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

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Supporting Information

Correction of hot electron contamination in mass-selected threshold photoelectron spectroscopy

Of the two PEPICO methods we discuss, mass-selected threshold photoelectron spectroscopy (ms-TPES), in which electrons with kinetic energy > 1 meV are discarded, achieves better electron kinetic energy resolution. Because the position-sensitive electron detector measures only a two-dimensional projection of the 3-D electron velocity distribution, electrons hitting the center of the detector comprise both threshold electrons and all energetic electrons with velocity vectors nearly perpendicular to the detector plane. The contribution of these "hot" electrons to the signal in the center of the detector must be removed to reveal the underlying threshold photoelectron signal. For each m/z ratio, the contribution of the hot electrons can be removed by subtracting a scaled portion of the coincident electron signal in an annulus around the center spot of the electron detector, revealing the true intensity of near-threshold electrons.1

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TPES of the individual C₄H₆ and C₅H₈ compounds

**Figure S1a–e:** Threshold photoelectron spectra (TPES) and mass-selected TPES (ms-TPES) (the latter is simply the photoelectron-photoion coincidence (PEPICO) signal) of two C₄H₆ and three C₅H₈ isomers. Because of beamtime limitations, the TPES of 1-pentyne was not recorded.
because its first, sharp peak is at the highest photon energy of our mixture measurements and is easily distinguishable from the other isomers.
False coincidence background

As mentioned in the manuscript, the false coincidence background in the multiple-start-multiple-stop coincidence detection technique is constant (with Poisson noise).\textsuperscript{2} Furthermore, if the ionization processes are dominated by the formation of a particular ion with a certain $m/z$, this ion will dominate the false coincidence signal in the other ms-PEVMIs, as well. Therefore, during the deconvolution of the PEVMI, the false-coincidence background may also need to be subtracted. By subtracting a false-coincidence-only electron image from a TOF window of identical width, the effect of false coincidences can be removed from the velocity map image as shown in Figure S2(a–e).

**Figure S2a–e:** Effect of false-coincidence background on the photoelectron velocity map images (PEVMIs). The PEVMI of a mixture containing all six C$_4$H$_6$ and C$_5$H$_8$ compounds at $h\nu = 9.611$ eV (a) is dominated by butyne (b), and the false coincidence background is evident in the $m/z = 68$ ms-PEVMI (c) and can be corrected to yield (d). This ms-PEVMI can then be fitted with the PEVMI of isoprene and cyclopentene to yield the reconstructed ms-PEVMI shown as (e).
Effect of measurement time on (ms-)PEVMI quality

To establish detection limits, the decomposition and reconstruction was also carried out by decreasing the amount of experimental data for both the mixture and the pure sample PEVMI. At an integration time of 14.4 s and 335 000 total counts, the image shown in Figure S3(b) could still be reconstructed with an error of 0.2% and yielding mixing coefficients less than 10% different from the original data. A reduction of 500, i.e. an integration time of 3.6 s and 85 000 total counts meant that the fine structure in the low count areas in the PEVMI was lost and the cyclopentene contribution (measured by a PES peak only 40 meV away from an intense peak in the butadiene spectrum) could not be established reliably from the ms-PEVMI. At an integration time of 1.8 s and 38 000 total counts, butadiene could still be resolved from the pentenes by mass selection (with a $S/N$ of >500) but, at 2700 electron counts in the ms-PEVMI, the signal level was insufficient for any isomer identification.

Figure S3a–d: Signal reduction of the 9.310 eV PEVMI of the 6-component mixture (a) by a factor of 125 (b), 500 (c), and 1000 (d). Image (b), corresponding to an integration time of 14.4 s, does not lead to significant information loss. At 3.6 s, in (c), the loss of fine structure means that the cyclopentene contribution cannot be established accurately, and at 1.4 s in (d), only approximate qualitative assignments are possible.

* Smaller datasets can be achieved post-measurement by trimming the experimental data files that are simply a long train of particle detection events with absolute timestamps (and, for electrons, x, y coordinates).
References