

# Combustion Reactions Followed by Photoelectron Photoion Coincidence Spectroscopy

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## Introduction

We study bimolecular and unimolecular chemical reactions. We seek a technique that is:

- Universal (applicable to a broad range of molecules & atoms)
- Selective (able to identify similar species unambiguously)
- Sensitive (detecting even radicals or intermediates, with short lifetimes or low abundance)
- Time-resolved (at least on the microsecond timescale)
- Multiplexed (meeting all these goals simultaneously)

Synchrotron Photoionization Mass Spectrometry meets these goals, but can we do better?

## Photoelectron Photoion Coincidence Spectroscopy

Photoelectron spectroscopy (PES) offers greater selectivity than photoionization (PI) spectroscopy because transitions to final cation states appear as peaks in PES. Unfortunately, electrons have the same mass regardless of the mass of the neutral one ionizes. However, Photoelectron Photoion Coincidence Spectroscopy can provide mass-selected photoelectron spectra.

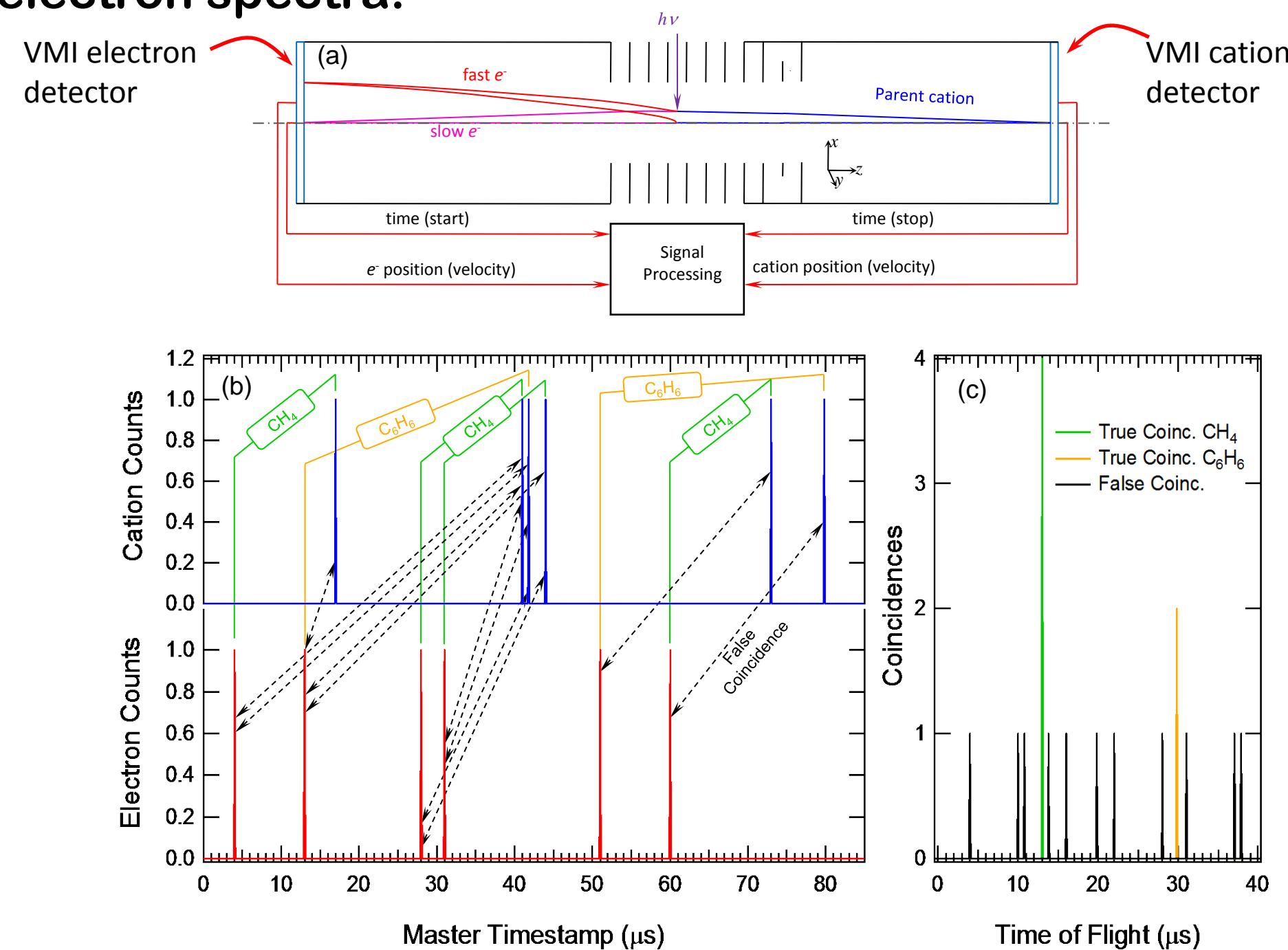


Fig. 1 PEPICO schematic, illustrating true and false coincidences

## PEPICO provides a more definitive spectral fingerprint

We mixed two C<sub>4</sub>H<sub>6</sub> hydrocarbons and analyzed them by PEPICO and PI spectroscopy.

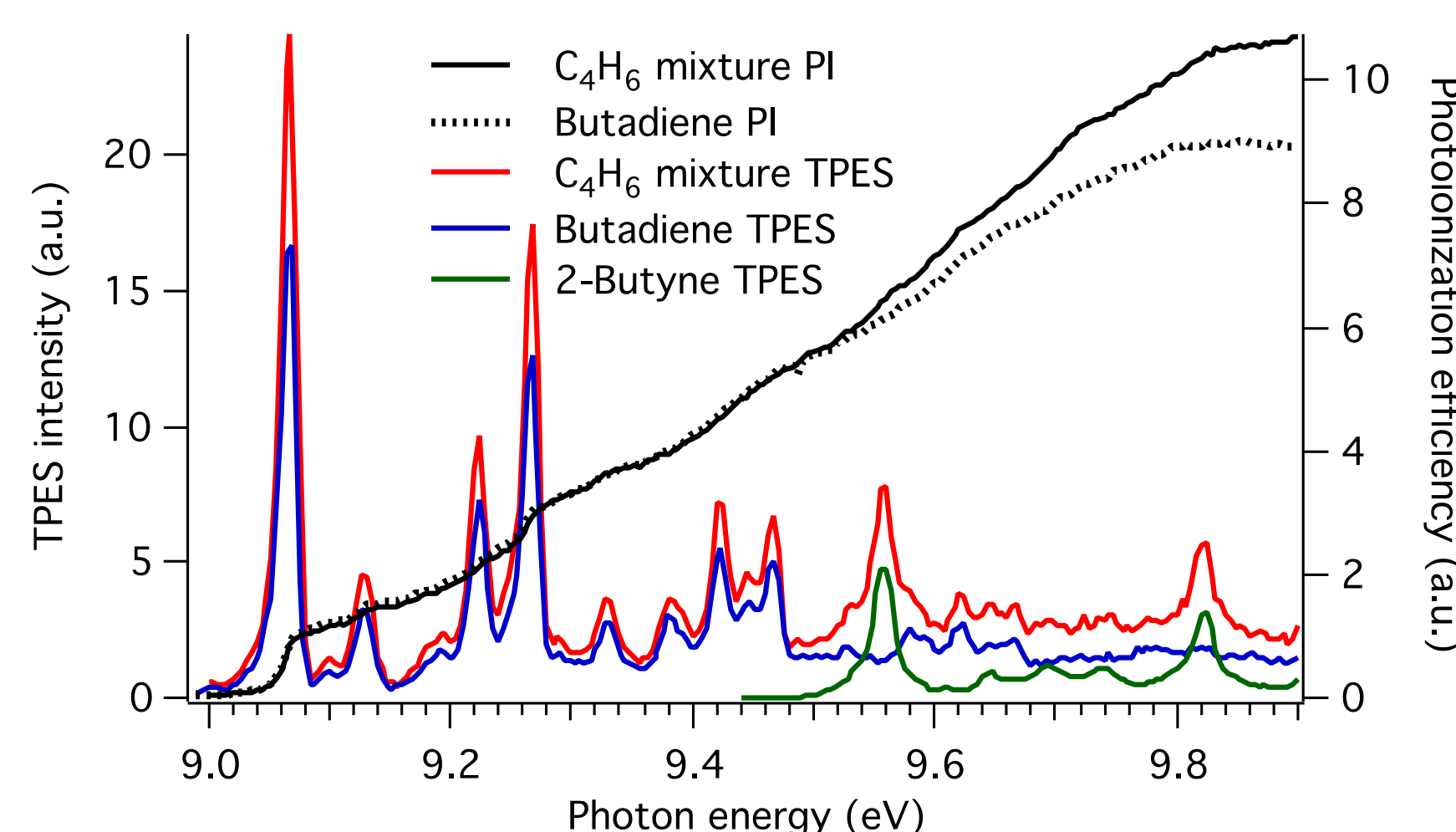


Fig. 2 Threshold photoelectron spectrum (TPES) of the 1,3-butadiene and 2-butyne mixture, together with the photoionization spectra extracted from the same data

## Combustion Reactions Followed by PEPICO (CRF-PEPICO)

We designed a prototype instrument to study time-resolved chemical reactions with PEPICO.

Key goals are:

- Cation mass resolution  $m/\Delta m > 1000$ .
- Dynamic range at least  $10^5$ .
- Photoelectron spectra with fixed or tunable VUV light
- Ability to study reactions carried out in a photolysis flow tube reactor

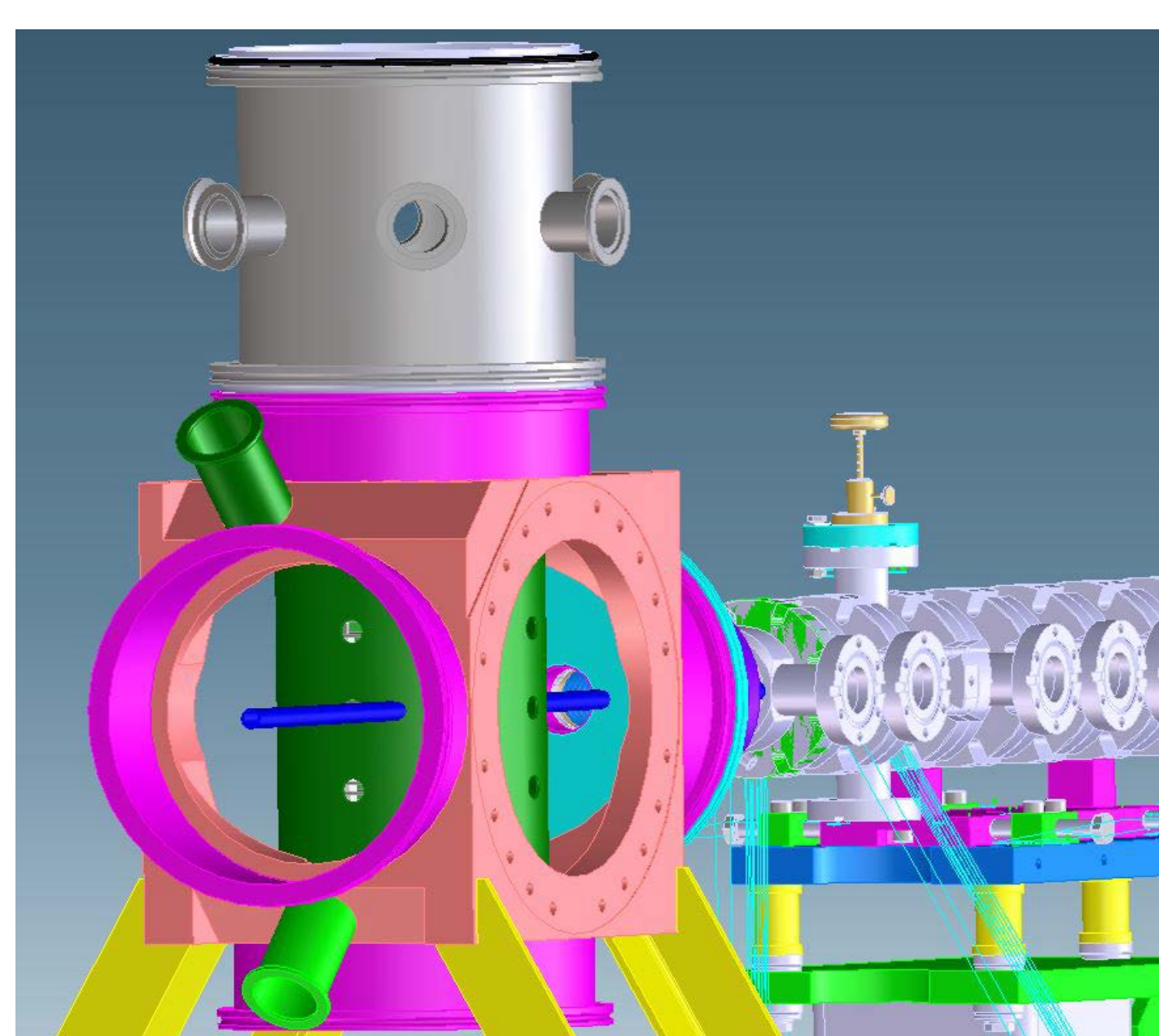
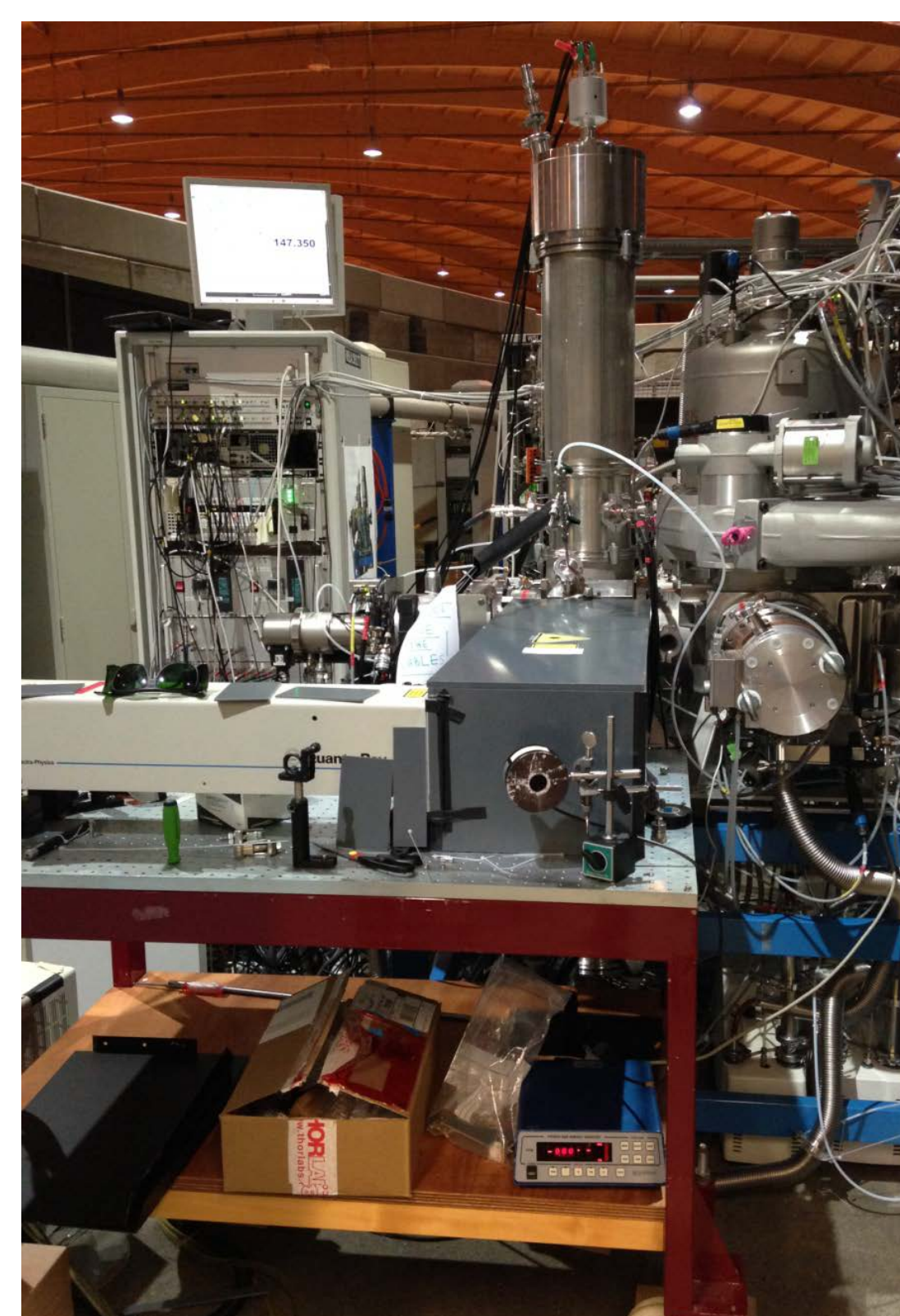


Fig. 3 CRF-PEPICO experimental setup including the gas filter, Mu-metal shielding cylinder around the charged particle optics colored in green and the flow tube in blue.



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## Velocity Map Imaging (VMI) Electron and Ion Optics

The CRF-PEPICO experiment performs velocity map imaging of photoelectrons and photoions, using two with Roentdek DLD-40 fast delay line detectors. Each electrostatic plate in the electron and ion optics has an individually controlled voltage. Our goal is to have a single extraction field (for electrons and cations) but two independent lenses for velocity map imaging.

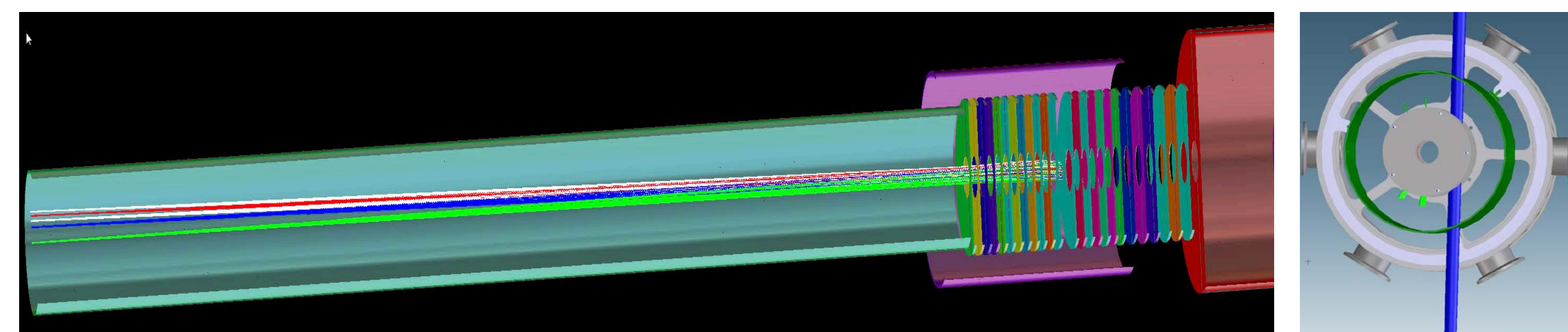
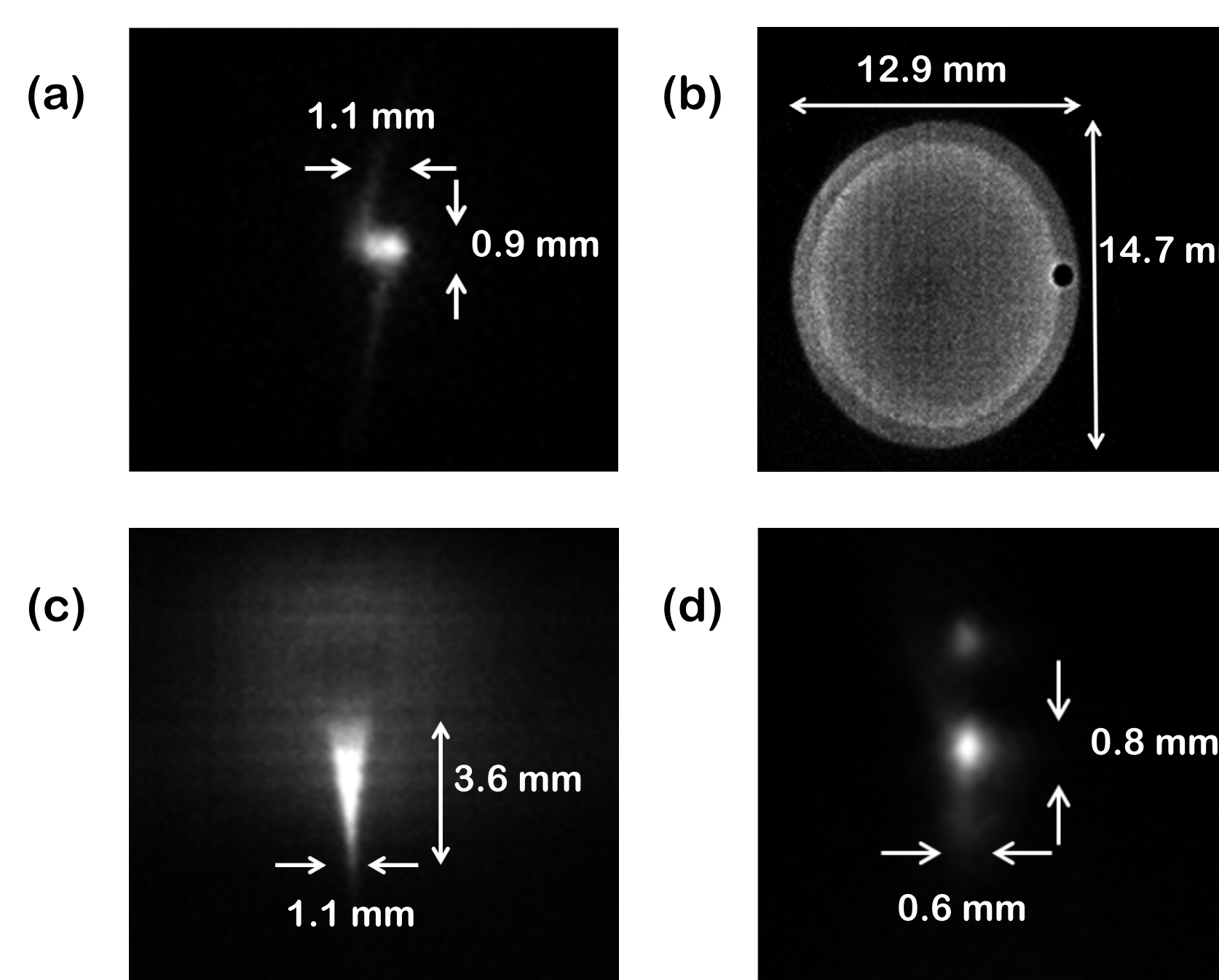


Fig. 4 3D SIMION model of the electron and ion optics, showing VMI focusing of electrons from 0 to 1 eV (left) and the beginning of the ion flight tube (right); 3D view of the electron/ion optics with the flight tube (blue) and the magnetic shielding cylinder (green).



Ionization of Ar atoms provides a test case. Using 7 extraction and 4 VMI plates on the electron side, and 4 extraction plates and 10 VMI plates on the ion side, the mass resolving power of more than 300 was achieved. Ion images recorded from gas exiting the low-pressure flow tube, or a supersonic expansion, allows us to visualize the velocity distributions of these two sources.

Fig. 5 Velocity mapped images obtained at 250 V cm<sup>-1</sup> extraction field of Ar (a) photoelectrons excited at threshold, (b) photoelectrons excited with  $h\nu = 16.500$  eV. The two circular patterns correspond to the <sup>2</sup>P<sub>3/2</sub> and <sup>2</sup>P<sub>1/2</sub> electronic states of Ar\*. (c) Ar ion image from the flow tube reactor, and (d) Ar ion image from a supersonic expansion

## Kinetics of the CH<sub>2</sub>I + O<sub>2</sub> Reaction

To test the CRF-PEPICO apparatus for study of bimolecular chemical reactions, we chose the CH<sub>2</sub>I + O<sub>2</sub> reaction. Photolysis of CH<sub>2</sub>I<sub>2</sub> at 355 nm produced CH<sub>2</sub> radicals. We monitored CH<sub>2</sub>I<sup>+</sup> and the corresponding photoelectron spectrum as a function of time following the photolysis laser. We obtain  $k = 1.78 \pm 0.019 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  for the rate coefficient of the CH<sub>2</sub>I + O<sub>2</sub> reaction. This value is in a good agreement with two previous measurements of this reaction by Masaki et al. ( $k = 1.6 \pm 0.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , J. Phys. Chem. 1995) and Timonen et al. ( $k = 1.39 \pm 0.01 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , PCCP 2006).

$h\nu = 9.19 \text{ eV}$ ;  $P_{\text{reactor}} = 1.7 \text{ mbar}$

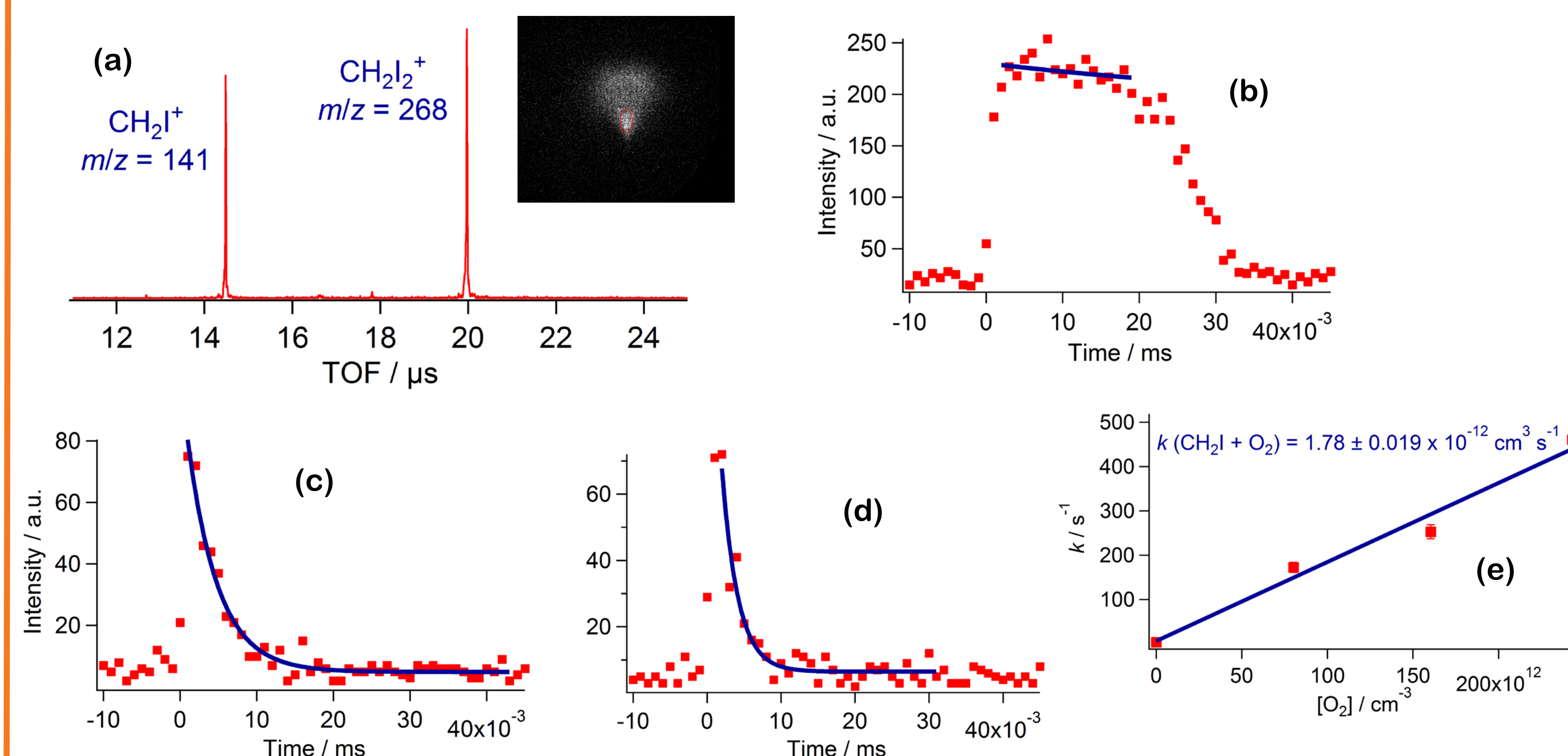


Fig. 6 (a) Time-of-flight mass spectrum of photolytically generated CH<sub>2</sub>I<sup>+</sup> at 9.19 eV along with the total ion image recorded (the region of interest is marked with red circle). Time-resolved CH<sub>2</sub>I<sup>+</sup> at (a) 0.0 cm<sup>-3</sup>, (b)  $0.80 \times 10^{14}$  cm<sup>-3</sup> (c)  $1.60 \times 10^{14}$  cm<sup>-3</sup> oxygen concentrations. (d) First order rate constants vs. [O<sub>2</sub>] yield the bimolecular rate coefficient.

## Detection of a Criegee Intermediate

A target in the CRF-PEPICO test experiments was Criegee intermediate CH<sub>2</sub>OO (formaldehyde oxide), a key species in tropospheric ozonolysis of alkenes. The reacting mixture was ionized at 10.00 eV by synchrotron VUV radiation. We detected CH<sub>2</sub>OO, but in concentrations too small to obtain a full photoelectron spectrum during our beamtime at the synchrotron. Nevertheless, these experiments demonstrate the power that CRF-PEPICO promises for the study of free radical reactions with improved selectivity, but also for the acquisition of clean photoelectron spectra of a free radical when many other species are present.

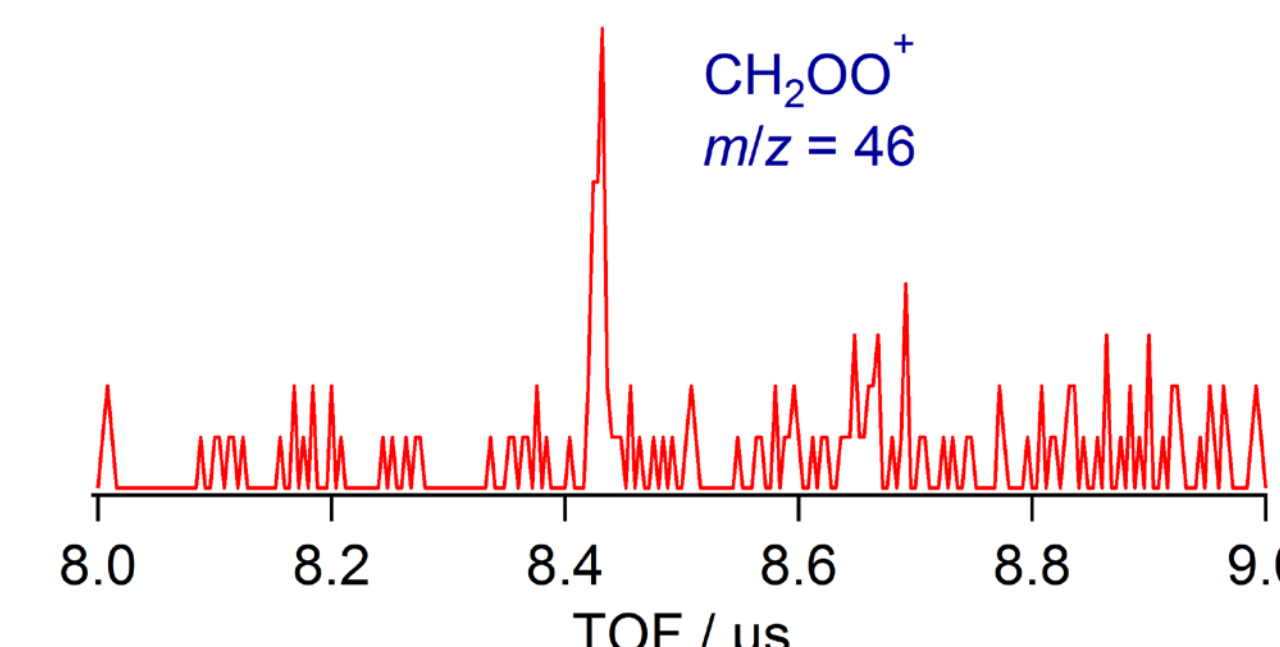


Fig. 7 CRF-PEPICO mass spectrum of the Criegee intermediate at  $h\nu = 10.00$  eV.

