

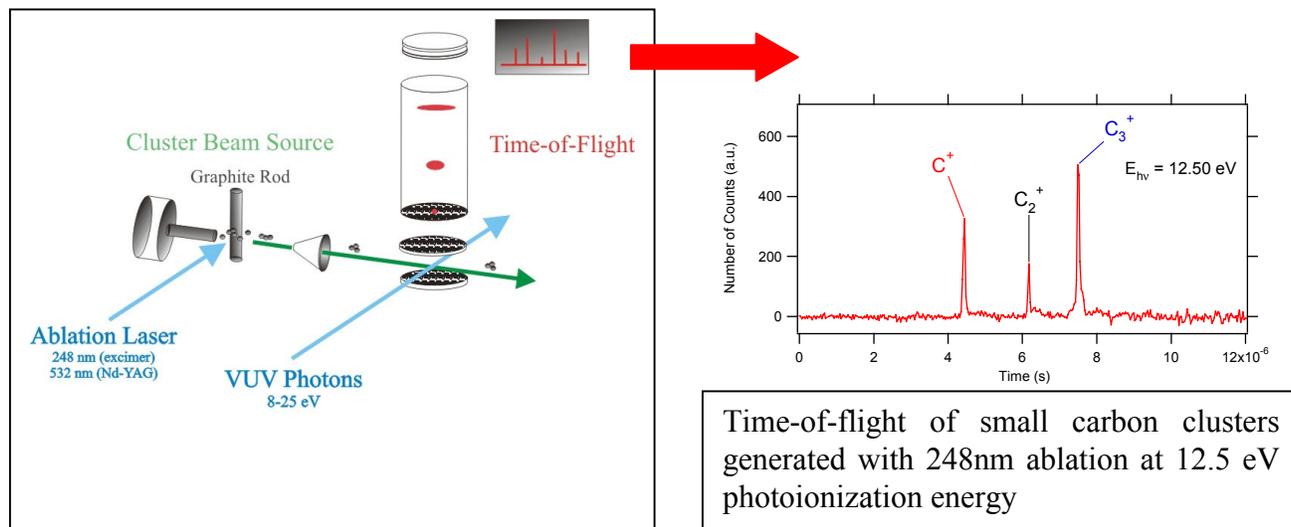
## Photoionization of small carbon clusters

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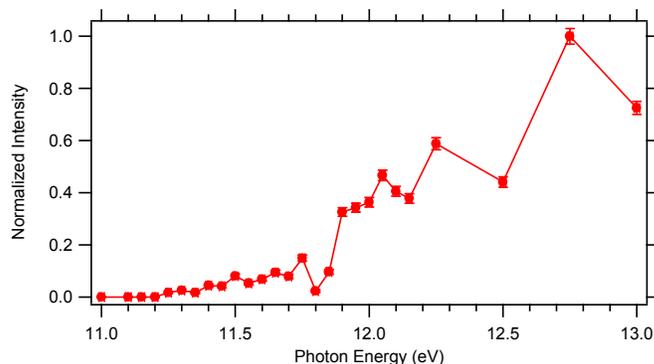
Clusters have always been used as a medium to understand the transition of chemical properties from the gas phase to the bulk. Small carbon clusters are ubiquitous in outer space and in our own environment are critical intermediates in flame chemistry and soot formation. They have also been invoked as precursors of large carbon molecules including aromatic species and fullerenes. The first spectroscopic observation of a cluster of carbon atoms was reported over a century ago, when Huggins investigated the spectra of comets<sup>1</sup>. There has been an extensive body of work performed on small carbon cluster anions, however there is a paucity of data when it comes to the neutrals and the cations<sup>2</sup>. We have initiated a program at the chemical dynamics beamline to study the properties of clusters using tunable VUV radiation. To this effect we have built a new endstation at the Chemical Dynamics Beamline (9.0.2.), Advanced Light Source in Berkeley. As a first test we have performed photoionization mass spectrometry studies on small carbon clusters and measured their ionization energies. Laser ablation on graphite and subsequent supersonic jet cooling is the method of choice for generating carbon clusters<sup>3</sup>. We have used both 248 nm (excimer) and 532 nm (Nd-YAG) laser radiation to generate the clusters. After being skimmed once the clusters are photoionized in a linear time-of-flight (TOF) mass spectrometer using tunable VUV radiation as shown in the figure below.



We have generated photoionization efficiency (I.E.) curves for C, C<sub>2</sub> and C<sub>3</sub> by scanning the 3 meter monochromator in the energy range of 10 to 13 eV. For C<sub>2</sub> and C<sub>3</sub>, to the best of our knowledge, these are the first direct I.E. measurements. There is considerable controversy in the reported I.E. for the carbon trimer. Estimates for the I.E. for C<sub>3</sub> were provided by 2 and 3 photon ionization experiments by Rohlffing et. al.<sup>4</sup> and they lie between 9.98 and 11.61 eV. Measurements<sup>5</sup> using charge-transfer bracketing techniques, wherein carbon cluster cations are reacted with compounds of known I.E.'s to determine whether a charge-transfer reaction occurs,

generates a value of  $12.97 \pm 0.1$  eV. It is likely that ionization of linear ( $^1\Sigma_g^+$ )  $C_3$  to the most stable bent ( $^2B_2$ ) isomer of  $C_3^+$  is likely to face substantial Franck-Condon effects which may have influenced some of these measurements. Latest theoretical calculations<sup>6</sup> using B3LYP density functional theory suggests 12.22 eV as I.E., however CCSD(T) ab-initio calculations indicate adiabatic ionization energies for  $C_3$  at 11.79 eV.

Below, we show a low resolution scan for the carbon trimer generated via 248 nm laser ablation. The dip at 11.8 eV is due of absorption of VUV light by Ar in the gas filter. We use a gas filter to remove high harmonics that are generated in the undulator along with the fundamental light. A cursory examination of the data indicates an I.E. around 11.6 eV.



PIE curve for  $C_3$  generated by 248 nm ablation

We are re-examining the  $C_3$  data using 532 nm laser ablation and higher resolution. Preliminary results suggest a 11.6 eV I.E. as correct as is the step nature of the photoionization curve. We are also in the process of examining the photoionization of other carbon clusters in the range of  $C_4$  to  $C_{10}$ . Future use of an imaging detector run in coincidence with photoelectron detection should deliver information on the electronic structure for each cluster. We also plan to use the ablation apparatus to generate novel clusters using a judicious combination of carrier gas and ablation material.

## References

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