

High-Resolution Double Velocity Map Imaging Photoelectron Photoion Coincidence Spectrometer for Gas-Phase Reaction Kinetics

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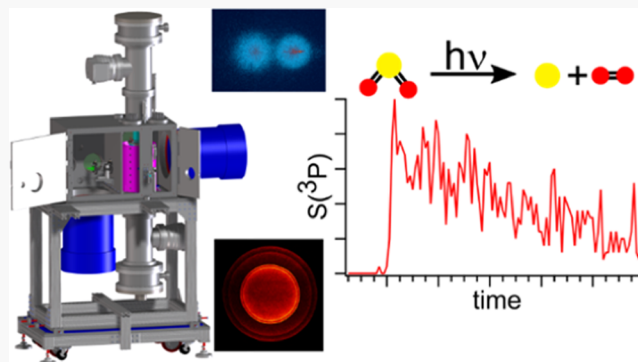


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ABSTRACT: We present a new photoelectron photoion coincidence (PEPICO) spectrometer that combines high mass resolution of cations with independently adjustable velocity map imaging of both cations and electrons. We photoionize atoms and molecules using fixed-frequency vacuum ultraviolet radiation. Mass-resolved photoelectron spectra associated with each cation's mass-to-charge ratio can be obtained by inversion of the photoelectron image. The mass-resolved photoelectron spectra enable kinetic time-resolved probing of chemical reactions with isomeric resolution using fixed-frequency radiation sources amenable to small laboratory settings. The instrument accommodates a variety of sample delivery sources to explore a broad range of physical chemistry. To demonstrate the time-resolved capabilities of the instrument, we study the 193 nm photodissociation of SO_2 via the $\tilde{\text{C}}(^1\text{B}_2) \leftarrow \tilde{\text{X}}(^1\text{A}_1)$ transition. In addition to the well-documented $\text{O}(^3\text{P}_j) + \text{SO}(^3\Sigma^-)$ channel, we observe direct evidence for a small yield of $\text{S}(^3\text{P}_j) + \text{O}_2(^3\Sigma_g^-)$ as a primary photodissociation product channel, which may impact sulfur mass-independent fractionation chemistry.



1. INTRODUCTION

Photoionization mass spectrometry (PIMS) is a powerful tool to study unimolecular and bimolecular reactions in the gas phase. The Sandia time-resolved multiplexed photoionization mass spectrometer (MPIMS)¹ has been successfully used to detect reaction intermediates and explore reaction mechanisms in combustion,^{2,3} atmospheric,^{4–6} and extraterrestrial chemistry.^{7,8} Coupled to a source of tunable vacuum ultraviolet (VUV) radiation for single-photon “soft” ionization, this method allows one to interrogate the chemistry of reacting neutral molecules as a function of kinetic time, mass, and photoionization (PI) energy. Different isomers of a species, e.g., conformers (rotational isomers) or structural isomers, are detected at the same mass-to-charge (m/z) ratio but may be distinguished and quantified by the onset and shape of their PI spectra. As powerful as this method is, when several isomers are detected at a single m/z ratio, identification and quantification become increasingly challenging because PI spectra usually lack definitive peaks, which are the basis for molecular signatures in many other spectroscopic techniques. Instead, in PI spectroscopy, the total ion yield as a function of photon energy is typically a smoothly rising curve, with inflections instead of sharp peaks. The PI spectrum is often further complicated by the competition between direct ionization, autoionization, and photodissociation that can affect the shape of the PI spectrum. Despite these complications, conformer-specific reaction rate constants in

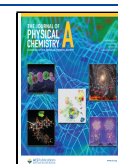
important atmospheric reactions of Criegee intermediates have been measured with the MPIMS.⁹

Photoelectron spectroscopy (PES) is a more information-rich photoionization technique to distinguish different isomers, where spectra with sufficient resolution provide vibrational and even rotational features that are useful as molecular fingerprints. In PES, the quantization of cation rovibronic states causes quantization of the electron kinetic energies, creating distinct peaks in the photoelectron spectrum.¹⁰ However, despite some pioneering efforts,¹¹ photoelectron spectroscopy has historically not been an attractive method to study mixtures of neutral species, as found in many chemical reactions. Although the photoions from a mixture of neutrals can be separated by their m/z ratios, PES provides only the photoelectron kinetic energies, and hence, one obtains a sum of photoelectron spectra when a mixture of neutrals is ionized. Such composite spectra are usually too complex to be useful, due to overlapping spectra of many species, which can make the analysis difficult to impossible.

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To utilize the advantages of PES and PIMS at the same time, one needs to combine the two techniques. In photoelectron photoion coincidence (PEPICO) spectroscopy, photoions are detected in coincidence with photoelectrons. The arrival time difference between an electron and its corresponding ion defines the m/z value of the latter and enables one to extract a photoelectron spectrum associated with each m/z ratio: the (ion) mass-resolved photoelectron spectrum. PEPICO spectrometers have a long history of achievements in thermochemistry,^{10,12–14} unimolecular dissociation dynamics,¹⁵ and ultra-fast studies of chemical reactions.^{16–20} Early versions of double imaging, also known as i^2 PEPICO spectrometers, i.e., with velocity map imaging and position-sensitive detectors for both electrons and cations, explored molecular frame photoelectron angular distributions²¹ and dissociative photoionization.²² Recently, PEPICO has blossomed as a sensitive and selective method for the analysis of multicomponent reacting mixtures, first with an imaging detector only for photoelectrons,^{23,24} and later by the i^2 PEPICO instruments at the Swiss Light Source^{25,26} and the SOLEIL synchrotrons.^{27,28} These double-imaging instruments have been used to explore a wide range of problems in physical chemistry.^{26,29–42}

The data collection requirements for a time-resolved PEPICO instrument are significant. Modern detectors and electronics allow for continuous data acquisition in a multiple-start multiple-stop approach, where each electron/cation pair detected within a chosen time window is termed a coincidence.⁴³ The continuous acquisition mode is a good match to the quasi-continuous light of modern synchrotrons and can handle large ionization count rates. An electron/cation pair that originates from a single neutral species is called a true coincidence, and the time difference between the arrival of the electron and cation at their respective detectors yields a time-of-flight (TOF) mass spectrum of the cations. By contrast, a false coincidence is an electron/cation pair that did not originate from the same neutral species but is detected within the chosen coincidence time window. False coincidences form a flat, “white noise” background over the entire span of the mass spectrum. Although one can subtract this false-coincidence background, its Poisson-noise remains, limiting the dynamic range and potentially obscuring small signals, which are especially important to detect in chemical reaction studies. Nevertheless, we have been pursuing technical advances for the last several years to create a new time-resolved, multiplexed PEPICO instrument for the detailed study of chemical reaction mechanisms.

In an earlier publication, we presented a prototype instrument (CRF-PEPICO), realized at the Swiss Light Source, to test the major design concepts for the instrument described here. The CRF-PEPICO prototype built upon advances from an earlier i^2 PEPICO instrument.²⁶ The CRF-PEPICO makes use of an ion deflector together with position-sensitive detectors to image both cations and electrons. Dynamic deflection of the cations enables false-coincidence rejection by linking the time of ionization with the arrival position on the detector.⁴⁴ The CRF-PEPICO also incorporates charged-particle optics that allow for the installation of a slow-flow side-sampled quartz reactor enabling chemical reaction studies in a collisional environment. The CRF-PEPICO has a moderate mass resolution of $m/\Delta m = 780$ and performs well in mass-resolved threshold photoelectron spectroscopy experiments using tunable VUV light.

In this paper, we present a new and substantially improved PEPICO instrument, which builds on insights from the CRF-PEPICO prototype. From inception, we designed our new instrument to study gas-phase reaction kinetics, complementing MPIMS and improving our ability to distinguish different isomers or conformers. In addition, it also incorporates pulsed and continuous supersonic molecular beam sources and has the flexibility to accommodate other sources and experimental approaches in the future. Our design goals for the new instrument are the following:

- (1) The instrument should provide high mass resolution, comparable to or better than the MPIMS ($m/\Delta m \gtrsim 1500$), to distinguish between isobaric ions that have the same nominal mass but slightly different exact masses, e.g., CH_2CO vs C_3H_6 .
- (2) The instrument should provide high-resolution velocity map imaging (VMI) of electrons—providing photoelectron spectra and angular distributions—and cations, to distinguish between parent ions and fragment ions arising from dissociative ionization. The goals of high mass resolution and good velocity mapping oppose each other. Linear time-of-flight spectrometers achieve their best mass resolution via linear electric fields that are the basis of Wiley–McLaren space focusing,⁴⁵ whereas velocity mapping requires curved electric fields that form electrostatic lenses.⁴⁶
- (3) The instrument should provide high-resolution photoelectron spectra from both tunable and fixed-frequency VUV sources. Although tunable sources such as synchrotrons enable the most powerful approaches, such as threshold and slow-electron photoelectron spectroscopy,⁴⁷ operation at a fixed VUV energy can be more efficient given limited experimental time^{14,48} and is easier to implement in small laboratory settings. This goal requires that the VMI covers a sufficiently wide range of electron kinetic energies (eKE) with the desired resolution. We want to be able to detect electrons with kinetic energies up to 6 eV with a fixed-frequency source and a desired resolving power of better than 1%, corresponding to 10 meV at 1 eV of eKE.
- (4) The instrument should handle large ionization count rates (~ 100 kHz) to enable studies at photon energies where minor species (reaction products or intermediates) are ionized in the presence of high signals from an excess reactant or other molecules present in much higher concentrations.
- (5) The system should analyze the raw experimental data in real time, including the inversion of the velocity map images, allowing the operator to adjust experimental parameters quickly for efficient use of available experimental time.
- (6) The instrument should be mobile and robust for use both at remote synchrotrons and in our home laboratory.

In the following sections, we describe the new instrument and report its performance. For this work, we did not have access to a synchrotron and instead used a gas-discharge lamp to generate VUV radiation for the experiments described herein. To test the time-resolved operation of this instrument, we measured the photodissociation of SO_2 at 193 nm, and we report a new, minor photodissociation channel that produces $\text{S}(^3\text{P}_j) + \text{O}_2(^3\Sigma_g^-)$.

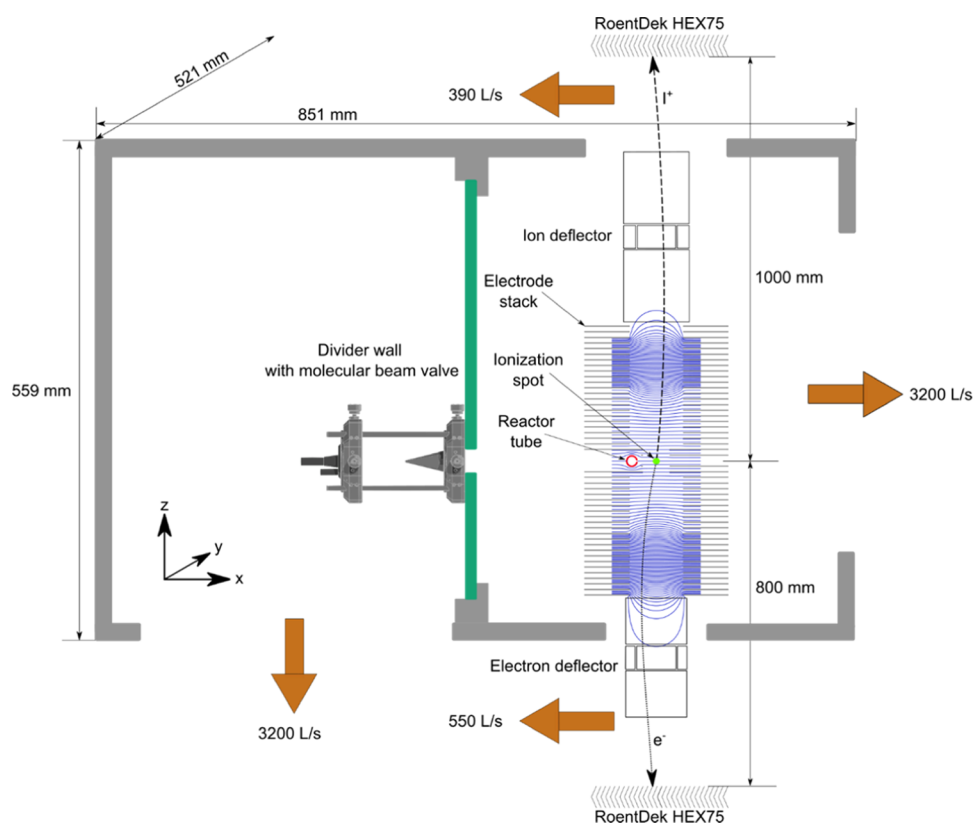


Figure 1. Schematic cross section of the PEPICO experiment. Green: Removable divider wall with molecular beam valve and skimmer assembly. Blue: Equipotential lines with 50 V separation from SIMION simulation with the 120 V/cm extraction field in the center. Red: Reactor tube perpendicular to the XZ plane. Light green: VUV radiation parallel with the reactor. Orange arrows indicate turbomolecular pumps.

II. EXPERIMENTAL SECTION

II.I. Hardware. Figure 1 shows a schematic of the instrument. The rectangular vacuum chamber is pumped by two 3200 L/s turbomolecular pumps. The ion and electron flight tubes each have an additional turbo pump, 390 L/s on the ion side and 550 L/s on the electron side, to improve the vacuum close to the detectors. The turbomolecular pumps are backed by two 500 L/min dry multilobe pumps. When used at a synchrotron, the chamber must be aligned to the fixed photon beam of the light source. Therefore, the frame of the chamber glides freely on a sheet of ultra-high-molecular-weight polyethylene that is the top surface of a supporting platform anchored to the ground. With this design, the platform can be securely attached to the floor, while pusher screws threaded into the platform provide fine lateral translation and rotation in the x,y -plane of the frame with low friction. The height of the chamber can be adjusted with threaded studs on swivel feet, providing full motion in x, y, z , pitch, roll, and yaw. See Figure S1 for a rendering of the CAD model of the chamber and the frame.

The heart of the instrument is the charged-particle optics stack, within which the sample gas is crossed by VUV light from a discharge lamp, in this work, or monochromatized synchrotron radiation in the future. To address goal (1) of the introduction, high mass resolution in TOF mass spectrometers requires Wiley–McLaren space focusing, which corrects, to first order, for the different birth positions along the TOF axis (the z -axis in Figure 1) of a group of ions. The elegant solution of Wiley and McLaren uses electrodes with conducting meshes to generate two regions of constant electric potential gradient:

the lower electric field of the extraction region in which ions are formed and a higher-field acceleration region.⁴⁵ Although the original ion imaging apparatus of Chandler and Houston⁴⁹ used electrodes with meshes, the later breakthrough of velocity map imaging⁴⁶ eliminated these meshes, which generated curved electric fields that map particles with equal perpendicular momenta onto the same position on a detector, regardless of the birth positions of the ions or electrons. Inspired by the work of Lin et al.,⁵⁰ and following up on the prototype design at the Swiss Light Source,²⁶ we accommodate these two opposing requirements by designing large-diameter, closely spaced, mesh-free charged-particle optics that allow for a large separation of the constant potential gradient (extraction) and curved-field regions, yielding almost perfectly linear fields close to the ionization volume. The result is high mass resolution, with good imaging due to the curved fields far away from the center. The VMI fields for cations and electrons are independently adjustable.

Photoelectrons and photoions are accelerated in opposite directions and detected on two RoentDek HEX75 time- and position-sensitive microchannel plate (MCP) detectors with 75 mm active diameters. The front face of the ion detector is 1000 mm above the ionization point, whereas the electron detector face is 800 mm below the ionization point. Each detector provides six delay-line signals (two per delay line) that define the (x, y) position of charged-particle impact and a capacitively coupled signal from the front MCP that carries information on the absolute detection timestamp of a charged particle. Using this timestamp, if we were to ionize with an isolated few-ps or shorter light pulse, we could measure the full 3D velocity vector of both cations and electrons. However, for use with

VUV sources that are continuous (our discharge lamp) or quasi-continuous (multibunch 3rd generation synchrotron sources), we cannot obtain the electron TOF because we do not know the time of ionization. Note that Garcia et al.,²⁷ in their double-imaging PEPICO spectrometer, created a modified Wiley–McLaren imaging design that has aspects of both spatial and velocity imaging. In a subsequent double-skimmed molecular beam modification, they achieved the best mass resolution recorded to date in a PEPICO instrument of $m/\Delta m = 1700$ (FWHM).²⁸ By contrast, our cation detection uses purely VMI imaging and yet achieves a mass resolution (see Section III.I) of $m/\Delta m = 6700$ (FWHM).

The electrodes consist of 48 circular 1 mm thick stainless steel disks, each with an outer diameter (OD) of 160 mm. The inner diameter (ID) of each plate is 60 mm except for the 4 electrodes surrounding the ionization point, which have 30 mm IDs. Along the *z*-direction, the center-to-center electrode spacing is 6.25 mm. The 26 inner electrodes around the center are connected together through a resistor chain using uncoated 10 M Ω resistors (MG716 from Caddock Electronics Inc.). The resistors are installed directly between the electrodes inside the vacuum chamber and form a voltage divider to generate a linear electric field inside the center of the ion optics. All other electrodes are connected to individual high-voltage power supplies except for the three electrodes furthest away from the center on the ion side, which are held at the flight tube potential. Therefore, reconfiguration of the electric fields and the dimensions of the extraction and imaging regions is possible without breaking vacuum. All data presented here were recorded with a 120 V/cm electric field in the ionization region. We simulated the charged-particle optics in SIMION⁵¹ with extraction field strengths between 50 and 140 V/cm and they perform well over this range. The ability to change the extraction field strength offers a number of advantages, most importantly the ability to adjust the final image magnification on both detectors. Specifically, the electron kinetic energy corresponding to electrons at the detector edge can be adjusted from 2.7 to 6.9 eV over this extraction field range. Furthermore, mass resolution increases with increasing extraction field, whereas photoelectron kinetic energy resolution is improved at lower field strengths. Changing the extraction field is also useful to measure unimolecular rate constants of dissociative photoionization processes over a wide range of rates.⁵²

Above the electrode plates on the ion side is an einzel lens with its center electrode segmented into four equal quadrants by vertical cuts to enable raster scanning of the ions for false-coincidence rejection as described in an earlier publication.⁴⁴ The center of the einzel lens is 250 mm above the center of the ion optics. The einzel lens is made from an aluminum tube with ID = 62.7 mm and OD = 73.0 mm held by a 3D-printed cylindrical polyether ether ketone (PEEK) holder. Above the einzel lens, an aluminum tube with ID = 86.4 mm and OD = 88.9 mm is held at the same potential as the final three plates, creating a field-free flight tube that extends upward to the cation detector. A 19 mm long cylindrical tube with ID = 111.8 mm encloses the front of the MCPs and surrounds the open end of the flight tube. The flight tube and the front of the MCP are held at the same potential as the last electrode of the ion optics. There are no meshes installed in the flight path.

The charged-particle optics are surrounded by a 356 mm tall cylindrical (ID = 254 mm, OD = 258 mm) Mu-metal shield that has many holes to improve gas conductance for pumping.

The Mu-metal cylinder is cut into 4 separate quadrants for easy installation and removal. When electrons exit the electrode plates in the $-z$ -direction, they enter an einzel lens made from a Mu-metal tube (ID = 63.5 mm, OD = 67.6 mm) with the center electrode segmented into four quadrants. After the einzel lens, electrons enter a field-free flight tube consisting of a Mu-metal cylinder (ID = 88.9 mm, OD = 93.0 mm) surrounded by a second cylinder (ID = 111.8 mm, OD = 116.6 mm) of a different alloy (SUPRA 50) with a higher magnetic saturation level. Both cylinders have holes for pumping, but they are staggered so that the electrons never have a direct line of sight to the vacuum chamber wall and always have at least one layer of magnetic shielding.

To enable a wide variety of experiments, the system was designed to be compatible with different sample inlet sources. The simplest is an effusive inlet consisting of a 1/4" copper tube that is connected to a feedthrough with a metering valve. The end of the tube is directed away from the ionizing radiation so that emitted molecules must suffer multiple thermalizing collisions before ionization, ensuring isotropic, thermalized speed distributions.

The second inlet source is a low-pressure reactor tube (ID = 10.5 mm, OD = 12.7 mm) that enables kinetics studies of unimolecular and bimolecular reactions in a collisional environment. The reactor tube runs through the chamber from the front to the back (along the *y*-axis) and passes through the charged-particle optics. The reactor has a pinhole in its side wall from which gas expands forming a continuous molecular beam. The two innermost electrodes on the charged-particle optics stack are cut along a chord 17 mm from the center to make room for the reactor tube (see Figure S2). The distance from the pinhole to the center of the electrode plates is 21 mm. Gas flow into the reactor tube is controlled by calibrated mass flow controllers. The pressure inside the reactor is regulated by a proportional-integral-derivative (PID) controlled butterfly exhaust valve, through which the reactor is connected to a 300 L/min dry scroll pump. Unimolecular photodissociation and bimolecular chemical reactions are initiated by a 15 ns laser pulse from an excimer laser (Coherent, Compex 110) aligned collinear and concentric to the reactor tube, with the light entering the reactor from the front of the instrument. We use a 4 Hz laser repetition rate, but higher and lower rates are possible if one adjusts the bulk gas flow speed so that photolyzed gas is completely replaced with fresh gas before the next laser pulse. For the reactor data presented here, we used a stainless steel reactor with a 200 μ m diameter pinhole. With the current pumping speeds, the useable pressure range of this reactor is 1–10 Torr. In the future, we will also use a quartz reactor as used previously in the MPIMS and the prototype CRF-PEPICO instruments.^{1,26}

A third inlet source is an Amsterdam Cantilever Piezo Valve (ACPV2), generating supersonic expansions, skimmed by a 2 mm diameter skimmer on a removable wall that can be slid into the chamber, dividing it into two separate regions for differential pumping. The molecular beams from sources 2 and 3 have a direct line of sight to the 3200 L/s pump on the right side of the chamber to minimize molecular scattering back to the ionization region. Typical operating conditions of the piezo valve were repetition rates of 600–1000 Hz at a backing pressure of 20–60 psi with a valve opening time of 35–50 μ s. With these conditions, the pressure on the valve side of the divider wall was 10^{-5} – 10^{-4} Torr, while the pressure in the

ionization chamber stayed below 10^{-6} Torr and typically $<5 \times 10^{-7}$ Torr. The chamber is designed to accommodate other sources and approaches in the future, such as high-pressure (>1 –100 atm), pyrolysis, pump-probe ionization, or heterogeneous catalysis reactors.

VUV light from a synchrotron or a gas-discharge lamp enters the chamber in the back and propagates along the $-y$ -direction, perpendicular to the gas expansion. To aid alignment and minimize scattered light, we have 3 light baffles in front of the charged-particle optics. The light baffles are anodized aluminum cylinders (OD = 0.5") with conical tips (80° full included angle). The light baffles are installed in x,z translation stages with an increasing center bore size along the light path. The VUV light is detected on an SXUV-100 photodiode (Opto Diode Corporation) after passing through the charged-particle optics. The photodiode is mounted at a 45° angle to the y -axis to minimize back reflection into the center of the ionization region. We commissioned this instrument with a discharge lamp (HIS13, Omicron) using Ne-I (primarily 16.85 and 16.67 eV) and Ar-I (primarily 11.83 and 11.62 eV) continuous VUV radiation.

II.II. Data Acquisition and Processing. Before discussing the acquisition and processing of raw data, it is helpful to describe the final data products that are interpreted by the user in the exploration of chemical reaction mechanisms. These data can be succinctly described as follows:

- (1) Mass spectra as a function of time. Here "time" may mean kinetic time relative to photolytic initiation of a chemical reaction but could mean any general repeatable time sequence, such as periodic gas pulses from a pulsed valve. This information provides the most direct view of the relevant chemistry by identifying the masses of the neutrals that are present as a function of time.
- (2) Ion mass-selected and time-resolved photoelectron VMI, from which photoelectron spectra and angular distributions may be extracted. This information distinguishes different neutral isomers detected at the same m/z ratio and may contain additional chemical dynamics information.
- (3) Internal energy-selected cation VMI from ions in coincidence with electrons of a certain eKE. This information can distinguish parent ions (which have minimal kinetic energy) from fragment ions formed via dissociative ionization (which contain kinetic energy release from the recoil of a neutral co-fragment).

The user may implement many additional filters to view subsets of the data from an experiment, which can be used to confirm or refute interpretations. We now describe the methods for acquiring and processing the raw data to produce this higher-level information.

For compatibility with the quasi-continuous nature of synchrotron radiation, all electric fields except the ion deflection fields (not utilized in the present work) are static. Electrons and ions formed by photoionization are continuously extracted and detected on time- and position-sensitive RoentDek delay-line detectors. Delay-line signals from the detectors are amplified (FAMP8, RoentDek) and sent through a constant fraction discriminator (CFD8c and CFD7x, RoentDek) before being recorded by two fast time-to-digital converters (TDC8HP, RoentDek). The TDCs are operated in an untriggered (primary-clock) mode, where all incoming signals are (absolute) time-stamped and passed to a personal

computer (PC). To enable real-time analysis of data, the PC has an Intel Core i9 12-core CPU running at 3.5 GHz with 64 GB memory and 1TB of fast SSD storage. On the PC, we run our in-house developed photoelectron photoion coincidence spectrum acquisition and analysis software, PepicoSandals (PS from here on).

In PS, all TDC events are sorted by a detector and absolute clock time and then submitted to two separate CPU threads converting the delay-line timing information into coordinates using algorithms provided in the resort64c library provided by RoentDek. From the resulting two lists of ion and electron arrival times and detector coordinates, all events that occurred within one second are bundled together into a raw data package marked with the VUV photon energy and flux (for photon energy scans). Each package is submitted into the main PS processing queue and archived in an HDF5 file by another separate CPU thread. The main queue is emptied by the coincidence analysis thread, which performs either a multiple-start multiple-stop analysis as described by Bodi et al.⁴³ or performs a false-coincidence rejection analysis as described by Osborn et al.⁴⁴ We analyzed all data in this work using the multiple-start multiple-stop approach with a 40 μ s wide time window, within which an electron and ion must arrive to be counted as a coincidence. Varying the width of this window allows the user to select the maximum detectable ion mass.

Each coincidence event is an electron–ion pair and contains the absolute arrival time of the electron, the time difference between the electron and the ion impacts at their respective detectors, the (x, y) detector coordinates of the electron and ion, and the kinetic time. The kinetic time is the difference between the electron timestamp and a chemistry-relevant event, e.g., a photodissociation laser pulse for photolysis-initiated kinetic experiments, or a pulsed valve opening. All of the timestamps have 25 ps resolution and are relative to the clock that synchronizes the TDCs. The timestamps from the TDCs have 24 bits of timing information, which only covers 419 μ s, but rollover markers are included in the data stream to enable infinitely long measurements. In PS, the timestamps are stored using 64-bit integers and the clock does not reset during an experiment. All coincidences from a one-second window are combined into a coincidence events package, which is held in random access memory until a user-set memory capacity threshold is reached, after which the package is deleted. The coincidences are added to histograms that display the electron and ion positions, as well as the ion TOF (or mass) spectrum and kinetic time traces of all recorded coincidences at the current photon energy.

The user can set up coincidence filters using various criteria, which can be freely combined with each other. Typical filter criteria enabling analysis of a subset of the total data are ion TOF (or alternatively, m/z ratio), (kinetic) time range, regions of interest (ROI) on either or both imaging detector(s), or photon energy range. Each coincidence filter runs in its own separate CPU thread and processes all coincidence packages currently held in memory. If packages are missing because the filter was created after they were removed from memory, the missing packages are quickly regenerated from the raw data saved in the HDF5 file. Each coincidence filter contains several histograms, based on the selected filter criteria. During acquisition, when a new coincidence package is available, each filter thread is awakened, processes the package, populates the filter-owned histograms, and displays the data on the graphical user interface. The detector velocity map images are

efficiently inverted using the DAVIS algorithm described by Harrison et al.⁵³ The filter histogram data can be exported into HDF5 files and then be further analyzed using Python or IGOR scripts.

We have tested PS with artificially generated data at count rates up to 200 kHz and the performance was always sufficient to accomplish coincidence analysis and filtering in real time (<1000 ms computation time per coincidence package). Coincidence analysis and filtering typically take 50–200 ms per package. In the lab, we tested the instrument with count rates up to 60 kHz and it showed stable performance. A potential bottleneck is the conversion of the TDC data to position coordinates, which we have not yet tested at higher count rates. If necessary, this computation could likely be parallelized by distributing the task over more CPU threads.

III. RESULTS AND DISCUSSION

III.I. Static Performance. To test VMI performance for electrons and cations, we used the supersonic beam source with atomic and molecular gases seeded in helium at varying concentrations and backing pressures. The gas was ionized by VUV radiation from a discharge lamp using Ne-I lines. We do not have a monochromator in the current setup and all frequencies generated by the discharge enter the chamber. The Ne-I discharge mainly produces photons with 16.85 and 16.67 eV with relative intensities quoted by the lamp manufacturer of 1:0.15.

Figure 2A shows the electron velocity map image (VMI) in coincidence with Ar^+ and Kr^+ from a molecular beam containing 20% Ar and 20% Kr in He. No corrections are needed to circularize the images, indicating good magnetic shielding. The photoelectron spectra show the expected spin–orbit splitting of 0.177 eV for Ar^+ and 0.666 eV for Kr^+ .⁵⁴ Due to the fact that we have both 16.85 and 16.67 eV photon energies present, each spin–orbit level gives rise to two peaks with a separation of 0.18 eV. To better visualize this peak splitting, we fit a Gaussian (green line in Figure 2B) to the ^{84}Kr peak at 2.85 eV, with variable position, width, and amplitude. Next, we fit three additional Gaussians to the remaining ^{84}Kr photoelectron peaks ($^2\text{P}_{3/2}$ with 16.67 eV radiation, $^2\text{P}_{1/2}$ with 16.85 eV, and $^2\text{P}_{1/2}$ with 16.67 eV), where only the peak amplitude is allowed to vary. The resulting fit agrees well with the data, which shows the signal near 2.0 and 2.7 eV in Figure 2B arises from ^{84}Kr . For argon, we resolve only 3 signals because the $^2\text{P}_{3/2}$ peak from 16.67 eV excitation lies under the $^2\text{P}_{1/2}$ peak from 16.85 eV excitation. The fractional energy resolution for these energetic electrons is $\sim 4\%$. We expect higher-energy resolution when using collimated synchrotron VUV radiation and note that Tang et al. have achieved 2.8% electron energy resolution on their PEPICO spectrometer.²⁸ SIMION simulations of our charged-particle optics design with this source predict a photoelectron energy resolution of $\sim 1\%$ for energetic electrons. We note that both our electron and ion images have the zero speed position slightly offset from the detector center. We have evidence that this error is due to a slight angular misalignment of the charged-particle optics, which we will correct in future work.

Figure 3 shows the cation VMI of a 25 μs time slice from the center of molecular beam pulses containing 10% hydrogen, 1% methane, 0.5% argon, 0.1% krypton, and 0.1% xenon in helium at 60 psi backing pressure. The molecular beam propagates to the right on the image with the zero speed position marked by a yellow cross. The diffuse signal surrounding the zero speed

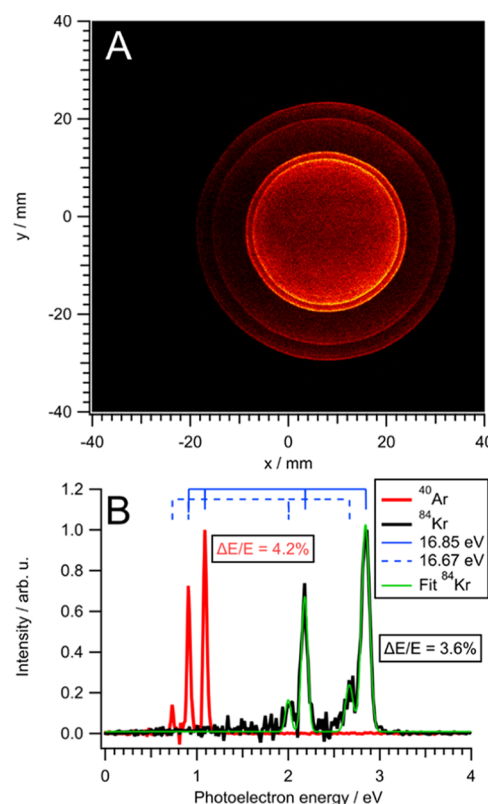


Figure 2. (A) Velocity map image of photoelectrons in coincidence with Ar^+ and Kr^+ ions. (B) Photoelectron spectra inverted from the image in (A) of electrons in coincidence with Ar^+ (red) and Kr^+ (black). The blue combs denote the expected photoelectron energies for electrons corresponding to the $^2\text{P}_{3/2}$ and $^2\text{P}_{1/2}$ states of Ar^+ and Kr^+ from ionization at 16.85 eV (solid line) and 16.67 eV (dashed line). The green line is a combination of 4 Gaussians fitted to the Kr signal; see the main text for details.

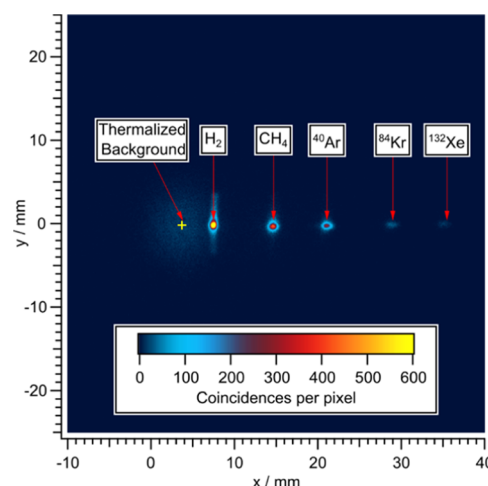


Figure 3. Ion velocity map image of a 25 μs time slice from the center of the molecular beam pulse. The yellow cross denotes the zero speed position.

position represents ions from the collisionally thermalized background gas of all five species. As expected for thermalized gases, speed distributions of all five species follow Maxwell–Boltzmann statistics, as shown in Figure S3. The thermal background spot is useful for the speed calibration because the center of this distribution provides the zero speed

The ion spots from the gas of the molecular beam pulse form tightly localized spots, indicating good velocity mapping conditions. The spots corresponding to heavier species appear further to the right on the image, underscoring the fact that velocity map imaging could be more accurately described as momentum map imaging. The spots become less circular with increasing mass, which we explain as follows. First, all species from the molecular beam travel with the same average speed along the x -axis—determined by the speed of the helium carrier gas—and are mapped on the image according to their momentum (mv), which is linearly proportional to their mass. Second, the spots corresponding to heavier ions are more stretched along the x -axis because the velocity spread of the gas pulse is constant for all species, but the corresponding spread in momentum is proportional to mass, becoming larger for the heavier ions. If the distance of each ion spot from the zero speed position in the (x , y) plane is plotted versus mean TOF (along the z -coordinate), these data lie on a line and a fit yields the speed of the molecular beam of 1766 m s^{-1} in this particular case. See Figure S4 for the distance versus TOF plot as well as a speed profile of the Xe ions (Figure S5), with a fitted speed ratio of $v/(\Delta v) = 25$ for the supersonic expansion.

Figure 4 shows the mass spectrum of xenon recorded with the molecular beam valve and the same gas mix used in Figure

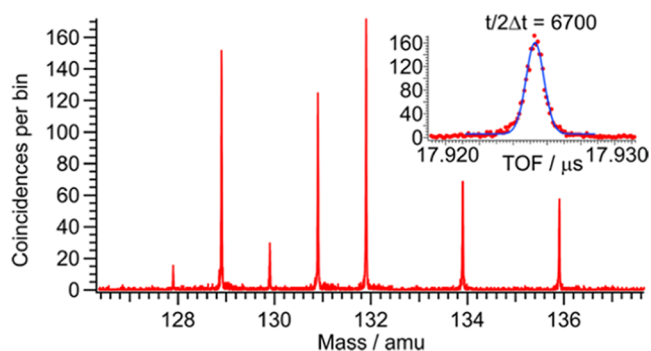


Figure 4. Mass spectrum of xenon. Inset: Enlarged view of the ^{132}Xe time-of-flight peak (red dots) with a Gaussian fit to the data (blue line).

3 at a backing pressure of 20 psi. The data was processed using an ROI filter on the Xe spot on the ion VMI to discriminate against the thermal background. The spectrum shows the natural isotope pattern of xenon and demonstrates the high mass resolution ($m/(\Delta m) = t/(2\Delta t) = 6700$) of our instrument. The peak shape is nearly Gaussian (inset Figure 4), enabling simple deconvolution of signals from isobaric species. We calibrated the mass axis using the TOF signals of H_2 , CH_4 , Ar, ^{84}Kr , and ^{132}Xe (see Figure S6). To test the accuracy of the mass calibration, we compared the measured masses of Kr and Xe isotopes that were not included in the mass calibration to their exact literature masses and found a mean absolute error of $3.8 \times 10^{-4} \text{ amu}$, demonstrating exceptional mass accuracy of $\sim 3 \text{ ppm}$. See Section 4 of the SI for details on the mass calibration. If the reactor tube inlet source is used instead of the molecular beam, the mass resolution is reduced because the gas is not expanded supersonically and has a larger velocity spread along the TOF dimension. The mass resolution with the reactor tube is still better than the instrument design goal at $m/\Delta m > 2600$. Our mass resolution is significantly higher than any other PEPICO instrument of which we are aware^{18,22,25–28} and will

avoid the need to combine low-mass-resolution PEPICO experiments with high mass-resolution ionization measurements (that do not detect electrons) to constrain the chemistry of isobaric neutrals such as $\text{C}_4\text{H}_8\text{O}$ (72.0575 amu) vs C_5H_{12} (72.0939 amu), as in the work of Pieper et al.⁴⁸ Separating two such species requires mass resolution >2000 , which is easily achieved by our design. For reference, Figure S7 shows cation and electron VMI images together with mass and photoelectron spectra from the same dataset.

To characterize the kinetic energy release (KER) of heavy particles, we employ dissociative ionization of SO_2 seeded at 0.3% in a supersonic helium expansion. Figure 5A shows an image of the SO^+ fragment ion generated by dissociative ionization. Unlike the compact spots in Figure 3, the molecular beam spot of SO^+ (centered at $x = 22 \text{ mm}$ in Figure 5A) is

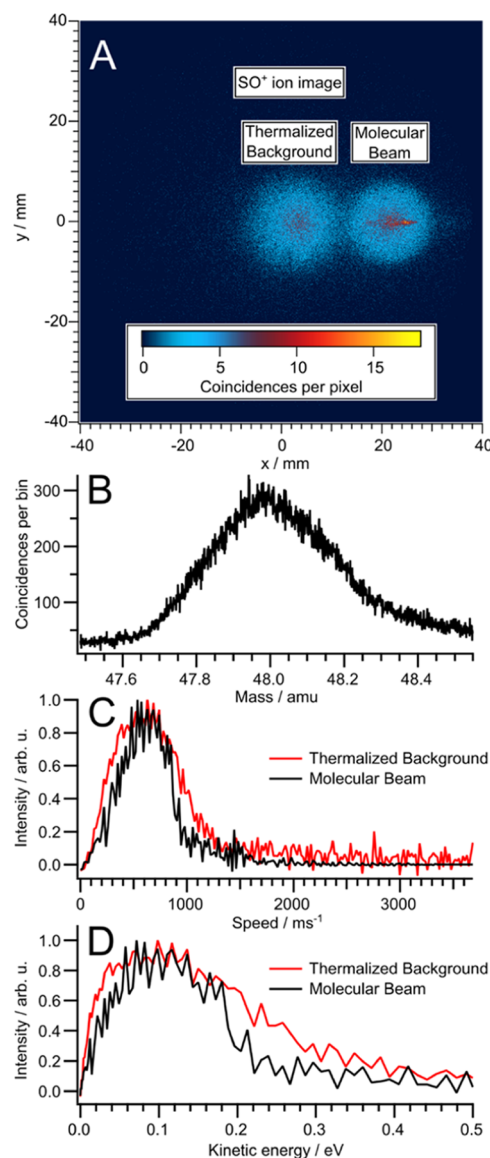


Figure 5. (A) Ion VMI of SO^+ ions from dissociative ionization of a supersonic molecular beam of SO_2 . (B) Mass spectrum of coincidences near m/z 48 including all coincidences shown in panel (A). (C) Speed distributions of the two ion spots, obtained by using a mask on the ion detector to include only coincidences of either the thermal background or molecular beam ions. (D) Same data as in (C) but converted to kinetic energy.

broad due to KER as SO^+ recoils from the neutral O atom co-fragment. The highly circular speed distribution of SO^+ fragment ions from supersonically cooled SO_2 offers additional evidence that the charged-particle optics are tuned well and the ions are properly velocity map imaged. Note that SO^+ arising from dissociative ionization of thermalized background SO_2 is more diffuse and has a slightly larger radius due to the neutral gas having a broader speed distribution compared to the narrow speed distribution of supersonically cooled SO_2 . When interpreting the intensities of the two distributions in Figure 5A, it is important to note that the data cover a 250 μs time window centered on the gas pulse, but the gas pulse itself is only $\sim 60 \mu\text{s}$ long. If we had chosen a 60 μs window to plot the data, the thermal background ions would be about a factor of 4 weaker. We chose the present time integration limits to make the signals arising from thermal and cold SO_2 molecules nearly the same, which makes it easier to evaluate by eye the difference in their total speed distributions. To be more quantitative, speed and kinetic energy distributions of SO^+ fragment ions are shown in Figure 5C,D, respectively.

The elliptical higher intensity signal (red) slightly right of the center of the SO^+ molecular beam spot in Figure 5A is caused by false coincidences involving SO_2^+ . As evident from Figure 5A, the SO^+ recoil is isotropic and leads to broadening of the mass peak in the TOF (z -axis) direction, shown in Figure 5B. To analyze all SO^+ coincidences, we select a mass range of 47.5–48.5 amu. Because most of the ions created in this experiment are SO_2^+ from direct ionization of the molecular beam, these ions contribute to the vast majority of the false coincidences, and the wide mass window required to include all SO^+ ions leads to a significant contribution to the image in Figure 5A from false coincidences. Although false coincidences are randomly distributed across the whole mass spectrum, all SO_2^+ ions, regardless of whether they are paired with the proper electron (true coincidence) or another electron (false coincidence), are still tightly focused at the same spot on the cation VMI. Therefore, the false coincidences formed by combinations of electrons and SO_2^+ ions that give rise to an apparent m/z of 47.5–48.5 amu will show up in the location of the SO_2 ion spot that is centered at $x = 25 \text{ mm}$. By using an ROI filter selecting only ions from the intense spot at $x = 25 \text{ mm}$, we obtain a mass spectrum that mainly shows SO_2 signals (m/z 64). By integrating over a TOF window that is the same size as the one shown in Figure 5B but shifted to a TOF range where only false coincidences occur we can quantify the number of false coincidences contributing to the VMI in this region. See Figure S8 for the ROI selected ion VMI and mass spectrum. One could eliminate these false coincidences by excluding data from this rather small portion of the cation VMI image or by utilizing the false-coincidence rejection technique.⁴⁴

III.II. Time-Resolved Performance: 193 nm Photodissociation of SO_2 . To demonstrate the ability of our new instrument to investigate dynamic systems, we measured the photodissociation of SO_2 with 193 nm light, which excites the $\text{C}(^1\text{B}_2) \leftarrow \tilde{\text{X}}(^1\text{A}_1)$ transition. This well-studied photodissociation reaction^{55–64} generates $\text{O}(^3\text{P}_j) + \text{SO } \text{X}(^3\Sigma^-)$, with Abe et al.⁵⁷ concluding that these are the “sole primary photodissociation products”. Therefore, it provides a useful test system producing an atom and a diatomic molecule as photoproducts. These experiments were performed with a stainless steel low-pressure reactor tube. Various dilutions of SO_2 in helium were flowed through the reactor at a total

pressure of 2 Torr. Radiation (193 nm, 15 ns pulsewidth, 11 mJ cm^{-2} fluence) from an excimer laser at 4 Hz repetition rate photodissociated SO_2 . All species in the molecular beam formed from the pinhole expansion were ionized by VUV radiation from the discharge lamp using either Ne-I light (16.85 and 16.67 eV) or Ar-I light (11.62 and 11.83 eV).

Figure 6 shows kinetic time profiles and ion VMIs from the SO_2 photodissociation experiment when Ne-I light is used for

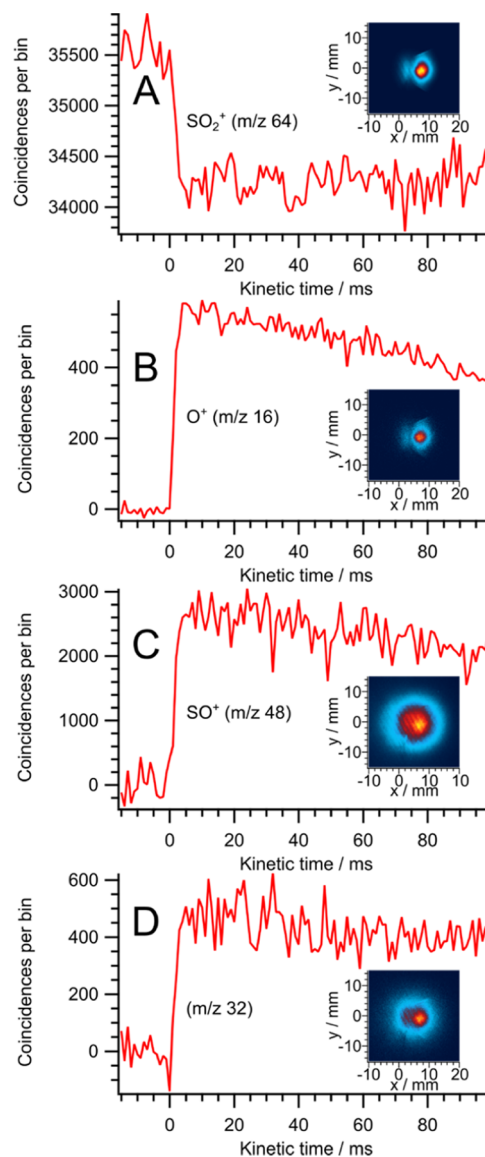


Figure 6. Time traces of SO_2^+ (A), O^+ (B), SO^+ (C), and m/z 32 (D) from the dissociation of SO_2 with 193 nm laser pulses (45,000 laser shots in this dataset). The neutrals are ionized by Ne-I radiation (16.85 and 16.67 eV). The insets show the ion VMIs with identical magnification in all panels.

ionization. The SO_2 concentration in this experiment was $3.4 \times 10^{15} \text{ molecules cm}^{-3}$ with a total mass flow rate of 38 sccm. Panel A shows a sharp depletion of SO_2 at the time when the laser fired ($t = 0 \text{ ms}$) with $\sim 4\%$ of the SO_2 being dissociated by the 193 nm laser pulse. The time trace is essentially a step function and the SO_2 concentration is stable until the photolyzed gas is pumped out of the reactor after 100 ms. The lack of any reformation of SO_2 implies that the rate of $\text{O} +$

$\text{SO} + \text{M} \rightarrow \text{SO}_2 + \text{M}$ is negligible under our conditions on the 100 ms timescale. The SO_2 ion image shows two speed distributions: a thermal background (centered at $x = 2$ mm) from SO_2 that did not emerge directly from the reactor tube, and a more intense feature centered at $x = 7$ mm representing SO_2 in the molecular beam. A molecular beam expansion from a 2 Torr reservoir generates much weaker cooling than the hard supersonic expansions in Figure 3, resulting in a much lower speed ratio for SO_2 . Figure 6B,C,D shows O^+ , SO^+ , and a species with m/z 32, respectively. All time traces have sharp, instrument response function limited rise times and then decay slowly until they are pumped out of the reactor after 100 ms. The O atoms (represented by the O^+ signal) show the fastest decay, probably due to loss on the stainless steel surface of the reactor. It is important to remember that these O atoms are formed by photodissociation of SO_2 at a pressure of 2 Torr inside the chemical reactor and are therefore thermalized by collisions (mostly with helium) before expansion into the vacuum chamber, followed by ionization. Therefore, we should not expect these O atoms to retain any KER imparted by photodissociation dynamics, and indeed the VMI image shows a relatively compact speed distribution.

By contrast, the ion VMIs of the SO^+ and m/z 32 ions are significantly larger, showing evidence for kinetic energy release following dissociative ionization. SO^+ ions are formed by two processes. The first process is dissociative ionization of SO_2 by the Ne-I radiation, which should display KER as demonstrated in the supersonic expansion experiments of Figure 5. This source of SO^+ should display the same time trace as Figure 6A because these ions represent SO_2 neutrals. The second source of SO^+ is from neutral SO radicals in the molecular beam that were generated by SO_2 photodissociation in the reactor tube. Similar to the O atoms that are their co-fragments, the SO neutrals should not retain any KER after collisional thermalization in the reactor tube. Note that dissociative ionization of SO_2 is happening both before and after the photodissociation laser fires. The average pre-photolysis signal is subtracted from the time traces in Figure 6B–D, which therefore displays the laser-induced change in signals due to photodissociation.

Most of the m/z 32 signal is due to S^+ formed by dissociative ionization of SO neutrals and therefore shows almost the same time profile as the SO radical contribution to Figure 6C. The thermodynamic appearance energy of S^+ from SO is 15.74 eV (1.11 eV lower than the Ne-I photon energy), based on known heats of formation.^{65,66} This channel, however, is not the only contributor to the m/z 32 signal. Filtering the coincidences by different ROIs on the ion VMI reveals position dependencies in the time traces, where ions with large KER have a time trace with the same shape as the SO neutrals, but ions that are close to the center of the distribution at $x = 7$ mm (Figure 6D, inset) show a faster decay. The mass spectrum of these ions shows two sharp peaks at 31.972 ± 0.007 and 31.993 ± 0.008 amu corresponding to $^{32}\text{S}^+$ (exact mass: 31.97207 amu) and $^{16}\text{O}_2^+$ (exact mass: 31.98984 amu) ions. A minor impurity of O_2 is always present in the vacuum chamber and we always see it as a non-time-resolved peak in our mass spectra, whereas the S^+ peak is time-resolved. See the SI, Figures S9–S11 for a mass spectrum near m/z 32 and ROI-filtered time traces.

One advantage of time-resolved PEPICO data is its high dimensionality, which provides many ways to dissect the same dataset to extract deeper and corroborating physical insights. As an example, we show in Figure 7 several projections of the dataset just described but focusing only on coincidences

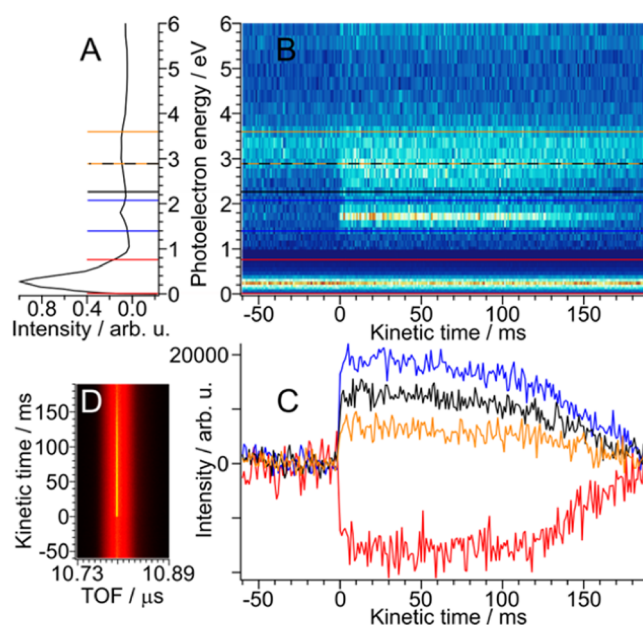


Figure 7. Time-resolved PEPICO data of m/z 48 (SO^+) from SO_2 photodissociation, ionized with Ne-I radiation. To improve S/N, the electron detector was rebinned coarsely at 1 mm per pixel. (A) Photoelectron spectrum integrated over the whole 250 ms kinetic time range. (B) 2D image of photoelectron spectra with 1 ms kinetic time binning, where the photodissociation laser fires at 0 ms. The data displayed between 0 and 1 eV is scaled differently to improve clarity; see the main text for details. (C) Kinetic time traces for photoelectron kinetic energy ranges 0–0.75 eV (red), 1.4–2.07 eV (blue), 2.26–2.89 eV (black), and 2.89–3.6 eV (orange). (D) 2D image of ion TOF signal vs kinetic time showing a broad non-time-resolved feature due to dissociative ionization of SO_2 and a sharp time-resolved feature due to SO radicals formed by the laser after 0 ms.

associated with m/z 48 (SO^+). All 4 panels show different projections of the same dataset and contain coincidences from the 10.73 to 10.89 μs TOF range. The 2-D kinetic time vs TOF plot in Figure 7D shows a very high mass resolution (i.e., narrow along the TOF dimension) time-resolved peak superimposed on a broad mass peak that appears to have no time dependence. The data in Figure 7D implies that two neutral species are represented by the cation signal of SO^+ . Next, the 2-D cut of photoelectron spectra vs kinetic time in Figure 7B can be projected as a time-integrated photoelectron spectrum in Figure 7A (see Figure S12 for a higher-resolution photoelectron spectrum) or as kinetic time traces integrated over specific photoelectron energies in Figure 7C. The average pre-photolysis signal was subtracted from the time traces in Figure 7C. The portion of Figure 7B between 0 and 1 eV was rescaled to improve the visibility of small intensity changes on top of a large background. The horizontal lines in Figure 7A,B depict the color-coded integration limits used in Figure 7C. To interpret these projections, we draw on existing knowledge of the photoelectron spectroscopy of SO_2 and SO, combined with knowledge of the photodissociation products of SO_2 excited at 193 nm.

The red trace in Figure 7C shows signal reduction after the laser fires at 60 ms. The only species present before the 193 nm laser fires is SO_2 , and we know it photodissociates at 193 nm. Therefore, the red trace in Figure 7C likely represents the laser-induced destruction of SO_2 . Remembering that the primary VUV photon energy is 16.85 eV, the photoelectron

peak from 0 to 0.75 eV corroborates this hypothesis: the 16.85 eV VUV photon energy and the known 15.93 eV appearance energy of SO^+ from SO_2 only allow eKE from 0 to 0.92 eV. By contrast, the time traces in blue, black, and orange in Figure 7C increase after the laser fires; these signals therefore likely represent the $\text{SO X}(^3\Sigma^-)$ formed by photodissociation of SO_2 excited at 193 nm. This hypothesis can be corroborated by the known photoelectron spectroscopy of SO , where Dyke et al.⁶⁷ measured a compact Franck–Condon envelope for excitation to the $\text{SO}^+ \text{b}(^4\Sigma^-)$ state, spanning eKE = 1.65–1.91 eV, and an extended Franck–Condon envelope for the $\text{SO}^+ \text{a}(^4\Pi)$ state, spanning eKE = 2.25–3.35 eV. Circling back to Figure 7D, one sees that the very narrow mass peak that increases abruptly after the laser fires represents SO , whereas the broad signal represents SO_2 . The broadness results from the kinetic energy release imparted to the fragment ion SO^+ recoiling from a neutral O atom in the dissociative ionization of SO_2 . Finally, we emphasize that these conclusions drawn from the mass and photoelectron spectra are complementary to conclusions drawn from the kinetic energy release in the cation VMI images of SO^+ already discussed in Figure 6C. This example demonstrates the many opportunities to cross-check the validity of hypotheses using the multidimensional data available from this instrument.

III.III. Production of $\text{S}(^3\text{P})$ from the 193 nm Photodissociation of SO_2 . To further explore the time trace and VMI image of m/z 32 in Figure 6D, we acquired additional data on the 193 nm photodissociation of SO_2 using lower-energy VUV photons (11.62 and 11.83 eV) from an Ar discharge lamp. Figure 8 shows the time trace of SO in panel A

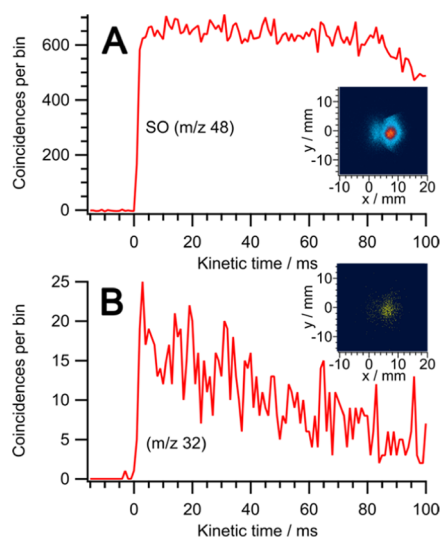


Figure 8. Time traces representing SO (A) and S atoms (B) from the dissociation of SO_2 with 193 nm laser pulses (57,600 laser shots in this dataset). The reaction intermediates are ionized by Ar-I radiation (11.62 and 11.83 eV). The insets show the ion VMIs.

and m/z 32 in panel B from this experiment. We lowered the SO_2 number density to 4.9×10^{14} molecules cm^{-3} to reduce rates of possible bimolecular chemistry. The mass flow rate was higher in this experiment (48 sccm); therefore, the gas was pumped out of the reactor at an earlier kinetic time compared to the data in Figure 6. The threshold for dissociative ionization of SO_2 to SO^+ is 15.930 ± 0.005 eV.⁶⁸ Therefore, dissociative ionization is energetically forbidden and we do not

expect or observe any KER in the SO^+ ion VMI. Instead, all observed SO^+ represents SO neutrals formed by the photodissociation of SO_2 . The m/z 32 ions also do not show any KER at this photon energy and their time trace looks very different compared to the m/z 32 signal observed with Ne-I light (Figure 6D). The m/z 32 signal in Figure 8B decays faster with time than any other of the observed species, implying that it must represent a reactive neutral species. Time-resolved mass spectra (Figure S13) show peaks at m/z 32 and 34 in an $\sim 100:4$ ratio, as expected for the $^{32}\text{S}:^{34}\text{S}$ the isotope ratio. The VUV radiation at 11.83 eV is sufficient to ionize $\text{S}(^3\text{P}_2)$, which has $\text{IE} = 10.36001 \pm 0.00012$ eV.⁶⁹ The electrons in coincidence with the m/z 32 ions have $\text{eKE} = 1.45 \pm 0.03$ eV (see Figure S14), which agrees within error with the expected energy (1.47 eV) of electrons from S atoms ionized at 11.83 eV. Note that the m/z 32 signal from ionization with Ar-I light is weak, such that the photoelectron spectrum in Figure S14 is quite noisy. We observe a signal at $\text{eKE} = 1.26 \pm 0.03$ eV, which is at the expected energy (1.26 eV) for photoelectrons from ionization of $\text{S}(^3\text{P}_2)$ with 11.62 eV light, but it is not clearly discernible above the noise level. Although the manufacturer-stated relative intensity of 11.62 to 11.83 eV photon energies from an argon discharge is 1:0.5, our photon energy intensity ratio appears to be different.

To confirm that the observed m/z 32 signal is indeed caused by S atoms, we ran a separate experiment in which we flowed 2% O_2 in He through the reactor and ionized it with the Ar-I light. The AIE of O_2 is 12.0697 eV,⁷⁰ well above the expected photon energies of Ar-I light, but the discharge lamp also produces some light from the Ar-II lines (13.30 and 13.48 eV) and we observe a small O_2^+ signal. We measure 31.977 ± 0.009 amu for the m/z 32 signal from the SO_2 photodissociation experiment and 31.994 ± 0.007 amu when flowing 2% O_2 in He, in good agreement with the exact masses of ^{32}S and $^{16}\text{O}_2$. We verified that the mass calibration did not drift between the two experiments by also analyzing the mass spectrum of H_2O (a contaminant present in both experiments, $\text{AIE} = 12.62$ eV⁷¹). See the SI, Figure S15 for mass spectra of m/z 32 from SO_2 photodissociation, as well as O_2 and H_2O . Together, the exact mass, photoelectron spectrum (Figure S14), isotope ratio (Figure S13), and time trace in Figure 8B provide strong evidence that we are detecting $\text{S}(^3\text{P})$ atoms. We propose that these atoms are primary photodissociation products from 193 nm photodissociation of SO_2 .

A skeptical reader may question whether the observed S atoms could be formed by bimolecular or termolecular reactions of the photoproducts in the reactor. Table 1 shows four reactions to consider in this system,^{65,66,72–75} where (reaction R1b) would produce S atoms. The two termolecular reactions are highly exothermic, whereas the bimolecular reactions are both endothermic.

Second-order rate coefficients for the two termolecular reactions in Table 1 are at the pressure of 2 Torr He bath gas appropriate for the present experiments. Note that although Naidoo et al.⁷⁴ made their measurements of reaction R2a only in argon bath gas, the measurements of reaction R1a by Cobos et al.⁷³ yield similar rate coefficients in Ar and He and we expect little difference between these two monatomic rare gases for reaction R2a. The $\sim 4\%$ photodissociation fraction of SO_2 by the 193 nm laser pulse yields initial number densities of the photoproducts $[\text{O}]_0 = [\text{SO}]_0 \sim 2 \times 10^{13} \text{ cm}^{-3}$. Under these conditions, the rates of reactions R2a and R2b are too slow to consume any appreciable amount of $\text{O}(^3\text{P})$ atoms.

Table 1. Possible Bimolecular and Termolecular Reactions Following SO₂ Photodissociation

reaction	ΔH_{rxn} (kcal/mol) ^a	k (cm ³ molecule ⁻¹ s ⁻¹)
$\text{O}(^3\text{P}_j) + \text{SO}(^3\Sigma^-) + \text{M} \rightarrow \text{SO}_2(^1\text{A}_1) + \text{M}$ (R1a)	−131	4×10^{-14b}
$\text{O}(^3\text{P}_j) + \text{SO}(^3\Sigma^-) \rightarrow \text{S}(^3\text{P}_j) + \text{O}_2(^3\Sigma_g^-)$ (R1b)	+6	$<4 \times 10^{-14c}$
$\text{O}(^3\text{P}_j) + \text{SO}_2(^1\text{A}_1) + \text{M} \rightarrow \text{SO}_3(^1\text{A}_1') + \text{M}$ (R2a)	−83	6.4×10^{-17d}
$\text{O}(^3\text{P}_j) + \text{SO}_2(^1\text{A}_1) \rightarrow \text{SO}(^3\Sigma^-) + \text{O}_2(^3\Sigma_g^-)$ (R2b)	+13	$<1 \times 10^{-16e}$

^aThermochemical values from refs 65, 66, 72. ^bRef 73. ^cUpper limit derived from ref 73. ^dRef 74. ^eRef 75.

Note that we do observe a very weak signal at the m/z of SO₃ (IE = 12.82 eV⁷⁶) when using 16.85 eV radiation, but it is not time-resolved and likely arises from an impurity in the reactant SO₂ gas. Turning to (R1), if the second-order reaction R1a were the only loss mechanisms for the photoproducts, the $t_{1/2} = (k[\text{O}])^{-1}$ time required for 50% of SO₂ to be reformed would be 1.2 s, much longer than our timescales. Reaction R1b, which could produce S atoms, is endothermic by 6 kcal/mol and would also have a $t_{1/2} \sim 1.2$ s for S atom formation, which is inconsistent with the measured ~ 2 ms rise time of S(³P) in Figure 7B. Because we can see no feasible pathway for bimolecular chemistry to produce S atoms in this system, we conclude that S(³P)_j + O₂(³Σ_g[−]) is a primary photodissociation channel of SO₂ at 193 nm. To our knowledge, this product channel has not been reported in the literature. Although we cannot yet quantify the S atom photodissociation quantum yield, it must be small to have evaded earlier detection. In future work, we will quantify this product channel, which, even if small, may impact mass-independent fractionation mechanisms of sulfur isotopes relevant to the atmospheric photochemistry of the Great Oxygenation Event in Earth's history.^{77–79}

IV. CONCLUSIONS

We have developed a new double-imaging PEPICO instrument and demonstrated its ability to measure mass- and time-resolved photoelectron spectra, along with kinetic energy release spectra of the heavy atomic and molecular fragments after ionization. At present, the experiment has three sample inlet source configurations: effusive gas delivery, a side-sampled reactor tube for kinetics experiments under collisional conditions, and supersonic pulsed or continuous expansions. We performed all experiments with fixed-frequency VUV radiation. The ability to generate mass-resolved photoelectron spectra without access to tunable VUV synchrotron radiation enables isomer-specific probes of chemical reactions in standard laboratory settings. By contrast, the more common method of photoionization mass spectroscopy requires tunable VUV radiation for definitive isomer quantification. However, our PEPICO instrument will be more powerful when coupled with tunable, monochromatic, quasi-continuous synchrotron radiation, enabling, for example, high-resolution threshold or slow photoelectron spectroscopy.⁸⁰ We will pursue such experiments in the future, as access to synchrotrons reopens.

Our new instrument provides excellent mass resolution ($m/\Delta m = 6700$ with the supersonic beam source) and mass accuracy of ~ 3 ppm, coupled with independently adjustable velocity map imaging of both cations and electrons. We accomplished these opposing goals using a long stack of large-diameter, mesh-free charged-particle optics to separate the linear electric fields needed for mass resolution from the

curved electric fields needed for velocity mapping. This performance should make it a powerful tool to study unimolecular and bimolecular chemistry in a collisional environment, along with spectroscopy and dynamics using supersonic expansions. The design is sufficiently flexible to enable future studies using additional sources such as high-pressure chemical reactors,⁸¹ ultrafast pump-probe spectroscopy, and heterogeneous catalysis.

The capabilities of this new instrument provide direct evidence that the photodissociation of SO₂ via the $\tilde{\text{C}}(^1\text{B}_2) \leftarrow \tilde{\text{X}}(^1\text{A}_1)$ transition produces a small yield of S(³P)_j + O₂(³Σ_g[−]) as a primary photodissociation product channel, in competition with the major O(³P)_j + SO(³Σ[−]) channel. The observation of S atoms from this photodissociation, which we will explore further in the future, may have implications for mass-independent fractionation of sulfur on the early Earth.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.1c10293>.

Rendering of the PEPICO instrument, details of the center electrodes, speed distributions of thermalized and supersonic gas sources, mass calibration and mass accuracy, dissociative ionization of SO₂, details of nominal mass 32 products from SO₂ photodissociation, photoelectron spectra of S(³P), mass spectra of ³²S vs ¹⁶O₂ (PDF)

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Notes

The authors declare no competing financial interest.

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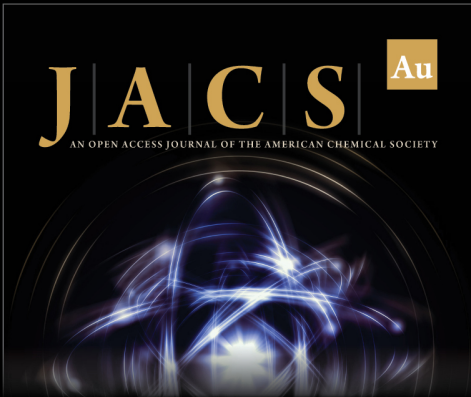
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