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Equilibrium structure and vibrational spectra of sila-adamantane

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The recent synthesis of a four-fold silylated sila-adamantane molecule ($C_{24}H_{72}Si_{14}$, T_d), [J. Fischer, J. Baumgartner, and C. Marschner, *Science* **310,** (2005) 825] is the first attempt of making the silicon analogue of adamantane. It has adamantane-like Si_{10} core, capped by methyl and silymethyl ligands. We report its electronic structure, vibrational spectrum, and the infra-red and Raman spectra calculated within the density functional formalism using large polarized Gaussian basis sets. The properties of sila-adamantane are compared with exact silicon analogue ($Si_{10}H_{14}$) of adamantane. Results show that replacing hydrogens in $Si_{10}H_{16}$ by methyl and silymethyl ligands results in expansion of the Si_{10} core and are responsible for large number of peaks in the Raman spectrum. The Si-C stretch at 664 cm^{-1} and methyl deformations frequencies compare well with recent measurements of vibrational frequencies of methylated silicon surface.

PACS numbers:
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I. INTRODUCTION

Silicon is of considerable interest in nanotechnology and in semiconductor industry. In bulk phase, silicon has diamond lattice like carbon. The diamond structure can be built by translating the smallest unit of the carbon lattice called adamantane. The adamantane has 10 carbon atoms that are capped by hydrogen atoms that passivate the dangling bonds of carbon atoms in the sp^3 bonding. The adamantane and a few low-order diamondoids have been synthesized[1]. Recently, isolation of several new lower- and medium-order diamondoids from petroleum oil was reported by the Molecular Diamond Technologies Group at Chevron-Texaco[2]. This has led to a renewal of interest in the chemistry and physics of the diamondoids[3].

The search for silicon analogue of adamantane, called sila-adamantane $Si_{10}H_{16}$, has so far been unsuccessful. There has been however some progress. A recent report by Ficher, Baumgartner and Marschner (FBM) of synthesis of silylated sila-adamantane is a breakthrough in the synthesis of sila-adamantane[4]. Instead of hydrogen atoms as capping elements as in the exact silicon analogue of adamantane, silicon atoms in sila-adamantane are capped by methyl and trimethylsilyl groups (Cf. Fig. 1). It was characterized using the nuclear magnetic resonance (NMR) spectroscopy. The ultra-violet and visible spectra were also measured which showed strong absorption at 222 nm (5.58 eV). Followed by this report, Piccheri reported electronic structure of $C_{24}Si_{14}H_{72}$ within Perdew-Burke-Ernzerhof density functional model. He reported structural parameters calculated using the 3-21G* basis sets and density fitting methodology[5].

In the present article, we report the electronic structure of sila-adamantane examined within the density functional theory using large polarized Gaussian basis sets. Furthermore, at the same level of theory we calculate vibrational frequencies, the infra-red and Raman spectra. We also calculate these properties for exact silicon analogue of adamantane ($Si_{10}H_{16}$), and compare them with those of sila-adamantane $C_{24}Si_{14}H_{72}$ to examine the effect of methyl and silymethyl ligands.

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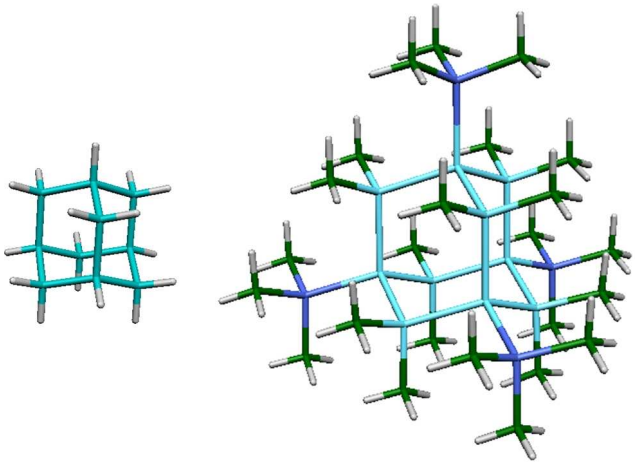

FIG. 1: (Color online) The optimized structures of sila-adamantane $Si_{10}H_{16}$ and silylated sila-adamantane $C_{24}Si_{14}H_{72}$.

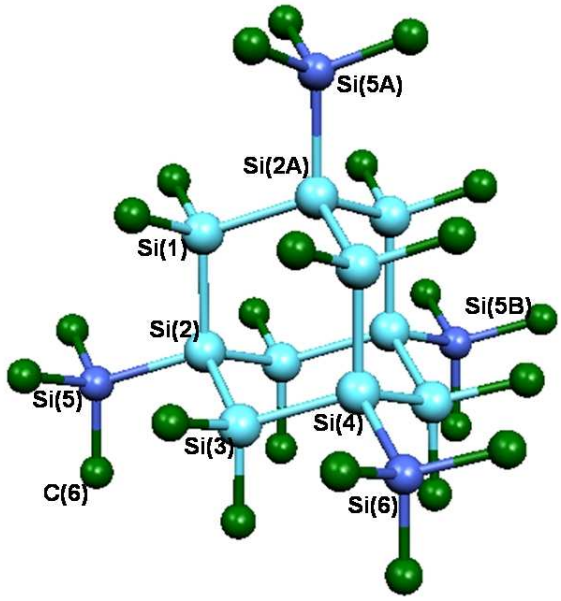

FIG. 2: (Color online) The optimized structure of $C_{24}Si_{14}H_{72}$ without hydrogens. The Si atoms that are part of the silymethyl ligands are shown in dark blue for clarity. The atomic labels are identical to those in experimental structure from Ref. 4.

II. FORMALISM

Our calculations are performed within the Kohn-Sham formulation[6] of the density functional theory[7] using NRLMOL code[9]. The molecular orbitals are expressed as linear combination of Gaussian functions. The exchange-correlation effects are described within the generalized gradient approximation using Perdew-Burke-Ernzerhof[8] parameterization. For a reliable prediction of properties, we use large polarized basis sets that are specially optimized for the PBE functional[10]. Thus the basis for Si contains 6 s-, 5 p-, and 3 d-type Gaussians each contracted from 16 primitive functions. For C, 12 primitive functions were used to contract 5 s-, 4p-, and 3 d-type basis functions. The basis for H consist of 4 s-, 3 p-, and 1 d- type basis functions. In total 2614 basis functions were used in calculation of $C_{24}Si_{14}H_{72}$. Additional diffuse functions were used for the calculations of polarizabilities. The exchange-correlation contribution to matrix elements and total energy are obtained numerically using efficient numerical grids employed in NRLMOL[9]. The vibrational frequencies were obtained by diagonalizing the dynamical matrix built from the forces computed at perturbed geometries. Finally, the infra-red and Raman spectra were computed from the dipole moment and polarizability derivatives, respectively.

III. RESULTS

The optimized structure of $Si_{10}H_{16}$ and $C_{24}Si_{14}H_{72}$ are shown in Fig. 1. The $C_{24}Si_{14}H_{72}$ is also shown without hydrogens in Fig. 2. To distinguish the Si atoms that belong to silymethyl-ligand, these four atoms are shown in dark blue. The $Si_{10}H_{16}$ core in $C_{24}Si_{14}H_{72}$ is clearly seen. The atoms have labels exactly identical to those given in the supplementary information of the experimental study in Ref. 4. Both structures were optimized within the T_d symmetry. The bond distance between two silicon atoms (Si(1)-Si(2)) that belong to the tetrahedral adamantane core (Si(10)) is 2.39 Å, in good agreement with experimental value of 2.36 Å. In case of $Si_{10}H_{16}$, this bond length is calculated to be 2.36 Å. The Si-$SiCH_3$ bond length (Si(2)-Si(5) distance) is also 2.39 Å while the experimental value is 2.35 Å. The bond angle between the Si-Si bonds from the Si_{10} core (Si(2)-Si(1)-Si(2A)) in $C_{24}Si_{14}H_{72}$ is 110° and is in excellent agreement with the experimental value of 110.3^o. Similarly, very good agree-

ment is observed for the dihedral angle between three bonds from the Si_{10} core (Si(2A)-Si(1)-Si(2)-Si(3)). The predicted angle is 59.8^o while experimental value is 59.9^o. These bond angles are essentially similar in $Si_{10}H_{16}$ (angles 110.1^o and $59.\ 7^o$). As the bond angles and dihedral angles in $Si_{10}H_{16}$ are essentially similar to those in the Si_{10} core in $C_{24}Si_{14}H_{72}$, it appears that replacing hydrogens by methyl and trimethylsilyl ligands leads to an expansion of the Si_{10} core.

IV. ELECTRONIC STRUCTURE PROPERTIES

The fully occupied highest occupied molecular orbital (HOMO) of $C_{24}Si_{14}H_{72}$ is three fold degenerate and has T_2 symmetry while its LUMO has A_1 symmetry. The HOMO-LUMO (HL) gap is 4.16 eV. For the $Si_{10}H_{16}$, the HL gap is 4.82 eV. The HL gaps reported earlier with a smaller 3-21G* orbital basis and the density fitting methodology are in the range 4.38-4.53 eV depending on the choice of exchange-correlation parameterization[5]. We also calculated the HOMO-LUMO gap for the $Si_{10}H_{16}$ using the time dependent DFT (TDDFT) and using the Perdew-Wang GGA as implemented in ABINIT[11]. The calculated gap using TDDFT of 4.6 eV is only marginally larger than the PBE-DFT gap. The optical gaps of $Si_{10}H_{16}$ have been studied using more complex quantum Monte Carlo and GW approximations[12]. These methods give value of 9.2 eV for the optical gaps. Our attempts to compute the TDDFT optical gap for $C_{24}Si_{14}H_{72}$ were not successful due to large memory requirement.

V. VIBRATIONAL SPECTRA

A. $Si_{10}H_{16}$

The $Si_{10}H_{16}$ cage has T_d point group symmetry. It has in total 72 vibrational modes which could be classified as $5A_1 + A_2 + 6\ E + 7T_1 + 11\ T_2$. Of the total 11 T_2 modes that are infra-red active, only four have appreciable intensity. The calculated IR spectra is shown in Fig. 3. The first absorption is at 716 cm^{-1} (7.61 D/Å^2) due

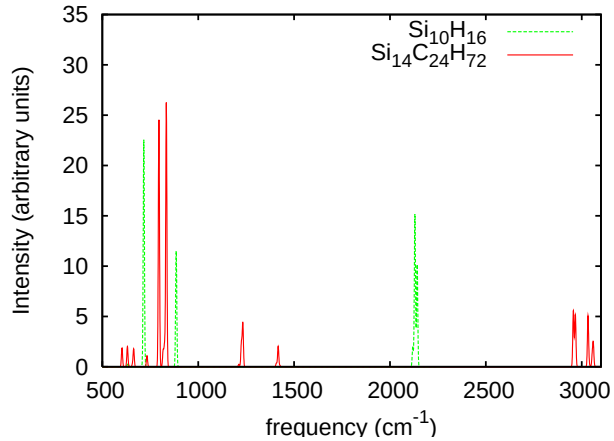

FIG. 3: (Color online) The infra-red spectra of $Si_{10}H_{16}$ and $C_{24}Si_{14}H_{72}$.

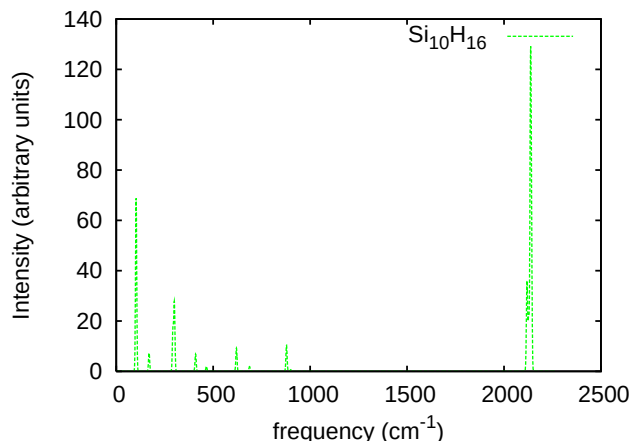

FIG. 4: (Color online) The Raman spectra of $Si_{10}H_{16}$.

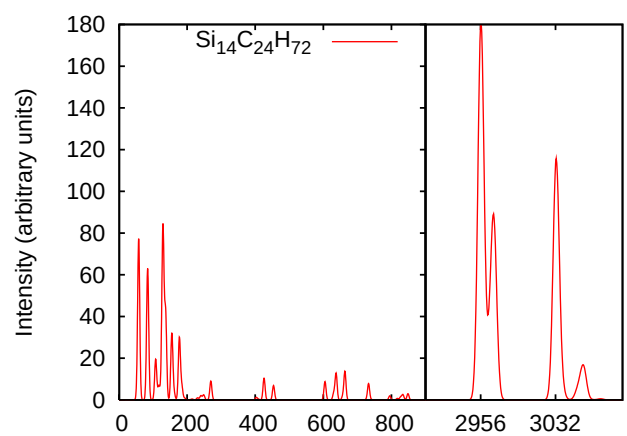

FIG. 5: (Color online) The Raman spectra of $C_{24}Si_{14}H_{72}$. It is split into low frequency region 50-1000 cm^{-1} and high frequency 2800-3100 cm^{-1} (CH stretches) region.

to the SiH_2 wagging. The mode at 885 cm^{-1} (3.85 D/Å^2) corresponds to the bending (scissor) mode of SiH_2. The peaks for the two SiH stretching modes are at higher frequencies of 2130 cm^{-1} and 2141 cm^{-1} are coalesced in the figure. The quantities in bracket are intensities.

The Raman spectra of $Si_{10}H_{16}$ is shown in Fig. 4. There are $5A_1$, 6 E, and 11 T_2 Raman active modes. The fully symmetric A_1 mode at 2137 cm^{-1} is the symmetric SiH stretch and is the most intense (intensity 130 Å^4/amu). The absorption due to fully symmetric stretch of Si-Si bonds (breathing of silicon cage) occurs at lower (due to larger mass) frequency of 299 cm^{-1} . The second most intense absorption is seen at lower wave number of 102 cm^{-1} with intensity of 68 Å^4/amu. This is three fold degenerate T_1 mode due to rocking motion of SiH_2. The Raman active doubly degenerate mode at 103 cm^{-1} is due to the deformation of silicon cage. The absorptions at larger frequencies (> 600 cm^{-1}) involve SiH_2 deformations and SiH stretches. Less intense absorption are 620 cm^{-1} (SiH_2 twist, intensity 9 Å^4/amu), 688 cm^{-1} (SiH_2 and SiH rocking, intensity 2 Å^4/amu), and 878 cm^{-1} (SiH_2 scissor, 10 Å^4/amu).

B. $C_{24}Si_{14}H_{72}$

We computed the vibrational frequencies, within the harmonic approximation, with different possible orientations of methyl groups that are consistent with the T_d symmetry. In all cases we find 9 imaginary frequencies for $C_{24}Si_{14}H_{72}$ due to the rotation of CH3 group. These rotations seen in the gas phase will be frozen in the crystalline state. The total 324 vibrational modes in the $C_{24}Si_{14}H_{72}$ can be classified as $17A_1$ + 10 A_2 + 27 E + $37T_1$ + 44 T_2. There are a total of 44 IR active modes. The calculated infra-red absorption spectrum is displayed in Fig. 3. The two conspicuous peaks at lower frequencies of 795 cm^{-1} (8 D/Å^2) and 834 cm^{-1} (9 D/Å^2) are due to the $SiCH_3$ rocking/wagging motions. These modes are similar to the SiH_2 wagging and rocking seen in $Si_{10}H_{16}$. The weak absorption at 1232 cm^{-1} (1.4 D/Å^2) is the Si-CH_3 umbrella mode. The three peaks at higher frequencies in the frequency range 2956-3032 cm^{-1} with intensities of 1.3-1.4 D/Å^2 are due to the symmetric and asymmetric C-H stretches. A number of vibrational modes results in weak absorption, with intensities less than 1 D/Å^2. These are Si-C asymmetric stretch at 664 cm^{-1} (0.6 D/Å^2), Si-Si-Si deformation at 631 cm^{-1} (0.7 D/Å^2), Si-C symmetric stretch at 603 cm^{-1} (0.6 D/Å^2), CH_3 deformation at 1417 cm^{-1} (0.7 D/Å^2), and C-H symmetric stretch at 3060 (0.8 D/Å^2). The compilation of the frequencies is given in Table I.

TABLE I: The IR active frequenters for the $C_{24}Si_{14}H_{72}$. The stretch of absorptions is given in bracket with following abbreviations: w: weak, vs: very strong, m: medium. The experimental numbers are for methylated silicon(111) surface obtained by high-resolution electron energy loss spectroscopy (HREELS)[13] and transmission infra-red (TIR)[14] spectroscopy.

Freq. (cm^{-1})	HREELS	TIR	Mode description
664 (w)	678		Si-C asymmetric stretch
603 (w)			Si-C symmetric stretch
631 (w)			Si-Si-Si deformation
796(vs)			$SiCH_3$ bending
834(vs)			CH_3 rocking
1233(m)		1257	CH_3 Umbrella
1417 (w)	1424	2856	CH_3 deformation
2956 (m)		2909	C-H symmetric stretch
2969 (m)	2916	2909	C-H symmetric stretch
3032 (m)	2989	2928	C-H asymmetric stretch

The Raman spectrum of $C_{24}Si_{14}H_{72}$ is shown in Fig. 5. The spectrum can be split into two parts: the absorptions in the low-intermediate frequency range (60-200 cm^{-1}) and intense absorptions in the frequency range 2900-3100 cm^{-1} . The doubly degenerate absorption at 59 cm^{-1} (77 Å^4/amu) involves rocking like motion of Si-Si$(CH_3)_3$. This mode is depicted in Fig. 6. The absorption at 84 cm^{-1} (63 Å^4/amu) is due to a doubly degenerate mode that results in deformation of Si-Si-Si bonds in the Si_{10} core similar to the mode at 103 cm^{-1} seen in $Si_{10}H_{16}$. The triplet degenerate mode also due to the distortion of Si_{10} core at 85 cm^{-1} is merged with the peak at 84 cm^{-1} . These two modes are shown

in Fig. 7. The weak absorptions at 108, 155 cm^{-1} are due to methyl rotations. The most intense peak in the low frequency region at 130 cm^{-1} (85 $Å^4$/amu) is due to non-degenerate A_1 mode that results in breathing motion of Si atoms to which $Si(CH_3)_3$ ligands are attached. The breathing motions of rest of Si atoms in Si_{10} core (to which two CH_3 groups are attached) leads to an absorption at 177 cm^{-1} ($Å^4$/amu).

The intense absorptions at higher frequencies are due to CH stretches. The first peak at 2956 cm^{-1} (160 $Å^4$/amu) is due to A_1 CH stretch where CH_3 belongs to the $Si(CH_3)_3$ group. The A_1 CH stretch in the two methyls attached to silicon atoms leads to absorption at slightly higher frequency 2969 cm^{-1} . The three-fold degenerate asymmetric CH stretches absorb at 3032-3033 cm^{-1} (102 $Å^4$/amu) and is also infra-red active.

The most obvious difference between the Raman spectra of $Si_{10}H_{16}$ and $C_{24}Si_{14}H_{72}$ is the presence of the intense peak at 2130 cm^{-1} for the $Si_{10}H_{16}$ involving SiH bonds and the high frequency modes involving CH bonds in the methylated $C_{24}Si_{14}H_{72}$ cluster. It may be mentioned here that there are several very low intensity modes between 1000-1500 cm^{-1} for the $C_{24}Si_{14}H_{72}$. However, the intensities of these peaks are comparatively very small and hence may not be used for identification purposes.

The passivation of dangling bonds at the silicon surfaces by hydrogenation, chlorination and alklation (ethylation, methylation etc) has been a subject of several studies due to technological importance of silicon. Two groups have reported experimental studies of vibrational modes of methylated silicon surface have been reported[14]. Although the sila-adamantane core studied here is a very small unit of silicon crystal, it is interesting to compare the frequencies due to Si-C stretching and methyl deformations. Yamada and coworkers[13] assign the vibration of 678 cm^{-1} to Si-C which compare well with 664 cm^{-1} Si-C asymmetric stretch. The CH_3 stretch and deformation freuenqcies compare well (Cf. I).

VI. CONCLUSION

The equilibrium structure of recently synthesized of silylated sila-adamantane $C_{24}Si_{14}H_{72}$ was obtained within the density functional theory, using large polarized Gaussian basis sets and the semi-local PBE approximation to the exchange-correlation functional. The calculated geometrical parameters are in very god agreement with experimental values. The Si_{10} core in the optimized $C_{24}Si_{14}H_{72}$ is dilated with respected to the silicon analogue of adamantane $Si_{10}H_{16}$. The calculation of vibrational frequencies indicate that some of the methyl ligands are freely rotating in the gas phase. The infra-red and Raman spectra of $C_{24}Si_{14}H_{72}$ is reported for the first time. The comparison of spectra for the $C_{24}Si_{14}H_{72}$ with that of $Si_{10}H_{16}$ do not show any similarity since in both the structures only the Si core is similar. The $Si_{10}H_{16}$ shows intense peaks corresponding to stretching of the Si-H bonds which are missing in the $C_{24}Si_{14}H_{72}$ due to absence of SiH bonds. On the other hand, the presence of methyls are evident in the low frequency peaks for the $C_{24}Si_{14}H_{72}$ and also in very high frequency peak arising from the CH bonds.

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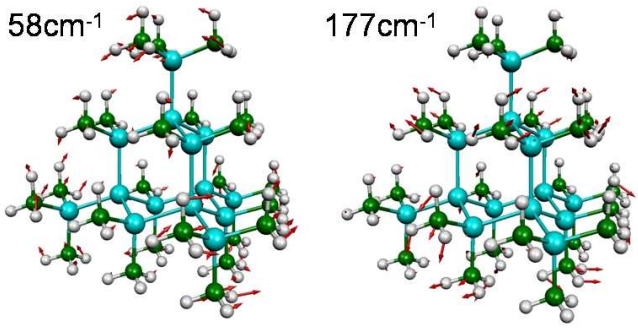

FIG. 6: (Color online) The portrayal of vibrational modes: Left: doubly degenerate mode at 59 cm^{-1} , Right: Nondegenerate mode at 177 cm^{-1} due to breathing motion of Si atoms of Si_{10} core. (See text for more details).

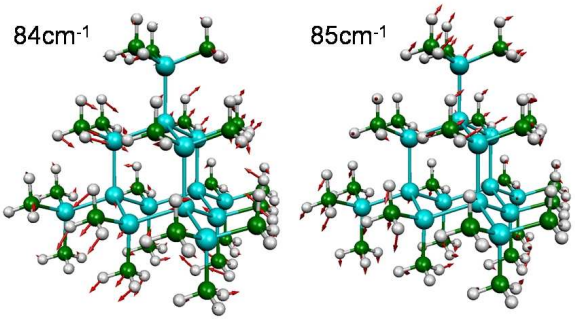

FIG. 7: (Color online) The depiction of Raman active vibrational modes due to distortion of Si_{10} core: Left: doubly degenerate mode at 84 cm^{-1} , Right: Triply degenerate mode at 85 cm^{-1} .

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