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Metallocarbohedrenes: A new class of molecular clusters with cage structure

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The chemistry of a new class of molecular clusters having closed cage structure, called metallocarbohedrenes or metcars, is described. These molecules of general formula M_8C_{12}, where M is a metal, were discovered in mass spectrometry experiments. By reacting laser-evaporated metal with hydrocarbons and cooling the reaction mixture in an inert atmosphere of helium, a number of metcar ions containing Ti, V, Hf, Zr, Mo, Cr and Fe have been produced by different workers. The chemistry of these ions is gradually unfolding with several groups putting efforts in experimental and theoretical studies.

SOME of the current excitements in chemistry are centred around molecular clusters. It was nearly nine years ago that C_{60} was discovered[1]. The observation of a magic peak in the mass spectrum at $m/z = 720$ while studying carbon clusters formed in the laser evaporation of graphite culminated in the discovery of C_{60}. The unusual stability of this cluster was then attributed to a cage-like structure. Similar molecules, C_{70}, C_{76}, C_{78}, etc., were soon found, proving the existence of a class of molecular clusters called fullerenes. After five years of extensive theoretical and experimental investigations, a method for their bulk synthesis was discovered[2]. This spurred intense research activity all over the world; over one thousand research papers have been published in this area in the last four years[3].

The fascination of chemists for magic peaks and numbers cannot be over-emphasized. Discovery of magic peaks, when related to giant molecular species with high symmetry and unusual chemistry, causes excitement in all facets of science. The most recent excitement is due to an interesting class of molecular clusters called metallocarbohedrenes or, in short, metcars. This article presents a brief account of the body of information available today. Some of the future research possibilities are presented.

Metcars: chemistry in plasma

There are three research groups currently active in the experimental studies of metcars. The first group is of Prof. A. W. Castleman Jr in Penn State. The other two are those of Dr. M. A. Duncan in the University of Georgia and Prof. M. T. Bowers in the University of California, Santa Barbara. The discovery occurred during an investigation of the dehydrogenation reactions of hydrocarbons induced by metal ions, atoms and clusters by the Castleman group[4]. The apparatus for the experiment was a time-of-flight (TOF) mass spectrometer (MS) coupled with a laser vaporization source. In a typical experiment, the second harmonic of a Nd:YAG laser (532 nm, 20 mJ/pulse) is directed on to a metal surface. The evaporated metal ions, atoms and clusters react with hydrocarbons (CH_4, C_2H_4, C_2H_2, C_3H_6, etc.). The products of the reaction pass through a 5 mm skimmer. The ionic cluster spectrum is obtained by pulsing the TOF lens field. Neutral clusters formed in the reaction can be photoionized by a second Nd:YAG laser; ions are accelerated in a static TOF field. The ions after the flight are detected by a microchannel plate detector. Experiments were carried out with a reflectron also. MS experiments have also been performed with a selected ion drift tube (SIDT) apparatus. This consists of a laser evaporation source, a quadrupole mass analyser for initial mass selection, a drift tube reactor for ion/molecule reactions, followed by a quadrupole mass analyser for final mass analysis of the product ions.

The experimental set-up of Duncan's group is similar[5]. The metal of interest is evaporated from a rotating rod by using either a XeCl excimer (308 nm) or the second harmonic of a Nd:YAG laser (532 nm). The plasma of metal atoms, ions and clusters reacts with CH_4 or C_2H_4 seeded in helium. The cation clusters resulting from this reaction are cooled by supersonic expansion and are mass-analysed by reflectron mass spectrometry. For the measurement of mass distribution, the cation clusters are accelerated by a pulsed electric field. In the photodissociation experiments, the primary ion is mass-selected and photodissociation occurs at the turning region of a reflectron. The flight time in the remaining drift tube region gives the mass spectrum of the daughter ions. Prof. Bowers and co-workers use an ion chromatography apparatus with laser desorption[6].

During the course of investigating the dehydrogenation reactions of hydrocarbons by titanium atoms, ions and clusters, Castleman and co-workers[4] accidentally found an unusually intense magic peak at 528 amu in their mass spectrum (Figure 1). The initial experiment was with methane. Soon it was found that several hydrocarbons such as acetylene, ethylene, propylene and benzene gave the same product. In order to establish definitively the identity of the species, studies were performed with hydrocarbons of varying isotopic composition. Isotopic labelling with deuterium showed that the magic peak does not have any hydrogen. ^{13}C labelling showed that 12 carbon atoms are present in the molecule. High-resolution isotope distribution pattern confirmed the presence of 8 titanium atoms. Thus, the cluster responsible for the magic peak was proved to be due to $Ti_8C_{12}^+$.

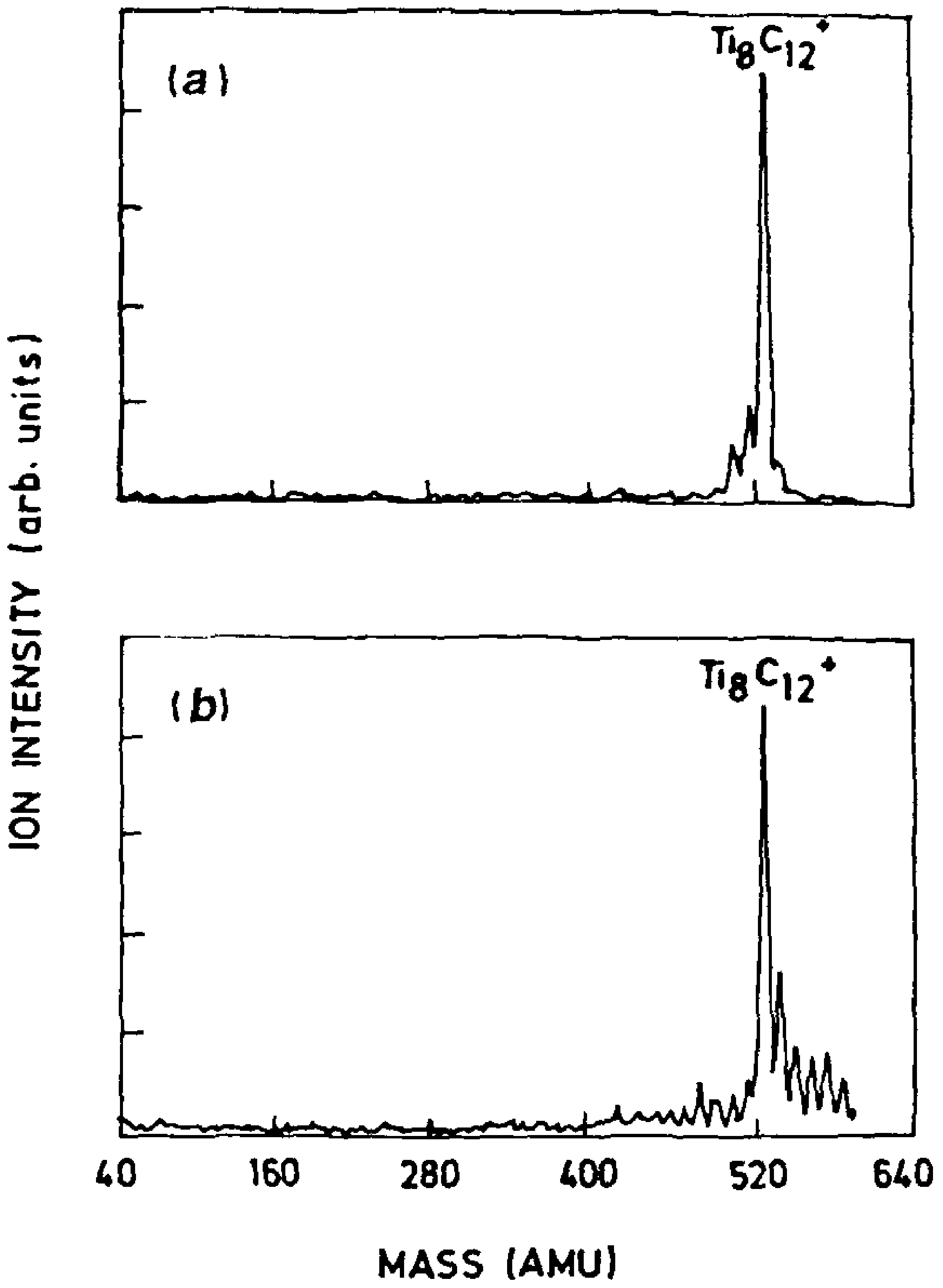

Figure 1. *a*, Mass distribution of clusters generated by reacting laser-evaporated titanium with CH_4 *b*, Mass spectrum of clusters obtained with C_2H_2 Note the magic peak corresponding to $Ti_8C_{12}^+$ at *m/z* = 528 (Adapted from ref 4, with permission)

Unusual abundance of the cluster was explained as being due to its structure; it has been proposed that the structure of the ion and the corresponding neutral molecule is the highly symmetric pentagonal dodecahedron[4] (Figure 2). In this structure, each carbon is bonded to two titanium and one carbon through σ bonds. Each titanium is bonded to three carbons through Ti–C bonds. The remaining valence electrons could be involved in metal–carbon double bonding. The other alternative is that 6 pairs of C–C π bonds are formed and the

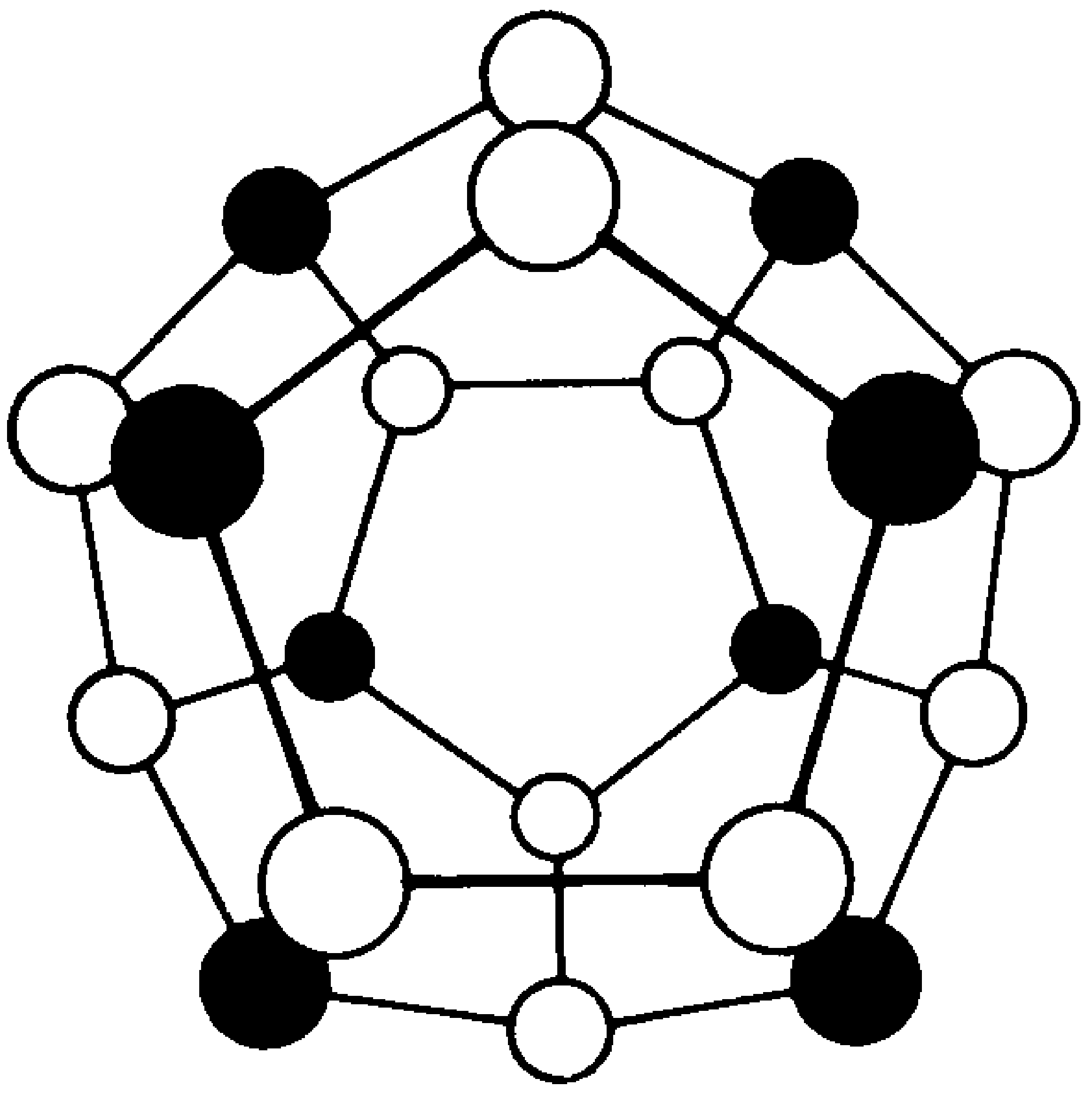

Figure 2. The proposed pentagonal dodecahedron structure for M_8C_{12} The titanium and carbon atoms are represented by filled circles and open circles, respectively Each carbon is bonded to two titaniums and one carbon and each titanium is bonded to three carbons (Adapted from ref 4, with permission)

remaining π electrons are involved in metal–metal interactions. It should be mentioned that neither metal–metal interaction nor metal–carbon back bonding is unusual in metal–carbon systems such as carbene and carbyne complexes.

Ti_8C_{12} is similar to C_{20}, an unstable molecule with severe strain and degeneracy of bonding. Since Ti can participate in bonding through d–sp hybridized orbitals, the presence of two titaniums in pentagonal ring will reduce the strain. The π bonding in the dodecahedron will be facilitated by the better overlap of the $d\pi$–$p\pi$ orbitals. Ti is more electropositive than carbon. The dodecahedron with eight Ti atoms can have a paired neutral ground state. Altogether, the above arguments suggest a stable electron bond structure. The stability of the structure has been demonstrated by collision-induced dissociation (CAD) studies.

Experiments were performed to titrate the metal atoms present in the cluster that are available for bonding. Reactions of mass-selected Ti_8C_{12} with ND_3 yielded a product with eight ND_3 units. This result showed that *titanium atoms are exposed at the cluster surface and are* similarly coordinated.

Dodecahedral structure is not unique to Ti_8C_{12} stoichiometry. Other compositions such as Ti_7C_{13}, Ti_6C_{14}, etc., can also have the same structure. However, replacement of the titaniums with carbons would destroy the structure of high symmetry. In such a structure, some pentagonal rings will have less than two titanium atoms. It is unlikely that one titanium atom will effectively reduce the strain in the ring. Therefore, it is believed that such clusters would undergo further reactions in the reactor to form more stable clusters such as Ti_8C_{12}.

The magic peak was observed for negative ions also. This, along with the high intensity of the mass peak, suggests that the neutral analogue would also be stable. Although experiments have not proved the existence of larger clusters, available results suggest that a class of similar molecules with larger cage structures are possible. Clusters of M_8C_{12} variety should also be possible with other transition metals. These molecules are collectively called metallocarbohedrenes or metcars.

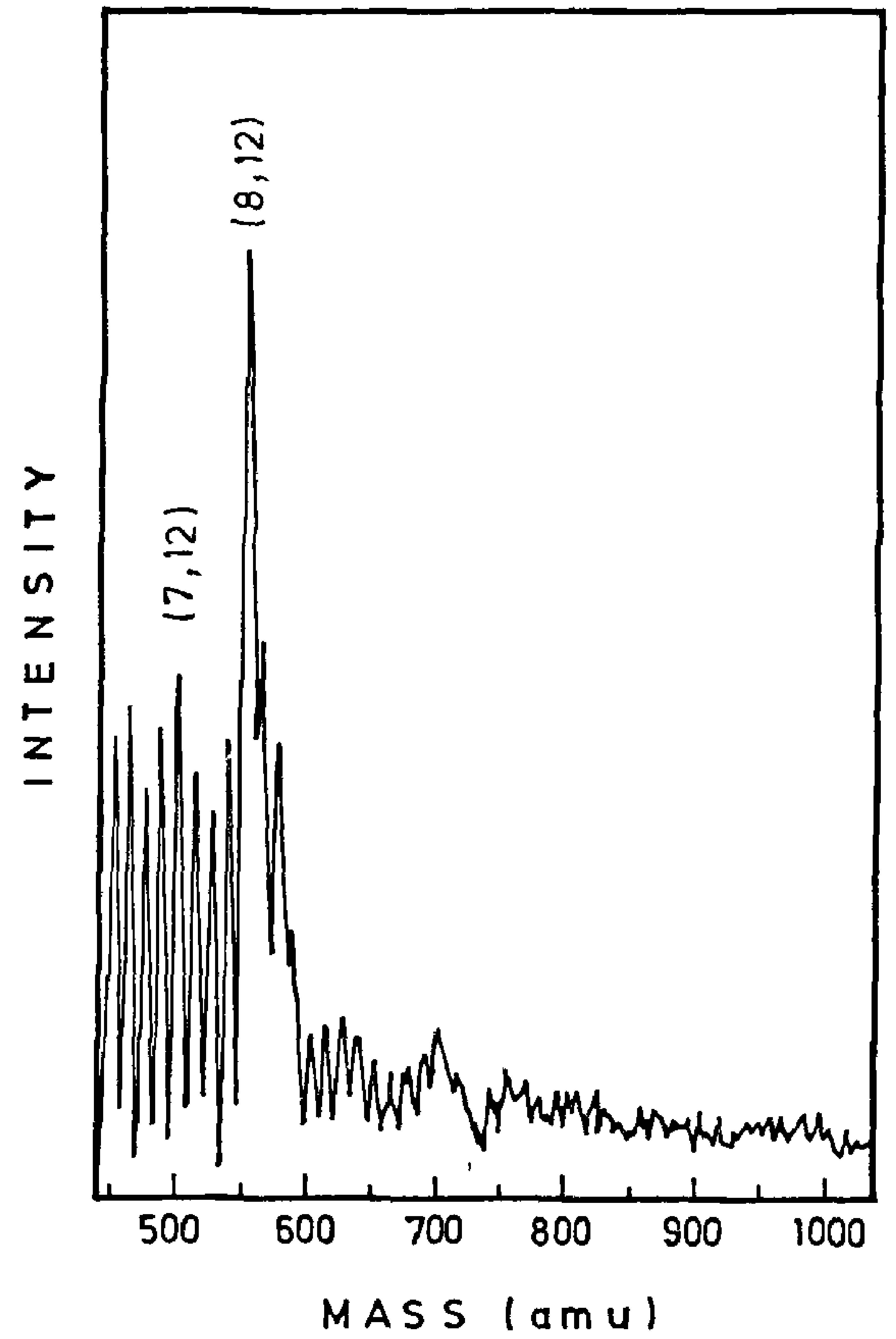

Figure 3. Mass spectrum of the vanadium–carbon cluster ions obtained upon the reaction of laser-evaporated vanadium with CH_4 Ions corresponding to one and two carbon attachments to the magic cluster V_8C_{12} are also seen (From ref. 7, used with permission)

Extension to V, Zr and Hf

Castleman and co-workers later extended their investigations to other metal–carbon systems, particularly to early transition metals. Figure 3 shows the spectrum obtained with vanadium and methane[7]. Isotope-labelling experiments, as before, proved that no hydrogens are present in the magic peak. Experiment with zirconium and hafnium also established the presence of magic clusters[7] of composition $M_8C_{12}^+$. Since Zr and Hf have a similar electronic structure to that of titanium, it is likely that the structures of $Zr_8C_{12}^+$ and $Hf_8C_{12}^+$ are similar to that of $Ti_8C_{12}^+$. In the case of vanadium, although there is an extra electron, it was suggested that the structure is similar.

Evidence for the proposed structure was obtained from ND_3 reaction studies. The reaction of mass-selected $V_8C_{12}^+$ with ND_3 yielded $V_8C_{12} \cdot 8ND_3^+$, showing that all the vanadium atoms are similarly coordinated. It is proposed that the C–C and V–C σ bonds form the basic structure. The remaining valence electrons form a delocalized π system. It is also possible that the remaining electrons in vanadium are involved in metal–metal bonding.

In Zr_mC_m an unusual growth pattern has been found[8]. Even after the formation of the first cage, the cluster growth continues. But rather than increasing the cluster size, multicage structures are formed. The general growth mechanism as observed in fullerenes is not followed. The double cage with $Zr_{13}C_{22}$, the triple cage with $Zr_{18}C_{29}$, the quadruple cage with $Zr_{22}C_{35}$, etc., are observed. The different cage structures are observed as intensity anomalies in the mass spectrum. It should be noted that a typical mass spectrum of a metal–carbon cluster system such as Ti_mC_n exhibits magic numbers at (14, 13), (24, 24), (32, 32), etc., which are consistent with cubic structures. Since similar cluster distribution is not seen in Zr_mC_n, it was suggested that cage structures were responsible for the pattern. Metcars of Ti and Zr have been formed by direct laser vaporization of the respective carbides also[9].

Beyond early transition metals

Later studies by the Duncan group showed that clusters of similar type are possible with other transition metals also. In these experiments, performed similarly by the laser vaporization of metal rods, Pilgrim and Duncan[5] found the presence of magic peaks of $M_8C_{12}^+$ stoichiometry with Cr, Mo and Fe. In the case of Cr and Mo, $M_8C_{12}^+$ clearly stands out as magic peaks (Figure 4). In the case of Fe, no single magic peak exists, but 8/12 stoichiometry is prominent and is followed by a truncation in the spectrum.

All the above-mentioned studies showed that metcar cluster formation is general and would occur with a number of metals. While Ti, V, Zr, Hf, Mo and Cr form metcars readily, for Fe metcar formation competes with other reactions, leading to structures of different stoichiometries. The presence of magic peaks in positive, negative and photoionization studies shows that neutral clusters should be stable.

Binary metal metcars of Ti and the metals Y, Nb, Mo, Ta and W have been produced by direct laser vaporization of a mixture of Ti carbide and the metal[10]. It is interesting that individual metals Ta, Y and W have not shown the tendency to form metcars. These substitutions are not as extensive as those found with Zr.

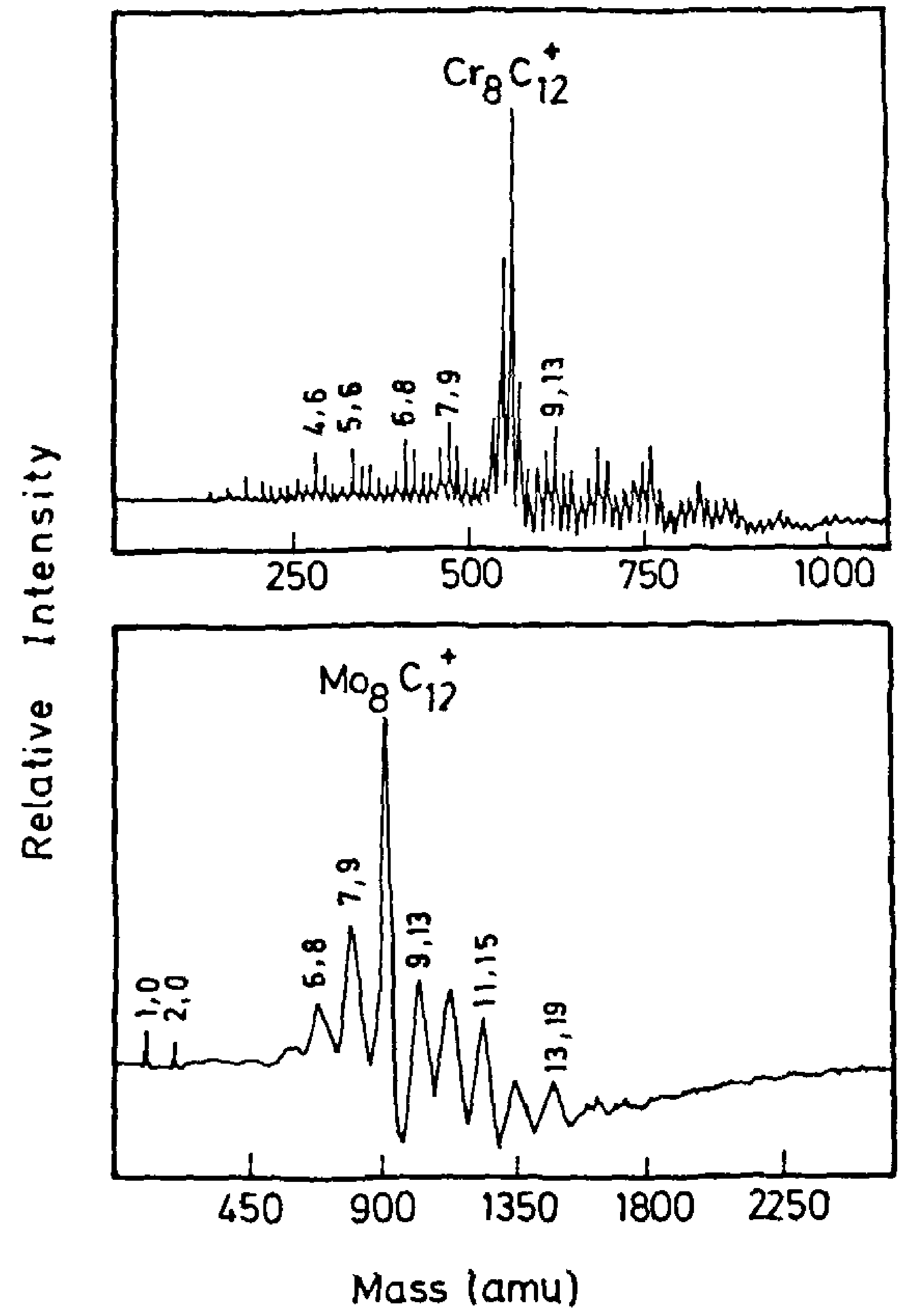

Figure 4. Mass spectra of Cr (*a*) and Mo (*b*) – carbon clusters obtained upon the reaction of laser-evaporated metal with C_2H_2. Clusters of a variety of stoichiometries are seen, but there is definite intensity enhancement at the metcar composition. (From ref 15, with permission.)

Mechanism of formation

Studies concerning the mechanism of formation suggest that metal–carbon clusters first develop multiple-ring structures via the successive addition of MC_2 units. A stable cage structure corresponding to M_8C_{12} closes suddenly[11]. The formation mechanism of metcars was studied by investigating the cluster distribution of ionic and neutral clusters.

In Figure 5*a*, *b* are shown the cluster distributions of ionic and neutral clusters of the Ti/C system. It is clear from the spectra that neutral clusters also show prominence. In addition to this, other clusters of the type (4, 8), (5, 10), (6, 12) and (7, 13) are also abundant. For the smaller cluster size, TiC_2 is prominent; other clusters of the type (2, 4) and (3, 6) are also important. For the

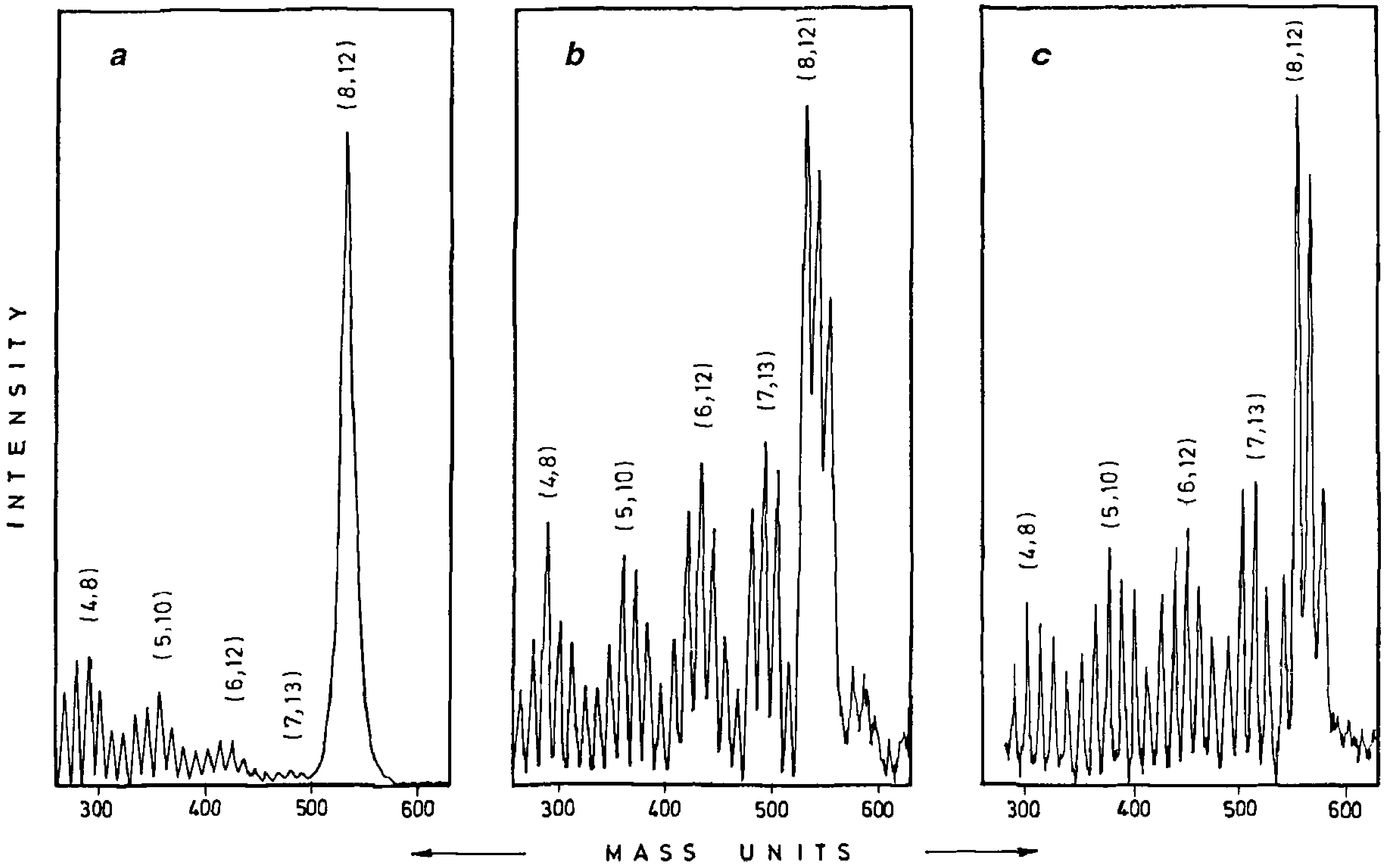

Figure 5. Mass spectra of (*a*) ionic $Ti_mC_n^+$, (*b*) neutral Ti_mC_n and (*c*) neutral V_mC_n The neutral spectra were obtained with 355 nm radiation of a power of 1 × 10^6 W/cm^2 (From ref 11, used with permission)

photoions of V_mC_n also, the magic peak V_8C_{12} is the base peak as seen from Figure 5 *c*. For this system, other clusters of the type (4, 8), (5, 10), (6, 12) and (7, 13) are seen. At higher laser powers, intensities of M_3C_6 and M_3C_8 become comparable to that of M_3C_6. This could be due to the contribution from fragmentation. Other than this effect, the spectra remain identical at different laser fluences. The magic peak and the distribution of masses remain the same at all fluences investigated. Similarly, the spectra remain similar at all laser wavelengths. The wavelengths investigated are 266, 355, 532 and 1064 nm. This is an important experiment since the formation of photoions may involve multiphoton processes.

The presence of $(MC_2)_n$ (M = Ti, V) peak in the mass spectrum with enhanced abundance for $n < 7$ shows that MC_2 units are important in the formation of metcars[11]. This growth breaks down at $n = 8$, consistent with a close cage structure. In the proposed structure, a minimum of 20 atoms are required to form a cage. For a smaller cluster, there are several sites in which MC_2 units can be added. As the cluster size increases, closed cage structures become possible, $M_7C_{13}^+$ marks the formation of a cage. Upon further MC_2 addition, a symmetric structure is formed and the excess carbon atoms boil off (Figure 6). This explanation also means that a few of the extra carbon atoms can be attached to the cage as $M_8C_{13}^+$ or $M_8C_{14}^+$. In the metastable decomposition experiment[12], it has been observed that one carbon atom is loosely bound in M_8C_{13} and two are loosely bound in M_8C_{14}. The abundance of peaks of M_8C_{13} and M_8C_{14} is due to the stability of the M_8C_{12} structure itself. No magic peaks of the type (9, 11) or (10, 10) are observed, showing that the M_8C_{12} structure is unique. The maximum number of metal atoms that can be incorporated to the structure is eight, in accordance with the stronger metal–carbon bonds than the metal–metal bonds.

Photodissociation and metastable decomposition experiments[13] were performed on metcars. For $Ti_8C_{12}^+$, the foremost decomposition channel is through the loss of Ti atom. In the absence of photoabsorption, the loss of Ti^+ is insignificant, suggesting that the ionization potentials (IP) of Ti_mC_n are lower than that of Ti.

Later experiments with titanium–graphite mixed rods[14] exhibited the same kind of cluster distribution as was seen with the metal and hydrocarbons. In these experiments, a pressed and homogenized graphite–titanium composite rod was laser-evaporated and the

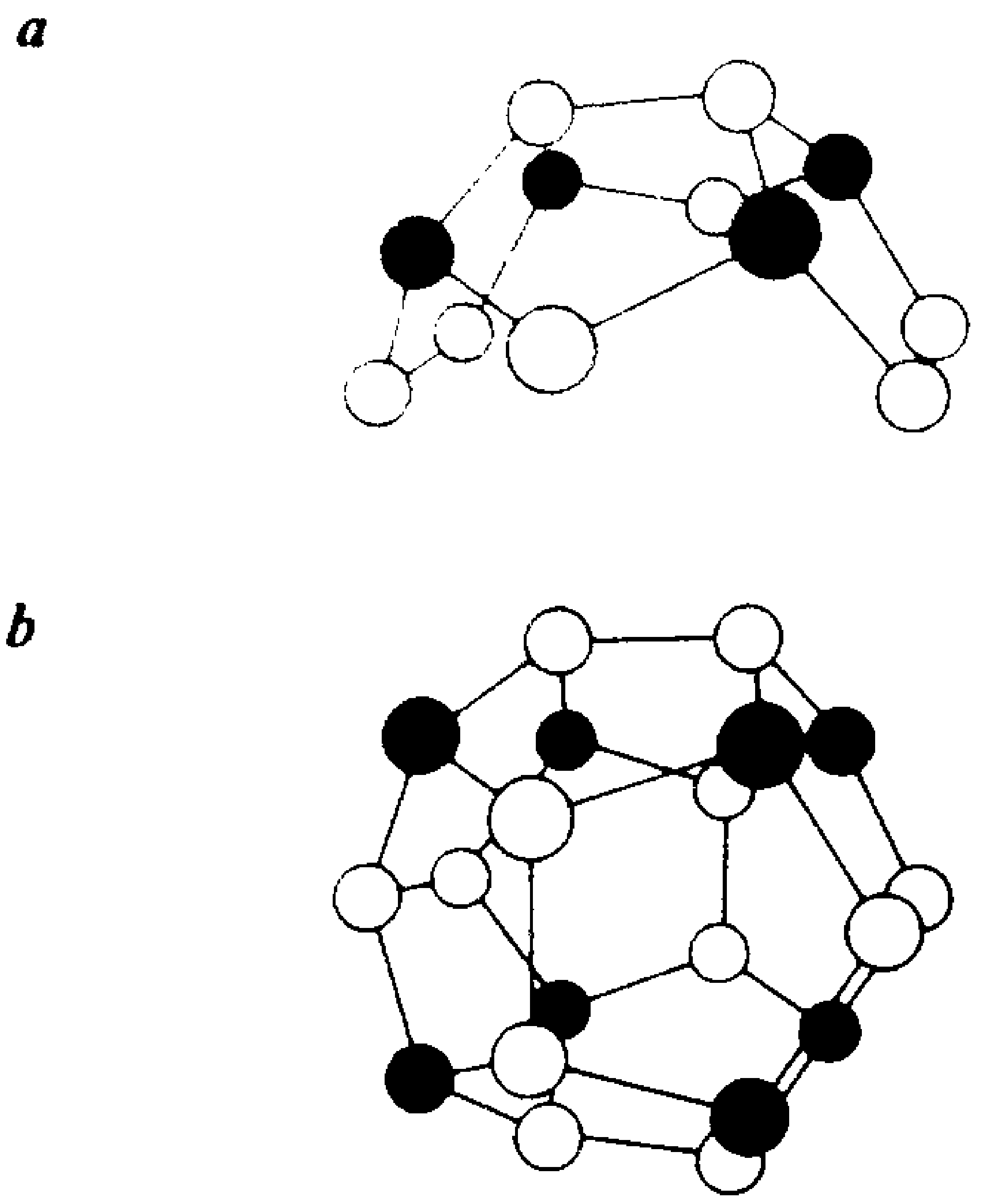

Figure 6. All illustration of the formation mechanism of metcars MC_2 units add sequentially to form e g M_4C_8 and the cage closes suddenly at M_8C_{12} with the elimination of excess carbon atoms (From ref 11, used with permission.)

products were cooled in a supersonic expansion. The experiment proved that the formation of metcars occurs as a result of interaction between Ti and C atoms. If hydrocarbons are present, dehydrogenation reactions only facilitate the formation of carbon atoms.

Dissociation of metcars

Using a reflectron time-of-flight spectrometer, Pilgrim and Duncan performed photodissociation experiments[15]. Figure 7 shows the photodissociation mass spectra of Ti and Zr metcars. The spectra are plotted with a computer difference technique where a negative peak indicates the depletion of the parent ion signal and the positive peaks indicate the fragment ions. The spectrum of $Ti_8C_{12}^+$ shows peaks due to (5, 12), (6, 12) and (7, 12) clusters, indicating that decomposition occurs through metal atom losses. Vanadium, molybdenum and iron metcars show the same pattern of sequential metal atom losses. Iron and chromium metcars lose more number of metal atoms for the same laser power compared to titanium and vanadium metcars. This can be understood from the bonding characteristics.

Bonding in metcars can be understood in terms of the strong C=C bonds and *M*–C σ bonds. The repulsion between d electrons of the metal and the π electrons of the C=C units become important in later transition metals. Thus, metcar structures will be less stable for later transition elements. Consequently, they fragment much more readily than Ti and V metcars.

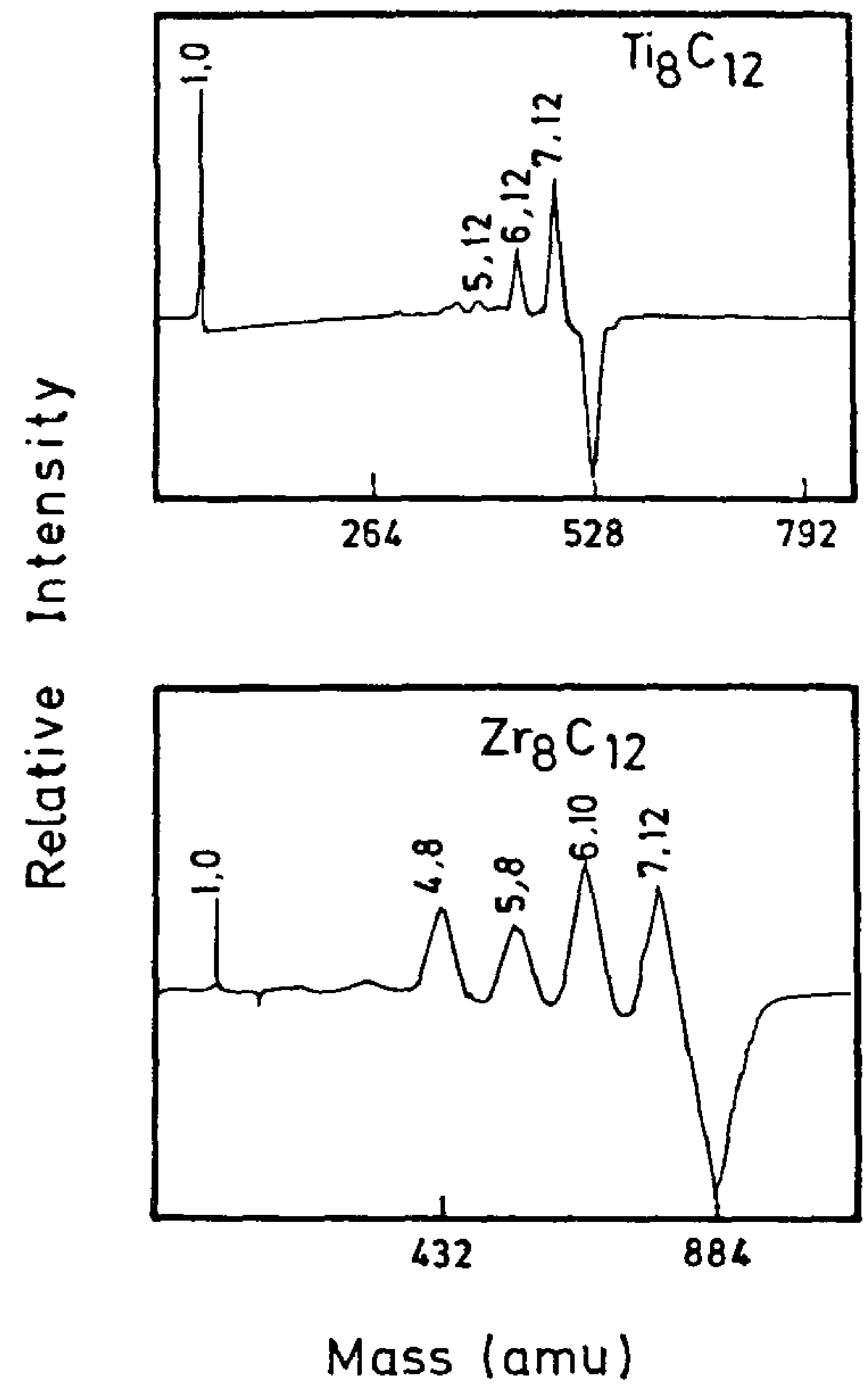

Figure 7. Photodissociation mass spectra of $Ti_8C_{12}^+$ obtained with 532 nm laser Negative peaks represent the depletion of the mass-selected parent ion and the fragment ions appear as positive peaks (From ref. 5, with permission)

In the case of zirconium, a qualitatively different behaviour is observed. The most important peaks in the spectrum are due to (7, 12), (6, 10), (5, 8), (4, 6) and Zr. This would mean that the initial fragmentation occurs via a metal atom loss, followed by MC_2 losses. This is in accordance with the importance of MC_2 units in the formation of metcars, as suggested by Castleman and colleagues. In metcars, M–(C=C) σ bonding is weaker than C=C bonds. Decomposition of a majority of metcars by the successive loss of metal atoms is consistent with this picture of bonding. It appears that the M–C_2 interaction is strong in the case of zirconium metcar compared to other systems.

Metcars are not the only possible structures in metal–carbon systems. Bulk structures of TiC, VC and ZrC, etc., all show face-centred cubic (fcc) crystal pattern. For similar metal–carbon systems of Ta_mC_n and Nb_mC_n, nanocrystal fcc structures are observed. This suggests that in metal–carbon systems, there can be two types of structures: (i) metcar and (ii) cubic[13]. In one particular system, only one form of clusters are present. This seems to suggest that thermodynamic stability of one particular form in a system might be responsible for the observed behaviour.

Under certain experimental conditions, both metcars and cubes are seen in the Ti/c system[13]. It is important to know whether these growth patterns are independent and one can be forced to the other by changing the experimental conditions. It should be mentioned that a theoretical investigation has suggested that the formation of either of these clusters depends on the experimental conditions. Experiments using niobium showed that the two structures develop independently. No cubic clusters are seen under carbon-rich conditions. It has been shown that thermodynamics of the reactions are not the only factor determining the formation of certain clusters, kinetics too play a dominant role.

Reactions of metcars

The reactivity of metcars, in particular that of $Ti_8C_{12}^+$, has been investigated at thermal energies[16]. Reactions with polar molecules such as H_2O, ND_3 and methanol showed that the first solvation shell of the ion can accommodate eight molecules. Even after increasing the reagent pressure to very high levels, no further attachment was seen. At low partial pressures, one to eight attachments are seen. In Figure 8 the reaction products with methanol are shown.

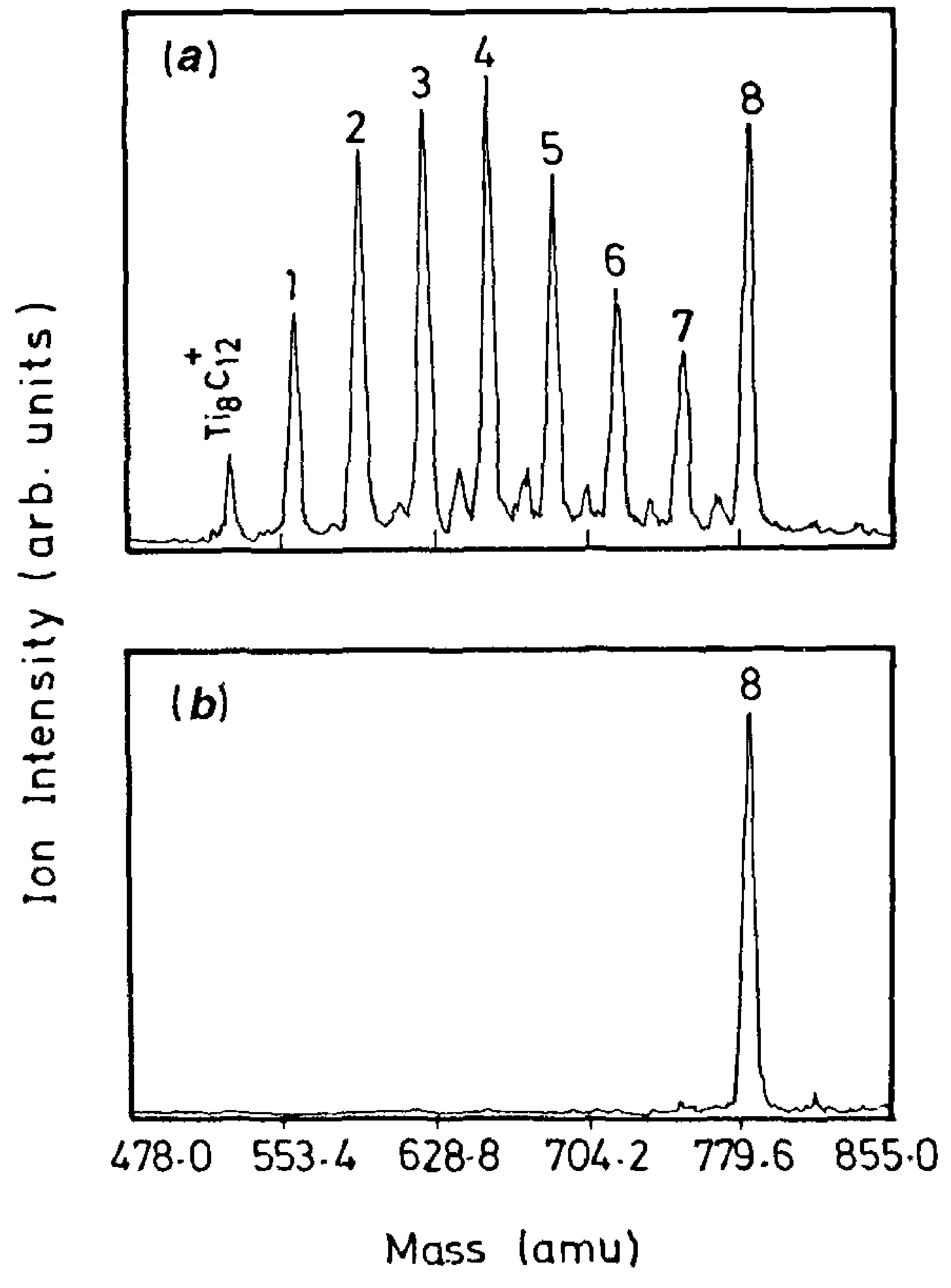

Figure 8. Mass spectra of the reaction products of methanol with $Ti_8C_{12}^+$ *a*, low partial pressure of methanol, *b*, much higher partial pressure of methanol (From ref 16, used with permission)

In the case of π-bonding molecules such as ethylene and benzene, only four molecules get attached to the metcar ion[16]. Even after increasing the partial pressures of the reagent gases to high values, no more additions were observed. Ti_8C_{12} was not shown to react appreciably with oxygen and methane.

Reactions of $Ti_8C_{12}^+$, $Nb_8C_{12}^+$ and $Ti_7NbC_{12}^+$ with acetone and methyl iodide have also been investigated[17]. Association reactions dominate in the case of acetone. In the case of the iodide, abstraction of I is observed. The bonding strength of $Ti_8C_{12}^+$–I has been determined to be larger than 56 kcal/mol. The substitution of Ti with Nb affects greatly the reactivity.

The reactivity behaviour can be understood on the basis of bonding in these molecules. Although the valence electrons of the metal atoms are used up in bonding, titanium has d orbitals capable of receiving charge. In addition, since titanium is more electropositive, its electron density will be significantly less than carbon. Both of these would make it form addition compounds with polar molecules. In addition to ion–dipole interactions, there could be ion–quadrupole and ion-induced dipole interactions. These interactions could be strong enough to hold ions and ligands together if polarizabilities and quadrupole moments of the ligands are large. Both benzene and ethylene have large polarizabilities, which would explain the complex formation. The difference in the number of π-bonding and polar ligands could be due to the differences in the interaction orientation and $Ti_8C_{12}^+$–ligand strengths. The repulsive interaction of the C=C bonds and the ligands will depend on the ligand orientation; this would be different in both the cases.

The reactivity of $V_8C_{12}^+$ studied in FTICR shows a significantly different trend[18]. Reaction with O produces $V_8C_{10}^+$ and two CO molecules. The parent ion coordinates with four molecules of MeCN or benzene. $V_8C_{12}^+$ coordinates with four molecules of H_2O. Reaction with the second molecule of H_2O results in dehydrogenation, forming $V_8C_{12}(H_2O)O^+$, and subsequent reaction yields $V_8C_{12}(H_2O)_3O^+$. These studies are consistent with T_d or D_{2d} structures with four metals in each of the different coordination sites.

Theoretical studies

Initial theoretical investigations by Lin and Hall[19] showed that the highly symmetric structure of the T_h point group is stable. Calculations done in the structure involve M–(C=C) σ bonds. The high stability is due to the dπ–pπ interaction. Each metal atom has a local C_{3v} symmetry and contributes three orbitals for σ bonding.

Later studies[20] suggested that the T_d structure, in which the 12 carbon atoms form a cylindrical closed chain capped by two M_4 units, is more stable in the case of Ti, Zr, Hf, V, Mo and W metcars. This structure is stabler than the T_h structure by more than 200 kcal/mol.

Ab initio calculations by Rohmer *et al.*[21] on Ti_8C_{12} showed that the singlet state of the T_h point group has a weak HOMO–LOMO gap (1.7 eV) and the promotion of an electron pair from $4a_g$ to the triply degenerate $4t_g$ will lead to a stabilized triplet state. Populating $4t_g$ with one more electron pair creates yet another triplet state. This state is the most stable state within the constraints of the T_h point group. However, these states, owing to electronic degeneracy, are subjected to Jahn–Teller distortion. The degeneracy can be removed by allowing all the four electrons in the partially occupied molecular orbitals to be accommodated in two orbitals. The resulting D_{2h} closed shell state is shown to be 28.5 kcal/mol more stable than the state within the constraints of the T_h point group. In this optimized structure, three C–C and Ti–C distances are found. The HOMO energy is 5.2 eV, significantly smaller than that of C_{60} (7.6 eV), computed with a double ζ basis set. The predominant character of the frontier orbitals is due to the metal; the carbon π orbital appears at 9.2 eV. Similar distortions exist for V_8C_{12} also. Without distortion, the ground state of Ti_8C_{12} is shown to be a triplet with all C–C distances equal to 1.40 Å and Ti–C distances equal to 1.98 Å. It has also been shown by qualitative reasoning based on Huckel theory[22] that full electron pairing occurs with trigonal D_{3d} structure, not with the T_h structure. Similar calculations have been performed on Zr, V, Fe and Si analogues as well[23,24]. In all the cases, metcars are stable, and even though distortions from the ideal structure occur, they remain remarkably spherical.

The electronic structure M_8X_{12}, where M represents d metal or sp metal elements and X = B, C or N, has also been investigated[25]. The study attributes the exceptional stability of the Ti_8C_{12} system to the strong Ti–C σ bonds. Such cage structures might not be optimal for metals such as Ca and Zn. If appropriate elements are substituted in place of Ti and C, the electronic structure can be significantly different. For example, Sb_8B_{12} has a closed-shell singlet ground state with a substantial HOMO–LUMO gap and, therefore, should be chemically more stable.

Calculations performed using the density functional theory[26] also show significant distortion to the cluster geometry. The binding energy per atom is about 6.6 eV, and the bonding mechanism is found to be different from fullerenes. The structure can be viewed as a distorted metal cube. The C_2 units are placed on the faces of this cube.

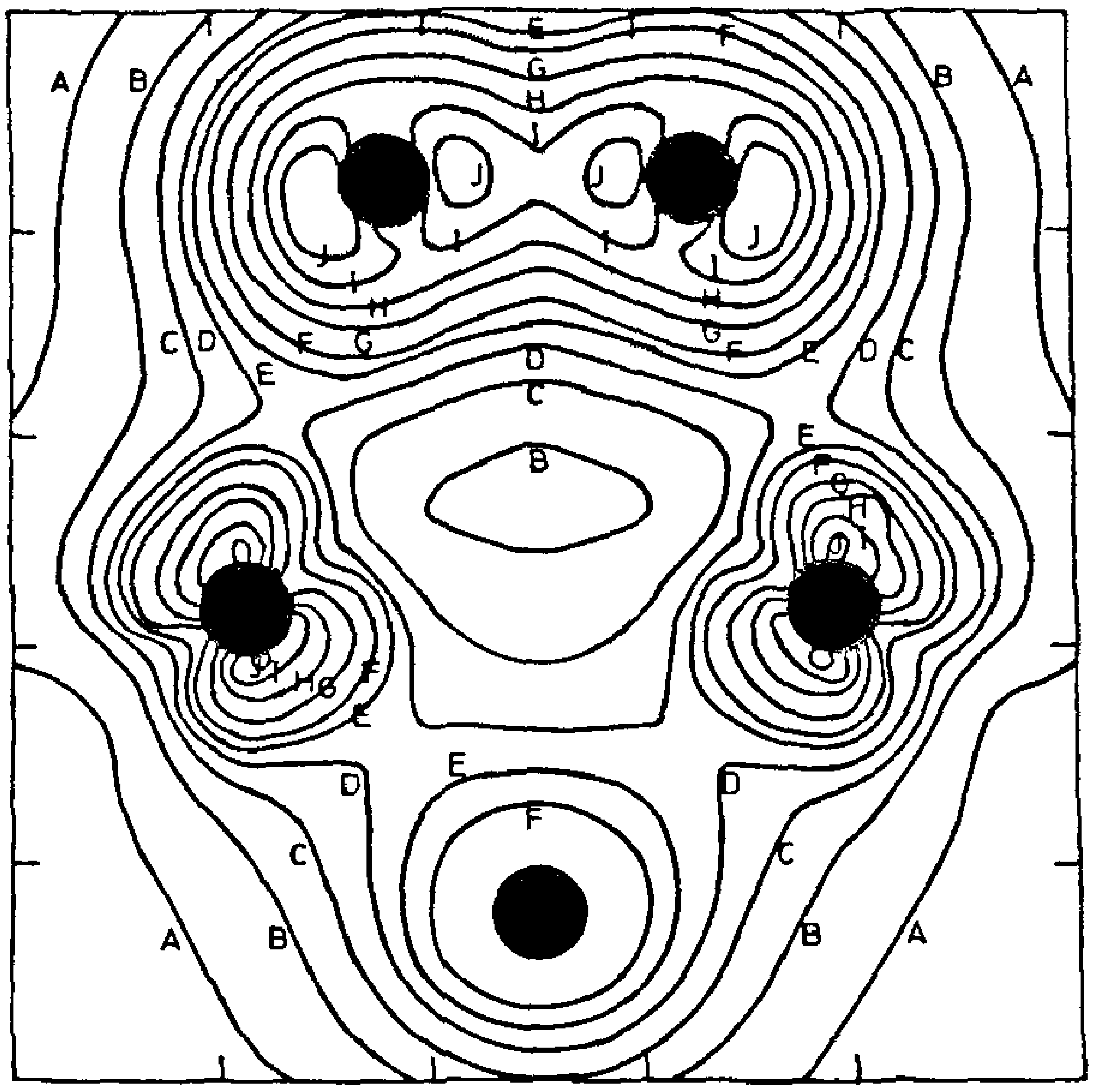

Figure 9. Computed charge density profile of a pentagonal face of Ti_8C_{12}. The top two and the bottom one are C atoms and the middle two are Ti atoms. The bottom carbon atom is slightly off the plane The method is based on LCAO-MO and density functional approximation A = 0.01, B = 0.03, C = 0.05, D = 0.07, E = 0.09; F = 0.11; G = 0.15, H = 0.19, I = 0.23, J = 0.27. (From ref 30, used with permission)

Ab initio calculations with configuration interaction have been performed for both Sc_8C_{12} and Ti_8C_{12} structures[27]. The highly symmetric T_h structure gives an A_g ground state for Sc_8C_{12} but a ^9A_g state for Ti_8C_{12}. The stability seems to arise from the overall topology of the cage. It is possible that the structure may undergo distortion to form lower-symmetry structures. There could also be isomers of higher stability.

Calculations performed using the LCAO–MO method and the density functional approximation[28–30] also showed that Ti_8C_{12} is stable and its structure is a distorted dodecahedron. The binding energy per carbon atom is quite high (6.1 eV). The density of states is high near the Fermi energy[30]. These states are derived from hybridization between Ti 3d and C sp electrons. The cluster is only weakly magnetic. The calculated IP of the molecule is about 6 eV. The calculated electron density profile in a pentagonal ring is shown in Figure 9. There is a pile-up of electrons along Ti–C and C–C bonds but very little density is seen along the Ti–Ti bond. This is consistent with the short C–C and Ti–C distances. The picture of bonding shows significant charge transfer from titanium to carbon. The type of bonding, the binding energy per atom, the ionization potential, the C–C distance, etc., of metcars show significant differences from C_{60}, suggesting that metcars, like fullerenes, are a different class of molecular clusters.

The dodecahedral structure is not the only predicted one. Rohmer *et al.*[31] predicted a distorted dodecahedron with seven possible conformations. Pauling[32] proposed a structure in which Ti atoms occupy the corners of a cube and a pair of carbon atoms occupy the centres of each face. In the structure proposed by Khan[33], the Ti atoms form a cube and a cage of 12 carbon atoms is trapped in it. Ion mobility studies have been used to verify which of these structures really exist[34]. The experimentally determined mobilities suggest that none of the cubic structures exists. The most likely structure is that proposed by Castleman's group[4] or that proposed by Rohmer *et al.*[31].

The electronic structure and stability of metcars and cubic structures containing Ti and C or N have been studied by *ab initio* density functional approach[35]. Metcars and cubes have comparable binding energies per atom for carbides. For the metal–nitrogen systems, cubes are more stable. The formation of a specific structure depends on the experimental conditions. Theoretical studies are in agreement with the experiments[11].

A theoretical study has been performed on the optical properties of metcars[36]. This study using the spherically averaged pseudopotential model combined with density functional formalism shows that Ti_8C_{12} has a static polarizability α of 50 a.u., only little lower than that of C_{60}. The collective plasma resonance is around 12 eV, which may be detected in photoelectron spectroscopy, as in the case of C_{60}.

Theoretical studies[37] on the reactivity of Ti_8C_{12} suggest that the C_2 units can coordinate with transition metal ligands such as $Pt(PH_3)_2$. In such complexes a net transfer of two electrons to Ti_8C_{12} occurs. The metal centres can also accommodate electron donors such as CO. The study suggests that the electron-deficient nature may make Ti of one metcar to interact with C_2 of another molecule. This type of associated clusters may be present in the evaporated soot.

Epilogue

It should be clear from the above discussion that metallocarbohedrenes have generated immense excitement in chemistry, physics and materials science. The unique bonding of this class of molecules would make it possible for them to show different kinds of chemistry. Some of the chemical properties could be important in catalysis. Since the molecule is predicted to be metallic, conductivity and magnetism of materials derived from metcars will be important. A method for the bulk synthesis and chemical processes for purification should be developed. There have been attempts along this line and Ti_8C_{12} has been detected in soot obtained by arc evaporation of a Ti–C composite[38]. There have been no developments beyond this point in the synthesis and characterization. Gas phase studies have definitively established that neutral metallocarbohedrene molecules are stable. By applying proper synthetic methods it should be possible to make them in bulk. Their reactivity towards molecules such as oxygen is not high, showing that these molecules would be air-stable. They form addition compounds with polar molecules, which would make it possible to extract them with polar molecules. With the advancements in the chemistry of fullerenes, it would be interesting to apply similar chemistry to a completely different kind of closed cage structures.

It should be apparent from the discussion that quantum leaps in scientific frontiers, particularly in chemical sciences, today require state-of-the-art instrumentation. Almost all of the frontier developments in molecular chemistry are due to bringing together different tools of scientific research. Foremost amongst them are the methods of mass spectrometry.

Molecular cluster research continues to show remarkable growth. The discovery of closed cage structures opens up immense possibilities. The development in just one class of molecules, namely fullerenes, itself has been enormous. With the rapid advancement in instrumentation, it is definite that more excitements would occur in the years to come. An important point to note is that chemistry is now discovered and understood in the gas phase in minute amounts. The translation of this chemistry to condensed phase often requires several years of effort. Modern chemistry is often born in mass spectrometers with the assistance of tools such as lasers and supersonic nozzles. It is important to initiate work along similar lines in India because immense possibilities are awaiting to be explored.

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RESEARCH ARTICLE

Correlating more than two particles in quantum mechanics

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A few years ago, Greenberger, Horne and Zeilinger showed that quantum nonlocality effects, already well-known for systems of two correlated particles, are more spectacular with three particles or more. For observing these effects, one has to initially put the system in an entangled quantum state that is very specific, and not necessarily easy to produce. We discuss some properties of these states and we propose an experimental scheme which allows to create them by successive applications of the postulate of measurement in quantum mechanics. The procedure should, in principle, allow the creation of the desired correlations in systems containing a relatively large number of particles. We propose to apply it to single paramagnetic ions stored in traps, through the measurement of the rotation of the plane of polarization of a laser beam interacting with the ions (quantized Faraday effect).

ONE of the great contributions of Einstein, with Podolsky and Rosen[1], later completed by the celebrated theorem of Bell[2], was to show that the most surprising feature of quantum mechanics is not indeterminism, as was initially thought, but nonlocality. While Von Neumann's arguments, attempting to prove that the results of quantum mechanics cannot be reproduced by deterministic theories, have been shown by Bell to be not conclusive[3], the Bell theorem provides quantitative and general criteria about locality violation. Now, it is a delicate matter to decide in what sense exactly quantum mechanics is nonlocal, or, more generally, to word a precise definition of what is a local theory[4]; this question, at the border of physics and philosophy, is probably still a matter of debate, and we will not discuss it here. What is clear, anyway, is that we do not have an equivalent of the Bell theorem for indeterminism so that, for the moment at least, believing or not believing in the fundamentally nondeterministic character of microscopic processes is more or less a matter of taste. In fact, it is not impossible that the fundamental theory of microscopic processes will, one day, include a (nonlocal) deterministic mechanism behind what