ON THE STRUCTURE OF METAL CARBIDE CLUSTERS AND NANO-CRYSTALS.

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In gas-phase cluster science the metal carbide clusters play a special role. In 1992 Castleman and coworkers reported the observation of a new class of clusters, the M_8C_{12} "met-cars". The (8,12) (i.e. the number of metal atoms, the number of carbon atoms) stoichiometry was found to be very stable, and a near-spherical cage structure was proposed. Later, Duncan *et al.* observed another stable configuration, the $M_{14}C_{13}$ cluster, which is thought to be a piece of a face-centered cubic (FCC) lattice, and these clusters are therefore named "nano-crystals". Both clusters cannot be isolated, and no spectroscopic data, which can either confirm or disprove the proposed structures, has been obtained. Their advocated stability is primarily derived from the corresponding "magic" peaks in the mass spectrum.

Here, tunable pulsed infrared (IR) radiation from the free electron laser FELIX is used to selectively excite neutral metal carbide clusters, directly, via their vibrational modes to very high internal energies. For the strongly bound clusters a process called "thermionic emission" can occur, emitting an electron in order to release its excess energy. The resulting ions are detected via a reflectron time-of-flight mass spectrometer.

In the case of titanium carbide clusters, a whole set of masses is found to be stable in the gas phase. Besides (8,12) and (14,13), also bigger clusters having the FCC structure are observed to be stable. By tuning the wavelength of FELIX while monitoring the number of ions, the first infrared spectra of any of these species are obtained, which reveal structural information. In this way the (8,12) stoichiometry is concluded to have C–C bonding whereas $Ti_{14}C_{13}$ has remarkable similarities to bulk TiC.

Furthermore, all the heavier nano-crystals have surprisingly identical spectra showing a single resonance at around 20 micron, which is now believed to account for the infrared emission feature observed by the ISO satellite, originating from AGB stars who are in the later stages of their life.