

Vibrationally Resolved Photoelectron Spectra of TiC_x^- ($x = 2-5$) ClustersXue-Bin Wang, Chuan-Fan Ding, and Lai-Sheng Wang*[†]

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Vibrationally resolved photoelectron spectra are obtained for the small TiC_x^- ($x = 2-5$) clusters. Adiabatic electron affinities (EAs) and low-lying electronic states are measured for the neutral TiC_x clusters. While the EAs are similar for the series of clusters, 1.542 eV for TiC_2 , 1.561 eV for TiC_3 , 1.494 eV for TiC_4 , and 1.748 eV for TiC_5 , the observed ground-state vibrational frequencies decrease for the larger clusters: 560 cm^{-1} for TiC_2 , 650 cm^{-1} for TiC_3 , 440 cm^{-1} for TiC_4 , and 240 cm^{-1} for TiC_5 . The results are interpreted using ring-type structures that are known to be the ground-state structure for similar YC_x and LaC_x clusters. The current results provide the first and only spectroscopic and electronic information that will be valuable to test future theoretical calculations to understand the detailed structure and bonding of these simple titanium carbon clusters.

The interaction between transition metal and carbon is important in understanding several cluster materials, including endohedrofullerenes, catalytic growth of carbon nanotubes, and metallocarbohedrenes (metcar). Metcars, containing 8 metal atoms and 12 carbons, were found to form particularly for the early transition metals, $\text{Ti}_8\text{C}_{12}^+$ being the most prototypical.^{1,2} However, despite intensive research on the metcars over the past several years, the structure and bonding of these unique clusters are still not well understood. Experimentally, this information may be obtained by studying small titanium carbide clusters, Ti_mC_n . Understanding the detailed structure and bonding of the small carbide clusters systematically should lead to valuable insight into the growth and formation of the metcars.³⁻⁷

Photoelectron spectroscopy (PES) of size-selected anions is particularly powerful in providing electronic and spectroscopic information for these clusters. We have been interested in investigating the electronic structure of the metcars using PES.⁸⁻¹⁰ In this Letter, we report the first vibrationally resolved PES spectra for a series of simple titanium carbon clusters, TiC_x^- ($x = 2-5$). Vibrational frequencies, electron affinities (EAs), and rich low-lying electronic excited states are obtained for these clusters.

The experiments are conducted on a magnetic-bottle time-of-flight PES apparatus equipped with a laser vaporization supersonic cluster source.¹¹ A pulsed laser beam, 532 nm from a Q-switched Nd:YAG laser, is focused down to a 1 mm diameter spot onto a pure titanium carbide (TiC) disk target to generate the desired TiC_x^- clusters, which can also be produced by vaporizing a pure Ti target with a hydrocarbon-seeded He carrier gas. However, the use of the pure TiC target eliminates the possibility of H-containing species, which may contaminate the Ti_nC_m^- clusters due to the broad isotope distribution of Ti. The Ti_nC_m^- clusters, entrained into a He carrier gas, undergo a supersonic expansion and are skimmed once to form a collimated beam. The negative clusters are then extracted perpendicularly from the beam by a high-voltage pulse into a field free time-of-flight (TOF) tube for mass analyses. The cluster of interest is mass-selected and decelerated before being

detached by a laser beam (532 and 355 nm) from a second Q-switched Nd:YAG laser. The photoelectrons are collected at nearly 100% efficiency by the magnetic bottle and analyzed in a 3.5 m long TOF tube. The photoelectron TOF spectra are converted to electron-binding energy spectra, calibrated by the known spectrum of Cu^- . The present resolution is better than 30 meV for 1 eV electrons.

We have obtained data for a wide range of Ti_nC_m^- clusters. In the present letter, we report on the vibrationally resolved PES spectra for the simplest series containing only one Ti atom. The TiC^- diatomic species and other clusters containing a single C atom are not observed under our experimental conditions with substantial abundance and are not studied presently. This is probably due to the fact that the C or C^- atomic species are not very abundant in the plasma.

The spectra of TiC_x^- ($x = 2-5$) are shown in Figures 1 and 2 at 355 and 532 nm, respectively. The 355 nm spectra reveal many low-lying excited states with partially resolved vibrational structures for the neutral TiC_x clusters, as labeled by the letters in Figure 1. The 532 nm spectra each display well-resolved vibrational structure for the ground state, except for that of TiC_5^- , where vibrational structure is only partially resolved. At the lower photon energy, the spectra are better resolved due to the energy dependence of resolution in the TOF-type electron analyzer. We also observed strong photon energy dependence for certain features. Notably, the A and B features of TiC_2^- and the B feature of TiC_4^- are enhanced at 532 nm while the A feature of TiC_3^- is observed to be slightly reduced at 532 nm. Weak hot band features can also be seen as tails on the low binding energy side in each spectrum. A very weak feature shown in the 355 nm spectrum of TiC_5^- at 1 eV (Figure 1, labeled as “?”) is due to a slight contamination of Ti_2C^- , which has the same mass as TiC_5^- . This contamination is not present in the 532 nm spectrum of TiC_5^- (Figure 2). The observed energies and vibrational frequencies are listed in Table 1 for all four clusters. The lowest binding energy feature in each spectrum represents the adiabatic EA of the corresponding neutral cluster and can be determined relatively accurately because of the vibrational resolution. There are also higher energy features in each spectrum that are not listed in Table 1 due to poorer statistics at the higher binding energies.

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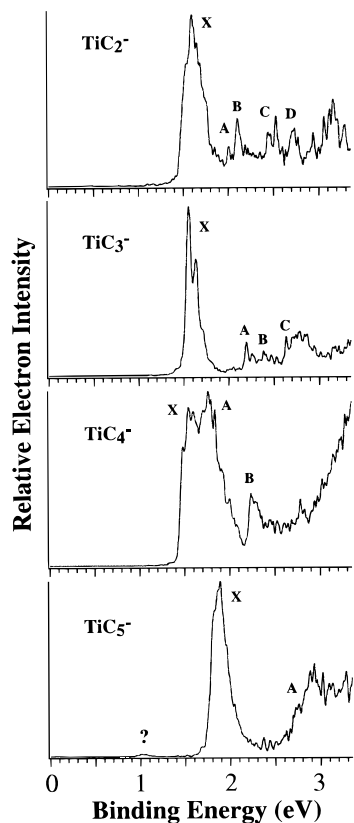


Figure 1. Photoelectron spectra of TiC_x^- ($x = 2-5$) at 355 nm (3.49 eV). The letters indicate individual electronic states observed for the neutral clusters. Binding energies for these states are listed in Table 1.

Several observations can be made about the spectra: (1) the EAs are similar for all the clusters, and there seems to be a slight even-odd alternation: TiC_x clusters with an odd number of C's having slightly higher EAs than the neighboring TiC_x clusters with an even number of C's; (2) there is a rather high density of low-lying electronic excited states; (3) the ground-state vibrational frequency, most likely due to the totally symmetric mode, increases from TiC_2 to TiC_3 and decreases from $\text{TiC}_3 \rightarrow \text{TiC}_4 \rightarrow \text{TiC}_5$. The detailed interpretation of all the observed features will require accurate theoretical calculations. We will attempt to give a preliminary interpretation and hope that these results will inspire more theoretical efforts. A preliminary explanation is possible based on theoretical information available for other MC_x clusters, particularly for YC_x and LaC_x , which have received more theoretical attention.¹²⁻¹⁴

The only small TiC_x clusters calculated previously are the TiC and TiC_2 species.^{3,15} The calculated binding energy (D_e) for TiC is ~ 3.0 eV and the vibrational frequency between 700 and 800 cm^{-1} .¹⁵ TiC_2 has been calculated to be a C_{2v} molecule where Ti is side-bonded to the C_2 .³ Because of the high EA of C_2 , the $\text{Ti}-\text{C}_2$ bonding is characterized by both covalent and ionic characters. There are no calculations on the higher TiC_x clusters. However, extensive theoretical studies have been done on the related YC_x and LaC_x clusters for $x = 2-6$.^{12,13} The most favorable structures for these clusters are all ring-type.¹² In particular, the YC_2 and LaC_2 are similar to TiC_2 , all having C_{2v} structures.

Although bulk TiC carbide is a refractory material with very high cohesive energy, the binding energy in the TiC molecule is rather small, about half of the binding energy of a $\text{C}-\text{C}$ bond. Therefore, the higher TiC_x clusters may all have ring-type structures similar to YC_x and LaC_x . TiC_3 most likely has the ring structure since it would be much less favorable to gain an extra $\text{Ti}-\text{C}$ bond by breaking a much stronger $\text{C}-\text{C}$ bond in

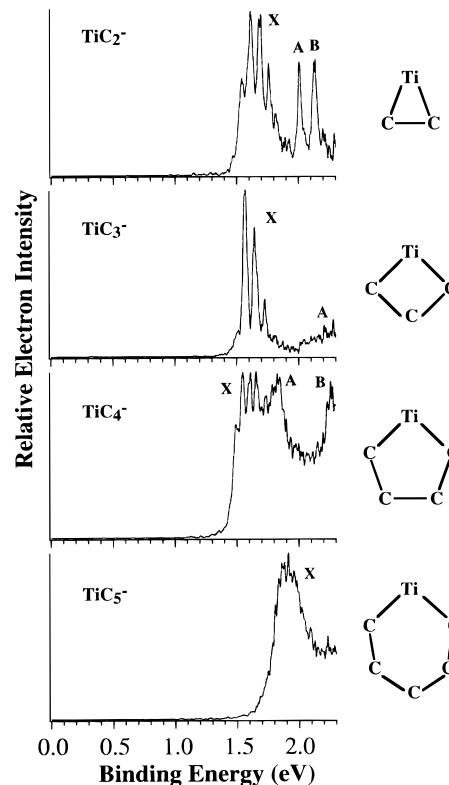


Figure 2. Photoelectron spectra of TiC_x^- ($x = 2-5$) at 532 nm (2.33 eV), showing vibrationally resolved spectra for the ground-state features. Note the strong photon energy dependence of the A and B states of TiC_2 . Schematic ring-type structures proposed for the clusters are also shown.

TABLE 1: Observed Binding Energies (BE) and Spectroscopic Constants for the Ground and Low-Lying Excited States of TiC_x ($x = 2-5$)

| | | BE (eV) | term value (eV) | vib. freq. (cm^{-1}) ^a |
|----------------|---|-------------------------|-----------------|--|
| TiC_2 | X | 1.542 (20) ^b | 0 | 560 (50) |
| | A | 2.004 (20) | 0.462 (28) | |
| | B | 2.115 (25) | 0.573 (32) | |
| | C | 2.440 (30) | 0.898 (36) | 720 (50) |
| | D | 2.708 (60) | 1.166 (63) | |
| TiC_3 | X | 1.561 (15) ^b | 0 | 650 (30) |
| | A | 2.195 (30) | 0.634 (23) | 500 (60) |
| | B | 2.395 (30) | 0.834 (23) | 500 (60) |
| | C | 2.635 (30) | 1.074 (23) | |
| TiC_4 | X | 1.494 (20) ^b | 0 | 440 (40) |
| | A | 1.680 (60) | 0.186 (63) | |
| | B | 2.235 (40) | 0.750 (45) | |
| TiC_5 | X | 1.748 (50) ^b | 0 | 240 (60) |
| | A | 2.695 (50) | 0.947 (70) | |

^a Totally symmetric mode. ^b The BE of the ground-state represents the adiabatic electron affinity.

an alternative CTiC_2 type structure. However, for TiC_4 and TiC_5 , alternative structures, such as C_2TiC_2 and C_2TiC_3 , may be comparable to the ring-type structures since two extra $\text{Ti}-\text{C}$ bonds are gained. Our observed electron affinities and the ground-state vibrational frequencies for the TiC_x clusters provide indirect evidence supporting the ring-type structures, which are schematically shown in Figure 2 next to each spectrum.

In the TiC_x^- anions, the extra electron likely occupies orbitals of Ti 4s3d character. Thus the EA of the neutral cluster is expected to be sensitive to the environment or coordination of the Ti atom. In previous works on metal oxides, such as MO_x type clusters,¹⁶ we found that the EA always increases with the number of O atoms in the MO_x clusters. The fact that the TiC_x clusters all have rather similar EAs suggests that the environment

around Ti is probably similar in all the clusters, consistent with the ring-type structures, as shown in Figure 2. Furthermore, it is well-known that the EAs of the linear C_x clusters exhibit even-odd alternations for $x < 10$.¹⁷ We suspect that the weak even-odd alternation in the EAs of the TiC_x clusters is related to that of the pure C_x clusters, further supporting the ring-type structures.

The resolved vibrational frequencies for the TiC_x clusters should be due to the totally symmetric modes that are allowed in the photodetachment transition. The observed frequencies for the ground states show interesting trends, which can be rationalized using the ring-type structures. The 560 cm^{-1} frequency observed in TiC_2 should be due to the Ti-C₂ stretching mode. Interestingly, this frequency is nearly identical with that recently observed for YC_2 (561.1 cm^{-1}).¹⁸ The frequency observed in TiC_3 is surprisingly higher than that of TiC_2 . This can be explained by the particular vibrational mode involved. The TiC_3 ring should have two symmetric ring-breathing modes, one involving the C-C motion on the opposite corners and the other involving the Ti-C stretching along the 2-fold axis. The observed frequency should be due to the latter mode since the detached electron is expected to be from an orbital of mostly Ti 4s3d character. The frequency of this mode should be comparable to that of the Ti-C diatomic. Indeed, the 650 cm^{-1} frequency observed for TiC_3 is very close to the $700\text{--}800\text{ cm}^{-1}$ calculated for TiC .¹⁵ The decrease of the observed vibrational frequencies in TiC_4 and TiC_5 may be attributed to the increasing ring sizes. The larger rings are also expected to be floppy, consistent with the broad Franck-Condon envelopes observed in the ground states of TiC_4 and TiC_5 .

Finally, it is interesting to compare the current TiC_x clusters to the FeC_x clusters that were studied previously.¹⁹⁻²² The FeC_x clusters in the same size range have quite different EAs with strong size dependence.²⁰⁻²² FeC_4^- and FeC_5^- both give broad and complicated PES spectra, suggesting large geometry changes between the anions and the neutrals. It was suggested that the very small FeC_x clusters have linear structure and that there is a linear to ring transition from FeC_3 to FeC_4 . There is evidence from both PES and ion mobility experiments that FeC_5^- exists in two isomer forms, the linear chain and the ring.^{19,22} Comparatively, the TiC_x clusters all appear to have the ring structures. This is probably due to the stronger Ti-C bonding, compared to the Fe-C bonding.

In conclusion, we report the first vibrationally resolved photoelectron spectra of a series of TiC_x clusters for $x = 2\text{--}5$. The observed electron affinities and ground-state vibrational frequencies are tentatively interpreted to support ring-type structures for these clusters. Ab initio calculations will be needed to confirm this interpretation. Clearly, theoretical calculations on these clusters and other small Ti_nC_m clusters

are much desired if one is to elucidate the growth and the structure and bonding of the Ti_8C_{12} metcar. The data presented here will be valuable to test such future calculations.

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