

Structural Identification of Metcars

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The ground-state structure of the metcar Ti_8C_{12} is investigated using first-principles computer simulations. Comparison with recent experimental data on the vibrational spectrum of gas phase Ti_8C_{12} allows one to identify the geometrical structure of the clusters studied in the experiment. The present combination of predictive first-principles computer simulations and detailed experimental measurements of the vibrational spectra of clusters offers the first viable tool for structural identification of cluster shapes.

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Nearly one decade has passed since the spectacular discovery by Castleman's group [1] of Ti_8C_{12} and other metcars. At present, and in spite of the tremendous research effort carried out since then (for a review and exhaustive list of references, see Ref. [2]), no one can tell the equilibrium structure of Ti_8C_{12} . From the initial T_h structure proposed by Castleman and collaborators—depicted in Fig. 1—to the more recently proposed structures with associated group symmetries T_d and D_{2d} —also depicted in Fig. 1—no compelling argument has been advanced so far and no piece of experimental information exists which, alone, can decide for (or exclude) any of the competing structures proposed to date. Furthermore, it is noteworthy that most of the theoretical arguments advanced to date in favor or against a specific metcar shape were based on energetic considerations alone. As is well known, such arguments are only valid at $T = 0$ K.

It is within such a scenario that recently van Heijnsbergen *et al.* [3] have succeeded in determining, for the first time, the infrared (IR) vibrational spectrum of the Ti_8C_{12} metcar in the gas phase. The technique employed was resonant enhanced multiphoton ionization using a tunable IR laser (IR-REMPI), a technique which had already been used, with success, in a similar determination of the IR spectra of the fullerenes C_{60} and C_{70} , also in gas phase [4], and which takes advantage of the fact that, for these systems, the dissociation energy is larger than the ionization potential, which favors deexcitation of the clusters via thermionic emission. More recently, the same technique proved very useful in supporting the formation of titanium carbide during a short phase of catastrophic mass loss in dying, low-mass stars [5].

As is well known, the vibrational spectrum of a cluster can provide invaluable information regarding its geometry [6–8]. As such, it is highly desirable to compute the vibrational spectrum of Ti_8C_{12} in a reliable way and hope that, by comparing with the available experimental data, one is able to decide which structure is most likely associated with the gas-phase clusters traveling in the experimental

setup of Ref. [3]. Such is the purpose of this Letter in which we compute, for the first time, the vibrational spectra of the metcar Ti_8C_{12} , for its various symmetric and non-symmetric (see below) structures which show up as local minima in the potential energy hypersurface of 54 dimensions associated with this cluster. Two main conclusions can be drawn, based on our first-principles structural optimizations and calculations of the IR spectra of Ti_8C_{12} , carried out at several levels of approximation to density

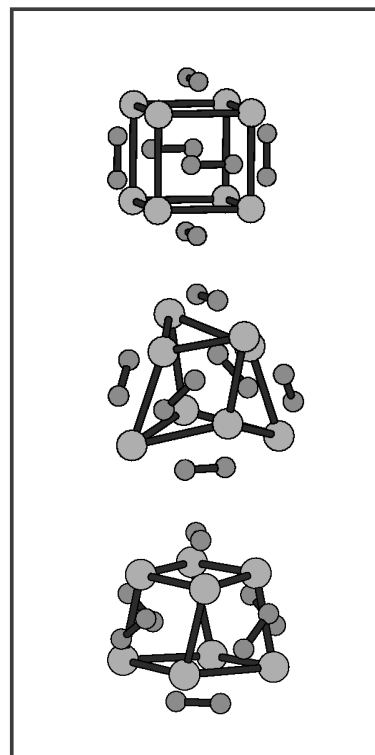


FIG. 1. The optimized, symmetric seed structures of Ti_8C_{12} obtained in this work are depicted, exhibiting a T_h (top panel), T_d (middle panel), and D_{2d} (lower panel) symmetry. These structures were used as a starting point for symmetry unconstrained structural optimizations (see main text for details).

functional theory (DFT): (i) The optimal structures of Ti_8C_{12} are not always symmetric, revealing subtle Jahn-Teller distortions via which they may acquire additional stability. (ii) The IR spectra associated with each of these candidate structures are sufficiently different to enable us to assign to the experimental spectrum [3] a D_{2d} -like structure found here as a result of our first principles structural optimizations of Ti_8C_{12} . The present results provide a very interesting possibility for those clusters of which the IR spectra can be recorded, since it is demonstrated here that a comparison between the experimental and theoretical spectra can be used as an efficient tool for the structural identification of clusters.

All calculations were carried out making use of the ADF program package [9], which enables us to compute all properties of interest to this work at different levels of approximation to DFT. In practice, one solves the Kohn-Sham equations by projecting them in a finite, localized basis set of Slater-type orbitals. For carbon, we used the frozen-core approximation and a triple zeta basis augmented with two polarization functions, which has proved successful in connection with fullerenes [8]. For titanium we used a triple zeta all electron basis with diffuse functions available in the package. For the exchange-correlation functional we took that of Vosko *et al.* [10] for the local density approximation (LDA) calculations and that of Perdew *et al.* [11] for the generalized gradient approximation (GGA) calculations. Both types of approximations have been shown to provide reliable results for both structural and electronic properties of organometallic clusters [6,7,12]. Therefore, we used both approximations as well as different flavors (e.g., spin polarized, spin unpolarized, etc.) in order to confirm that indeed, the results reported here do not depend on the level of approximation used. Consequently, in what follows all numerical values as well as the IR spectra presented correspond to results obtained with spin-unpolarized GGA computations.

Within such an *ab initio* framework, one can calculate, for a given set of atomic coordinates, many electronic prop-

erties such as the cohesive energy, effective one-electron energies, highest-occupied–lowest-unoccupied molecular orbital (HOMO-LUMO) gap, bandwidth, etc. Furthermore, one can relax the structure so as to minimize the total energy of the cluster, by means of a conjugate gradient technique. The vibrational spectrum of a cluster can then be determined by diagonalizing the Cartesian displacement matrix explicitly constructed in ADF. Finally, the computation of the static polarizability of the cluster—for which the inclusion of polarization functions in the basis set proves crucial [13]—has been carried out. As is well known, additional information on the cluster shape can be inferred from the knowledge of its directional polarizabilities [14].

For the highly symmetric structures displayed in Fig. 1, with (from top to bottom) T_h , T_d , and D_{2d} symmetry, respectively, our results essentially reproduce those previously obtained by equivalent computational implementations in what concerns their energetics [2]. As such, the energetically most stable structure has a T_d symmetry which, at the level of spin-unpolarized GGA, has the HOMO partially occupied. All structures were optimized with the underlying symmetry restricted. Subsequently, and using the same computational framework, we applied random perturbations to these three structures, corresponding to random displacements of one or more atoms of the cluster with respect to their equilibrium positions, thereby breaking their intrinsic symmetry. After each random perturbation, we performed a conjugate gradient optimization of the structures without imposing any symmetry constraints. As a result we obtained several asymmetric local minima, of which two are highly stable. These, together with the results obtained for the three symmetric structures depicted in Fig. 1, are characterized in Table I. Since these two minima reveal no special symmetry, we label them with reference to the high-symmetry structure that we used as a “seed” for perturbation, appending an asterisk to distinguish these from the seed structures. This notation relies on the fact that the T_d^* and D_{2d}^* structures

TABLE I. Results for the various quantities computed for the five structures of Ti_8C_{12} considered in this work. The quantity Δ represents the difference in cohesive energy between the most stable structure found in this work—denoted by T_d^* —and the actual structure (see main text for details). In the remaining lines, the values for the static polarizability of Ti_8C_{12} are tabulated (in \AA^3) along the principal axes of the cluster. Since these values provide a measure of the relative length of each principal axis of the cluster, one can classify the structure according to the corresponding shape of the ellipsoid [16]: spherical, prolate, oblate, or triaxial. $\langle\alpha_0\rangle = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$ provides the value for the average polarizability of each structure.

geometry	T_h	D_{2d}	T_d	D_{2d}^*	T_d^*
HOMO-LUMO gap, eV	0.60	0.43	0.00	0.45	0.08
Δ , eV	15.14	1.15	0.35	1.81	0.00
Polarizability, \AA^3	(spherical)	(prolate)	(spherical)	(triaxial)	(triaxial)
α_{xx}	52.44	51.36	51.31	52.26	54.11
α_{yy}	52.44	50.47	51.31	50.20	52.36
α_{zz}	52.44	50.47	51.31	49.63	51.40
$\langle\alpha_0\rangle$	52.44	50.77	51.31	50.70	52.62

closely resemble the original seed structures. Yet, there is a sizable change of stability for these two nonsymmetric structures, as reflected in the changes of both the cohesive energy and the HOMO-LUMO gaps. In evolving from the T_d to the T_d^* structure, one observes that basically a rearrangement of the Ti atoms in the skeleton takes place, changing from a spherical to a triaxial shape (cf. Table I), whereas the carbon dimers maintain their bond lengths and relative orientation. A similar situation applies, to a lesser extent, for the difference between the D_{2d} and D_{2d}^* structures, in which case the Ti skeleton evolves from a prolate to a triaxial shape (cf. Table I). Similar to what happens with the T_d^* structure, which develops a small HOMO-LUMO gap of less than 0.1 eV, one finds that the corresponding HOMO-LUMO gap associated with the D_{2d}^* structure is slightly larger than the gap of the symmetric seed. At any rate, it is worth mentioning that the HOMO-LUMO gaps associated with the D_{2d} -based structures are much larger than those associated with the T_d -based structures, at all levels of approximation to DFT.

From Table I, one can observe that the average static polarizability of T_d^* is the largest. To be noted as well is that the nonsymmetric nature of the T_d^* geometry makes the polarizability values along the three principal axes all different.

For the five minima we computed the associated vibrational spectra. The results are shown in Fig. 2, together with the experimental spectrum obtained in Ref. [3], which corresponds to the shaded curve present in all plots. The results show a remarkable feature, associated with the high-energy side of the IR spectra: Indeed, the spectra of the T_h structure displays a three-peak structure, whereas the T_d structures show a two-peak structure and the D_{2d} structures show a single-peak structure. All theoretical spectra were obtained in GGA, and the vibrational peaks have been folded with normalized Gaussian functions with a full width at half maximum of 40 cm^{-1} , chosen to fit the overall experimental width observed. It is noteworthy that, as a result of this folding, the single peak obtained for the D_{2d} structures results from the merging of a main peak and a smaller peak corresponding to two different E_1 -type vibrations of the symmetric cluster. A similar situation can be inferred from the experimental spectrum, which exhibits shoulders at the edge of the main peak at $\approx 1400\text{ cm}^{-1}$. Similarly, the peak in the middle of the three-peak structure obtained for the T_h structure has a shoulder which evidences the occurrence of a small peak lying close in energy with the main peak of the IR-spectrum. Finally, the two-peak line shape associated with the T_d structures results from four peaks which are pairwise quasidegenerate. These peak structures were found to be present at all levels of approximation to DFT. In view of this procedure, it is clear that a single-peak structure is the only one compatible with the experimental data of Ref. [3].

Common to all structures, the theoretical IR spectra concentrate a sizeable strength in the low end of the spectra, divided among two main peaks, at ≈ 250 and

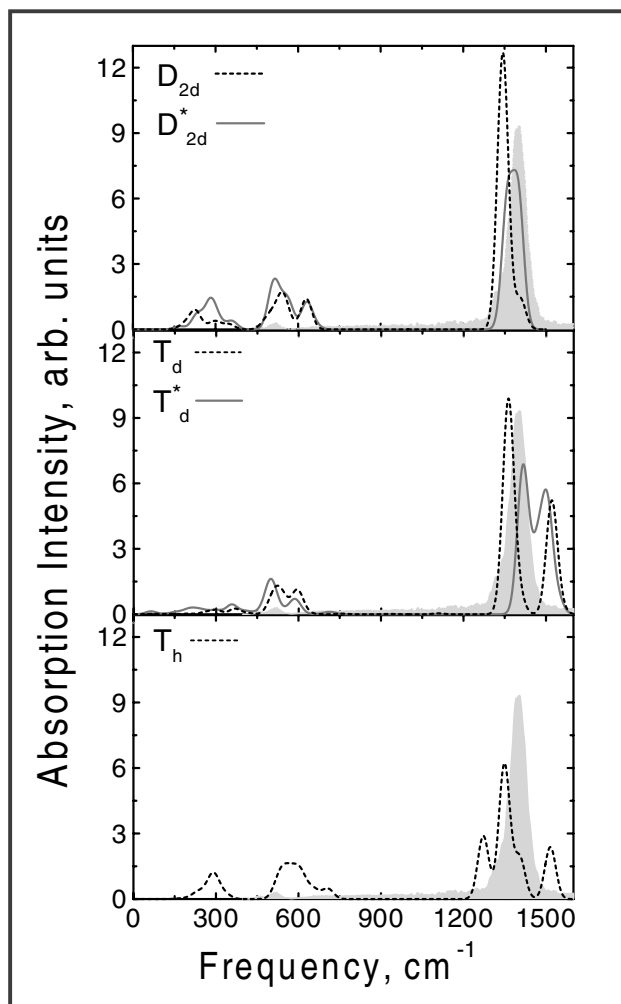


FIG. 2. Comparison between the computed infrared absorption spectra for all five structures (three symmetric and two nonsymmetric) obtained here as local minima of Ti_3C_{12} , and the experimental spectrum of Ref. [3]. The upper panel shows the comparison for the D_{2d} -like minima, the middle panel depicts the comparison for the T_d -like minima, whereas the lower panel shows the comparison for the T_h minimum. In all panels, the experimental data correspond to the shaded curve. The dashed lines represent the results for the symmetric minima, whereas the solid lines represent the results for the nonsymmetric minima.

$\approx 500\text{ cm}^{-1}$. Since the experimental spectra scanned frequencies in the interval $[400, 1650]\text{ cm}^{-1}$, this means that theoretical peaks obtained at $\approx 250\text{ cm}^{-1}$ lie outside the experimental energy window and cannot be accounted for by these experimental results. Furthermore, the statistics underlying the experimental data of Ref. [3] change as the energy changes [15], which means that the experimental data display a different normalization at different energies, as opposed to the theoretical spectra which are uniquely normalized, thereby lending physical meaning to the relative strength associated with each peak. As a result, one cannot directly compare the relative strength between the theoretical and experimental peaks, being left with the peak positions. In keeping with these considerations, one

may conclude that the agreement between the theoretical and the experimental data is very good, allowing us to assign a D_{2d} -like shape to the clusters flying in the experimental apparatus of Ref. [3].

As pointed out in Ref. [3], the high-energy region of the IR spectra is expected to receive contributions associated mostly with vibrations of the di-carbon system, whereas the low-energy part of the spectra is expected to be more directly associated with the vibrations of the titanium skeleton. Indeed, at this level of approximation—GGA to DFT—the vibrational frequency of the carbon dimer occurs at 1670 cm^{-1} for an intercarbon distance of 2.5 bohr. These results can be directly compared to the distances between carbon atoms in the D_{2d} and D_{2d}^* structures—all at ≈ 2.6 bohr—and also the high-frequency peak of the vibrational spectrum corresponding to these structures, at $\approx 1370\text{ cm}^{-1}$. However, the changes within the titanium skeleton as one evolves from the D_{2d} to the D_{2d}^* (and, for that sake, from the T_d to the T_d^*) structures, with associated modifications of the IR spectra, put in evidence the role played by the titanium-carbon coupling in the resulting IR spectrum. In this respect, one should point out that DFT is known to accurately describe the carbon-based systems, as well as the titanium-carbon compounds, lending credibility to the results obtained herewith. Comparing the two structures T_d^* and D_{2d}^* , one observes that the di-carbon bond length in the T_d^* structure is 2.5 bohr, whereas for the D_{2d}^* it is nearly 2.6 bohr. For the Ti-Ti bond lengths, we have from 5.4 to 5.6 bohr for the T_d^* structure and 5.3 to 5.5 bohr for the D_{2d}^* structure. Finally, we have bond lengths between 3.6 and 4.2 bohr for the Ti-C bond lengths in the T_d^* structure, to be compared with the interval 3.8 and 4.1 bohr for the D_{2d}^* structure.

In view of these results, one concludes that the structure with an associated IR spectrum which best fits the experimental peak positions does not correspond to that of the most stable cluster found. However, it is also clear that the Ti_8C_{12} clusters flying in the experimental apparatus of Ref. [3] are not at $T = 0\text{ K}$, at which energy arguments alone are strictly valid. Indeed, at finite temperature, clusters are both energy and entropy driven towards stability [16,17] and, in what concerns entropy, its role is expected to be more pronounced in the T_d -like structures than in the D_{2d} -like structures, due to the much smaller HOMO-LUMO gaps of the former structures. In other words, it is likely that entropy will contribute, at finite temperatures, to change more effectively the topology of the free-energy hypersurface in the vicinity of the T_d minima (as compared to the $T = 0$ energy hypersurface) than in the vicinity of the D_{2d} minima. As a result the D_{2d} structures may become more abundant at finite temperatures, as one expects to happen in the cluster beam of Ref. [3].

To summarize, it is found that the most stable geometry of Ti_8C_{12} corresponds to a T_d -like, nonsymmetric structure. However, by comparing with the experimental data from Ref. [3], one is led to conclude that the most abundant structure present in the gas-phase experiments corresponds to a D_{2d} -like structure. Indeed, of all spectra calculated, only those associated with the D_{2d} -like structures are compatible with the experimental results. Furthermore, not only do these structures have a high stability but they also display the largest HOMO-LUMO gaps of all structures computed here. Of all the local minima identified so far for Ti_8C_{12} the T_d^* obtained here corresponds to the structure in which the interatomic bonds are largest. Taking into account the well-known tendency of LDA and GGA to underestimate the bond lengths, it is expected that real Ti_8C_{12} clusters will span a somewhat larger effective volume.

The results obtained here for Ti_8C_{12} can be readily generalized to the vast family of metcars. The bottleneck of all the calculations is the accurate determination of the global minimum structure, which may turn out to be nonsymmetric. Work along these lines is in progress.

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- [1] B. C. Guo, K. P. Kerns, and A. W. Castleman, Jr., *Science* **255**, 1411 (1992); B. C. Guo *et al.*, *ibid.* **256**, 511 (1992).
 - [2] M. M. Rohmer and M. Bénard, and Josep-M. Poblet, *Chem. Rev.* **100**, 495 (2000).
 - [3] Deniz van Heijnsbergen *et al.*, *Phys. Rev. Lett.* **83**, 4983 (1999).
 - [4] G. von Helden *et al.*, *Phys. Rev. Lett.* **79**, 5234 (1997).
 - [5] G. von Helden *et al.*, *Science* **288**, 313 (2000).
 - [6] Koblar Jackson *et al.*, *Phys. Rev. B* **55**, 2549 (1997).
 - [7] Arlin Briley *et al.*, *Phys. Rev. B* **58**, 1786 (1997).
 - [8] G. K. Gueorguiev and J. M. Pacheco, *J. Chem. Phys.* **114**, 6068 (2001).
 - [9] G. te Velde and E. J. Baerends, *J. Comput. Phys.* **99**, 84 (1992).
 - [10] S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.* **58**, 1200 (1980).
 - [11] J. P. Perdew *et al.*, *Phys. Rev. B* **46**, 6671 (1992).
 - [12] J. M. Pacheco and J. L. Martins, *J. Chem. Phys.* **106**, 6039 (1997).
 - [13] S. J. A. van Gisbergen, J. M. Pacheco, and E. J. Baerends, *Phys. Rev. A* **63**, 063201 (2001).
 - [14] I. Moullet *et al.*, *Phys. Rev. Lett.* **65**, 476 (1990).
 - [15] Deniz van Heijnsbergen (private communication).
 - [16] J. M. Pacheco and R. A. Broglia, *Phys. Rev. Lett.* **62**, 1400 (1989).
 - [17] O. Gentzen and M. Brack, *Phys. Rev. Lett.* **67**, 3286 (1991).