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Infrared spectroscopy of Ti_8C_{12} 'met-car' cations

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Abstract

Neutral titanium carbide clusters are produced in the gas phase with a standard laser vaporization source and stored in an ion trap for 250 ms after ionization. During this time, the ions are irradiated with infrared light from a free electron laser. Multiphoton absorption and dissociation occurs when the IR light is in resonance with an infrared-allowed vibrational transition. Monitoring the amount of ionic fragments as a function of the IR wavelength yields the infrared spectrum of the parent. The infrared spectrum of the Ti_8C_{12} cation is recorded and compared to the spectrum of the neutral species. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

With the development of pulsed-nozzle laser vaporization sources, a wide variety of exotic clusters have been produced in the gas phase. Chemical and physical properties of atomic clusters containing metal, semiconductor and/or carbon have been investigated extensively [1–3]. Unlike condensed or supported clusters, however, the structural properties of gas phase clusters have been the subject of much debate and remain largely uncharacterized.

One area of interest involves the metal carbide, nitride, and oxide clusters [4–16]. In order to reveal structural information, experiments have been carried out in a number of ways. The earliest conclusions were based on observations of anomalous intensity distributions in mass spectra. Extremely intense mass peaks, indicating a high abundance of clusters with a certain composition, have led to the discovery of fullerenes in the mid 1980s this way. A similar experiment on metal containing carbon clusters unveiled some 'magic' stoichiometries in their mass spectra. Ti_8C_{12} was the first to be found special by Castleman and coworkers [4]. Later studies showed that this stoichiometry is also preferred by other transition metals, such as V, Zr, Hf [5,6], Fe, and Cr [7], and they were referred to as metallo-carbohedrenes or 'met-cars' in short. A structure was proposed of a cage-like cluster with 12 five-membered rings, each containing two metal and three carbon atoms (T_h symmetry). More recent theoretical efforts have suggested a tetrahedral structure with T_d symmetry, depicted in Fig. 2 [17–20]. Ion mobility

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experiments showed that the structure is near spherical, but could not make a distinction between the two symmetries [21], and chemisorption reactivity studies have suggested either eight or four equivalent metal atoms on the surface depending on conditions [22,23].

Spectroscopic measurements on met-cars have been successful in only a few cases. Sakurai and Castleman [24] measured ionization potentials (IPs) via near threshold photoionization spectroscopy. The values they found for the IPs of Ti_8C_{12} and Zr_8C_{12} are 4.40 and 3.95 eV, respectively. Wang, Li, and Wu employed photoelectron spectroscopy (PES) on $Ti_8C_{12}^-$ and other anions [12], obtaining electronic information on the anion and the electron affinity (EA) of the neutral (1.16 ± 0.05 eV (vertical)), consistent with the orbital occupation expected for the T_d structure.

Mass-selected photodissociation experiments on the met-car species were also carried out [7–9], showing that the decomposition of Ti_8C_{12} when irradiated with green light (532 nm) occurs by a sequence of neutral Ti atom losses, whereas Zr_8C_{12} loses ZrC_2 units. Further investigations on titanium carbide clusters by Pilgrim and Duncan revealed the existence of other 'magic' peaks in the mass spectrum attributed to face centered cubic nanocrystalline structures [8,9].

Quite recently, the use of a free electron laser (FEL) opened up new opportunities for acquiring vibrational spectra of gas phase clusters via a technique called infrared resonance enhanced multiphoton ionization (IR-REMPI) [25,26]. We have reported and analyzed the infrared spectra of titanium carbide clusters obtained in this way [10], followed by more recent studies on ZrO [14], VC [13], and MgO [27] clusters. Interestingly, these investigations have even led to the identification of TiC nanocrystals in the surroundings of dying stars [11].

The IR-REMPI technique can be used for obtaining data on neutral clusters and it is selective for extremely stable species (in general $D_0 \gg IP$). After absorption of many photons, stable clusters can thermally ionize, and the resulting ions can be mass-selectively detected, whereas less strongly bound clusters will dissociate instead. Investigating the spectroscopy of cations, on the other hand, requires a different detection scheme. The free electron laser can also be used for multiphoton photofragmentation spectroscopy of mass-selected ions. Similar to IR-REMPI, this technique is called infrared resonance enhanced multiphoton dissociation (IR-REMPD). However, while REMPD has been applied previously to weakly bound ionic clusters [28–33], this method may be problematic for strongly bound species such as metal carbides. Recently, Oomens et al. [34] applied IR-REMPD to polycyclic aromatic hydrocarbon (PAH) cations, produced by ionization of neutral PAHs effusing from an oven.

In the present experiments IR-REMPD is applied to titanium carbide met-car cluster ions stored in an ion trap. The Ti_8C_{12} cluster is a good candidate for a proof-of-principle experiment for two reasons. First of all, experimental conditions can be adjusted such that Ti_8C_{12} is produced in high abundance. Secondly, as already observed in IR-REMPI spectra of neutral Ti_8C_{12}, the absorption cross-section for the C–C stretch mode in Ti_8C_{12} is extremely high. Both factors compensate for the relatively low ion densities that can be achieved in the trap and make it possible to obtain clear photodissociation signals.

Other than serving as a proof-of-principle experiment, there are more interesting reasons to choose Ti_8C_{12}. This experiment also creates the opportunity to compare the spectrum of a stable neutral metal cluster to its corresponding cation for the first time. Investigations on clusters require their ionization for detection. This is usually accomplished with photoionization, in which ionization potentials, cross-sections and/or fragmentation processes provide unwanted complexity in mass spectra. Consequently, there is often confusion about 'magic numbers' in mass spectra and the roles of neutral versus cation stability, as in the case of Ti_8C_{12}. The IR-REMPI spectra showed that this met-car is stable as a neutral and supports the proposed presence of C_2 units in its structure. For the ion, however, no spectroscopic information is available in order to confirm or disprove a similar structure, or to determine whether or not a significant rearrangement will take place upon ionization.

2. Experimental

The experimental setup used in the present experiments is depicted in Fig. 1. Most of the experimental details shown here have been described elsewhere [10,11,13,14,34]. However, an important adjustment is made for the purpose of IR-REMPD in that the normal time-of-flight (TOF) extraction plates are replaced by a quadrupole ion trap. This trap consists of a 2 cm inner diameter toroidal ring and two hyperbolic endcap electrodes. The three electrodes are biased with typically 1000 V, and extraction of the trapped ions toward the reflector is achieved by applying a voltage dip of 200 V on the endcap nearest to the reflector. In addition to the bias voltage, the ring electrode is fed with a fixed 1 MHz radio frequency (RF) voltage with a tunable amplitude adjusted for the masses of interest (typically 1000–2000 V_{p-p}). As shown in the inset, small (1 mm diameter) apertures have been drilled in the ion trap to enable access of the molecular beam and the different laser beams. In these experiments, no collision gas is used for stabilizing the ion trajectories.

The excimer laser providing the UV is operated with KrF, and 1–2 mJ of 248 nm radiation is coupled into the ion trap. The neutral clusters entering the trap are ionized by this light and trapped for 250 ms. During this time, the trapped ions can be irradiated with infrared laser pulses generated by the free electron laser for infrared experiments (FELIX) [35]. The output of FELIX comes in macropulses of 5 μs duration at a repetition rate of 5 Hz. Each macropulse contains a series of 0.5–5 ps micropulses at a repetition rate of 1 GHz. A macropulse contains up to 100 mJ of energy and the bandwidth is Fourier transform limited. The tuning range is 40–2000 cm^{-1}, although only the region from 400 to 1660 cm^{-1} is used in the present experiments. The infrared light is focused in the center of the trap by a concave mirror and backreflected by a second one in order to double the number of micropulses interacting with the stored ions. No neutral beam is present in the trap when the IR light is applied.

When the infrared light of FELIX is tuned in resonance with an infrared allowed transition, the trapped ions can absorb multiple photons. For this, the vibrational anharmonicity has to be small compared to the laser bandwidth and/or internal vibrational redistribution (IVR) must occur rapidly. The train of micropulses, separated by 1 ns in the temporal profile of the FELIX macropulse, is favorable for this to happen. If the ions are heated sufficiently, dissociation occurs. The resulting fragment ions and the remaining parent ions remain confined in the trap as long as the RF voltage is on. To extract the contents of the trap, the RF is switched off just before the voltage dip of one of the endcaps as described before. The ions are accelerated and mass-analyzed in the reflectron TOF mass spectrometer. The fragment ion yield and/or

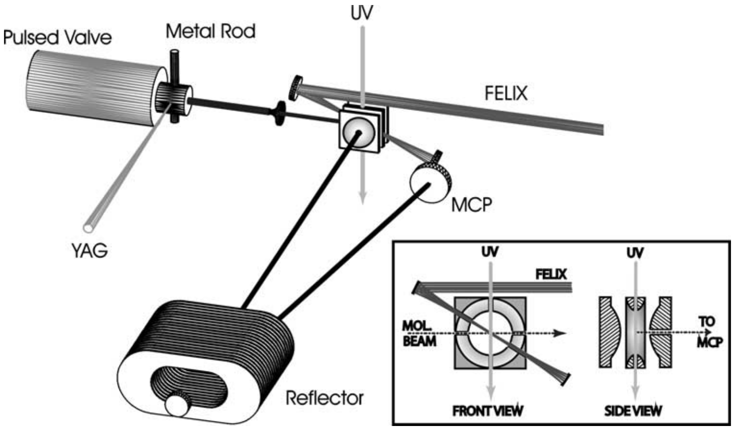

Fig. 1. A schematic diagram of the molecular beam machine with the ion trap used for ion storage and extraction.

the depletion of the parent ion is recorded with a digital oscilloscope as a function of the IR wavelength to obtain a spectrum.

3. Results and discussion

Fig. 2 shows two mass spectra that originate from neutral metal carbide clusters which are ionized with 248 nm photons, and are stored in the ion trap for 250 ms. The upper trace demonstrates the mass distribution of the ions produced initially by photoionization. The lower trace shows the fragmentation which occurs when the ions are irradiated with two macropulses (each 40 mJ) of FELIX light. The mass peaks obtained in these spectra have relatively low resolution because of the extraction process out of the ion trap. Furthermore, the small apertures in the ion trap cause the ion yield in this configuration to be lower than that in a standard molecular beam experiment using TOF plates.

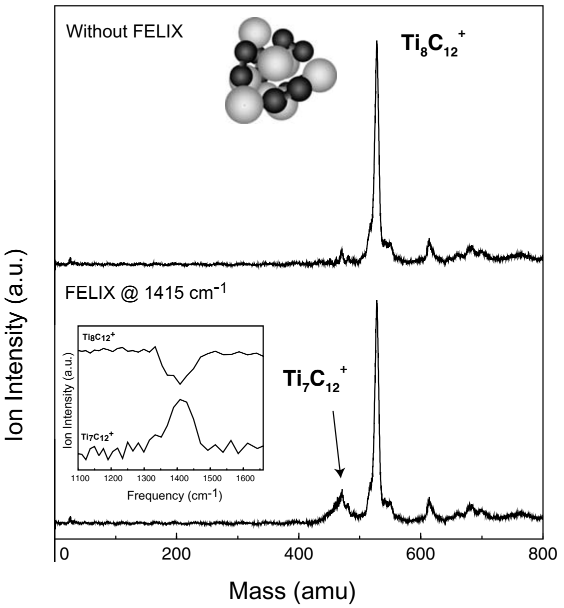

Fig. 2. Two mass spectra of titanium carbide ions stored in a trap for 250 ms. The upper trace shows the mass distribution in the trap without any IR light applied. In the lower trace the masses in the ion trap have been exposed to FELIX at 7.3 μm, leading to dissociation of $Ti_8C_{12}^+$to$Ti_7C_{12}^+$. The inset shows an IR-REMPD spectrum of $Ti_8C_{12}^+$ (upper trace) showing a clear depletion peak at around 1415 cm^{-1}. As a result, the ion yield of $Ti_7C_{12}^+$ increases in this region (lower trace).

Both mass spectra look very similar. A large ion signal is obtained at a mass corresponding to that of the well-known Ti_8C_{12} cation among several weaker peaks from other titanium carbide species. As seen in the upper trace, only a small amount of $Ti_7C_{12}^+$ is produced in the ion trap after UV ionization. When FELIX is applied and tuned to 7.3 μm, however, a significant increase is observed in the number of $Ti_7C_{12}^+$ ions (lower trace). From visible laser photodissociation experiments, it is already known that $Ti_7C_{12}^+$ is a fragment of $Ti_8C_{12}^+$ [7]. In order to verify the source of this ion and to obtain an infrared spectrum for $Ti_8C_{12}^+$, the amount of the different titanium carbide species are recorded as a function of the FELIX wavelength.

The inset in Fig. 2 displays the intensity of $Ti_7C_{12}^+$ and $Ti_8C_{12}^+$ while FELIX is scanned in the region between 1100 and 1660 cm^{-1}. Although FELIX is actually tuned from 400 to 1660 cm^{-1}, a significant change in ion intensity is only observed for these clusters in the displayed frequency range. Other titanium carbide cluster ions show no measurable frequency dependence as a function of the FELIX wavelength.

For $Ti_8C_{12}^+$ depletion of the ion signal is observed at 1415 cm^{-1}. At the same frequency, an increase in the ion signal for $Ti_7C_{12}^+$ can be observed. The intensities of the peaks have been scaled in this figure for comparison. Comparing absolute values, only 40% of the depleted parent ions can be detected in the $Ti_7C_{12}^+$ fragment channel. A plausible explanation might be the translational energy fragments receive upon dissociation, leading to unstable trajectories in the trap and loss of signal.

From these spectra it is clear that $Ti_8C_{12}^+$ is the parent dissociating to $Ti_7C_{12}^+$ when it is irradiated with IR light at 1415 cm^{-1} (IR-REMPD). Although the infrared spectrum of the Ti_8C_{12} cation could be extracted by just using the photo-depletion spectrum, the ion yield of $Ti_7C_{12}^+$ is used for this, because of its (almost) zero background.

This is the first infrared spectrum for any gas phase metal cluster cation and a comparison can be made with previous results on the correspond-

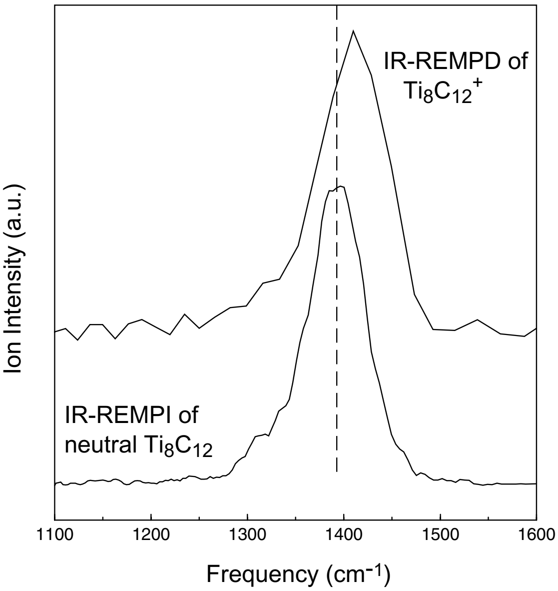

Fig. 3. Comparison of the infrared spectra of the Ti_8C_{12} neutral and cation. Relative to the spectrum of the neutral, a blue shift of about 20 cm^{-1} is observed for the cation.

ing neutral system [10]. Fig. 3 compares the IR-REMPD spectrum of the Ti_8C_{12} cation obtained here with the IR-REMPI spectrum of neutral Ti_8C_{12}. It is readily seen that, after careful laser calibration, a blueshift is observed for the cation of about 20 cm^{-1}. The FWHM of both peaks are comparable (82 cm^{-1} for the cation versus 71 cm^{-1} for the neutral) and the same asymmetric behavior in the lineshape is observed with a more gradual intensity increase on the low frequency side. The mode at 1415 cm^{-1} for the Ti_8C_{12} cation is logically associated with a C–C stretching mode analogous to the assignment of the 1395 cm^{-1} peak for the neutral. Removing an electron barely shifts the resonance, indicating that no significant structural rearrangement takes place upon ionization. The asymmetric shape observed in both spectra originates from the anharmonicity of the normal mode in resonance, and is typical for a multiphoton absorption process. Unfortunately, the dissociation threshold for the Ti_8C_{12} cation is not accurately known, preventing a more detailed comparison between the IR-REMPI spectrum (with the known IP) and the IR-REMPD spectrum.

Besides the region shown in Fig. 3, the infrared spectrum for the neutral has two more resonances around 500 cm^{-1}, believed to belong to modes involving metal–carbon stretches. Their infrared intensity in the IR-REMPI spectrum is already an order of magnitude less compared to the high frequency mode at 1395 cm^{-1}, and these modes could not be observed for the ion.

Taking the theoretically most stable structural model for Ti_8C_{12}, which has tetrahedral (T_d) symmetry, the molecular orbitals of the met-car are $(1a_1)^2(1t_2)^6(1e)^4(1t_1)^6(2a_1)^2$ for the 20 valence electrons available (the other 12 valence electrons are localized in the six C_2-units) [9,20]. The molecular orbitals $1a_1, 1t_2$, 1e, and $1t_1$ are bonding orbitals and the $2a_1$ orbital, which is also the highest occupied one in the ground state (HOMO), is an antibonding orbital. The lowest unoccupied molecular orbital (LUMO) is the triply degenerate $2t_2$ antibonding orbital. So the Ti_8C_{12} anion, neutral, and cation have degenerate $^2T_2$, non- degenerate $^1A_1$, and non-degenerate $^2A_1$ electronic ground states, respectively. Both the low IP and the low EA can be easily understood in this picture. In their discussion of the photoelectron spectrum, Wang and Cheng [12] argue that since the HOMO for the anion is degenerate, $Ti_8C_{12}^-$ is subject to Jahn–Teller distortion in contrast with the neutral and cation. As a result, a geometry change is expected when the HOMO electron in the anion is detached. However, both the neutral and cation are non-degenerate, and ionizing the neutral would not give rise to a significant geometry change. Removing one electron from the $2a_1$ orbital only results in an increase in the overall bond order by a half, indicating a more strongly bound cluster.

The comparison between the infrared spectra of the Ti_8C_{12} neutral and cation in Fig. 3 supports this idea. Upon ionization, a small blue-shift is observed for this vibrational resonance, implying a stronger bond and confirming that the molecular orbitals influence the stretch vibration of the C_2-units. This vibration is identified in both cases, suggesting a similar structure containing C_2 units for both the ion and the neutral. Accordingly, the stability of the Ti_8C_{12} ion parallels the neutral, consistent with the high abundance of this cluster in mass spectra observed by different groups with different approaches involving ions and neutrals.

4. Conclusions

The results shown here demonstrate the feasibility of obtaining infrared spectra of strongly-bound metal clusters via IR-REMPD in an ion trap. Neutral clusters are ionized and held in the ion trap, while excitation on the vibrational modes of the ions leads to fragmentation. This is achieved with an unusual yet powerful IR laser, focused into the trap. Dissociation lifetimes are compensated for because the ions are stored another 250 ms before extraction to the detector. In this respect, trapped ion photodissociation has an advantage over other experimental detection schemes. By recording the ion yield of both parent and fragment ions as a function of IR wavelength, infrared spectra can in principle be obtained for any ionized cluster in the trap. Comparing this technique to IR-REMPI, the clusters under investigation are now ions rather than neutrals, and the technique is not restricted to clusters with high stability. The present design of the ion trap, however, results in weaker signals because of the small molecular beam aperture and because the ion trajectories in the trap do not overlap well with the IR laser, prohibiting their efficient excitation. Future design improvements are expected to increase the available ion density and the detection sensitivity.

In the present experiments IR-REMPD is applied to titanium carbide met-cars. When FELIX is tuned to 7.3 μm, dissociation of $Ti_8C_{12}^+$ is observed via loss of a Ti atom. By tuning FELIX, infrared spectra are taken for $Ti_8C_{12}^+$ showing a peak at 1415 cm^{-1}. This mode is assigned to the C–C stretch vibration in the ion. When comparing to the neutral infrared spectrum, a blue-shift of 20 cm^{-1} is observed for this mode. This suggests that the cation is a stronger bonded cluster than the neutral. This is consistent with theory, which predicts the HOMO electrons to be antibonding. Furthermore, the similarities in the infrared spectra of both the Ti_8C_{12} neutral and cation indicate that there is no significant structural rearrangement upon ionization and that there is conservation of the relatively high stability for this cluster. Although this is rather speculative, it is tempting to conclude that the T_d symmetry remains intact when an electron is removed.

The experiment presented here invites an ensemble of other candidates to be investigated. Other metal carbide systems, such as the cubic nanocrystals, can be studied via their dissociation behavior. Moreover, this technique can be applied to other, somewhat less stable systems, such as metal–ligand complexes. Since dissociation thresholds are much lower for these species than for metal carbide clusters, IR-REMPD is expected to be more efficient, allowing the detection of weaker vibrational modes.

Recently, preparations have been made to conduct another type of experiment in this setup. Adding a second pulsed valve near the ion trap region allows investigations of the reaction dynamics of the molecules and clusters of interest. Ti_8C_{12} is well known for instance to oxidize, forming $Ti_8C_{12}O$. Pulsing oxygen into the ion trap while $Ti_8C_{12}^+$ ions are stored may induce this reaction to occur. Employing IR-REMPD on the oxidized met-cars should then induce new features in its infrared spectrum, possibly revealing more information on its structure.

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