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DFT and NBO analysis of Self Assembly Material Isobutyltrimethoxy Silane and formation of SAM

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ABSTRACT

In this work, we report a combined experimental and theoretical study on molecular structure, vibrational spectra and NBO analysis of Isobutyltrimethoxylsilane. Density functional theory (DFT),B3LYP/6-311++G (d,p) basis set was used for the optimization of the ground state geometry and simulation of the Infrared and Raman spectra of this molecule. Calculated geometrical parameters fit very well with the experimental ones.The Self Assembled Monolayer of Isobutyltrimethoxylsilane on Si/SiO2 substrate was prepared and the resulting surface was studied using AFM.

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Introduction

Self assembled monolayer is a layer of molecular thickness formed by the self-organization of molecules in an ordered manner by chemisorptions on a solid surface. SAM has recently become very popular due to their potential applications to biosensors, nanotechnology and biomolecular electronics [1-4]. Surface topography and roughness of SAM's are determined by Atomic Force Microscopy. Atomic Force Microscopy is successfully applied to various materials including glasses, metals, polymers, semiconductors, biomaterials etc [5]. The use of silane based monolayer has many important advantages. One of the advantages is the high stability of the monolayer, because of the covalent network formed between the surface and the silane molecules. This consists ideally two bonds between the molecules and an additional bond formed with the surface. These intra molecular bonds can be used to form a laterally polymerized, resulting in an improved stability of the monolayer [6]. In this work, Isobutyl trimethoxy silane is used for the formation of Self-assembled monolayer (SAM). We have also characterized the vibrational spectral analysis of ISBTMS using FTIR and FT Raman spectroscopy, with the assistance of quantum chemical computations. Natural bond orbital analysis, HOMO-LUMO energies and molecular charges are also calculated.

Experimental Details

The AR grade Isobutyl trimethoxy silane (IBTMS) was purchased commercially from Sigma Aldrich and was used as received. The solvent toluene and other inorganic chemicals of GR grade were obtained from Merck. FT-IR spectra of the present liquid sample IBTMS kept in the liquid window has been recorded using a Agilent Cary 630 spectrometer in the wave number range 400–4000 cm⁻¹ with the spectral resolution of 2 cm⁻¹. The FT-Raman spectrum of ISBTMS was obtained in the range 4000 – 50 cm⁻¹ using BRUKER RFS 27 FT-Raman Spectrometer. The spectral Resolution is 2 cm⁻¹.

Sample preparation and formation of SAM

The spin coating technique is used for preparation of SAMs in this experiment, as an interesting alternative to the more

volumetric ratio H2SO4/H2O2) for few minutes or until the visible reaction stops, taking extreme caution while using very strong oxidant piranha solution, due to its violent reactivity towards organic matter. The silicon wafers were again rinsed with ultrapure water and dried under N2 gas. The IBTMS was diluted with toluene, [7,8] to form 0.01 M, 0.05 M, and 0.1 M solutions. It was found that the solution concentration played a vital role in the formation of SAM of silane. Since at lower concentrations, it was found to form incomplete island like structures and higher concentrations favored multi layers formation. A smooth monolayer was formed at 0.01 M concentration by spin coating technique. The monolayer formation was optimized with different speeds and a speed of 5000 rpm yielded best result. The spin coating was performed under the anhydrous conditions of a glove box (MBraun M-20). Later, the substrates were exposed to ammonia and hydrochloric acid vapors for a few hours at room temperature to enhance the hydrolysis of silane and to promote the bonding to SiO₂ surface. The substrates were then rinsed in the toluene to remove the multilayer and physically adsorbed materials. SAM characterization Surface topography and roughness were determined by Atomic Force Microscopy (AFM) (Seiko Instruments) using the tapping mode with a single crystal Si tip with a resonant frequency of 300 kHz, with 0.5 kHz scanning speed. Height and

common method of submerging the substrate in a silane solution

[7]. Four inch diameter silicon wafers with a native oxide

layer(p-type, h100i orientation, 20-30 Ω cm resistivity and

surface roughness .19 nm) were cut into samples of 1 cm by 1

cm and then, the substrates were first sonicated for 10 min in

propanol, acetone and ultrapure water (Millipore Direct-O18 M

 Ω -cm resistivity). It was then cleaned with piranha solution (3:1

the manufacturer-provided software. Fig. 1 shows the morphology of the films obtained from the AFM studies for different concentration along with phase images and its height profiles. It was found that at 0.01 M concentration the films were uniform.

phase images were collected simultaneously and analyzed using



32425



Fig 1. AFM micrographs - Formation of SAM of ISBTMS on Si/SiO₂ wafers for different concentration

Computational Details

The entire quantum chemical calculations have been performed at Density functional theory(DFT) method hybrid Becke's three-parameter Lee-Yang-Parr correlation functional (B3LYP) with 6-311++G(d, p) basis set using the Gaussian 09W program [9]. The optimized structural parameters have been evaluated for the calculations of vibrational frequencies, by assuming Cs point group symmetry. As per the results of calculations, the unscaled calculated frequencies, reduced mass, force constant, infrared intensity, Raman activity, depolarization ratios and optimized parameters like bond lengths, bond angles and dihedral angles are obtained. In order to fit the theoretical wave numbers to the experimental wave numbers, an overall scaling factor has been introduced by using a least square optimization of the computed to the experimental data. The calculated vibrational wave numbers are scaled by 0.9679 for B3LYP/6-311++G (d, p) basis set. The PEDs are computed from quantum chemically calculated vibrational frequencies using VEDA program [10]. Gauss view program has been used to view visual animation and also for the verification of the normal modes assignment.

Results and Discussion

There are 29 atoms in isobutyl Trimethoxysilane and so there can be 81 (3N-6) normal modes of vibration. The spectral bands are due to the internal vibrations of butyl group, methoxy silane group. The vibrational analysis is based on the FT IR spectrum and FT Raman spectrum. The optimized structure of ISBTMS along with the atom numbering schemes is shown in figure 2. The experimental FTIR and FT-Raman spectra of ISBTMS are shown in figure 3 and 4 respectively.

Methoxy Silane group Vibrations

The Si-O-CH₃ symmetric stretching vibrations are generally observed in the region 810-800cm⁻¹[11]. In ISBTMS, Si-O-C symmetric stretching vibrations are observed at 810 cm⁻¹as very strong band in IR and the related calculated value is 801cm⁻ ¹. The CH₃ asymmetric and symmetric stretching vibration of Si-O-CH₃ group are generally observed in the region 2990-2925 cm⁻¹and 2850-2820cm⁻¹[13]. The medium band in IR at 2955 cm⁻¹and very strong band in Raman at 2946 cm⁻¹ are assigned as asymmetric CH₃ stretching vibration. The calculated value also coincides with the experimental value. The symmetric CH₃ stretching vibration is observed at 2843 and 2870 cm⁻¹ in IR and Raman. The corresponding calculated value is 2889 cm⁻¹ and it coincides with the literature value (2860 cm⁻¹). The weak band in Raman at 1456 cm⁻¹ is assigned as CH₃ deformation vibration. The Si-O-C asymmetric deformation vibration is observed at 403 cm⁻¹, as weak band in Raman and the calculated value ultimately coincides with the literature value (470-330 cm⁻¹). The O-C stretching vibration are usually observed in the region 1380-1050 cm-1[25]. The very strong band in FTIR at 1082 cm-1 is assigned stretching vibrations of methoxy silane group. Various other deformation and torsional modes of the methoxy silane group have also been observed.

Butyl group Vibrations

In IBTMS, the butyl group ((CH₃)₂CH-CH₂), is attached to the Silicon atom. The CH₃ stretching vibrations are normally observed in the range 3000-2800cm⁻¹[11, 12]. The observed medium band in IR at 2955 cm⁻¹ and a very strong band in Raman at 2945 cm⁻¹ are assigned as methyl symmetric stretching, and the corresponding calculated value is 2945 cm⁻¹. The C-H asymmetric value of butyl CH₃ group in Raman at 1456 cm⁻¹ is attributed to the asymmetric deformation mode. The CH₃ symmetric deformation vibrations of butyl group are generally observed in the range 1365, 1390cm⁻¹. In ISBTMS, the medium bands observed in IR at 1369 cm⁻¹ and the weak bands observed at 1387 cm⁻¹ are assigned for the deformation of isobutyl group. The asymmetric and symmetric methylene stretching vibrations normally occur at 2915-2940, 2870-2840 cm⁻¹ [11], respectively. In ISBTMS, the CH₂ asymmetric stretching mode is observed as a strong band at 2910 cm⁻¹ in Raman and the symmetric stretching vibration is mixed with methyl symmetric stretching and is observed at 2873 cm⁻¹ in IR. The observed weak band in IR at 1231 cm⁻¹ and medium band in Raman at 1227 cm⁻¹ are assigned to C-C stretching vibrations. Various other deformation and torsional modes of the butyl have also been observed.

Natural Population Analysis

The NBO analysis provides an efficient method for studying intermolecular and intramolecular bonding. It also provides a convenient basis for intermolecular charge transfer or conjugative interactions in molecular system.NBO theory allows the assignment of the hybridization of atomic lone pair of the atoms involved in bond orbitals. Some electron donor orbital, acceptor orbital and the interacting stabilization energy resulted from the second order micro disturbance theory are reported [14, 15].

$$E(2) = \Delta E_{ij} = q_i \frac{F(ij)^2}{\varepsilon_j - \varepsilon_i}$$

Where q_i is the ith donor orbital occupancy, ε_i and ε_i are diagonal elements and F(ij) is the off diagonal NBO Fock matrix element. The larger E(2) value, the more intensive is the interaction between electron donors and electron acceptors, i.e. the more donating tendency from electron donor to electron acceptor and the greater the extent of conjugation of the whole system [24]. Delocalization of electron density between occupied lewis type and NBO orbitals formally unoccupied non -lewis NBO orbitals correspond to a stabilizing donor-acceptor interaction. NBO analysis has been performed on the title molecule (ISBTMS) at the 6-311++G (d,p) level in order to elucidate the delocalization electron density within the molecule. The occupancies and energies of bonding lone pair molecular orbitals (LP) and anti-bonding (BD*) molecular orbitals of the ISBTMS are predicted at 6-311++G (d,p) level of theory and is presented in Table 1.

The second order perturbation theory analysis of the Fockmatrix in NBO shows strong intramolecular hyperconjugative interactions are presented in table 3.The intra molecular interaction are formed by the orbital overlap between bonding (C-H), (C-C), (C-Si) to the anti (C-H), (C-C), (Si-O) bond orbital which results intra molecular charge transfer causing stabilization of the system. The intra molecular interactions of the σ (C1 – C5) distributes to C5-C7, C5-C8, C7-H12 and C8-H9 leading to the stabilization of 3.14, 2.76, 6.19and 6.65256 Kcal/mol respectively. The same kind of interaction between the electron donating group, such as LP (2) O19 to σ *(Si 14 - O29), and LP (2) O29 to σ *(Si14 - O20) are considerably very large with 45.56376 and 39.8317KJ/mol, respectively. The energy contribution LP (2) O20 to σ *(C21 - H22) and LP (1) O20 to σ *(Si14 - O19) are 30.13, 18.7 kJ/mol respectively. The other examples of these interactions are summarized in Table 3.





Fig 4. Observed FTRaman spectrum of ISBTMS Charge Analysis

The charge distribution on a molecule has a significant influence on the vibrational spectra. The mulliken charge distribution of the molecule is calculated at the GAUSSIAN '09 with the B3LYP/ 6-311++G (d,p) basis set as given in Table 2. Distribution of positive and negative charges is vital in increasing or decreasing of bond length between atoms. In this molecule oxygen atom, carbon atom exhibits a negative charge, which are donor atoms. Hydrogen atoms exhibit a positive charge, which is an acceptor atom. Silicon atom have a more positive charge (0.983257) because electron withdrawing inductive effect of Oxygen atom.

HOMO-LUMO analysis

The highest occupied molecular orbital's (HOMOs) and the lowest-lying unoccupied molecular orbital's (LUMOs) are named as frontier molecular orbital's (FMOs). The FMOs play an important role in the optical and electric properties, as well as in quantum chemistry and UV–VIS spectra [16]. A molecule having a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity and low kinetic stability [17, 18]. HOMO, which can be thought the outer orbital containing electrons, tends to give these electrons as an electron donor and hence the ionization potential is directly related to the energy of the HOMO. On the other hand LUMO can accept electrons and the LUMO energy is directly related to electron affinity [19]. In ISBTMS, the HOMO is located over the Oxygen group. By contrast, the LUMO is located over the silane group (except all CH3 group).The energy difference between the highest occupied molecular orbital and the lowest unoccupied molecular orbital is 0.92 eV. The ISBTMS is more polarizible because it having a small energy gap.



Fig 5. Isodensity plot of ISBTMS Hyperpolarizibility Calculations

The first hyperpolarizabilities (β_{total}) of this novel molecular system and related properties (β , α and α_0) of ISBTMS were calculated using B3LYP/6-31G (d) basis set, based on the finite – field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. Polarizabilities and hyperpolarizabilities characterize the response of a system in an applied electric field [20]. They determine not only the strength of molecular interactions as well as the cross sections of different scattering and collision process and also the nonlinear optical properties (NLO) of the system [21-22].

First hyper polarizability is a third rank tensor that can be described by 3 x 3 x 3 matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [21,23]. The components of β are defined as the coefficients in the Taylor series expansion of energy in an external electric field.

$$E = E^{0} - \mu_{\alpha}F_{\alpha} - \frac{\alpha_{\alpha\beta}F_{\alpha}F_{\beta}}{2!} - \frac{\alpha_{\alpha\beta\gamma}F_{\alpha}F_{\beta}F_{\gamma}}{3!} + \cdots$$

Where E_0 is the energy of the unperturbed molecules, F_α the field at the origin μ , $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ are the components of dipole moments, polarizability and the first hyperpolarizabilities, respectively.The total static dipole moments μ ,the mean polarizabilities α_0 ,the anisotropy of the polarizabilities α and the mean first hyperpolarizabilities β_{total} , using the x,y and z components they are defined as[22] The total static dipole moment is

 $\mu = (\mu_{x+}^2 \mu_{y+}^2 \mu_z^2)^{1/2}$

Table 1 NRO Deculte Showing	a the Formation of Lowis (and non lowic orbitals of ISBTMS
rable 1. NDO Results Showing	g the Formation of Lewis a	and non-lewis orbitals of 15D 1105

Bond (A-B)	ED(e)	ED%(A)	ED%(B)	NBO	S%	P%
$\sigma(C_1 - H_2)$	1.98886	62.30	37.70	0.7893(sn3.12)C	24.29	75.71
0(01 112)	-0 48857	02.50	51.10	0.6140(s100)	100	/5./1
$\sigma(C_1 - H_2)$	1 98899	61.61	38 39	0.7849(sn3.19)C	23.84	76.16
0(01 113)	-0.48775	01.01	50.57	0.7049(sp5.19)c 0.6196(s100)	100	/0.10
$\sigma(C_{1} - H_{2})$	1 98937	62 30	37.70	0.7893(sn3.12)C	24.29	75 71
0(01 - 114)	-0 48937	02.50	51.10	0.7099(sp3.12)C 0.6140(s100)	100	13.11
$\sigma(C_1 - C_2)$	1 98440	49.86	50.14	0.7061(sn2.62)C1	27.61	72 39
0 (01 05)	-0 58876	47.00	50.14	0.7001(sp2.02) C1 0.7081(s100)C5	29.70	70.30
$\sigma(C_{1}, H_{2})$	1 96822	60.95	39.05	0.7807(sn2.94)C5	25.70	74.61
0 (05 - 116)	-0.46395	00.75	37.03	0.7007(sp2.94)C3 0.6249(s100)H6	100	/4.01
$\sigma(C_{z} - C_{z})$	1 98143	60.95	39.05	0.0249(s100)110 0.7807(sp2.94)C5	25 39	74 61
0(05 0/)	-0 59296	00.75	37.05	0.6249(s100)H6	100	/4.01
$\sigma(C_{z} - C_{z})$	1 98404	32.47	67 53	0.5698(sp4.07)C5	19.72	80.28
0(05 - 08)	-0 58701	52.47	07.55	0.5070(3p4.07)C5	17.72	00.20
	0.50701			0.8218(sp2.29)08	30.39	69.61
$\sigma(C_{\pi},H_{\mu})$	1 97569	84.47	15 53	0.0210(sp2.22)000	31.17	68.83
0(07 1112)	-0.48802	04.47	15.55	0.3940(sp3.77)Si12	20.94	79.06
$\sigma(C_{\pi} - H_{10})$	1 97658	63 33	36.67	0.7958(sp3.12)C9	24.25	75.75
0(07 113)	-0.48935	05.55	50.07	0.6056(s100)H10	100.00	15.15
$\sigma(C_{a}, S_{i}, \iota)$	1 95957	63 33	36.67	0.7958(sn3.12)C9	24.25	75 75
0(07 5114)	-0.49160	05.55	50.07	0.6056(s100)H10	100.00	15.15
$\sigma(C_{2} - H_{2})$	1 98922	72.42	27.58	0.8510(sn2.63)C9	27.53	72 47
0(08 119)	-0 48349	12.42	27.50	0.0510(3p2.05)C)	21.55	12.41
	-0.+05+7			0.5251(sp2.68)Si12	27 19	72.81
$\sigma(C - H_{12})$	1 98866	62.70	37.30	0.5251(sp2.00)5112 0.7918(sp3.19)C9	27.17	76.14
0(08 - 1110)	-0.48401	02.70	57.50	0.6107(s100)H13	100	70.14
$\sigma(C_{0} - H_{11})$	1 98888	26.93	73.07	0.5190(sn2.86)Si12	25.94	74.06
0(08 - 11]])	-0.48450	20.75	73.07	0.5190(sp2.60)5112 0.8548(sp2.64)C14	27.45	72 55
	-0.40450			0.0540(sp2.04)C14	27.45	12.55
σ(Si ₁₄ - O ₁₉)	1.98017	26.93	73.07	0.5190(sp2.86)Si12	25.94	74.06
	-0.81059			0.8548(sp2.64)C14	27.45	72.55
$\sigma(Si_{14} - O_{20})$	1.97851	62.91	37.09	0.7932(sp2.86)C14	24.14	75.86
	-0.79651			0.6090(s100)H15	100	
$\sigma(Si_{14} - O_{29})$	1.97956	63.23	36.77	0.7952(sp3.12)C14	24.25	75.75
	-0.79488			0.6064 s(100)	100	
$\sigma(C_{15} - H_{16})$	1.99464	62.93	37.07	0.7933(sp3.16)C14	24.03	75.97
	-0.51425			0.6089 s(100) H 21	100	
$\sigma(C_{15} - H_{17})$	1.99675	62.91	37.09	0.7932(sp3.14)C16	24.14	75.86
(15 17)	-0.51658			0.6090 s(100) H17	100	
$\sigma(C_{15} - H_{18})$	1.99550	63.23	36.77	0.7952(sp3.12)C16	24.25	75.75
	-0.51662			0.6064 s(100) H18	100	
$\sigma(C_{15} - O_{10})$	1.99524	62.93	37.07	0.7933(sp3.16)C16	24.03	75.97
0(015 019)	-0.83254	02.95	57.07	.6089 s(100) H19	100	15.51
$\sigma(0, 0)$	1 00/3/			sp 1.60	38.45	61 55
$O(O_{20} - O_{21})$	0.83404			sp 1.00	30.43	01.55
	-0.83404	-	41.00		25.01	54.10
$\sigma(C_{21} - H_{22})$	1.99558	58.72	41.28	0.7663(sp2.87)	25.81	74.12
	-0.52024	-		0.6425	99.96	0.04
$\sigma(C_{21} - H_{23})$	1.99657	58.80	41.20	0.7668(sp2.86)	25.88	74.05
	-0.52237			0.6419(sp0.00)	99.96	0.04
$\sigma(C_{21} - H_{24})$	1.99453	59.09	40.91	0.7687(sp2.89)	25.71	74.22
	-0.51857			0.6396(sp0.00)	99.96	0.04
$\sigma(C_{25} - H_{26})$	1.99471	59.21	40.79	0.7695(sp2.88)	25.77	74.16
25 207	-0.51719			0.6387	99.96	0.04
$\sigma(C_{25} - H_{27})$	1,99593	58.77	41.23	0.7666(sp2.87)	25.82	74 11
S(C25 112/)	-0.51937	20.11	11.20	0.6421	99.96	0.04
	1.00(24	50 10	41.54	0.7646(am2.99)	25.70	74.00
$O(C_{25} - H_{28})$	1.99024 0.52144	38.40	41.54	0.7040(sp2.88)	23.13	74.20 0.04
(2)	-0.32140		10.55	0.0445	99.90	0.04
$\sigma(C_{25} - O_{29})$	1.99533	31.91	68.09	0.5649(sp3.33)	23.01	76.73
	-0.83140			0.8252(sp2.17)	31.50	68.44

Audline Jini M N et al./ Elixir Vib. Spec. 82 (2015) 32425-32432

Atom	Mulliken Charge	Natural Charge
10	0 576717	
<u>гс</u> 2Ц	-0.370717	0.20157
211	0.161039	0.20137
30	0.142991	0.19833
4H	0.133962	0.19269
50	0.224629	-0.21893
6H	0.17/102	0.18038
7C	-0.910509	-0.89401
8C	-0.564914	-0.57176
9H	0.138338	0.19931
10H	0.163975	0.20120
11H	0.138288	0.19465
12H	0.222629	0.23596
13H	0.198337	0.22972
14Si	0.983257	2.26198
15C	-0.271509	0.17182
16H	0.141903	-0.18700
17H	0.177944	0.17482
18H	0.139614	0.15815
190	-0.404803	-0.92358
200	-0.437416	-0.92658
21C	-0.269634	-0.19055
22H	0.140425	0.16276
23H	0.154235	0.16471
24H	0.154760	0.17342
25C	-0.316004	-0.19104
26H	0.154142	0.17607
27H	0.165899	0.16428
28H	0.156255	0.15757
290	-0.338217	-0.92024

Table 2. Charge Analysis of ISBTMS

 Table 3. Second - Order Perturbation Theory analysis of Fock Matrix in NBO basis corresponding to the intramolecular bonds of ISBTMS molecule

corresponding				
Donor NBO(i)	E.D/e	Acceptor NBO(j)	E.D/e	E ⁻ /Kcalmol ⁻⁺
σ(C ₁ - H ₂)	1.98886	$\sigma * (C_5 - H_6)$	0.02609	2.45
	-0.48857		0.40429	
$\sigma(C_1 - H_3)$	1.98899	$\sigma * (C_5 - C_7)$	0.01988	3.33
	-0.48775		0.38601	
σ(C ₁ - H ₄)	1.98937	$\sigma * (C_5 - C_8)$	0.01559	3.16
	-0.48937		0.39863	
σ (C ₁ - C ₅)	1.98440	$\sigma * (C_8 - H_0)$	0.00590	1.59
- (-1 -5)	-0.58876	- (-0)/	0.42623	
$\sigma(C - H)$	1 96822	$\sigma^*(C_{-},S_{1,j})$	0.06315	3 54
$0(C_5 - \Pi_6)$	-0.46395	$0 (C_7 - S_{1_{1_4}})$	0.00313	5.54
(0, 0)	-0.40375	*(0 11)	0.27044	1.50
$\sigma(C_5 - C_7)$	1.98143	$\sigma * (C_1 - H_3)$	0.00633	1.50
	-0.59296		0.42087	
$\sigma(C_5 - C_8)$	1.98404	$\sigma * (C_1 - H_4)$	0.00624	1.65
	-0.58701		0.41701	
$\sigma(C_7 - H_{12})$	1.97569	$\sigma * (C_1 - C_5)$	0.01600	3.40
	-0.48802		0.39561	
$\sigma(C_7 - H_{13})$	1.97658	$\sigma * (C_{5} - C_{8})$	0.01559	3.36
	-0.48935		0.39863	
$\sigma(C_7 - Si_{14})$	1.95957	$\sigma * (Si_{14} - O_{20})$	0.09466	3.17
() 14)	0.49160	(14 20)	0.27112	
$\sigma(C_{e} - H_{o})$	1.98922	$\sigma * (C_1 - C_5)$	0.01600	3.24
0(08 119)	-0 48349	0 (01 05)	0 39561	0.2.
$\sigma(C_{0} - H_{10})$	1 98866	$\sigma^*(C_{1}-H_{2})$	0.02609	2 45
0(08 - 1110)	-0.48401	0 (05 116)	0.02007	2.43
$\sigma(C \mid \mathbf{H})$	1 00000	σ*(C C)	0.40427	2 20
$O(C_8 - \Pi_{11})$	1.90000	$0^{-1}(C_5 - C_7)$	0.01966	5.59
(0: 0)	-0.48430	*(0: 0)	0.58001	2.20
$\sigma(S1_{14} - O_{19})$	1.98017	$\sigma (S1_{14} - O_{29})$	0.09833	2.29
	-0.81059		0.27640	
$\sigma(S_{1_{14}} - O_{20})$	1.97851	$\sigma *(S_{1_{14}} - O_{19})$	0.07696	4.09
	-0.79651		0.28213	
$\sigma(Si_{14} - O_{29})$	1.97956	σ *(Si ₁₄ – O ₂₀)	0.09466	2.45
	-0.79488		0.27112	
$\sigma(C_{15} - H_{16})$	1.99464	σ *(Si ₁₄ -O ₁₉)	0.07696	2.12
	-0.51425		0.28213	
$\sigma(C_{15} - H_{18})$	1.99550	$\sigma *(Si_{14} - O_{19})$	0.07696	0.76
(15 10	-0.51662		0.28213	
$\sigma(C_{21} - H_{22})$	1.99558	σ *(Si14-O20)	0.09466	0.62
- (- 21 22)	-0.52024		0.27112	
$\sigma(C_{21} - H_{24})$	1 99453	σ *(Si 14 -020)	0.09466	2.14
0(021 1124)	-0 51857	0 (51 11 020)	0.027112	2.11
$\sigma(C_{11} - H_{11})$	1 00/71	$\sigma *(Si 14 - 0.20)$	0.00833	2.24
$O(C_{25} - \Pi_{26})$	0.51710	0 (51 14 - 027)	0.07635	2.24
LD (1) O 10	-0.31719	-*(0:14,000)	0.27040	4.60
LP(1)019	1.94122	σ *(Si 14 - O20)	0.09400	4.60
	-0.46948	*(0:14 000)	0.2/112	10.00
.LP(2)019	1.90029	σ *(Si 14 - O29)	0.09833	10.89
	-0.30547		0.27640	
LP(1)O20	1.94114	σ *(Si 14 - O19)	0.07696	4.47
	-0.48684		0.28213	
. LP (2) O 20	1.90429	σ *(C 21 - H22)	0.01956	7.20
	-0.30799		0.38504	
LP (1) O 29	1.94186	σ *(C 25 - H26)	0.01478	3.81
	-0.48307		0.39652	
LP (2) O 29	1.90111	σ *(Si 14 - O20)	0.09466	9.52
	-0.30481		0.27112	

Table 4. The electric dipole moment (μ), the average hyperpolarizability (α) and the first hyperpolarizability

(p _{tot}) of ISBTMS		
Parameters	B3LYP/6-31G(D)	
$\mu_{\rm x}$	-3.8393	
μ_{y}	-1.4298	
μ_z	0.3641	
μ	4.1131	
α_{xx}	-70.1315	
α_{xy}	3.8170	
$\alpha_{\rm vv}$	-77.7322	
α _{xz}	4.1043	
α_{vz}	1.6095	
α _{zz}	-77.2079	
α ₀	-111.18537 x10 ⁻²³ esu	
α	-15.157 x 10 ⁻²³ esu	
β _{xxx}	-45.7522	
β _{xxv}	7.2776	
β _{xyy}	-14.0530	
β _{vvv}	-12.0405	
β _{xxz}	-0.0471	
β _{xyz}	0.3568	
β_{xzz}	-0.9137	
β_{vzz}	-0.3392	
β _{vyz}	0.4582	
β _{zzz}	0.3102	
β_{tot}	5.5645434 x 10 ⁻³¹ esu	

The isotropic polarizability is $\begin{aligned}
\alpha_0 &= \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \\
\text{The polarizability anisotropy invariant is} \\
\Delta \alpha &= 2^{-1/2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xz}^2]^{1/2} \\
\text{and the first hyperpolarizability is} \\
\beta_{tot} &= (\beta_{x+}^2 \beta_{y+}^2 \beta_z^2)^{1/2} \\
\text{and} \\
\beta_x &= \beta_{xxx} + \beta_{yyy} + \beta_{zzz} \\
\beta_y &= \beta_{yyy} + \beta_{xxy} + \beta_{yyz} \\
\beta_z &= \beta_{zzz} + \beta_{xxz} + \beta_{yyz} \\
\beta_z &= \beta_{zzz} + \beta_{xxz} + \beta_{yyz}
\end{aligned}$

The B3LYP/6-31G (d) calculated the first hyperpolarizability value of ISBTMS 5.5645434 x 10^{-31} esu and other parameters are collected in table 4.

Conclusion

The analysis of surface morphology of Isobutyl trimethoxy silane monolayer using AFM indicates the monolayer formation at lower concentration, where the average thickness of the film is around 1nm .The structure of IBTMS was optimized by DFT method with basis sets 6-311++G(d,p) using Gaussian 09 Software. The optimized geometry, the vibrational frequencies of the title compound have been calculated and have been found to agree well with experimentally reported values. A plot of the highest occupied molecular (HOMO) and that of the lowest occupied molecular (LUMO) is also made. The ISBTMS is more polarizible because it having a small energy gap. The first hyperpolarizability value of ISBTMS is $5.5645434 \times 10^{-31}$ esu.

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