Infrared spectroscopy of gas-phase clusters using a free-electron laser

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Introduction

Laser vaporization in pulsed nozzle sources has made it possible to produce a fantastic variety of atomic clusters. For carbon clusters, variations on these methods made it possible to produce C_{60} and the related fullerenes and nanotubes in macroscopic quantities and to study them using conventional spectroscopy. However, most clusters produced in the gas phase, especially those containing metals, remain largely uncharacterized. Among these are transition metal-carbide,-oxide and -nitride clusters,

The free-electron laser FELIX [1] at the FOM Institute "Rijnhuizen" is ideally suited for a large variety of experiments in gas phase molecular physics. In particular, its wide wavelength tuning range, covering (almost) the full 'molecular fingerprint' region, combined with high power and fluence make FELIX ideally suited to excite gas-phase species such as gas-phase clusters. When FELIX is tightly focussed and resonant with an IR active mode of the cluster, the excitation of the cluster can become very high. For hot clusters, several cooling pathways exist and for strongly bound species with low lying ionization potentials, the thermal emission of an electron (thermionic emission) can become the dominant process. We exploit this thermionic emission to record IR spectra of strongly bound gas-phase clusters. Here, results from experiments of titanium carbide clusters are presented [2,3].

Titanium carbide clusters were investigated before using mass spectrometric techniques. The Ti_8C_{12} "met-cars" clusters were first reported by Castleman and coworkers [4]. They proposed a structure in which both metal and carbon are present in the wall of a symmetric cage with 12 five-membered rings on its surface (T_h symmetry). The $Ti_{14}C_{13}$ cluster was suggested to have a 3x3x3 nanocrystalline cubic structure [5]. Neither the Ti_8C_{12} nor the $Ti_{14}C_{13}$ clusters have been isolated, and there is no spectroscopic data which can confirm or disprove the proposed structures

Experimental

The clusters of interest are produced by pulsed laser vaporization from a solid metal rod in an expansion containing several percent reactant gas. A scheme of the setup is shown in Figure 1. About 20-30 mJ of a frequency doubled Nd:YAG laser (Spectra Physics GCR 150) are focused on the metal surface. The metal rod can have a diameter of 6 or 12 mm and is rotated and translated to regularly expose a fresh spot on the surface. Gas from a pulsed valve (R.M. Jordan Inc.) quenches the laser plasma, clustering and chemical reactions occur and the clusters and carrier gas expand into vacuum. When performing experiments on metal-carbides, 5 % CH_4 (or $^{13}CH_4$) is seeded in argon. For metal oxides, 1-5 % O_2 in argon and for experiments on metal nitrides, 1-5 % N_2 in argon is used. The beam is skimmed and enters the region between the acceleration plates of a reflectron Time Of Flight (TOF) mass spectrometer (R.M. Jordan Inc.) that is 20 cm downstream of the cluster source. Ions produced directly in the source plasma are blocked with an electric field (500-1000 V/cm) perpendicular to the molecular beam that is located directly after the skimmer, about 5 cm prior to the TOF region.

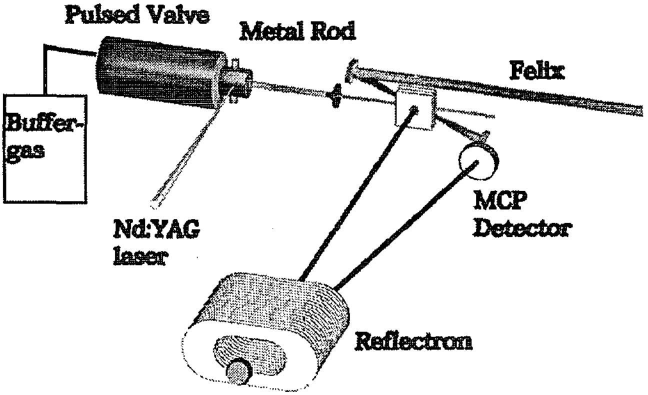


Figure 1: Scheme of the experimental setup. Neutral clusters are generated by laser vaporization techniques. Ions that are created after interaction with FELIX are anayzed in a time of flight mass spectrometer.

The FELIX beam enters the chamber above the axis of the molecular beam and is focussed on the cluster beam using a 7.5 cm focal length gold mirror. The laser beam is focussed back using a 3.75 cm focal length mirror thus effectively doubling the micropulse repetition rate and thus the fluence that clusters are exposed to. The molecular beam moves with a typical beam velocity of 600 m/s. The IR laser beam focus will be, depending on wavelength, between tens of microns to several hundreds of microns in size. The clusters will thus not be exposed to the entire FELIX macropulse but see only up one microsecond of it.

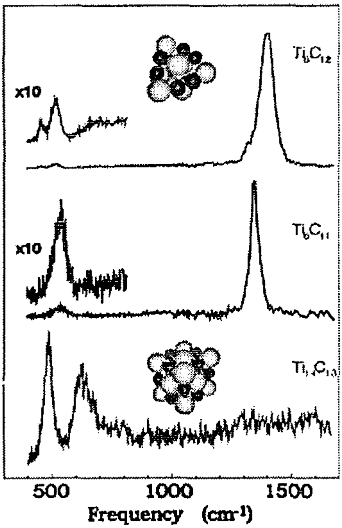
To be able to resonantly pump a large amount of energy into a cluster, the available energy per μs is thus a crucial factor. One feature that really distinguishes FELIX from most other free-electron lasers is that FELIX has the highest output energy per micro-second throughout its tuning range of 5 – 250 μm. The light output consists of macropulses that are 5 μs long and come at a repetition rate of 10 Hz. Each macropulse consists of micropulses that come at a repetion rate of 1 GHz (1 ns spacing) or 25 MHz (40 ns spacing). The micropulse length can be adjusted and range from 300 fs to several ps. The bandwidth is transform limited and can range from 0.5 % FWHM of the central wavelength to several percent. In the 1 GHz mode, the output energy can be up to 150 mJ / macropulse.

Results and Discussion

Figure 2 shows the spectra of three selected clusters as the infrared ionization laser is tuned through the region of 400 to 1670 cm^{-1}. It is immediately apparent that there is a strong wavelength dependence to the ionization yield and that this wavelength dependence is different for the different cluster masses measured. The Ti_8C_{12} "met-cars" cluster has a strong resonance centered at 1395 cm^{-1} (1345 cm^{-1} for the ^{13}C cluster), while the $Ti_{14}C_{13}$ cluster has no measurable resonance in this wavelength region. The frequencies measured can be associated with vibrational resonances for specific structural patterns in these clusters. The 1395 cm^{-1} band in Ti_8C_{12} is logically associated with a C--C stretching mode. The $Ti_{14}C_{13}$ cluster has two resonances in the longer wavelength region at 630 and 485 cm^{-1} (610 and 475 cm^{-1} for the ^{13}C cluster). The low frequency features are particularly strong for the $Ti_{14}C_{13}$

cluster. Bulk TiC with the well-known rock-salt structure, has surface phonon resonances in this region [6].

For Ti_8C_{11} and Ti_8C_{12}, the measured IR spectra are consistent with those expected for the so called "met-car" structures [4]. All larger clusters show IR spectra that are indicative for bulk-like nanocrystalline structures [5]. The spectra of all those larger clusters do not depend strongly on cluster size and show resonances at positions where k=0 phonons of the TiC (100) surface are known to be [6].



The infrared resonance-enhanced multiphoton ionization spectra obtained for the Ti_8C_{12}, Ti_8C_{11} and $Ti_{14}C_{13}$ clusters are shown. In each spectrum the indicated parent molecular ion yield is measured while tuning the infrared wavelength. The structures proposed previously for Ti_8C_{12} and $Ti_{14}C_{13}$ are shown in the figure.

Surprisingly, strongly bound gas phase clusters can also be of importance in astrophysics. In an active collaboration with a group of astrophysicists, we identified a well-known emission feature observed at wavelengths around 20.1 microns in spectra of post-asymptotic giant branch (post-AGB) stars, to the emission of titanium-carbide clusters. For more than a decade, the strange infrared glow coming from certain red giant stars had puzzled astronomers. Originally identified by the Dutch-American IRAS satellite in 1988, this emission became known in the astronomical community as the '21-micron mystery' [7]. Although it was known that meteorites contain micrometer-sized graphite grains with embedded titanium carbide grains, and although isotopic analysis had identified asymptotic giant branch stars as the birth sites of these grains, the possibility that the mysterious 21-micron emission might originate from titanium carbide crystals was never considered. Only after our laboratory measurements revealed the spectroscopic signature of titanium carbide nano-crystals, the mystery was unambiguously solved. In the figure, an IR spectrum of TiC clusters as measured at Rijnhuizen is shown (lower trace). This can be compared to the emission spectrum of a post-AGB star. Clearly, the match is very good.

The results shown here represent the first infrared spectra of gas phase metal clusters. Infrared spectroscopy is particularly problematic for these species due to the intrinsically weak absorption in this region and the limited availability of intense tunable light sources. The method presented here is uniquely suited to strongly bound clusters with low ionization energies, a condition which is met for many pure metal clusters and metal compound clusters. The IR-REMPI method using widely tunable free electron lasers therefore provides unprecedented opportunities to probe the structures and dynamics of size-selected metal, non-metal and semiconductor atomic clusters in the isolated gas phase environment. Recent results on metal-carbide, -oxide and –nitride clusters will be presented in the talk.

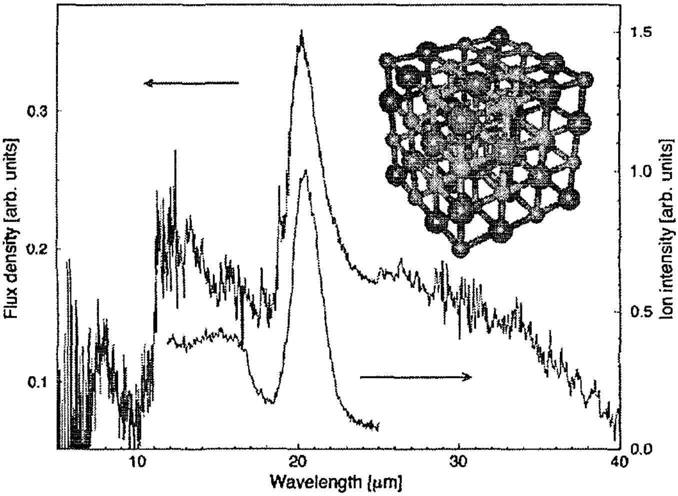


Figure 3: The emission spectrum from the post--AGB object SAO 96709, taken by the ISO satellite (upper trace, left axis) and the wavelength spectra of TiC nanocrystal clusters recorded in the laboratory (lower trace, right axis). Also shown is a pictorial representation of a typical (4x4x4 atom) TiC nanocrystal.

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