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Structural parameters, barriers to internal rotation, normal coordinate analysis and quantum mechanics calculations of 1,1,1-trimethyldisilane

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Abstract

The molecular structure, vibrational frequencies and barriers to internal rotation of the staggered and eclipsed conformations of 1,1,1-trimethyldisilane, $\text{H}_3\text{SiSi}(\text{CH}_3)_3$, have been studied using ab initio molecular orbital calculations. In these calculations, up to 6-311 + G(d,p) basis set at the levels of RHF and MP2 with full electron correlation were employed as well as the hybrid density functionals at the theoretical level of B3LYP. From these data, the energy difference between the staggered and eclipsed conformations has been determined with an average of 318 cm^{-1} (0.91 kcal/mol) in favor of the staggered rotamer, while, the eclipsed form has been barred due to the presence of an imaginary torsion frequency. The $-\text{SiH}_3$ and $-\text{CH}_3$ barriers of 1.05 and 1.98 kcal/mol, respectively, have been predicted from potential function scans at MP2/6-31(d) basis set with full electron correlations. The r_o Si–H bond distance of 1.4885 \AA has been obtained from the observed Q-branch in the gaseous infrared spectrum. The calculated infrared and Raman spectra were obtained using harmonic vibrational frequencies, infrared intensities and Raman activities from RHF/3-21G(d) in addition to MP2 and B3LYP levels at 6-31G(d) basis set. The current study provides a complete vibrational assignment for all the vibrational modes, which is supported by normal coordinate analysis, force constants and potential energy distributions. The results are discussed and theoretical values are compared to experimental values whenever possible.

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Keywords: 1,1,1-Trimethyldisilane; Normal coordinate analysis; Vibrational frequencies; Ab initio calculation; Barriers to internal rotation

1. Introduction

Silyl groups can be used to derivatize and protect various substrate during synthetic procedures (blocking and deblocking agents). The molecular structure

and conformational interchange of disilane (DS) and hexamethyldisilane (HMDS) have been investigated earlier on the basis of free internal rotation around the Si–Si bond [1–4]. However, vibrational studies, ab initio calculations [5–8] and gas phase electron diffraction (GED) studies [9] show hindered internal rotation leaving the staggered rotamer as the only conformer found in all phases. The structure of 1,1,1-trimethyldisilane, $\text{H}_3\text{SiSi}(\text{CH}_3)_3$, (TMDS) molecule is to some extent similar to DS and HMDS [10], due to

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the existence of both SiH_3 and $\text{Si}(\text{Me})_3$ moieties, respectively. Recently, partial vibrational assignments have been reported [11] and the photoabsorption spectra [12] and decomposition kinetics for TMDS have been reported as well [13].

To the best of our knowledge, the vibrational spectra of TMDS has not been thoroughly investigated due to the exclusion of methyl stretching modes and deformation frequencies [11]. Thus a new determination of the force fields in TMDS was timely to bring these vibrational modes to light. To verify the internal barriers to rotation of the silyl ($-\text{SiH}_3$) and methyl ($-\text{CH}_3$) groups in TMDS, we decided to reinvestigate its molecular structure using potential energy surface scan. These barriers are correlated to the theoretical and experimental values [14–19] whenever possible to observe whether the Si–Si rotational energy barrier in TMDS differ significantly from that obtained for DS and HMDS molecules [10, 20]. To fill these gaps, GAUSSIAN 98 ab initio calculations [21,22], normal coordinate analysis, and force field constant calculations for TMDS under C_{3v} selection rules were employed. A combined frequency computations at RHF/3-21G(d), MP2/6-31G(d) with full electron correlation and B3LYP/6-31G(d) basis sets were carried out and a complete vibrational assignment for all the vibrational modes of the staggered rotamer is provided. All the results are reported herein and compared with those obtained earlier for similar molecules.

2. Computational details

2.1. Ab initio calculations

For 1,1,1-trimethyldisilane (TMDS), energy minima with respect to nuclear coordinates were obtained by the simultaneous relaxation of all geometric parameters using the gradient method of Pulay [23]. The optimized geometry at the level of restricted Hartree–Fock (RHF) calculations using 6-31G(d) basis set were used as a starting point utilizing Møller Plesset many body perturbation theory (MP2) with full electron correlation [24] up to the 6-311 + G(d,p) computational levels for the fully staggered ($-\text{SiH}_3$ is staggered to SiC_3 skeleton) and eclipsed ($-\text{SiH}_3$ is eclipsing the SiC_3 skeleton)

conformations. Furthermore, hybrid Density Functional Theory calculations (DFT) [25,26] at the Becke3LYP theoretical level [27–29] have also been carried out as a compromise between accuracy and feasibility. Both MP2 and DFT levels have reproduced the experimental conformational stabilities and vibrational wavenumbers of isolated molecules reasonably well [30]. Some key structural parameters, rotational constants, dipole moments as obtained from 3-21G(d), 6-31G(d), 6-311 + G(d,p), at the RHF, MP2 and B3LYP for the staggered and eclipsed conformers are presented in Table 1. Total energies and the energy differences (ΔE) between both rotamers are given in Hartrees (1 H = 627.5095 kcal/mol) and listed in Table 2. All computational calculations were carried out on PIII 700 MHz, IBM PC computer using LCAO-MO SCF GAUSSIAN 98 ab initio calculations [22], while the molecular point group symmetry for TMDS was constrained to C_{3v} symmetry for both eclipsed and staggered rotamers.

2.2. Normal coordinate analysis

A normal coordinate analysis was performed for TMDS (C_{3v}), where the vibrational modes are spanned (grouped) into $10A_1$ (Raman and IR active), $5A_2$ (–) and 15 doubly degenerate species which is Raman and IR active.

Fifty independent internal coordinates have been used to form forty five symmetry coordinates (Table 3) using the traditional method of Wilson [31]. The internal coordinate definitions and the numbering of atoms adopted in the current study are shown in Fig. 1. For the normal coordinate analysis, the following procedure has been used to transform ab initio results into the form required for iterative normal coordinate program. The Cartesian coordinates obtained for the optimized structures were fed into a G-matrix program, where the B-matrix has been used to convert the ab initio force fields in Cartesian coordinates to a force field in the desired internal coordinates. All the diagonal elements of the obtained force field constants have been assigned scaling factors and fed into a force constant program similar to the one written by Schachtschneider [32]. Initially, all scaling factors have been kept fixed at a value of 1.0 to produce the pure ab initio calculated vibrational

Table 1

Bond distances (Å), angles (degrees) dipole moments (Debye), rotational constants (MHz) and energies (Hartrees) for the staggered and eclipsed rotamers of 1,1,1-trimethyldisilane molecule as obtained from RHF, MP2 and DFT

Structural parameters	CEP ^a (d,p)	RHF/3-21G(d)		MP2/6-31G(d)		B3LYP/6-31G(d)		MP2/6-311 + G(d,p)		B3LYP/6-311 + G(d,p)		ED	
	Stagg.	Eclip.	Stagg.	Eclip.	Stagg.	Eclip.	Stagg.	Eclip.	Stagg.	Eclip.	Stagg.	HMDS ^b (Stagg.)	DS ^c (Stagg.)
$r(\text{SiC})$	1.892	1.892	1.892	1.888	1.888	1.899	1.899	1.881	1.882	1.894	1.894	1.877 ± 0.003	
$r(\text{SiSi})$	2.360	2.360	2.349	2.354	2.342	2.372	2.362	2.359	2.348	2.377	2.366	2.340 ± 0.009	2.331 ± .0003
$r(\text{CH}_9=\text{CH}_{12}=\text{CH}_{15})$	1.102	1.088	1.088	1.095	1.095	1.094	1.097	1.095	1.095	1.095	1.095	1.127 ± 0.009	
$r(\text{CH}_{10})^d$	1.101	1.088	1.088	1.094	1.094	1.096	1.096	1.094	1.094	1.094	1.094	1.127 ± 0.009	
$r(\text{SiH}_3=\text{SiH}_4=\text{SiH}_5)$	1.493	1.482	1.482	1.491	1.491	1.493	1.493	1.481	1.481	1.491	1.491		1.492 ± 0.003
$\angle(\text{SiSiC}_6=\text{SiSiC}_7=\text{SiSiC}_8)$	109.7	109.4	109.3	109.7	109.6	109.5	109.5	109.6	109.6	109.6	109.5	108.4 ± 0.4	
$\angle(\text{SiSiH}_3=\text{SiSiH}_4=\text{SiSiH}_5)$	111.1	111.4	111.3	111.5	111.3	111.9	111.7	111.1	110.9	111.5	111.4		110.3 ± 0.4
$\angle(\text{H}_9\text{Csi})^e$	110.5	110.8	110.8	110.6	110.5	110.7	110.6	110.5	110.4	110.6	110.5	108.7 ± 0.8	
$\angle(\text{H}_{10}\text{Csi})^f$	111.5	111.3	111.3	111.4	111.5	111.5	111.6	111.5	111.5	111.5	111.5	108.7 ± 0.8	
$\angle(\text{H}_3\text{SiH}_4)$		107.5	107.6	107.4	107.6	107.0	107.1	107.7	107.7	107.4	107.5		108.6 ± 0.4
$\angle(\text{C}_6\text{Si}_2\text{C}_7)$		109.5	109.6	109.3	109.4	109.4	109.5	109.3	109.4	109.4	109.5	110.5 ± 0.4	
$\angle(\text{H}_9\text{C}_6\text{H}_{10})$		107.7	107.7	107.8	107.7	107.7	107.6	107.8	107.7	107.7	107.6	110.3 ± 0.8	
$\angle(\text{H}_{10}\text{C}_6\text{H}_{11})$		107.7	107.8	107.7	107.8	107.6	107.7	107.7	107.8	107.6	107.7	110.3 ± 0.8	
$\pi(\text{C}_6\text{SiSiH}_3)$		0.0	180.0	0.0	180.0	0.0	180.0	0.0	180.0	0.0	180.0		
$\pi(\text{H}_{10}\text{C}_6\text{Si}_2\text{H}_9)^g$	119.9	119.9	119.8	119.8	119.8	119.9	119.8	119.8	119.7	119.8	119.7		
$\pi(\text{H}_{11}\text{C}_6\text{Si}_2\text{H}_9)^h$	119.9	119.9	119.8	119.8	119.8	119.9	119.8	119.8	119.7	119.8	119.7		
<i>A</i>		3014	3010	3031	3028	2992	2990	3050	3046	3010	3006		
<i>B</i>		1879	1889	1881	1893	1858	1867	1883	1894	1859	1869		
<i>C</i>		1879	1889	1881	1893	1858	1867	1883	1894	1859	1869		
$ \mu_a = \mu_b $		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0		
$ \mu_c = \mu_t $		1.229	1.242	1.176	1.262	1.368	1.382	1.071	1.068	1.176	1.185		

^a Values are obtained from Ref. [11].

^b Values are obtained from Ref. [9].

^c Values are obtained from Ref. [40].

^d $\text{CH}_{10} = \text{CH}_{11} = \text{CH}_{13} = \text{CH}_{14} = \text{CH}_{16} = \text{CH}_{17}$.

^e $\angle\text{H}_9\text{C}_6\text{H}_{10} = \angle\text{H}_9\text{C}_6\text{H}_{11} = \angle\text{H}_{12}\text{C}_7\text{H}_{13} = \angle\text{H}_{12}\text{C}_7\text{H}_{14} = \angle\text{H}_{15}\text{C}_8\text{H}_{16} = \angle\text{H}_{15}\text{C}_8\text{H}_{17}$.

^f $\angle\text{H}_{10}\text{C}_6\text{H}_{11} = \angle\text{H}_{13}\text{C}_7\text{H}_{14} = \angle\text{H}_{16}\text{C}_8\text{H}_{17}$.

^g $\pi(\text{H}_{10}\text{C}_6\text{Si}_2\text{H}_9) = \pi(\text{H}_{13}\text{C}_7\text{Si}_2\text{H}_{12}) = \pi(\text{H}_{16}\text{C}_8\text{Si}_2\text{H}_{15})$.

^h $\pi(\text{H}_{11}\text{C}_6\text{Si}_2\text{H}_9) = \pi(\text{H}_{14}\text{C}_7\text{Si}_2\text{H}_{12}) = \pi(\text{H}_{17}\text{C}_8\text{Si}_2\text{H}_{15})$.

Table 2

RHF, MP2 and B3LYP energies in Hartrees for eclipsed and staggered conformations of 1,1,1-trimethyldisilane molecule

	Staggered	Eclipsed	ΔE^a (cm ⁻¹)
At 3-21G(d) basis set			
RHF level	-694.9407623	-694.9393152	318 ^b
MP2 level	-695.4071197	-695.4053771	382 ^c
B3LYP level	-697.0384730	-697.0369085	344 ^d
At 6-31G(d) basis set			
RHF level	-698.4429792	-698.4416844	284 ^b
MP2 level	-699.0381372	-699.0364989	360 ^c
B3LYP level	-700.5612454	-700.5599127	292 ^d
At 6-311 + G(d,p) basis set			
RHF level	-698.5250615	-698.5236748	304 ^b
MP2 level	-699.5080002	-699.5067384	277 ^c
B3LYP level	-700.6542684	-700.6529028	300 ^d

Calculations have been carried out with full electron correlation.

^a Utilizing all levels at different basis sets, an average ΔE of 318 cm⁻¹ (0.91 kcal/mol \equiv 3.8 kJ/mol) has been obtained.

^b $\Delta E_{av} = 302$ cm⁻¹ (0.86 kcal/mol \equiv 3.6 kJ/mol) from RHF utilizing all basis sets.

^c $\Delta E_{av} = 340$ cm⁻¹ (0.97 kcal/mol \equiv 4.1 kJ/mol) from MP2 utilizing all basis sets.

^d $\Delta E_{av} = 312$ cm⁻¹ (0.89 kcal/mol \equiv 3.7 kJ/mol) from B3LYP utilizing all basis sets.

frequencies at RHF/3-21G(d) basis set. Subsequently a scaling factors of 0.9, 0.8 and 1.0 for stretches, bends and torsions have been utilized to obtain the scaled frequencies as well as the potential energy distribution (PED) of the vibrational modes. Whereas, a scaling factor of 0.9 has been utilized for all coordinates except for methyl and silyl torsions (where a scaling factor of 1.0 was used) to obtain the scaled frequencies for MP2/6-31G(d) calculations. The same scaling factors have been used in previous studies [10,18], in view of the fact that, Hartree–Fock (HF) frequencies are too high by about 10% or so [33–35]. On the contrary, a scaling factor of 0.9 for stretching and bending modes of ν SiH, δ HCH, and δ HCSi and 0.95 for ν CH stretching modes and 1.0 for heavy atom stretches, bends and torsion modes (ν SiSi, ν SiC, δ CSiC, δ CSiSi, τ CH₃ and τ SiH₃) have been implemented for B3LYP/6-31G(d) frequencies.

Table 4 summarizes, the fixed scaled and unscaled frequencies, infrared intensities, Raman activities, depolarization ratios beside the PED's, for complete description of the symmetry coordinates, see Table 3. For brevity, the produced PED's at RHF/3-21G(d) have

been omitted since the produced PED's from all levels were essentially similar. Minor exceptions were observed, such as SiH₃ symmetric deformation (ν_7) was found to be a pure vibrational mode (88% S₇) at RHF/3-21G(d). The resultant ab initio force fields [RHF/3-21G(d), MP2/6-31G(d) and B3LYP/6-31G(d)] in internal coordinates are compared with the values obtained from CEP calculations [11] in Table 5.

2.3. Simulated infrared and Raman spectra

To assist vibrational assignments, the vibrational spectra of TMDS were predicted by means of frequencies, infrared intensities and Raman scattering activities (Table 4) from MP2 and B3LYP levels at 6-31G(d) basis set in addition to RHF/3-21G(d) calculations.

Infrared intensities were calculated based on the dipole moment derivatives with respect to the Cartesian coordinates. The derivatives were taken from the ab initio calculations transformed to normal coordinates by the following equation

$$\left(\frac{\partial \mu_u}{\partial Q_i}\right) = \sum_j \left(\frac{\partial \mu_u}{\partial X_j}\right) L_{ij}$$

where the Q_i is the i th normal coordinate, X_j is the j th Cartesian displacement coordinate, and L_{ij} is the transformation matrix between the Cartesian displacement coordinates and normal coordinates. The infrared intensities were calculated by the following equation

$$I_i = \frac{N\pi}{3c^2} \left[\left(\frac{\partial \mu_x}{\partial Q_i}\right)^2 + \left(\frac{\partial \mu_y}{\partial Q_i}\right)^2 + \left(\frac{\partial \mu_z}{\partial Q_i}\right)^2 \right]$$

the Raman scattering cross section, $\partial \sigma_j / \partial \Omega$, which is proportional to the Raman intensity, can be calculated from the scattering activities and the predicted frequencies for each normal mode using the relationship [36–39]

$$\frac{\partial \sigma_j}{\partial \Omega} = \left(\frac{2^4 \pi^4}{45}\right) \left(\frac{(\nu_0 - \nu_j)^4}{1 - \exp\left[\frac{-hc\nu_j}{kT}\right]} \right) \left(\frac{h}{8\pi^2 c \nu_j} \right) S_j$$

where ν_0 is the excitation frequency, ν_j is the vibrational frequency of the j th normal mode, and S_j is the corresponding Raman scattering activity. To obtain the polarized Raman scattering cross sections,

Table 3
Symmetry coordinates* for 1,1,1-trimethyldisilane molecule

Species	ν_i	Definition	Symmetry coordinate ^a
A ₁	ν_1	CH ₃ antisymmetric stretch	$S_1 = (2a_1 - a_2 - a_3) + (2b_1 - b_2 - b_3) + (2c_1 - c_2 - c_3)$
	ν_2	CH ₃ symmetric stretch	$S_2 = (a_1 + a_2 + a_3) + (b_1 + b_2 + b_3) + (c_1 + c_2 + c_3)$
	ν_3	SiH ₃ symmetric stretch	$S_3 = r_1 + r_2 + r_3$
	ν_4	CH ₃ antisymmetric deformation	$S_4 = (-2\theta_3 + \theta_1 + \theta_2) + (-2\rho_3 + \rho_1 + \rho_2) + (-2\eta_3 + \eta_1 + \eta_2) + (-2\phi_1 + \phi_2 + \phi_3) + (-2\sigma_1 + \sigma_2 + \sigma_3) + (-2\lambda_1 + \lambda_2 + \lambda_3)$
	ν_5	CH ₃ symmetric deformation ‘umbrella’	$S_5 = (\theta_1 + \theta_2 + \theta_3) + (\rho_1 + \rho_2 + \rho_3) + (\eta_1 + \eta_2 + \eta_3) - (\phi_1 + \phi_2 + \phi_3) - (\sigma_1 + \sigma_2 + \sigma_3) - (\lambda_1 + \lambda_2 + \lambda_3)$
	ν_6	CH ₃ antisymmetric deformation	$S_6 = (-2\theta_3 + \theta_1 + \theta_2) + (-2\rho_3 + \rho_1 + \rho_2) + (-2\eta_3 + \eta_1 + \eta_2) - (-2\phi_1 + \phi_2 + \phi_3) - (-2\sigma_1 + \sigma_2 + \sigma_3) - (-2\lambda_1 + \lambda_2 + \lambda_3)$
	ν_7	SiH ₃ symmetric deformation ‘umbrella’	$S_7 = (\alpha_1 + \alpha_2 + \alpha_3) - (\beta_1 + \beta_2 + \beta_3)$
	ν_8	SiC ₃ symmetric stretch	$S_8 = d_1 + d_2 + d_3$
	ν_9	SiSi symmetric stretch	$S_9 = R$
	ν_{10}	SiC ₃ symmetric deformation ‘umbrella’	$S_{10} = (\gamma_1 + \gamma_2 + \gamma_3) - (\delta_1 + \delta_2 + \delta_3)$
A ₂	ν_{11}	CH ₃ antisymmetric. Stretch	$S_{11} = (a_2 - a_3) + (b_2 - b_3) + (c_2 - c_3)$
	ν_{12}	CH ₃ antisymmetric. Deformation	$S_{12} = (\theta_1 - \theta_2) + (\rho_1 - \rho_2) + (\eta_1 - \eta_2) - (\phi_2 - \phi_3) - (\sigma_2 - \sigma_3) - (\lambda_2 - \lambda_3)$
	ν_{13}	CH ₃ antisymmetric. Deformation	$S_{13} = (\theta_1 - \theta_2) + (\rho_1 - \rho_2) + (\eta_1 - \eta_2) + (\phi_2 - \phi_3) + (\sigma_2 - \sigma_3) + (\lambda_2 - \lambda_3)$
	ν_{14}	(CH ₃) ₃ torsions	$S_{14} = \tau_2 + \tau_3 + \tau_4$
	ν_{15}	SiH ₃ torsion	$S_{15} = \tau_1$
E	ν_{16}	CH ₃ antisymmetric stretch	$S_{16a} = 2(a_2 - a_3) - (b_2 - b_3) - (c_2 - c_3)$ $S_{16b} = (b_2 - b_3) - (c_2 - c_3)$
	ν_{17}	CH ₃ antisymmetric stretch	$S_{17a} = 2(2a_1 - a_2 - a_3) - (2b_1 - b_2 - b_3) - (2c_1 - c_2 - c_3)$ $S_{17b} = (2b_1 - b_2 - b_3) - (2c_1 - c_2 - c_3)$
	ν_{18}	CH ₃ symmetric stretch	$S_{18a} = 2(a_1 + a_2 + a_3) - (b_1 + b_2 + b_3) - (c_1 + c_2 + c_3)$ $S_{18b} = (b_1 + b_2 + b_3) - (c_1 + c_2 + c_3)$
	ν_{19}	SiH ₃ antisymmetric stretch	$S_{19a} = 2r_1 - r_2 - r_3$ $S_{19b} = r_2 - r_3$
	ν_{20}	CH ₃ antisymmetric deformation	$S_{20a} = 2(\theta_1 - \theta_2) - (\rho_1 - \rho_2) - (\eta_1 - \eta_2)$ $S_{20b} = (\rho_1 - \rho_2) - (\eta_1 - \eta_2)$
	ν_{21}	CH ₃ rock	$S_{21a} = 2(2\theta_3 - \theta_1 - \theta_2) - (2\rho_3 - \rho_1 - \rho_2) - (2\eta_3 - \eta_1 - \eta_2)$ $S_{21b} = (2\rho_3 - \rho_1 - \rho_2) - (2\eta_3 - \eta_1 - \eta_2)$
	ν_{22}	CH ₃ symmetric deformation ‘umbrella’	$S_{22a} = 2(\theta_1 + \theta_2 + \theta_3) - (\rho_1 + \rho_2 + \rho_3) - (\eta_1 + \eta_2 + \eta_3) - 2(\phi_1 - \phi_2 - \phi_3) + (\sigma_1 + \sigma_2 + \sigma_3) + (\lambda_1 + \lambda_2 + \lambda_3)$ $S_{22b} = (\rho_1 + \rho_2 + \rho_3) - (\eta_1 + \eta_2 + \eta_3) - (\sigma_1 + \sigma_2 + \sigma_3) + (\lambda_1 + \lambda_2 + \lambda_3)$
	ν_{23}	SiH ₃ antisymmetric deformation	$S_{23a} = 2\alpha_1 + \alpha_2 + \alpha_3$ $S_{23b} = \alpha_2 - \alpha_3$
	ν_{24}	CH ₃ rock	$S_{24a} = 2(\phi_2 - \phi_3) - (\sigma_2 - \sigma_3) - (\lambda_2 - \lambda_3)$ $S_{24b} = (\sigma_2 - \sigma_3) - (\lambda_2 - \lambda_3)$
	ν_{25}	CH ₃ rock	$S_{25a} = 2(2\phi_1 + \phi_2 + \phi_3) - (2\sigma_1 + \sigma_2 + \sigma_3) - (2\lambda_1 + \lambda_2 + \lambda_3)$ $S_{25b} = (2\sigma_1 + \sigma_2 + \sigma_3) - (2\lambda_1 + \lambda_2 + \lambda_3)$
	ν_{26}	SiC ₃ antisymmetric stretch	$S_{26a} = 2d_1 - d_2 - d_3$ $S_{26b} = d_2 - d_3$
	ν_{27}	SiH ₃ rock	$S_{27a} = 2\beta_1 - \beta_2 - \beta_3$ $S_{27b} = \beta_2 - \beta_3$
	ν_{28}	SiC ₃ antisymmetric deformation	$S_{28a} = 2\gamma_1 - \gamma_2 - \gamma_3$ $S_{28b} = \gamma_2 - \gamma_3$
	ν_{29}	(CH ₃) ₃ torsions	$S_{29a} = 2\tau_2 - \tau_3 - \tau_4$ $S_{29b} = \tau_3 - \tau_4$
	ν_{30}	SiC ₃ rock	$S_{30a} = 2\delta_1 - \delta_2 - \delta_3$ $S_{30b} = \delta_2 - \delta_3$

^a Symmetry coordinates are not normalized, for internal coordinates definition see Fig. 1.

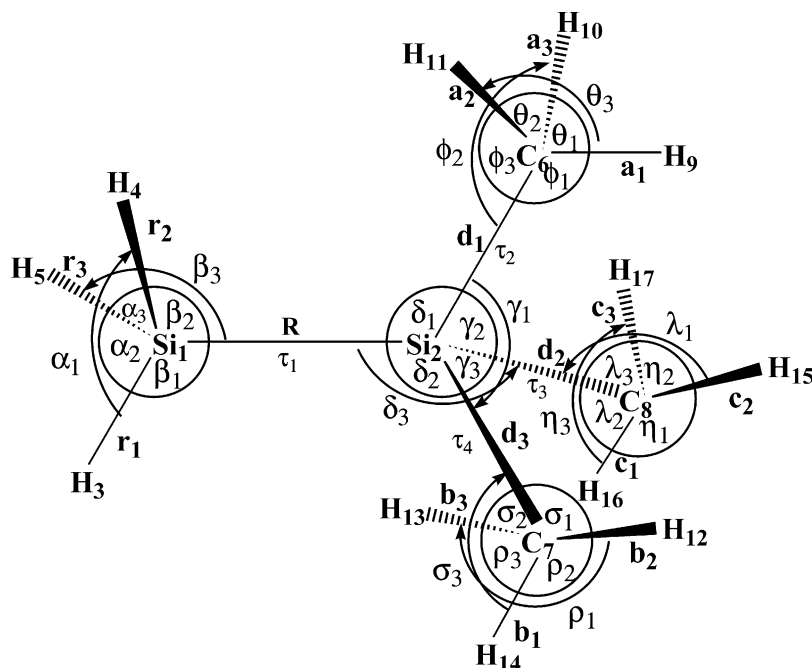


Fig. 1. Atom numbering and internal coordinates of the fully *staggered* 1,1,1-trimethyldisilane.

the polarizabilities are incorporated into S_j by $S_j[(1 - \rho_j)/(1 + \rho_j)]$ where ρ_j is the depolarization ratio of the j th normal mode. The Raman scattering cross sections and calculated frequencies, together with a Lorentzian function, were used to obtain the calculated Raman spectrum. The simulated infrared and Raman spectrum of TMDS together with the theoretically determined scaled vibrational wave-numbers are shown in Figs. 2 and 3, respectively. Unfortunately, the gaseous infrared and Raman liquid spectra recorded by Zink and Hassler [11] were not illustrated and the CH stretching and bending frequencies have been omitted. However, we believe the predicted infrared and Raman spectra provide an excellent support for the proposed vibrational assignment.

It is clear that the scaled frequencies from all levels of calculations are very similar in the low lying frequency region (below 800 cm^{-1}) as illustrated in the calculated infrared spectra (Fig. 2), which ensures that the three scaling factors which have been used are most likely good. The predicted IR intensities from the levels of B3LYP and MP2 are almost the same, except $\sim 1000\text{--}850\text{ cm}^{-1}$. The simulated Raman spectra (Fig. 3) from RHF, B3LYP are very similar and

comparable with the one predicted by MP2 level with minor changes in intensities which could be validated only with an experimental spectrum of TMDS.

3. Results and discussion

3.1. Molecular structures

To the best of our knowledge there is neither microwave (MW) nor electron diffraction structural data reported for TMDS molecule. Therefore, the computed geometrical parameters are compared with the values of DS [40] and HMDS [9] as obtained from GED studies (Table 1). When comparing same levels of calculations at the same basis set, bond lengths of staggered and eclipsed conformers are indistinguishable, except for the SiSi distance which varies by about 0.01 \AA . The SiSi and SiH distances of the staggered TMDS agrees within $0.01\text{--}0.02\text{ \AA}$ to that of DS [40] and HMDS molecule [9]. Although, the local symmetry of the $-\text{CH}_3$ group in the geometry matrix follow the C_s symmetry, it turns to be C_{3v} rotor where the C–H distances differ slightly by 0.001 \AA at MP2

Table 4
Observed and calculated frequencies (cm^{-1}) for 1,1,1-trimethyldisilane molecule

Species	Vib. No.	Fundamental	RHF/3-21G*		MP2/6-31G(d)		IR int. ^c	Raman act. ^d	Obs. ^e IR _g /R _i	PED ^f	B3LYP/6-31G(d)					
		Unscaled/scaled CPE [11]	Ab initio	Fixed scaled ^a	Ab initio	Fixed scaled ^b					Ab initio	Fixed scaled ^g	IR int. ^c	Raman act. ^d	PED ^{f,h}	
A ₁ (p)	ν ₁	ν _{as} CH ₃		3250	3084	3189	3026	22.2	197.5	2965 ⁱ /–	100S ₁	3112	3034	28.4	220.6	99S ₁
	ν ₂	ν _{as} CH ₃		3180	3017	3097	2938	3.6	308.8	2915 ⁱ /–	100 ₂	3041	2964	7.1	295.1	99S ₂
	ν ₃	ν _s SiH ₃	2303/2119	2255	2138	2274	2157	92.2	199.5	2138/2127	100S ₃	2209	2095	115.1	223.1	100S ₃
	ν ₄	δ _{as} CH ₃		1641	1468	1539	1460	6.3	0.1	1428 ⁱ /–	72S ₄ ,28S ₆	1509	1431	12.0	0.1	72S ₄ ,28S ₆
	ν ₅	δ _s CH ₃ [*]		1474	1318	1373	1303	5.6	0.9	1268 ⁱ /–	99S ₅	1336	1268	6.7	0.8	99S ₅
	ν ₆	ρ CH ₃	912/839	1010	904	959	910	1.1	1.8	901/897	33S ₆ ,44S ₇ ,12S ₄	930	887	55.6	1.1	33S ₆ ,42S ₇ ,12S ₄
	ν ₇	δ _s SiH ₃ [*]	1002/922	924	826	895	849	442.8	0.8	836/819	55S ₇ ,29S ₆ ,11S ₄	868	826	481.1	0.8	56S ₇ ,30S ₆ ,11S ₄
	ν ₈	ν _s SiC ₃	652/600	634	601	643	610	16.9	15.2	625/624	89S ₈	613	611	22.9	15.2	90S ₈
	ν ₉	ν _s SiSi	413/412	386	364	430	408	3.7	19.6	413/412	82S ₉	407	406	10.8	19.6	82S ₉
	ν ₁₀	δ _s SiC ₃ [*]	220/202	213	192	211	200	4.6	2.0	–/218	83S ₁₀	207	206	8.3	2.0	82S ₁₀ ,10S ₉
A ₂ (–)	ν ₁₁	ν _{as} CH ₃		3254	3087	3197	3033	ia	ia	ia	100S ₁₁	3120	3041	ia	ia	100S ₁₁
	ν ₁₂	δ _{as} CH ₃		1624	1453	1516	1438	ia	ia	ia	68S ₁₂ ,32S ₁₃	1487	1411	ia	ia	68S ₁₂ ,32S ₁₃
	ν ₁₃	ρ CH ₃	718/661	813	727	730	693	ia	ia	ia	68S ₁₃ ,32S ₁₂	706	670	ia	ia	69S ₁₃ ,32S ₁₂
	ν ₁₄	CH ₃ torsion		148	148	168	168	ia	ia	ia	100S ₁₄	152	152	ia	ia	100S ₁₄
	ν ₁₅	SiH ₃ torsion		86	86	99	99	ia	ia	ia	100S ₁₅	91	90	ia	ia	100S ₁₅
E (dp)	ν ₁₆	ν _{as} CH ₃		3255	3088	3197	3033	11.2	92.0	2965 ⁱ /–	100S ₁₆	3121	3042	15.8	106.9	100S ₁₆
	ν ₁₇	ν _{as} CH ₃		3248	3082	3188	3025	1.2	22.3	2965 ⁱ /–	100S ₁₇	3111	3032	1.4	28.2	99S ₁₇
	ν ₁₈	ν _s CH ₃ [*]		3097	3017	3077	2938	3.7	1.2	2915 ⁱ /–	100S ₁₈	3040	2963	11.3	1.1	99S ₁₈
	ν ₁₉	ν _{as} SiH ₃	2296/2113	2249	2134	2286	2169	144.7	86.8	2138/2127	100S ₁₉	2218	2104	155.0	100.0	100S ₁₉
	ν ₂₀	δ _{as} CH ₃		1636	1463	1529	1451	7.9	11.6	1428 ⁱ /–	89S ₂₀	1500	1423	14.4	20.1	86S ₂₀ ,10S ₂₁
	ν ₂₁	δ _{as} CH ₃		1627	1455	1520	1442	0.1	27.7	1428 ⁱ /–	90S ₂₁	1491	1414	0.5	32.2	87S ₂₁ ,10S ₂₀
	ν ₂₂	δ _s CH ₃ [*]		1463	1309	1362	1292	31.6	1.1	1268 ⁱ /–	98S ₂₂	1324	1257	43.8	0.2	97S ₂₂
	ν ₂₃	δ _{as} SiH ₃	1025/943	1018	911	982	932	60.7	22.0	931/929	96S ₂₃	953	904	97.5	32.9	95S ₂₃
	ν ₂₄	ρ CH ₃	912/839	982	880	913	866	48.6	3.7	836/832	75S ₂₄	884	847	38.9	9.4	73S ₂₄
	ν ₂₅	ρ CH ₃	805/741	883	792	809	767	5.1	2.3	749/747	77S ₂₅ ,11S ₂₆	779	746	3.6	2.4	70S ₂₅ ,19S ₂₆
	ν ₂₆	ν _{as} SiC ₃	728/670	741	699	723	686	9.3	6.5	695/695	78S ₂₆ ,10S ₂₅	691	682	10.1	9.8	68S ₂₆ ,18S ₂₅ ,12S ₂₄
	ν ₂₇	ρ SiH ₃	467/429	527	472	515	488	12.6	9.7	496/497	87S ₂₇	503	479	15.5	15.6	87S ₂₇
	ν ₂₈	δ _{as} SiC ₃	216/199	208	186	202	192	2.2	1.6	–/218	85S ₂₈	205	203	4.3	1.7	96S ₂₈
	ν ₂₉	CH ₃ torsion		161	159	185	185	0.1	0.1	–/–	92S ₂₉	165	165	0.1	0.1	91S ₂₉
	ν ₃₀	ρ SiC ₃	139/128	135	122	131	125	1.7	1.0	–/143	86S ₃₀	132	132	2.6	1.1	79S ₃₀ ,10S ₂₉

* Umbrella vibrational mode for SiH₃ or SiC₃ and each of CH₃ groups.

^a Scaled ab initio calculations with factors of 0.9 for stretches and 0.8 for the bends, and 1.0 for torsion using the RHF/3-21G(d) basis set.

^b Scaled ab initio calculations with factors of 0.9 for stretches and bends, and 1.0 for torsion using the MP2/6-31G(d) basis set.

^c Calculated infrared intensities in km/mol.

^d Calculated Raman activities in Å⁴/amu.

^e Frequencies are taken from the infrared spectrum of the gas [11].

^f Contributions less than 10% are omitted.

^g Scaled ab initio calculations with factors of 0.9 for CH stretching, HCH and HCSi bending modes, 0.95 for SiH stretch 1.0 for heavy atom stretches and bends, and torsions using the B3LYP/6-31G(d) basis set.

^h Contributions for S₆ is 56S₆, 22S₄, 11S₇, 10S₁₀ and for S₇ is 88S₇ at RHF/3-21G(d).

ⁱ Observed from the infrared spectrum of trimethylsilane in the gas phase [44].

Table 5

Ab initio unscaled diagonal force constants for 1,1,1-trimethyldisilane molecule

Coordinate involved ^a	Types of vibration	Local coordinate ^b	Force constant in mdyne/Å				% (RHF – B3LYP/ RHF)	% (MP2 – B3LYP/ MP2)
			CEP(d,p) ^c (Ncm ⁻¹)	RHF/3-21G(d)	MP2/6-31G(d)	B3LYP/6-31G(d)		
SiSi	Stretch	<i>R</i>	1.83	1.431	1.835	1.630	13.9	11.2
SiH ₃	Stretch	<i>r</i> ₁	3.0–3.11	2.913	2.883	2.819	3.2	2.2
SiC ₆	Stretch	<i>d</i> ₁	3.04–3.18	3.006	2.992	2.720	9.5	9.1
C ₆ H ₉	Stretch	<i>a</i> ₁	–	5.734	5.483	5.238	8.6	4.5
C ₆ H ₁₀	Stretch	<i>a</i> ₂	–	5.767	5.526	5.288	8.3	4.3
H ₃ SiH ₄	Bend	<i>α</i> ₁	0.55–0.56	0.441	0.419	0.398	9.7	5.0
H ₃ SiSi	Bend	<i>β</i> ₁	0.39	0.325	0.307	0.295	9.2	3.9
C ₆ SiC ₈	Bend	<i>γ</i> ₁	0.71–0.8	0.558	0.554	0.545	2.3	1.6
C ₆ SiSi	Bend	<i>δ</i> ₁	0.52	0.467	0.460	0.445	4.7	3.2
H ₉ C ₆ H ₁₀	Bend	<i>θ</i> ₁	0.43–0.49	0.567	0.502	0.484	14.6	3.6
H ₁₀ C ₆ H ₁₁	Bend	<i>θ</i> ₃	0.37–0.48	0.564	0.496	0.479	15.1	3.4
H ₉ C ₆ Si	Bend	<i>φ</i> ₁	–	0.455	0.379	0.357	21.5	5.8
H ₁₀ C ₆ Si	Bend	<i>φ</i> ₂	–	0.453	0.379	0.359	20.7	5.3
SiH ₃ torsion	Bend	<i>τ</i> ₁	–	0.000	0.000	0.000	0.0	0.0
CH ₃ torsion	Bend	<i>τ</i> ₂	–	0.005	0.007	0.005	0.0	28.6

Force constants in mdyne/Å unless otherwise notified.

^a For atom numbering and internal coordinates definitions, see Fig. 3, assuming C_s symmetry for the CH₃ group.^b *r*₁ = *r*₂ = *r*₃; *d*₁ = *d*₂ = *d*₃; *a*₁ = *b*₁ = *c*₁; *a*₂ = *a*₃ = *b*₂ = *b*₃ = *c*₂ = *c*₃; *α*₁ = *α*₂ = *α*₃; *β*₁ = *β*₂ = *β*₃; *γ*₁ = *γ*₂ = *γ*₃; *δ*₁ = *δ*₂ = *δ*₃; *θ*₁ = *θ*₂ = *ρ*₁ = *ρ*₂ = *η*₁ = *η*₂; *θ*₃ = *ρ*₃ = *η*₃; *φ*₁ = *σ*₁ = *λ*₁; *φ*₂ = *φ*₃ = *σ*₂ = *σ*₃ = *λ*₂ = *λ*₃; *τ*₂ = *τ*₃ = *τ*₄.^c Force constants in terms of vibrational modes rather than those in internal coordinates as obtained from Ref. [11].

and B3LYP levels regardless of the employed basis set or the level of calculations (Table 1). Nevertheless the predicted CH distances of TMDS are found to be shorter by about 0.1 Å than that of HMDS [9]. The three levels of calculations predicts the length of the Si–C (sp³) bond to be in the range of 1.888–1.899 Å (Table 1) in agreement with GED study [41] which is larger than that of HMDS by ~0.01 Å [9].

Bond angles are either similar or vary within ±0.1°, except for for ∠ SiSiH which varies by 0.1–0.2° (Table 1). For instance, the staggered angles of ∠ SiSiC, ∠ H₉CSi, and ∠ H₉CH₁₀ are less than that of the eclipsed form by ~0.1°. However, the ∠ HSiH, ∠ CSiC, ∠ H₁₀CSi, and ∠ H₁₀CH₁₁ of the staggered are predicted to be larger than the high energy form. Furthermore, the bond angles of the staggered form agree within 0.1° with those predicted by Ref. [11] at CEP(d,p) level except for the ∠ HCSi which varies by 0.1–0.3°. Moreover, the bond angles obtained from the current study agree within 3° compared to the values obtained from GED for DS and HMDS [9,40].

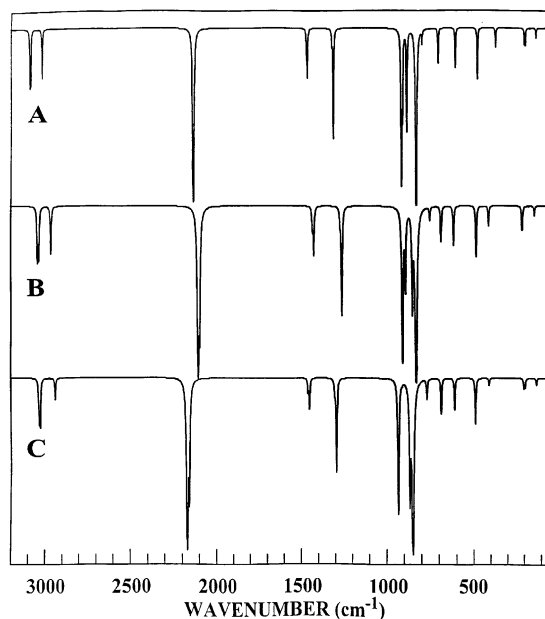


Fig. 2. Predicted infrared spectrum of staggered 1,1,1-trimethyldisilane at: (A) RHF/3-21G(d); (B) B3LYP/6-31G(d); (C) MP2/6-31G(d) with full electron correlation.

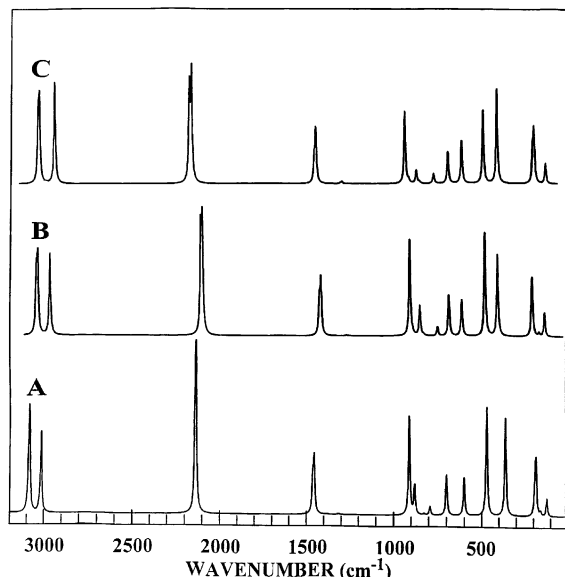


Fig. 3. Predicted Raman spectrum of staggered 1,1,1-trimethyldisilane at (A) RHF/3-21G(d); (B) B3LYP/6-31G(d); (C) MP2/6-31G(d) with full electron correlation.

3.2. Vibrational frequencies and force constants

The frequency calculations showed that the staggered form has real frequencies, however, the eclipsed form has one imaginary frequency and is a transition state [42]. The staggered conformer is found to be more stable than the eclipsed form by an average of 318 cm^{-1} (0.91 kcal/mol) from all levels and all basis sets (Table 2). This average ΔE is comparable to that of $\sim 378\text{ cm}^{-1}$ which was obtained for DS using RHF and MP2 at 6-311++G(d,p) basis set, and $\sim 359\text{ cm}^{-1}$ for HMDS from RHF level at 3-21G(d) and 6-31G(d) basis sets [10]. It is worth mentioning that, comparable ΔE values were obtained from DFT and RHF, where ΔE differs only by $\pm 26\text{ cm}^{-1}$. Furthermore, B3LYP and MP2 calculations gives an energy difference for the gas phase that is to some extent larger than those obtained from RHF level except for the 6-311 + G(d,p) basis set.

The reported ab initio force constants in the current study (Table 5) could be used in initiating an experimental study of equilibrium molecular geometry of TMDS similar to GED study [43]. It is obvious from Table 5 that, differences between RHF and DFT diagonal force constants are fairly close, for the SiSi, SiH, SiC stretches, CSiC and CSiSi deformations as

well as SiH₃ torsions. However, better accuracies are noticeable for other force constants predicted from the levels of MP2 and DFT at the same basis set (Table 5). Practically, small valence interaction force constants are considered negligible such as SiH and CH stretches. However, large interactions are expressed in methyl rocking, SiH₃ symmetric deformation (umbrella mode) as well as SiC₃ antisymmetric stretch and rocking. The resulting force fields representing, stretch–stretch, stretch–bend and bend–bend interactions can be obtained from the author.

3.3. Vibrational assignment

The conformational analysis using vibrational spectroscopy is based on the results of normal coordinate analysis with the force field. Three different scaling factors were applied in order to improve the concordance between the computed and the experimental vibrational spectral data. Table 4 lists the gas phase infrared and liquid Raman data obtained in the course of earlier work on TMDS and trimethylsilane (TMS), (CH₃)₃SiH because both molecules obey C_{3v} selection rules [11,44].

Due to the absence of methyl stretching fundamentals of TMDS [11], it will be correlated with the observed bands of TMS [44]. The CH stretches for the three methyl groups spanned to 1A₂ (–), 2A₁ and 3E species. From Table 4, three coinciding vibrational modes are observed and assigned to $\nu_{\text{as}}\text{CH}_3$ (ν_1 , ν_{16} and ν_{17}) scaled at (3026, 3033 and 3025) cm^{-1} , respectively, which was observed at 2965 cm^{-1} . In the same way, the $\nu_{\text{s}}\text{CH}_3$ (ν_2 and ν_{18}) has been assigned to the observed band at 2915 cm^{-1} which was scaled at 2938 cm^{-1} . However, ν_{11} could not be observed because it is vibrationally inactive.

Two infrared-active stretching vibrations (ν_3 and ν_{19}) are expected but only one Q-branch recorded at 2138 cm^{-1} [11] in the infrared gaseous spectrum which was undoubtedly assigned to SiH₃ stretching modes. It is apparent that, ν_3 and ν_{19} were consistent with those scaled at 2138 and 2134 cm^{-1} by RHF/3-21G(d) basis set, respectively. MP2/6-31G(d) basis set estimates the same fundamentals at 2157 and 2169 cm^{-1} which are a little bit high, however, B3LYP deduced them at relatively low wavenumbers, respectively (Table 4). The r_0 (SiH) bond length was calculated utilizing the following formula

of: $r_o(\text{SiH}) = 1.8729 \text{ \AA} - 1.798 \times 10^{-4} \nu_{\text{iso}}(\text{SiH})$, cm^{-1} [45]. There is a reasonable agreement with the value of 1.4885 \AA for r_o Si–H bond which is shorter by 0.0025 \AA to those predicted by ab initio calculations at MP2/6-31G(d) and B3LYP/6-311 + G(d,p) basis sets with an error of 1.7% (Table 1). However, MP2/6-311 + G(d,p) predicts a distance which is shorter by 0.0075 \AA .

Also, the bands in the region of $1300\text{--}1450 \text{ cm}^{-1}$ were not included [11], thus CH_3 antisymmetric (ν_4 , ν_{20} and ν_{21}) and symmetric (ν_5 and ν_{22}) deformations remain unassigned for TMDS. However, they could be correlated to the spectral data of HMDS [10] and TMS [44]. The antisymmetric methyl deformations, A_1 and $2E$ were assigned to the observed band at 1428 cm^{-1} in the infrared gas spectrum of TMS [44]. Likewise, CH_3 symmetric deformations were observed at 1254 and 1246 cm^{-1} for HMDS [10] and at 1268 cm^{-1} for TMS [44].

A minor change in the positions of $\delta_s \text{SiH}_3$ (ν_7) and ρCH_3 (ν_6) which have been assigned earlier to the observed bands at 897 and 819 cm^{-1} , respectively, from the liquid Raman spectrum should be noted [11]. These two fundamentals should be interchanged when inspecting the PED's (Table 4) as well as the scaled frequencies predicted from both MP2 and B3LYP levels. The calculated PED's reveal a strong mixing of $\delta_s \text{SiH}_3$ (ν_7) which is $\sim 55\%$, $\sim 29\%$ methyl rocking (S_6), and 11% methyl antisymmetric deformation (S_4), at MP2 and B3LYP levels. On the other hand, the methyl rock (ν_6) is extensively mixed with $\sim 44\%$ SiH_3 symmetric deformation (ν_7) and 12% CH_3 antisymmetric deformation (ν_4) at both MP2 and B3LYP levels (Table 4) which is similar to that attained from RHF level. However, little mixing was observed between (ν_{12} and ν_{13}) and (ν_{25} and ν_{26}) fundamentals. Practically all other vibrational modes are pure fundamentals to a high extent.

As expected, the proposed vibrational assignment of the skeleton modes ($\nu_s \text{SiC}_3$, $\delta_s \text{SiC}_3$, $\nu_{\text{as}} \text{SiC}_3$, $\nu_s \text{SiSi}$, $\delta_{\text{as}} \text{SiC}_3$ and ρSiC_3) is completely consistent with a former study of TMDS [11]. The observed bands for TMDS agrees within $\pm 20 \text{ cm}^{-1}$ with the reported values of TMS [44] and HMDS [10] except for ρSiC_3 mode. The SiSi stretch were assigned to the observed at 413 and 412 cm^{-1} in the infrared gas and Raman liquid spectra, respectively [11], which lie between

the νSiSi for HMDS (404 cm^{-1}) and DS (343 cm^{-1}) molecules [10]. Hence, the SiSi stretch is increasing in the following order, HMDS (404 cm^{-1}) < TMDS (413 cm^{-1}) < DS (432 cm^{-1}) which is consistent with weighing factors of the neighboring atom(s).

From the current and earlier studies [10,46], it is believed that the estimated frequencies obtained by RHF/3-21G(d) still provides a relatively strong support for the vibrational assignment regardless of their closeness to the experimental data compared to those obtained from either MP2 and B3LYP levels at the 6-31G(d) basis set.

3.4. Silyl and methyl barriers

From previous investigations [14–19], the silyl torsional mode appears as the sum and difference bands with the νSiH vibrational mode. The same method could not be used here, since the IR gaseous spectrum of TMDS was not published [11]. Moreover, the silyl and methyl torsional modes (ν_{15} and ν_{14}) are vibrationally inactive under the C_{3v} symmetry, which is unscaled at 99 and 168 cm^{-1} , respectively, at MP2/6-31G(d), and the active methyl torsional mode (ν_{29}) was not observed [11]. Accordingly, it was not possible to obtain barriers to internal rotations experimentally. In a recent study, Tarek A. Mohamed et al. have found that the silyl torsional barriers obtained from MP2/6-31G(g) calculations agree reasonably well with those determined experimentally [18,19]. Thus, the $-\text{SiH}_3$ and $-\text{CH}_3$ barriers to internal rotations around SiSi and SiC, respectively, were obtained by means of ab initio potential surface scan (PSS) at RHF and MP2 levels at 6-31G(d) basis set with full electron correlation in the latter case. To obtain $-\text{SiH}_3$ and $-\text{CH}_3$ barriers, the C_6SiSiH_3 and $\text{H}_9\text{C}_6\text{SiSi}$ dihedral angles were varied by 15° increments while all geometrical parameters of the staggered form were kept constant. The estimated Si–Si torsional barrier (V_3 potential function) of TMDS is found to be 0.89 and 1.05 kcal/mol (312 and 369 cm^{-1}) from RHF/6-31G(d) and MP2/6-31G(d) basis sets, respectively. These values are consistent with an average of $\sim 1.14 \text{ kcal/mol}$ obtained for DS ($1.26 \pm 0.02 \text{ kcal/mol}$) and HMDS (1.02 kcal/mol) from the experimental results [20] and RHF/6-31G(d) basis set [10], respectively. Such consistency is understandable since TMDS is semi DS and semi

HMDS due to the presence of the SiH_3 and $\text{Si}(\text{CH}_3)_3$ moieties, respectively. From the current study, it is obvious that the Si–Si barrier height for DS, TMDS and HMDS does not differ significantly [10,20,40]. Employing PSS at RHF/6-31G(d) and MP2 = full/6-31G(d) basis sets, the threefold barrier of the methyl rotor is found to be 1.8 and 1.97 kcal/mol (630 and 689 cm^{-1}), respectively. A lower value of 1.36 ± 0.48 kcal/mol (476 ± 167 cm^{-1}) has been obtained for methyl barrier in tetramethylsilane from GED [47] since the adjacent neighbors are $-\text{SiCH}$ and SiSiH_3 , respectively. However, the accuracy of the SiSi ($-\text{SiH}_3$) and SiC ($-\text{CH}_3$) barrier heights reported here, could be judged quantitatively upon recording the methyl torsion in far infrared gas spectrum. The significant barrier heights of both silyl and methyl groups in TMDS were in favor of hindered internal rotation around SiSi and SiC bonds.

4. Conclusion

The main geometric parameters of the staggered and eclipsed rotamers are very similar where the distances and angles are differing by 0.01–0.02 Å and 0.1° , respectively. The determined V_3 potential function (~ 0.97 kcal/mol) for both SiH_3 and CH_3 groups (~ 1.88 kcal/mol) were in favor of hindered internal rotation around SiSi and SiC bonds which are close to the silyl barriers for DS and HMDS molecules. The SiSi stretching mode increases in the following order, HMDS (404 cm^{-1}) < TMDS (413 cm^{-1}) < DS (432 cm^{-1}). RHF and DFT levels provide a solid support for the vibrational assignments of molecules having single conformations at ambient temperature with low cost and more feasibility compared with MP2 calculations.

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