Predicted Infrared and Raman Spectra for Neutral Ti$_8$C$_{12}$ Isomers

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Using a density-functional based algorithm, the full IR and Raman spectra are calculated for the neutral Ti$_8$C$_{12}$ cluster assuming geometries of T$_h$, T$_d$, D$_{2d}$ and C$_{3v}$ symmetry. The Ti$_8$ pentagonal dodecahedron is found to be dynamically unstable. The calculated properties of the relaxed structure having C$_{3v}$ symmetry are found to be in excellent agreement with experimental gas phase infrared results, ionization potential and electron affinity measurements. Consequently, the results presented may be used as a reference for further experimental characterization using vibrational spectroscopy.

I. INTRODUCTION

In 1992, Castleman and co-workers$^{[1]}$ discovered the first of a family of magic number clusters, called metallocarbohedrenes, amidst a metal-carbon cluster distribution produced using a laser plasma reactor source. Metallocarbohedrenes, or Met-Cars for short, are clusters of stoichiometry M$_8$C$_{12}$ (M = V, Zr, Hf, Ti, Nb, Mo, Fe, C)$_2$ or Ti$_8$-M$_1$C$_{12}$ (M = Zr, Hf, Nb, Mo, Ta, W, Si, Y, Nb, Mo, Ta, W).$^{[2]}$ Bearing an unusual 2:3 metal-carbon reduced stoichiometric ratio, a pentagonal dodecahedral cage structure having T$_h$ point group symmetry was proposed by Castleman to account for ligand titration experiments which suggested that the eight metal atoms had similar coordination.$^{[3]}$ Shortly thereafter, Dance$^{[4]}$ proposed a tetracapped tetrahedron of T$_d$ symmetry and later showed that the T$_h$ dodecahedron was higher in energy by 15 eV. Other geometries have also been proposed including structures belonging to the C$_{3v}$ point group.$^{[5,6]}$ Comparison of the drift time of mass selected Ti$_8$C$_{12}^+$ with calculated mobilities for various structures reinforces the proposed hollow cage structures instead of more closely packed cubic structures.$^{[7,8]}$

Despite the considerable amount of interest in the chemical and physical properties of Met-Cars, the equilibrium geometry is still not known.$^{[9]}$ If these M$_8$C$_{12}$ clusters are to be realized as new materials, production and isolation in macroscopic quantities is imperative. Early experiments by Castleman et al. showed that Met-Cars exposed to air were stable for short periods of time possibly due to protection by soot.$^{[10]}$ Most recently, Selvan and Pradeep also approached the bulk synthesis problem, using an arc-discharge$^{[11]}$. Infrared spectra of the soot after exposure to air over the course of 30 minutes showed the disappearance of a band at 665 cm$^{-1}$ and the emergence of others at 1457, 1122, and 872 cm$^{-1}$.

The “appearing” bands were assigned to methylene wagging, C-C bond stretching, and methylene rocking modes, respectively. As discussed below, the highest energy "appearing" mode (1457 cm$^{-1}$) also is close to the energy range associated with Met-Cars. Time-lapse variations across IR spectra cannot be used to declare the presence of a "new" material when the disappearing or emerging peak(s) are not known or expected to be signatures of the species under investigation.

Recently, the infrared spectra for neutral Ti$_8$C$_{12}$, as well as for Ti$_8$C$_{11}$ and Ti$_{14}$C$_{13}$, have been measured in the gas phase by infrared multiphoton excitation using a pulsed linear accelerator.$^{[12]}$ Though the measurement represents the vibrational signature for a free Met-Car, it serves as the first available experimental reference applicable for use in the identification of the presence of Ti$_8$C$_{12}$ in unpurified samples. Recently, Gueorguiev and Pacheco$^{[13]}$ have calculated the infrared absorption spectrum for the Ti$_8$C$_{12}$ . Their calculations have shown the Met-Cars with distorted T$_d$ geometry to be the lowest energy ones while the experimental IR-absorption spectrum compares better with the calculated spectrum for the D$_{2d}$ structure. This is clearly a finite temperature effect. However, the width of the experimental peak near 1400 cm$^{-1}$ is much larger than predicted by the above mentioned article. Neither the experimental or theoretical works give strong evidence that there is Met-Car infrared intensity near the 665 cm$^{-1}$ range. Therefore an additional calculation aimed at this question is useful. Another motivation of the present work is to identify the symmetry of the lowest energy structure within the density functional theory. A comparison of the theoretical IR absorption spectra with experiment will certainly be helpful in this regard. However, due to the fact that the existing experimental measurements were carried out at finite temperature, the characterization of the ground state structure through IR measurement may be unreliable. We show in the following that at finite temperature in which the experiments are carried out, the spectra is a mixture of low lying isomers leading to a large width of the high frequency peak. In this paper, we present the complete vibrational modes for a D$_{2d}$ structure and a C$_{3v}$ trigonal pyramid Ti$_8$C$_{12}$ as determined from all-electron density functional studies. Apart from the IR absorption spectrum, we also present our calculated Raman scattering spectrum for these structures. This is the first calculated Raman spectrum of Ti$_8$C$_{12}$ . The reliability of our predicted Raman frequencies can be assessed based on agreement between the calculated IR spectrum and the gas phase IR results or other exper-
mentally determined properties.

II. COMPUTATIONAL DETAILS

The geometrical and electronic structures of Ti$_8$C$_{12}$ molecule of different structures were studied using density functional theory. The calculations were performed with the NRLMOL code, within the generalized gradient approximation to the exchange-correlation energy. The Kohn-Sham orbitals were expanded in a basis of linear combination of atomic orbitals where each orbital is expanded in a Gaussian basis set centered on the atoms. An optimized basis set was employed to speed up the calculations. The basis for the Ti atom consists of 7 s-type, 5 p-type and 4 d-type orbitals each of which are constructed from a linear combination of 19 Gaussians. For C atom, 5 s-type, 4 p-type and 3 d-type functions were used which in turn are composed of 12 Gaussians. A variational integration mesh was used for the analytical computation of the potential. Spin-polarized calculations were performed taking all electrons into account. The optimization of the clusters was symmetry adapted. The massively parallel version of the code was used and the calculations were carried out on a cluster of PCs. The geometry optimizations were carried out by using the limited-memory Broyden-Fletcher-Goldfarb-Shanno (LBFGS) scheme of minimization. The geometry optimizations were carried till the forces on the atoms were below 0.001 a.u. For each geometry, the self-consistency cycle was carried out till the energy differences were less than 0.000001 a.u.

To calculate the vibrational frequencies, a dynamical matrix was constructed by first displacing the atoms by $\pm$ 0.08 a.u. and calculating the forces. The vibrational frequencies of the molecules were calculated by a direct diagonalization of the dynamical matrix. The details of the method can be found in Ref. Spin-polarized calculations were performed taking all electrons into account. The Raman and infrared intensities were obtained from the derivatives of the vibrational frequencies and the Raman and IR intensities were calculated by a direct diagonalization of the dynamical matrix. The details of the method can be found in Ref. The Raman and infrared intensities were obtained from the derivatives of the dipole moment and the polarizability tensor which in turn were obtained by applying an electric field of strength 0.005 a.u. For a high precision calculation of the vibrational frequencies and the Raman and IR intensities, the energies of the displaced geometries were converged to a tolerance of $1.0 \times 10^{-8}$ a.u.

III. RESULTS AND DISCUSSION

The earlier reports of the Met-Car structure have shown the Ti$_8$C$_{12}$ clusters with a T$_d$ geometry to be lower in energy than the one with T$_h$ symmetry. It may be recalled here that Dance have shown a barrierless reaction pathway between T$_h$ and the T$_d$ structures he considered. The path was constrained with the D$_2$ symmetry. On the other hand, Chen et al. have proposed a D$_{2d}$ structure to be more strongly bound. To obtain possible candidate structures for the low energy isomers, we have performed the geometry optimizations for different structures with T$_d$, T$_h$, C$_{3v}$, D$_{2d}$, D$_{2h}$, and D$_2$ point group symmetries. Calculations for the lower symmetry structures albeit similar to the higher symmetry ones, were carried out so as not to rule out any low symmetry structures. The lowest energy structures, which are unique are shown in Fig. We have carried out the optimizations for two structures with the D$_{2d}$ symmetry in which the carbon dimers are oriented differently. We use a $\ast$ to distinguish between them. The one labeled as D$_{2d}$ has a structure close to the C$_{3v}$ structure and therefore is not shown in Fig. Similarly, we have not shown the structure of the D$_{2h}$ geometry since it is close to the T$_h$ structure. Also, one of the T$_d$ structures, labeled as T$^*$_d is close to the C$_{3v}$ and therefore is not shown.

The geometry optimization has revealed the structure with C$_{3v}$ symmetry to be the lowest energy structure among the structures considered here. The energies of all the calculated optimized structures relative to the energy of C$_{3v}$ structure are given in Table. We wish to point out here that a similar structure with T$_g$ symmetry (T$^*$_d) was found to be slightly higher in energy (0.13 eV). The lower order of the C$_{3v}$ symmetry group removes some of the degeneracies at the Fermi level. A fully unsymmetrized optimization leads to a structure lower in energy by only 0.01 eV. Therefore, we accept the C$_{3v}$ structure as the lowest energy structure among the ones examined in this work. We believe that this structure is the same as the distorted T$_d$ reported in Ref. The T$_d$ and T$_h$ structures shown in Fig. are significantly higher in energy, respectively, by 14.94 and 14.5 eV than the C$_{3v}$ structure. The energy difference between the T$_d$ and T$_h$ isomers is small (0.44 eV). The D$_{2d}$ structure is also found to lie higher in energy by 0.06 eV than the C$_{3v}$ structure. The other structures with D$_{2d}$ and D$_2$ symmetry are still higher by $\sim$ 2 eV.

To get more information about the stability of the different conformers, we have calculated the atomization energies and the vertical ionization potential (vIP) as well as the vertical electron affinities (vEA). These values, along with the magnetic moments, and the HOMO-LUMO gaps are summarized in Table. We found that while the T$_h$ structure has magnetic moment 4 $\mu_B$, the other structures are found to possess a smaller magnetic moment of 2 $\mu_B$. The calculated binding or atomisation energy of all the different structures are high which suggest that these clusters are highly stable. The vertical IP and EA are calculated by assuming the structure of the charged cluster to be same as the neutral one. The relative values of the vIP and vEA indicate the relative stability of the clusters with different geometry. Surprisingly, the higher energy isomers exhibit higher ionization potentials. The vertical IP of the T$_d$, D$_{2d}$, and the C$_{3v}$ structures range between 4.51-4.61 eV. The earlier reported values of calculated vIP for the T$_d$ structure ranges between 4.37 - 4.7 eV whereas the adiabatic IP is 4.43 eV. The vIP or IP reported for other structures
are considerably higher than the experimental value. For the lowest energy structure with $C_{3v}$ symmetry, we have calculated the adiabatic IP. In this case, the geometry of the charged cluster was allowed to relax. The calculated ionization potential (4.47 eV) is in excellent agreement with the recently determined value (4.4 ± 0.02 eV) from near threshold photoionization efficiency curves for the Ti$_8$C$_{12}$.

The vertical electron affinity of the Ti Met-Cars were reported for $T_d$ and $T_h$ structures. While the experimental vertical electron affinity is 4.16 ± 0.05 eV, the adiabatic affinity of 1.05 ± 0.05 eV is lower. The vEA calculated in the present work for the $C_{3v}$, $D_{2d}$ and $T_d$ structures are relative higher while the $D_{2h}$ shows a very low vEA (Table I). The calculated adiabatic electron affinity of the $C_{3v}$ structure is 1.00 eV which is in excellent agreement with the experimental value of 1.05 eV.

Apart from the $C_{3v}$ anionic structure, we have optimized the geometries of the $T_d$ and the $D_{2d}$ structures also. The anionic $T_d$ and $C_{3v}$ are degenerate with an energy difference of 0.004 eV while the $D_{2d}$ anion lies 0.015 eV above. The low electron affinity and the high ionization potential of the Ti$_8$C$_{12}$ signifies the low reactivity of this cluster.

The energy ordering among the isomers and the good agreement with experimental IP and EA gives us confidence that $C_{3v}$ structure is a likely candidate for the lowest energy structure within GGA.

Another possible way of identifying the structure will be through the infrared absorption spectrum. Recently, Heijnsbergen et al. have carried out the measurement of infrared resonance-enhanced multiphoton ionization spectrum (IR-REMPI) of the Ti$_8$C$_{12}$ clusters within the frequency range of 400 cm$^{-1}$ to 1600 cm$^{-1}$. The IR-REMPI spectrum closely resembles the conventional infrared absorption spectrum in peak position and relative intensity. This experiment reports a broad peak of the IR-REMPI spectrum centered around 1395 cm$^{-1}$. A comparison of the calculated spectrum with the measured spectrum can shed light on the possible candidate structures of the highly stable Ti$_8$C$_{12}$ and also in identifying the Met-Cars in a mixed environment. The vibrational spectrum of the high lying structures with $T_h$, $T_d$, $D_2$ and $D_{2h}$ symmetries have several imaginary frequencies which further indicates these structures to be highly unstable. We, therefore, concentrate on the analysis of the vibrational modes and the IR and Raman spectrum of the two lowest energy structures, namely, the $C_{3v}$ and $D_{2d}$ structures.

Pacheco et al. have recently reported calculated IR absorption spectrum for the Met-Car with $T_d$, $T_h$ and $D_{2d}$ structures and unsymmetric structures which are Jahn-Teller distorted. They have shown that while the Jahn-Teller distorted $T_d$ structure is the lowest energy structure, the absorption spectrum of the $D_{2d}$ structure matches the experimental spectrum best. They suggest that at finite temperature, the clusters with $D_{2d}$ symmetry are most abundant. The calculated spectra in Ref. were broadened by a Gaussian of FWHM of 40 cm$^{-1}$ which merges the closely spaced peaks. For the sake of completeness, we also calculated the IR spectra for the $D_{2d}$ structure reported in Ref. The starting geometry differs from the other $D_{2d}$ structure in the orientations of the carbon dimers. This structure, upon optimization, distorts largely from the starting geometry. The final structure is shown in Fig. which we refer to as $D_{2d}$. This structure, although high in energy with respect to the $C_{3v}$, is stable with no imaginary frequency associated with it. However, the IR spectrum shows peaks at frequencies lower than in the experimental spectrum - one at 1357 cm$^{-1}$ and a much larger one at 1310 cm$^{-1}$. Since this structure lies high in the energy scale, we concentrate on the IR spectra of the geometries labeled as $C_{3v}$ and the $D_{2d}$.

Although both the $C_{3v}$ and the $D_{2d}$ symmetry groups are subgroups of the $T_d$ symmetry group, they are independent. The small energy difference of 0.06 eV between them suggests the possibility of a symmetry breaking reaction path connecting the $C_{3v}$ and $D_{2d}$ structures. Indeed, there exists such a path shown in Fig. The plot shows the small energy difference between the two structures. However, an estimate of the vibrational frequencies for such an anharmonic potential ruled out the possibility that at low or room temperature the Met-Cars can vibrate between the two structures. This fact again establishes that at zero temperature, it is likely to conform to the $C_{3v}$ structure.

The experimental spectrum was measured between 400 - 1600 cm$^{-1}$ range. Therefore, we present our calculated spectrum in this frequency range in Fig. The spectra shown in Fig. in the upper two panels were broadened with a Gaussian of full width half maximum (FWHM) of 6 cm$^{-1}$ as well as 40 cm$^{-1}$. The high resolution spectrum shows two clear peaks at 1393 cm$^{-1}$ and 1442 cm$^{-1}$ for the $C_{3v}$ structure (Fig. lower panel) while the $D_{2d}$ structure shows peaks at 1354 cm$^{-1}$ and 1393 cm$^{-1}$. At temperature $T=0$ K, both the structures have strong absorption peaks near 1400 cm$^{-1}$. The smearing of the peaks with a gaussian of FWHM of 40 cm$^{-1}$ merges both the peaks and brings the spectra closer to the experimental one. In the experimental spectra, we detect a shoulder near 1364 cm$^{-1}$ which is clearly reproduced for the $C_{3v}$ spectra but at a higher frequency. Although the shape of the IR absorption spectrum is correctly reproduced for the calculated $C_{3v}$ spectra, the spectra is shifted slightly towards high energy region. The peaks of the $D_{2d}$ spectra at 1354 and 1393 cm$^{-1}$ have comparable intensities and a smearing with Gaussian of FWHM of 40 cm$^{-1}$ does not show a shoulder clearly and the broad peak is to the left of the experimentally observed peak. In the low frequency region around 500 cm$^{-1}$, the experimental spectrum shows peaks at 455 and 520 cm$^{-1}$, which are correctly reproduced in case of $C_{3v}$ structure and slightly shifted to higher frequency in case $D_{2d}$ structure. Based on this observation and as well as the fact that the $C_{3v}$ energy is lower than the $D_{2d}$, we believe that at temperature $T=0$K the IR spectrum will be dominated by
that of the C_{3v} structure. We have estimated the shift in
the frequency of the highest peak of the C_{3v} structure
due to the anharmonicity of the potential to be about 10
cm^{-1}. These estimates also showed that the lowest eight
excitations would encompass a broadening of nearly 30
cm^{-1}.

Given that the experimental IR spectra was associated
with clusters hot enough to undergo thermionic emission,
the effect of thermal fluctuations will be strong in the exper-
imentally measured IR spectra. Therefore a statistically
weighted spectra of all the low-lying structure will
better reproduce the experimental IR absorption spec-
trum. In Fig. 4, we show the weighted spectra of the C_{3v}
and the D_{2d} structures which are within a range of 0.06
eV. In the Fig. 5, we show the calculated weighted IR
absorption for temperatures T=300K, 750K and 1100K.
At room temperature, the spectra is dominated by the
C_{3v} structure and weighted spectra has a peak shifted
towards the high energy region. However, as the tem-
perature is increased, the contribution from the D_{2d} struc-
ture increases and the spectra shows two close peaks for
750 K. At still higher temperature of 1100K, the peak due
to the C_{3v} is reduced. The noticeable feature is that the
width of the experimental peak is better reproduced in
the weighted spectra. The contribution from other iso-
mers will become important at still higher temperature.
Another noteworthy point is that the low energy region of
the spectrum is better reproduced at room temperature.

For the purpose of comparison with any probable fu-
ture experimental investigation, we also present our cal-
culated Raman scattering spectra for both C_{3v} and D_{2d}
geometries. This is the first calculated Raman spectra
for Ti_8C_{12}. These plots are shown in Fig. 6. The Ra-
man active modes are seen at lower frequencies which
arises due to the Ti-Ti stretch mode and also twisting of
the C-C bonds. These modes will change the volume of
the cluster and hence the polarizability which will lead
to Raman activities. The scattering intensities at high
frequencies are low for both the structures. The spectra
shown in Fig. 5 has been convoluted with a Gaussian of
FWHM 6 cm^{-1}. A larger value of FWHM will smear out
most of the fine structures seen in the plots. A few weak
peaks are seen in the region around 1400 cm^{-1} where the
IR activity is most strong. In the Raman spectra of both
the C_{3v} and D_{2d} structures, the most prominent peaks
occur in the region between 100 to 200 cm^{-1} which are
nearly similar (Fig. 5). Therefore, Raman spectra in this
low frequency region will not help in distinguishing the
ground state structure between C_{3v} and D_{2d}. However,
the spectra between 300 - 600 cm^{-1} are distinguishable
as can be seen from Fig. 5. A measurement of the Ra-
man spectrum can greatly influence the debate over the
equilibrium geometry of the Met-Cars.

IV. CONCLUSIONS

In conclusion, we have carried out extensive density
functional calculations on the electronic structure and
the vibrational states of the Ti_8C_{12} for different geomet-
ries. We find the geometry with C_{3v} symmetry to be the
lowest energy structure. A study of the vibrational
states show that the calculated IR absorption spectra
for this geometry compares best with the experimental
one. We find another structure with D_{2d} symmetry as a
competing structure with an energy difference of only
0.06 eV. We find that a symmetry breaking reaction path
exists from the D_{2d} to the C_{3v} structure. However,
our estimates of the vibrational modes in the potential
surface between the C_{3v} and D_{2d} ruled out any possi-
bility of cold clusters vibrating between the two closely
placed geometries. We estimate the reaction barrier to
be about 600K. We point out that the experiments may be
associated with hot clusters and show that the overall
width of the high frequency IR spectra supports a high
temperature mixture of C_{3v} and D_{2d}. The two peak
character observed in our calculations could reduce to a
shoulder structure with small perturbation of IR inten-
sity and peak positions. We also present our calculated
Raman spectra for these two low-lying structures. An ex-
perimental measurement of the Raman spectra may help
in deciding the ground state geometry of the Ti_8C_{12}.

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TABLE I: The energies of the clusters relative to the lowest energy structure, the atomisation energies ($E_b$), spin and the HOMO-LUMO gap ($\Delta$) of the Ti$_8$C$_{12}$ clusters of various symmetries. All values are in eV.

| Cluster | Relative $E_b$ (eV) | $S$ | $\Delta$ (eV) | $vIP$ | $vEA$ |
|---------|---------------------|-----|------------|------|------|
| C$_{3v}$ | 0.00                | 7.08 | 1         | 0.12 | 4.61 | 0.89 |
| T$_h$   | 14.50               | 6.36 | 2         | 0.05 | 4.82 | 1.40 |
| T$_d$   | 14.94               | 6.34 | 1         | 0.22 | 5.68 | 2.09 |
| T$_{d^*}$ | 0.13               | 7.08 | 1         | 0.33 | 4.54 | 1.08 |
| D$_{2d}$ | 0.06               | 7.08 | 1         | 0.13 | 4.51 | 0.93 |
| D$_{2d^*}$ | 1.78              | 7.00 | 1         | 0.44 | 5.35 | 1.35 |
| D$_{2h}$ | 14.47               | 6.36 | 1         | 0.25 | 6.26 | 0.66 |
| D$_2$   | 1.99                | 6.99 | 1         | 0.07 | 5.18 | 1.53 |

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FIG. 1: The optimized geometries of the Ti$_8$C$_{12}$ with various symmetries.

FIG. 2: A possible reaction path from the D$_{2d}$ to the C$_{3v}$ isomer. The x-axis shows the distances along the reaction path from the C$_{3v}$ isomer.
FIG. 3: The calculated IR intensities for Ti$_8$C$_{12}$. The upper panel shows the absorption spectra for D$_{2d}$ geometry and the lower one shows the same for C$_{3v}$ geometry. The solid lines represent the experimental spectra. The dash-dotted line shows the calculated spectra broadened with a gaussian of FWHM of 6 cm$^{-1}$ while the dashed line shows the one broadened with 40 cm$^{-1}$. The convoluted curves are not renormalized. The theoretical intensities are in (D/Å)$^2$amu$^{-1}$. The experimental data are scaled down for comparison with theoretical data.
FIG. 4: The calculated IR intensities of the Ti$_8$C$_{12}$ at different temperatures. The theoretical curves were convoluted with Gaussian of FWHM of 40 cm\(^{-1}\).

FIG. 5: The Raman scattering spectra of the low-lying D$_{2d}$ and the C$_{3v}$ structures. The spectra are broadened with a Gaussian of 6 cm\(^{-1}\).