Ionization Potentials for the Titanium, Zirconium, and the Mixed Metal Met-Cars

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Photoionization spectra of the titanium and zirconium metallocarbohedrene clusters (Met-Cars) of the stoichiometry $Ti_{8-x}Zr_xC_{12}$ ($x = 0-4$, 8) have been investigated near threshold. Study of the photoionization efficiencies of these species at different photon energies led to a determination that the ionization potentials (IP's) for the titanium and zirconium Met-Cars, Ti_8C_{12} and Zr_8C_{12}, are 4.40 ± 0.02 and 3.95 ± 0.02 eV, respectively. The IP's for the binary metal Met-Cars, $Ti_{8-x}Zr_xC_{12}$ ($x = 1-4$), were also determined, and it was found that the IP decreases continuously from that of the pure titanium Met-Car toward that of the pure zirconium Met-Car as the number of substituting zirconium atoms increases.

I. Introduction

Ever since the discovery in our group of metallocarbohedrene clusters (or Met-Cars for short), which are exceptionally stable species with the stoichiometry M_8C_{12} (M = Ti,[1] V, Zr, Hf,[2] Nb,[3] Cr, Fe, Mo[4]) or $Ti_{8-x}M_xC_{12}$ (M = Zr, Hf,[5] Y, Nb, Mo, Ta, W, and Si[6,7]), many experimental and theoretical studies have been conducted to explore their properties as a new class of material. Among them, determining their ionization potentials (IP's) and electron affinities contributes to an understanding of their electronic structures.[8] In addition, knowledge of their IP's is important to elucidate the unique feature of the observed delayed ionization of these species.[9−11] Furthermore, comparison between theoretically predicted and experimentally measured IP's provides a good test for both types of investigation, which hence bridges the gap between theoretically constructed pictures of Met-Cars and experimental observations.

Results of previous theoretical[12−17] and experimental[18−20] studies of the IP's of pure metal Met-Cars are summarized in Table 1. The upper part of Table 1 contains two groups of calculated IP's; one for Met-Cars of a pentagonal dodecahedral cage structure with T_h symmetry first proposed by our group,[1] and the other for those of a tetrahedral cage geometry with T_d symmetry, which was predicted by Dance to be the most stable structure.[21] Considering these predicted numbers, it is found that the two types of Met-Cars have significantly different IP's. For instance, for the titanium Met-Car, the IP has been calculated to be equal to or greater than 5.3 eV for T_h-symmetry Met-Cars whereas it has been predicted to be equal to or less than 4.7 eV for T_d-symmetry Met-Cars. A similar trend is found for the zirconium Met-Car although the number of the calculations is fewer. Therefore, this suggests that, by measuring the IP's of the Met-Cars experimentally, progress may be made toward answering the controversy about the geometric structure of Met-Cars, which has been discussed for several years.[1,5,17,21−36]

As for experimental studies about the IP's of the Met-Cars, only very limited investigations have been conducted. Two of them involved study of the collision-induced dissociation of $M_9C_{12}^+$ (M = Ti, V) and demonstrated that the IP for the titanium (or vanadium) Met-Car is lower than the IP of a titanium (vanadium) atom (6.82 eV for Ti and 6.74 eV for V).

TABLE 1: Ionization Potentials (eV) for the Titanium, Vanadium, Zirconium, and Niobium Met-Cars[a]

	Ti_8C_{12}	V_8C_{12}	Zr_8C_{12}	Nb_8C_{12}	ref
	Theoretical Calculations				
symmetry					
T_h	6.02[b]				12
	5.33	5.92	4.89		13
	5.92				14
	5.4				15
T_d	4.5				15
	4.37	5.53	3.99		16
	4.7[b]/4.60[c]	5.5[b]	4.2[b]/4.10[c]	5.4[b]	17
	Experimental Measurements				
method[d]					
CID	<6.82				18
CID		<6.74			19
PI	4.9 ± 0.2	>5.76	>5.76	>5.76	20

[a] Unless noted, theoretically calculated IP's are not specified to be either vertical or adiabatic in the references. [b] Vertical IP's. [c] Adiabatic IP's. [d] CID: collision-induced dissociation. PI: photoionization. See text for details.

These upper limits were determined on the basis of observation that, as a result of dissociation of the $M_9C_{12}^+$ ion, the positive charge is carried by the Met-Car instead of the evaporated atom, i.e., $M_9C_{12}^+ \rightarrow M + M_8C_{12}^+$. This result implies that the IP of the Met-Car is lower than that of the metal atom.[18,19]

A more straightforward method to determine the IP's, i.e., photoionization spectroscopy, was employed for Met-Cars by Brock and Duncan.[20] They obtained 4.9 ± 0.2 eV for the IP of the titanium Met-Car. For vanadium, zirconium, and niobium Met-Cars, it was concluded that the IP's exceed 5.76 eV, which was equal to the highest photon energy available with their photoionization laser setup. However, the values of the IP's were determined indirectly by studying the dependence of signal intensities upon the power of the ionization laser employed in their study; photoionization efficiency (PIE) curves near threshold, which are commonly utilized in IP measurements, were not investigated. Therefore, the disagreement in Table 1 between the prior experimentally measured and theoretically predicted IP's does not necessarily mean the accuracies of the theoretical calculations were insufficient.

Stimulated by the inconsistencies between the theoretical and experimental values, we recently conducted a photoionization

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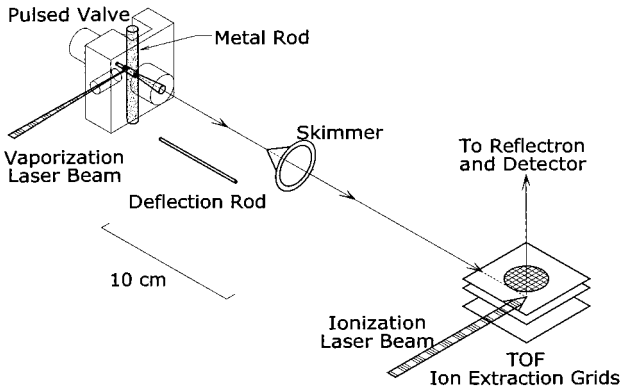

Figure 1. Schematic of the experimental setup: cluster source, deflection rod, skimmer, TOF lens, and the laser beam paths.

spectroscopy study of the pure and mixed titanium−zirconium Met-Cars to determine their IP's with a more direct approach. The objective of this paper is to present the measured PIE spectra and IP values deduced from the experiments. In addition, the discrepancy between the IP's determined in the present study and those by Brock and Duncan is discussed. The measured IP's are compared with the theoretically predicted values, and are also rationalized with a recent finding by our group about the delayed ionization of Met-Cars.

II. Experimental Section

The apparatus used in this work was a time-of-flight (TOF) mass spectrometer coupled with a laser-induced plasma reactor as a cluster source and a dye laser for photoionization (Figure 1). A plasma reaction was induced in the presence of a gas jet by impinging a strong laser beam of 532-nm light from a Nd:YAG laser (Spectra Physics GCR-150) focused by a lens of 70-cm focal length onto a metal rod of 6.35 mm in diameter. The gas jet, which was composed of a mixture of methane (15% in volume) and helium, was ejected from a pulsed valve (General Valve 99-43-900; a modified version of a standard General Valve Series 9 with a short pulse duration[37]) operated at an absolute stagnation pressure of about 700 kPa. The laser power employed for vaporization in the present experiments was set so that a dominant Met-Car peak was seen in the mass spectra;[38] a detailed description is given later in this section. A fresh metal surface of the metal rod was exposed on each laser shot by a rotational and translational motion controller. Mixed metal Met-Cars were produced with alloy rods (The Metron Group) of titanium and zirconium. To produce mixed metal Met-Cars of various stoichiometry, alloy rods of 9 or 15% molar ratio of zirconium content were used. The vaporized metal atoms and the gas from the valve were mixed in a cylindrical "waiting room"[39,40] of 3-mm inner diameter and 10-mm length, in the cluster source body, which was made of Teflon, where plasma-induced dehydrogenation of methane molecules, followed by formation of metal−carbon clusters, took place.

The clusters of both neutrals and ions were ejected from the waiting room through a conical nozzle, resulting in a supersonic cluster-beam expansion in vacuum. To investigate only neutral clusters, an electric potential of about +200 V dc was applied to a metal rod located parallel to the cluster beam at a distance of 10 mm so that all initially charged species were deflected out of the neutral beam path. The neutral clusters then entered the second vacuum chamber after passing through a skimmer of 2-mm opening. Irradiation of ultraviolet light from a dye laser (Lambda Physik FL 2001, about 10-ns pulse duration) equipped with a BBO frequency-doubling crystal, pumped by

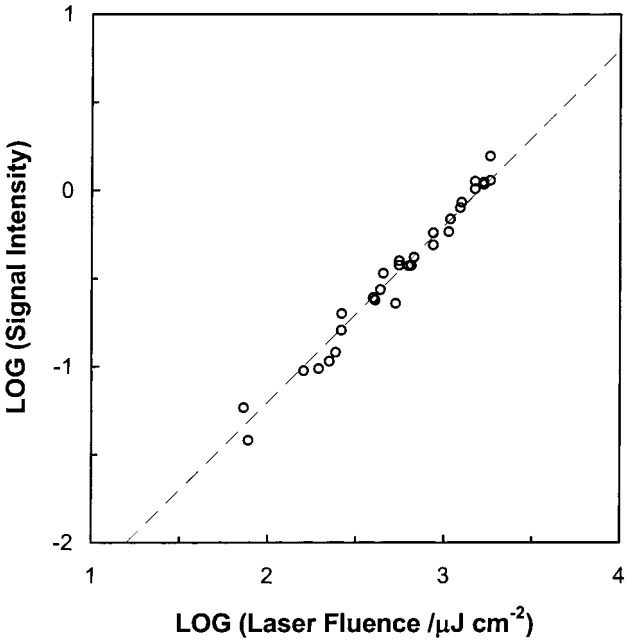

Figure 2. Photoionization laser power dependence of the Ti_8C_{12} Met-Car at a photon energy of 4.59 eV (270 nm) for the range between 0.070 and 1.8 mJ cm^{-2}. The dashed line represents the slope for linear dependence.

an excimer laser (308 nm, Lambda Physik EMG 201 MSC), accomplished ionization of the neutral clusters in a constant electric field of about ∼740 V/cm. This field was established between the TOF ion extraction grids, utilizing an arrangement where the electric field was perpendicular to the neutral cluster beam. In the present study, several laser dyes were used to cover the range of photon energy from 3.9 to 5.6 eV. The ionized clusters were then analyzed by a reflectron TOF mass spectrometer, followed by chevron microchannel plates (Galileo) for ion detection. The ion signal was amplified, averaged with a CAMAC data-acquisition system, and recorded on a PC. Each spectrum was obtained through data accumulated for 2500 or 5000 laser shots in a constant experimental setting. The timing of the vaporization and ionization lasers, the pulsed valve, and the motion controller for the metal rod was synchronized by a multichannel trigger generator operated at a 30-Hz repetition rate. During operation, oil diffusion pumps maintained the vacuum at about 1×10^{-2} Pa in the cluster source chamber and below 5×10^{-4} Pa in the ionization/mass spectrometer chamber.

The fluence of the *ionization* laser was maintained sufficiently low so that single-photon excitation processes dominated. This was established by monitoring laser power dependence of the peak intensity of the Met-Cars about every 0.1 eV above the IP's to verify linearity (Figure 2). The linearity was usually assured in the power range of up to about 1.5 mJ cm^{-2}. For PIE measurements, the fluence was maintained typically in the range of 400−800 μJ cm^{-2} for sufficient peak intensities.

As mentioned above, the power of the *vaporization* laser for cluster formation was set so that the Met-Car peak was prominent. In our previous study of the titanium−carbon cluster system, it was established that the mass distribution of the Ti−C clusters is highly dependent on the power of the vaporization laser for cluster formation, and more importantly that the titanium Met-Car, Ti_8C_{12}, is dominantly produced when the vaporization laser power is sufficiently high.[38] Similarly, it was found during the present study that the zirconium and titanium−

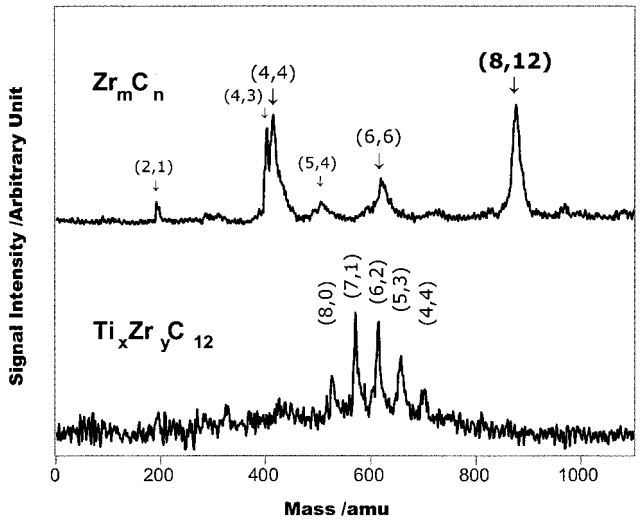

Figure 3. Photoionization mass spectra of (a) neutral zirconium−carbon and (b) neutral titanium−zirconium−carbon clusters. The data were smoothed without losing primary features. In (a), the designation (*m*, *n*) stands for the Met-Car of Zr_mC_n. The ionization photon energy and laser fluence were 4.20 eV (295 nm) and 0.67 mJ cm^{-2}, respectively. In (b), (*x*, *y*) stands for the Met-Car of $Ti_xZr_yC_{12}$. The ionization photon energy and laser fluence were 4.59 eV (270 nm) and 1.2 mJ cm^{-2}, respectively. The rod used to obtain the mass spectrum was composed of 85% titanium and 15% zirconium in molar ratio.

zirconium mixed Met-Cars were produced abundantly when the vaporization laser power was sufficiently high, while the Met-Car peaks were barely seen at lower vaporization laser powers. Mass spectra of zirconium−carbon and titanium−zirconium−carbon clusters obtained under the high vaporization laser power conditions are shown in Figure 3. In the mass spectra of Zr−C clusters, however, several species were seen in addition to the zirconium Met-Car. For example, the peak that corresponds to Zr_8C_{12} is too wide and appears to have a tail to the right. This is probably due to species with a slightly higher mass than Zr_8C_{12}, such as Zr_8C_{13}.[41] Nevertheless, the tail disappeared when the photon energy of the ionization laser was reduced and did not interfere with the IP measurement of the zirconium Met-Car near threshold. For the Ti−Zr−C clusters, the mass spectrum in Figure 3 has a hump superimposed on the peaks of mixed metal Met-Cars. Again, it is probably due to species of stoichiometries different from Met-Cars. The hump was smaller and negligible when the ionization photon energy was close to the ionization threshold of the Met-Cars and did not disturb the IP measurement, especially in establishing zero levels during the measurements of peak intensity.

To obtain PIE curves of the Met-Cars, the photon energy of the ionization laser was scanned at a step of 0.02−0.05 eV, and peak intensities of the Met-Cars were determined from mass spectra. The measured peak intensities were normalized with respect to the ionization laser fluence and plotted against photon energy. The procedure employed to determine the IP's of the Met-Cars from the PIE curves thus obtained is described in detail in the next section.

III. Results and Discussion

A. IP's for the Pure Titanium and Zirconium Met-Cars. The ionization efficiency plots for the titanium and zirconium Met-Cars near threshold are shown in Figure 4. In the photon energy ranges near threshold, i.e., 4.17−4.68 eV for Ti_8C_{12} and 3.89−4.05 eV for Zr_8C_{12}, respectively, several points of different intensities are plotted at the same photon energy. This is because

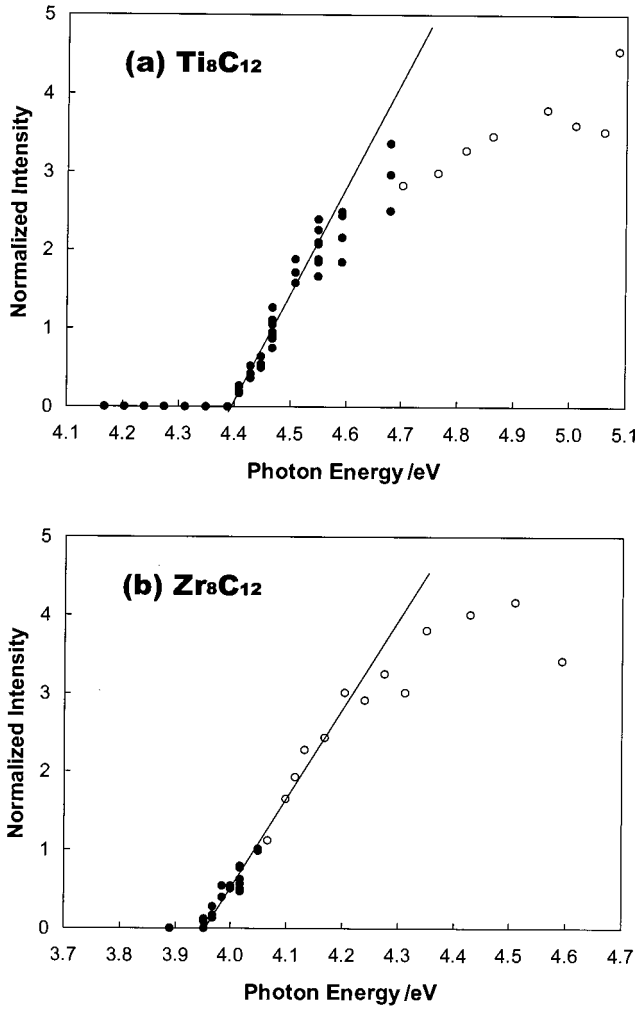

Figure 4. PIE plots for the pure titanium and zirconium Met-Cars. For the threshold photon energy range, each point represents the peak intensity of the cluster in mass spectra obtained through data accumulated for 2500 laser shots, after normalization with respect to the ionization laser fluence (solid circles). For higher photon energy ranges which were studied with laser dyes different from those of the threshold ranges, points show averaged intensities for each photon energy (open circles). Data sets which were obtained with different laser dyes were connected so that averages of normalized intensities at a boundary coincide. The lines are the regressions of the points measured between 4.39 and 4.55 eV for Ti_8C_{12}, and between 3.98 and 4.20 eV for Zr_8C_{12}, respectively. Estimated error in peak intensity, mainly due to white noise, is about ±0.2 in the scale.

the photon energy scan was repeated back and forth in the range using a single laser dye. Therefore, the scattering of the points represents the magnitude of fluctuation in measuring signal intensities in the threshold range. Each point corresponds to a peak intensity of the Met-Cars in mass spectra obtained through data accumulated for 2500 laser shots, after normalization with respect to the ionization laser fluence. In the higher photon energy ranges covered by different laser dyes, only averaged intensities are plotted. Laser dyes used to cover the photon energy ranges were Coumarin 540A (4.17−4.68 eV) and Coumarin 503 (4.68−5.09 eV) for Ti_8C_{12} and Kiton Red 620 (3.89−4.05 eV), Rhodamine 610 (4.05−4.13 eV), Rhodamine 590 (4.13−4.31 eV), and Coumarin 540A (4.22−4.59 eV) for Zr_8C_{12}.

In each plot, the ionization efficiency decreases as the photon energy becomes lower. Regarding the photon energy ranges higher than those shown in Figure 4, it was established by scanning the photon energy up to 5.64 eV that the Met-Car peaks

maintained high, nonzero intensities under single photon absorption conditions. This observation indicates that the sharp onsets shown in Figure 4 correspond to the ionization thresholds of Ti_8C_{12} and Zr_8C_{12}.

Focusing on the thresholds, the tailing feature, which is often observed in PIE measurements of polyatomic systems, was not clearly seen. This is perhaps due to the fact that the Met-Car peak in the mass spectra was buried in noise at the threshold. More specifically, the estimated error in measuring the peak intensities in the mass spectra is about ± 0.2 in the scale and is mainly attributable to white noise. When the real peak intensity is below 0.2, no peak was discernible and the intensity was read as zero (e.g., points at 4.39 eV and below in the titanium Met-Car's PIE plot). On the other hand, when the real peak intensity was slightly above 0.2, the peak was recognized and the intensity was measured as nonzero. Therefore, the tails might have been undervalued in the threshold range.

Because the tailing feature was not significant and the PIE plots are nicely fitted by straight lines, the linear extrapolation method[42] was adopted in the present study to deduce the IP's, instead of other procedures[43−46] that are preferably utilized when a PIE curve has a distinct tail. The IP's determined by following these considerations were 4.40 ± 0.02 and 3.95 ± 0.02 eV for the titanium and zirconium Met-Cars, respectively. The errors were estimated by evaluating the scattering of the data points near threshold due to possible fluctuation of the instruments and the noise in the mass spectra.

Referring again to Table 1, it is noticed that there is significant discrepancy between our data and those by Brock and Duncan. That is, our IP's are lower by 0.5 eV for Ti_8C_{12}, and by more than 1.8 eV for Zr_8C_{12}. Therefore, following the above IP assignment with the data in Figure 4, we conducted two additional PIE measurements. Those experiments were intended to investigate whether the temperature of the Met-Cars affected the PIE plots and ultimately the IP assignment. For example, if a measurement is conducted at high temperatures, the IP tends to be assigned to a lower than actual value. Indeed, it is a valid question to ask whether the temperatures of our clusters might be higher since our experiments are conducted at a high vaporization laser power to produce abundant Met-Cars. Thus, an investigation was undertaken to answer whether this temperature effect contributed to the difference between our IP's and those determined by Brock and Duncan.

First, a PIE measurement was conducted at a higher vaporization laser power, keeping other experimental conditions unchanged. The idea was that an increased vaporization laser power should induce a plasma of a higher temperature in the cluster source, which might result in production of warmer clusters and perhaps cause a more significant tail in the PIE plot. The findings showed that, within limits of error, the PIE plot of the titanium Met-Car which was obtained by doubling the vaporization laser power was essentially identical and did not display a significant tail. Accordingly, a shift to a lower value in IP assignment was not observed, and the IP was determined to be the same. We concluded that the high vaporization laser power did not affect our IP assignment.

For the second experiment, we modified our cluster source. That is, instead of the conical nozzle described in the Experimental Section and in Figure 5a, a straight nozzle for extensive cooling was used, as shown in Figure 5b. In conducting similar measurements, Hackett and co-workers utilized a straight nozzle that was thermally contacted with a refrigerator. This arrangement was employed in their study in order to control temperatures of metal and metal-oxide clusters produced by a laser

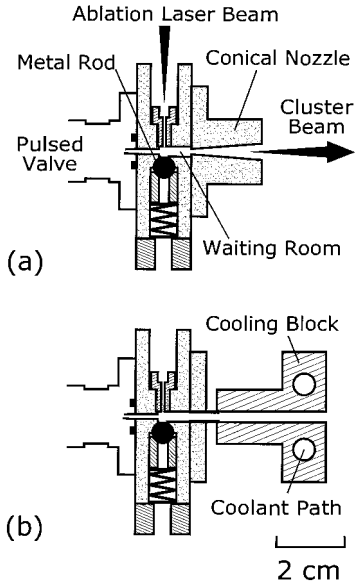

Figure 5. Comparison of the two different types of the cluster sources (a) with a conical nozzle and (b) with a straight tube for intensive cooling. Sand-patterned pieces were made with Teflon, while hatched ones were made of metals.

vaporization method with a pulsed valve.[47] Our nozzle construction was based on their geometric design to acquire similar cooling effects. However, it should be noted that, even with the similar cooling nozzle, it was uncertain until studied whether the temperatures of their clusters and those of Met-Cars in the present study would be comparable, since many factors would be different between the two experiments, such as the heat capacities of the clusters and carrier gases, the temperatures of the clusters at the moment when they were produced, the residence times in the nozzles, etc. Therefore, we chose the straight nozzle design as an effective way of cooling clusters, as established by the prior work, we tested the new experimental setup, and after sufficient efficiency of cooling clusters was established as described below, we studied the effects of temperature on the IP measurements of Met-Cars.

A straight channel of 32-mm length and 3-mm inner diameter was drilled in a brass block capable of being cooled to about -190 °C by feeding liquid nitrogen through it. This was connected to the main body of the cluster source via a metal tube of 9-mm length and 2.9-mm inner diameter. Since the cluster source main body was made of Teflon, the temperatures of the rest of the cluster source were maintained at about room temperature. The temperature of the cooling block was monitored by a thermocouple. Experiments were conducted on titanium Met-Cars.

Complete descriptions of the experimental observations with this new nozzle will be given elsewhere,[48] and only results that are important for the investigation of temperature effects on the IP measurements are described here. The most significant effect of the new experimental setup with the straight nozzle was that methane molecules, which were abundant in the cluster source, become clustered to the Met-Cars under low-temperature conditions, and that the resulting complexes were observed as additional peaks in the mass spectra.[49,50] Under an assumption that the association was physisorption of methane with weak bonds to the surface of the Met-Cars, this observation proved the straight nozzle was effective to sufficiently cool Met-Cars (and methane, and probably helium, too).[51]

After this observation, the IP of the titanium Met-Car was investigated with the straight nozzle being cooled and hence in

the presence of coexisting methane−Met-Car complexes. Importantly, no significant shift to a higher value in IP assignment was observed. Therefore, from the results of the two experiments, it was concluded that there is no influence of the internal energy content of our clusters on the IP assignments.

After these investigations about the temperature effects, another question still remained unanswered: Why are the IP's by Brock and Duncan[20] substantially different from the IP's determined in the present study? At the moment, we do not have any evidence to explain the discrepancy. The fact that we used different methods to deduce the IP's does not explain the difference; at wavelengths exceeding the IP, we always observed the ionization laser power dependence in our experiment to be equal to unity. For example, the dependence at 4.86 and 4.77 eV for Ti_8C_{12} was 1.00 and 0.96, respectively, while Brock and Duncan reported the dependence was 1.29 for 4.84 eV and 1.52 for 4.75 eV. We can only speculate that, in the experiment by Brock and Duncan, some coexisting species disturbed their IP measurement. This might be either from species of stoichiometries different from pure Met-Cars, or from possible isomers of Met-Cars,[52] and in both of the cases, they must have higher IP's. As a result of convolution of the coexisting species, once the photon energy was reduced below the ionization threshold of the high IP species, the power dependence measured during the scan of the ionization photon energy might have appeared to be greater than unity, and this could lead to IP's being assigned to the higher values.

Apart from this issue, comparison of the IP's of the titanium and zirconium Met-Cars determined in the present study with the theoretically predicted IP's listed in Table 1 prompts an interesting consideration: What structure of the Met-Cars is more appropriate to explain the measured IP's? For both the titanium and zirconium Met-Cars, the measured IP's agree quite well with the IP's calculated with T_d symmetry imposed. It is obvious that the T_h-symmetry Met-Cars could not be detected by the near-threshold photoionization efficiency study even if they coexisted with the T_d-symmetry Met-Cars, provided the IP's of the T_h-symmetry Met-Cars are as high as what have been predicted. However, assuming the quality of the density functional calculation is high in estimating IP's for clusters of the elements and the size studied here, the good agreement between theory and experiments leads to the conclusion that the T_d-symmetry Met-Cars are present in considerable amounts.

Other than prompt ionization, another phenomenon previously observed for Met-Cars is delayed ionization. Two crucial parameters must be considered in accounting for this ionization mechanism, i.e., the IP's of the Met-Cars and their bond strength. The IP's were determined to be about 4 eV in the present study, while the bond energies were estimated to be about 9 eV for Met-Car cations based on collision-induced dissociation experiments.[18,19] Since the bond strength in the neutral Met-Cars are theoretically calculated to be approximately the same as that of the cations, it is clear that the Met-Cars satisfy the criterion for the delayed ionization, i.e., the energy for the weakest bond in an ionizing species must be considerably higher than its IP. It should be noted that, as part of another study in our laboratory, we investigated the delayed ionization of Met-Cars and found that parametrization of the data leads to an estimate of IP values that are comparable with the ones directly measured in the present study.[11]

B. IP's for the Titanium−Zirconium Mixed Met-Cars. The ionization efficiency plots for the titanium−zirconium mixed Met-Cars near threshold are shown in Figure 6. Since the peak intensities of the mixed metal Met-Cars were considerably lower than those of the pure metal Met-Cars, attaining high-quality mass spectra required data accumulation of 5000 laser shots at higher ionization laser powers. Error for the peak intensities due to noise was estimated to be ±0.2 in the scale. Two laser dyes were used to cover the photon energy range shown in Figure 6, i.e., Coumarin 540A above 4.31 eV and Rhodamine 590 below it. For the Met-Cars of higher zirconium contents, peak intensities were quite low due to the mixing ratio of the two metals in the alloy rod used in the present study (see Figure 3), and this caused large uncertainties in IP assignment of the $Ti_5Zr_3C_{12}$ and $Ti_4Zr_4C_{12}$ clusters. Clearly, the tailing effect was not seen for any of the Met-Cars in Figure 6, and the reason

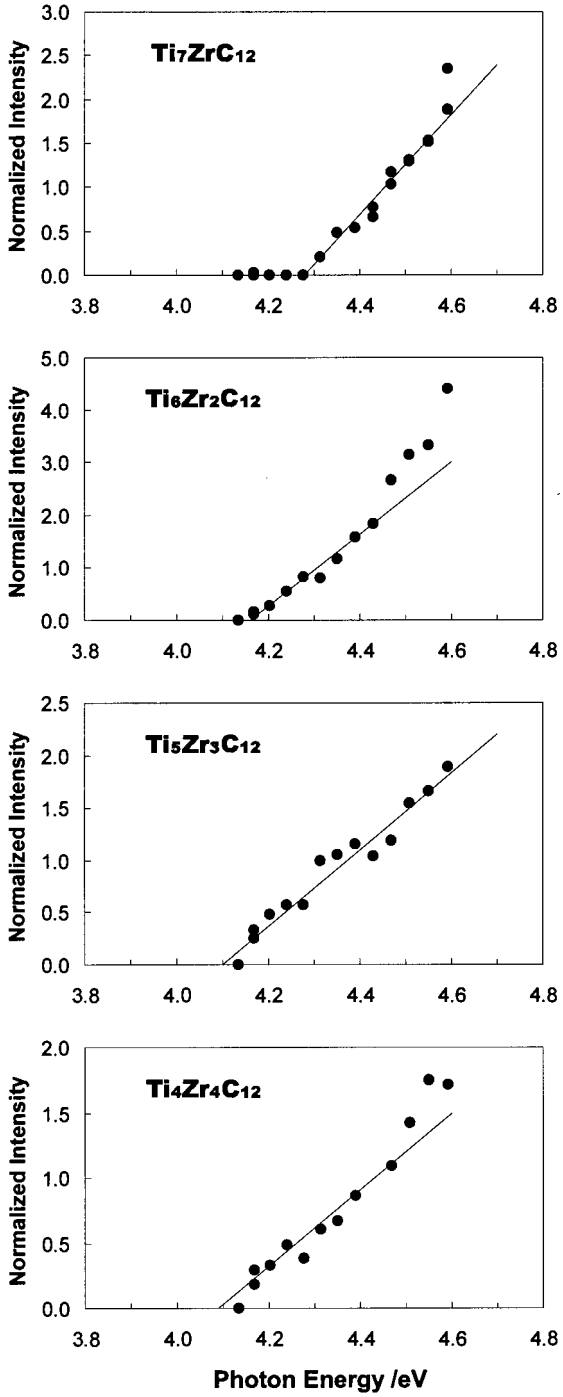

Figure 6. PIE plot for the $Ti_{8-x}Zr_xC_{12}$ ($x = 1-4$) clusters. Each point represents the average of two or more data points which were individually obtained by accumulating data for 2500 or 5000 laser shots. Error in which all original points fall is about ±0.2 in the scale. The lines are drawn to guide eye.

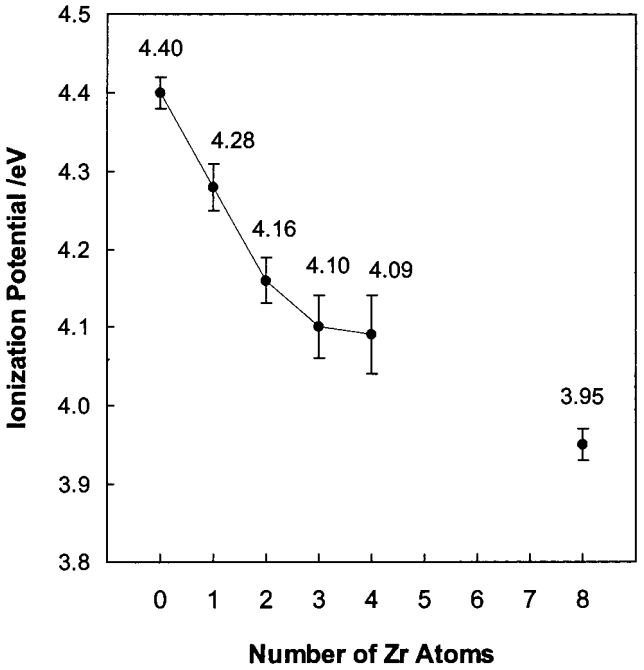

Figure 7. Ionization potentials for the $Ti_{8-x}Zr_xC_{12}$ ($x = 0-4$, 8) clusters.

for it seems to be the same as what was discussed for the PIE plots of the pure metal Met-Cars. Following these considerations, the IP's of the mixed metal Met-Cars are assigned to be 4.28 ± 0.03, 4.16 ± 0.03, 4.10 ± 0.04, and 4.09 ± 0.05 for (Ti, Zr) = (7, 1), (6, 2), (5, 3), and (4, 4), respectively, and they are plotted in Figure 7 with the IP's for the pure metal Met-Cars. Starting with the IP of the pure titanium Met-Car, it decreases continuously as the number of substituting zirconium atoms increases. Moreover, the first and second zirconium atom substitutions, i.e., from (Ti, Zr) = (8, 0) to (7, 1) and then to (6, 2), at first cause large decreases in the IP values, followed by a leveling off to small changes in the range where the metal ratios are about 1:1.

Each of the measured IP's for the mixed metal Met-Cars represents the IP for a geometric isomer of the lowest IP among the Met-Cars of the same stoichiometry. For example, two types of isomers may exist for $Ti_6Zr_2C_{12}$, for any geometric structure assumed, one in which the two zirconium atoms occupy neighboring metal sites with each other, and another in which the two zirconium atoms are separated. It is expected that they may have different electronic structures and hence different IP's. On the other hand, according to the estimation through density functional calculations of the stabilities for these types of isomers for the T_d-symmetry Met-Cars,[17] they are likely to be similarly stable and to exist at comparable concentrations. While the near-threshold photoionization study could not distinguish them, predicting and comparing the IP's of the isomers of the mixed metal Met-Cars by theoretical calculations will be beneficial in terms of understanding the electronic structure of those Met-Cars, in conjunction with estimating the absolute IP's.

IV. Conclusions

The ionization potentials for the titanium and zirconium Met-Cars were determined to be 4.40 ± 0.02 and 3.95 ± 0.02 eV, respectively. The IP's for the binary metal Met-Cars, $Ti_{8-x}Zr_xC_{12}$ ($x = 1-4$), were also determined, and it was found the IP decreases continuously from that of the pure titanium Met-Car toward that of the pure zirconium Met-Car as the number of substituting zirconium atoms increases. Assuming a high degree of accuracy in the density functional calculations, comparison of the IP's individually obtained from experimental and theoretical investigations indicates the T_d-symmetry Met-Cars explain the observed IP's quite well. The establishment of the low IP values provides a further basis for attributing the delayed ionization dynamics observed in Met-Cars to a thermionic emission mechanism.

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References and Notes

(1) Guo, B. C.; Kerns, K. P.; Castleman, A. W., Jr. *Science* **1992**, *255*, 1411.
(2) Guo, B. C.; Wei, S.; Purnell, J.; Buzza, S. A.; Castleman, A. W., Jr. *Science* **1992**, *256*, 515.
(3) Wei, S.; Guo, B. C.; Deng, H. T.; Kerns, K.; Purnell, J.; Buzza, S. A.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 4475.
(4) Pilgrim, J. S.; Duncan, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 6958.
(5) Cartier, S. F.; May, B. D.; Castleman, A. W., Jr. *J. Chem. Phys.* **1994**, *100*, 5384.
(6) Cartier, S. F.; May, B. D.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 5295.
(7) Deng, H. T.; Guo, B. C.; Kerns, K. P.; Castleman, A. W., Jr. *Int. J. Mass Spectrom. Ion Processes* **1994**, *138*, 275.
(8) The electron affinities for the Ti, V, Cr, Zr, and Nb Met-Cars were reported in the following papers: Wang, L. S.; Li, S.; Wu, H. *J. Phys. Chem.* **1996**, *100*, 19211. Li, S.; Wu, H.; Wang, L. S. *J. Am. Chem. Soc.* **1997**, *119*, 7417.
(9) May, B. D.; Cartier, S. F.; Castleman, A. W., Jr. *Chem. Phys. Lett.* **1995**, *242*, 265.
(10) Cartier, S. F.; May, B. D.; Castleman, A. W., Jr. *J. Chem. Phys.* **1996**, *104*, 3423.
(11) Kooi, S. E.; Castleman, A. W., Jr. *J. Chem. Phys.* **1998**, *108*, 8864.
(12) Reddy, B. V.; Khanna, S. N.; Jena, P. *Science* **1992**, *258*, 1640.
(13) Grimes, R. W.; Gale, J. D. *J. Phys. Chem.* **1993**, *97*, 4616.
(14) Li, Z. Q.; Gu, B. L.; Han, R. S.; Zheng, Q. Q. *Z. Phys. D* **1993**, *27*, 275.
(15) Lou, L.; Nordlander, P. Unpublished, referred to in ref 20.
(16) Dance, I. G. Unpublished, referred to in ref 20.
(17) Muñoz, J.; Pujol, C.; Bo, C.; Poblet, J.-M.; Rohmer, M.-M.; Benard, M. *J. Phys. Chem.* **1997**, *101*, 8345.
(18) Kerns, K. P.; Guo, B. C.; Deng, H. T.; Castleman, A. W., Jr. *J. Chem. Phys.* **1994**, *101*, 8529.
(19) Kerns, K. P.; Guo, B. C.; Deng, H. T.; Castleman, A. W., Jr. *J. Phys. Chem.* **1996**, *100*, 16817.
(20) Brock, L. R.; Duncan, M. A. *J. Phys. Chem.* **1996**, *100*, 5654.
(21) Dance, I. *J. Chem. Soc., Chem. Commun.* **1992**, 1779.
(22) Guo, B. C.; Kerns, K. P.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1993**, *115*, 7415.
(23) Deng, H. T.; Kerns, K. P.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1996**, *118*, 446.
(24) Cartier, S. F.; May, B. D.; Castleman, A. W., Jr. *J. Phys. Chem.* **1996**, *100*, 8175.
(25) Yeh, C. S.; Afzaal, S.; Lee, S. A.; Byun, Y. G.; Freiser, B. S. *J. Am. Chem. Soc.* **1994**, *116*, 8806.
(26) Byun, Y. G.; Freiser, B. S. *J. Am. Chem. Soc.* **1996**, *118*, 3681.
(27) Byun, Y. G.; Lee, S. A.; Kan, S. Z.; Freiser, B. S. *J. Phys. Chem.* **1996**, *100*, 14281.
(28) Bowers, M. T. *Acc. Chem. Res.* **1994**, *27*, 324.
(29) Lee, S.; Gotts, N. G.; von Helden, G.; Bowers, M. T. *Science* **1995**, *267*, 999.
(30) Lin, Z.; Hall, M. B. *J. Am. Chem. Soc.* **1993**, *115*, 11165.
(31) Lou, L. ; Nordlander, P. *Chem. Phys. Lett.* **1994**, *224*, 439.
(32) Dance, I. *J. Am. Chem. Soc.* **1996**, *118*, 6309.
(33) Rohmer, M.-M.; Bénard, M.; Henriet, C.; Bo, C.; Poblet, J.-M. *J. Chem. Soc., Chem. Commun.* **1993**, 1182.
(34) Rohmer, M.-M.; Bénard, M.; Bo, C.; Poblet, J.-M. *J. Am. Chem. Soc.* **1995**, *117*, 508.
(35) Bénard, M.; Rohmer, M.-M.; Poblet, J.-M.; Bo, C. *J. Phys. Chem.* **1995**, *99*, 16913.
(36) Poblet, J.-M.; Bo, C.; Rohmer, M.-M.; Bénard, M. *Chem. Phys. Lett.* **1996**, *260*, 577.
(37) Huang, Y.; Sulkes, M. *Rev. Sci. Instrum.* **1994**, *65*, 3868.
(38) Sakurai, H.; Castleman, A. W., Jr. *J. Phys. Chem. A* **1997**, *101*, 7695.
(39) Milani, P.; de Heer, W. A. *Rev. Sci. Instrum.* **1990**, *61*, 1836.

(40) Maruyama, S.; Anderson, L. R.; Smalley, R. E. *Rev. Sci. Instrum.* **1990**, *61*, 3696.

(41) This tail is not due to the delayed ionization of Zr_8C_{12} because the mass spectrum was obtained under a single-photon ionization condition where multiphoton processes, e.g., the delayed ionization, may hardly occur.

(42) Saunders: W.; Clemenger, K.; de Heer, W.; Knight, W. *Phys. Rev. B* **1985**, *32*, 1366.

(43) Watanabe, K. *J. Chem. Phys.* **1954**, *22*, 1564.

(44) Kappes, M. M.; Schär, M.; Röthlisberger, U.; Yeretzian, C.; Schumacher, E. *Chem. Phys. Lett.* **1988**, *143*, 251.

(45) Limberger, H. G.; Martin, T. P. *J. Chem. Phys.* **1989**, *90*, 2979.

(46) Bergmann, T.; Martin, T. P. *J. Chem. Phys.* **1989**, *90*, 2848.

(47) There are many cluster studies that utilized some sort of cooling devices. However, we adapted their method because their studies were similar to ours in terms that they used a laser vaporization cluster source with a pulsed valve and, moreover, because they provided experimental evidence for the cooling efficiency of their nozzle. See: Collings, B. A.; Amrein, A. H.; Rayner, D. M.; Hackett, P. A. *J. Chem. Phys.* **1993**, *99*, 4174. Yang, D.-S.; Zgierski, M. Z.; Rayner, D. M.; Hackett, P. A.; Martinez, A.; Salahub, D. R.; Roy, P.-N.; Carrington, T., Jr. *J. Chem. Phys.* **1995**, *103*, 5335.

(48) Sakurai, H.; Castleman, A. W., Jr. To be published.

(49) It was confirmed by an experiment with deuterated methane, CD_4, that the adsorbate was methane; fragments of CH_4, e.g., CH_3, and other chemicals from impurity, e.g., water, were excluded.

(50) This observation provides another piece of evidence that the neutral titanium Met-Car was abundant in the cluster beam, and hence proves it is a stable species. More description will be given in ref 48.

(51) This observation of the methane association does not rule out the possibility that the Met-Cars produced with the conical nozzle were cold in the original source configuration. The differences between the conical and straight nozzles were not only cooling efficiency but also mixing conditions between Met-Cars and methane molecules. In other words, the straight nozzle provided a longer mixing time and a higher methane concentration than the conical nozzle before the whole gaseous species expanded into the vacuum, and this might be the difference whether the methane association was observed or not.

(52) One of the reviewers suggested the possible existence of isomers to explain the discrepancy. In the reviewer's argument, our clusters were grown under hotter conditions, and upon cooling may have been annealed into a more stable structure of a lower IP than those produced by Brock and Duncan.