DELAYED IONIZATION IN TRANSITION METAL-CARBON CLUSTERS

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Introduction

Mass spectrometric studies of several single and binary metal transition metal carbon cluster systems, produced in a laser vaporization source, reveal species that undergo delayed ionization. Pulsed extraction and blocking fields, in a time-of-flight mass spectrometer, allow the study of delayed ionization over a time window of several microseconds after excitation with a pulsed laser. In systems where metallocarbohedrenes (Met-Cars) are produced, the Met-Cars are a dominate delayed species[1,2]. Delayed behavior is investigated over a range of photoionization wavelengths and fluences. In order to determine the degree to which the delayed ionization is thermionic in character, the experimental data have been compared to Klots' model for the thermionic emission from small particles.

Experimental

The instrument used in this investigation is a reflectron time-of-flight (TOF) mass spectrometer. A laser vaporization/plasma reactor source is mounted on axis with the spectrometer whereby a rotating quarter inch diameter metal rod is vaporized with a Nd:YAG laser (second harmonic, 532 nm) at a set delay after a pulsed valve is fired. Typically, pure methane is used as the reactant gas. The generated plasma is cooled as it expands through a nozzle into a differentially pumped chamber.

Ions produced in the source are rejected before the ionization/extraction region by applying a voltage to a wire mesh mounted before the skimmer.

A modified TOF lens assembly, based on the design of Recknagel[3], is used to investigate the delayed ionization. All species ionized during the ionization laser pulse (266 nm, 355 nm, 532 nm, or 590 nm) can be deflected off the axis of the spectrometer in less then one hundred nanoseconds (in the mass range of interest.). The blocking time can be scanned to investigate the delayed ionization over a time window after excitation with the pulsed laser.

Typically the blocking time is scanned from -1.00 μsec to + 0.90 μsec and the ions are extracted at +1.00 μsec.

Results and Discussion

The transition metals titanium, zirconium, niobium, and vanadium are investigated in the present study. Binary metal systems are also investigated where titanium is alloyed with yttrium, zirconium, niobium, and tantalum. Figure 1 shows a comparison of the prompt ions and the delayed ions present in the titanium - carbon cluster system. Note that the Met-Car, $Ti_8C_{12}^+$, is the dominant delayed species. Similar spectra are observed for all transition metal - carbon cluster systems studied, although in other systems, additional delayed species are observed.

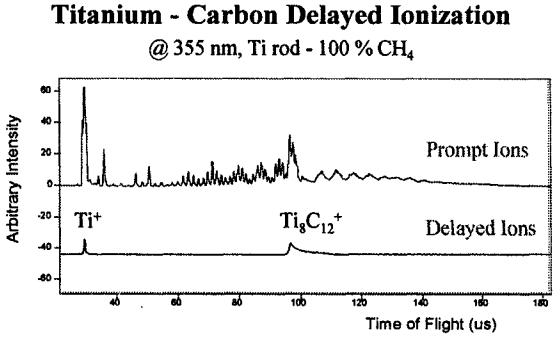

Figure 1. Time of flight spectra of prompt and delayed ions.

We have compared our experimental data with Klots' model for the quasiequilibrium rate constants for thermionic emission from small particles[4], using a method similar to that of Recknagel[3] et al.

The adjustable parameters in the model include the ionization potential of the species, laser wavelength, laser fluence, particle radius, photoabsorption cross

section, particle size (number of atoms), and initial temperature.

We use the ionization potential measured by Brock and Duncan[5] for $Ti_8C_{12}^+$ (4.9 ± 0.2 eV). Laser fluence is measured and the laser wavelengths used are 266 nm, 355 nm, 532 nm, and 590 nm. The two unknown quantities adjusted to fit the experimental data are initial temperature and photoabsorption cross section.

Figure 2 shows a plot of the normalized delayed ion intensity vs. the blocking time for the titanium Met-Car. The parameters used in the model calculation are laser fluence = 80.0 mJ/cm^2, particle radius = 2.5981 A, photoabsorption cross section = 1.0 * 10^{-17} cm^2, and an initial temperature of 300 K.

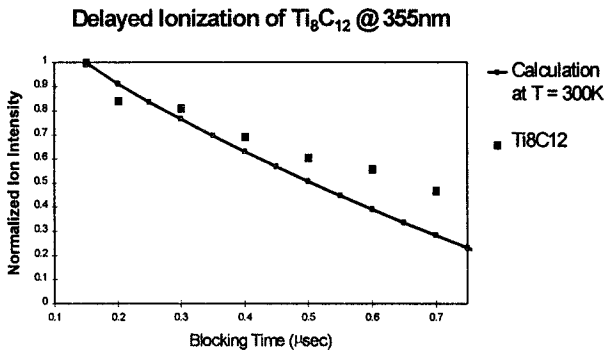

Figure 2. Titanium Met-Car delayed ion yield as a function of blocking time.

Conclusions

Delayed ionization is observed in all single metal and binary metal Met-Car systems studied. The Met-Cars typically are the dominate delayed ion species in the transition metal - carbon cluster systems studied.

Good agreement between Klots' model and the experimental data is achieved, supporting the conclusion that the observed delayed ionization is thermionic in character. Also, the delayed ionization is not observed to be wavelength dependent, but is observed to be fluence dependent. This supports the assumption that the energy is being distributed over all possible states, and the observed delayed ionization is not due to a specific long lived state.

We also observe that the delayed ionization behavior of the various Met-Car species studied is dependent on the identity of the transition metal incorporated into the cage structure.

The nature of the observed delayed atomic ion is currently being investigated in our laboratory.

Acknowledgments

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