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What a (True) Coincidence!

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In Photoelectron Photoion Coincidence Spectroscopy (PEPICO), a gas-phase molecule is ionized by a vacuum-ultraviolet photon and both the photoelectron and the photoion from a single neutral molecule are detected in coincidence. In threshold PEPICO (TPEPICO), photoions are collected in coincidence with only the near-zero kinetic energy electrons and one slice of the TPEPICO data gives the mass-selected threshold photoelectron spectrum.

The continuous nature of the multiple-start-multiple-stop coincidence acquisition, utilized now at most PEPICO research centers, allows rapid data collection, maximizes the duty cycle and, since every coincidence event has an absolute timestamp, makes PEPICO well suited for kinetics experiments, as a selective detection technique.

Recently, the utility of PEPICO has been demonstrated as a universal, isomer-selective and sensitive analytical technique for time-resolved quantitative analysis of bimolecular chemical reactions. Towards this goal, we have built a new PEPICO spectrometer, CRF-PEPICO, utilizing simultaneous velocity map imaging for both cations and electrons, while also achieving good cation mass resolution through space focusing. With this new instrument, we have also demonstrated a new approach to dramatically increase the dynamic range in PEPICO spectroscopy by combining temporal ion deflection with a position-sensitive ion detector, suppressing the false coincidence background.

A few recent examples to highlight the power of PEPICO spectroscopy are presented here. The simplest alkylperoxy radical, CH_3OO, formed by reacting photolytically generated CH_3 radicals with O_2, was investigated using the new CRF-PEPICO apparatus at the Swiss Light Source. Modeling the experimental photoion mass-selected threshold photoelectron spectrum using Franck–Condon simulations yielded the most accurate adiabatic ionization energy of this species. Dissociative photoionization of CH_3OO generates the CH_3^+ fragment ion and the appearance energy of this fragment ion, using the methyl cation as the anchor, yields a CH_3OO heat of formation that reduced the uncertainty of the previously determined value by a factor of 5. Statistical simulation of the CH_3OO breakdown diagram provides a molecular thermometer of the free radical's internal temperature, which was confirmed to be slightly over room temperature, indicating quick thermalization.

Small unsaturated resonance-stabilized hydrocarbon radicals play a crucial role in producing PAHs, responsible for molecular weight growth processes that ultimately lead to soot formation. The ability of propargyl radicals to react with themselves makes it key species in molecular weight growth. However, most of these reactions do not produce just a single isomer, rather, a progression through various isomers towards the global energy minimum. The large number of isomers makes unambiguous separation and quantification difficult but the several isomer-specific peaks in mass-selected photoelectron spectra can be much more distinguishable than photoionization spectra. To study the C_6H_6 isomerization pathways, we have performed pyrolytic iPEPICO experiments with continuous flow of a high-energy C_6H_6 isomer, 1,5-hexadiyne, in argon through a temperature-controlled oven (25–500℃) just prior to the iPEPICO ionization region. Analysis of the temperature-evolution of the photoelectron spectra shows clear correlations between decay and formation of various C_6H_6 isomers. Our data shows no evidence for 1,2,4,5-hexatetraene and indicates that fulvene appears at lower temperatures than benzene.

Summary

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