

Predicted infrared and Raman spectra for neutral Ti_8C_{12} isomersTunna Baruah,^{1,2} Mark R. Pederson,^{2,*} M. L. Lyn,³ and A. W. Castleman, Jr.³¹*Department of Physics, Georgetown University, Washington, D.C. 20057*²*Center for Computational Materials Science, Code 6390, Naval Research Laboratory, Washington, D.C. 20375*³*Departments of Chemistry and Physics, Pennsylvania State University, University Park, Pennsylvania 16802*

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Using a density-functional based algorithm, the full infrared and Raman spectra are calculated for the neutral Ti_8C_{12} cluster assuming geometries of T_h , T_d , D_{2d} , and C_{3v} symmetry. The T_h 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.

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I. INTRODUCTION

In 1992, Castleman and co-workers [1,2] 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 $M_8\text{C}_{12}$ ($M = \text{V}, \text{Zr}, \text{Hf}, \text{Ti}, \text{Nb}, \text{Mo}, \text{Fe}, \text{Cr}$) [1–4] or $\text{Ti}_{8-x}\text{M}_x\text{C}_{12}$ ($M = \text{Zr}, \text{Hf}, \text{Nb}, \text{Mo}, \text{Ta}, \text{W}, \text{Si}, \text{Y}, \text{Nb}, \text{Mo}, \text{Ta}, \text{W}$) [5–7]. 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 [1]. Shortly thereafter, Dance [8,9] 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 [10–13]. Comparison of the drift time of mass selected $\text{Ti}_8\text{C}_{12}^+$ with calculated mobilities for various structures reinforces the proposed hollow cage structures instead of more closely packed cubic structures [14,15].

Despite the considerable amount of interest in the chemical and physical properties of Met-Cars, the equilibrium geometry is still not known [13]. If these $M_8\text{C}_{12}$ clusters are to be realized as new materials, production and isolation in macroscopic quantities is imperative. Early experiments by Castleman and co-workers showed that Met-Cars exposed to air were stable for short periods of time possibly due to protection by soot [16]. Most recently, Selvan and Pradeep also approached the bulk synthesis problem, using an arc-discharge [17]. Infrared spectra of the soot after exposure to air over the course of 30 min 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 infrared (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_8C_{12} , as well as for Ti_8C_{11} and $\text{Ti}_{14}\text{C}_{13}$, have been measured in the gas phase by infrared multiphoton excitation using a pulsed linear accelerator [18]. 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_8C_{12} in unpurified samples. Recently, Gueorguiev and Pacheco [19] have calculated the infrared-absorption spectrum for the Ti_8C_{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 [18] or theoretical [19] 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_8C_{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

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first calculated Raman spectrum of Ti_8C_{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 experimentally determined properties.

II. COMPUTATIONAL DETAILS

The geometrical and electronic structures of Ti_8C_{12} molecule of different structures were studied using density-functional theory [20]. The calculations were performed with the NRLMOL code [21] within the generalized gradient approximation (GGA) to the exchange-correlation energy [22]. 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 [23] 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 [24]. 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 [25] 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 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 ± 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. [26]. 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 1.0×10^{-8} a.u.

III. RESULTS AND DISCUSSION

The earlier reports of the Met-Car structure have shown the Ti_8C_{12} clusters with a T_d geometry to be lower in energy than that with T_h symmetry. It may be recalled here that Dance [9] 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.* [11] 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_2 ,

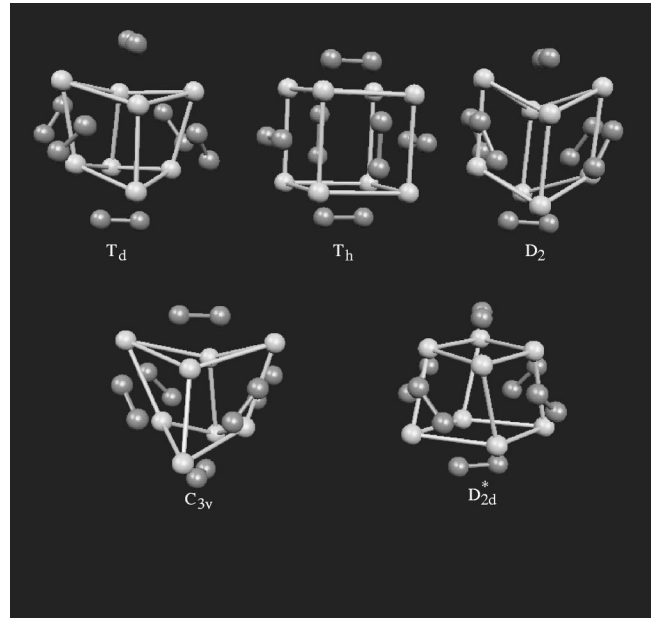


FIG. 1. The optimized geometries of the Ti_8C_{12} with various symmetries.

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. 1. 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 * 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. 1. 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 I. We wish to point out here that a similar structure with T_d 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. [19]. The T_d and T_h structures shown in Fig. 1 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 ~ 2 eV.

To get more information about the stability of the different conformers, we have calculated the atomization energies

TABLE I. The energies of the clusters relative to the lowest-energy structure, the atomization energies (E_b), spin and the HOMO-LUMO gap (Δ) of the Ti_8C_{12} clusters of various symmetries. All values are in eV.

	Relative energy	E_b	S	Δ	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

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 I. 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 atomization 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 [13]. 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_8C_{12} [27].

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 1.16 ± 0.05 eV, the adiabatic affinity of 1.05 ± 0.05 eV [28] is lower. The VEA calculated in the present work for the C_{3v} , D_{2d} , and T_d^* range between 0.89–1.08 eV. The VEA for other structures are relatively 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 [28]. 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_8C_{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.* [18] have carried out the measurement of infrared resonance-enhanced multiphoton ionization spectrum (IR-REMPI) of the Ti_8C_{12} clusters within the frequency range of 400–1600 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_8C_{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. Gueorguiev and Pacheco [19] 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. [19] were broadened by a Gaussian of full width at half maximum (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. [19]. 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. 1 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. 2. 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

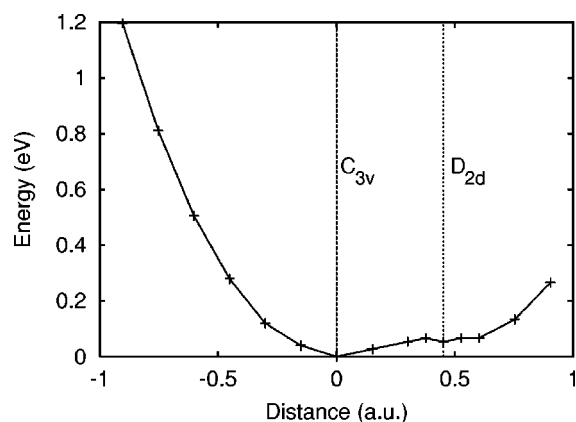


FIG. 2. A possible reaction path from the D_{2d} to the C_{3v} isomer. The x axis shows the distances along the reaction path from the C_{3v} isomer.

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. 3. The spectra shown in Fig. 3 in the upper two panels were broadened with a Gaussian of FWHM of 6 cm^{-1} as well as 40 cm^{-1} . The

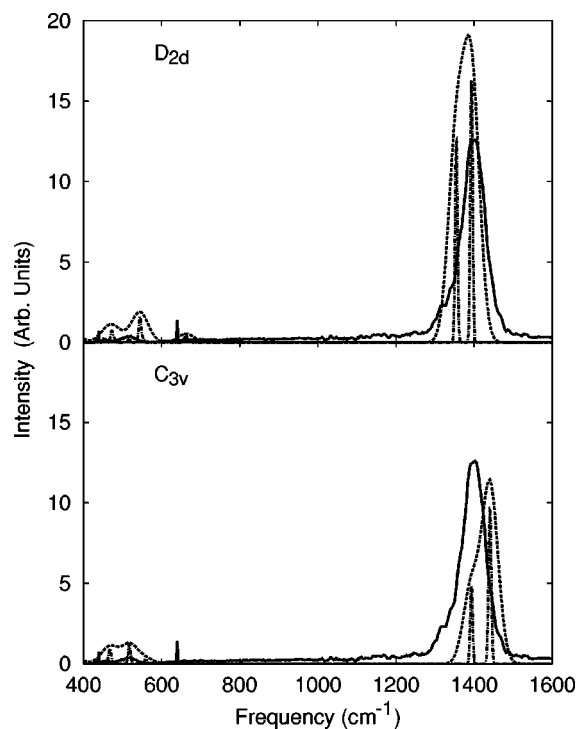


FIG. 3. The calculated IR intensities for Ti_8C_{12} . The upper panel shows the absorption spectra for D_{2d} geometry and the lower one shows the same for C_{3v} geometry. The solid lines represent the experimental spectra. The dash-dotted line shows the calculated spectra broadened with a Gaussian 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 $(\text{D}/\text{\AA})^2 \text{amu}^{-1}$. The experimental data are scaled down for comparison with theoretical data.

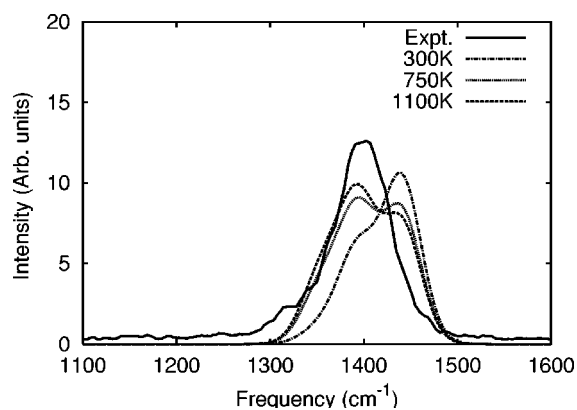


FIG. 4. The calculated IR intensities of the Ti_8C_{12} at different temperatures. The theoretical curves were convoluted with a Gaussian of FWHM of 40 cm^{-1} .

high-resolution spectrum shows two clear peaks at 1393 cm^{-1} and 1442 cm^{-1} for the C_{3v} structure (Fig. 3, 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 experimentally measured IR spectra. Therefore a statistically weighted spectra of all the low-lying structure will better reproduce the experimental IR-absorption spectrum. 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. 4, we show the calculated weighted IR absorption for temperatures $T=300$, 750 and 1100 K. At room temperature, the spectra is dominated by the C_{3v} structure and weighted spectra has a peak shifted towards the high-energy region. How-

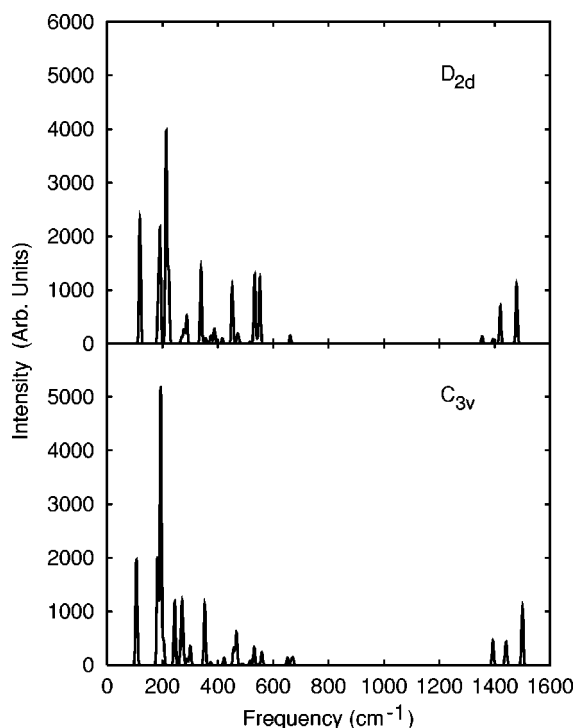


FIG. 5. The Raman-scattering spectra of the low-lying D_{2d} and the C_{3v} structures. The spectra are broadened with a Gaussian of 6 cm^{-1} .

ever, as the temperature is increased, the contribution from the D_{2d} structure increases and the spectra shows two close peaks for 750 K. At still higher temperature of 1100 K, 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 isomers 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 future experimental investigation, we also present our calculated 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. 5. The Raman 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 intensi-

ties at high frequencies are low for both the structures. The spectra shown in Fig. 5 has been convoluted with a Gaussian of $\text{FWHM } 6 \text{ cm}^{-1}$. 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 and 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 $300\text{--}600 \text{ cm}^{-1}$ are distinguishable as can be seen from Fig. 5. A measurement of the Raman 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 geometries. 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 possibility of cold clusters vibrating between the two closely placed geometries. We estimate the reaction barrier to be about 600 K. 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 intensity and peak positions. We also present our calculated Raman spectra for these two low-lying structures. An experimental measurement of the Raman spectra may help in deciding the ground-state geometry of the Ti_8C_{12} .

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