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13. ABSTRACT ***(Maximum 200 Words)***

Attaining the ability to produce materials through cluster assembly offers great potential advantages, namely the prospect of forming nanoscale materials having selected optical, electronic, or structural properties on the one hand, or useful catalylic, reactive or energy storage characteristics on the other. The work conducted as part of this program involved investigations of the properties of transition metal compounds comprised of nitride, carbides and oxides, with attention to their varying electronic nature with cluster size, and composition. Findings are reported from three interrelated phases of work: (1) forming and studying cluster building blocks, elucidating their properties, investigating methods to accomplish their production in the bulk, and assessing their potential for use as cluster assembled materials; (2) studying the excitation and relaxation dynamics of the clusters following photoexcitation, with attention to providing an understanding of their behavior in terms of observed delayed electron and atomic ion emission; and providing baseline data for assessing theoretical approaches for handling the dynamics of systems having a large number of free electrons; and (3) undertaking studies which provide insight into the potential catalytic behavior of selected clusters, Met-Cars and CAMs, including investigations that serve to identify the fundamentals of catalysis of selected reactions.

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INTRODUCTION AND STATEMENT OF OBJECTIVES

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.

The work conducted under the auspices of this program was addressed to the study of interrelated issues dealing with the dynamics and formation of selected cluster types, with the overall objective 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 provided information on the reactive properties of the clusters and uncovered methods for the production of building blocks having the desired stoichiometry, size, and properties. In addition, the findings gave 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.

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 extended our earlier studies devoted to investigations of transition metal compounds in terms of elucidating their properties and developing methods for their production and

assembly. The program dealt in large measure with investigations of the dynamics of cluster formation, growth, and reactivity, including excitation and relaxation phenomena encountered in probing the properties under study.

The program has been directed to three interrelated scientific themes of work, all involving investigations of the properties of transition metal compounds comprised of nitride, carbides and oxides, with attention to their varying electronic nature with clusters size, composition and degree of aggregation. The findings summarized below demonstrate the prospect of being able to form new materials with desired catalytic or reactive characteristics such as those that might provide constituents of energetic materials or additives to fuels, as well as the design of new materials of selected structural, electronic, or optical characteristics.

OVERVIEW OF ACCOMPLISHMENTS DURING THE GRANT PERIOD

In efforts to lay the foundation for tailoring the design of new materials, attention has been placed on studies of the evolving electronic band structures of transition metal-carbon materials of varying sizes and compositions, providing underlying fundamental concepts governing their properties. The work has built heavily on a femtosecond laser system acquired through a DURIP grant which is incorporated in the femtosecond spectroscopy-molecular reaction dynamics facility operating in our laboratory. The construction of a photoelectron spectrometer with funds provided from a DURINT grant was completed, providing a primary tool for the future program; and, two major cluster deposition facilities donated to us by the Intel Corporation were reconstructed, which will aid in assembling deposits of CANaMs.

During the grant period, attention has been given to three major undertakings: 1) elucidating the electronic and reactive states of Met-Cars through the study of their excitation and relaxation

dynamics; 2) developing approaches for synthesizing CANaMs of unique properties, including methods for effecting the selection of clusters of desired composition and sizes, depositing them on surfaces and characterizing the produced nanoscale materials; and 3) exploring methods for storing highly energetic materials through cluster stabilization. A brief summary of accomplishments in each area is given in what follows. Details are provided in the various papers written on the basis of findings from this grant; some are in print while others are in various stages of publication as noted in the listing provided.

1) Studies of Met-Cars: Excitation and Relaxation Processes

The recent interest in the study of electronic structure in nanoscale materials has spawned more fundamental work in excitation and relaxation dynamics in systems of finite size. One primary activity has been devoted to unraveling the unique electronic properties of Met-Cars through several approaches. In one major activity, a detailed study was made to identify one of the evolving electronic bands of states characteristic of these nanoscale materials of caged geometry. Through the implementation of the femtosecond pump-probe technique pioneered by Zewail, the excited state dynamics of various vanadium-carbon clusters were explored. Recent studies of vanadium Met-Cars have led to the discovery of a band of electronic states in the vicinity of 2 eV that displays a range of electronic relaxation lifetimes which show appreciable variation with comparatively small changes in photon energy. See

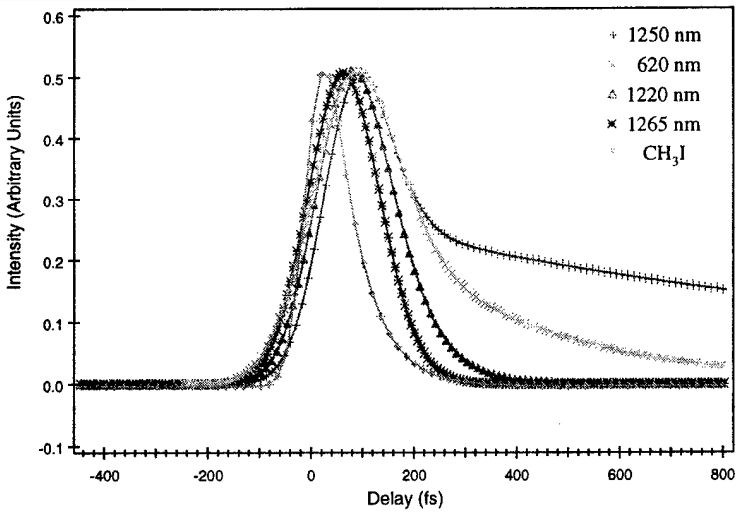

Figure 1 Pump-probe traces of V_8C_{12} at various wavelengths.

Figure 1 and group publications (GP) 522, 531 and 543 listed at the end of this report. In support of enabling a more in-depth study of the molecular properties of Met-Cars, the construction of a new high-intensity cluster source and associated photoelectron energy analyzer were undertaken and are now being implemented.

In addition to revealing the time-resolved behavior of V_8C_{12}, studies focusing on other metal-carbon species (see GP522 and GP543) led to further insights into various potential chromophoric subunits within the Met-Cars. In comparison to species of smaller size, the Met-Cars display increased delocalized electronic character, and their relaxation processes likely include efficient electron-phonon coupling and electron-electron scattering as found in other systems of low ionization potential (IP). The new findings begin to uncover the complexity of the density of excited electronic states involved, and the concomitant relaxation dynamics. They provide a challenge to theoreticians who are engaged in studies of electron dynamics in metallic-like systems. Other experiments have revealed wavepacket motion upon populating the excited state, as detailed in GP531.

Since the discovery of the family of Met-Cars by our group in the early 1990's,[1,2] many interesting phenomena have been observed. Possibly, one of the most exciting characteristics of the Met-Car family is the observation of a large degree of delayed ionization (GP533, GP547),[17] a process observed in only a few other systems, namely ones where the IPs of the clusters are lower than their binding energy (BE). When this condition is met (i.e. IP < BE), the clusters, upon excitation with sufficient energy to ionize, eject an electron following a pronounced delay in time. Those states seen in Figure 1 to possess extended relaxation dynamics are thought to contribute to the delayed ionization phenomenon.

Growing interest is arising in this area due to questions raised by various theoretical groups about the general phenomenon,[18] with suggestions that various relaxation mechanisms likely contribute to a process that was previously thought to be explainable solely in terms of a thermionic emission model. A new reverse field technique to study delayed ionization was implemented in our laboratory during the grant period, and it has been shown to be especially amenable to probing the details of the process at both long and short times, and with a high degree of temporal and intensity resolution. Figure 2 depicts the delayed ionization of Met-Cars as measured with this apparatus. See GP533 and GP542.

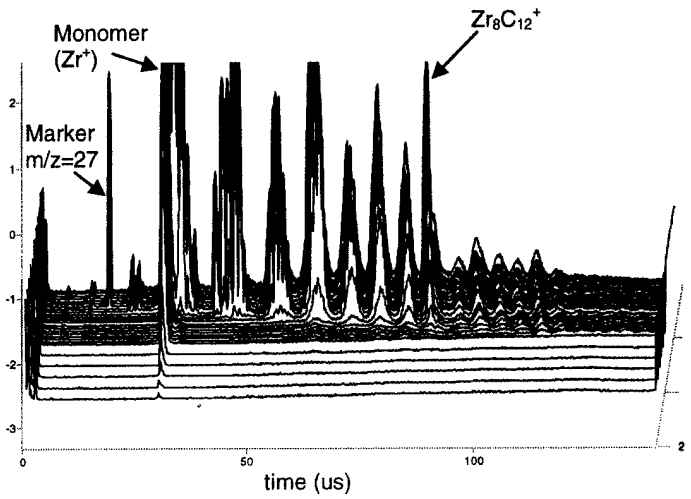

Figure 2 3-D plot of zirconium carbide clusters spectra at increasing delay time from top to bottom (0.05 μs, 0.20 μs steps). The last spectrum displaying the marker peak is the zero time. Note the long delay of the Met-Car and the atomic ion, Zr+.

The time it takes for delayed ionization to occur is approximately one billion times slower than prompt ionization. Clearly, there must be an energy storage mechanism active in the clusters that inhibits the ejection of an electron, even when the clusters are imparted with sufficient energy to undergo prompt ionization. The nature of this energy storage mechanism has not been fully resolved in the case of clusters and other systems of discrete size; some evidence suggests statistical processes in accord with thermionic emission, while other evidence points to behavior associated with excited state phenomena.[18] The thermionic model assumes that the energy, once imparted to the cluster, is stored in its vibrational modes, whereupon all of phase space is sampled.

Equipped with our new method, we successfully measured the delayed ionization of the zirconium Met-Car and C_{60}. These new experiments include the study of delayed ionization that occurs on shorter time scales than were previously measurable. We have been successful in accounting for the new findings (GP557) with the thermionic emission model, which we have modified to more accurately account for the experimental conditions. The modified model fits the data surprisingly well, even considering the new observations at short delay times. These measurements have begun to shed new light on competing processes such as fragmentation of the highly excited species, which will be studied further in the future program.

One such fragmentation process of great interest is the observation of a delayed atomic ion, only observed in the Met-Car system (GP542).[17] An interesting observation showed that, as the delay between the interaction of the ionization laser with the molecular beam and the pulsing of the extraction field is increased, the persistence of the Zr^+ is delayed in time. This is quite unexpected behavior since the atomic ion obviously does not have any vibrational modes in which to store ionization energy. Recent experiments reported in publications GP533 and GP542 provide conclusive evidence that the appearance of the delayed atomic ion is associated with the Met-Car. This phenomenon is not currently understood and will be one subject of study in the next grant period.

As part of our continuing effort to understand the process of multicharging in clusters effected by relatively modest laser fluences, and also to assist in furthering the development of the method we devised for arresting intermediates in fast reactions via Coulomb explosion (GP465), a new technique (MEKER; Minimum Excess Kinetic Energy Required for an ion to be detected) was developed during the grant period. It enables the analysis of high energy multicharged cations produced by Coulomb explosion in a time-of-flight mass spectrometer (TOF-MS). The technique employs energy gating through a manipulation of electric potentials in the Wiley-McLaren lens assembly, and the use of a reflecting electric field. In order to establish

the validity of the new method, water clusters of sizes up to about 20 molecules were first studied. These were irradiated with femtosecond laser pulses to generate protons and multicharged oxygen atoms, and kinetic energy releases of large magnitude were successfully measured, validating the usefulness of this new method. See GP526. Other contributions were made in the area of covariance analysis for assigning the parentage of cluster species involved in the energy release measurements; see GP529 and GP535.

2) Design and Synthesis of CANaMs

a) Deposition of Mass-Selected Cluster Species:

Another major goal has been to develop methods to isolate Met-Cars in quantities sufficient for characterizing their properties in the condensed state. We have now made some very exciting and promising new achievements in this area. Utilizing information acquired from our work dealing with laser ablation and direct laser vaporization of metal-graphite composites,[19] we have found appropriate experimental conditions for acquiring modestly high intensities of Met-Car clusters that can be mass selected and deposited in quantities suitable for analysis by electron diffraction methods. Through the use of the reflectron time-of-flight method extensively developed in our laboratory over many years,[20] we have built a new machine and have been able to acquire soft-landed deposits of zirconium-carbon clusters gated at the Zr_8C_{12} mass. Electron diffraction images showed the existence of nanocrystals with face-centered cubic (fcc) structure having a lattice parameter in excess of 15 Å (Figure 3), a value indicative of cluster assembly. The species correspond to neither oxides nor stoichiometric carbides. The observed lattices of fcc structure

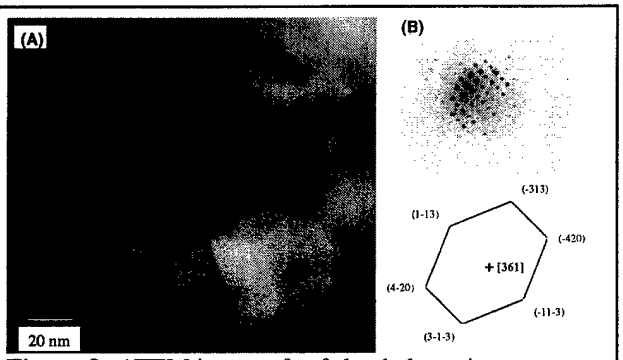

Figure 3 a)TEM image of soft-landed species mass gated at the Met-Car and (b) corresponding diffraction analysis showing an fcc lattice structure with a lattice parameter of 15 Å

are in general agreement with recent theoretical calculations on cluster assembled Met-Cars.[21] Details are provided in GP546.

In addition to the nanocrystals discussed above, several other interesting features were observed in the micrographs (Figure 4). Copious quantities of circular and oblate patterns were observed. In several images, these oblate features were observed to closely resemble images of carbon nanotubes. Currently, the origin and formation of these features is not well understood; however, future experiments should aid in the resolution of these issues. It is significant to note that the concept of nanotubular Met-Cars has been treated theoretically,[22] with the conclusion that such structures can stably exist.

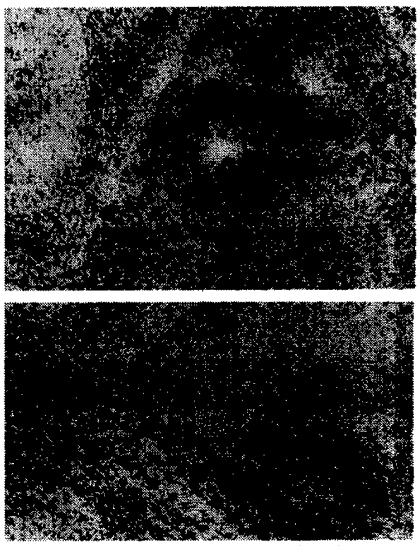

Figure 4 Circular (top) and oblate (bottom) features from TEM images obtained from mass-gated Met-Cars deposition

b) Studies of Other Cluster Building Blocks:

Work is in progress to lay foundations for the production of other materials produced using the concept of cluster assembly. At the present time, particular attention is being devoted to silicon, silicon oxide, and tungsten oxide cluster systems which may be particularly attractive as coatings or substrates for supporting nanoscale materials. The current theme of this work is to investigate the evolving stoichiometry of the clusters upon their growth, and to ascertain what factors influence them to progress toward the bulk crystalline structure as opposed to a unique nanoscale arrangement.

i) Silicon and Silicon Oxides

Currently, there is great technological interest in silicon nanostructures due to confinement-induced optical and electronic properties.[23] Recent reports have shown that, through soft-landing techniques similar to those employed in our group, regular arrays of "magic" silicon

clusters like those described here can be deposited onto a surface,[24-28] opening the door for numerous technological advances. In the past, experiments in our laboratory were conducted on silicon and silicon oxide clusters. More recently, our attention has turned to probing the reactive properties of the smaller clusters that act as building blocks for larger nanostructures. Oxygen etching experiments (GP541) confirmed earlier results[29,30] that identify several cationic clusters with exceptional stability, specifically Si_n^+ where n = 4, 6, 9, and to a lesser extent 13, 14, and 23. A sequential etching reaction mechanism was observed, showing that clusters with exceptional stability not only appeared to be inert towards oxygen, but also evolved as favored reaction products. The same technique was employed in the study of the anionic silicon clusters, resulting in our finding of several exceptionally stable clusters not previously reported.

General trends in the measured rate constants of the smaller species are found to fit well with theoretical predictions of cluster stabilities based on geometrical and electronic considerations. Several different growth mechanisms have been found for the size range above n = 18, and our experiments provide valuable information on the probable stopping points in the morphological transition from prolate to more spherical structures. The oxygen etching technique therefore shows great promise in the characterization of silicon and silicon-containing clusters. Details of our recent findings in this area are presented in GP541.

ii) Embryonic Form of Tungsten Oxide

Contrary to the conventional understanding that atomic clusters behave very differently from their bulk, we have found, in collaboration with Jena and others (see GP556) that a small cluster containing only four tungsten and twelve oxygen atoms, $(WO_3)_4$, bears all the hallmarks of bulk tungsten oxide, WO_3. This observation, based on a synergistic approach involving mass spectrometry, photo-electron spectroscopy, and first principles molecular orbital theory, illustrates the existence of a class of materials whose embryonic forms are tiny clusters with structures analogous to the bulk.

Tungsten oxide materials are important for technological applications such as substrates for film growth, and electrochromic devices. It should be noted that WO_3 was the first electrochromic material discovered that is able to change its optical properties under the action of a voltage pulse.[31] Significantly, we have found that a small cluster, $(WO_3)_4$, has the same inter-atomic bond lengths, atomic arrangements, electronic structure, and energy gap between the highest occupied and lowest unoccupied molecular orbital as the bulk tungsten oxide. In addition, a systematic study of $(WO_3)_x$ (where x = 1 – 4) clusters shows that the W-W bond is broken in W_2O_m clusters when the oxygen content reaches the bulk composition (m = 6). The electron affinities (EA's) and vertical detachment energies of all the $(WO_3)_x$ clusters are nearly the same, indicating that the bulk bonding characteristics are developed even in the smallest cluster having the bulk composition (GP556). It is possible that other embryonic crystalline species may be discovered.

3) Nanostructured High Energy Density Matter: Studies of Aluminum Clusters

Another phase of our current work is devoted to the concept of developing methods for storing materials of high energy content, aluminum being a particularly interesting possibility. Newly acquired information on reactivities of the cluster building blocks is pointing the way to selecting appropriate candidates as counterions for stabilizing nanoscale deposits of these materials. Continuing gas-phase studies of the aluminum cluster system have focused on the introduction of counterions that might stabilize the closed-shell Al_{13}^-, Al_{23}^-, and Al_{37}^-. As we are aware of potential applications in the area of high-energy fuels, our recent efforts have focused on the study of combustible organic species. Experiments were undertaken to attempt the chemical formation of neutral ionic "salts" where an aluminum cluster anion would be bound to a methyl cation.

Thermodynamic considerations (see GP552) confirm that if a reaction between CH_3I and an aluminum cluster yielded an iodide ion, then there must be a substantial amount of interaction

energy between the cluster and the methyl group. Such a reaction was identified, but not confirmed to involve the closed shell species. A comparison of relative reaction rates to previously measured EA's led to the conclusion that the interaction energy between the aluminum clusters and CH_3 that led to the formation of I^- must actually be covalent in nature. Although the exact nature of the covalent bond is currently unknown, the free electron nature of aluminum is known to play a large role in the chemical behavior of its clusters, and so it is possible that the clusters act as superatoms, binding to CH_3 through interactions of the clusters' valence electrons. It is also possible, however, that individual atoms within the clusters engage in the binding in order to sate "dangling bonds".

Although we have not as yet found the most suitable counterion to stabilize the closed shell aluminum species, we did discover a novel neutralization reaction yielding seemingly stable clusters of the type Al_nCH_3. It is thought that these clusters hold promise as candidates for dopants in cryogenic fuels and, more generally, as building blocks for CANAM's. The simplicity of the neutralization scheme also makes this process attractive as a method for the introduction of metal cluster species into molecular electronics. Very recent experiments with HI revealed the surprising highly stable species $A\ell_{13}I$, with the aluminum cluster retaining its integrity. This finding provides strong evidence for the prospect of using the Jellium concept to devise new cluster assembled materials. Work along these lines is continuing.

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