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High-Resolution Time-Resolved PEPICO with Tunable Vacuum Ultraviolet Photoionization

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Abstract

Recently we presented a new time-resolved, double-imaging photoelectron photoion coincidence (i^2 PEPICO) spectrometer for the study of chemical reactions using fixed frequency, single-photon vacuum ultraviolet ionization. Here we describe new capabilities and insights from this instrument when coupled with tunable ionizing radiation. We interrogate the gas expansion dynamics of a side-sampled chemical reactor tube, revealing clear evidence for viscous flow in the expansion before ionization. Cation imaging can be used to restrict detected signal to only the direct molecular beam, removing contributions from background and reflected gases. We characterize the peak shape and mass resolution of the instrument, provide new insight and clarification regarding collections efficiencies, and consider the noise sources and resulting signal-to-noise in PEPICO experiments. We quantify the temporal instrument response function and show that velocity map imaging of cations may be used to eliminate the transit time delay and reduce the temporal blurring inherent in ex-situ sampling geometries. The resulting time resolution of 7 μ s is a significant improvement compared to previous instruments. We discuss methods to quantify and address the ubiquitous problem of background electrons ejected from metal surfaces in photoelectron spectrometers. Finally, we compare variants of mass-selected photoelectron spectroscopy, provide an example of quantitative analysis using PEPICO, and present evidence for unexpected products in the 193 nm photodissociation of CH_3OH that underscores the value of universal imaging approaches.

1 Introduction

The study of bimolecular reactions in a controlled collisional environment is a valuable approach in physical chemistry that bridges the gap between single-collision reactive scattering in crossed molecular beams and approaches that simulate complex real-world environments, such as atmospheric simulation chambers or 1-dimensional flames. Although laser-based spectroscopies are powerful tools for *in situ* interrogation of bimolecular reactions, they usually lack the universality of single-photon ionization methods, which convert neutral molecules into cations and electrons to monitor neutral chemistry. Recently, we reported on a new time-resolved photoelectron photoion coincidence (PEPICO) spectrometer designed for kinetics studies of gas-phase reactions pertinent to combustion, atmospheric, and interstellar chemistry.¹ That report described the performance of the instrument using fixed-frequency vacuum ultraviolet (VUV) ionizing radiation from a noble-gas discharge lamp. However, the most powerful implementation of such instruments is realized when combined with continuously tunable VUV light sources such as synchrotrons. By scanning the photon energy, cation mass-selected threshold photoelectron spectra (ms-TPES) (or slow photoelectron spectra, SPES) and photoionization (PI) spectra can be recorded, providing unique isomer-specific spectral fingerprints that enable species identification in gas-phase reaction experiments.²⁻⁴ We refer readers less familiar with photoelectron and PEPICO spectroscopy to two review articles by Baer and Tuckett,⁵ and Fischer and Pratt,⁶ which discuss the history of the technique and recent advances in its use in physical chemistry.

Fixed wavelength experiments also become more powerful at synchrotron facilities because the photon energy may be chosen to exploit resonances in the photoionization spectrum, enhancing signals for specific species. Conversely, the photon energy may be set below the ionization energy of a species one wishes to avoid detecting in order to more sensitively detect weaker signals of species with lower ionization energies. Detection sensitivity is also improved due to the higher photon flux of monochromatized synchrotron radiation, up to 10^{14} photons s^{-1} . Furthermore, thanks to the collimated photon beam and the small source

size, synchrotron sources provide VUV radiation at much higher brightness than incoherent laboratory VUV sources. In this article our discussions center on the use of rapidly and broadly tunable, moderate bandwidth (1–10 meV), high-brightness, quasi-continuous VUV sources to probe chemical reaction dynamics and kinetics. Significantly smaller photon energy bandwidth (0.01 meV or smaller) may be obtained from pulsed laser sources combined with non-linear VUV generation techniques.^{7–9} These laboratory-based photon sources enable impressive rotationally-resolved photoionization and zero-electron kinetic energy (ZEKE) spectroscopy.⁹ However, their repetition rates are generally limited to < 100 Hz and they are not rapidly tunable over wide photon energy ranges. These sources work well for high-resolution spectroscopy in cold, pulsed supersonic expansions. By contrast, the quasi-continuous nature of synchrotron VUV sources, combined with their ability to tune in seconds over multiple eV bandwidths means synchrotron VUV radiation is still unchallenged for the purpose of probing time-resolved chemical reactions on microsecond timescales with high sensitivity. Moderate bandwidth synchrotron VUV sources work well with dispersive photoelectron spectroscopy achieved with velocity-map imaging detectors, and we focus on these types of instruments in this article.

Although high signal count rates are generally desirable, they pose technical challenges for the data acquisition and processing in coincidence spectroscopies such as PEPICO. High count rates lead to a large background of false coincidences that can mask weak signals from minor but important chemical species. Advances in data acquisition¹⁰ and novel experimental approaches to suppress false coincidences¹¹ mitigate these problems.

In this paper, we present performance metrics of the instrument that were not previously reported by us,^{1,11} and that advance performance compared to existing instruments. We also clarify certain metrics in the context of existing literature. We focus especially on metrics that require tunable VUV radiation, which impact the ability to study isomer-resolved photodissociation and the ensuing chemical kinetics. These metrics include gas expansion dynamics, mass resolution, collection efficiencies of charged particles, signal-to-

noise ratios and dynamic range, the temporal instrument response function, comparisons between types of photoelectron spectra, and extraction of quantitative isomer mole fractions. As an example of the insights that may be gleaned from highly multiplexed experiments such as this, we present preliminary data of unexpected results from methanol photodissociation at 193 nm.

2 Experimental

The details of the instrumental apparatus are described in the original report¹ and will be briefly outlined here. The PEPICO spectrometer is a double (*i.e.*, electrons and cations) velocity map imaging (*i*²PEPICO) instrument with charged-particle optics tuned for high mass resolution, while simultaneously yielding high kinetic energy resolution of electrons and ions. We achieve these competing goals using a grid-free, charged-particle optics stack with 48 electrodes that separates the curved electric fields needed for velocity-map imaging from the linear gradient Wiley–McLaren space-focusing fields needed for high mass resolution.

The instrument is designed so that multiple sources of gaseous samples may be easily interchanged. A molecular beam valve producing short, supersonic pulses of gas can be installed on a removable wall that creates a differential pumping region inside the chamber. This source is useful for spectroscopy experiments where cold samples with only a few populated quantum states are desired. For studies of gas-phase chemistry in a collisional environment, a 12.7 mm OD / 10.5 mm ID flow reactor made from stainless steel or borosilicate glass can be installed inside the charged-particle optics. Figure 1 shows a schematic of the central part of the ion optics with the reactor tube installed. Reactions are initiated by photodissociation of a suitable precursor by an excimer laser pulse (Coherent, Compex 110), which propagates down the reactor tube. The reactor can be operated at pressures between 1–10 torr and is sampled via a 200 μm diameter pinhole in the reactor side wall. Gas expands through the pinhole into high vacuum with typical operational pressure of 1–10 $\times 10^{-7}$ torr,

over a base pressure of 3×10^{-8} torr. The molecular beam propagating along the $+x$ direction is intersected by VUV light traveling in the $-y$ direction. After the interaction regions the VUV beam flux is monitored by an SXUV-100 photodiode held at a 45 degree angle to the incoming beam, with the specularly reflected beam from the photodiode captured in a beam dump inside vacuum. Photoions and photoelectrons are extracted along the $\pm z$ direction, velocity focused, and imaged onto two Roentdek Hexanode delay line detectors, each with 75 mm active diameter.

Electrons and cations are detected in delayed coincidence. A true coincidence means detection of the electron and cation pair formed in the photoionization of a single neutral species. A false coincidence is any other electron/cation pair. The term delayed coincidence acknowledges that electrons reach the detector ≈ 30 ns after the ionization event, whereas cations require 2–40 μ s to reach their detector, depending on their mass-to-charge (m/z) ratio. The experimental data can be analyzed in real time using our custom software, Pepi-coSandals (spectrum acquisition and analysis software), allowing for optimal use of limited experimental time at synchrotron light sources.

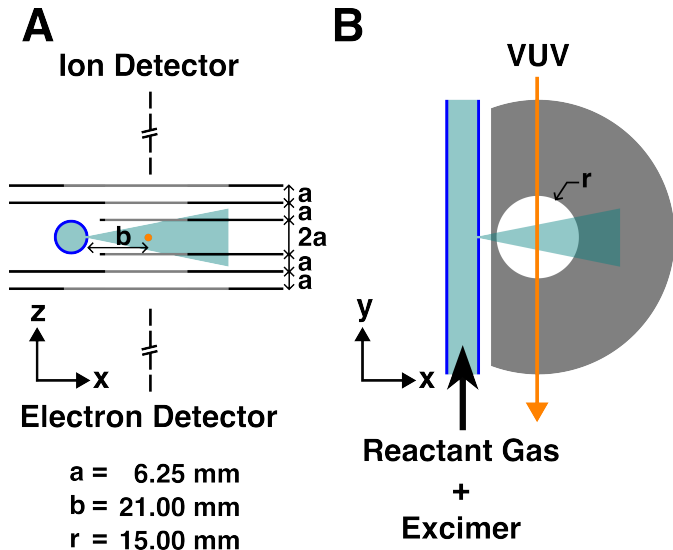


Figure 1: Schematic side-view (A) and top-view (B) of the center of the charged-particle optics showing cut electrodes (black/grey) with a flow-reactor tube (dark blue) installed. The light blue triangle depicts the molecular beam expanding from the reactor pinhole.

Most of the data presented here were recorded with a reactor tube made from borosilicate glass. To minimize the distance d_x between the pinhole and the ionization point, the reactor tube is embedded in the charged-particle optics by cutting the two innermost electrodes along a chord as shown in Fig. 1. To minimize surface patch potentials, we coated the outer surface of the reactor tube with black carbon followed by graphite paint (Ted Pella Inc., PELCO 16056 and 16053) and electrically grounded the reactor tube. The orange ionization point in Fig. 1A is at a potential of 0 V. The black coating also prevents ultraviolet excimer laser photons from reaching the microchannel plate detectors, preventing generation of spurious counts. We have found that, when using a quartz reactor tube together with 193 nm excimer photons, the electron detector still triggered at the time of laser firing. Borosilicate reactors can be used to eliminate this problem, as borosilicate’s transmission is negligible at 193 nm.

In our initial design, all 48 electrodes were uncoated stainless steel. The VUV photon energies used for ionizing gas-phase species are above the work function of stainless steel, and stray photons hitting a metal surface will generate background photoelectrons. Recently, we coated the four electrodes closest to the VUV beam path with Vantablack (Surrey Nanosystems), a proprietary nanostructured, conductive carbon coating, which led to a 3–4 $\times$ reduction in background electrons. Photoelectrons from metal surfaces are a ubiquitous problem in photoelectron spectroscopy.^{12–14} As one attempts to reduce these photoelectrons, we find it helpful to minimize the ratio of (electron count rate) / (VUV photocurrent), where the VUV photocurrent is proportional to VUV flux. The normalization to VUV flux helps one compare different approaches for reducing background photoelectrons on a quantitative basis.

We performed experiments at the Chemical Dynamics Beamline (9.0.2.3) of the Advanced Light Source (ALS) synchrotron at Lawrence Berkeley National Laboratory in five different measurement campaigns between December 2021 and June 2024. The VUV light at beamline 9.0.2.3 is generated by a 3-m undulator with undulator harmonics attenuated using a gas filter containing argon or helium depending on the photon energy. Three meters downstream

of the gas filter, the linearly polarized light, with the $\mathbf{E}$ vector along the x axis, is dispersed by a concave spherical grating ($600 \text{ lines mm}^{-1}$) and re-focused onto an adjustable horizontal monochromator exit slit. The VUV beam is focused to a $65 \mu\text{m}$ spot at the exit slit and then diverges with a full-angle of 1.66 mrad (corresponding to an effective f-number of $f/600$) as it enters the PEPICO chamber. The PEPICO instrument is attached to the beamline with the ionization point 637 mm downstream of the slit, yielding a beam diameter of $\approx 1 \text{ mm}$ in the ionization region. We calibrate the photon energy to the (8s) autoionizing Rydberg resonance of Xe at 12.5752 eV .

3 Results and discussion

3.1 Data acquisition and data structures

Before presenting new results, we summarize the salient characteristics of the multi-dimensional data produced by the Sandia PEPICO spectrometer. A more complete description can be found in our first article on this instrument¹ and related concepts in recent review articles.^{5,6} Unlike a traditional mass spectrometer (which detects only the cation from an ionization event) or a traditional photoelectron spectrometer (which detects only the electron), a PEPICO spectrometer detects and correlates both charged particles. Although cations and electrons may be analyzed separately, the fundamental concept in PEPICO spectroscopy is that of a true coincidence, *i.e.*, the detection of both the electron and the cation from the same ionization event. All other detected electron / cation pairs are false coincidences. Based on electron and cation impact times and positions at the respective detectors, coincidences may be sorted (or filtered) in numerous useful ways to create datasets that convey physical meaning.

Datasets of coincidences may be visualized as functions of complementary independent variables, such as time-of-flight (ToF), which yields mass spectra of the cations, cation velocity components (v_x, v_y, v_z), electron kinetic energy and angular distributions correlated with

each peak in the mass spectrum, or kinetic time profiles of coincidence detection relative to a sudden external perturbation of the neutral sample, such as a photodissociation laser pulse. All these correlations may also be a function of the VUV photon energy.

We utilize the multi-start / multi-stop (MM) technique for data collection,¹⁰ in which the detection of all charged particles is timestamped by a master clock that does not reset during the duration T_{tot} of data acquisition. Here, we denote event times from the master clock with capital T , and event times within a time-of-flight spectrum or with respect to a laser pulse (chemical kinetic time) with lower case t . Each detected electron provides a "start" timing signal, and is paired with every cation (each one providing a "stop" signal) detected within a user-chosen time range after each electron that we denote ToF_{max} . On our instrument $\text{ToF}_{\text{max}} = 40 \mu\text{s}$ enables detection of cations up to m/z 650 ($z = 1$, because cations are singly charged), but any time range may be chosen in post-processing the raw data.

In analyzing raw data, we apply coincidence filters that restrict the ranges of chosen independent variables to construct physically meaningful observables. The most common coincidence filter selects from the full dataset only those coincidences of a recognizable peak in the mass spectrum at a near-integer m/z ratio. Additional filters may be added to select data from chosen regions of the electron and cation detectors, and/or from a particular time window relative to the photodissociation laser trigger. Coincidence filters are usually implemented during data collection to facilitate data collection decisions, but the raw dataset may be post-processed as many times as needed with any combination of coincidence filters to gain chemical insight. We now characterize the instrument's performance for interrogating unimolecular and bimolecular chemical reactions.

3.2 Gas expansion dynamics

Quartz and borosilicate glass reactor tubes have been in use for many years in gas-phase reaction studies using photoionization mass spectrometry (PIMS),¹⁵⁻¹⁷ yet the nature of the

gas expansion dynamics from a reactor tube at 1–40 torr pressure is not well studied. The cation VMI of our new instrument enables us to investigate the neutral expansion dynamics from these reactor tubes, which impacts how such data are interpreted in time-resolved chemical kinetics experiments. These experiments typically seed small mole fractions of heavier molecules (≥ 16 amu) in a light, non-reactive bath gas, usually He. We therefore use Xe diluted in He to explore gas expansion dynamics in this section. The expansion dynamics lies on the spectrum from purely effusive molecular flow to supersonic viscous flow. Figure 2 presents data from flows of 5×10^{-5} mole fraction Xe in He as a function of reactor pressure from 1–9 torr. Panels A–C show VMI images of Xe^+ that map the neutral Xe velocity at 1, 5, and 9 torr total pressure. We determined the zero speed position in the laboratory frame of reference on the detector by ionizing background H_2O that has a thermalized Maxwell–Boltzmann (MB) velocity distribution, as discussed in our first paper.¹ The average velocity of the thermalized gas is 0 m s^{-1} and the zero speed position is shown by the black crosses at $x = 1.9 \text{ mm}$, $y = -2 \text{ mm}$.

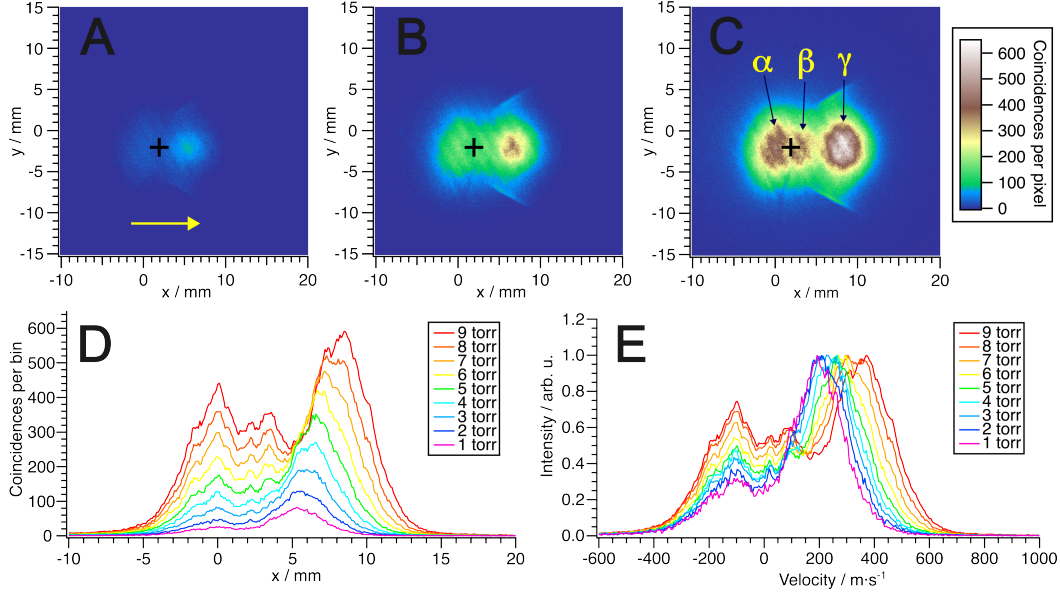


Figure 2: Xe coincidences from a reactor pressure scan with a fixed mole fraction of 5×10^{-5} Xe in He. **Top row:** Ion images of Xe^+ ions at a reactor pressure of **A:** 1 torr, **B:** 5 torr and **C:** 9 torr. The black cross in panels **A–C** denotes the position of zero velocity and the arrow in **A** shows the direction of the gas expansion centerline. **D:** Profile slice through the ion images at $y = -2 \pm 0.5$ mm. **E:** Intensity profiles from panel (**D**) plotted as a function of velocity and normalized to the largest peak.

The VMI images show interesting structures that are most prominent in the 9 torr image. Fig. 2D extracts Xe coincidence intensity vs. x position on the detector in a 1 mm wide horizontal slice around the expansion centerline. Dividing ion position in panel D by ion ToF yields the velocity distribution along the molecular beam axis in panel E.

The sampling geometry is such that we only probe a small solid angle of the reactor gas momentum space in the y and z dimensions around p_x (see below for a discussion of translational temperatures along the z axis). The v_x distribution of the sampled gas can therefore be approximated as the speed distribution of the 3D MB distribution. The measured most probable speed at $P = 1$ torr occurs at $v_x \approx +200 \text{ m s}^{-1}$, which corresponds closely to the most probable speed of Xe at 300 K, $v_{mp} = \sqrt{\frac{2k_B T}{m}} = 194 \text{ m s}^{-1}$. (In this section T denotes absolute temperature). By contrast, the most probable speed of He at 300 K is 1116 m s^{-1} . From this comparison, we conclude that the expansion is nearly effusive at $P = 1$ torr. As pressure increases, the most probable Xe velocity in the distribution

monotonically increases to $v_x = +400 \text{ m s}^{-1}$ at $P = 9 \text{ torr}$. This observation, combined with the fact that the most prominent features in the VMI images of Fig. 2 are centered at positive velocities along the molecular beam axis leads us to conclude that the the rightmost feature (γ) in Fig. 2C represents Xe atoms entrained in the helium molecular beam expansion. With increasing total pressure, Xe is accelerated due to viscous flow interactions with the lighter He atoms in the molecular beam. The most probable speed of a hard He supersonic expansion from a 300 K reservoir⁵ is $v_{mp} = \sqrt{\frac{5k_B T}{m}} = 1765 \text{ m s}^{-1}$. Although the effects of viscous flow are clear in our expansions from side-sampled chemical reactor tubes, they cannot be described as hard supersonic expansions.

The center feature (β), labeled in Fig. 2C, is centered near the position of zero velocity, and we assign this feature to Xe atoms thermalized by multiple collisions with the chamber walls prior to ionization. The leftmost feature (α) in Fig. 2C appears to contain two components. The more prominent one peaks at a virtually pressure-independent velocity of $v_x \approx -100 \text{ m s}^{-1}$, whereas a shoulder near $v_x \approx -210 \text{ m s}^{-1}$ grows in with increasing pressure. Based on the negative velocity of these two components, these Xe atoms are moving *towards* the reactor tube, and we assign this feature to Xe atoms from the molecular beam that are reflected from the mu-metal shielding that surrounds the charged-particle optics before being ionized by the VUV beam. Note that at our maximum operating chamber pressure of $1 \times 10^{-6} \text{ torr}$, the mean free path in the chamber is larger than 10 m. Therefore, gas-chamber wall collisions vastly outnumber gas-gas collisions.

If a single reflection converted the molecular beam into a Maxwell-Boltzmann distribution with a diffuse source, photoionization of singly reflected species would only sample negative velocities along x , leading essentially to an enhancement of the β feature at $x < 0$ in the image with a most probable v_x of 0 m s^{-1} and an *average* $\langle v_x \rangle_{v_x < 0} = -\sqrt{\frac{2kT}{\pi m}} = -110 \text{ m s}^{-1}$. This is only in serendipitous agreement with the measured *most probable* velocity. As gas molecules may leave the charged particle optics for good and the alignment with the ionizing beam is constantly being lost after each reflection, the nascent molecular beam represents

the strongest feature in the image, after which α represents the sample reflected once. Twice reflected molecules cannot clearly be resolved between the β and γ features any more, and multiple reflections are summed up as an essentially converged Maxwell–Boltzmann distribution in β . Thus, we see the once reflected gas molecules crossing the ionizing beam in α , which have already undergone some randomization and, as their average speed only increases mildly with pressure, also some thermalization after a single wall collision.

Informed by this characterization of the gas dynamics from the side-sampled reactor tube, it is clear that one should include in a kinetic dataset only coincidences from the molecular beam feature γ on the cation detector in Fig. 2C. This region of the cation VMI represents neutral species that originated from the reactor tube, have had no collisions with the chamber walls, and a negligible probability of collisions with background chamber gases. These observations underscore the importance of cation VMI to address sampling effects experimentally.¹⁸

3.3 Times of flight

3.3.1 Electron time of flight

Time-of-flight mass spectrometry is an inherently pulsed technique, requiring a start signal when a cation begins its flight and a stop signal when the cation impacts the detector. The time difference between these signals is the true ToF. In our PEPICO spectrometer, all 48 electrodes are held at stable DC potentials, the molecular beam is continuous, and the VUV radiation from the synchrotron is essentially continuous (60 ps pulses at 500 MHz repetition rate). Therefore, ionization events are distributed almost randomly in time and we cannot control the time of ionization for any neutral. In this situation, the pulsed nature of time-of-flight mass spectrometry is realized by each electron acting as a start signal. We therefore define the ToF as

$$\text{ToF} = T_i - T_e, \tag{1}$$

where T_i and T_e are the detection times of the ion and electron at their respective detectors. $T_e < T_i$ holds for true coincidences due to the much larger cation mass relative to m_e . Because the cation is created within a DC electric field, its true ToF begins at the time of ionization T_{ioniz} . The fundamental equation relating mass to ToF is

$$\text{ToF} = \beta + \alpha \sqrt{\frac{m}{z}}, \quad (2)$$

where m is the cation mass, z is the charge, and α and β are parameters determined by calibration to signals of known m/z ratios. A typical calibration is shown in Fig. S1.

Our instrument achieves excellent mass accuracy of ≈ 3 ppm.¹ A new insight we provide here is that the parameter $\beta = -30.542 \pm 0.003$ ns, returned from the fit to eq. 2, measures the mean time-of-flight of the electrons $\langle \text{ToF}_e \rangle$ from the ionization volume to the electron detector. Stated another way, the true ToF of the cations is, on average, 30.542 ns longer than the ToF we define in eq. 1, and therefore the time of each ionization event may be tabulated as

$$T_{ioniz} = T_e + \beta = T_e - \langle \text{ToF}_e \rangle. \quad (3)$$

In an ideal PEPICO experiment, one would measure the the 3-D velocity vector of each electron. However, note that the 0.003 ns uncertainty in $\langle \text{ToF}_e \rangle$ is the uncertainty of the mean value, not a measure of the breadth of the velocity distribution $v_{z,\text{elec}}$ along the time-of-flight axis. Our reconstruction of photoelectron spectra¹ provides the distribution of kinetic energies of an ensemble of electrons, but, lacking the $v_{z,\text{elec}}$ values on an event-by-event basis, we cannot extract each electron's 3-D velocity vector, which would be valuable for measuring molecular frame photoelectron angular distributions.¹⁹

3.3.2 Cation time of flight: Peak shape, mass resolution, and translational temperature

If one includes coincidences from the entire area of the cation detector, the peak shape in the mass spectrum of a stable molecular species emitted from the reactor tube is a broad base with a sharp peak superimposed in the center (Fig. S2A). The sharp peak arises from the molecular beam (feature γ , Fig. 2C), whereas the remaining areas of the cation VMI image produce the broad base in the mass spectrum. As discussed above, one should generally include only the data from the molecular beam, and we now quantify the mass resolution using this restriction.

As a reference for the best mass resolution from this instrument, Figure 3A shows the ToF peak of ^{132}Xe from a hard, singly skimmed supersonic expansion using a pulsed molecular beam valve with 1 % Xe in He and a 20 psi backing pressure. The velocity spreads $\Delta v_x, \Delta v_y$ under these conditions are significantly smaller than from the reactor tube source, enabling a small region-of-interest (ROI) on the cation detector to encompass all the useful coincidences from the molecular beam.¹ The peak shape is Gaussian, with a mass resolution from this hard expansion of $m/\Delta m = 11\,170 \pm 120$, which is a significant improvement compared to the best previous PEPICO mass resolution $m/\Delta m = 2\,062$ from Vredenburg et al.²⁰ As discussed by Baer and Tuckett,⁵ the FWHM of a mass spectral peak in a perfectly designed time-of-flight spectrometer is a function of only the cation mass, the translational "temperature" of the precursor neutrals in the $\pm z$ direction, and the electric field at the point of ionization as follows:

$$\text{FWHM} = 22.33 \times \frac{\sqrt{mT}}{F}, \quad (4)$$

where m is the ion mass in dalton, T the absolute temperature in K, F the extraction field in V cm^{-1} , and the FWHM is in ns. For our extraction field of 120 V cm^{-1} , the hard supersonic expansion corresponds to a z -axis translational "temperature" of 0.14 K. This very low effective temperature results from the long distance (33 cm) between the pulsed

valve and the ionization cylinder of 1 mm diameter, resulting in a small velocity spread along the z direction. Sensitivity could be improved by shortening these distances with some reduction of mass resolution. One should remember that supersonic expansions are non-equilibrium environments, and hence the term "temperature," although used ubiquitously, is not rigorously appropriate: the internal energy of molecules in such expansions are almost always higher than the translational "temperature" would imply.

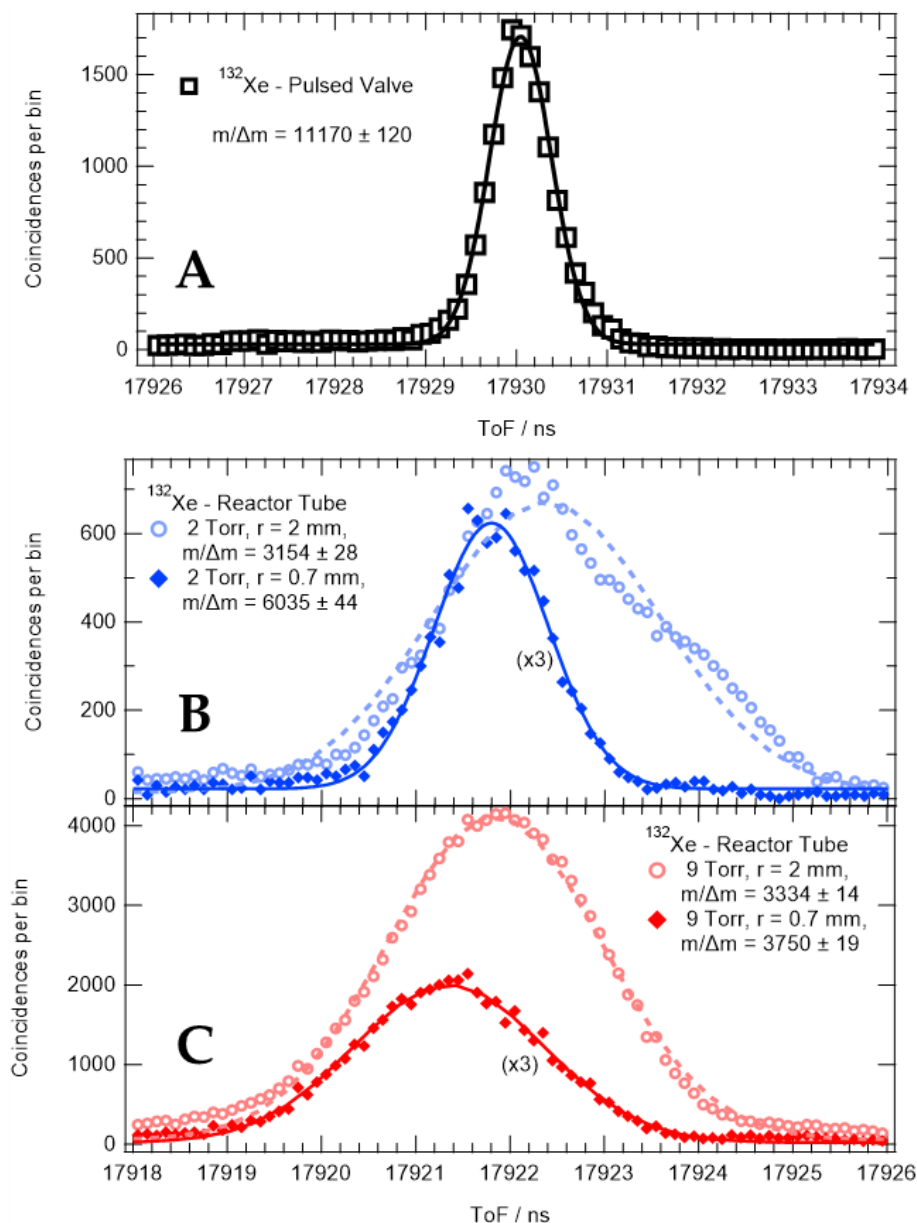


Figure 3: Time-of-flight mass spectra showing mass resolution [$m/\Delta m = \text{ToF}/(2\Delta\text{ToF})$] of the ^{132}Xe mass peak (A) from the hard supersonic expansion with a pulsed molecular beam valve and (B, C) from the mild supersonic expansion from the reactor tube at two different pressures of 2 and 9 torr. Lines are Gaussian fits to the data points. For the reactor tube, an improved mass resolution can be achieved if the circular ion detector ROI is reduced from 2 to 0.7 mm radius, but this choice discards $\approx 85\%$ of the peak area. For detailed discussion on the pressure dependence and the selection of ROI, see Supporting Information.

In chemical kinetics experiments, the unskimmed beam from the reactor tube, the lower backing pressure, and the shorter 21 mm distance between the expansion orifice and the

ionization region reduces mass resolution. Figs. 3B and C show Xe time-of-flight spectra from Xe seeded in He at 2 and 9 torr reactor pressures. Choosing a cation ROI with 2 mm radius includes almost all of the molecular beam spot shown in Fig. 2C, and yields $m/\Delta m = 3\,154 \pm 28$ and $m/\Delta m = 3\,334 \pm 14$ for 2 and 9 torr, respectively. For reference, this latter mass resolution corresponds to a z -axis translational "temperature" of 1.5 K. As collisional cooling is minimal in the expansion, this value is a consequence of sampling a small solid angle of the expansion. Choosing a smaller circular ROI with radius of 0.7 mm on the molecular beam spot, the mass resolution improves to $m/\Delta m = 6\,035 \pm 44$ at 2 torr and $m/\Delta m = 3\,750 \pm 19$ at 9 torr. Using the smaller ROI reduces the integrated area under the curve by a factor 6 to 7. We usually operate with 2 mm radii ROIs for best signal-to-noise ratio. If a higher mass resolution is required to distinguish two species, one can achieve this goal by reducing the size of the ROI while sacrificing signal. However, when increasing the mass resolution in this way, the peak height is not reduced as much as the peak area, and hence dynamic range increases as we discuss in Section 3.5. The Supporting Information contains a more detailed analysis of correlation between cation position on the detector and TOF peak shape and resolution (see Figures S3–S5).

3.4 Collection efficiencies

As discussed by Baer and Tuckett,⁵ coincidence experiments benefit from high collection efficiencies for both electrons and cations. This is because the *product* of the electron and cation collection efficiencies determine the probability of coincidence detection, rather than only the cation (or electron) collection efficiency as in triggered time-of-flight mass spectrometry (or photoelectron spectroscopy). For consistency with earlier work,^{5,10} the electron and cation collection efficiencies we define are the product of two quantities: (1) the fraction of the full 4π solid angle of cations (or electrons) that impact the active area of a detector, and (2) the quantum efficiency of the detector system that converts the impacted charged particle into a detected event. We assume that the electrons and cations originate from the

same volume, *i.e.*, the volumetric overlap between the VUV and gas beam is identical for the electrons and cations imaged onto their respective detectors, which is to be expected in a symmetric experiment, such as ours, for charged species within the kinetic energy range of the VMI detectors. The goal of this section is to clearly define collection efficiencies, provide an example of their measurement, and clarify how these concepts can best inform data collection decisions.

In earlier implementations of PEPICO and threshold-PEPICO (TPEPICO) spectroscopy,⁵ it was difficult to transport the full 4π solid angle of electrons and cations to their respective detectors. Fortunately, velocity map imaging with fast imaging detectors makes it straightforward to collect the full 4π solid angle of all charged particles, especially at low to moderate kinetic energies. By contrast, the quantum efficiency for charged particle detection is always less than 100% in detectors that use microchannel plates to amplify the signal of an individual charged particle. To make the best use of experimental time, it is wise to define and monitor collection efficiencies, enabling educated choices regarding data acquisition parameters and detector maintenance.

Before discussing the practical measurement of collection efficiencies we define some relevant concepts and nomenclature. Let J (s^{-1}) denote the average ionization rate of the neutrals being interrogated. The detected count rate of electrons J_e or cations J_i may be expressed as⁵

$$J_e = \eta_e J \tag{5}$$

$$J_i = \eta_i J \tag{6}$$

where η_e and η_i are the unitless electron and cation collection efficiencies, respectively. Equations 5 and 6 are a system of two equations with three unknowns, where J_e and J_i are directly measured single-particle count rates, whereas the three variables on the right hand sides must be determined. In particular, the ionization rate J cannot be measured directly but may be

extracted as described below.

In contrast to the single-particle properties just described, a coincidence is a two-particle property formed by correlating an electron with a cation. As discussed in Section 3.3, mass-resolved quantities are only available from true coincidences. If G_C^{tr} denotes the number of true coincidences detected in total acquisition time T_{tot} (s), then the true coincidence count rate J_C^{tr} (s^{-1}) is

$$J_C^{\text{tr}} = G_C^{\text{tr}}/T_{\text{tot}} \quad (7)$$

Because detection of a coincidence requires the detection of an electron (the start signal) followed by detection of a cation (the stop signal), it follows that the true coincidence count rate J_C^{tr} may be expressed as the electron count rate multiplied by the ion collection efficiency:

$$J_C^{\text{tr}} = \eta_i J_e \quad (8)$$

Equivalently, the true coincidence count rate may be written as the ion count rate multiplied by the electron collection efficiency

$$J_C^{\text{tr}} = \eta_e J_i \quad (9)$$

The reader may find it helpful to consider the limiting case $\eta_e = \eta_i = 100\%$ to rationalize the derivation of eqs. 8 and 9.

Extracting the two collection efficiencies from experimental data reduces to measuring J_C^{tr} , J_e , and J_i needed to solve eqs. 8 and 9, with appropriate corrections to account for the fact that J_C^{tr} is a two-particle property whereas J_e and J_i are single-particle properties. We clarify that eqs. 8 and 9 require the true coincidence count rates, not the total coincidence count rates, a fact may be ambiguous in the literature.^{5,10} In addition, one need not restrict the kinetic energy of photoelectrons to threshold electrons when evaluating collection efficiencies, which is another point of ambiguity in the literature.^{5,21}

Collection efficiencies are most easily measured by collecting two datasets: one with—labeled

A—and one without—labeled B—a single ionizable gas added to whatever background species may unavoidably be present. Fig. 4 shows a portion of the TOF mass spectrum from dataset A, with a sample of 0.035% Xe in He ionized at 12.339 eV. Because $J_e(A)$, and $J_i(A)$ are not mass-resolved, we must remove any contributions to these count rates that do not result from Xe ionization, such as dark counts on both detectors, photoelectrons from VUV interacting with metal surfaces, and the presence of any impurity gas species ionizable at the photon energy being used. To do this we acquire dataset B, flowing pure He through the reactor tube, which should contain only these unwanted contributions. The corrected electron and cation count rates containing only the contributions from Xe are

$$J_e(\text{Xe}) = J_e(A) - J_e(B) \quad (10)$$

$$J_i(\text{Xe}) = J_i(A) - J_i(B) \quad (11)$$

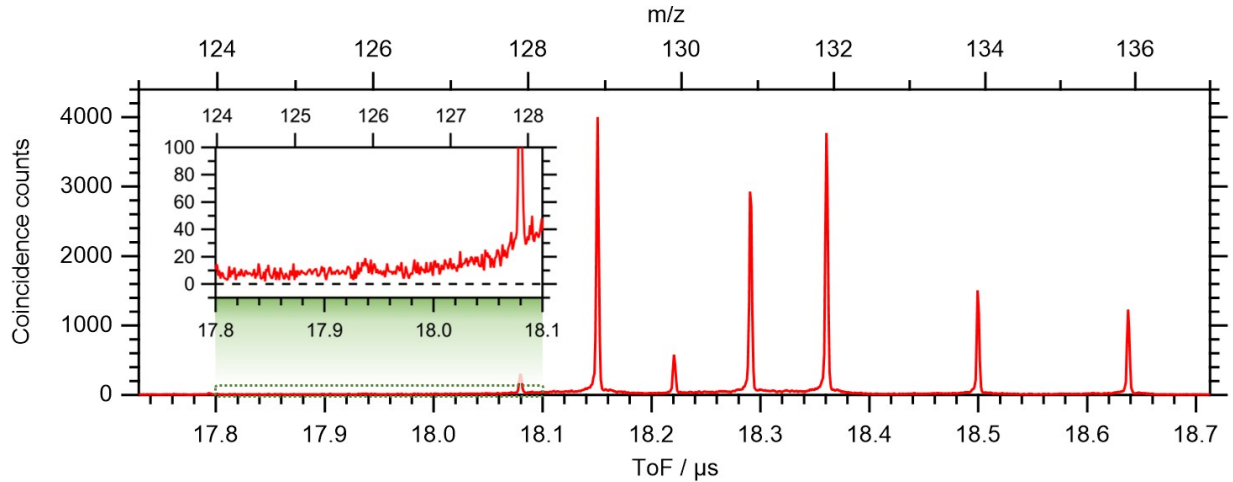


Figure 4: Time-of-flight mass spectrum of the seven stable isotopes of Xe (mole fraction 0.035%) in He at 10 torr total pressure ionized at 12.339 eV, with single-particle count rates of $J_e = 21\,100\text{ s}^{-1}$, $J_i = 34\,500\text{ s}^{-1}$. Coincidences are filtered to include only a 2 mm radius ROI on the cation detector centered on feature γ of Fig. 2C.

We determine $J_C^{\text{tr}}(\text{Xe})$ from the mass spectrum in Fig. 4, which shows peaks due to the seven stable Xe isotopes on a flat, non-zero baseline (see inset). A key feature of the

MM data acquisition scheme¹⁰ is that false coincidences are randomly distributed in time, forming a background that increases in magnitude with acquisition time but with a slope of zero in the time-of-flight spectrum. The average value of this baseline per time-of-flight bin (1 ns in Fig. 4) in the flat region from 17.8–18.0 μ s is 8.76 counts per bin. After subtracting this background level, the spectrum contains, on average, only true coincidences. Hence $J_C^{\text{tr}}(\text{Xe})$ is the integral of the background-subtracted mass spectrum over the TOF range containing all the Xe peaks. Combining this value with $J_e(\text{Xe})$ and $J_i(\text{Xe})$ in eqs. 8 and 9 yields $\eta_e = 35\%$ and $\eta_i = 57\%$. The total ionization rate $J(\text{Xe})$ may then be obtained via eq. 5 or 6.

The electron and ion images from this dataset confirm that we collect the full 4π solid angle of electrons and cations. We therefore attribute the collections efficiencies solely to the quantum efficiency of charged particle detection in our microchannel plate delay line detectors and associated electronics. These collection efficiencies are in line with "good" collection efficiencies noted by Baer and Tuckett.⁵ Note that the MCP quantum efficiency will decrease over time as the integral charge having passed through each plate increases, and the reduction in collection efficiency vs. MCP age can inform the experimentalist whether replacement (or detector rotation, in the case of spatially inhomogeneous detection efficiency drops, to expose a new area) is needed. Along with the possibility of restricting the ion detector image to the region due to the molecular beam signal (see above), the possibility to identify and address such spatial inhomogeneities also underscores the importance of imaging detection if microchannel plates are used.

3.5 Signal to noise and dynamic range

We now evaluate how instrument design affects signal-to-noise ratios of major and minor species and the dynamic range of the experiment. Bodi et al.¹⁰ discussed signal and noise sources in PEPICO measurements, with additional perspective from Baer and Tuckett.⁵ Electron/cation pairs that form true coincidences are correlated in time and yield peaks in

the mass spectrum of width w . As shown in Fig. 3, our ToF peak shapes are Gaussian. To compare signal intensities, we define their width w as 5.15σ , or $2.19 \times \text{FWHM}$, which contains 99% of a peak's area. Using multi-start / multi-stop data collection, the total number of true coincidences integrated over all mass spectral peaks during an experimental time T_{tot} is

$$G_{\text{C}}^{\text{tr}} = \eta_e \eta_i J T_{\text{tot}} \quad (12)$$

whereas the number of true coincidences in a single peak labeled A, with fractional peak area α , is

$$G_{\text{C}}^{\text{tr}}(\text{A}) = \alpha \eta_e \eta_i J T_{\text{tot}} \quad (13)$$

By contrast, false coincidences are distributed randomly in time-of-flight because they are uncorrelated electron/cation pairs that did not arise from ionization of a single atom or molecule. Electrons and cations from all sources contribute to the false coincidence background underneath peak A. As a result, the number of false coincidences in a dataset within peakwidth w_{A} is the total number of start events, i.e., detected electrons ($\eta_e J T_{\text{tot}}$), multiplied by the average number of cations ($\eta_i J w_{\text{A}}$) that arrive within a mass spectral time-of-flight window w_{A} after each start event.

$$G_{\text{C}}^{\text{f}}(\text{A}) = \eta_e \eta_i J^2 T_{\text{tot}} w_{\text{A}} \quad (14)$$

Note that true coincidences increase with the total ionization rate J , whereas false coincidences increase with J^2 .

Here we note that although one could define the total false coincidences in a dataset G_{C}^{f} , and a corresponding total false coincidence count rate J_{C}^{f} , these values are not inherently meaningful because they depend linearly on the user-chosen value ToF_{max} . More specifically, as long as ToF_{max} is large enough to detect the heaviest cations in a sample, doubling ToF_{max} would not change G_{C}^{tr} or J_{C}^{tr} , but it would double the apparent false coincidence count rate. In

the end, the critical false coincidences are those that fall within the span of each peak in the mass spectrum. All others that fall outside of a mass spectral peak can be disregarded. As a consequence, the only meaningful number of false coincidences to consider are those defined by eq. 14, which lie underneath a particular mass spectral peak A of true coincidences. The number of *these* false coincidences does not depend on the arbitrary value ToF_{max} .

We now consider the signal-to-noise ratio in a PEPICO experiment. The two main sources of noise that impact peak A are 1) the Poisson counting statistics—or shot noise—of the true coincidences forming peak A, and 2) the false coincidences underneath peak A. Because the standard deviation in a Poisson distribution is the square root of the number of events, we have

$$\text{Shot Noise} = \delta G_C^{\text{tr}}(\text{A}) = \sqrt{\alpha \eta_e \eta_i J T_{\text{tot}}} \quad (15)$$

$$\text{False Coincidence Noise} = \delta G_C^{\text{f}}(\text{A}) = J \sqrt{\eta_e \eta_i T_{\text{tot}} w_A} \quad (16)$$

and because these two noise sources are uncorrelated we may add them in quadrature:

$$\delta G_C(\text{A}) = \sqrt{\left[\delta G_C^{\text{tr}}(\text{A})\right]^2 + \left[\delta G_C^{\text{f}}(\text{A})\right]^2} = \sqrt{\alpha \eta_e \eta_i J T_{\text{tot}} + \eta_e \eta_i J^2 T_{\text{tot}} w_A} = \sqrt{\eta_e \eta_i J T_{\text{tot}} (\alpha + J w_A)} \quad (17)$$

Hence the signal to noise of peak A is

$$\frac{S}{N}(\text{A}) = \frac{G_C^{\text{tr}}(\text{A})}{\delta G_C^{\text{tr}}(\text{A})} = \frac{\alpha \eta_e \eta_i J T_{\text{tot}}}{\sqrt{\eta_e \eta_i J T_{\text{tot}} (\alpha + J w_A)}} = \alpha \sqrt{\frac{\eta_e \eta_i J T_{\text{tot}}}{\alpha + J w_A}} \quad (18)$$

Equation 18 has two important limiting cases. If peak A is a major peak in the mass spectrum, then $\alpha \gg J w_A$. Shot noise dominates total noise, and the S/N becomes

$$\frac{S}{N}(\text{A, major peak}) \approx \sqrt{\alpha \eta_e \eta_i J T_{\text{tot}}} = \sqrt{G_C^{\text{tr}}(\text{A})} \quad (19)$$

For large peaks, with negligible false coincidence background noise, S/N increases with the square root of both ionization rate and total experiment time, and is independent of peak width w_A . If one can increase the VUV flux, the ionization rate J will increase, improving signal to noise for all major peaks. The other limiting case occurs for small amplitude peaks ($\alpha \ll Jw_A$) where false coincidence noise dominates, and the S/N becomes

$$\frac{S}{N}(\text{A, minor peak}) \approx \alpha \sqrt{\frac{\eta_e \eta_h T_{\text{tot}}}{w_A}} \quad (20)$$

Remembering from eq. 14 that the false coincidences underneath peak A depend on the square of the ionization rate, it can be tempting, when one is struggling to resolve a minor peak in a PEPICO experiment, to halve the VUV flux, therefore reducing the false coincidence rate by a factor of four while reducing the signal by only a factor of two. Unfortunately, eq. 20 shows that this change will have no effect on the S/N of such minor peaks, because the S/N is independent of J when false coincidence noise dominates. Instead, avenues to increase S/N for minor peaks include increasing ion and electron collection efficiencies, signal averaging longer, decreasing peak width w_A by increasing the mass resolution, or employing false coincidence rejection techniques.¹¹ In summary, this analysis shows that the S/N of major peaks increases with increasing ionization rate whereas the S/N of minor peak is unaffected by ionization rate. Therefore, in a fixed acquisition time, one should generally choose at the highest achievable count rates, consistent with other experimental constraints, in order to maximize S/N .

To conclude this section, we provide typical experimental parameters to make the above relationships more concrete. Consider the case of methanol photodissociation, where we present some unexpected results in Section 3.9. We photodissociate CH_3OH with a 193 nm laser pulse and probe the system using VUV photons at 11.0 eV, which is above the ionization energy of methanol. A typical experiment uses $[\text{CH}_3\text{OH}] = 2.3 \times 10^{15} \text{ molecules cm}^{-3}$ with laser fluence of $4.2 \times 10^{16} \text{ photons cm}^{-2} \text{ pulse}^{-1}$ that photodissociates 1.5% of the methanol sample, reducing $[\text{CH}_3\text{OH}]$ by $3.4 \times 10^{13} \text{ molecules cm}^{-3}$. We therefore expect a major peak

Table 1: Typical PEPICO parameters: detection of major and minor species

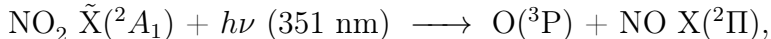
Parameter	Value	Unit	Description
J	50 000	s^{-1}	Ionization rate
T_{tot}	1000	s	Total acquisition time
ToF_{max}	40 000	ns	Maximum ToF tabulated
t_{bin}	0.1	ns	ToF bin width
η_e	0.35		Electron collection efficiency
η_i	0.57		Cation collection efficiency
J_e	17 500	s^{-1}	Total electron count rate
J_i	28 500	s^{-1}	Total cation count rate
J_{C}^{tr}	9 975	s^{-1}	Total true coincidence count rate
w	3.5	ns	TOF peakwidth capturing > 99% peak area
$\alpha(\text{CH}_3\text{OH})$	0.99985		Methanol (major) peak fraction
$G_{\text{C}}^{\text{tr}}(\text{CH}_3\text{OH})$	9.97×10^6		CH_3OH true coincidences
$G_{\text{C}}^{\text{f}}(\text{CH}_3\text{OH})$	1746		False coincidences under CH_3OH peak
$\delta G_{\text{C}}^{\text{tr}}(\text{CH}_3\text{OH})$	3 158.1		Shot noise from CH_3OH true coincidences
$\delta G_{\text{C}}^{\text{f}}(\text{CH}_3\text{OH})$	41.8		False coincidence noise under peakwidth w
$\delta G(\text{CH}_3\text{OH})$	3 158.4		Total noise of CH_3OH signal
$S/N(\text{CH}_3\text{OH})$	3 158		S/N of CH_3OH concentration measurement
$\alpha(\text{P})$	0.00015		Product P (minor) peak fraction
$G_{\text{C}}^{\text{tr}}(\text{P})$	1 496		Product P true coincidences
$\delta G_{\text{C}}^{\text{tr}}(\text{P})$	38.7		Shot noise product P true coincidences
$\delta G_{\text{C}}^{\text{f}}(\text{P})$	41.8		False coincidence noise under peakwidth w
$\delta G(\text{P})$	56.9		Total noise of product P signal
$S/N(\text{P})$	26		S/N of Product P concentration measurement
Jw	0.00018		Jw metric from eq. 18

from CH_3OH^+ at m/z 32.026. Consider a minor product P from this photodissociation with a 1% branching fraction, and therefore a concentration $[\text{P}] = 3.4 \times 10^{11}$ molecules cm^{-3} . In this example, we assume all species have the same photoionization cross section, and assume that CH_3OH and product P are the only species observed, with peak fractions after photodissociation of $\alpha(\text{CH}_3\text{OH}) = 0.99985$, and $\alpha(\text{P}) = 0.00015$, representing major and minor peaks, respectively, from the above discussion. We use mass resolution $m/\Delta m = 3300$, consistent with Fig. 3C, resulting in a mass spectral peakwidth for species near 30 amu of $w = 3.5$ ns. Typical experimental parameters and results are shown in Table 1.

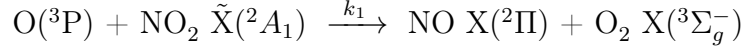
The methanol concentration measurement has a S/N ratio of 3 158, completely dominated by shot noise, as expected for the largest peak in the mass spectrum. By contrast, the minor product P has $\alpha \approx Jw$, and hence the shot noise and false coincidence noise for species P are nearly equivalent, with a resulting S/N of 26 for the time-integrated intensity of species P. Although this S/N is sufficient for measuring the branching fraction of species P, it would not be sufficient for a plot of the concentration of P vs. kinetic time presented in the next section. We note that background electrons ejected from metal surfaces will generate additional false coincidences that will reduce the S/N for minor peaks where false coincidence noise makes a significant contribution, highlighting the value of reducing background electrons. Nevertheless, the high mass resolution of our PEPICO spectrometer, resulting in a small value $Jw \approx 0.0002$ provides excellent dynamic range of more than 10,000 at $S/N > 10$ for the minor peak without the use of false coincidence rejection techniques.¹¹

3.6 Temporal instrument response function

In kinetics experiments, the true chemical time history is inevitably delayed and broadened by the temporal instrument response function (IRF), as discussed by Taatjes.²² As with the MPIMS apparatus,²³ we characterize the temporal IRF of our side-sampled chemical reactor by 351-nm photodissociation of NO_2 ,



measuring the kinetic time profile of the NO radical signal. This photodissociation occurs in less than 400 fs—instantaneous on the timescale of our experiment—yielding only $\text{O}(^3\text{P}) + \text{NO}$.²⁴ Therefore, the rise of NO produced directly from photodissociation, with amplitude c_1 , should solely be determined by our IRF. However, the bimolecular reaction



also produces NO, with amplitude c_2 , on a slower timescale with time-constant $\tau = (k_1[\text{NO}_2])^{-1}$, where $k_1(298 \text{ K}) = 1.03 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.^{25–28} If all $\text{O}(^3\text{P})$ is consumed by reaction with NO_2 in great excess, then $c_1 = c_2$. The NO_2 photodissociation system therefore provides a means to evaluate both the IRF and the instrument’s ability to measure bimolecular rate coefficients.

The experimental time profile of NO in Fig. 5(a) is coincidence signal $G_{\text{NO}}(t_{\text{raw}})$ vs. raw kinetic time referenced to the periodic laser pulse

$$t_{\text{raw}} = T_e - T_{\text{laser}}(n) \quad (21)$$

where $T_{\text{laser}}(n)$ is the master-clock timestamp of the n^{th} laser pulse at laser repetition rate R , and n is evaluated for each detected electron as

$$n = \lfloor R T_e \rfloor \quad (22)$$

The NO time trace in Fig. 5(a) appears to show only a single rise. On closer inspection, Fig. 5(b) reveals a faster rise that we assign to NO from photodissociation and a slower rise of NO from the bimolecular reaction. We fit the NO coincidence signal to the functional form of eq. 23, which convolves a Heaviside step function $H(t)$ —representing the sudden production of NO via photodissociation—with a Gaussian (standard deviation σ) that broadens the IRF due to velocity spread in the molecular beam and other sources of temporal broadening.

$$\begin{aligned}
G_{\text{NO}}(t) &= G_0 + A \left[\frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(t-t_0)^2}{2\sigma^2}} \otimes \left\{ c_1 + c_2(1 - e^{-\frac{t}{\tau}}) \right\} H(t) \right] \\
&= G_0 + A \int_{-\infty}^{\infty} \left[\frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(t'-t_0)^2}{2\sigma^2}} \left\{ c_1 + c_2(1 - e^{-\frac{t-t'}{\tau}}) \right\} H(t-t') \right] dt' \\
&= G_0 + \frac{A}{2} \left[c_1 \left\{ \text{erfc}\left(-\frac{t-t_0}{\sqrt{2}\sigma}\right) \right\} + c_2 \left\{ \text{erfc}\left(-\frac{t-t_0}{\sqrt{2}\sigma}\right) - e^{\frac{\sigma^2}{2\tau^2} - \frac{t-t_0}{\tau}} \text{erfc}\left(\frac{\sigma}{\sqrt{2}\tau} - \frac{t-t_0}{\sqrt{2}\sigma}\right) \right\} \right] \quad (23)
\end{aligned}$$

The laser pulse reaches the reactor tube at $t = 0$ (vertical dashed line in Fig. 5(b)), whereas the step transition of $H(t)$ and the mean of the Gaussian occur at time t_0 , which is delayed from the laser pulse by the mean transit time $\langle t_d \rangle$ required for NO to traverse the distance $d_x = 21 \pm 0.5$ mm (see Fig. 1) from the pinhole to the center of the VUV beam. G_0 is a signal offset, A is the overall amplitude, and τ is the time constant of the bimolecular reaction defined above. The black line in Fig. 5(b) shows the best fit function with residuals plotted above. Here, we fix $c_1 = c_2 = 0.5$. Of the five fitted parameters, G_0 and A are necessary but nugatory; the important parameters are $t_0 = 34 \pm 2$ μs , the Gaussian FWHM $b (= 2.355\sigma) = 24 \pm 8$ μs , and the bimolecular reaction time constant $\tau = 155 \pm 12$ μs . Combining τ with $[\text{NO}_2]$ yields our measurement of $k_1(298\text{K}) = 1.00 \pm 0.08 \times 10^{-11}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, in good agreement with the literature value of k_1 .

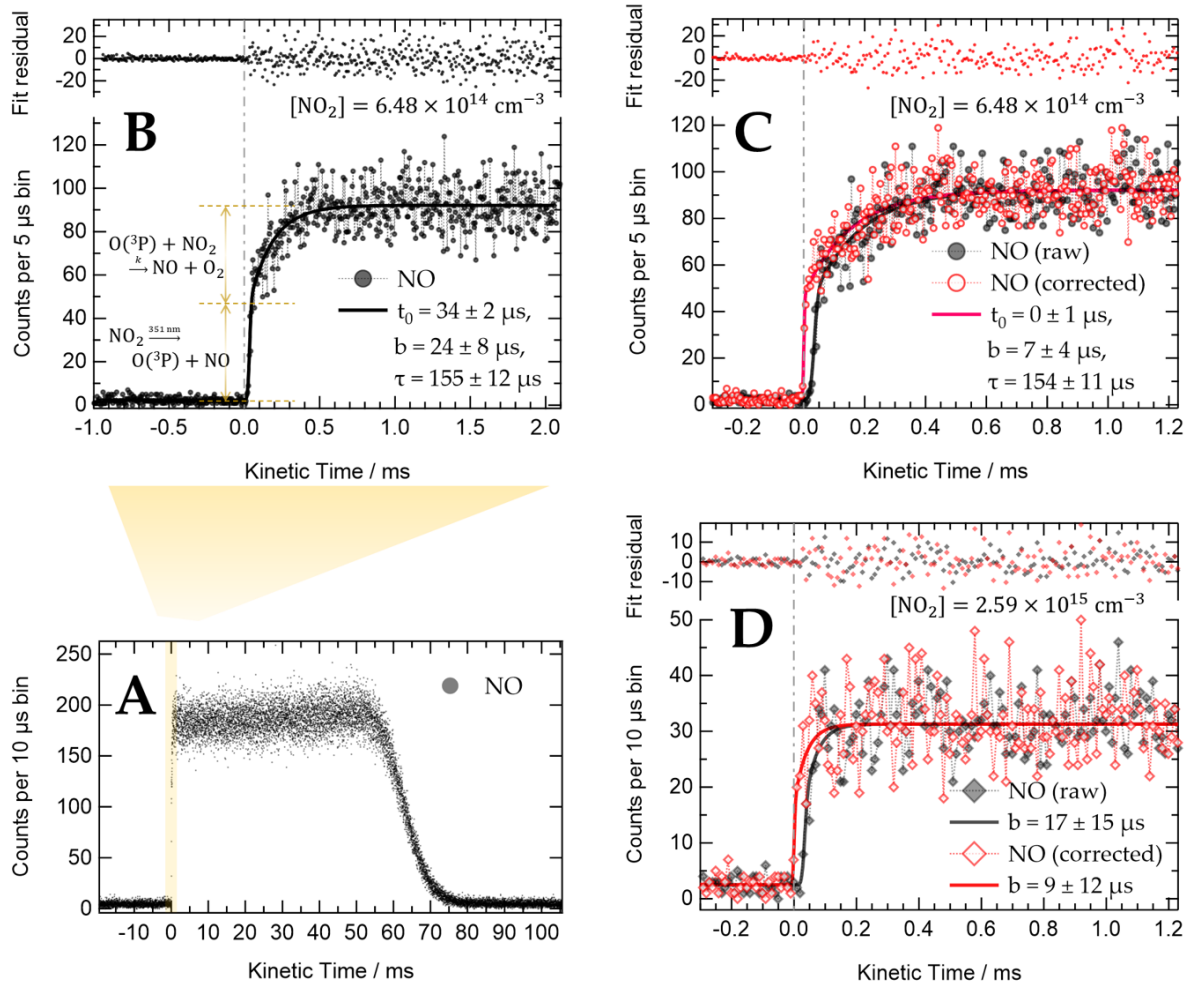


Figure 5: (A) Complete NO time trace following NO_2 photodissociation at laser repetition rate $R = 8$ Hz. (B) A 3 ms range of the same data (grey circles) in which both the faster NO (photodissociation) and the slower NO (bimolecular reaction) may be distinguished. The laser pulse arrives at $t = 0$ (vertical dashed line). The black line shows a fit to the data (see text) with residuals above (dots). Panel (C) compares the same data (grey circles) and fit (black line) to the transit-time corrected data (red circles, see text) and a fit to that data (red line) with residuals (red dots). Panel (D) shows both raw and transit-time corrected data from a different experiment with $4\times$ higher $[\text{NO}_2]$, with (red open diamonds) and without (black filled diamonds) transit time correction. All data use a cation ROI of 3 mm radius to include only the NO in the molecular beam.

To understand the physical origin of the IRF, remember that the photodissociation of NO_2 occurs inside the reactor tube in a collisional environment, whereas our measurement of this chemistry happens *ex situ*, by sampling, ionizing, and detecting species in a collisionless, high-vacuum environment. The first NO^+ cations we observe represent NO radicals formed

by photodissociation of NO_2 that happen to be at the pinhole—the origin of the molecular beam—when the 15-ns laser pulse arrives in the reactor at time $t = 0$. These NO radicals require, on average, $t_0 = \langle t_d \rangle = 34 \mu\text{s}$ to travel the fixed distance $d_x = 21 \pm 0.5 \text{ mm}$ before being ionized by the VUV beam. In this context, we can define a corrected kinetic time for each coincidence event i as

$$t_{\text{corr}}(i) = t_{\text{raw}}(i) - \langle \text{ToF}_e \rangle - \langle t_d \rangle \quad (24)$$

that subtracts both the mean electron flight time (of order 30 ns) and the much larger mean neutral transit time of order 30 μs .

However, we can improve on this correction through the multi-dimensional nature of PEPICO data by extracting the transit time of each individual NO molecule. Remembering that the x -coordinate of each NO^+ impact on the cation detector represents the v_x component of each neutral NO radical, and that the transit distance d_x is identical (within 5%) for all NO radicals, we can extract the transit time

$$t_x(i) = \frac{d_x}{v_x(i)} = \frac{d_x}{\left[\frac{\Delta x(i)}{\text{ToF}(i)} \right]} \quad (25)$$

for each NO coincidence i . We then create an improved, event-by-event version of eq. 24 as

$$t_{\text{corr}}(i) = t_{\text{raw}}(i) - t_x(i) \quad (26)$$

for each event i , where we have neglected $\langle \text{ToF}_e \rangle$.

The event-by-event corrected coincidences, $G_{\text{NO}}(t_{\text{corr}})$, are shown as the red data points in Fig. 5C, with the red line showing the fit of eq. 23 to this corrected data. As expected, the parameter $t_0 = \langle t_d \rangle$ returned by the fit is now $0 \pm 1 \mu\text{s}$, reflecting the fact that the corrected coincidences have the transit time delay removed. Furthermore, the broadening (or blurring) of the time trace due to the non-negligible spread in neutral velocities (see feature γ in Fig. 2C and E) has been reduced by a factor of 3.5, to a FWHM of $b = 7 \pm 4$

μs . This value, which is the rise time of NO from photodissociation in Fig. 5C (red points), represents our best kinetic time resolution. However, we note that even this value may be an upper limit because the data are binned in $5\ \mu\text{s}$ time bins, and one cannot expect to evaluate kinetic time resolution more finely than the binning size. Although we could bin more finely, this dataset’s S/N would not support finer binning. We note that the transit-time corrected data yields a bimolecular time constant τ that is unchanged within error, which is expected because, even in the uncorrected data of Fig. 5B, τ is more than six times larger than the Gaussian broadening due to the NO v_x speed distribution.

As a final test, Fig. 5D shows a dataset acquired with four times larger $[\text{NO}_2]$. The poorer S/N of this dataset (due to shorter acquisition time) forces us to use a coarser time binning of $10\ \mu\text{s}$. Taking into account the $4\times$ larger $[\text{NO}_2]$, we fix τ at its expected value of $39\ \mu\text{s}$ and fit only the t_0 and the Gaussian FWHM. The transit-time corrected data (red) provides a FWHM value for Gaussian blurring ($b = 9 \pm 12\ \mu\text{s}$) consistent to the previous dataset, albeit with reduced precision. The randomly scattered residuals show that the NO rise due to the now-faster bimolecular reaction is again consistent with the literature rate coefficient, providing evidence this instrument can measure pseudo-first order rate coefficients as fast as $25,000\ \text{s}^{-1}$. We note that the alignment of the excimer laser beam path to the reactor tube must be carefully optimized to achieve the best time resolution, which is ca. 2 orders of magnitude faster than the $\approx 400\ \mu\text{s}$ time resolution typical of the Multiplexed Photoionization Mass Spectrometer.²³

3.7 Dispersive, threshold, and slow photoelectron spectroscopy

As discussed by Fischer and Pratt,⁶ there are multiple ways to measure the photoelectron spectrum of a molecule, but all methods are based on two fundamental approaches. A dispersive PES is recorded using a fixed VUV photon energy, generally well above the ionization energy of the molecule, with the photoelectron spectrum constructed by analyzing the kinetic energies of the ejected electrons. By contrast, a threshold photoelectron spectrum

(TPES) requires a tunable source of VUV, and is recorded by scanning the photon energy while collecting only electrons with zero (or near-zero) kinetic energy. This approach yields a peak in the TPES as each energy level of the cation (electronic, vibrational, rotational, etc.) becomes energetically accessible with increasing photon energy. Dispersive PES instruments have the advantage that they can operate with fixed-frequency light sources and the angular distribution of the photoelectrons can yield information about the photoionization dynamics. TPES offers the possibility of much higher energy resolution, which in some instruments is limited only by the bandwidth of the light source but requires the complexity of a tunable light source. This tunable excitation of the neutral allows one to explore how resonant excited states of the neutral (Rydberg states, shape resonances) couple to the final cation and outgoing electron, as well. With TPES, there is generally no access to electron angular distributions, and most of the electrons produced when above the ionization threshold are ignored due to their non-zero kinetic energies, leaving precious signal unutilized.

The advent of velocity-map imaging enabled a third option that combines attractive aspects of dispersive PES and TPES. First demonstrated in the negative ion community by Neumark and co-workers,²⁹ the variant for neutral photoionization demonstrated by Pouilly et al. is called slow photoelectron spectroscopy (SPES).³⁰ In SPES a photoelectron velocity map image is acquired at each photon energy in a scan, with the image inverted to give the dispersive PES at each photon energy. The result is a 2D matrix of electron kinetic energy versus photon energy. The SPES is generated by integrating this dataset over a range of electron kinetic energies (from 0 to eKE_{max}). The advantage of SPES over TPES is that, by including a range of energetic electrons, a better signal to noise ratio is obtained with negligible degradation of energy resolution, especially in molecular cases where the resolution may be limited by rotational structure of the molecule rather than the spectrometer or the light source. One potential drawback of SPES is the image inversion step. Many inversion methods propagate noise from large radii in the image, where higher kinetic energy electrons are detected, to the center, where threshold electrons are detected. This extra noise would

degrade S/N of the low kinetic energy electrons in SPES spectra but is not present in TPES spectra (because image inversion is not needed). However, we use the MELEXIR maximum entropy reconstruction algorithm which does not suffer from this limitation.³¹ We conclude that in most cases the choice of SPES with a reasonable integration boundary is advantageous over TPES due to improved S/N without reduction in resolution.

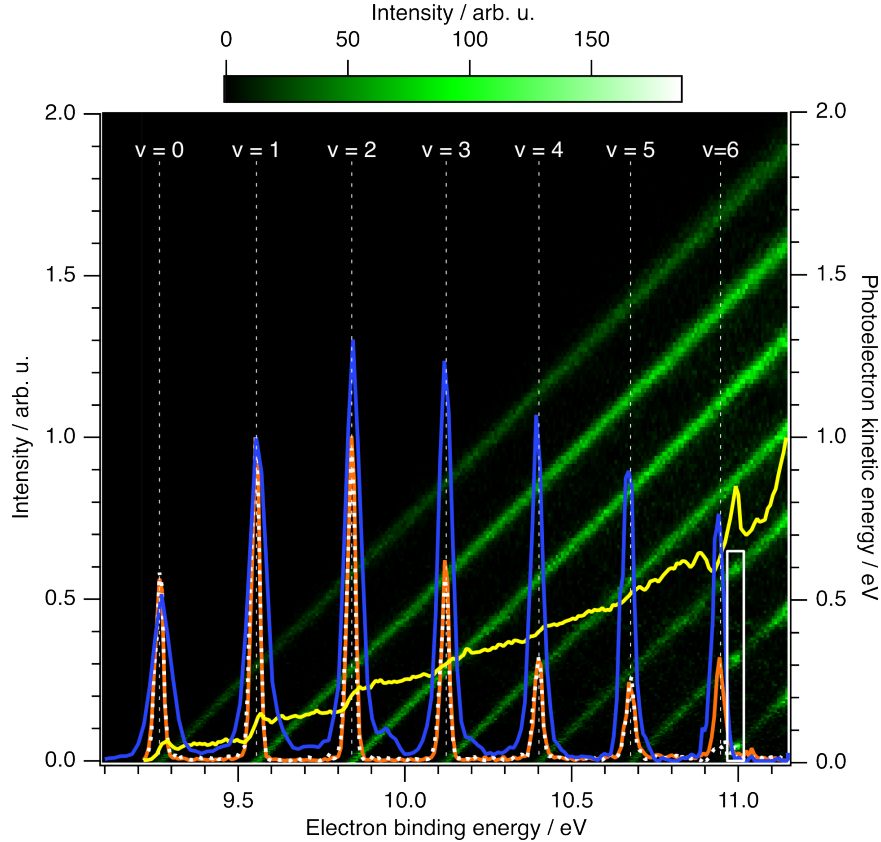


Figure 6: Photoelectron and photoionization spectra of nitric oxide. The dispersive photoelectron spectrum (**blue solid line**) is acquired at $h\nu = 11.144$ eV. The other spectra are acquired in a single photon energy scan (equivalently electron binding energy) from 9.216 to 11.144 eV in 8 meV steps. The background shows a 2D plot of photoelectron kinetic energy (columns, right ordinate) vs. photon energy. An autoionizing resonance (**white box**) is highlighted. The photon energy scan produces the SPES (**white dotted line**) for $eKE < 0.01$ eV, SPES (**orange solid line** plotted underneath the white dotted line) for $eKE < 0.1$ eV, and photoionization spectrum (**yellow solid line**).

Using NO as a test case, we explore these various modes of data acquisition in Fig. 6, flowing 0.25% NO in He through the reactor tube at a pressure of 8 torr. We first recorded a single dispersive photoelectron spectrum at a fixed photon energy of 11.144 eV. Our method

for image inversion and calibration of the electron kinetic energy is described in supporting information (Figs. S7 – S9). This dispersive PES is shown in blue in Fig. 6. We then acquired data by scanning the photon energy from 9.216 to 11.144 eV with a step size of 8 meV. The yellow curve is the photoionization (PI) spectrum, which is the number of coincidences of electrons with m/z 29.998 cations vs. photon energy. The same PI spectrum could be obtained on a photoionization spectrometer such as the MPIMS instrument³² by plotting NO^+ ion signal vs. photon energy. With a pure NO sample, the PI spectrum is equivalent to the total electron yield from a photoelectron spectrometer.

The background of the figure plots the 2-D matrix of photoelectron kinetic energy versus electron binding energy (or photon energy). Each vibrational quantum state of NO^+ gives rise to a diagonal line on this plot. For this reason SPES can be understood as a multiplexed version of constant ion state (CIS) spectroscopy, in which the contributions of multiple final ion states may be monitored simultaneously rather than sequentially.⁶ Integrating along these diagonal lines up to a cutoff photoelectron kinetic energy of 0.01 eV (0.1 eV) yields the SPES, given in the yellow dotted line (orange solid line) traces. To accomplish this integration we shift each pixel row to the left by the photoelectron kinetic energy of that row, and sum over all rows below the cutoff kinetic energy, analogous to the procedure outlined by Pouilly et al.³⁰ All traces except the PI spectrum were normalized to 1 at the $v = 1$ peak. The TPES spectrum is essentially identical to the SPES spectrum with the cutoff at 10 meV and was omitted from the figure for clarity. From our SPES data we extract $\text{AIE}(\text{NO}) = 9.264$ eV, in good agreement with the literature value of 9.26431 ± 0.00005 eV.³³ We note this agreement with the literature and our measurement of $\text{AIE}(\text{acetaldehyde})$ *vide infra* confirms the accuracy of the ALS beamline 9.0.2.3 monochromator when calibrated to a single reference energy at 12.5752 eV.

The vibrational branching ratios (from the area under the curve of each peak) in the fixed frequency PES does not match the SPES. As discussed by Southworth et al.,³⁴ the vibrational branching ratios in the photoelectron spectrum of NO acquired at photon energies

above 18 eV agree with calculated Franck–Condon Factors.³⁵ However, for photon energies from 11–18 eV, the branching ratios and the angular distributions of photoelectrons vary significantly with photon energy due to a σ shape resonance or the effects of interchannel coupling mechanisms. For this reason, we do not expect the dispersive PES and SPES/TPES peak areas (or heights) to agree quantitatively.

Both SPES traces are essentially identical to each other and to the threshold photoelectron spectrum except for the peak corresponding to the $v = 6$ vibrational level of the cation. Here, the peak in the 0.1 eV kinetic energy cutoff SPES is significantly larger than for the TPES or the 0.01 eV SPES. The reason for this enhancement can be understood from the 2-D photoelectron kinetic energy matrix (background of Fig. 6). If one follows the diagonal signal of the $v = 4$ to $v = 6$ states up to 11 eV binding energy one sees a peak in the intensity on each of these signal lines (marked with a white box in the figure). These intensity peaks are due to an autoionizing resonance^{36,37} that increases the absorption cross section and also the ionization yield. The autoionizing resonance also gives rise to a sharp peak in the photoionization spectrum at the same energy. For the SPES including $eKE < 0.1$ eV, the autoionization contributes to the $v = 6$ signal, whereas this contribution is missing when the limit $eKE < 0.01$ eV is chosen. These comparisons are a reminder that calculated photoelectron spectra intensities based on Franck–Condon factors may not correspond to either dispersive or SPES/TPES spectra when processes other than direct ionization to the continuum are operative. Such differences in photoelectron peak intensities in truly non-resonant excitation photoelectron spectra vs. resonantly excited photoelectron spectra have been discussed in detail.³⁸

Comparing the PI with the PE spectrum, we see steps in the PI spectrum at the photon energies that correspond to vibrational energies of NO^+ . In the case of NO these steps are well pronounced for the low cation vibrational states up to $v = 2$ but are much more subtle for the higher vibrational quantum states. Photoelectron spectra are usually more feature rich than PI spectra when moderate bandwidth VUV radiation (e.g., 10 meV) is used for

excitation. In this case, PI spectra often rise smoothly with increasing photon energy with few features. Significantly narrower bandwidth VUV radiation, available from laser-based VUV sources, usually resolve more features in PI spectra, such as Rydberg series converging to each rotational and vibrational level of the cation. For moderate VUV bandwidths used here, we find that the combination of PI and SPES spectra, both available from a single photon energy scan, provide the most definitive spectral fingerprints for isomer resolved studies.

Another noteworthy point: although single frequency PES and SPES/TPES may not agree in the intensity distribution, they agree in peak positions, barring resonant ionization process as explored in detail by Guyon’s pioneering work.³⁹ Because photon energy scans take a considerable amount of time, especially if one needs to signal average at each photon energy to obtain sufficient signal-to-noise for kinetic time profiles, it is often advantageous to do a single frequency experiment and use the available beam time for signal averaging. This is especially true if the highest kinetic energy resolution is not required. More complex questions revealed by the fixed frequency dataset may then be explored with a dataset taken over an informed choice of photon energies that yields time-resolved SPES spectra of all the species in the reacting mixture.

3.8 Isomer quantification via photoelectron spectroscopy

Photoionization mass spectrometry has a proven history of quantitative analysis of chemically reacting systems, including isomer branching fractions of neutrals that appear at the same m/z in a mass spectrum.¹⁷ Quantification relies on the measurement of absolute photoionization cross sections, tabulated in databases,⁴⁰ that are used to convert measured signals into concentrations according to

$$G = \Lambda \alpha_M \sigma C, \tag{27}$$

where G is signal intensity, σ is photoionization cross section, C is concentration, and α_M is the relative mass discrimination factor that is often empirically described by a power function of m/z (see Supporting Information). Λ represents a mass-independent proportionality constant. A linear combination of absolute PI spectra, used as basis functions, are fit to the unknown PI spectra at each m/z ratio, with the fit coefficients providing the fractional abundances.

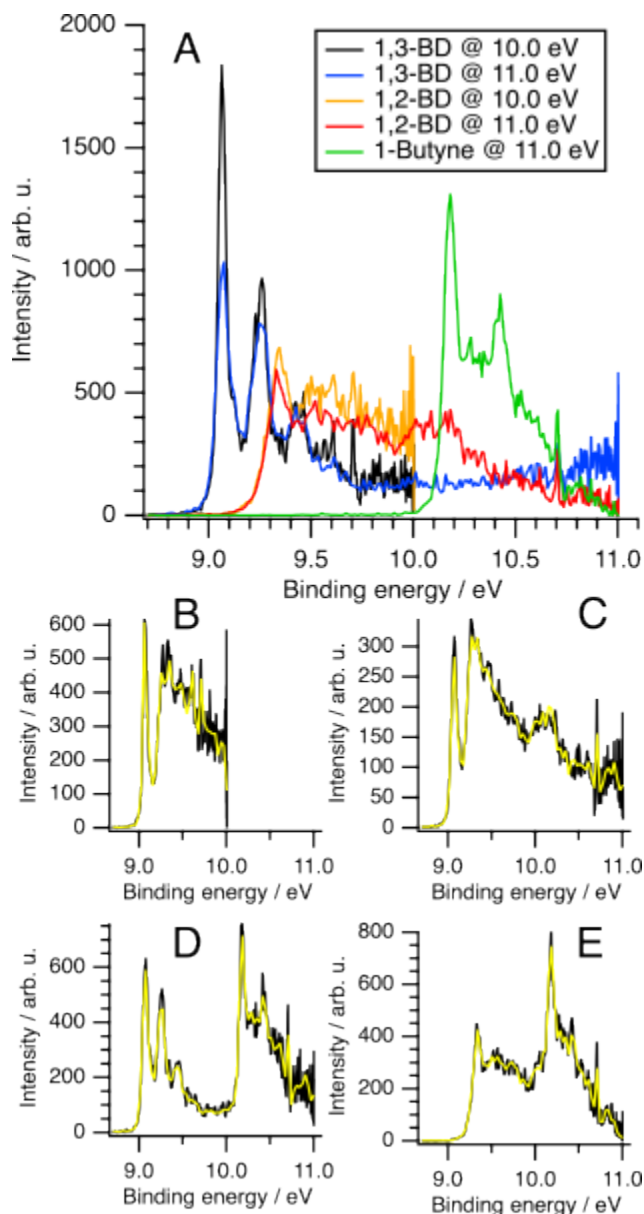


Figure 7: **A** Dispersive photoelectron spectra of pure C_4H_6 isomers at 10.0 and 11.0 eV. **B-E** (black) Photoelectron spectra of various mixes of multiple isomers of C_4H_6 . (yellow) Fit of linear combination of pure isomer spectra. **B** Mixing ratio 1,2-BD : 1,3-BD = 2.336 at 10.0 eV. **C** Mixing ratio 1,2-BD : 1,3-BD = 1.502 at 11.0 eV. **D** Mixing ratio 1,3-BD : 1-Butyne = 2.499 at 11.0 eV. **E** Mixing ratio 1,2-BD : 1-Butyne = 5.004 at 11.0 eV.

As demonstrated in the previous section, one clear advantage of PEPICO spectroscopy for reaction studies over PI spectroscopy is the feature richness of photoelectron spectra. The same approach to quantitative analysis as with PI spectra may be used with PEPICO-derived photoelectron spectra, but because vibrational branching ratios in PES may depend

on the photon energy, as discussed in the previous section, the choice of PES basis functions must be made with care. The simplest approach is to use fixed-frequency dispersive photoelectron reference spectra acquired at the same photon energy used in probing the unknown chemical reaction. In this case, the integrated area of each isomer’s photoelectron spectrum is proportional to that isomer’s absolute PI cross section at this photon energy.

To demonstrate this capability using our PEPICO instrument, we prepared several mixtures of three different C_4H_6 (m/z 54.047) isomers, namely 1,3-butadiene (1,3-BD), 1,2-butadiene (1,2-BD), and 1-butyne. We measured the dispersive PES for each pure compound at 10.0 and 11.0 eV photon energies to provide basis function spectra, as shown in Fig. 7A. We then recorded the PES of the mixtures of isomers at the same two photon energies in Fig. 7B-E. The PES of the m/z 54 isomer mixtures are well fit by linear combinations of the pure PES basis functions. The prepared mole fractions and the ones recovered from the fit are given in Table 2 and are within an error of $\pm 3\%$. This result confirms that we can use this instrument to quantitatively study kinetics of isomers that cannot easily be distinguished by other methods. However, one caveat is that isomerically pure samples of known concentration need to be available for recording reference photoelectron spectra. For the case of reactive species, such as free radicals, such isomerically pure samples must be created *in situ*, which, although challenging, has been done many times with MPIMS^{41–43} and recently with PEPICO.⁴⁴

Table 2: C_4H_6 isomer experimental and recovered mixing ratios.

Photon Energy	Species	Mole Fraction	Mole Fraction from Fit	Error
11 eV	1,3-BD	0.3997	0.3883	−2.95%
	1,2-BD	0.6003	0.6117	+1.87%
10 eV	1,3-BD	0.2998	0.3070	+2.34%
	1,2-BD	0.7002	0.6930	−1.04%
11 eV	1,3-BD	0.7142	0.7101	−0.58%
	1-Butyne	0.2858	0.2899	+1.43%
11 eV	1,2-BD	0.8334	0.8357	+0.27%
	1-Butyne	0.1666	0.1643	−1.37%

TPES or SPES spectra of pure species may also be used as basis functions for quantitative

fits to unknown reaction mixtures. However, due to the possibility that vibrational branching ratios depend on the photon energy, in this case the photon energy scan range, and ideally the spectral point spacing, should be identical between reference and unknown spectra. These issues complicate the development of quantitative databases for PES spectra, although at least one such database exists.⁴⁵

One final point relates to quantification of species probed at different m/z ratios. In this case one must account for the different instrument sensitivity for detection as a function of m/z ratio. We call this quantity the mass discrimination factor, which is denoted α_M in eq. 27 and is described in more detail in Supporting Information. This sensitivity is seldom uniform in any instrument, and must be calibrated. We acquire the mass discrimination factor by ionizing a reference mixture containing known mole fractions of H_2 , Ar, Kr, and Xe at 16.85 eV, where the PI cross sections are known with high accuracy. The mass discrimination factor depends on the nature of the gas expansion, and hence could depend on total pressure, temperature, and gas composition in the reactor. We provide an example of mass discrimination factor determination in the Supporting Information.

3.9 Unexpected results from universal, multiplexed detection

A major advantage of universal, highly multiplexed experiments such as this time-resolved PEPICO spectrometer is that they may reveal unexpected chemical product channels. Conversely, a danger with diagnostics that are sensitive to only a limited set of species, such as laser-induced fluorescence (LIF), is that one will only observe the species one chooses to interrogate, and for LIF the possible outcomes are limited to only those species that fluoresce after excitation. To demonstrate the usefulness of coincidence detection in gas phase reaction experiments we present preliminary results of the photodissociation of methanol.

A mixture of 0.725% CH_3OH in He flowed through a borosilicate reactor at 10 torr and CH_3OH was photodissociated with 193 nm laser pulses ($43 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$). The products were ionized at 10.409 eV. The details of this experiment will be reported in a separate paper.

Here, we highlight an unexpected product at m/z 44.03. The photoion mass-selected PES (ms-PES) is given in Fig. 8 together with reference PES of acetaldehyde and vinyl alcohol. Both C_2H_4O isomers are clearly present following methanol photodissociation. We observe a peak for acetaldehyde at 10.229 eV binding energy with a FWHM of 0.028 eV, in excellent agreement with the reference PES and adiabatic ionization energy (AIE) of acetaldehyde (10.228 ± 0.002 eV) determined by Yenchu et al.⁴⁶ The reference PES for vinyl alcohol from Matti et al.⁴⁷ agrees well with our data after being blue-shifted by 50 meV. We required a similar energy offset between the PES from Matti et al. and PI spectra of vinyl alcohol recorded on the MPIMS instrument,⁴⁸ which we attributed to an error in energy calibration of Matti et al. However that determination was based on the comparison of PES to PI spectra, rather comparing spectra of the same type.

By contrast, Fig. 8 shows a single, dispersive ms-PES containing both C_2H_4O isomers. We calibrate the position to kinetic energy conversion of our electron detector using Xe (see Figs. S8 – S9) with accuracy of 5 meV across the electron detector. The AIE of acetaldehyde is accurately retrieved from our spectrum, which also confirms the accuracy of the VUV photon energy. As a result, we expect similar accuracy for the vinyl alcohol binding energies because both isomers are present in the same spectrum, which is further confirmation of an energy calibration error in the Matti et al. data. Clearly, the acetaldehyde and vinyl alcohol isomers arise from bimolecular chemical reactions because methanol contains only one carbon atom. The time traces of these species (not shown) have risetimes of 1 - 3 ms depending on the methanol concentration. These time traces will help identify the pathways of the bimolecular chemistry that forms acetaldehyde and vinyl alcohol in a future publication.

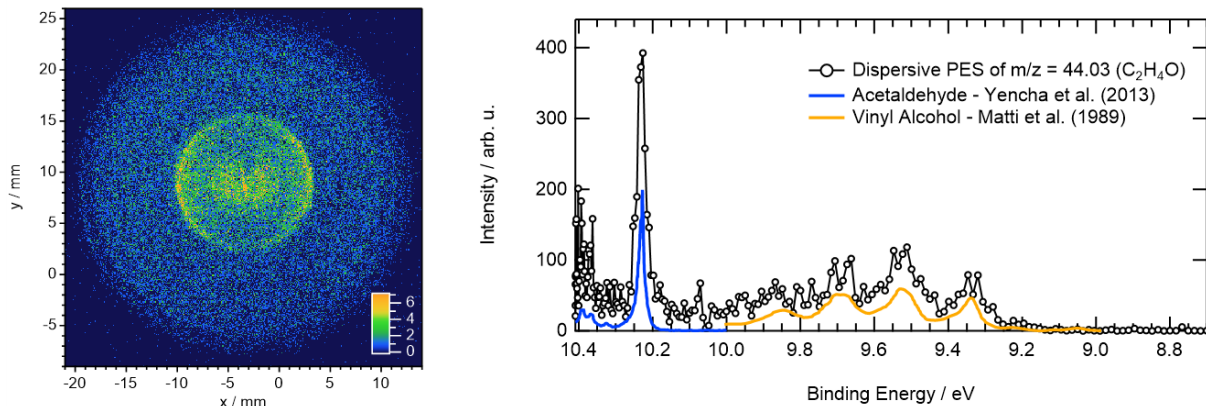


Figure 8: Dispersive photoelectron image (left) and ms-PES (right, open circles) of m/z 44 from methanol photodissociation at 193 nm ionized at $h\nu = 10.409$ eV. Reference photoelectron spectra for acetaldehyde⁴⁶ (blue) and vinyl alcohol⁴⁷ (orange, 40 meV blue-shifted) are overlaid for comparison.

4 Conclusions

This work and our previous publication¹ demonstrate the value of time-resolved i^2 PEPICO spectroscopy to explore multi-channel chemical reactions and reaction sequences with isomeric selectivity. Here we provide insights to the design and function of such instruments that extend and clarify previous work. The velocity map imaging capabilities of the instrument reveal viscous flow in molecular beam expansions from side-sampled reactor tubes at pressures of 2–10 torr. Cation imaging allows one to restrict datasets to include only those species in the molecular beam expansion, eliminating signals from background and reflected gases. We quantify the mass spectral peak shapes and mass resolution, with effective translational temperatures of < 2 K along the time-of-flight axis, as determined by the sampling geometry and corresponding to a mass resolution of at least 3000 for reactor tube studies. Mass resolution of this magnitude can distinguish isobaric species (e.g., O vs. CH_4) by m/z alone. Furthermore, cation imaging allows the experimentalist to trade signal for increased mass resolution as needed in post-processing. Interestingly, the mass spectral calibration procedure allows one to extract the average electron flight time, although at present, retrieval

of the full 3-D velocity vector of each photoelectron is unattainable.

We present a comprehensive discussion of collection efficiencies in PEPICO including a practical example of their evaluation. Collection efficiencies are useful to assess instrument performance and inform decisions on detector maintenance. Considering both true and false coincidences, we evaluate contributions of shot noise and false coincidence noise to the signal-to-noise and dynamic range of a PEPICO experiment. The S/N of major peaks will always be determined by shot noise, whereas for the smallest peaks, at the limit of dynamic range, false coincidence noise will dominate. We show that narrow mass spectral peaks resulting from high mass resolution are one of the best ways to improve dynamic range in PEPICO.

We evaluate the temporal instrument response of the instrument, showing that it is delayed by transit from the expansion orifice to the VUV beam, and broadened by the spread of neutral velocities in the expansion. Leveraging the power of cation velocity map imaging, the transit time delay may be eliminated and the broadening of the temporal response reduced by a factor of 3.5 by correcting the transit time on an event-by-event basis. The resulting temporal resolution is $7\ \mu\text{s}$, and even this value may be an upper bound, limited by S/N in the present experiments that prevents finer time binning of the coincidences.

We compare dispersive photoelectron spectra taken with fixed-frequency VUV radiation to threshold and slow photoelectron spectroscopies, considering the relative advantages of each approach. For an instrument with high-quality electron imaging, we conclude that slow photoelectron spectroscopy can provide the same electron kinetic energy resolution as threshold PES but with improved S/N . Finally we demonstrate that PEPICO spectroscopy may be used for quantitative analysis of isomer distributions with mole fraction accuracy of a few percent. Universal detection approaches such as i^2 PEPICO increase the chance that unexpected outcomes of a chemical reaction will be detected, as we demonstrate with the observation of the acetaldehyde and vinyl alcohol isomers of $\text{C}_2\text{H}_4\text{O}$ following the photodissociation of CH_3OH in a collisional environment. Finally, we found that light baffling along the incoming VUV path coupled with a nanostructured carbon coating on the central

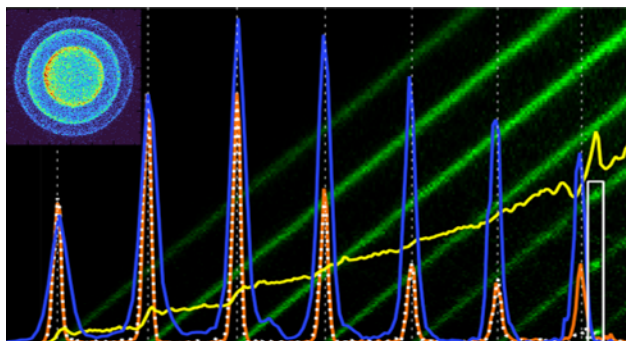
charged particle optics can significantly reduce the background electron signal from stray VUV photons impacting metal surfaces. The ratio of electron count rate to VUV flux (measured by a photodiode in our case) is a useful metric to monitor during modifications and alignment to reduce background electrons.

5 Associated Content

Supporting Information Available

Mass calibration fits determining electron time-of-flight, Mass spectral peak shapes vs. neutral velocity and reactor pressure, simulations of mass spectral peak shapes, signal linearity, inversion methods for photoelectron velocity map images, energy calibration of the electron detector, mass discrimination factors, background electrons and their reduction.

TOC Graphic



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6.1 Notes

The authors declare no competing financial interest.

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