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6. AUTHOR(S)
A.W. Castleman, Jr.
Department of Chemistry

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Pennsylvanai State University
University Park, PA 16802

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The studies devoted to chemical dynamics yielded direct information on the reactive properties of the clusters and provided further information on developing methods for the production of building blocks having the desired stoichiometry, size and properties. In addition, the work provided insights into the electronic properties which influence the stability of cluster assembled materials that may function as catalysts for selected reactions, or be resistant to chemical attack for other applications.

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A. W. Castleman, Jr.
Final Technical Report (Agency Award No.: F49620-99-1-0099)

DURIP 99 ULTRAFAST LASER DYNAMICS: EXPLORING THE FORMATION AND PROPERTIES OF CLUSTER MATERIALS

INTRODUCTION:

Currently, there is extensive interest in the prospect of developing new materials that can be tailored to display unique properties that will differ from those of bulk extended solids. Indeed, through the concept of cluster assembly, there is the prospect of designing and producing ones that may exhibit unique optical, electronic, or structural properties on the one hand, or perhaps useful catalytic or reactive characteristics on the other.

This grant was devoted to assembling a new facility to investigate interrelated issues dealing with the dynamics and formation of selected cluster types. The overall objective was to lay the foundation for strategies to be employed in the ultimate development of cluster assembled materials (CAMs) of nanoscale dimensions. The studies devoted to chemical dynamics yielded direct information on the reactive properties of the clusters and provided further information on developing methods for the production of building blocks having the desired stoichiometry, size, and properties. In addition, the work provided insights into the electronic properties which influence the stability of CAMs that may function as catalysts for selected reactions, or be resistant to chemical attack for other applications.

As described in what follows, the main properties under consideration in our work hinge largely on the electronic states of the clusters and related nanoscale aggregates. In this context, we undertook studies devoted to investigations of transition metal

compounds in terms of elucidating their properties and developing methods for their production and assembly. The experimental program dealt in large measure with the assembly of an advanced femtosecond laser system and commentary investigations of the dynamics of cluster formation, growth, and reactivity, including excitation and relaxation phenomena encountered in probing the properties under study. The work built on a femtosecond laser system recently acquired and assembled through the DURIP funded program for which this document represents the final report.

THE ULTRAFAST LASER FACILITY

Our work focused on producing and investigating the properties of nanoscale materials as well as probing the interaction of clusters with intense, ultrashort laser pulses. We explored Met-Cars, with the goal of further understanding their formation, bonding, stability, and ionization dynamics. In addition, we have looked at the reactivity of aluminum and aluminum carbon clusters, which offer the prospect of being building blocks for materials of unique properties. Experiments are currently underway, employing a newly installed and characterized ultrafast laser system, to investigate the electron relaxation dynamics in the aforementioned Met-Car and aluminum containing clusters. In another aspect of our research, we have looked at the fundamental physics of the interaction of clusters with intense, ultrashort laser pulses and have provided insight into the Coulomb explosion process. We have adapted the Coulomb explosion process into a new method to investigate the intermediates in fast chemical reactions.

The Ultrafast laser facility was employed to conduce research in support of our AFOSR sponsored research grants: AASERT98: Investigations of New Classes of Molecular Materials and Clusters of Transition Metal Compounds: Building Blocks of

New Materials. It was also utilized in conducting research, which formed the basis for the Ph.D. dissertation of Dr. Steven Kooi, "Formation, Fragmentation, and Ionization Dynamics of Transition Metal-Carbon, Nitrogen, and Oxygen Clusters".

Since the discovery of Met-Car clusters in 1992, there has been interest in elucidating their electronic properties. Met-Car clusters, for example, are measured to have relatively low ionization potentials (IPs) despite being composed of elements with comparatively high IPs. Met-Cars are also observed to undergo delayed ionization under nanosecond pulsed photoionization, and this, coupled to the measured low ionization potentials, exemplifies the free electron nature in these clusters. Many details concerning the electronic structure of the Met-Car clusters are not well known due to the complexity of calculations on systems with numerous electrons. Herein we briefly summarize our work which represents the first time-resolved excited state measurements for any Met-Car system.

Ultrafast laser pump-probe techniques have been employed to study many systems, ranging from small metal or metal-containing clusters to large gas phase cluster aggregates. Studies of particular interest have recently focused on electron dynamics, with specific emphasis placed on elucidating the collective electronic effects of Met-Car clusters. Characterization of ultrafast pulses is thus vital for proper analysis and is necessary to ensure accurate interpretation of electronic lifetimes. A brief description of the laser system and pulse characterization techniques follow.

Femtosecond laser pulses are generated in a commercial Ti:Sapphire regenerative amplifier system (Spectra Physics (SP), Spitfire). The ultrafast laser system begins with a mode-locked Ti:sapphire oscillator (SP Tsunami), pumped by a 5 Watt diode pumped

solid state Nd:YAG continuous-wave laser (SP Millennia). The output of the Tsunami oscillator has a repetition rate of 82 MHz, typically centered at 800 nm, at a few nJ/pulse and ~20 fs. The output of the Tsunami is amplified in a regenerative amplifier (SP Spitfire), which is pumped by an intercavity frequency doubled 10 Watt Nd:YLF laser (SP Merlin).

The output of the regenerative amplifier, typically 1.2 mJ/pulse at 40 to 50 fs, centered at 800 nm and horizontally polarized, is split with a 50/50 beamsplitter and is either directed onto a high precision delay stage (Aerotech) or to an optical parametric amplifier (SP OPA-800). After the delay stage, the light can be frequency doubled (400 nm), tripled (266 nm), or quadrupled (~200 nm) in two commercial harmonic generation boxes. The harmonic crystals are optimized to preserve the sub 50 fs pulsewidth, therefore sacrificing power conversion efficiency.

The optical parametric amplifier has a collinear double pass geometry and is capable of producing ~50 fs pulses from 240 nm to 3.1 □m, through different harmonic generation or frequency mixing steps. To ensure that the crystals are properly aligned, such that the desired wavelength is generated, a fiber optic spectrometer (Ocean Optics SD2000) is utilized. This diagnostic equipment has the capability of analyzing light between 200 nm and 800 nm and between 650 nm and 1.1 μm by simply varying a grating. The spectrometer is also equipped with a calibration source and two fiber optics of different diameter. The pump pulse from the harmonic box(es) and probe pulse from the optical parametric amplifier are recombined and loosely focused, collinearly, intersecting the cluster beam perpendicularly between the extraction grids of our home built reflectron time-of-flight mass spectrometer.

To gain insight on shape of the concerned pulses, the output of the regenerative amplifier is characterized in a polarization gate frequency resolved optical gating (SP FROG) apparatus. This technique essentially resolves the pulsewidth and identifies the presence of frequency chirp in the pulse. An additional technique employed to characterize the concerned pulses is a simple cross correlation measurement. The cross correlation width of two laser pulses is readily determined by simply examining the pump-probe transient of a known molecular system, such as methyl iodide, directly in the molecular beam. The setup for such an experiment is straightforward in that the signal intensity of methyl iodide, for example, is simply plotted versus the time delay between the pump and probe pulses. In addition to the cross correlation of the laser, this technique provides an efficient way in identifying the exact overlap, time zero, of the two pulses.

During the pump-probe experiments the fluence of the pump and probe beams is carefully adjusted to minimize or eliminate ion production when only the pump or probe beam is present. Mass spectra are subsequently collected at set pump-probe delays on a digital oscilloscope (LeCroy 9304A) and analyzed on a personal computer.

In order to overcome the inherent instability in a laser vaporization source due to pulse to pulse fluctuations and long term drift in our pulsed valve, a rapid scan pump-probe data acquisition method is utilized in our work. This method essentially repeats a single pump-probe scan multiple times (typically five) compiling and averaging mass spectra for each specific time delay between the pump and probe pulse, thus minimizing long term signal intensity fluctuations.

The neutral vanadium and titanium carbon clusters were generated in a typical laser vaporization source. The surface of a quarter inch diameter transition metal rod is

vaporized with a Nd:YAG laser (Spectra Physics INDI-10) pulse, ~4 mJ/pulse and 8 ns, at an appropriate delay after a pulsed valve is actuated. Typically, pure methane at 4.5 atm backing pressure is used. Neutral and ionic species are formed in the vaporization source. The charged clusters are then deflected with an electric field before a skimmer, allowing only the neutral clusters to enter the time-of-flight extraction region.

RESULTS AND DISCUSSION

A mass spectrum showing a typical distribution of titanium carbon clusters formed from photoionization (400 nm, 50 fs, 24 μJ/pulse) of neutral species produced in the laser vaporization source is shown in Figure 1b. The cluster distribution is almost identical to the distribution observed under photoionization with a 355 nm, 10 ns Nd:YAG pulse, as shown in Figure 1a, with one significant difference. Note that while the overall distribution does not change substantially, the "tailing" of the titanium Met-Car peak to higher mass, present in the nanosecond ionization case is reduced or absent in the femtosecond photoionization spectrum. The "tailing" of peaks to higher mass is indicative of delayed ionization. When short enough excitation pulses are employed direct multiphoton ionization dominates the thermionic emission level is below our detection limits.

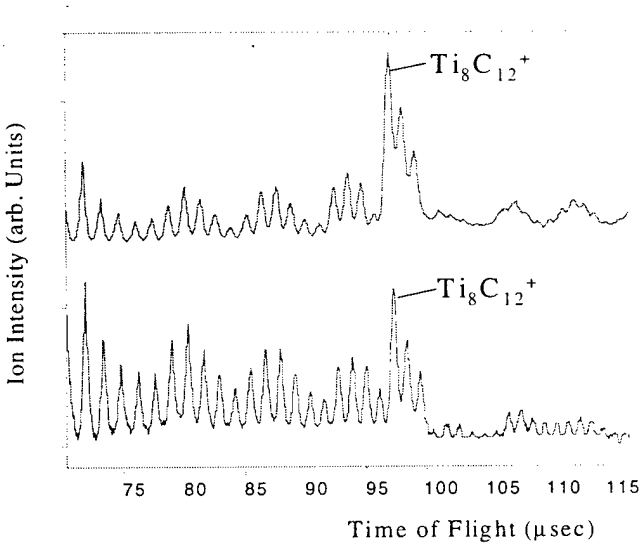

Figure 1. The top mass spectrum (a) shows the distribution of titanium-carbon clusters under photoionization at 355 nm, 10 ns pulsewidth, while the bottom mass spectrum (b) shows the distribution under photoionization at 800 nm, 40 fs pulsewidth.

Time resolved measurements: ultrafast dynamics

A mass spectrum showing a typical distribution of vanadium carbon clusters formed from photoionization (400 nm, 50 fs, 24 μJ) of neutral species produced in the laser vaporization source is shown in Figure 2. Again, the mass distribution is almost identical to the nanosecond photoionization spectrum at 355 nm. The Ultrafast dynamics of the titanium met-car is shown in Figure 3.

The data shown in Figure 3 agrees with the expected free electron nature in the Met-Cars. In addition, a longer lifetime component is observed in accord with expectations from the noted delayed ionization behavior when an electronic band is accessed. The short pulse capabilities of the new

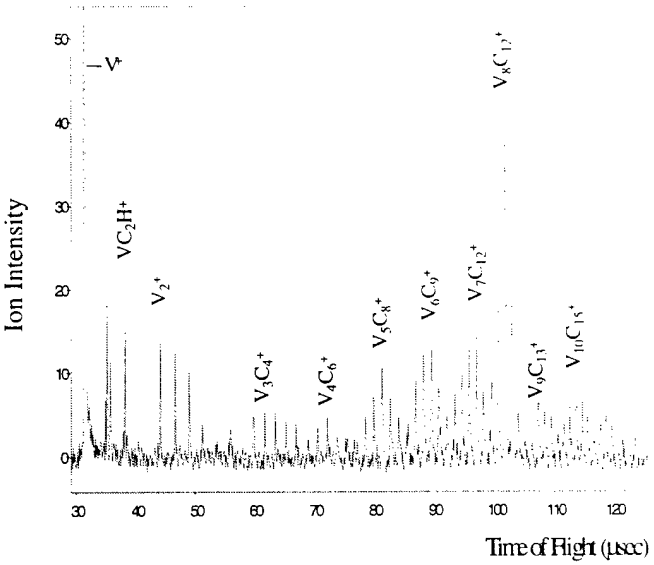

Figure 2 Mass spectrum of vanadium carbon clusters produced under 400 nm, 50 fs photoionization of neutral clusters generated in the laser vaporization source.

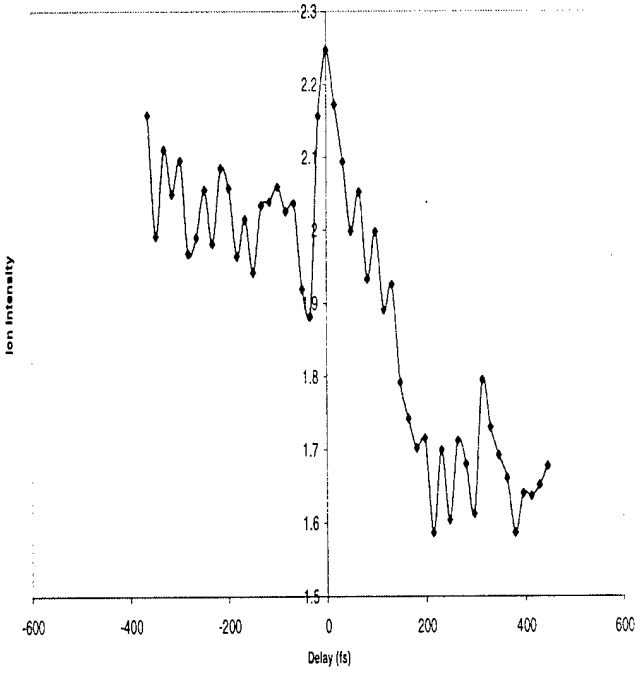

Figure 3. Pump probe transient observed for the Ti Met-Car, employing a 50 fs, 660 nm pump and 400 nm probe.

laser system allows us to measure extremely short excited state lifetimes, as are expected to be present in systems with many free electrons.

The ultrafast dynamics of vanadium carbon clusters have been investigated under 400 nm pump, 620 nm probe conditions. The pump-probe transient of the vanadium Met-Car is illustrated in Figure 4. Measurements of the ionization potential of V_8C_{12} indicate that one 400 nm photon and one 620 nm photon is sufficient to exceed the IP, however we expect that some fraction of the transient signal results from more than two photon absorption, due to the non-zero background.

The cross-correlation of the 400 nm pump and 620 nm probe beams is $\leq$ 86 fs while the observed response of the V_8C_{12} cluster is 225 fs (FWHM). This distinct difference indicates that a state (or band of states) with an appreciable lifetime is being accessed. The fact that the Met-Car response is noticeably longer than the autocorrelation and that these clusters are strongly bound, also suggests that the pump-probe response is too short to be attributable to a fragmentation process, either in the Met-Car cluster itself, or fragmentation of a larger cluster to form the Met-Car. The pump-probe response is thus more than likely a measurement of electronic relaxation. However, the pump-probe transients for all of the

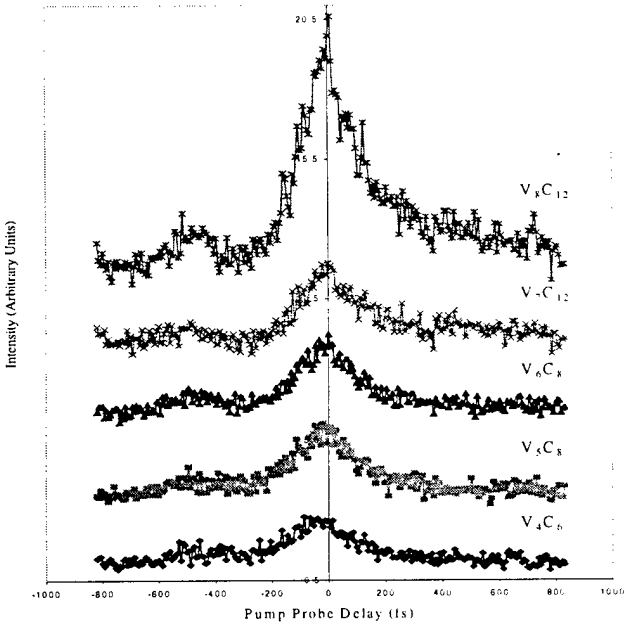

Figure 5 Pump-probe transients (pump: 400 nm, 50 fs, 24 μJ; probe: 620 nm, 50 fs, 20 μJ) observed for the vanadium-carbon clusters: V_4C_6, V_5C_8, V_6C_8, V_7C_{12}, and V_8C_{12} between delay times of –1 ps and +1 ps.

observed vanadium-carbon clusters with more than four metal atoms show a similar pump-probe response, as seen in Figure 5 with exponential decays on the order of a few hundred femtoseconds. This result suggests that the band of states accessed in the vanadium Met-Car is already present in clusters as small as the V_4C_x series.

However, upon closer inspection and curve fitting, a trend is noticed in the observed transients for V_4C_6, V_5C_8, V_6C_8, V_7C_{12}, and V_8C_{12}. To perform an appropriate analysis, the experimental data were first fitted using a typical least squares fitting method. There are several trends observed in the fitted and normalized transients, as plotted in Figure 6. First of all, a narrowing of the transient is observed with increasing cluster size. This is suggestive of the expected increased free electron character with increasing cluster size. Secondly, the maximum of the fitted transients shift to longer delay times with increasing cluster size. Finally, the V_4C_6 and V_5C_8 transients exhibit a single exponential decay, while the V_6C_8, V_7C_{12}, and V_8C_{12} transients display double exponential decays. The V_7C_{12} and V_8C_{12} clusters have almost identical fitted transients with one fast decay component and one

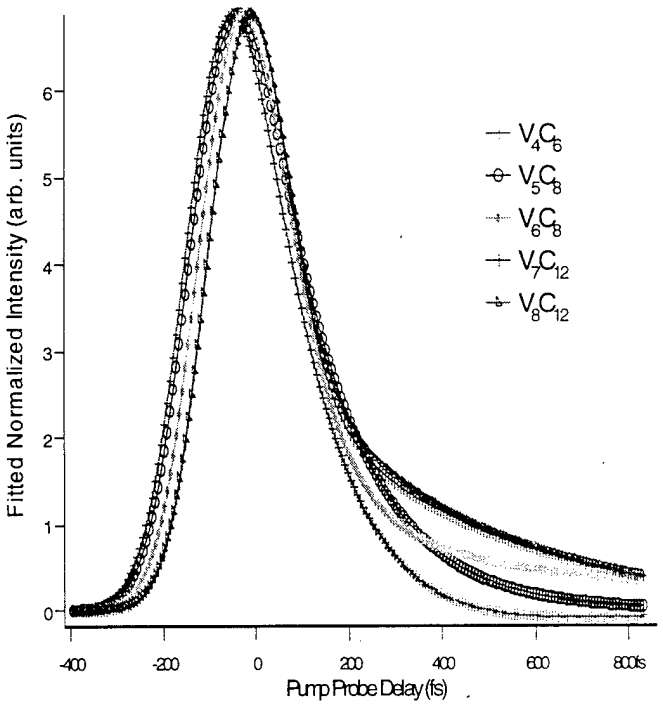

Figure 6 Summary of fits of experimental pump-probe data for V_4C_6, V_5C_8, V_6C_8, V_7C_{12}, and V_8C_{12}. Note that the transients become narrower with increasing size.

longer, several hundred femtosecond, decay. Since the excited states and band structure of the vanadium Met-Car lie above those of the analogous titanuim system, the lack of a plateau corresponding to delayed ionization is expected.

CONCLUSIONS:

The laser facility acquired and assembled through DURIP funding is unique. It is enabling a detailed investigation of the dynamics of electronic excitation and relaxation in cluster systems and hence providing important data on these phenomena. The findings will be of value in further elucidating the electronic properties of systems of restricted geometry and will also provide data for testing theoretical models which endeavor to account for the related relaxation processes. Related experimental work is continuing in our laboratory using this facility.