Predicted Structures for Ti_8C_{12} and Si_8C_{12} Dodecahedron Molecules

Robin W. Grimes* and Julian D. Gale

The Royal Institution of Great Britain, 21 Albemarle St., London W1X 4BS, UK

Quantum cluster calculations confirm the high stability of both M_8C_{12} clusters, their equilibrium geometries being distorted dodecahedrons; the charge transfer within the two cluster types and the electronic structures are shown to be markedly different.

There is now considerable literature concerning the properties of C_{60} and related clusters.[1] In addition to pure carbon materials, clusters have also been formed with a variety of metal ions in association with the cages.[1-3] Nevertheless, these structures are essentially variations on the C_{60} theme. In this light, the recent work of Guo *et al.*,[4] who described the formation of Ti_8C_{12} metallo-carbohedrene clusters, is of particular importance. In that study the Ti_8C_{12} dodecahedron clusters were formed through the reaction of laser vaporized titanium with a variety of hydrocarbon gases.[4] The resulting ionized clusters were analysed using mass spectroscopy which revealed a completely dominant so-called 'super magic' peak at 528 atomic mass units. By varying the isotopic composition of the reactants it was possible to establish that the clusters responsible for the peak had the composition Ti_8C_{12}. It was suggested that the dominance of the spectra by this cluster was due to Ti_8C_{12} assuming a particularly stable dodecahedron structure. In this configuration each constituent pentagon ring consists of three carbon and two titanium atoms [see Fig. 1(*a*)]. The stability of the molecular unit is then derived

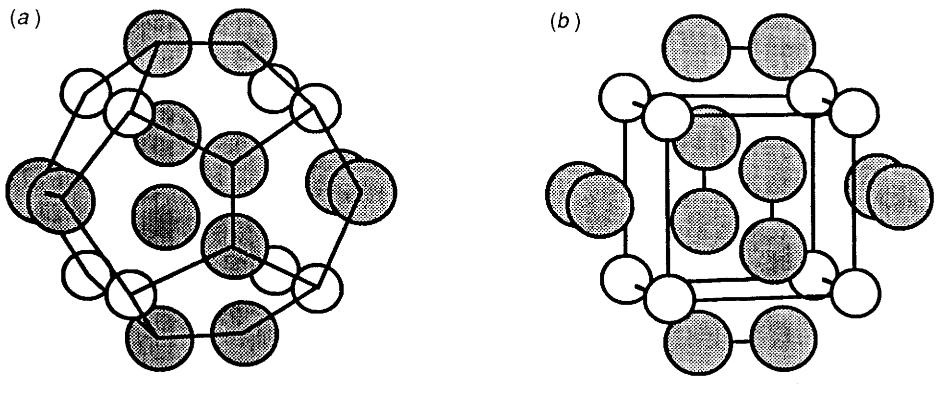

Fig. 1 Representations of the Ti_8C_{12} clusters. The shaded spheres are carbon, the smaller spheres are Ti.

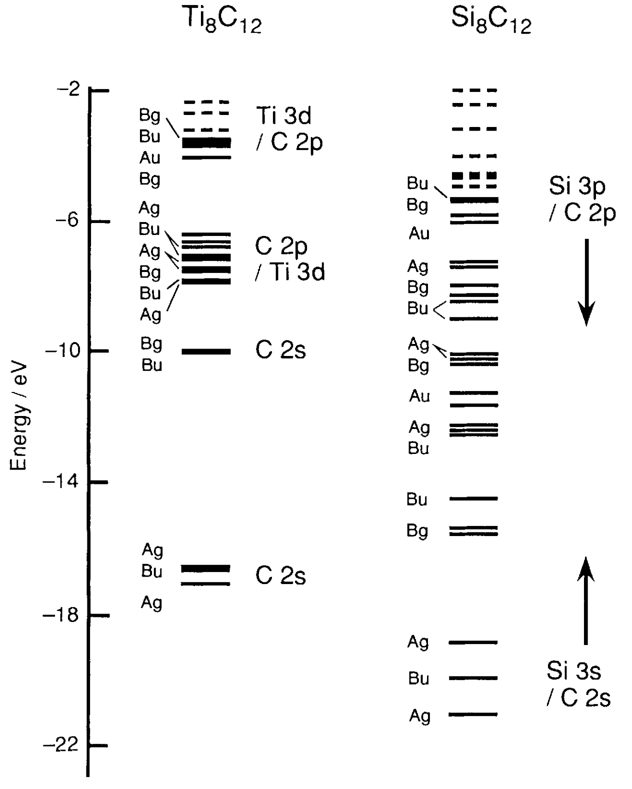

Fig. 2 Molecular orbital energies and symmetries within the D_{2h} point group: —— occupied, - - - unoccupied

Table 1 Calculated properties of M_8C_{12} clusters and the cluster fragments M_8 and C_2

Clusters:	Ti_8C_{12}	Si_8C_{12}
Distances/Å		
M–M	3.06	3.03
C–C	1.40	1.38
M–C	1.98	1.88
Centre of C_2 to centre of cube plane	0.94	0.74
Mulliken charges[a]	Ti: 0.75+ C: 0.50−	Si: 0.13+ C: 0.09−
Ground state multiplicity	3	5
Formation energy/eV from M_8 and $6C_2$	−58.62	−46.20
Ionization energy/eV	5.33	6.92
Location of hole in cluster M_8:	$\frac{2}{3}$	1
C_2:	$\frac{1}{3}$	0
Fragments (*d*/Å):		
M–M in M_8 cube	2.44	2.37
C–C in C_2 dimer	1.27[b]	1.31[c]

[a] The Hartree–Fock Mulliken charges for Ti_8C_{12} were +0.85 and −0.57 respectively. These are expected to alter slightly once the wavefunction is corrected for correlation. [b] This calculated ground state for C_2^- is the experimentally observed $^2\Sigma_g$ state; the experimental value is 1.31 Å.[12] [c] This calculated ground state for C_2^0 is the experimentally observed $^3\Pi u$ first excited state, which is only 0.09 eV above the actual 1 Σg ground state; the experimental value for $^3\Pi_u$ is 1.31 Å.[12]

from the network of s and p bonds formed between each atom and its three nearest neighbours. As an alternative model for the electronic structure it is possible to consider the cluster as a cube of eight metal–metal bonded titanium atoms surrounded by six C_2 dimers, one adjacent to each of the Ti_8 cube faces [see Fig. 1(*b*)]. The present work suggests that while the clusters behave essentially as single molecular units they do exhibit some features which make this alternative description sometimes useful.

In this study we shall employ quantum cluster methods to examine more closely the structural and electronic properties of the Ti_8C_{12} cluster and the as yet unknown analogous Si_8C_{12} cluster. Most calculations were based on the local density approximation (LDA).[5,6] A high quality double-numerical basis set[6] was used which included polarization functions: 3d on C and Si; 4p on Ti. Calculations were carried out with a D_{2h} molecular symmetry. For comparative purposes, Hartree–Fock (HF) calculations[7] at the LDA optimized geometry were also performed to corroborate certain of the results; an sd-Model Potential with a 41G valence contraction was used for Ti[8] and for C a 6-31G basis.[9] Both methods have been shown to be highly successful in reproducing the structural and electronic properties of molecular systems.[10]

The results of our LDA simulation studies on neutral and singly ionized clusters are presented in Table 1. In Fig. 2 we show the molecular orbital energies for neutral Ti_8C_{12} and Si_8C_{12}. In addition to providing predictions of physical properties, we shall focus our discussion of the results in terms of the insight provided into the molecular electronic structure.

Consider first the structure of the Ti_8C_{12} molecule. Table 1 shows that, as might have been expected, the predicted values of the Ti–C and C–C distances are not equal. This implies that the molecule is a distorted dodecahedron: in fact, the distance from the centre of the C–C bond to the centre of the cube defined by Ti_8 is larger than that required to form a regular dodecahedron. Perhaps then the molecule should be regarded more as a Ti_8 cube with six associated C_2 molecules as depicted in Fig. 1(*b*). However, if we consider the Mulliken charges we find that in Ti_8C_{12} both Ti and C are charged (see Table 1). In fact, each C_2 pair assumes a −1 charge although the calculated C–C distance for C_2^- is 0.13 Å less than that in Ti_8C_{12}.

If we now turn our attention to the Ti_8C_{12} molecular orbital energies in Fig. 2 it is immediately clear that the C 2s levels form two distinct groups separated by *ca.* 7 eV. Calculations on C_2 show a similar C 2s splitting of *ca.* 9 eV for both C_2^0 and C_2^-. The higher occupied levels also form two groups both of which are the result of overlap between C 2p and Ti 3d atomic orbitals; the group nearest the HOMO are slightly more Ti 3d in nature and the lower group are marginally more C 2p like. An identical distribution of orbital energies and triplet ground state was found using the HF method.

What we can conclude from these observations is that the Ti_8C_{12} molecule retains some of the characteristics of its constituent Ti_8 and C_2 components but is essentially a very highly bound molecular species. The high calculated binding energy reported in Table 1 would indeed result in a stable molecular species even under the conditions encountered in a molecular beam. Initial results from HF calculations indicate a very similar high binding energy. In this regard, it is perhaps worth drawing attention to the fact that that since the overall charge of the Ti_8 cube is +6, the Ti_8 cube has a complete set of 10 d electrons. This will certainly contribute to the stability of the molecule.

The results for the structure of the Si_8C_{12} molecule are very similar to those of Ti_8C_{12}; it is a distorted dodecahedron. This is despite the fact that the Mulliken charges for Si and C are almost zero (see Table 1). Indeed, electronically, Si_8C_{12} shows marked differences from Ti_8C_{12}. The ground state multiplicity of Si_8C_{12} is different from that of Ti_8C_{12}. Also, the molecular orbitals form a much more continuous distribution as shown in Fig. 2. This is due to strong Si 3s/C 2s and Si 3p/C 2p overlap. Si_8C_{12} is clearly a more 'covalent' molecule than

Ti_8C_{12}. Nevertheless, Si_8C_{12} is highly stable albeit slightly less stable than Ti_8C_{12}.

Lastly we draw attention to the calculated ionization properties (see Table 1). In particular, although the ionization energies of Ti_8C_{12} and Si_8C_{12} are *ca.* 5 and 7 eV respectively, the hole distribution is markedly different. In Ti_8C_{12} the hole is distributed on both species whereas in Si_8C_{12} it is located only on the Si_8 cube. The ionized energies reported here are for fully relaxed geometries. However, the photoionization energies are only *ca.* 0.04 eV higher in both cases and the relaxation accompanying ionization is not greater than 0.02 Å for any of the characteristic distances described in Table 1.

The work discussed in this communication represents a new direction in carbon cluster research. In particular, compared to conventional fullerenes, the cage incorporates a much higher proportion of species other than carbon. In addition, these clusters are significantly smaller in size. Thus, as suggested by Guo *et al.*,[4] these materials herald the beginning of a potentially rich new area of investigation. Indeed, as this manuscript was in preparation, new metallo-carbohedrenes have been reported in which the Ti atoms are replaced by V, Zr or Hf.[12]

Received, 4th June 1992; Com. 2/02954E

References

1 H. Schwartz, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 293.

2 T. Pradeep, G. U. Kulkarni, K. R. Kannan, T. N. Guru Row and C. N. R. Rao, *J. Am. Chem. Soc.*, 1992, **114**, 2272.

3 T. Guo, J. Changming and R. E. Smalley, *J. Phys. Chem.*, 1991, **95**, 4948.

4 B. C. Guo, K. P. Kerns and A. W. Castleman, Jr., *Science*, 1992, **255**, 1411.

5 DMol version 2.1, BIOSYM Technologies, San Diego, USA, 1991.

6 B. Delley, *J. Chem. Phys.*, 1991, **92**, 508.

7 CADPAC5 developed by R. D. Amos, *et. al.*, Cambridge, UK, 1992.

8 Y. Sakai, E. Miyoshi, M. Klobukowski and S. Huzinaga, *J. Comput. Chem.*, 1987, **8**, 226.

9 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1971, **56**, 2257.

10 See for example for LDA: B. Delley, *Chem. Phys.*, 1986, **110**, 329; S.-H. Chou, A. J. Freeman, S. Grigoras, T. M. Gentle, B. Delley and E. Wimmer, *J. Chem. Phys.*, 1988, **89**, 5177; and for HF: D. Jayatilaka, R. D. Amos and N. Koga, *Chem. Phys. Lett.*, 1989, **163**, 151.

11 K. P. Huber and G. Hertzberg, *Molecular Spectra and Structure IV: Constants of Diatomic Molecules*, van Nostrand Rheinhold, New York, 1979.

12 B. C. Guo, S. Wei, J. Purnell, S. Buzza and A. W. Castleman, Jr., *Science*, 1992, **256**, 515.