i/R}(E)$  that includes all energy-dependent variables of the species  $i$  in relation to a reference species  $R$  (usually argon) [4]. Here, these calibration factors were generated from cold-gas measurements of known gas compositions (*direct calibration*), or were estimated by the RICS (*relative ionization cross sections*) method [9], or a convolution of literature ionization cross sections with the known kinetic energy distribution of ionizing electrons (see [4] for details) was used. The accuracy of mole fractions thus relies on the exactness of these factors.

In the PI-MBMS experiment, the argon signal cannot be measured below its ionization threshold of 15.759 eV and thus cannot be used as a reference. The evaluation of species mole fractions therefore results from the direct use of tabulated photoionization cross sections and thus from their accuracy.

Effort has also been made to quantitatively evaluate data from the SLS PEPICO experiment [8]. It relies on the same basic principles, but modifications must be introduced to account for the continuous ionization and the electron/ion coincidence arrangement (see [8] for details). Even quantification of C<sub>2</sub>H<sub>4</sub>O isomers was possible. However, state selected cross section data is needed for quantification of TPEPICO.

### 3. Results and discussion

#### 3.1 Major species

Mole fraction profiles for major species including  $C_2H_4$ ,  $O_2$ ,  $H_2$ ,  $CO$ ,  $CO_2$ , and  $Ar$  resulting from the EI-MBMS and PI-MBMS experiments are in very good agreement. Also equilibrium values [25] reached in the exhaust gases at an estimated temperature of 2150 K are matched well (see Fig. S1 for details). Both datasets have been evaluated in a similar manner following an internal calibration strategy [4] based on the elemental C, H, and O balances and on a single cold-gas calibration measurement of a defined  $CO/CO_2$  mixture. Major progress was made in recent years to improve consistency of data measured with different MBMS setups [5,7].

#### 3.2 Quantification and identification of intermediates

The main intermediate in the decomposition of ethylene is acetylene ( $C_2H_2$ ). Figure 2 shows the mole fraction profiles of  $C_2H_2$ . Shape and position of the maxima are in good agreement between the different experiments but peak values are different. However, mole fractions for EI-MBMS rely on direct calibration whereas those from PI-MBMS were determined with photoionization cross sections. Figure 2 illustrates the influence of different cross section values from the literature on the acetylene mole fraction. With the most recent cross section value from Cool et al. [26], the peak mole fraction is 0.031, in reasonable agreement with 0.045 from EI-MBMS while slightly earlier determinations [27,28] lead to 0.069 and 0.019, respectively, spanning a factor of about 3.5. In this case the absolute mole fraction values from PI-MBMS measurements tend to be less accurate than in the EI-MBMS experiment and demonstrate the necessity of high-quality determination of cross sections. A quantification of the acetylene profile measured via the ion signal at the SLS is in reasonable agreement with the data shown. The profile is however, shifted to larger HAB in agreement with the slightly more fuel-rich flame conditions.

The simple example  $C_3H_4$  can illustrate difficulties encountered with several isomeric structures. Here, only two isomers, allene and propyne, must be distinguished and quantitatively measured. With their different ionization thresholds (allene, IE = 9.69 eV and propyne, IE = 10.36 eV) they can be independently quantified by PI-MBMS, as shown in Fig. 3, which provides the measured PIE curve (right) and the mole fractions of allene and propyne by PI-MBMS together with the sum mole fraction from the EI-MBMS. The EI-MBMS evaluation used the electron-ionization cross section of propyne because isomer separation

with PI-MBMS resulted in higher mole fractions of propyne. This choice leads to a noticeable difference between the  $C_3H_4$  mole fraction and the sum of allene and propyne. Identification becomes more difficult for cases with more structural isomers, where selection of a cross section for a particular isomer to evaluate EI-MBMS data may lead to errors in the interpretation if no independent isomer-specific information is available. Thus a precise determination of the isomeric composition is needed for high quality quantification.

For the purpose of the identification (and subsequent quantification) of isomers, the determination of the onset of the signal in an energy scan is crucial. These onsets can be identified with unprecedented accuracy using (T)PEPICO data. Figure 4 shows the electron signal of  $m/z = 50$  measured at the SOLEIL instrument together with the photoionization cross section of 1,3-butadiyne [3]. The onset of the photoion signal is quite clear in this example, but the defined peak of the TPEPICO-signal shows strikingly how this technique can improve the identification of species with the help of their thresholds even in the presence of overlapping photoelectron spectra from isomers. From the TPEPICO signals in Fig. 5a (compared from both SLS and SOLEIL instruments) and the low-resolution photoelectron spectra from the literature [29,30], it seems that the dominant contribution in the spectrum of  $m/z = 42$  is due to ketene ( $C_2H_2O$ , IE = 9.61 eV). Here, peak mole fraction determined by EI-MBMS and PI-MBMS also show higher values for  $C_2H_2O$  (EI-MBMS:  $C_3H_6$ :  $4.48 \times 10^{-4}$ ;  $C_2H_2O$ :  $6.35 \times 10^{-4}$ /PI-MBMS:  $C_3H_6$ :  $3.46 \times 10^{-4}$ ;  $C_2H_2O$ :  $6.8 \times 10^{-4}$ ). Figure 5b shows that TPEPICO spectra can contribute to isomer separation even when concentrations of the flame species are very small and lead to spectra with low S/N. In the TPEPICO spectrum the thresholds of acetone and propanal can be clearly distinguished while they overlap in the PIE curve.

First successful attempts of isomer selective species quantification from the photoelectron signal have been reported recently [8] for  $C_2H_4O$  from the SLS experiment. In Fig. 6 these mole fractions are plotted together with the results of the EI-MBMS experiment as well as the mole fractions of the isomers obtained by the PI-MBMS experiment. Good agreement can be found especially between the isomer-resolved PI and the TPES data. The small differences in peak mole fraction can probably be explained by the slightly different flame conditions.

Identification of species by PI-MBMS needs the measurement of PIE curves by scanning the electron energy. The necessity of energy scans is also given for TPEPICO experiments.

However, PEPICO offers even more advantages: As can be seen in the two-dimensional ring pattern in Fig. 7 (upper panel), a complete photoelectron spectrum can be measured simultaneously at fixed photon energy with the DELICIOUS III spectrometer at SOLEIL for all masses present in the mass spectra. This PES is sufficient to identify species and quantify contributions of different isomers to the total signal and allows, in principle, to abstain from the time-consuming energy scans. In Fig. 7 (lower panel) this is demonstrated for  $C_2H_2$ . Here, the PE-spectra measured at a fixed energy of 12 eV is shown in comparison to the TPEPICO-spectra in the 11-12 eV range. The comparison of TPEPICO with the photoion signal shows that the onset of ionization can be determined much more readily and with higher accuracy from TPEPICO. Although PEPICO has a lower spectral resolution, this method will allow relatively rapid systematic measurements of the flame chemistry, while retaining the capability to distinguish isomers.

#### **4. Summary and Conclusion**

A fuel rich premixed argon-diluted low-pressure ethylene-oxygen flame under comparable conditions was measured at four different MBMS-setups (Bielefeld University, Advanced Light Source (ALS), SOLEIL synchrotron and Swiss Light Source (SLS)), combining MBMS flame-sampling and different ionization and detection methods. The focus of this study was the inspection of the important properties of these methods for combustion chemistry analysis. Electron-ionization MBMS experiments offer the possibility of a quick and detailed 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. However, no isomer-selective information about the detected species can be obtained. Photoionization MBMS helps closing this informational gap, but the quantification relies on the quality of measured photoionization cross sections. Difficulties in the identification of isomers (with the help of PIE curves) can occur when PIE curve onsets are diffuse or cross sections of isomers overlap. Here, PEPICO experiments promise to be a powerful tool. While EI- and PI-experiments use only information from the generated ions, PEPICO provides further information from the ejected electrons. This information carried by the species-specific photoelectrons opens an additional dimension for reliable identification of intermediate species structure besides mass and photoionization spectra, and will be ultimately useful in flames where a large

number of structural isomers may be formed. PEPICO spectra should allow the recording of fingerprints (IPs, vibrational envelopes) of different species present in the flame, leading to their isomer identification by comparison with *ab initio* calculations or with data from the literature which is especially useful for radicals which have very similar ionization energies and cannot typically be resolved in the PI experiment.

## Acknowledgements

The Bielefeld team acknowledges generous partial support by Deutsche Forschungsgemeinschaft within the Collaborative Research Center SFB 686, TP B3. They wish to thank Julia Wullenkord, Harald Waterbör for their support and the general staff at SOLEIL for smoothly running the facility. Some of the experiments were carried out at the VUV beamline of the Swiss Light Source, Paul Scherrer Institute (PSI). The work was financially supported by the Swiss Federal Office for Energy (BFE Contract Number 101969/152433). AL and NH are supported by the U.S. Department of Energy (USDOE), Office of Basic Energy Sciences (BES) under Grand No. DE-AC04-94-AL85000 and DE-SC0001198 (the Energy Frontier Research Center for Combustion Science). The Advanced Light Source is supported by the Director, Office of Science, BES, USDOE under Contract No. DE-AC02-05CH11231.

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## Tables

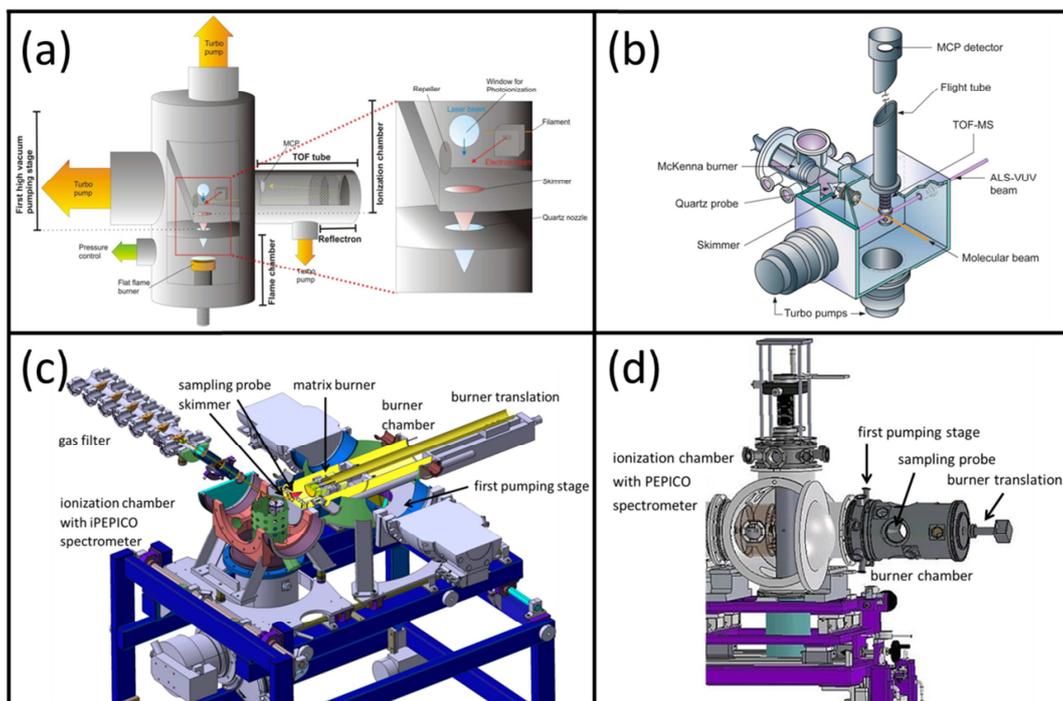
**Table 1:** Comparative summary of important instrument parameters.

	Bielefeld	ALS	SLS	SOLEIL
<b>burner</b>				
matrix material	bronze	stainless steel	bronze	bronze
diameter	6.4 cm	6.0 cm	6.0 cm	6.5 cm
<b>flame sampling system</b>				
probe material	quartz	quartz	quartz	quartz
probe angle	25°	tapered 25-40°	40°	25°
orifice diameter	500 μm	500 μm	500 μm	500 μm
distance probe/skimmer	~ 1cm	~ 1cm	~ 3 cm	~ 1cm
distance probe/ionization	22 cm	40 cm	14 cm	57 cm
<b>detection</b>				
	ToF-MS	ToF-MS	PEPICO	PEPICO
(m/Δm)	4000	3500	300	300
<b>ionization method</b>				
Source	filament	undulator	bending magnet	undulator
ionizing particle	electron	VUV photon	VUV photon	VUV photon
#electron/photons	1.00E+09	1.00E+14	1.00E+12	1.00E+14
energy range	5-70 eV	7.4-30 eV	5-30 eV	5-40 eV
energy resolution (E/ΔE)	1 eV (FWHM)	0.03 eV @ 10 eV	0.001 eV @ 10 eV	0.00008 eV @ 16 eV
<b>accessible data</b>				
burner profiles	yes	yes	yes	yes
PIE curves	no	yes	yes	yes
photoelectron spectra (PES)	no	no	yes	yes
mass-resolved PES	no	no	yes	yes
time requirement	12 hours	24 hours	24 hours	24 hours

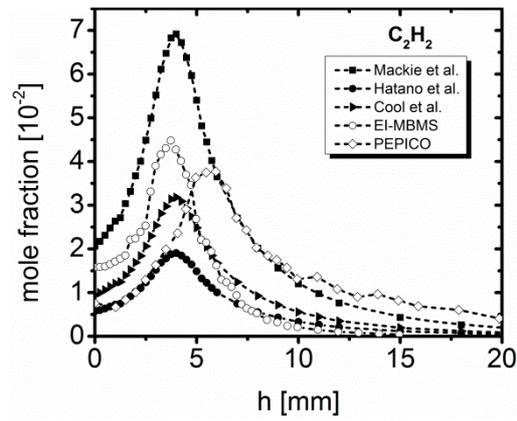
**Table 2:** Flame conditions used at the four different measurement systems in this study.

	Dilution [%]	$\phi$	Burner size [cm]	Ar [SLM]	O <sub>2</sub> [SLM]	C <sub>2</sub> H <sub>4</sub> [SLM]	Total flow [SLM]
EI-MBMS	25	1.7	6.4	1.14	2.18	1.23	4.55
PI-MBMS	25	1.7	6.0	1.00	1.91	1.09	4.00
SLS	50	1.8	6.0	2.00	1.25	0.75	4.00
SOLEIL	25	1.7	6.5	1.17	2.24	1.28	4.69

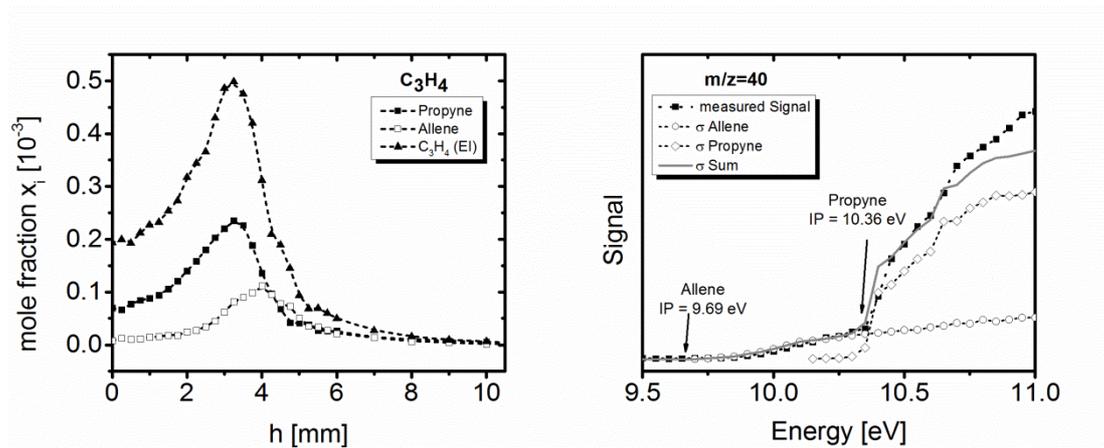
## Figures



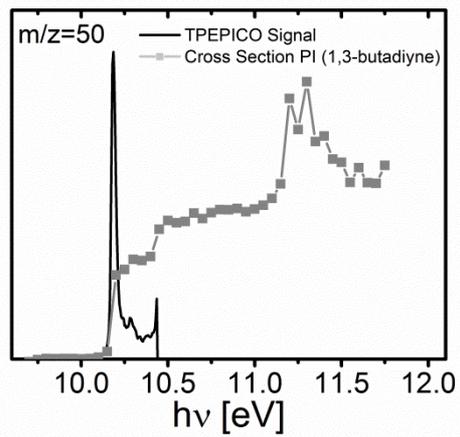
**Fig. 1:** Schemes of used instruments. (a) EI-MBMS (Bielefeld University), (b) PI-MBMS (ALS), and PEPICO-instruments at the SLS (c) and SOLEIL synchrotron (d).



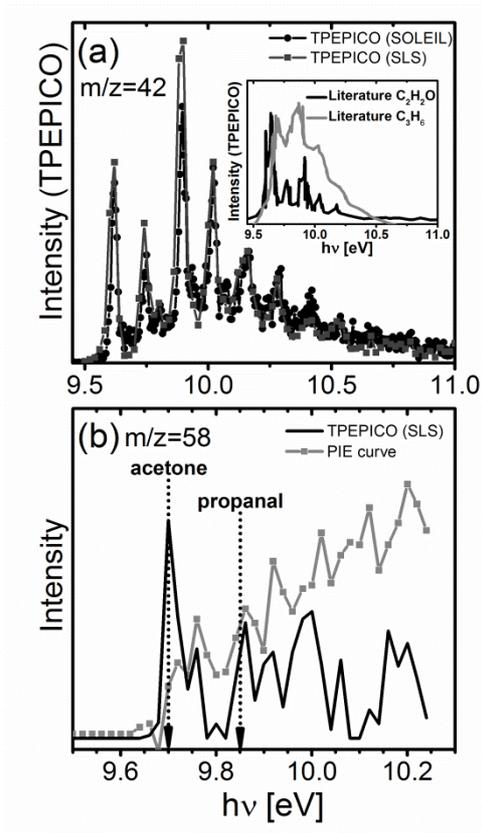
**Fig. 2:** Mole fraction profiles of  $C_2H_2$  measured with EI-MBMS, PI-MBMS, and PEPICO. In the EI-MBMS system, the species can be calibrated with direct gas measurements while the use of different PI cross sections [3,27,28] in the PI-MBMS experiment results in different mole fractions for the same experimental data. The PEPICO data were analyzed with the cross section of Cool.



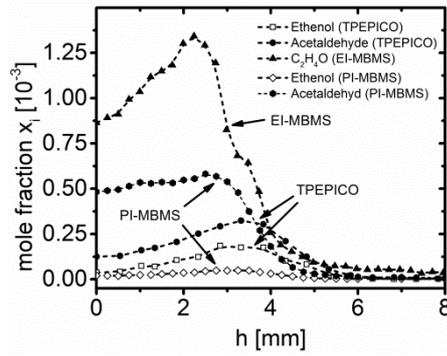
**Fig. 3:** Mole fraction profiles of the isomeric intermediate species  $C_3H_4$ , allene and propyne (left). PIE curve of  $m/z = 40$  measured by PI-MBMS at the Advanced Light Source.



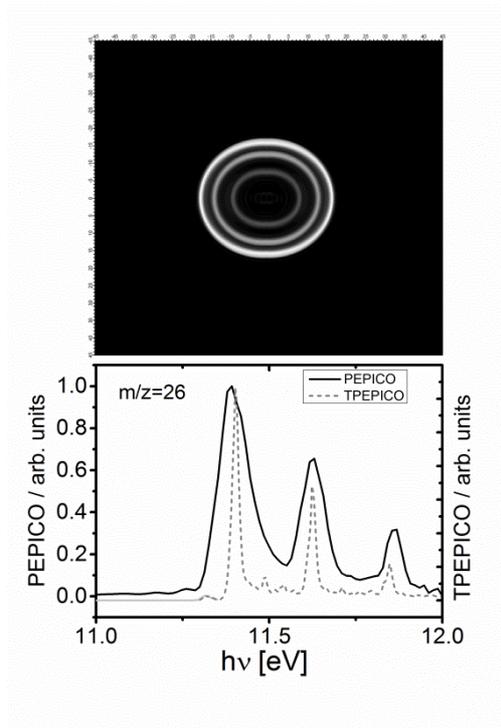
**Fig. 4:** Photoionization cross section of 1,3-butadiyne [3] and electron signal at  $m/z = 50$  measured with TPEPICO at SOLEIL synchrotron.



**Fig. 5:** (a) Threshold photoelectron spectra  $m/z = 42$  measured at SOLEIL synchrotron and Swiss Light Source sampled from the reaction zone of the flame. Literature PE spectra for ketene [30] and propene [29]. (b) Threshold photoelectron spectra  $m/z = 58$  (SLS).



**Fig. 6:** Mole fraction profiles of  $C_2H_4O$  (EI-MBMS) as well as mole fractions for ethenol and acetaldehyde from the PI-MBMS experiment from the ALS and the TPEPICO-experiment from the SLS [8].



**Fig. 7:** Inverted velocity map image (VMI) obtained at a fixed photon energy of 12 eV for mass 26 (upper panel). Photoelectron spectrum (PES) extracted from the VMI and TPEPICO spectrum in the energy range of 11-12 eV, both obtained with the SOLEIL set-up.

## Figure captions

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**Supplemental Material**

[Click here to download Supplemental Material: MBMS\\_ethylen\\_PEPICO\\_supplemental Material.pdf](#)

## Submission

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

Results produced by eXtyle 

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