

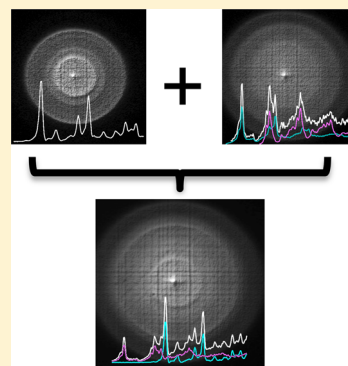
Mass-Resolved Isomer-Selective Chemical Analysis with Imaging Photoelectron Photoion Coincidence Spectroscopy

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S Supporting Information

ABSTRACT: Photoionization mass spectrometry is a powerful method for time- and space-resolved chemical analysis of reactants, intermediates, and products. Tunable synchrotron light enables isomer separation based on unique photoionization spectra; however, mixtures of three or more isomers can be difficult to resolve by this method. In this work we demonstrate, by measuring the photoelectron spectrum corresponding to each cation m/z ratio, that imaging photoelectron photoion coincidence spectroscopy provides a more detailed spectral fingerprint than photoionization spectra. This method offers increased selectivity for analyzing gas-phase mixtures of many components. Mixtures of two C_4H_6 and four C_5H_8 unsaturated hydrocarbons were analyzed, and the components could easily be identified based on mass-selected threshold photoelectron spectra (scanning the photon energy) or photoelectron velocity map images (PEVMIs) at a single or a few fixed photon energies. The PEVMI approach is more highly multiplexed, trading somewhat lower spectral resolution for faster data acquisition and photoelectron angular distributions.

SECTION: Spectroscopy, Photochemistry, and Excited States



A long-standing challenge in experimental gas-phase physical chemistry is to find a universal, multiplexed, sensitive, and selective detection method for neutral molecules that interrogates chemical reactions with high fidelity. Photoionization mass spectrometry (PIMS) meets these requirements. Molecular species, stable or unstable, can all be ionized, hence it is universal; with time-of-flight detection, a wide range of masses can be detected simultaneously, giving a multiplex advantage; with single-ion counting against a near-zero background, it is highly sensitive, and, with mass-to-charge selection, it is inherently selective.¹ PIMS offers further significant advantages: fragmentation can be controlled by tuning the photon energy, and isomers with different ionization energies can be distinguished by their photoionization (photon) spectra (ion intensity vs PI energy).

An example of such an experiment is the multiplexed chemical kinetic photoionization mass spectrometer (MPIMS) operating at the Chemical Dynamics Beamline of the Advanced Light Source at Lawrence Berkeley National Laboratory.¹ In addition to combustion studies,² this instrument enabled discoveries in terpene oxidation,³ Criegee intermediates and their reactions,^{4,5} and the chemistry of Titan, Saturn's largest moon.⁶ PIMS is also a powerful tool for analysis of flame chemistry and structure. For example, another apparatus at the ALS was used to measure the concentration versus height-above-burner of combustion intermediates in flames of modern fuel blends.⁷ Still, many reactions would benefit from enhanced selectivity in chemical detection. Specifically, it can be challenging to identify isomers and their mole fractions from

PI spectra when three or more are present at one mass-to-charge (m/z) ratio or when two have similar ionization energies.

In this work, we present imaging photoelectron photoion coincidence spectroscopy (iPEPICO) as a new approach that significantly increases the selectivity of PIMS while maintaining or even increasing the multiplex advantages of the MPIMS approach. We briefly review the PEPICO technique in the context of other techniques, present preliminary data on analysis of chemical mixtures of stable compounds, and discuss the advantages and disadvantages of this new application for PEPICO spectroscopy.

Photoelectron spectroscopy (PES) analyzes the photoelectron intensity as a function of electron binding energy. In the absence of resonances, the PI spectrum is essentially the integral of the photoelectron spectrum. PES offers greater selectivity than PI spectroscopy because transitions to final cation states appear as sharp peaks in PES but only as changes in the slope in a PI spectrum. This difference aids PES in the identification of each neutral molecule in a mixture.⁸ However, with a few exceptions,^{9,10} PES is rarely used to quantitatively analyze mixtures of neutral molecules because there is no unique way to correlate a given electron with the neutral that produced it if only electrons are detected.

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In contrast with PES, PEPICO spectroscopy extracts both the photoelectron *and* the photoion from the ionization region. The detection of a kinetic energy-selected electron marks the beginning of a time window (typically 5–50 μ s) to detect the corresponding cation by measuring its time-of-flight and hence its mass. The kinetic-energy distribution of the electrons detected in coincidence with a particular m/z cation creates a mass-resolved photoelectron spectrum (ms-PES). In threshold PEPICO (TPEPICO), photoions are collected in coincidence with only the near-zero kinetic energy electrons, using tunable photon energies.¹¹ In this case, the TPEPICO data provides mass-selected threshold photoelectron spectra (ms-TPES) for each m/z ratio.

If the ionization rate is low (e. g., most laboratory light sources), then the electron/ion pairs are well-separated in time and the ion detected within a suitable time-of-flight window after the electron very likely comes from the same neutral precursor molecule. Such an event is termed a *true* coincidence. A *false* coincidence denotes an electron/ion pair that did not arise from the same neutral molecule. Because of this, electron-ion coincidence experiments traditionally required low count rates to suppress the probability of false coincidences and to avoid signal paralysis. When count rates exceed the reciprocal of the coincidence time window, false coincidences make ever-increasing contributions to the data, affecting detection efficiency and signal-to-noise ratio. This problem explains why (T-)PEPICO has not been explored as a method for chemical analysis, where high total count rates are often required to enable detection of products with small mole fractions in a mixture.

A few years ago, we introduced a highly multiplexed coincidence detection technique, called multistart–multistop (MSMS) detection, on the Swiss Light Source iPEPICO experiment, which circumvented signal paralysis up to count rates of 10^6 s⁻¹.¹² With this technique, the false coincidence background is constant (with Poisson noise) throughout the time-of-flight spectrum. Furthermore, the false coincidence rate increases quadratically with the ionization rate, whereas the noise on the false coincidence background increases linearly, just as the true signal. Thus, the S/N ratio is independent of the ionization rate using the MSMS coincidence detection scheme.¹²

A decade ago, one of us took part in introducing photoelectron velocity map imaging (VMI) to PEPICO, enabling a broad range of electron kinetic energies to be analyzed simultaneously and to remove contributions of energetic electrons in TPEPICO while maintaining high collection efficiencies for threshold electrons.¹³ These two advances allow for the full utilization of intense synchrotron VUV sources that produce high electron/cation count rates, significantly increasing data throughput and signal-to-noise ratio in PEPICO experiments and providing near-unity duty cycle.^{12,14} These breakthroughs have generated renewed interest in PEPICO, and several new experiments have been recently built at synchrotron light sources.^{14–21} However, with the exception of a handful of pioneering experiments on free radicals,^{22–24} PEPICO has mostly been applied to pure samples of stable species. The main goal of the experiments presented here is to test the concept of imaging PEPICO as a powerful new method for mass- and isomer-selective analysis of chemical mixtures, applicable to transient species.

The experiments use the imaging photoelectron photoion coincidence (iPEPICO) endstation¹⁴ at the vacuum ultraviolet

(VUV) X04DB bending magnet beamline²⁵ of the Swiss Light Source. In brief, this apparatus features better than 1 meV electron kinetic energy resolution at threshold by VMI of the photoelectrons, detected with a Roentdek DLD40 detector; tunable synchrotron radiation in the 5–30 eV photon energy range; and a triggerless MSMS coincidence data acquisition technique.

Cyclopentene, isoprene, 1-pentyne, 1,4-pentadiene, and 2-butyne were purchased from Sigma–Aldrich as pure samples (99% purity, except for cyclopentene, 96%), while 1,3-butadiene was used as a 20 wt % solution in toluene. The pure samples and the mixtures were introduced into the experimental chamber at room temperature through an effusive inlet source. The photon energy was calibrated to Ar and Ne autoionization lines.

Imaging PEPICO (iPEPICO) spectroscopy uses a position-sensitive electron detector for multiplexed electron kinetic energy analysis by VMI and correction for hot electrons in ms-TPES spectra. With this technique, (mass-selected) threshold photoelectron spectra were collected in 4 meV photon energy steps for the pure samples and two mixtures: one of 2-butyne and 1,3-butadiene and one of all six C₄H₆ and C₅H₈ compounds. The raw data from the threshold photoionization iPEPICO experiment contain two types of spectra: both the threshold photoelectron spectrum (TPES), that is, the total threshold photoelectron signal (with no correlation to which neutrals produced these electrons) as a function of the photon energy, and the ms-TPES, that is, the coincidence events between threshold electrons and photoions within a selected time-of-flight (or m/z) window. Note that the TPES data do not equal the sum of all of the ms-TPES spectra because the TPES data are unaffected by the ion collection efficiency.

The TPES and the ms-TPES of the two mixtures are shown Figure 1a–c. Those of the pure compounds are shown in Figure S1 in the Supporting Information. The first mixture is composed of two C₄H₆ isomers, with roughly 95% 1,3-butadiene and 5% 2-butyne. Although the black traces in Figure 1a show that the simultaneously collected PI spectra can detect the presence of 2-butyne in this mixture, the peaks present in TPES spectra make the identification of 2-butyne much more definitive.

Figure 1b,c shows TPES of the more complex mixture containing two C₄H₆ and four C₅H₈ isomers. Coincident photoelectron/photoion pairs allow the separation of the TPES into the m/z = 54 and 68 ms-TPES, respectively and, in the m/z = 54 ms-TPES, both butadiene and butyne are easily identifiable. The m/z = 68 spectrum is more complex. The first, sharp feature coincides with the first peak in the isoprene TPES. Cyclopentene is also identifiable even though its origin transition is only separated by 40 meV from the second peak in the isoprene spectrum. The first peak in the 1,4-pentadiene TPES is clearly discernible near 9.6 eV in the ms-TPES of the mixture. Finally, the very strong first peak corresponding to 1-pentyne is identifiable at 10.08 eV.

Although the information content of the peaks in ms-TPES is clearly superior to the thresholds observed in PI spectra for the analysis of many-component mixtures in a mass- and isomer-selective manner, both methods share one downside: the need to scan the photon energy. Not only does this restrict experiments to tunable light sources, it also renders them less multiplexed. This limitation can be circumvented by analyzing the whole PEVMI obtained by iPEPICO, which contains, in our case, an \sim 0.8 eV wide section of the photoelectron

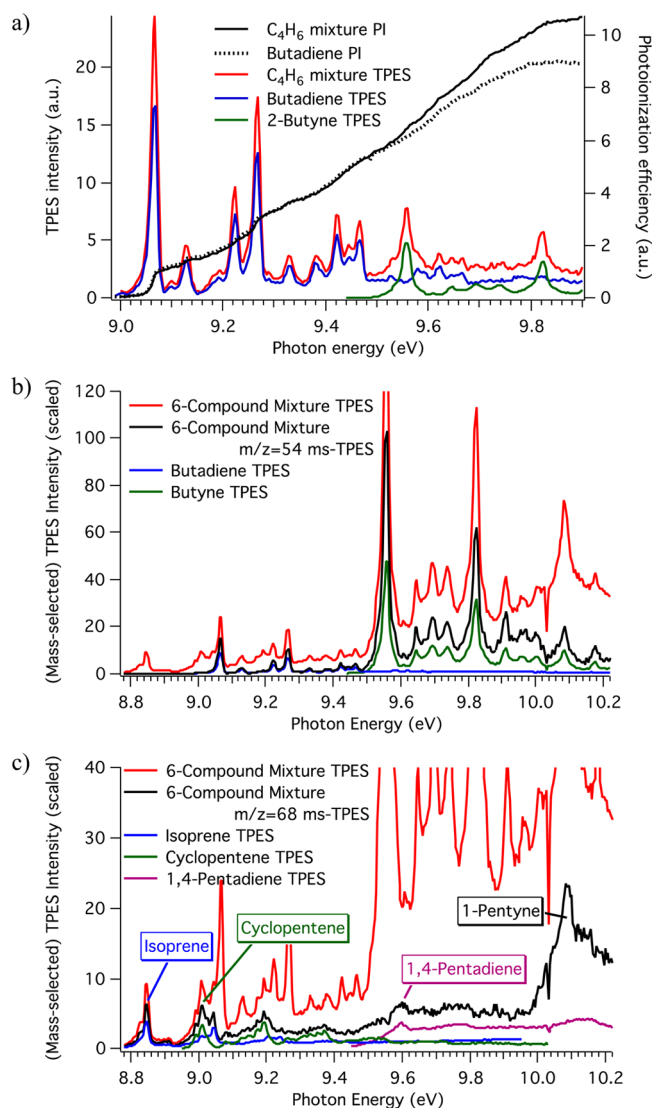
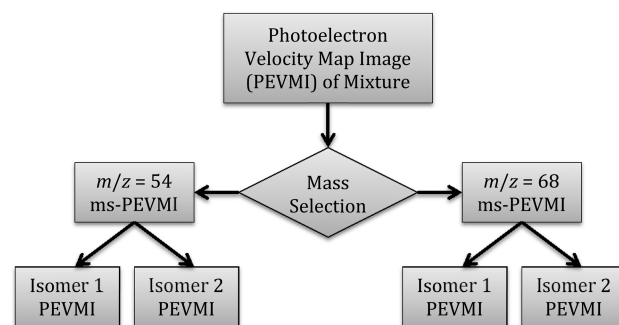


Figure 1. (a) Threshold photoelectron spectrum of the 1,3-butadiene and 2-butyne mixture shown along with the TPES of the individual compounds (scaled). Here the PI spectra of the mixture and of pure 1,3-butadiene are also shown for comparison. The latter are measured as the photoion signal in coincidence with electrons of any kinetic energy. (b) Total TPES, $m/z = 54$ ms-TPES of the six-compound mixture along with reference TPES of the two C_4H_6 isomers. (c) Total TPES, $m/z = 68$ ms-TPES of the same mixture along with reference TPES of some of the C_5H_8 isomers, showing features on the ms-TPES that are indicative of the four components.

spectrum and photoelectron angular distribution. Thus, in the second set of our proof-of-concept experiments, we have explored isomer identification by PEVMI analysis. Chart 1 shows how the photoelectron image can be used for mass- and isomer-selective identification by first decomposing the PEVMI into mass-selected photoelectron images (ms-PEVMI), keeping only the photoelectron events that are in coincidence with photoions of a single m/z . (Here the false-coincidence background may also need to be subtracted; for details, see a brief discussion and a visibly affected image in Figure S2 in the Supporting Information.) The ms-PEVMI is fit to a linear combination of the images of the pure compounds at the same photon energy. Small, random, and spatially uniform residuals between the observed ms-PEVMI from the mixture and the

Chart 1. Using the Full Photoelectron Velocity Map Image to Analyze a Complex Mixture



best-fit image serve as control that the decomposition into the constituent photoelectron images was successful and complete. It is important to emphasize that in the image analysis there is no need to use inverse Abel (or similar) transformations to reconstruct the 3-D kinetic energy distribution of the electrons, which would introduce significant noise into the reconstructed photoelectron images; rather, the “raw” 2-D photoelectron velocity images are directly used for chemical analysis.

PEVMIs were collected for the six-compound mixture at three photon energies: 9.160, 9.310, and 9.611 eV. In the first two images, isoprene, cyclopentene, and butadiene contribute, whereas the image at 9.611 eV also contains the first photoelectron peak of 2-butyne. To decompose the mixture PEVMI into single-species contributions, the PEVMIs of the individual components were recorded at the same photon energies. Figure 2a–c shows the image deconstruction process at $h\nu = 9.310$ eV. The PEVMI of the mixture, shown in Figure 2a, can be separated into mass-selected images, as shown in Figure 2b for $m/z = 54$ and 68. 2-Butyne does not ionize at this photon energy, and the PEVMI of pure butadiene (Figure 2b, left) fully reproduces the $m/z = 54$ ms-PEVMI. Isoprene and cyclopentene both contribute to the $m/z = 68$ ms-PEVMI, and a linear combination of their individual PEVMIs (in Figures 2b, right) was fit to the experimental data. The result in Figure 2c on the right shows very good agreement with the $m/z = 68$ ms-PEVMI with an rms deviation of 0.5% of the signal squared. When most ion peaks can be assigned to the known component PEVMIs, the total PEVMI can also be reconstructed, as shown in Figure 2c, bottom image.

Exploring dynamic range in detail is beyond the scope of this paper, but a preliminary analysis of detection limits has been performed nevertheless. The PEVMI shown in Figure 2a is based on 40 million electron counts and slightly more than 7 million coincidences taken in 1800 s of integration time. Under such circumstances, at close to 10^5 s $^{-1}$ ionization rate, true coincidences outnumber false ones by a factor of 20:1. However, because the false coincidences are distributed evenly across TOF, the S/N ratio, expressed in peak height over noise on the false coincidence background, is close to 17 000 for the $m/z = 54$ peak in the TOF spectrum. To establish detection limits, the decomposition and reconstruction were also carried out by decreasing the amount of experimental data for both the mixture and the pure sample PEVMI; details are given as Supporting Information.

In conclusion, imaging PEPICO shows great promise for quantitative, time- or space-resolved, isomer-resolved analysis of mixtures of gas-phase neutrals. Because final vibrational quantum states appear as peaks in mass-resolved photoelectron

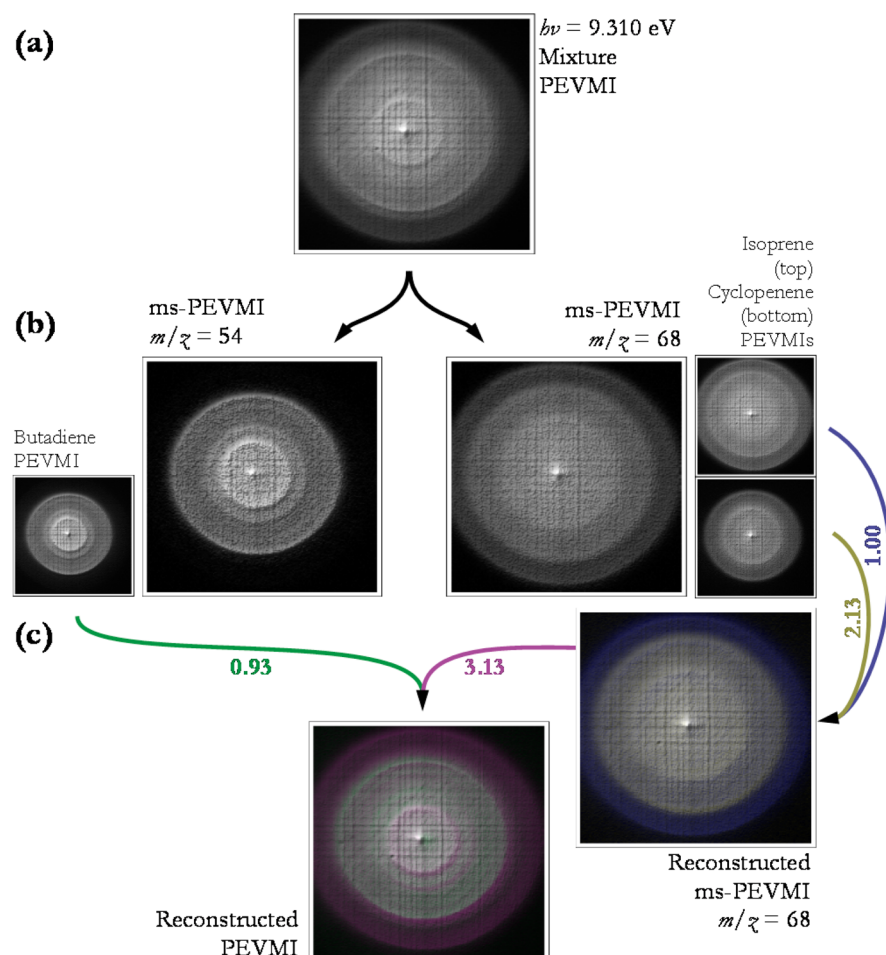


Figure 2. Mixture PEVMI in panel (a) can be separated into two ms-PEVMIs at $m/z = 54$ and 68 in panel (b), the latter of which corresponds to a mixture of isoprene and cyclopentene. The $m/z = 68$ ms-PEVMI is reconstructed based on the two pure sample PEVMIs in panel (c), and in linear combination with the butadiene PEVMI the total PEVMI is reproduced.

spectra rather than as steps seen in PI spectra, iPEPICO will provide higher selectivity than PI spectroscopy. ms-TPES, like PI spectroscopy, requires tunable photons, whereas PEVMI offers superior multiplexing, requiring only one or a few fixed VUV frequencies to cover the entire Franck–Condon envelope of the cation electronic states. Furthermore, in iPEPICO mode, the PI spectrum is also available from the raw data stream as the photoion signal in coincidence with photoelectrons of any kinetic energy, providing access to autoionizing resonance information. The possible downsides of iPEPICO versus PI mass spectrometry are (a) increased experimental complexity, (b) slightly lower (40%) signal level due to the additional requirement of photoelectron detection, and (c) limitations on dynamic range due to false coincidences. A proposed experimental approach to circumvent the latter disadvantage will be addressed in a subsequent publication.

By presenting these proof-of-concept results using iPEPICO to analyze complex mixtures, we hope to demonstrate the value of this method for the growing number of gas-phase time- and space-resolved chemical analysis experiments both at synchrotrons and in individual laboratories with fixed-frequency sources around the world.

■ ASSOCIATED CONTENT

● Supporting Information

Correction for hot electrons in TPES, the false coincidence background in ms-PEVMI, and the effect of measurement time on ms-PEVMI quality. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

[†]B.S.: On sabbatical at the Combustion Research Facility, Sandia National Laboratories.

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