

Article

Quantum Chemical Studies on Silicon Tetrafluoride and Its Protonated Analogues

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Abstract: For every heteronuclear molecule, protonation can occur at more than one site thus giving rise to more than one proton affinity. Experimentally, only one proton affinity (PA) value is reported for a molecule and the experiment does not specify the site for the protonation. In the present work, quantum chemical calculations are carried out on SiF₄ and its possible protonated analogues (HF₄Si⁺ and HSiF₄⁺) by employing several computational chemistry methods including the MP2 method with 6-311++G** and cc-pVDZ basis sets, the HF, B3LYP and the CCSD methods with the 6-311++G** basis set and the Gaussian 04 (G4) compound method with the aim of determining the protonated analogue that corresponds to the experimentally determined PA value. Also, bond distances, bond angles, rotational constants, dipole moments, infrared spectroscopy and HOMO-LUMO energies are calculated for the three molecular species; SiF₄, HF₄Si⁺ and HSiF₄⁺. From the results, the experimentally reported PA value is found to correspond to the protonated analogue in which the proton is attached to one of the fluorine atoms (HSiF₄⁺) instead of the one in which the proton is attached to the silicon atom. Except for the HOMO-LUMO energies which are best predicted by the B3LYP method, other parameters are found to be accurately predicted by the G4 compound method in comparison with available experimental results. These findings

have not only aided in providing the needed information which was lacking in literature about SiF₄ especially its protonated analogues, but these results also find applications in industries (such as in catalysis and synthesis) and in the chemical exploration of the interstellar medium (ISM).

Keywords: Protonation, Quantum Chemical Calculation, Fluorosilane, Frontier Orbital, Perturbation

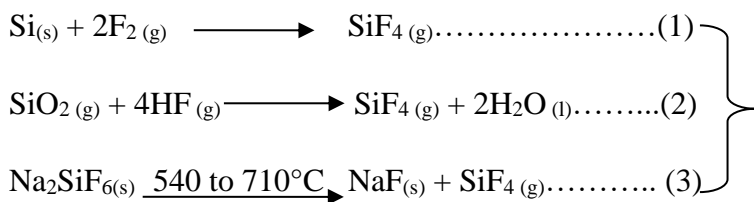
1. Introduction

The study of chemistry of today has grown past the use of test-tubes and chemicals to the use of computers. A reflection of the relevance of this way of studying chemistry is the 1998 Noble Prize award in chemistry which was divided equally and awarded between John A. Pople for his development of computational methods in quantum chemistry and Walter Kohn for his development of density-functional theory (Miller, 1999). The underlying force behind their success and the methods used is the Schrodinger's fundamental law of quantum mechanics which have been simplified by the currently available ab-initio methods. Given the position of the nuclei and the number of electrons, the ab-initio quantum chemical calculation methods can be used to solve the electronic Schrödinger equation to obtain useful information like the energy, electron densities and other properties of the system. Common classes of the ab-initio methods include; the Hartree-Fock methods e.g. HF, ROHF, UHF, the Post Hartree-Fock methods e.g. Møller–Plesset perturbation theory (MPn), Coupled-Cluster (CC) and the Multi-reference methods e.g. Multi-Configurational Self-Consistent Field (MCSCF) (Friesner, 2005).

Structures and properties of molecules can now be analyzed to supplement the experimental procedures and techniques. For instance, the Kohn's density-functional theory is now used in the calculation of the optimized or molecular geometry (bond length and angles), studying optimized geometries of molecules is therefore very important as it influences the colour of the substance, its reactivity, biological activity and its polarity (McMurry, 1992, Cotton *et al.*, 1999, Alexandros *et al.*, 2015). Further application of the ab-initio quantum chemical calculation is in the field of Material Sciences which focuses on structures, binding energies and catalysis with practical applications in modeling of conductivity for microelectronics, semiconductors and catalytic processes (Hammer *et al.*, 2000, Wu *et al.*, 1991, Raghavachari *et al.*, 2004). Biological applications focus mainly on modeling of enzymatic catalysis and most recently, the ab-initio quantum chemical calculations have also been applied to nanotechnology in the investigation of carbon nanostructures (Bettinger *et al.*, 2003).

In the field of Astrochemistry/Molecular Spectroscopy which is a young interdisciplinary science lying at the interface of chemistry, physics, astronomy and astrophysics in which over 200 molecular species have been astronomically observed from the different molecular clouds in the interstellar medium (ISM), ab-initio quantum chemical calculations have played a major role both in the laboratory (by aiding experimental molecular spectroscopy experiment) and in astronomical observation (by proving the spectroscopic parameters for astronomical searches for non-terrestrial molecular species that have not been probed experimentally in the laboratory and unstable species that are difficult to be studied in the terrestrial laboratories) (Etim and Aruan 2015, Etim et al., 2016, 2017, 2018, 2019, 2020).

Silicon tetrafluoride (tetrafluorosilane) is a colourless, volatile and narrow liquid range compound that was first synthesized by John Davy in 1812 (Davey, 1812). A substantial amount of it occurs naturally in volcanic plumes (Mori *et al.*, 2002, Schaefer, 2005). It finds uses in organic synthesis, catalyst, oil well drilling and microelectronics (Shimizu, 2001). Five methods have been identified for the laboratory scale production of SiF₄ (a) thermal dissociation of hexafluorosilicates (b) reacting silicon with fluorinating agents (c) fluorination of silicon tetrachloride (d) fluorination of silicon dioxide and (e) decomposition of fluorosilicic acid with concentrated acids (Soltani *et al.*, 2016). Some of these methods are represented in the chemical equations below:



(Chemical book, 2017, Bulanov *et al.*, 2003)

Apart from homonuclear molecules such as H₂, O₂, N₂, etc., with only one possible site for protonation, other molecular species (the heteronuclear species) can be protonated in more than one site, thus giving rise to more than one proton affinity value for a single molecular species. Experimentally, only a single proton affinity value is determined for each molecular species irrespective of the possible number of protonation site(s). Also, the experimental result does not specify where the proton is attached to. However, with the help of quantum chemical calculations, a proton can specifically be attached to each possible protonated site and the proton affinity calculated for each possible protonated system. With this ab-initio quantum chemical calculations approach, the protonated analogue corresponding to the experimentally determined PA value can be accurately assigned. Thus, this work aims at using ab-initio quantum chemical calculations to accurately determine the protonated analogue of SiF₄, corresponding to the experimentally determined PA value. Secondly, there have been paucity of fundamental/basic

experimental and computational information on SiF₄ and its possible protonated analogues, hence this research will also bridge this gap by providing these parameters such as bond distances, bond angles, rotational constants, dipole moments, infrared spectroscopy and HOMO-LUMO energies using the ab-initio quantum chemical calculations, the results will be compared with few available experimental results.

2. Materials and Methods

The quantum chemical calculations reported in this work were carried out using the Gaussian 09 suite of programs (Frisch *et al.*, 2009). The different computational chemistry methods employed in this work include the second order Moller-Plesset perturbation theory (MP2), the Hartree-Fock (HF), the Becke, three-parameter, Lee-Yang-Parr (B3LYP), the coupled cluster method including singles and doubles terms (CCSD) and the Gaussian 04 (G4) compound method. For the MP2 method, the 6-311++G** and cc-pVDZ basis sets are employed while only the 6-311++G** basis set is used in the HF, B3LYP and the CCSD methods. The choice of these methods and basis sets is based on experience in previous studies (Etim *et al.*, 2016, 2017, 2018, 2019, 2020). The use of different methods is necessary both in monitoring the consistency of the results and in determining which method is best in predicting a particular parameter or parameters in comparison with available experimental data.

The SiF₄ and its protonated analogues (HF₄Si⁺ and HSiF₄⁺) were optimized with the different methods mentioned above. For all the calculations reported in this work, only stable equilibrium structures are considered. This was verified via harmonic frequencies calculations with the equilibrium geometries having only real frequencies with no imaginary frequencies. The proton affinity (PA) is calculated as the difference in energy (electronic energy) between a neutral species and its protonated analogue. Zero point correction to energies is included in all the calculations reported here.

Except otherwise stated, the reported experimental data in this work are obtained from the NIST website.

Errors such as that for IR Spectroscopy were calculated as percentage error using the equation below:

$$\text{Error (\%)} = \frac{(\text{Calculated Value} - \text{Experimental Value})}{\text{Calculated Value}} \dots\dots\dots (4)$$

3. Results and Discussion

In this section, the results obtained following the methodology described above are presented and discussed.

3.1. Proton Affinity

In Table 1, the proton affinity values calculated for SiF₄ are presented. The experimental PA value (120.2 kcal/mol) of SiF₄ reported in the NIST website is also presented in the Table. In SiF₄, the proton has two possible sites for attachment, either to the Silicon atom or to any of them Fluorine atoms. The PA values corresponding to these two possibilities are shown in the table. In both cases, the G4 method predicts the PA value with the least error. Figure 1 shows the optimized structures of the SiF₄ and its protonated analogues. In all the different quantum chemical methods considered in this work, the protonated analogue in which the proton is attached to one of the Fluorine atoms has the closest PA value to the experimental value suggesting that reported experimental PA value corresponds to this protonated analogue. A simple stability check on the two protonated analogues of SiF₄ also reveals that the protonated species in which the proton is attached to one of the Fluorine atom is the most stable (as shown in Table 2) in all the computational methods employed in this work. This further supports the fact that the experimentally measured PA value corresponds to this protonated analogue in which proton is attached to F atom instead of the one in which the proton is attached to the Silicon atom. Also, the electron density is highest in fluorine as compared to silicon which supports the ease of attachment of proton to the fluorine atom. The above is in agreement with Etim *et al.*, 2018 and Ya-pin Tu, 2006 where they both pointed out that PA occurs at the site with the highest electron density or a site that is thermodynamically most favorable.

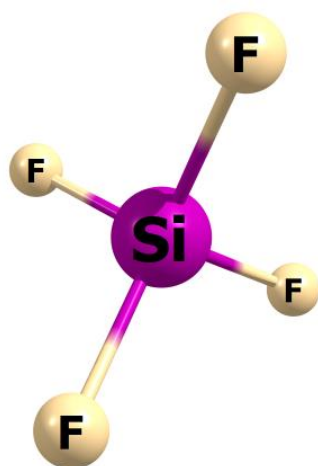
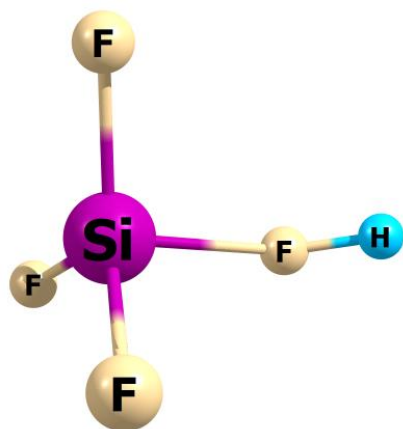
Table 1: Proton affinity values for SiF₄ (kcal/mol)

Molecule	Protonation Site				
	Method	Proton attached to F atom		Proton attached to Si atom	
		PA (kcal/mol)	Error	PA (kcal/mol)	Error
SiF ₄	HF/6-311++G**	113.181	7.019	75.907	44.293
	B3LYP/6-311++G**	114.043	6.157	88.219	31.981
	MP2/6-311++G**	116.626	3.574	89.093	31.107
	MP2/cc-pVDZ	122.619	-2.419	99.599	20.601
	CCSD/6-311++G**	123.203	-3.003	98.068	22.132
	G4	122.563	-2.363	101.348	18.852
	Experiment value	120.200	NA	120.200	NA

Table 2: Sum of electronic and zero-point Energies for HF_4Si^+ and HSiF_4^+ molecular species

Method	Energy (Hartree/Particle)*	
	HSiF_4^+	HF_4Si^+
HF/6-311++G**	-687.243	-687.183
B3LYP/6-311++G**	-689.438	-689.397
MP2/6-311++G**	-688.164	-688.120
MP2/cc-pVDZ	-687.960	-687.924
G4	-689.334	-689.3000

* Sum of electronic and zero-point Energies

**Fig. 1a:** Optimized structure of SiF_4 **Fig. 1b:** Optimized structure of HSiF_4^+ .

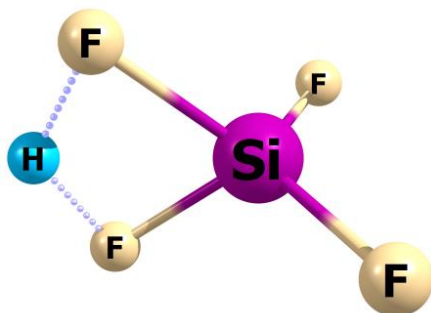


Fig. 1c: Optimized structure of HF_4Si^+

3.2. Bond Distances and Bond Angles

Figure 2 depicts the optimized geometry of SiF_4 and its protonated analogues with the numbering showing the connection of atoms. The bond length from silicon to the various atoms are as shown in Fig. 2 with Si as the central atom bearing 1 and F atoms with 2,3,4,5 while the proton is numbered 6 in the protonated species. SiF_4 can be protonated either through Si or through F atoms. SiF_4 has a tetrahedral geometry. Of the possible two protonated analogues, HSiF_4^+ showed a more stable geometry when proton is attached to the F atom while when the proton is attached to the silicon atom (as in HF_4Si^+), it optimizes to the structure in which the proton is in-between the two fluorine atoms. Table 3 presents the bond distances and bond angles obtained with the six different methods employed in this work for SiF_4 , HSiF_4^+ , and HSiF_4^+ . The observed experimental bond distance and bond angle of SiF_4 are also shown in the table. The Hartree-Fock method with the 6-311++G** basis set and the G4 method predict the bond distance between Silicon and Fluorine in SiF_4 to be 1.56 Å which is in a very good agreement with the experimental value of 1.554 Å reported by Takami, 1983.

Just like methane (CH_4), SiF_4 has an experimental bond angle of 109.47° and it's interesting that all the methods used in this study predicted it to a great level of accuracy as shown in Table 3. With the accuracy observed from the bond distance and bond angle for SiF_4 predicted from the various methods employed in this work, same level of accuracy is expected for the protonated species with no experimental values. Much precision is expected for the bond distances and bond angles of the protonated analogues with all the quantum chemical methods as presented in Table 3. Therefore, we can now confidently come to a conjecture that the bond angles of the protonated analogues depends on the coordinate in which the bond angle is taken and ranges from 90° - 120° for HSiF_4^+ and 70° - 120° for HSiF_4^+ .

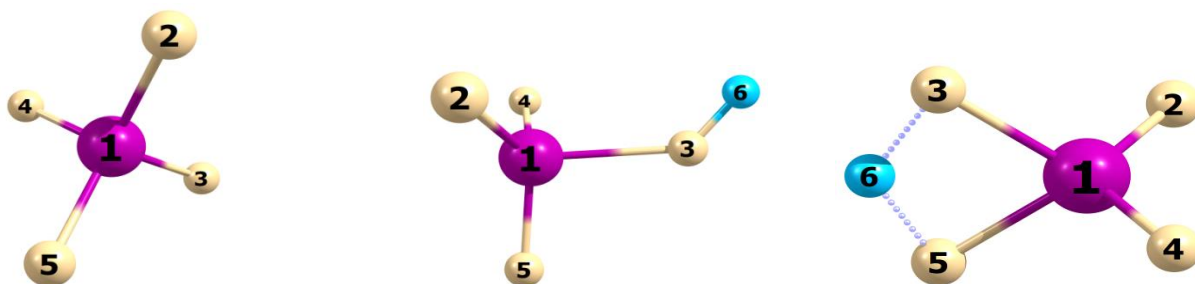


Fig. 2: Optimized geometries of SiF_4 , HF_4Si^+ and HSiF_4^+ respectively, showing the connections between atoms in numbers.

Table 3: Equilibrium geometries of SiF_4 and its protonated analogues

Molecule	Methods						Expt
	HF/ 6-311++G**	B3LYP/ 6-311++G**	MP2/ 6-311++G**	MP2/ cc-Pvdz	CCSD/ 6-311++G**	G4	
SiF_4							
Si-F	1.56	1.584	1.58	1.61	1.61	1.56	1.554
F-Si-F	109.5	109.48	109.47	109.47	109.47	109.46	109.4712
HF_4Si^+							
r(1-2)	1.524	1.553	1.549	1.586	1.582	1.537	
r(1-3)	1.797	1.846	1.841	1.880	1.873	1.814	
r(1-4)	1.524	1.552	1.548	1.586	1.582	1.537	
r(1-5)	1.520	1.548	1.544	1.582	1.578	1.533	
r(3-6)	0.929	0.953	0.946	0.953	0.950	0.951	
A(2-1-3)	100.0	100.0	99.80	99.30	99.30	100.6	
A(2-1-4)	116.2	116.3	116.3	116.4	116.4	116.0	
A(2-1-5)	117.8	118.0	118.1	118.5	118.5	117.7	
A(3-1-4)	100.0	100.0	99.90	99.50	99.40	100.7	
A(3-1-5)	98.90	98.00	97.90	97.10	97.10	98.40	
A(1-3-6)	137.0	132.3	131.0	126.4	127.3	126.0	
A(4-1-5)	117.8	118.0	118.1	118.5	118.5	117.7	
HSiF_4^+							
r(1-2)	1.515	1.544	1.540	1.578	1.574	79.5	
r(1-3)	1.653	1.691	1.687	1.727	1.721	1.670	
r(1-4)	1.515	1.544	1.540	1.578	1.574	1.529	
r(1-5)	1.653	1.691	1.687	1.727	1.721	1.670	
r(3-6)	1.200	1.227	1.210	1.212	1.207	1.224	
r(5-6)	1.200	1.227	1.210	1.212	1.207	1.224	
A(2-1-3)	112.7	112.7	112.6	112.7	112.7	112.8	
A(2-1-4)	120.4	120.2	120.6	120.9	120.9	119.5	
A(2-1-5)	112.7	112.7	112.6	112.7	112.8	112.8	
A(3-1-4)	112.7	112.7	112.6	112.7	112.8	112.8	
A(3-1-5)	78.20	78.60	78.50	76.90	76.70	79.70	
A(1-3-6)	80.60	79.90	78.90	79.10	79.50	79.20	

3.3. Rotational Spectroscopy

Rotational constants involve the gas phase measurement of transition energies between quantized rotational states of molecules. One of its significance lies in its application in the exploration and disquisition of chemical composition of interstellar mediums. Rotational transitions have been used to observe many currently known interstellar molecular species astronomically, its values which are most often a constant for a given molecular specie are termed rotational constants (Etim *et al*, 2017). For this study, the experimental rotational constant for the neutral SiF₄ is reported to be 4.13053 GHz (Takami and Kuze, 1983) while no experimental values are available for the two protonated analogues (HF₄Si⁺ and HSiF₄⁺). The lack of experimental rotational constants for the protonated species could be as result of their unstable nature (because they are ions) which makes it difficult for these species to be synthesized and studied in the terrestrial laboratory (Etim *et al*, 2017).

As shown in table 4, the results of the rotational constants for SiF₄ seem so interesting as five of the six methods employed predicted the rotational constants to the same accuracy with a good agreement with the experimentally observed value. These best methods include the Gaussian 4 theory G4, CCSD/6-311++G^{**}, MP2/cc-pVDZ, MP2/6-311++G^{**} and the B3LYP/6-311++G^{**} method except the HF/6-311++G^{**} method. Having predicted the rotational constants for the neutral molecule to a high level of accuracy, the rotational constants predicted by these methods for the protonated analogues with no experimentally measured values are expected to be very accurate as observed in the case of the neutral species. Thus, the rotational constants for the protonated species presented in Table 4 could be employed in the astronomically searches for these molecular species in the interstellar medium and other applications/studies that require the use of rotational constants.

Table 4: Rotational constants (GHz) for SiF₄ and its protonated analogues

Molecules	Methods						Expt
	HF/ 6-311++G ^{**}	B3LYP/ 6-311++G ^{**}	MP2/ 6-311++G ^{**}	MP2/ cc-Pvdz	CCSD/ 6-311++G ^{**}	G4	
SiF ₄							
A _e	4.047	4.122	4.122	4.122	4.122	4.122	4.13053
B _e	4.047	4.122	4.122	4.122	4.122	4.122	4.13053
C _e	4.047	4.122	4.122	4.122	4.122	4.122	4.13053
HF ₄ Si ⁺							
A _e	3.773	3.927	3.927	3.928	3.928	3.928	
B _e	3.727	3.877	3.877	3.877	3.877	3.877	
C _e	3.680	3.834	3.834	3.834	3.834	3.834	
HSiF ₄ ⁺							
A _e	4.050	4.050	4.050	4.050	4.050	4.050	
B _e	3.980	3.980	3.980	3.980	3.980	3.980	
C _e	3.980	3.980	3.980	3.980	3.980	3.980	

Dipole moment is an important parameter in interstellar chemistry because the intensities of rotational transitions scale with the square of the dipole moment, the higher the dipole moment, the higher the intensity of the lines. According to Tripathy *et al*, 2008, molecules with dipole moments have asymmetrical positive and negative charges, asymmetry is needed for polarity. SiF₄ has zero or no dipole moment because the 4 Si-F bonds are identical and symmetric and has the same approximate shape as carbon tetrachloride (it's the same molecule but with carbon replaced by the element one period down [Si] and 4 chlorines each replaced by the element one period up [F]), a well-known nonpolar solvent. While each individual Si-F bond is polar, the geometric symmetry causes the net charge on the molecule as a whole to cancel out. Thus the molecule is non-polar.

Table 5 contains the values of the dipole moment for all the quantum chemical calculation methods used in this study and they all accurately predicted the dipole moment of SiF₄ in accord to the experimental value of zero, we can therefore accept the values obtained by these same methods for the protonated analogues as their dipole moments since they are almost within the same level of precision.

Table 5: Dipole moments for SiF₄ and its protonated analogues

Molecular system	Methods						
	HF/6-311++G**	B3LYP/6-311++G**	MP2/6-311++G**	MP2/cc-pVDZ	CCSD/6-311++G**	G4	Expt.
SiF ₄	0	0	0	0	0	0	0
HF ₄ Si ⁺	4.462	4.411	4.570	4.500	4.500	4.364	
HSiF ₄ ⁺	4.536	4.052	4.536	4.457	4.457	3.859	

3.4. IR Spectroscopy

SiF₄ (a tetrahedral) and its protonated analogues are non-linear and will have 3N – 6 Vibrations with vibrational frequencies of 9 and 12 respectively. Due to degeneracy, the vibrational frequencies of the neutral molecule (SiF₄ which is 9) has been detected experimentally as 4 modes which includes; Degenerate deformation bending (V₂), Symmetrical stretching (V₁), Degenerate stretching (V₃) and Degenerate Deformation (V₄).

Table 6 shows the IR frequencies for SiF₄ and its protonated analogues; HF₄Si⁺ and HSiF₄⁺ while Figure 3, 4 and 5 respectively show the IR spectra of SiF₄, HF₄Si⁺ and HSiF₄⁺ at the HF/6-311++G** level. The spectra from other quantum chemical methods employed in this study are presented in the appendix.

Table 6: IR frequency for SiF₄ and its protonated analogues (HF₄Si⁺ and HSiF₄⁺)

Molecules	Methods					Experimental Values
	HF/6-311++G**	B3LYP/6-311++G**	MP2/6-311++G**	MP2/cc-pVDZ	G4	
SiF ₄						
C(Deg.def)	278.1498	252.0443	261.3824	240.766	261.3455	268
C „	278.1595	252.4075	261.3833	240.7672	261.6502	„
W(Deg.def)	400.5341	366.7954	377.8621	361.8971	383.7578	400
W „	400.5388	366.7954	377.8625	361.8974	384.0196	„
W „	400.5395	367.366	377.8626	361.8975	384.2442	„
S(Sym.stre)	836.5595	761.5948	779.809	731.1541	790.3004	800
B(Deg.stre)	1077.1555	995.6408	1012.7504	1013.8671	1039.6661	1032
B „	1077.1644	995.7663	1012.7516	1013.871	1039.8965	„
B „	1077.167	995.916	1012.752	1013.8714	1040.0211	„
HF ₄ Si ⁺						
C(Deg.def)	96.65760	125.5427	82.95200	-51.1174	-96.7414	
C	231.8799	207.6385	217.6588	196.1253	211.5847	
C	252.6899	228.1267	233.2988	212.4902	224.508	
W(Deg.def)	333.2612	306.8670	314.5234	300.4103	317.9221	
W	345.5068	314.8088	323.4111	308.4341	325.2812	
W	368.7109	332.8463	345.6907	334.6177	344.7658	
W	518.8281	472.5565	481.4921	500.6154	508.6936	
W	616.7225	619.8195	654.7623	674.8684	700.3923	
S(Sym.stre)	902.1976	824.1926	842.4900	817.8736	855.1219	
B	1195.8767	1106.247	1226.9822	1111.2165	1142.0142	
B	1214.1524	1134.6245	1146.8955	1128.6059	1159.9069	
B	3960.3437	3657.5946	3761.4068	3696.8039	3680.9841	
HSiF ₄ ⁺						
C(Deg.def)	-1836.4868	-1350.6818	-1391.398	-1236.459	-1265.747	
C	218.1938	193.2218	200.0879	183.8352	202.5375	
C	295.1506	272.1798	278.9123	266.9646	282.7068	
C	299.1161	277.3382	283.0506	267.9646	290.5592	
C	354.0863	321.8361	332.3841	327.8985	338.3015	
W(Deg.def)	615.9778	554.069	575.5397	574.8669	563.5941	
S(Sym.stre)	852.8613	762.4829	781.7736	764.1033	777.0373	
S	873.5083	854.5767	877.6456	931.0352	913.4596	
B(Deg.stre)	1080.4905	971.742	1011.9026	1000.1822	984.7522	
B	1097.3566	994.3596	1019.319	1032.3532	1029.6236	
B	1255.8735	1155.0535	1180.6355	1157.5611	1184.826	
B	1974.8682	1854.5823	1950.3435	1945.0435	1922.8034	

The error magnitude for the IR spectroscopy was obtained using eqn (4). A comparison of the six quantum chemical calculation methods employed in this work reveal that the B3LYP, MP2/cc-pVDZ, HF and MP2 methods recorded the largest average percentage error of magnitudes 5.22%, 5.05%, 3.56% and 2.80% respectively while the G4 method is the best method with the least average percentage error of 0.99%, a very low error compared to the other methods,

The G4 method still recorded the best prediction on the basis of specific frequency with specific values closer to the experimental values. However, the two protonated analogues have 12 vibrations respectively but none have been observed experimentally. On the basis of the accurate predictability of the G4 method for the neutral molecule, we are therefore resolving that the values predicted by the G4 method for the protonated analogues are more accurate and could thus be used for other investigations that require these values.

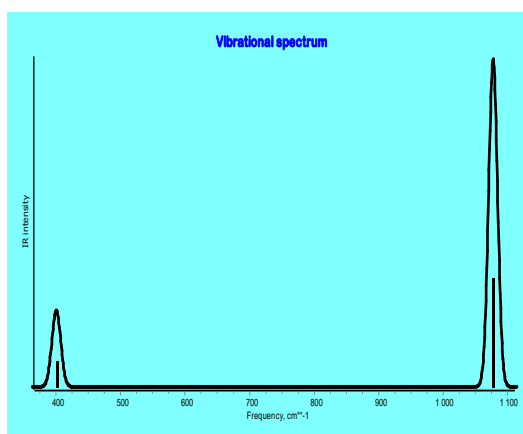


Fig. 3: Infrared spectrums of SiF_4 at HF/6-311++G** Method

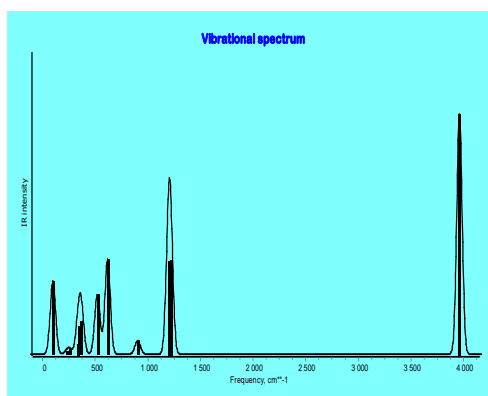


Fig. 4: IR Spectrum for HF_4Si^+ HF/6-311++G** Method

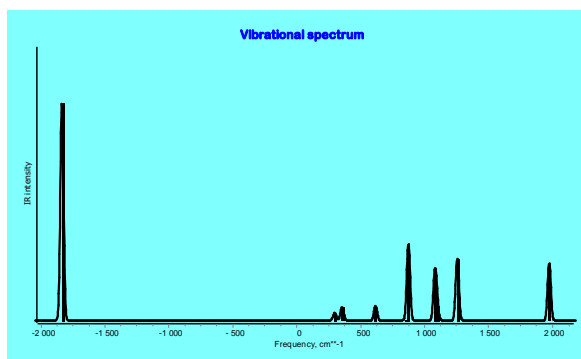


Fig. 5: IR Spectrum for HSiF_4^+ System at HF/6-311++G** method

3.5. HOMO-LUMO Energy

Molecular orbital is divided into two types, the Highest Occupied Molecular Orbital (HOMO) which has the highest energy and the Lowest Unoccupied Molecular Orbital (LUMO) which is lowest in energy. The difference in energy between the HOMO and the LUMO is referred to as the HOMO-LUMO Gap or Frontier orbitals. Excitation of molecules becomes easier when their HOMO-LUMO Gap converges or becomes smaller. HOMO-LUMO Gap is correlated to the strength, stability, valence band, conduction band and even the colour of the molecule in solution (Griffith *et al.*, 1957).

Generally, all the Ab-initio methods used in calculating the HOMO-LUMO Gap of SiF_4 and its protonated analogues gave values that are approaching zero and are quite smaller than the band gap of Si atom of 1.14 eV as reported by Streetman and Sanjay (2000), this finding is correct due to the presence of bonding orbitals in SiF_4 and its protonated analogues and in accord with finding of Atkins and de Paule (2000) that bonding orbitals are more stable and possesses lesser energy than antibonding orbitals

Of our six quantum chemical calculation methods employed, B3LYP/6-311++G** level of theory gave the best predictions with values approaching zero as contained in Table 7. Figures 6, 7 and 8 show the Molecular orbital diagrams with their HOMO-LUMO Gaps for HF/6-311++ G** level of theory for both SiF_4 and its protonated analogues.

Table 7: HOMO-LUMO energy for SiF_4 and its protonated analogues (in A.U.=atomic unit)

Molecules	Methods					
	HF/ 6-311++G**	B3LYP/ 6-311++G**	MP2/ 6-311++G**	MP2/ cc-pVDZ	CCSD/ 6-311++G**	G4
SiF_4	0.74074	0.42459	0.73908	0.82648	0.82858	0.72073
HSiF_4^+	0.75252	0.39005	0.74845	0.767	0.76904	0.74861
HF_4Si^+	0.78743	0.40724	0.77965	0.78015	0.78275	0.78217

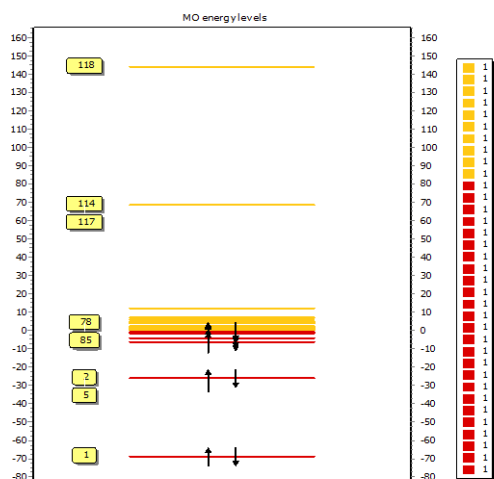


Fig. 6: MO Diagrams for SiF₄ at HF/6-311++ G**

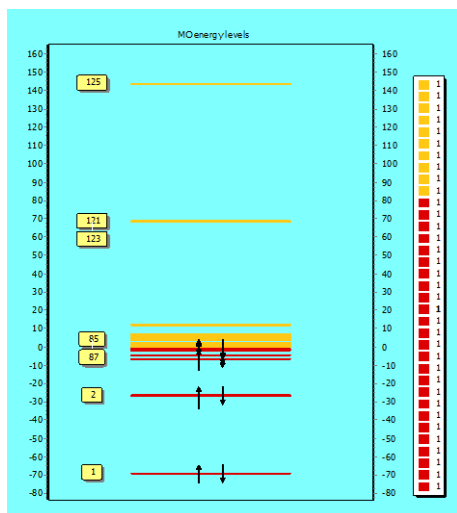


Fig. 7: MO Diagram for HF₄Si⁺ at HF/6-311++G**

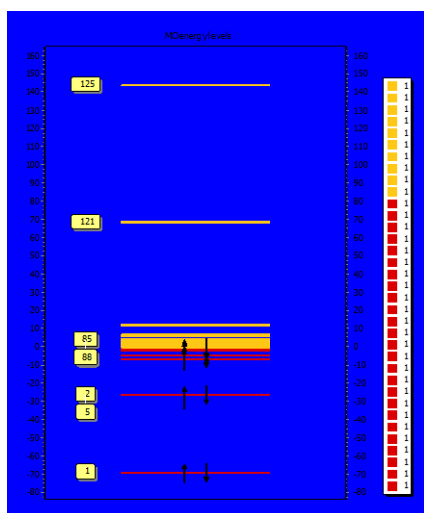


Fig. 8: MO Diagrams for HSiF₄⁺ System at HF/6-311++ G**

4. Conclusion

The protonation of Silicon Tetrafluoride has been studied using different quantum chemical calculation methods with the main aim of determining the best protonation site that corresponds to the experimentally measured proton affinity value. From the different methods used in calculating the PA values, it reveals that the best protonation site occurs when the proton is attached to one of the fluorine atom. The reported experimental PA value corresponds to this protonated analogue as against the protonated analogue in which the proton is attached to the silicon atom. This protonated analogue is found to be most stable, also, the electron density is highest in fluorine as compared to silicon which supports the ease of attachment of proton to the fluorine atom. Within the limit of this research, we have been able to confidently muster a conjecture that the bond angles of SiF_4 from the experimental finding is 109.47° while the bond angles of its possible protonated analogues (HF_4Si^+ and HSiF_4^+) depend on the coordinate in which the bond angle is taken and generally ranges from 90° - 120° for HF_4Si^+ and 70° - 120° for HSiF_4^+ . The G4 method had exceptionally stood out and outperformed the other methods in accurately calculating the rotational constants, proton affinity, IR Spectroscopy and even the dipole moment of the neutral molecule (SiF_4) when compared to the experimental values and as such we upheld the values obtained by the G4 method for the protonated analogue.

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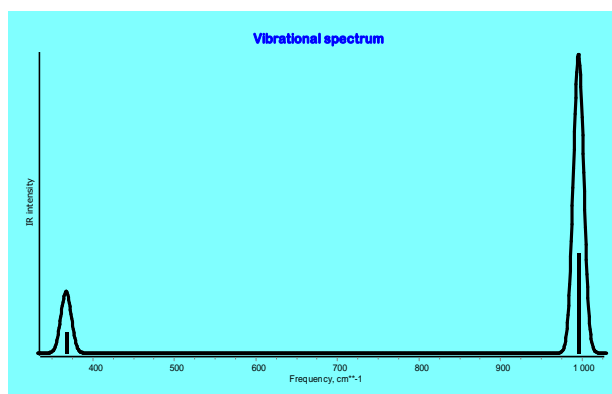
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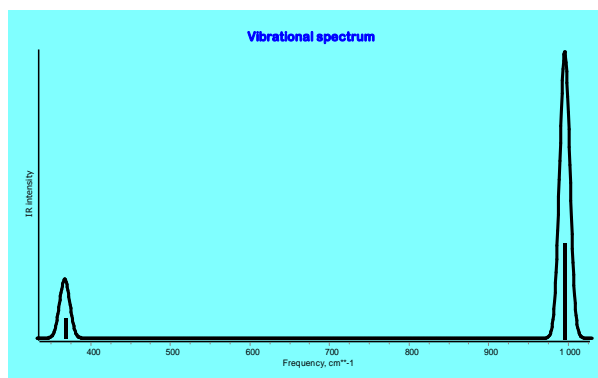
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Appendix

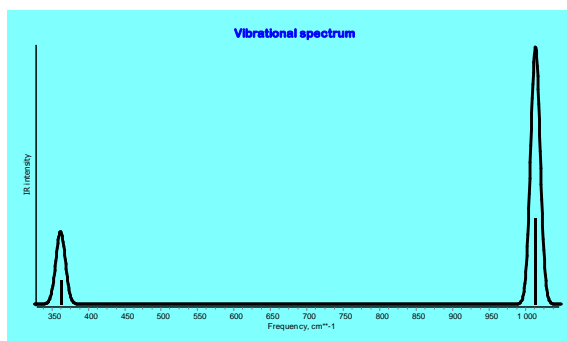
Infrared spectra of SiF₄ obtained at the different levels of theory/basis sets



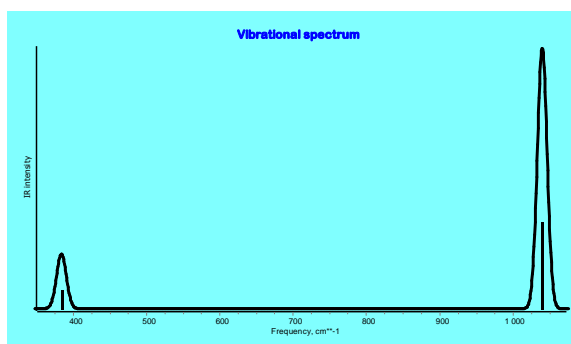
B3LYP/6-311++G**



MP2/6-311++G**

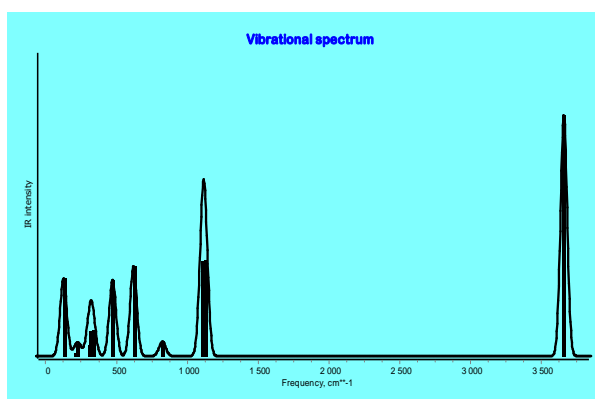


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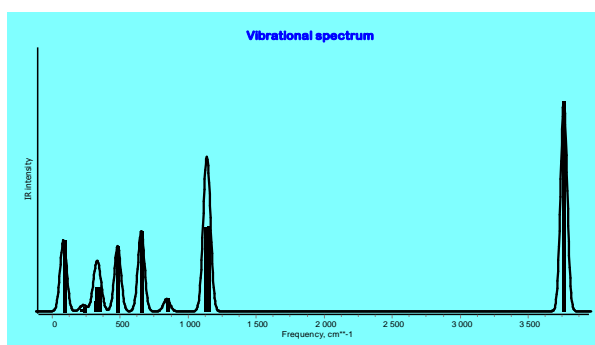


G4 Method

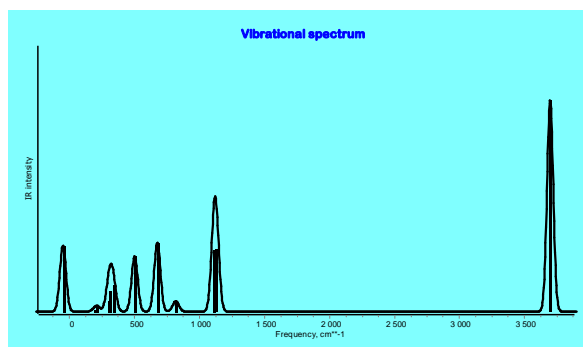
IR Spectra for HF₄Si⁺ System obtained at the different levels of theory/basis sets



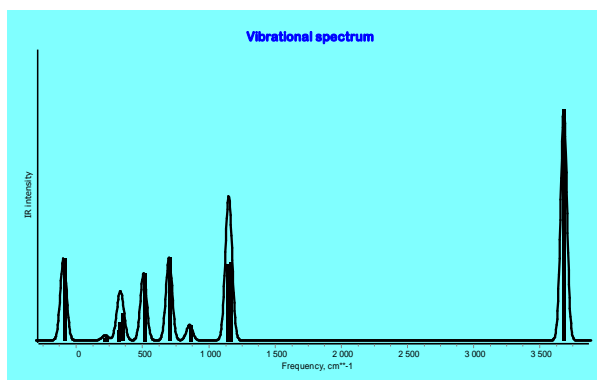
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MP2/6-311++G**

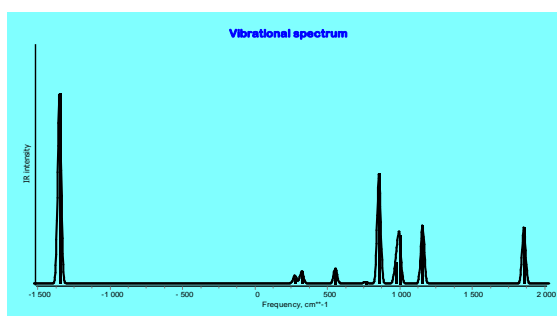


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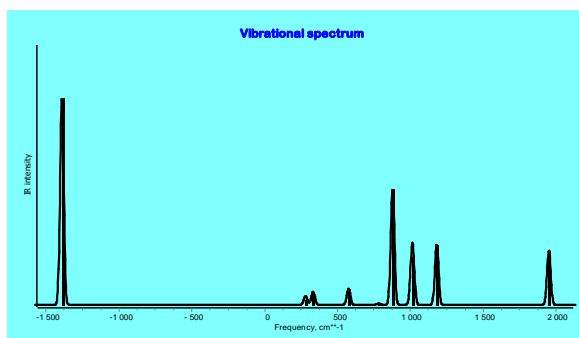


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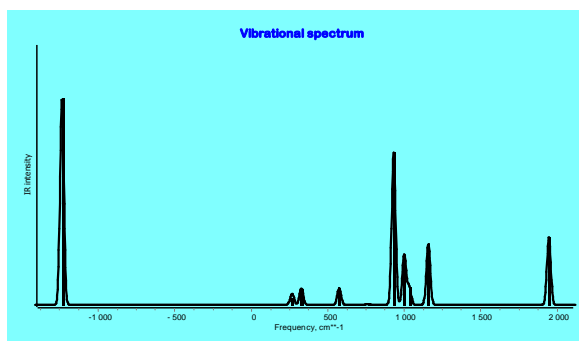
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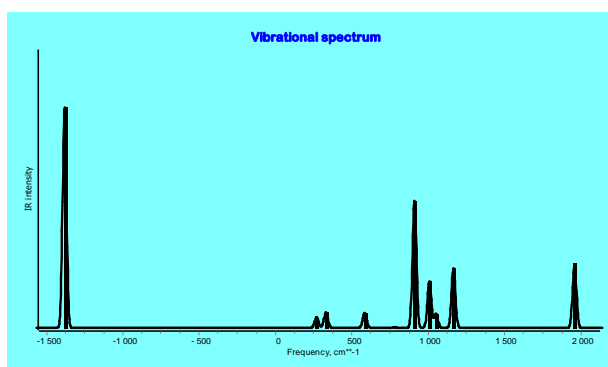
B3LYP/6-311++**



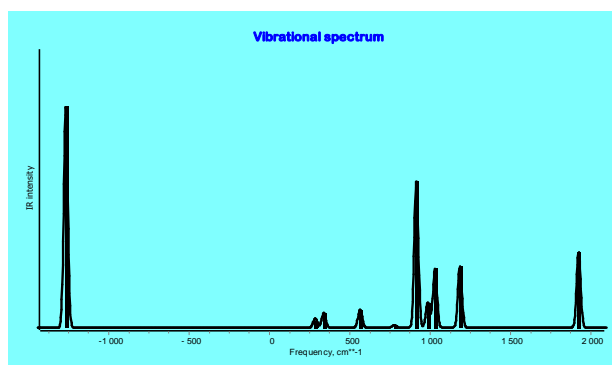
MP2/6-311++G**



MP2/cc-PVDZ



CCSD/6-311++G**



G4