Density Functional Theory Studies on Vibrational Spectra of Si_2H_5X (X = F, Cl, Br) and Their Isotopomers

Daiqian Xie,* Xuejun Xu, Ying Xue, and Guosen Yan

Department of Chemistry, Sichuan University, Chengdu 610064, China

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Density function theory calculations using the B3′ exchange functional and three correlation functionals of PW91, LYP, and P86 at the 6-31G** basis set level have been carried out to study the molecular structures and fundamental vibrational frequencies of Si_2H_5Cl, Si_2H_5Br, Si_2H_5F, and their isotopomers. The ab initio restricted Hartee−Fock (RHF) approach with the 6-31G** basis set has also been used to calculate the fundamental vibrational frequencies of Si_2H_5Cl, Si_2H_5Br, and their isotopomers. Comparsion of the calculated and the experimental results shows that the three DFT methods of B3PW91, B3LYP, and B3P86 predict more accurate fundamentals than the scaled RHF method with a scale factor of 0.9. The calculated DFT force constants with respect to the five Si−H(D) stretch modes for Si_2H_5Cl and its isotopomers have been scaled to the experimental data with a factor of 0.936 determined by a least-squares fitting to the experimental vibrational frequencies. The scale factor of 0.936 is then transferred from Si_2H_5Cl to both Si_2H_5Br and Si_2H_5F. The fundamental vibrational frequencies determined from the scaled derived-DFT force fields for Si_2H_5Cl, Si_2H_5Br, and their isotopomers are in good agreement with the experimental data. The predicted values and mode assignments of the vibrational frequencies of Si_2H_5F and its isotopomers are also reported.

Introduction

The monohalogenodisilanes occupy a prominent place in the chemistry of molecular silicon compounds. Their structures have been studied for about 30 years.[1−3] The structural parameters were first obtained from the microwave spectra of five isotopic species of disilanyl fluoride by Cox and Varma in 1965.[1] The infrared and Raman spectra of Si_2H_5I and Si_2D_5I have been reported as well as the microwave structures of Si_2H_5I.[3] The FTIR and Raman spectra have been reported and vibrational assignments made and force fields calculated for Si_2H_5Cl and Si_2D_5Cl.[2,4,5] The IR and Raman spectra of Si_2H_5Br and Si_2D_5Br were recorded and assigned with the aid of normal coordinate analysis by Schenzel and Hassler[6] in 1994 and the IR and Raman spectra of Si_2H_5Br and Si_2D_5Br were reported, again by McKean et al.[5] in 1995. The band assigned to the torsional $\nu_{18}(A_{1u})$ mode of fundamentals for Si_2D_5Br was not obtained from infrared and Raman spectra.[5] No experimental data are currently available for Si_2H_5F and Si_2D_5F.

Ab initio calculations of the equilibrium geometries of Si_2H_5Cl using HF/6-31G* have been reported, and the force field and spectral intensities of the molecule have been obtained from ab initio calculations at same calculation level by McKean et al.[4,5,7] The normal coordinate analysis using an ab initio force field was carried out, and a total of 14 factors were separately optimized and determined by a least-squares fitting to experimental vibrational frequencies.[5] Additionally, all absolute values of all scale factors (defined by Pulay's definite suggestion) with exception for one pertinent to torsional mode obtained by McKean et al.[5] for Si_2H_5Cl are lower than 0.9. The force field calculated by the Hartree−Fock (HF) equation with a basis set of double-ζ quality are qualitatively correct with mainly systematic errors, which could be corrected by an empirical scaling procedure. We[8] also successfully applied this method to study the vibrational spectrum of XSO_2NCO (X = F, Cl), in good agreement with experimental data. For some monohalogenodisilanes and their isomers, however, our studies of vibrational spectra and force field calculated using RHF/6-31G** with the SQM approach was less successful, supposedly due to less systematic errors from neglect of electron correlation.

Electron correlation was treated with three variants of density functional theory (DFT), which are involved in B3LYP,[9,10] B3PW91,[9,11] and B3P86.[9,12] These three DFT methods with Gaussian-type basis functions of 6-31G** show that these DFT methods can reproduce fundamental vibrational frequencies of Si_2H_5X (X = Cl, Br) and their deuterium isotopomers with a mean absolute deviation of 2.0 cm^{-1} and a mean absolute deviation of 5.5 cm^{-1} for non-SiH(D) stretching vibrations, whereas the scaled quantum mechanical (SQM) force field approach with one scale factor of 0.9 to scale the HF force field generates a deviation of 33.9 cm^{-1}. Larger deviations between results obtained from DFT calculations and experimental results are found for five Si−H(D) stretching modes for every species of Si_2H_5X (X = Cl, Br) and their deuterium isotopomers. Any failure to reproduce the ν(SiH) values for Si_2H_5X (X = Cl, Br) reflects an inadequate calculation of the usual effect of anharmonicity. One scale factor of 0.936 was obtained from a least-squares fitting to experimental frequencies for Si_2H_5Cl and its deuterium isotopomer and was utilized to scale DFT force constants pertinent to the Si−H(D) stretching modes determined from the DFT calculations. Then the factor of 0.936 was transferred to Si_2H_5Br and its deuterium isotopomer to give an a priori prediction of their fundamentals. The scaled DFT fundamentals are in very good agreement with experimentally observed frequencies; furthermore, the mean absolute deviation between results obtained from three DFT calculations involved in PW91/6-31G**, B3LYP/6-31G**, and B3P86/6-31G** and the experimental result is 6.0 cm^{-1} for Si_2H_5X and Si_2D_5X (X = Cl, Br). In this work, density function theory calculations using B3LYP/6-31G**, B3PW91/6-31G**, and B3P86/6-31G**

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TABLE 1: Local Internal and Symmetry Coordinates for Si_2H_5X (X = F, Cl, Br)

symmetric species	symmetry coordinate[a]	description
A′	$S_1 = (2)^{-1/2}(q_4 + q_5)$	Si−H_2^x sym str
	$S_2 = (2)^{-1/2}(q_2 + q_3)$	Si−H_2^a sym str
	$S_3 = q_1$	Si−H^s str
	$S_4 = r$	Si−X str
	$S_s = R$	Si−Si str
	$S_6 = -0.214(L_4 + L_5) + 0.893k - 0.234(n_4 + n_5)$	SiH_2X skel bend
	$S_7 = 0.913m - 0.174(L_4 + L_5) - 0.190(n_4 + n_5) - 0.183_k$	Si−H_2^x scis
	$S_8 = -0.812\alpha_1 - 0.413(\alpha_2 + \alpha_3)$	Si−H_3 asym def
	$S_9 = -0.414\alpha_1 - 0.407(\alpha_2 + \alpha_3) + 0.404\beta_1 + 0.409(\beta_2 + \beta_3)$	Si−H_3 sym def
	$S_{10} = 0.5.21(L_4 + L_5) - 0.478(n_4 + n_5)$	Si−H_2^x wag
	$S_{11} = 0.820\beta_1 - 0.405(\beta_2 + \beta_3)$	Si−H_3 rock
	$S_{12} = (2)^{-1/2}(q_4 - q_5)$	Si−H_2^x asym str
	$S_2 = (2)^{-1/2}(q_2 - q_3)$	Si−H_2^a asym str
	$S_{14} = (2)^{-1/2}(\alpha_2 - \alpha_3)$	Si−H_3 asym def
	$S_{15} = 0.5[(L_5 - L_4) + (n_4 - n_5)]$	Si−H_2^x twist
	$S_{16} = (2)^{-1/2}(\beta_2 - \beta_3)$	Si−H_3 rock
	$S_{17} = 0.5(L_4 - L_5 + n_4 - n_5)$	Si−H_2 rock
	$S_{18} = \tau$	Si−H_3 torsion

[a] Internal coordinates given in Figure 1.

were also carried out to study the molecular structures and fundamental vibrational frequencies of disilanyl fluoride and its deuterium isotopomer. The factor determined from Si_2H_5Cl and Si_2D_5Cl was then transferred to scale the force constants relevant to the Si−H(D) stretching modes for Si_2H_5F and its deuterium isotopomer to give an a priori prediction of their fundamentals.

Calculations

Ab initio molecular orbital calculations have been carried out for monohalogenodisilanes Si_2H_5X (X = F, Cl, Br) by using the GAUSSIAN 94 suite of programs.[13] We used HF theory and three variants of density functional theory (DFT) in which Becke's three-parameter exchange functional[9] are combined with three different correlation functionals, namely, Lee−Yang−Parr (LYP),[10] Perdew−Wang 91 (PW91),[11] and Perdew 86 (P86).[12] All calculations were performed with the 6-31G** basis set,[14−18] which is a double-ζ type with one set of polarization d-type functions on every heavy atom and one set of polarization p-type functions on the hydrogen atoms.

The ab initio harmonic force fields, infrared intensities, Raman activities, depolarization ratios, and vibrational frequencies of Si_2H_5X (X = F, Cl, Br) were obtained with all the above levels of theory. In order to obtain a more complete description of the molecular vibrations, the normal coordinate analysis using DFT (B3LYP/6-31G**, B3PW91/6-31G**, and B3P86/6-31G**) force fields of SiH_5Cl and SiD_5Cl has been carried out. The symmetry coordinates for Si_2H_5X (X = F, Cl, Br) are defined in Table 1. At first, the force constants matrix $\mathbf{F}_x$ in Cartesian coordinates was transformed to that $\mathbf{F}_R$ in nonredundant local internal coordinates. The quadratic force constants are scaled according to Pulay's SQM procedure[19] by the equation

$$\mathbf{F}_R{}^{\text{scaled}} = \mathbf{C}^{1/2}\mathbf{F}_R\,\mathbf{C}^{1/2} \tag{1}$$

where **C** is a diagonal matrix whose element of C_{ii} is defined as the *i*th scale factor to the local internal coordinate force constant, $\mathbf{F}_R$ and $\mathbf{F}_R{}^{\text{scaled}}$ are two matrices whose elements F_{ij} and F_{ij}' are the original force constant and the scaled one. The scale factors were initially taken from values reported by Pulay et al.[20] and were optimized using the nonlinear least-squares fitting to the experimental frequencies of Si_2H_5Cl and Si_2D_5Cl. The standard least-squares equation is[21]

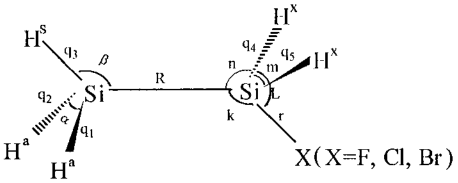

Figure 1. Geometry structure of Si_2H_5X (X = F, Cl, Br).

TABLE 2: Structural Parameters for Si_2H_5F[a]

parameters	HF/ 6-31G**	B3LYP/ 6-31G**	B3P86/ 6-31G**	B3PW91/ 6-31G**	exp[b]
$R(Si_1-Si_2)$	2.347	2.348	2.337	2.341	2.332
$R(Si_2-F)$	1.603	1.622	1.619	1.621	1.598
$R(Si_1-H^a)$	1.478	1.487	1.486	1.489	1.483[c]
$R(Si_1-H^s)$	1.480	1.489	1.489	1.491	1.483[c]
$R(Si_2-H^x)$	1.475	1.488	1.487	1.490	1.477[c]
$\angle Si_1Si_2F$	109.906	110.967	110.873	110.893	109.500
$\angle Si_1Si_2H^x$	111.063	110.350	110.315	110.306	110.368
$\angle Si_2Si_1H^a$	110.899	111.430	110.396	111.392	110.368
$\angle Si_2Si_1H^s$	108.320	107.892	107.839	107.861	110.368
$\angle Fsi_2H^x$	107.958	108.275	108.304	108.309	
$\angle H^aSi_1H^s$	108.774	108.559	108.596	108.952	108.333

[a] Bond lengths given in Å; bond angles given in degrees. [b] Experimental data taken from ref 1. [c] Assumed values taken from ref 1.

$$(\mathbf{J}^t\mathbf{W}\mathbf{J})\Delta\mathbf{C} = J^t\mathbf{W}\Delta\mathbf{\Phi} \tag{2}$$

where **W** is a diagonal matrix used to weight the observed frequencies, $\Delta\mathbf{\Phi}$ represents the differences between the observed and calculated frequencies, $\Delta\mathbf{C}$ indicates the calculated corrections to the force constant scale factors, and **J** is the Jacobi matrix with element $J_{ij} = (\partial\nu_i/\partial C_{jj})$. In this study, an individual Jacobi matrix element may be obtained as follows.[8]

$$J_{ij} = (\partial\nu_i/\partial C_{jj}) = (8\pi^2C^2\nu_i)^{-1} \times (\mathbf{L}_s{}^t\mathbf{U})_{ij} \times (\mathbf{L}_s{}^t\mathbf{U}\mathbf{C}^{1/2}\mathbf{F}_r)_{ij} \times C_{jj}{}^{1/2} \tag{3}$$

where **U** is the usual transformation matrix from local internal to symmetry coordinates and $\mathbf{L}_s$ is the eigenvector matrix of the vibratonal secular equation in symmetry coordinate space.

From the scaled quantum mechanical (SQM) force field, the vibrational frequencies and potential energy distributions (PED) were obtained using Wilson's GF matrix method.[22] A set of scale factors optimized by the least-squares fitting to the experimental frequencies of Si_2H_5Cl and Si_2D_5Cl was then transferred to Si_2H_5Br and Si_2H_5F. The DFT force field was scaled to give an a priori prediction of their fundamental frequencies. Similar calculations were also carried out utilizing the HF/6-31G** force field. A scaling factor of 0.9 with respect to all force constants were used to obtain the fixed scaled force field and resultant frequencies for Si_2H_5Cl, Si_2H_5Br, and their isotopomers.

Results and Discussion

Structure. All the geometrical parameters of disilyl chloride, disilyl bromide, and disilanyl fluoride were fully optimized by ab initio HF/SCF and DFT (using B3LYP, B3PW91, and B3P86) at the 6-31G** level. The equilibrium geometries of Si_2H_5X (X = F, Cl, Br) were found to be under C_s symmetry

TABLE 3. Structural Parameters for Si_2H_5Cl[a]

parameters	HF/ 6-31G**	B3LYP/ 6-31G**	B3P86/ 6-31G**	B3PW91/ 6-31G**	cal value[b]
$R(Si_1-Si_2)$	2.349	2.350	2.338	2.343	2.349
$R(Si_2-Cl)$	2.083	2.095	2.081	2.083	2.082
$R(Si_1-H^a)$	1.476	1.485	1.485	1.487	1.475
$R(Si_1-H^s)$	1.479	1.488	1.488	1.490	1.478
$R(Si_2-H^x)$	1.472	1.485	1.485	1.487	1.472
$\angle Si_1Si_2Cl$	109.625	110.056	109.919	110.116	109.710
$\angle Si_1Si_2H^x$	111.877	111.637	111.609	111.525	111.860
$\angle Si_2Si_1H^a$	109.913	110.160	110.049	110.107	111.000
$\angle Si_2Si_1H^s$	108.794	108.870	108.943	108.858	108.830
$\angle ClSi_2H^x$	107.135	107.370	107.441	107.438	107.160
$\angle H^aSi_1H^s$	109.274	109.099	109.164	109.149	109.590

[a] Bond lengths given in Å; bond angles given in degrees. [b] Calculated value taken from ref 4.

TABLE 4: Structural Parameters for Si_2H_5Br[a]

parameters	HF/ 6-31G**	B3LYP/ 6-31G**	B3P86/ 6-31G**	B3PW91/ 6-31G**
$R(Si_1-Si_2)$	2.346	2.347	2.334	2.340
$R(Si_2-Br)$	2.239	2.244	2.228	2.231
$R(Si_1-H^a)$	1.476	1.485	1.485	1.487
$R(Si_1-H^s)$	1.479	1.489	1.488	1.490
$R(Si_2-H^x)$	1.472	1.485	1.485	1.487
$\angle Si_1Si_2Br$	109.326	109.601	109.141	109.555
$\angle Si_1Si_2H^x$	112.047	111.779	111.962	111.728
$\angle Si_2Si_1H^a$	109.793	109.942	109.758	109.880
$\angle Si_2Si_1H^s$	109.074	109.409	109.657	109.347
$\angle BrSi_2H^x$	107.141	107.520	107.560	107.545
$\angle H^aSi_1H^s$	109.258	109.073	109.088	109.137

[a] Bond lengths given in Å; bond angles given in degrees.

with the two tops in a staggered conformation and the geometric structure of Si_2H_5X (X = F, Cl, Br) is shown in Figure 1. The DFT and RHF structural parameters of Si_2H_5F compared with experimental data[1] are given in Table 2. The fact that the structure parameters calculated using three DFT methods (B3LYP, B3PW91, and B3P86) with the 6-31G** basis set are in good agreement with the experimental results for Si_2H_5F shows that the DFT theoretical geometric structure is reliable with slight overestimation of the bond distances. For example, the Si−Si bond distance of disilanyl fluoride calculated using the B3 exchange functional and P86 correlation functional with the 6-31G** basis set is 2.337 Å, which is in good agreement with the experimental value[1] of 2.332 Å determined from microwave data. The Si−F bond distance for Si_2H_5F calculated using RHF/6-31G** is 1.603 Å, in better agreement with the experimental value[1] of 1.598 Å than the values calculated with DFT methods listed in Table 2. It appears that the DFT calculations using B3LYP/6-31G**, B3PW91/6-31G**, and B3P86/6-31G** slightly overestimate all bond distances of Si_2H_5F. All bond angles by RHF/6-31G** are in good agreement with experimental results.[1] The $SiSiH^x$ bond angle of Si_2H_5F calculated using B3LYP/6-31G** is 110.350°, which is in excellent agreement with 110.368° given in Table 2 determined from microwave data.[1]

Vibrational Spectra. 1. Monochlorodisilanes. Si_2H_5Cl and its deuterium isotopomer are studied thoroughly in Si_2H_5X (X = F, Cl, Br, I) and their deuterium isotopomers. The vibrational spectrum of Si_2H_5Cl has been extensively studied[2,4,5] and is well understood. Comparison between the calculated and observed results (Table 3) for Si_2H_5Cl and Si_2D_5Cl serves as a benchmark of the reliability of theoretical methods involved in B3LYP/6-31G**, B3PW91/6-31G**, B3P86/6-31G**, and RHF/6-31G**. Our DFT calculations using B3LYP/6-31G**, B3PW91/6-31G**, and B3P86/6-31G** have shown that DFT frequencies of Si_2H_5Cl and Si_2D_5Cl are in better agreement with experimental data, compared with the ab initio Hartree−Fock results. The calculated fundamental vibrational frequencies of Si_2H_5Cl and Si_2D_5Cl are compared with observed frequencies listed in Tables 5 and 6, respectively. Furthermore, the predicted infrared intensities, Raman activities, and depolarizations of Si_2H_5Cl are also reported in Table 7. Most of the observed frequencies of non-SiH(D) stretching modes are reproduced very well by DFT calculations using B3LYP/6-31G**, B3PW91/6-31G**, and B3P86/6-31G**. The mean absolute deviations between the DFT frequencies calculated in B3PW91/6-31G**, B3P86/6-31G**, and B3LYP/6-31G** and observed frequencies of non-SiH(D) stretching modes are found to be 4.3 cm^{-1} for Si_2H_5Cl and 4.5 cm^{-1} for Si_2D_5Cl, respectively. The frequencies of non-SiH(D) stretching modes obtained from the calculations using PW91/6-31G** for Si_2H_5Cl are in good agreement with observed results with a mean absolute deviation of 3.2 cm^{-1}. Larger deviations were found for the Si−H(D) stretching modes

TABLE 5: Observed and Calculated Frequencies[a] and Potential Energy Distribution (PED) for Si_2H_5Cl

				HF/6-31G**		B3LYP/6-31G**		B3P86/6-31G**		B3PW91/6-31G**		
sym[b]	vib no.	fundamental	exp[c]	unscaled	scaled[d]	unscaled	scaled[e]	unscaled	scaled[e]	unscaled	scaled[e]	PED[f]
A′	ν_1	$Si-H_2{}^a$ sym str	2178.8	2376.8	2254.5	2244.7	2171.2	2256.1	2182.3	2248.5	2174.9	71(2), 27(3)
	ν_2	$Si-H_2{}^x$ sym str	2172.0	2360.3	2238.8	2239.3	2166.1	2249.9	2176.5	2242.9	2169.7	85(1), 10(2)
	ν_3	$Si-H^s$ str	2157.9	2345.1	2224.4	2225.2	2152.5	2236.5	2163.4	2228.9	2156.2	68(3), 19(2)
	ν_4	$Si-H^x$ scis	959.4	1049.4	995.4	961.0	960.7	953	952.8	951.1	951.0	64(7), 32(8)
	ν_5	$Si-H_3$ asym def	939.6	1030.8	978.2	945.1	945.3	937.9	938.0	936.0	936.2	63(8), 30(7)
	ν_6	$Si-H_3$ sym def	879.4	988.3	937.4	893.7	893.6	884.1	884.0	881.9	881.8	68(9), 18(10)
	ν_7	$Si-H^x$ wag	806.2	899.2	852.7	820.3	820.0	811.3	811.0	809.6	809.4	78(10), 26(9)
	ν_8	$Si-Cl$ str	549.4	584.3	553.8	538.2	536.0	547.6	545.8	545.8	544.1	81(4), 15(11)
	ν_9	$Si-H_3$ rock	514.1	560.0	529.7	517.5	516.6	518.5	518.1	517.3	516.9	59(11), 18(5)
	ν_{10}	$Si-Si$ str	412.4	443.6	419.9	408.2	407.0	414.9	414.1	412.7	411.9	74(5), 15(11)
	ν_{11}	skel bend	124.7	137.1	129.6	124.6	124.2	123.4	122.9	124.1	123.8	121(6), 32(11)
A″	ν_{12}	$Si-H_2{}^a$ asym str	2181.3	2397.1	2256.6	2255.7	2181.9	2266.9	2192.7	2259.4	2185.5	60(13), 39(12)
	ν_{13}	$Si-H_2{}^x$ asym str	2172.0	2361.6	2240.0	2245.4	2171.9	2256.6	2182.7	2249.1	2175.5	61(12), 39(13)
	ν_{14}	$Si-H_3$ asym def	935.2	1030.3	977.3	945.3	945.2	938.9	938.8	936.9	936.7	97(14)
	ν_{15}	$Si-H_2{}^x$ twist	706.9	772.4	732.6	711.2	711.0	708.5	708.3	707.6	707.5	80(15)
	ν_{16}	$Si-H_2{}^x$ rock	592.0	653.2	619.3	596.2	595.9	592.3	592.0	591.2	590.9	38(17), 37(16)
	ν_{17}	$Si-H_3$ rock	360.3	404.1	383.2	361.3	361.3	356.4	356.3	356.4	356.3	76(16), 79(17)
	ν_{18}	$Si-H_3$ tors	108.0	104.9	99.4	101.2	101.0	103.4	103.4	102.0	102.0	98(18)

[a] Frequencies given in cm^{-1}. All calculated frequencies obtained from this work. [b] Symmetry species under C_s point group. [c] Taken from ref 5. [d] Scaling factors of 0.9 for all mode. [e] Scaling factors of 0.936 for Si−H stretches, 1 for others. [f] PED obtained from the normal coordinate analysis with the B3PW91/6-31G** force field in this work.

TABLE 6: Comparison of Observed and Calculated Frequencies[a] and Potential Energy Distribution (PED) for Si_2D_5Cl

sym[b]	vib no.	fundamental	exp[c]	HF/6-31G**		B3LYP/6-31G**		B3P86/6-31G**		B3PW91/6-31G**		PED[f]
				unscaled	scaled[d]	unsaled	scaled[e]	unscaled	scaled[e]	unscaled	scaled[e]	
A′	ν_1	Si−D^s str	1583.8	1706.6	1618.9	1625.1	1572.2	1633.8	1580.6	1628.2	1575.2	55(3), 46(2)
	ν_2	Si−D$_2^x$ sym str	1572.0	1704.2	1616.7	1606.9	1554.6	1613.2	1560.7	1609.6	1557.2	93(1), 5(2)
	ν_3	Si−D$_2$ sym str	1554.4	1678.9	1592.8	1590.6	1538.8	1598.2	1546.2	1593.0	1541.2	50(2), 45(1)
	ν_4	Si−D^x scis	695.0	773.9	734.2	702.4	702.4	695.9	695.0	694.4	694.4	63(7), 21(9)
	ν_5	Si−D$_3$ asym def	670.0	746.3	708.0	685.1	685.1	681.1	681.1	679.7	679.8	65(8), 9(10)
	ν_6	Si−D$_3$ sym def	658.0	731.4	693.8	668.7	668.7	663.5	663.6	662.4	662.4	21(9), 34(7), 29(8)
	ν_7	Si−D^x wag	602.9	671.2	636.8	611.7	611.7	605.5	605.5	604.5	604.5	60(10), 42(9)
	ν_8	Si−Cl str	524.3	544.9	516.9	509.5	509.5	520.3	520.3	518.7	518.7	81(4), 7(10)
	ν_9	Si−Si str	428.0	465.7	441.8	428.7	428.7	431.4	431.4	429.9	429.9	49(5), 26(11)
	ν_{10}	Si−D$_3$ rock	363.0	393.2	373.0	357.8	357.8	359.1	359.0	357.9	357.9	56(11), 33(5)
	ν_{11}	skel bend	117.0	128.2	121.6	116.3	116.3	114.8	114.8	115.7	115.7	121(6), 40(11)
A″	ν_{12}	Si−D$_2^a$ asym str	1594.8	1725.8	1637.2	1636.3	1583.0	1643.7	1590.3	1638.9	1585.6	64(13), 35(12)
	ν_{13}	Si−D$_2^x$ asym str	1586.9	1711.5	1623.6	1627.7	1574.7	1634.9	1581.7	1630.4	1577.3	64(12), 36(13)
	ν_{14}	Si−D$_3$ asym def	670.0	741.1	703.1	679.3	679.3	674.5	674.5	673.0	673.1	98(14)
	ν_{15}	Si−D^x twist	504.0	555.8	527.3	511.7	511.7	509.4	509.4	509.2	509.2	78(15)
	ν_{16}	Si−D$_2^x$ rock	462.0	506.5	480.5	463.7	463.7	461.0	461.0	460.4	460.4	44(17), 31(16)
	ν_{17}	Si−D$_3$ rock	260.8	292.2	277.2	261.2	261.2	257.5	257.5	257.6	257.6	81(16), 75(17), 40(16)
	ν_{18}	Si−D$_3$ tors	84.0	76.9	72.9	74.5	74.5	76.0	75.9	75.0	75.0	99(18)

[a] Frequencies given in cm^{-1}. All calculated frequencies obtained from this work. [b] Symmetry species under C_s point group. [c] Taken from ref 5. [d] Scaling factors of 0.9 for all mode. [e] Scaling factors of 0.936 for Si−D stretches, 1 for others. [f] PED obtained from the normal coordinate analysis using the P86/6-3IG** force field in this work.

TABLE 7. Infrared Intensity[a] and Raman Activity[b] of Fundamental Vibrational Frequencies for Si_2H_5X (X = F, Cl, Br)

		Si_2H_5Cl										
		IR int		Raman act			Si_2H_5Br[g]			Si_2H_5F[h]		
sym[c]	mode	exp[d]	cal[e]	cal[f]	cal[e]	depol	IR int	Raman act	depol	IR int	Raman act	depol
A′	ν_1		124.98	290.5	290.2	0.037	106.22	289.3	0.036	144.91	273.7	0.043
	ν_2		68.45	92.2	91.3	0.148	86.36	85.6	0.151	52.73	94.0	0.113
	ν_3		79.06	130.1	126.4	0.344	84.17	140.0	0.338	91.24	105.4	0.440
	ν_4		105.12	6.4	5.5	0.731	114.99	4.1	0.75	151.33	10.2	0.671
	ν_5		9.26	30.2	29.8	0.747	4.68	31.26	0.746	55.34	14.8	0.750
	ν_6	129	91.20	11.0	9.7	0.655	116.90	8.2	0.648	11.36	24.6	0.75
	ν_7	388	410.13	7.3	6.8	0.645	399.22	6.3	0.567	25.96	2.7	0.53
	ν_8	49	41.96	8.0	7.9	0.614	6.68	10.4	0.685	456.26	4.4	0.68
	ν_9	47	37.44	12.5	12.2	0.747	20.96	14.1	0.538	21.03	12.9	0.58
	ν_{10}	15	16.55	22.6	22.6	0.177	31.40	17.2	0.113	5.74	21.2	0.24
	ν_{11}		3.40	2.1	2.2	0.661	1.59	1.9	0.639	7.27	0.4	0.65
A″	ν_{12}		219.80	49.6	45.5	0.75	206.22	49.9	0.75	256.71	39.8	0.75
	ν_{13}		5.12	132.7	132.4	0.75	7.19	125.6	0.75	20.09	138.0	0.75
	ν_{14}		39.55	24.9	23.9	0.75	38.33	24.3	0.75	43.69	24.5	0.75
	ν_{15}	6.2	6.59	24.6	23.8	0.75	3.07	22.1	0.75	24.44	17.2	0.75
	ν_{16}		0.61	7.8	7.5	0.75	0.01	6.6	0.75	2.19	13.1	0.75
	ν_{17}	12.2	19.19	0.0	0.1	0.75	17.05	0.1	0.75	24.76	0.0	0.75
	ν_{18}		0.21	0.1	0.1	0.75	0.05	0.1	0.75	0.61	0.1	0.75

[a] Infrared intensities in km mol^{-1}. [b] Raman activity in A^4 amu^{-1}. [c] Symmetry species under C_s point group. [d] Taken from ref 5. The observed value of the sum of ν_1, ν_2, ν_3, ν_{12}, and ν_{13} is 377. The observed value of sum of ν_4, ν_5, and ν_{14} is 131. The observed value of sum of ν_{11} and ν_{18} 1.9. [e] Results obtained from calculations using PW91/6-31G**. [f] Taken from ref 5, obtained from ab initio HF calculations with the 6-31G* basis set. [g] Results obtained from calculations using PW91/6-31G**. [h] Results obtained from calculations using P86/6-31G**.

because these modes are strongly affected by anharmonicity. So the calculated force constants with respect to Si−H(D) stretching modes should be scaled by using a scale factor. The scale factor of 0.936 was obtained by a least-squares fitting to experimental vibrational frequencies by using the factor from Rauhut and Pulay's work as its original value.[20] As a result, the DFT-derived force constants obtained from calculations using B3LYP/6-31G**, B3PW91/6-31G**, and B3P86/6-31G** were scaled by using a factor of 0.936 relevant to Si−H(D) stretching modes and 1.0 corresponding to non-Si−H(D) stretching modes, respectively. In addition, the scaled DFT frequencies reproduce the observed fundamental vibrational frequencies of Si_2H_5Cl and its deuterium isotopomer with a mean absolute deviation of 5.0 cm^{-1}. A mean absolute deviation between the scaled theoretical frequencies, determined using PW91/6-31G** and the experimental values for Si_2H_5Cl is about 3.1 cm^{-1}.

Under C_s symmetry, the fundamental vibrational modes of Si_2H_5X (X = Cl, Br, F) and its deuterium isotopomer are distributed among two symmetry species: 11A′ + 7A″. Most of the A′ and A″ modes of the calculated assignment obtained from PEDs obtained from the B3PW91/6-31G** force field are in good agreement with assignment[4,5] with exceptions for ν_1 and ν_2. Our assignments of ν_1 and ν_2 modes are the reverse of the results obtained by McKean et al.[5]

2. Monobromodisilanes. For Si_2H_5Br and its deuterium isotopomer the HF minimal basis set calculations of vibrational fundamentals were carried out by McKean et al.[23] In this work, we carried out DFT calculations and the normal coordinate analysis to obtain fundamental vibrational frequencies, scaled DFT harmonic force field, and reassignments of some fundamental vibrational modes of Si_2H_5Br and its deuterium isotopomer. A mean absolute deviation of 20.7 cm^{-1} between the unscaled DFT frequencies and the experimental values for Si_2H_5-

TABLE 8: Comparison of Observed and Calculated Frequencies[a] and Potential Energy Distribution (PED) for Si_2H_5Br

	vib			HF/6-31G**		B3LYP/6-31G**		B3P86/6-31G**		B3PW91/6-31G**		
species[b]	no.	fundamental	exp[c]	unscaled	scaled[d]	unscaled	scaled[e]	unscaled	scaled[e]	unscaled	scaled[e]	PED[f]
A′	ν_1	Si−$H_2{}^a$ sym str	2178.0	2375.8	2253.6	2243.6	2170.2	2254.6	2180.8	2248.1	2174.6	77(2), 22(3)
	ν_2	Si−$H_2{}^x$ sym str	2170.0	2359.8	2238.4	2236.6	2163.5	2247.4	2174.0	2241.0	2167.8	86(1), 8(3)
	ν_3	Si−H^s str	2157.2	2343.0	2222.4	2223.6	2150.8	2234.4.	2161.4	2227.8	2155.0	69(3), 16(2)
	ν_4	Si−H^x scis	949.8	1047.3	993.4	959.0	958.8	950.6	950.4	948.2	948.0	58(7), 35(8)
	ν_5	Si−H_3 asym def	939.0	1029.0	976.4	942.9	943.0	934.5	934.6	932.5	932.6	59(8), 34(7)
	ν_6	Si−H_3 sym def	875.8	987.8	937.0	892.8	892.7	882.1	882.0	879.4	879.3	73(9), 14(10)
	ν_7	Si−H^x wag	786.1	884.1	838.4	806.6	806.3	797.6	797.4	795.8	795.6	83(10), 20(9)
	ν_8	Si−H_3 rock	519.0	577.0	547.3	523.5	523.4	518.7	518.6	517.8	517.7	78(11)
	ν_9	Si−Si Si−Br str	461.0	496.9	470.4	464.8	463.7	474.0	472.9	472.3	471.2	53(5), 47(4)
	ν_{10}	Si−Br str	380.0	402.1	380.5	379.4	78.5	388.4	387.4	385.6	384.7	53(4), 37(5), 12(11)
	ν_{11}	skel bend	107.0	111.2	105.3	100.6	100.4	98.2	98.0	99.0	98.8	121(6), 31(11)
A″	ν_{12}	Si−$H_2{}^a$ asym str	2181.8	2379.6	2257.1	2254.6	2180.9	2265.7	2191.6	2259.2	2185.3	66(13), 34(12)
	ν_{13}	Si−$H_2{}^x$ asym str	2171.4	2361.3	2239.8	2244.2	2170.7	2255.3	2181.5	2248.8	2175.2	65(12), 34(13)
	ν_{14}	Si−H_3 asym def	934.0	1031.1	978.1	946.0	945.9	938.3	938.2	936.2	936.0	97(14)
	ν_{15}	Si−H^x twist	690.6	770.2	730.6	711.3	711.2	708.5	708.4	707.8	707.7	81(15)
	ν_{16}	Si−H_3 rock	581.0	641.6	608.4	584.7	584.4	579.8	579.5	578.2	577.9	38(16), 35(17)
	ν_{17}	Si−$H_2{}^x$ rock	358.9	399.4	378.8	357.7	357.6	350.1	350.1	349.2	349.1	83(17), 74(16), 35(15)
	ν_{18}	Si−H_3 tors	96.0	115.2	109.3	104.1	104.1	97.2	97.2	95.6	95.6	98(18)

[a] Frequencies given in cm^{-1}. All calculated frequencies obtained from this work. [b] Symmetry species under C_s point group. [c] Taken from ref 5. [d] Scaling factors of 0.9 for all modes. [e] Scaling factors of 0.936 for Si−H stretches, 1 for others. [f] PED obtained from the normal coordinate analysis in this work.

TABLE 9: Comparison of Observed and Calculated Frequencies[a] and Potential Energy Distribution (PED) for Si_2D_5Br

	vib			HF/6-31G**		B3LYP/6-31G**		B3P86/6-31G**		B3PW91/6-31G**		
sym[b]	no.	fundamental	exp[c]	unscaled	scaled[d]	unscaled	scaled[e]	unscaled	scaled[e]	unscaled	scaled[e]	PED[f]
A′	ν_1	Si−$D_2{}^a$ sym str	1584.1	1705.6	1618.1	1624.1	1571.2	1632.3	1579.2	1627.6	1574.6	48(2), 52(3)
	ν_2	Si−$D_2{}^x$ sym str	1572.0	1703.5	1616.1	1605.0	1552.8	1612.8	1560.4	1608.2	1555.9	94(1), 5(2)
	ν_3	Si−D^s str	1554.3	1678.0	1591.9	1589.7	1537.9	1597.2	1545.3	1592.6	1540.7	47(3), 46(2)
	ν_4	Si−D^x scis	692.0	770.5	730.9	699.8	699.8	693.3	693.3	690.9	690.9	67(7), 19(9)
	ν_5	Si−D_3 asym def	667.0	744.7	706.5	682.5	682.5	677.3	677.3	675.9	675.9	71(8), 14(9)
	ν_6	Si−D_3 sym def	655.0	730.6	693.1	666.9	666.9	661.1	661.2	659.2	659.3	30(9), 32(7)
	ν_7	Si−D^x wag	587.7	660.1	626.2	602.2	602.2	595.9	595.9	694.5	594.5	69(10), 33(9)
	ν_8	Si−Si & Si−Br str	433.4	469.1	445.0	436.0	435.9	442.6	442.7	441.4	441.3	41(5), 42(4)
	ν_9	Si−Br str	418.0	452.0	428.8	420.1	420.8	423.8	423.9	422.4	422.4	28(4), 35(11), 17(5)
	ν_{10}	Si−D_3 rock	346.0	369.7	350.7	342.0	342.0	344.9	344.9	343.1	343.1	50(11), 25(5), 24(4)
	ν_{11}	skel bend	98.0	103.9	98.6	93.8	93.7	91.5	91.5	92.2	92.2	122(6), 37(11)
A″	ν_{12}	Si−$D_2{}^a$ asym str	1595.1	1726.2	1637.6	1635.4	1582.8	1643.5	1590.0	1638.8	1585.4	60(13), 39(12)
	ν_{13}	Si−$D_2{}^x$ asym str	1587.6	1711.3	1623.5	1626.9	1573.9	1634.9	1581.7	1630.3	1577.2	60(12), 39(13)
	ν_{14}	Si−D_3 asym def	667./0	741.7	703.6	679.8	679.8	674.0	674.0	672.6	672.6	98(14)
	ν_{15}	Si−D^x twist	498.2	554.5	526.0	511.8	511.8	509.6	509.6	509.1	509.1	75(15), 9(16)
	ν_{16}	Si−$D_2{}^x$ rock	446.7	493.0	467.7	450.8	450.8	447.8	447.8	446.7	446.7	41(17), 31(16)
	ν_{17}	Si−D_3 rock	258.4	289.0	274.1	258.9	258.9	253.4	253.4	252.8	252.8	79(16), 79(17), 37(15)
	ν_{18}	Si−D_3 tors	?	83.7	79.4	75.9	75.9	71.4	71.4	70.2	70.2	98(18)

[a] Frequencies given in cm^{-1}. All calculated frequencies obtained from this work. [b] Symmetry species under C_s point group. [c] Taken from ref 5. [d] Scaling factors of 0.9 for all mode. [e] Scaling factors of 0.936 for Si-D stretches, 1 for others. [f] PED obtained from the normal coordinate analysis in this work.

Br and its deuterium isotopomer is less than a mean absolute deviation of 34.4 cm^{-1} between SQM Hartree−Fock frequencies calculated at the 6-31G** level with a scale factor of 0.9 to scale all vibrational modes and the experimental values. It was shown that DFT frequencies of Si_2H_5Br and Si_2D_5Br are in better agreement with experimental data determined by McKean et al.,[5] compared with the ab initio Hartree−Fock results. The calculated fundamental vibrational frequencies of Si_2H_5Br and Si_2D_5Br are listed in Tables 8 and 9, together with comparison with observed frequencies determined by McKean et al.[5] The predicted infrared intensities, Raman activity, and depolarization values of Si_2H_5Br are also reported in Table 7. Most of the observed frequencies of non-SiH(D) stretching modes are reproduced very well by DFT calculations using B3LYP/6-31G**, B3PW91/6-31G**, and B3P86/6-31G** for Si_2H_5Br and Si_2D_5Br. A mean absolute deviation between the DFT calculated and observed frequencies of non-SiH(D) stretching modes for Si_2H_5Br and its deuterium isotopomer is found to be 6.7 cm^{-1}.

Because the DFT Si−H(D) stretching frequencies are not in satisfactory agreement with the observed results, the scale factor with respect to Si−H(D) stretching modes has been transferred from Si_2H_5Cl to Si_2H_5Br. The DFT-derived force constants obtained using B3LYP/6-31G**, B3PW91/6-31G**, and B3P86/6-31G** were scaled by factors of 0.936 pertinent to Si−H(D) stretching modes and of 1.0 corresponding to others. The scaled DFT frequencies reproduced the observed fundamental vibrational frequencies of Si_2H_5Br and its deuterium isotopomer with a mean absolute deviation of 7.0 cm^{-1}. The average error between the scaled B3PW91/6-31G** theoretical frequencies and the experimental values for Si_2H_5Br is determined to 5.2 cm^{-1}.

The following is a detailed discussion of the reassignment of the vibrational modes of Si_2H_5Br on the basis of comparison between the results obtained using the PW91/6-31G** force field and the normal coordinate analysis. In the IR spectrum of A′ modes for Si_2H_5Br, the bands at 2178.0 and 2170.0 cm^{-1} were respectively assigned by McKean et al.[23] to ν_1 due to the symmetric Si−$H_2{}^x$ stretching mode and ν_2 due to the symmetric Si−$H_2{}^a$ stretching mode. But from our calculated results, the ν_1 mode should be a contribution of Si−$H_2{}^a$ stretching vibration, while ν_2 should belong to the Si−$H_2{}^x$ stretching mode. McKean[23] assigned the band at 461.0 cm^{-1} (ν_9) to the Si−Br

TABLE 10: Calculated Frequencies[a] and Potential Energy Distribution (PED) for Si_2H_5F[a]

sym[b]	vib no.	fundamental	B3LYP/6-31G** unscaled	B3LYP/6-31G** scaled[c]	B3P86/6-31G** unscaled	B3P86/6-31G** scaled[c]	B3PW91/6-31G** unscaled	B3PW91/6-31G** scaled[c]	PED[d]
	ν_1	Si−H_2^a sym str	2237.1	2164.0	2249.2	2175.6	2241.2	2167.9	65(2), 33(3)
	ν_2	Si−H_2^x sym str	2233.0	2160.1	2245.1	2171.7	2237.4	2164.3	73(1), 16(2)
	ν_3	Si−H^s str	2219.4	2146.9	2231.3	2158.4	2223.5	2150.9	57(3), 23(1), 18(2)
	ν_4	Si−H^x scis	974.6	973.8	970.0	969.2	967.9	967.0	56(7), 13(10), 12(4)
	ν_5	Si−H^x wag	957.5	957.5	952.0	951.9	949.9	949.8	26(10), 34(7), 20(9)
	ν_6	Si−H_3 asym def	936.4	936.1	930.0	930.0	928.1	927.9	68(8), 16(10), 10(4)
	ν_7	Si−F str	866.9	866.9	866.8	866.2	863.0	862.4	70(4), 13(10)
	ν_8	Si−H_3 sym def	863.1	863.0	858.1	858.1	857.0	856.0	71(9), 28(10)
	ν_9	Si−H_3 rock	530.7	530.6	529.1	529.0	528.4	528.3	66(11), 11(5)
	ν_{10}	Si−Si str	418.9	418.3	424.1	423.5	422.7	422.2	84(5), 18(11)
	ν_{11}	skel bend	162.6	162.6	163.2	163.2	164.0	163.9	128(6), 43(11)
	ν_{12}	Si−H_2^a asym str	2246.2	2172.7	2258.4	2184.5	2250.4	2176.7	67(13), 32(12)
	ν_{13}	Si−H_2^x asym str	2234.5	2161.4	2247.2	2173.7	2239.2	2165.9	68(12), 32(13)
	ν_{14}	Si−H_3 asym def	942.2	942.1	936.0	935.9	933.8	933.7	96(14)
	ν_{15}	Si−H^x twist	761.4	761.3	759.0	758.8	758.7	758.6	74(15)
	ν_{16}	Si−H_2^x rock	629.4	629.1	626.1	625.8	625.1	624.8	40(17), 34(16)
	ν_{17}	Si−H_3 rock	367.6	367.6	365.4	365.4	366.6	366.5	84(16), 75(17), 46(15)
	ν_{18}	Si−H_3 tors	111.6	111.6	109.6	109.6	107.0	107.2	98(18)

[a] Frequencies given in cm^{-1}. All calculated frequencies obtained from this work. [b] Symmetry species under C_s point group. [c] Scaling factors of 0.936 for Si-H stretches, 1 for others. [d] PED obtained from the normal coordinate analysis in this work.

TABLE 11: Comparison of Observed and Calculated Frequencies[a] and Potential Energy Distribution (PED) for Si_2D_5F

sym[b]	vib no.	fundamental	B3LYP/6-31G** unscaled	B3LYP/6-31G** scaled[d]	B3P86/6-31G** unscaled	B3P86/6-31G** scaled[d]	B3PW91/6-31G** unscaled	B3PW91/6-31G** scaled[d]	PED[e]
A′	ν_1	Si−D^S str	1619.8	1567.1	1628.9	1575.9	1620.2	1567.4	56(3), 43(2)
	ν_2	Si−D_2^x sym str	1602.2	1550.2	1611.2	1558.8	1602.5	1550.5	90(1), 8(2)
	ν_3	Si−D_2^a sym str	1587.2	1535.6	1595.3	1543.4	1586.7	1535.1	48(2), 42(3), 8(1)
	ν_4	Si−F str	894.5	894.5	901.0	900.9	895.9	895.9	95(4)
	ν_5	Si−D^x scis	715.4	715.4	711.6	711.6	708.8	708.8	47(7), 23(9), 19(10)
	ν_6	Si−D^x wag	686.7	686.7	682.7	682.7	680.1	680.1	21(10), 42(8), 21(7)
	ν_7	Si−D_3 asym def	673.5	673.5	668.5	668.5	666.0	666.1	19(10), 55(8), 21(7)
	ν_8	Si−D_3 sym def	642.1	642.1	636.0	636.0	633.9	633.9	70(9), 26(10)
	ν_9	Si−Si str	437.8	437.8	440.3	440.3	438.7	438.6	44(5), 26(11)
	ν_{10}	Si−D_3 rock	367.4	367.4	368.4	368.4	367.4	367.4	47(11), 42(5)
	ν_{11}	skel bend	150.4	150.4	150.8	150.8	151.5	151.5	125(6), 55(11)
A″	ν_{12}	Si−D_2^a asym str	1629.1	1576.1	1638.1	1584.7	1629.2	1576.2	59(13), 40(12)
	ν_{13}	Si−D_2^x asym str	1619.7	1566.9	1628.8	1575.8	1620.0	1567.3	60(12), 40(13)
	ν_{14}	Si−D_3 asym def	676.9	676.9	672.2	672.2	669.4	669.4	97(14)
	ν_{15}	Si−D^x twist	563.5	563.5	561.2	561.1	560.0	559.9	60(15), 19(17)
	ν_{16}	Si−D_2^x rock	489.8	489.8	488.0	488.0	486.6	486.6	34(17), 33(16), 15(15)
	ν_{17}	Si−D_3 rock	265.6	265.6	264.0	264.0	264.5	264.5	86(16), 71(17), 48(15)
	ν18	Si−D_3 tors	83.7	83.7	83.0	82.9	81.3	81.3	99(18)

[a] Frequencies given in cm^{-1}. All calculated frequencies obtained from this work. [b] Symmetry species under C_s point group. [c] Referential parameters taken from ref 5. [d] Scaling factors of 0.936 for Si-D stretches, 1 for others. [e] PED obtained from the normal coordinate analysis in this work.

stretching mode. According to our normal coordinate prediction, the band at 461.0 cm^{-1} would likely be due to the Si−Si stretching vibration and the frequency of the Si−Br stretching is predicted to be 384.7 cm^{-1} (ν_{10}), corresponding to the experimental value of 380.0 cm^{-1}.

The calculated frequencies of the A″ modes are in good agreement with the experimental assignment.[5,23] A strong infrared band at 934.0 cm^{-1} with a weak Raman band at 936 cm^{-1} was assigned to ν_{14} of A″ mode by McKean et al.[5] On the basis of the PW91/6-31G** calculated result and the normal coordinate prediction, the medium intensity infrared band ν_{14} is due to the Si−H_3 antisymmetric deformation vibration. The impurity infrared band at 358.9 cm^{-1} observed by McKean et al.[5] and assigned to ν_{17} is predicted to be at 349.1 cm^{-1} with weak intensity due to the Si−H_2^x rock mode. The observed impurity Raman band at 96 cm^{-1} by McKean et al.[5] assigned to ν_{18}, in Si−Si torsional mode, is predicted at 95.6 cm^{-1} with very weak intensity by our calculations.

There are still some questions about the assignment of A″ modes of Si_2D_5Br. The main problem is that there is still no experimental data for ν_{18} due to the Si−Si torsion mode. The vibrational frequency of ν_{18} is predicted to be at 71.4 cm^{-1}. The strong intensity infrared band, close to the A′ mode of ν_5, at 657 cm^{-1} with a weak Raman band at 667 cm^{-1} was assigned to ν_{14} by McKean et al.[5] It was predicted to be at 674 cm^{-1} due to the antisymmetric Si−D_3 deformation mode. The strong infrared band at 258.4 cm^{-1} is predicted to be at 253.4 cm^{-1} with extensive mixing. It is made up of 40% SiD_3 rock, 40% SiD_2^x rock, and 19% SiD_2^x twist determined by the PED from our calculated results, although we refer to it as ν_{17}, in the SiD_3 rock mode.

3. Disilanyl Fluoride. DFT calculated results with B3PW91/6-31G**, B3LYP/6-31G**, and B3P86/6-31G** levels are firstly reported in Tables 10 and 11. In addition, the infrared intensities, Raman activities, and depolarization values of Si_2H_5F are also given in Table 7. To our knowledge, neither theoretical studies nor direct experimental results of fundamental vibrational frequencies for Si_2H_5F and its deuterium isotopomer have been reported.

Normal coordinate analysis has been carried out; moreover, the scale factor with respect to Si−H(D) stretching modes has been transferred from Si_2H_5Cl to Si_2H_5F because of successful

TABLE 12: Comparison of the Observed Vibratonal Frequencies[a] for Si−H Stretch Modes of Si_2H_5Cl, Si_2H_5Br, and Si_2H_5I

sym[b]	mode	Si_2H_5Cl	Si_2H_5Br	Si_2H_5I	mode descriptions[c]
A′	ν_1	2178.8	2178	2179	$SiH_2{}^a$ sym str
	ν_2	2172	2170	2166	$SiH_2{}^x$ sym str
	ν_3	2157.9	2157.2	2156	SiH^s str
A″	ν_{12}	2181.3	2181.8	2180	$SiH_2{}^a$ asym str
	ν_{13}	2172	2171.4	2171	$SiH_2{}^x$ asym str

[a] Frequencies given in cm^{-1}; taken from ref 5. [b] Symmetry species under C_s point group. [c] Mode descriptions for Si_2H_5Cl and Si_2H_5Br based on PW91/6-31G** vibrational energy decomposition analysis. Mode descriptions for Si_2H_5I involved in ν_1, ν_2, and ν_3 in agreement with those for Si_2H_5Cl and Si_2H_5Br listed in this table as well as ν_{12} of $SiH_2{}^x$ str and ν_{13} of SiH_3 str in different descriptions from those for Si_2H_5Cl and Si_2H_5Br, based on ref 3. Abbreviations used: str, stretch; sym, symmetry or symmetric; asym, asymmetric.

TABLE 13: Comparison of the Observed Vibratonal Frequencies[a] for Si−D Stretch Modes of Si_2D_5Cl, Si_2D_5Br and Si_2D_5I

sym[b]	mode	Si_2D_5Cl	Si_2D_5Br	Si_2D_5I	mode descriptions[c]
A′	ν_1	1583.8	1584.1	1584	SiD^s str
	ν_2	1572	1572	1566	$SiD_2{}^x$ sym str
	ν_3	1554.4	1554.3	1554	$SiD_2{}^a$ sym str
A″	ν_4	1594.8	1595.1	1594	$SiD_2{}^a$ asym str
	ν_5	1586.9	1587.6	?	$SiD_2{}^x$ asym str

[a] Frequencies given in cm^{-1}; taken from ref 5. [b] Symmetry species under C_s point group. [c] Mode descriptions are based on P86/6-31G** vibrational energy decomposition analysis. Mode descriptions for Si_2D_5I involved in ν_1, ν_2, and ν_3 in good agreement with those for Si_2D_5Cl and Si_2D_5Br listed in this table as well as ν_{12} of $SiD_2{}^x$ str and ν_{13} of SiD_3 str in different descriptions from those of Si_2D_5Cl and Si_2D_5Br, based on ref 3. Abbreviations used: str, stretch; sym, symmetry or symmetric; asym, asymmetric.

transference from Si_2H_5Cl to Si_2H_5Br. The DFT-derived force constants obtained from calculated results using B3LYP/6-31G**, B3PW91/6-31G**, and B3P86/6-31G** were scaled by using a factor of 0.936 pertinent to Si−H(D) stretching modes and using an factor of 1 correspond to non-SiH(D) stretching modes. Then the *a priori* predictions of fundamental vibrational frequencies for Si_2H_5F and its deuterium isotopomer are obtained.

As one can see from Table 8 for A′ modes of Si_2H_5F, the ν_1 mode is predicted to be a strong infrared band at 2175.6 cm^{-1} due to the $Si-H_2{}^a$ symmetric stretch mode. It is shown that two medium infrared bands at 2171.7 and 2158.4 cm^{-1} are respectively assigned to ν_2 of the $Si-H_2{}^x$ symmetric stretch mode and ν_3 of the $Si-H^s$ stretch. Extensive mixing is found for three A′ modes involved in bands at 969, 952, and 930 cm^{-1}, respectively, due to ν_4, ν_5, and ν_6. The mode of ν_4 assigned to the $Si-H_2{}^x$ scissors mode is made up of 56% $Si-H_2{}^x$ scissors, 13% $Si-H_2{}^x$ wag, and 12% Si−F stretch, and the mode ν_6 assigned to the $Si-H_3$ antisymmetric deformation mode is 68% $Si-H_3$ antisymmetric deformation, 16% $Si-H_2{}^x$ wag, and 10% Si−F stretch. The configuration of mode ν_5 is 34% $Si-H_2{}^x$ scissors, 26% $Si-H_2{}^x$ wag, and 20% $Si-H_3$ symmetric deformation, whereas it is designated as the $Si-H_2{}^x$ wag mode. The vibrational frequencies of Si−F and Si−Si stretching are predicted to be 862.4 cm^{-1} (ν_7) and 422.2 cm^{-1} (ν_{10}), respectively.

The ν_{12} of A″ modes is predicted to be the strong infrared band at 2184.5 cm^{-1}, the $Si-H_2{}^a$ antisymmetric stretch mode. The ν_{13} mode is predicted by our calculations to be the medium infrared band at 2173.7 cm^{-1} assigned to the $Si-H_2{}^x$ antisymmetric stretch mode. The medium infrared band at 365.4 cm^{-1} assigned to ν_{17} of the $Si-H_3$ rock is made up of 84% $Si-H_3$ rock, 75% $Si-H_2{}^x$ rock, and 46% $Si-H_2{}^x$ twist.

For A′ modes of Si_2D_5F, the frequency of the ν_1 mode is predicted to be at 1575.9 cm^{-1} due to the $Si-D^s$ stretch mode. The bands at 1558.8 and 1543.4 cm^{-1} are respectively assigned to ν_2 of the $Si-D_2{}^x$ symmetric stretch mode and ν_3 of the $Si-D_2{}^a$ symmetric stretch. There is extensive mixing in the A′ modes involved in bands at 711.6, 682.7, and 668.5 cm^{-1}, respectively, due to ν_5, ν_6, and ν_7. The mode of ν_5 assigned to the $Si-D_2{}^x$ scissors mode is made up of 47% $Si-D_2{}^x$ scissors, 23% $Si-D_3$ symmetric deformation, and 19% $Si-D_2{}^x$ wag; in addition, the mode ν_7 assigned to the $Si-D_3$ antisymmetric deformation mode is 55% $Si-D_3$ antisymmetric deformation, 21% $Si-D_2{}^x$ scissors, and 19% $Si-D_2{}^x$ wag. The configuration of mode ν_6 is 42% $Si-D_3$ antisymmetric deformation, 21% $Si-D_2{}^x$ scissors, and 21% $Si-D_2{}^x$ wag. It is designated as $Si-D_2{}^x$ wag mode.

The frequency of ν_{12} is predicted by the calculated results to be at 1584.7 cm^{-1} due to the $Si-H_2{}^a$ antisymmetric stretch mode for A″ modes of Si_2D_5F. The ν_{13} mode is predicted to be a band at 1575.8 cm^{-1} assigned to the $Si-H_2{}^x$ antisymmetric stretch mode. The band at 488.0 cm^{-1} assigned to ν_{16}, $Si-H_2{}^x$ rock mode, is made up of 34% $Si-H_2{}^x$ rock, 33% $Si-H_3$ rock, and 15% $Si-H_2{}^x$ twist. Similarly, the band at 264 cm^{-1} assigned to the mode of ν_{17}, $Si-H_3$ rock mode, is made up of 41% $Si-H_3$ rock, 36% $Si-H_2{}^x$ rock, and 23% $Si-H_2{}^x$ twist.

We made a comparison among vibrational fundamental frequencies for Si−H stretching modes from experimental results for Si_2H_5Cl, Si_2H_5Br, and Si_2H_5I (and their deuterium isotopomers) listed in Table 12 (and Table 13).[4,5] There is almost no difference among fundamental vibrational frequencies for Si−H stretching modes on the molecules of Si_2H_5Cl, Si_2H_5Br, and Si_2H_5I except for ν_2 of the A′ modes with a little discrepancy within 6 cm^{-1} and also almost no difference among fundamentals for Si−D stretching modes for Si_2D_5Cl, Si_2D_5Br, and Si_2D_5I except for ν_2 of the A′ modes with a little discrepancy within 6 cm^{-1}.[4,5] In addition, comparison of the force constants for Si−H(D) stretch modes obtained from DFT calculations and

TABLE 14: Comparison of Scaled DFT[a] Force Constants[b] for Si−H(D) Stretching in Si_2H_5Cl, Si_2H_5Br, and Si_2H_5F

	Si_2H_5Cl				Si_2H_5Br[d]			Si_2H_5F[d]		Si_2H_5I[e]	
	cal[c]	LYP[d]	PW91[d]	P86[d]	LYP	PW91	P86	LYP	PW91	P86	exp
$f_x(SiH^x)$	2.7207	2.7035	2.7129	2.7302	2.6977	2.7090	2.7243	2.8643	2.6927	2.7118	2.690
$f_s(SiH^s)$	2.6830	2.6755	2.6858	2.7044	2.6709	2.6822	2.6982	2.8475	2.6758	2.6946	
$F_a(SiH^a)$	2.7165	2.7128	2.7208	2.7390	2.7110	2.7213	2.7371	2.8780	2.7022	2.7214	
$F_{as}'(H^aH^s)$	0.0283	0.0174	0.0168	0.0167	0.0174	0.0168	0.0168	0.0198	0.0179	0.0177	
$f_a'(H^aH^a)$	0.0277	0.0173	0.0168	0.0167	0.0171	0.0166	0.0164	0.0197	0.0178	0.0177	
$f_x'(H^xH^x)$	0.0272	0.0164	0.0165	0.0163	0.0148	0.0149	0.0150	0.0209	0.0196	0.0194	

[a] DFT density function theory calculations using B3PW91/6-31G**, B3LYP/6-31G**, and B3P86/6-31G**. Abbreviations: PW91, B3PW91/6-31G**; LYP, B3LYP/6-31G**; P86, B3P86/6-31G**. [b] Force constants given in mdyn $Å^{-1}$. [c] Taken from ref 5. [d] This work. [e] Taken from ref 3; the force constant for $Si-H(D)_3$ stretch modes is 2.682 mdyn $Å^{-1}$.

experimental data for Si_2H_5X (X = F, Cl, Br) indicates that the force constants for Si−H(D) stretch modes are transferable from one monohalogenodisilane to another; please refer to Table 14. So five original experimental fundamentals for Si−H(D) stretching modes of Si_2H_5Cl (and Si_2H_5Cl) are chosen as the referential parameter for Si−H(D) stretching modes for Si_2H_5F (and Si_2H_5F). A mean absolute deviation between the scaled P86/6-31G** theoretical frequencies for Si−H streching modes of Si_2H_5F and the referential parameters listed in Table 12 is 1.7 cm^{-1}, and a mean absolute deviation between the scaled P86/6-31G** theoretical frequencies for Si−D streching modes of Si_2D_5F and the referential parameters listed in Table 13 is 10.6 cm^{-1}. The fact that the scaled DFT frequencies for Si−H(D) stretching modes are in good agreement with the referential parameters listed in Tables 12 and 13 shows that the scale factor of 0.936 with respect to Si−H(D) streching modes is reasonable.

Conclusion

Comparison of the experimental fundamental vibrational frequencies of Si_2H_5Cl, Si_2H_5Br, and their isotopomers and the results obtained from the calculations using density functional (B3PW91, B3LYP, and B3P86) and RHF methods shows that all of B3PW91, B3LYP, and B3P86 are superior to the scaled RHF approach with the scale factor of 0.9 for the molecular vibrational problem. A factor of 0.936 with respect to Si−H(D) stretching modes fit for Si_2H_5Cl, Si_2H_5Br, and their isotopomers is obtained to have the DFT (B3PW91/6-31G**, B3P86/6-31G**, and B3LYP/6-31G**) Si−H(D) stretching frequencies in satisfactory agreement with the observed results. The experimental assignment of the fundamental vibrational frequencies for Si_2H_5Cl, Si_2H_5Br, and their isotopomers has been checked, and reassignment of some vibrational modes is proposed, on the basis of the IR intensities determined from DFT calculations and the PED obtained from the scaled DFT force field. The fundamental vibrational frequencies and the force field for Si_2H_5F and its isotopomer have been obtained from DFT calculations using B3WP91/6-31G**, B3LYP/6-31G**, and B3P86/6-31G**. The scale factor of 0.936 pertinent to Si−H(D) stretch modes to scale DFT force constants is transferred from Si_2H_5Cl to Si_2H_5Br and Si_2H_5F. The assignments of the fundamental vibrational frequencies of Si_2H_5F and their isotopomers are made on the basis of our calculated results. The DFT calculations and the normal coordinate analysis on Si_2H_5F and its isotopomer are valuable for providing prediction of the future experimental vibrational spectrum of them.

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