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# Letters

# Relaxation Dynamics of Electronically Excited Nanoscale Metal–Carbon Complexes: Vanadium–Carbon Clusters

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**ABSTRACT**

**First measurements of the relaxation dynamics of electronically excited states in nanoscale transition metal–carbon species are reported. In this communication, time-resolved measurements, made with the femtosecond laser pump–probe technique by employing 50 fs pulses at 620 and 400 nm, reveal the excited-state dynamics in vanadium–carbon clusters including the vanadium Met-Car, $V_8C_{12}$. Size dependent trends are observed in the pump–probe transients, which suggest a more extensive free electron character in the larger clusters as compared to the smaller species.**

**Introduction.** Ultrafast laser pump−probe techniques have been employed to study a wide range of systems.[1] In terms of metal or metal containing clusters, early studies have focused mainly on small systems such as alkali metal dimers[2,3] and trimers,[4] and the silver trimer.[5,6] However, recent studies by Gerber and co-workers have extended pump−probe excited-state measurements to larger gas-phase metallic or semi-metallic cluster systems such as silicon, $Cd_xTe_y$,[7] and arsenic.[8] Ultimately, as more is learned about these systems, it might be possible to control energy relaxation via the tuning of cluster size. Moreover, such experiments provide insight into the mechanisms of electronic relaxation into bands of various energies. Femtosecond photoionization and photofragmentation studies of large gas-phase sodium[9] and mercury[10] clusters and pump−probe investigations of metal clusters supported on surfaces[11,12,13] have also been reported.

In the femtosecond photoionization studies of $Cd_xTe_y$ clusters, a "magic" stoichiometry of $Cd_5Te_{29}^+$ was observed that was not previously found under nanosecond photoionization conditions performed at 308, 450, or 500 nm.[7] This observation was attributed to the ability to perform fragmentation free multiphoton ionization with femtosecond laser pulses, whereby direct prompt ionization competed favorably with dissociation processes in intermediate excited states. The ionization and fragmentation dynamics of the $Cd_xTe_y$ clusters, at 800 nm, were also investigated using the pump−probe photoionization scheme at delay times from −20 to +20 ps. All clusters showed a fast decay on a one to four ps time-scale, but the monomer ions, $Cd^+$ and $Te^+$, showed both a long-time delay increase in intensity and a ps time-scale decrease in overall intensity. These observations, and the large kinetic energy of the ionic fragments, were interpreted as evidence that the monomer ions result from fragmentation of larger multiply charged clusters. Excited states in the atoms have lifetimes on the ns time-scale and were not observed in this experiment.

In the arsenic cluster studies, a commercial molecular beam epitaxy (MBE) effusion cell was employed as the cluster source.[8] Again, through the use of femtosecond

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pulses, fragmentation free multiphoton ionization was employed to directly probe the neutral cluster distribution. Although the cluster beam was almost entirely composed of the arsenic tetramer, the ultrafast dynamics of the arsenic monomer, dimer, trimer, and tetramer were investigated between −250 and +380 fs with 100 fs, 620 nm pump and probe pulses. Within the time resolution of the experiment, all species showed the same temporal behavior, corresponding to the autocorrelation of the two laser pulses.

In addition to the above referenced studies of metals and semiconductors, pump−probe experiments[14,15] have also been performed on $C_{60}$. The first pump−probe experiment[15] performed on $C_{60}$ employed 248 nm pump and probe photons. The pump−probe transient for $C_{60}$ matched the autocorrelation trace obtained with nitric oxide gas, and this result suggests that instead of populating an intermediate state, the excitation mainly induces a direct two photon ionization. Hertel and co-workers[14] performed a one color pump−probe experiment on $C_{60}$ with 90 fs, 620 nm pulses. It was presumed that one 620 nm photon saturated the $^1T_{1g}-^1A_g$ transition, from which three additional photons are required to ionize. An oscillatory structure was present in the pump−probe transient with a period of about 110 fs, and this was attributed to the vibrational excitation of the intermediate $^1T_{1g}$ state, with a frequency of $311 \pm 24$ cm$^{-1}$. Other studies have investigated the ultrafast fragmentation[16,17] and Coulomb explosion[18] of $C_{60}$ with femtosecond laser pulses.

Since the discovery[19] of Met-Car nanoscale clusters in 1992, there has been interest in elucidating their electronic properties. Met-Car clusters, for example, are measured[20] to have relatively low ionization potentials (IPs) despite being composed of elements with comparatively high IPs. Met-Cars are also observed to undergo significant delayed ionization[21−23] 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. However, Met-Cars have attracted considerable interest from the theoretical community.[24] Herein, we present the first time-resolved excited-state measurements of the electronic relaxation dynamics in vanadium−carbon clusters including the vanadium Met-Car, $V_8C_{12}$.

**Experimental Section.** The neutral vanadium−carbon clusters are generated in a typical laser vaporization source. The surface of a quarter inch diameter vanadium rod is vaporized with a Nd:YAG laser (Spectra Physics INDI-50) 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.

The femtosecond laser pulses are generated in a commercial Ti:sapphire regenerative amplifier system. The ultrafast laser system begins with a mode-locked Ti:sapphire oscillator (Spectra Physics (SP) Tsunami), pumped by a 5 W diode pumped solid state Nd:$YVO_4$ continuous-wave laser (SP Millennia). The output of the Tsunami oscillator, typically centered at 800 nm, has a pulse energy of a few nJ/pulse and a pulse width of ∼20 fs. The output of the Tsunami is amplified in a regenerative amplifier (SP Spitfire), which is pumped by an intercavity frequency doubled 10 W 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 beam splitter 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, tripled, or quadrupled in two commercial harmonic generation boxes. The harmonic crystals are optimized to preserve the sub 50 fs pulse width, therefore sacrificing power conversion efficiency. Typically, the second harmonic efficiency is ∼10% of the fundamental pump, whereas the third harmonic efficiency is ∼2% and the fourth harmonic efficiency is ∼0.3%. The pulses from the regenerative amplifier are characterized in a polarization gate frequency resolved optical gating (FROG) apparatus to determine the pulse width and to ascertain the presence and elimination of any frequency chirp in the pulse. The cross correlation of the two laser pulses is determined by examining the pump−probe transient of a known molecular system, directly in the molecular beam.

The optical parametric amplifier has a collinear double pass geometry and is capable of producing ∼50 fs pulses from 240 nm to 3.1 mm, through different harmonic generation or frequency mixing steps. 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. The zero delay time between the pump and probe pulses is identified by the known nearly prompt response of methyl iodide.[25] After replacing the methyl iodide source chamber with the lava source, the low mass species response, being similar to the response of $CH_3I$, is assigned the same zero.

During pump−probe experiments, the fluence of the pump and probe beams are carefully adjusted to minimize or eliminate ion production when either the pump or the probe beam is individually present. Any ion created is accelerated and travels a total of three meters to a multichannel plate detector. Mass spectra are collected at set pump−probe delays on a digital oscilloscope (LeCroy 9304A).

To overcome the inherent instability in our 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. 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.

**Results and Discussion.** *Time-Resolved Measurements:*

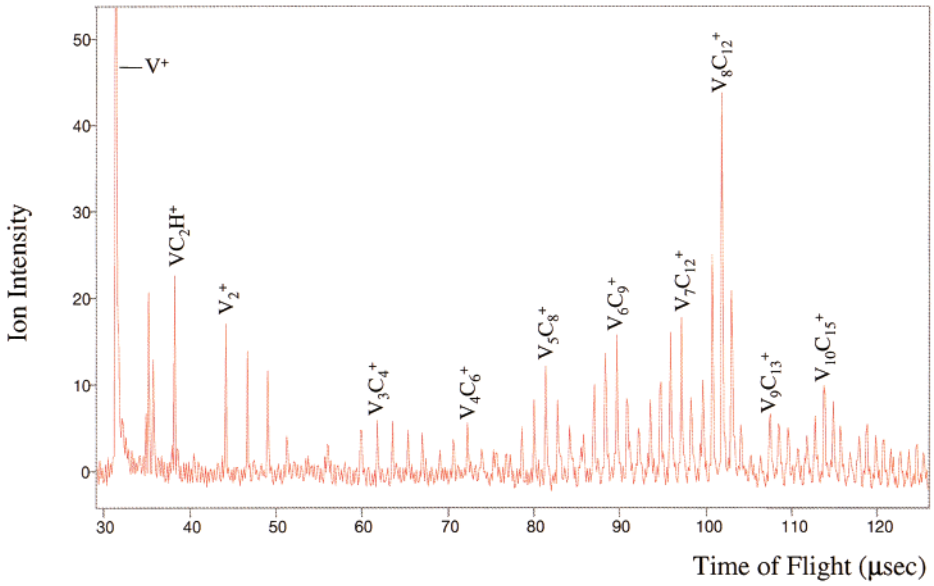


**Figure 1.** Mass spectrum of vanadium carbon clusters produced under 400 nm, 50 fs photoionization of neutral clusters generated in the laser vaporization source.

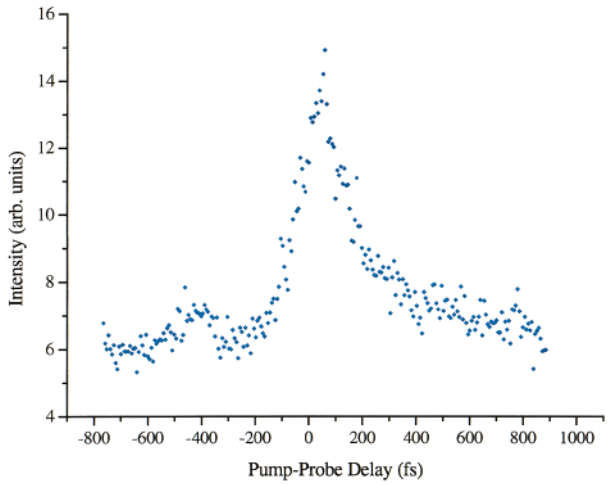


**Figure 2.** Pump-probe transient (pump: 400 nm, 50 fs, 24 mJ; probe: 620 nm, 50 fs, 20 mJ) observed for the vanadium Met-Car cluster between delay times of −1 ps and +1 ps.

*Ultrafast Dynamics.* A mass spectrum showing a typical distribution of vanadium−carbon clusters formed from photoionization (400 nm, 50 fs, 24 mJ) of neutral species produced in the laser vaporization source is shown in Figure 1.

The ultrafast dynamics of vanadium−carbon clusters were investigated under 400 nm pump, 620 nm probe conditions, and the pump−probe transient of the vanadium Met-Car is illustrated in Figure 2. Preliminary 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. We expect, however, that due to the nonzero background, some fraction of the transient signal results from the absorption of other photon combinations.

The cross-correlation of the 400 nm pump and 620 nm probe beams is ≤ 86 fs, whereas 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,[26] 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 attributed to the temporal dependence of the electronic relaxation. It should be noted that the pump−probe transients for all of the observed vanadium−carbon clusters with more than four metal atoms show a similar pump−probe response, as seen in Figure 3, with exponential decays on the order of a few hundred femtoseconds. This result suggests that a common chromophore[27] is being accessed that is present in clusters as small as the $V_4C_x$ series up through the Met-Car, $V_8C_{12}$.

Additionally, upon closer inspection and curve fitting, individual trends in the observed transients for $V_4C_6$, $V_5C_8$, $V_6C_8$, $V_7C_{12}$, and $V_8C_{12}$ are evident. The experimental data, except for the small feature centered around −450 fs, were fitted using a typical least-squares fitting method, accounting for the cross correlation of the pump and probe pulses. The trends observed in the fitted and normalized transients, as plotted in Figure 4, begin with the narrowing of the transient with increasing cluster size. This narrowing is suggestive of the expected increased free electron character with increasing cluster size. Second, the maxima of the fitted transients shift to longer delay times with increasing cluster size. This shift suggests that the possible chromophore response is not initiated until the relaxation dynamics of the proximate states are affectedly relaxed. The band of states that are influencing the delayed response could perhaps illustrate phonon relaxation modes and conceivably be responsible for the double exponential decay fitting for $V_6C_8$, $V_7C_{12}$, and $V_8C_{12}$. Although 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 longer, several hundred femtosecond, decay.

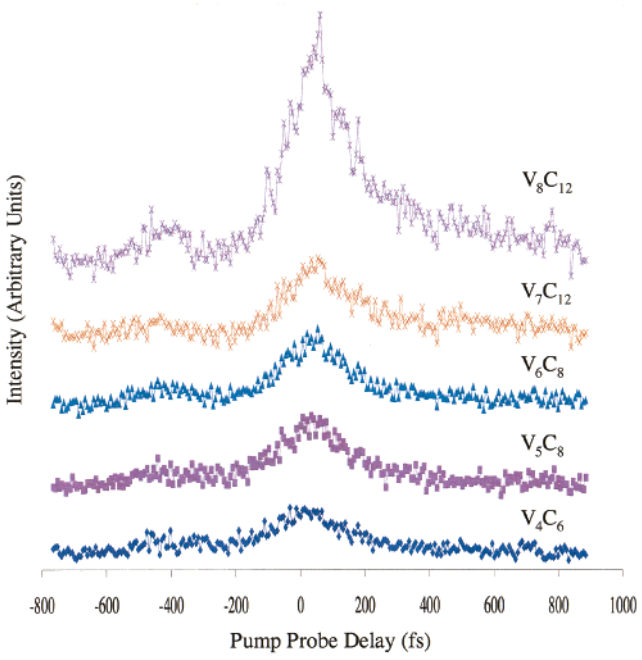


**Figure 3.** Pump-probe transients (pump: 400 nm, 50 fs, 24 mJ; probe: 620 nm, 50 fs, 20 mJ) observed for the vanadium−carbon clusters: $V_4C_6$, $V_5C_8$, $V_6C_8$, $V_7C_{12}$, and $V_8C_{12}$ between delay times of −1 and +1 ps.

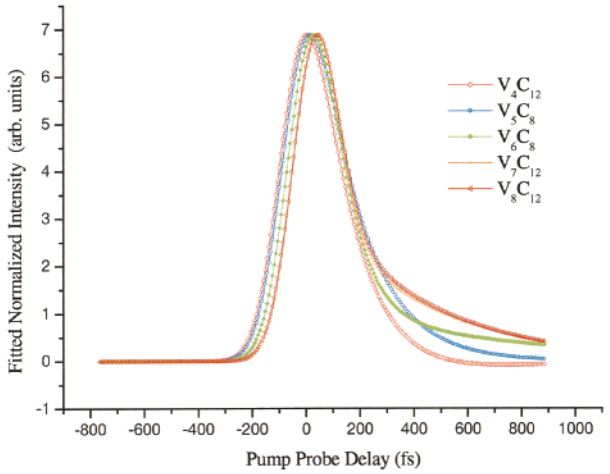


**Figure 4.** Summary of the fits of experimental pump−probe data for $V_4C_6$, $V_5C_8$, $V_6C_8$, $V_7C_{12}$, and $V_8C_{12}$. Note that the transients become narrower with increasing cluster size and evolve from single to double exponential decay behavior.

The $V_4C_6$ and $V_5C_8$ transients, also shown in Figure 4, exhibit a single-exponential decay.

**Conclusions.** The first measurements of the electronic relaxation dynamics in vanadium−carbon clusters are presented. The two color pump−probe transients show an asymmetric response, significantly longer than the cross correlation of the pump and probe beams, indicative of excitation into available bands. Future studies will extend the study to investigate wavelength and fluence effects on the relaxation dynamics observed in not only the Met-Car cluster, but also in the additional clusters of the distribution. Preliminary studies show a pronounced difference in the observed excited-state dynamics for the small (i.e., less than three metal atoms) clusters, whereas the clusters containing four or more vanadium atoms exhibit a similar pump−probe response and again, suggest the presence of a common chromophore. The pump−probe response is observed to narrow as the cluster size increases. This result suggests that the larger nanoscale complexes have more free electron character, and therefore, the rate of energy relaxation is higher in the larger clusters. We are hopeful that the current experiment will prompt further theoretical work on these systems, specifically in regard to their excited-state dynamics.

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