

## “Gas Phase Ion Thermochemistry through Imaging Photoelectron Photoion Coincidence Mass Spectrometry”

James P. Kercher, Department of Chemistry, Hiram College

### Impact

The funding from the American Chemical Society Petroleum Research Fund has been an extremely important component in attracting undergraduate students to the chemistry and physics majors. Students who have been supported by this grant have continued their education in numerous graduate programs in the areas of physical chemistry, polymer chemistry, and organic chemistry. Several others are research chemists at a variety of regional and international companies. Students are introduced to data collection methods, numerical analysis, and computational methods that they are not exposed to in other ways. The greatest impact is the travel aspect of the project where students spend 1 week working in Switzerland. For almost all students supported by this grant, it is the first time they travel abroad. I believe this type of experience is a critical component in a liberal arts education. Students are also able to routinely present our work at local and regional meetings.

The grant has had a very important impact on my career as a teacher and mentor. The financial support has allowed me to incorporate computational chemistry into the physical chemistry department curriculum. As a professor at a small liberal arts college, it can be challenging to balance teaching and service responsibilities with scholarship and this grant allows me to maintain an active research program involving undergraduate students.

### The Experiment

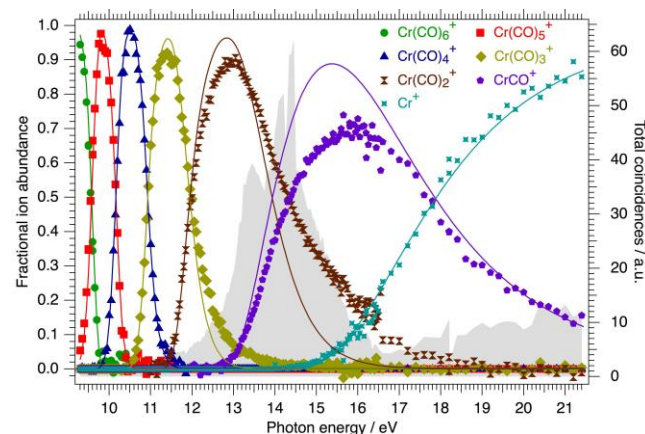
The *i*<sup>2</sup>PEPICO apparatus at the VUV beamline of the SLS, with close to 1 meV energy resolution, the ability to suppress hot electrons, the capability to image electrons and ions, and the available software for modeling complex dissociation reactions is ideally suited for the obtaining accurate thermochemistry for gas phase species. This experiment generates energy selected ions by measuring the ions in coincidence with zero energy electrons. The electrons and ions provide the start and stop signals, respectively to generate an ion time of flight spectrum, from which we obtain dynamical information such as dissociation rates and energies for fragmentation products. Over this reporting period we have finalized our results on Cr(CO)<sub>6</sub> and submitted the manuscript for publication, conducted temperature controlled experiments on ethyl chloride and its deuterated counterpart, and investigated a series of methylated butanes.

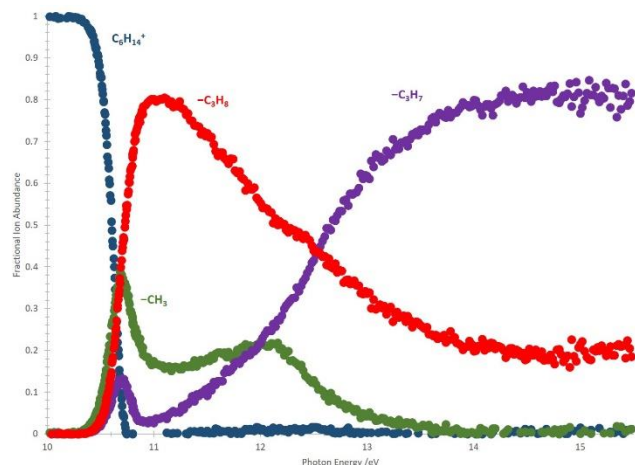
### Research Progress

#### Chromium hexacarbonyl, Cr(CO)<sub>6</sub> – submitted for publication

The fragmentation processes of internal energy selected chromium hexacarbonyl cations, Cr(CO)<sub>6</sub><sup>+</sup>, were investigated by imaging photoelectron photoion coincidence (iPEPICO) spectroscopy at the vacuum ultraviolet

(VUV) beamline of the Swiss Light Source (SLS). In the 9.3 to 21.5 eV photon energy range, Cr(CO)<sub>6</sub><sup>+</sup> dissociates by six sequential carbonyl ligand losses. The fragment ion fractional abundances along with the time-of-flight mass spectra for the first three metastable CO-loss channels were modeled using a statistical approach. Between 12 and 16 eV, the statistical model overestimates the degree of fragmentation, which is explained by enhanced kinetic energy release in impulsive CO loss on repulsive electronic states of the parent ion Cr(CO)<sub>6</sub><sup>+</sup>, as confirmed by TD-DFT calculations. This is the first reported example for an embedded non-statistical unimolecular dissociation regime, bracketed by statistical regimes at low and at high energies. The statistical model was employed to derive 0 K appearance energies for Cr(CO)<sub>n</sub><sup>+</sup> (n = 0–5). The measured Cr–CO bond dissociation energies in [(CO)<sub>n</sub>Cr–CO]<sup>+</sup> (n = 0–5), and the enthalpies of formation of the chromium carbonyl ion series were also determined.





### ***Methylated Butane Series***

More recently, unimolecular dissociation reactions for a series of energy-selected methylbutane cations were investigated at the VUV beamline of the SLS. Rate constants, dissociative ionization pathways and threshold photoelectron spectra (TPES) have been measured for the following energy-selected methylbutane cations: methylbutane, 2,3-dimethylbutane, 2,2,3-trimethylbutane, and 2,2,3,3-tetramethylbutane. The goal of this experiment is two-fold. First, the lowest energy dissociation reactions potentially occur through H-transfer reactions leading to the isobutene ion.

If the reaction is slow, rate constants for H-transfer reactions can be determined, and tunneling contributions may be evident. These can be

compared to theoretical results obtained from a 1-D model using an Eckart barrier. In the event the reactions are fast at threshold, they either do not involve H atom transfer reactions, or H-transfer takes place below the dissociative photoionization barrier, which means that accurate energetics can be obtained for the lowest energy pathway, and can be used in ion cycles to derive new thermochemistry. Preliminary data has been collected and the reactions occurring near threshold are more complicated than initially thought. The  $-CH_3$  and  $-C_3H_7$  fragment ions appear to be formed from multiple reaction pathways.

### ***Light and Heavy Ethyl Chloride, $C_2H_5Cl$ and $C_2D_5Cl$***

The dissociation dynamics of energy-selected ethyl chloride,  $C_2H_5Cl$ , and deuterated ethyl chloride,  $C_2D_5Cl$ , ions using the iPEPICO and new double electron and ion velocity image focusing  $i^2$ PEPICO experimental apparatus were investigated. The goal of the project is to determine the kinetic energy release distribution following the HCl/DCI loss pathway, which occurs via a hydrogen transfer reaction. The dissociation rates and energetics of the competing dissociation pathways, HCl loss at low energies and chlorine radical loss at higher energies, were measured. These studies will lead to better understanding of the kinetic energy release distribution, tunneling through a reverse activation barrier, and the isotope effect in the H atom transfer reaction leading to HCl loss. This work builds on our previous studies on light and heavy acetone and should complement the work on the series of methylbutanes.