

A new high resolution double velocity map imaging photoelectron photoion coincidence spectrometer for gas-phase reaction kinetics

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We present results of commissioning experiments of a new photoelectron photoion coincidence (PEPICO) instrument designed for studying gas phase reaction kinetics of transient species with high mass and energy resolution. PEPICO spectroscopy yields multidimensional data sets consisting of ion mass resolved photoelectron and photoionization spectra as well as kinetic time profiles of all species. Mass-selected photoelectron spectra are powerful molecular fingerprints that enable studies of isomers that cannot be distinguished by conventional photoionization mass spectrometry.

This new instrument makes use of a very large ion optics electrode stack that separates the linear electric fields at the point of ionization from curved fields at the end for velocity map imaging (VMI). This approach enables very good VMI performance while at the same time giving excellent mass resolution with $m/\Delta m > 6000$. The most powerful PEPICO experiments can be performed at synchrotrons using tunable VUV light, but this instrument also performs well with fixed energy sources amenable to smaller laboratory settings. We will show results of experiments performed at the Advanced Light Source in Berkeley as well as at Sandia using a gas discharge lamp.

To test the time-resolved capabilities of our instrument we studied the photodissociation of SO_2 with 193 nm light via the $\tilde{C}({}^1\text{B}_2) \leftarrow \tilde{X}({}^1\text{A}_1)$ transition. This reaction forms $\text{O}({}^3\text{P}_j) + \text{SO}({}^3\Sigma^-)$, but we also observed direct evidence for a small yield of $\text{S}({}^3\text{P}_j) + \text{O}_2({}^3\Sigma_g^-)$ that has not been reported in the literature previously.

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