International Journal of Modern Analytical and Separation Sciences, 2020, 8(1): 28-44

International Journal of Modern Analytical and Separation Science **ISSN: 2167-7778**

Journal homepage: www.ModernScientificPress.com/Journals/IJMAS.aspx *Florida, USA*

Article

Suspected Error in Some Experimentally Reported Proton Affinity Values: Insight from Quantum Chemical Calculations

Emmanuel E. Etim [1,*]; Oko Emmanuel, Godwin [1]; Sambo, Ifiok Friday[2]; Sulaiman Adeoye Olagboye [3]

[1]*Department of Chemical Sciences, Federal University Wukari, PMB 1020, Wukari, Taraba State, Nigeria*

[2]*Department of Chemistry, Akwa Ibom State University, Ikot Akpaden*

[3]*Department of Chemistry, Ekiti State University, Ado -Ekiti, Nigeria*

Author to whom correspondence should be addressed; E-Mail: emmaetim@gmail.com

Article history: Received 22 June 2020, Revised 1 August 2020, Accepted 3 August 2020, Published 24 September 2020.

Abstract: The phenomenon "error" is such a sensitive phenomenon in sciences and chemistry in particular due to its impact to lives, processes and studies and so the quest to completely eradicate or minimize errors. In this work, we report some molecules whose experimental proton affinity values are suspected to have shrouded some errors. These molecules include: NO, OF, SF_6, CH_3Br, CH_3Cl, and CH_3SH. Quantum chemical calculations methods which have been used to accurately determine the proton affinity values for different molecular species in our previous studies are applied in this study to calculate the proton affinity values for theses molecular species with experimentally measured proton affinity values. In each of the systems, the large disparity between the experimentally measured PA values and the ones determined via the different quantum chemical calculation methods suggest possible errors in the experimentally reported values.

Keywords: Error; Proton affinity PA; Computational value; Experimental value; Ab-Initio methods; Protonated analogues.

1. Introduction

The high accuracy and consistency of quantum chemical calculation cannot be overemphasized especially the Ab-initio method as they have enabled solutions to many chemical parameters such as structures, energies, interaction and properties with little or without errors at all when compared with experimental evaluations to an extent that we can now confidently accept or reject an experimental observations using the quantum chemical calculations and its methods as a basis (Helgaker, 2012) Quantum chemical calculations stand a chance of bringing to perfection the experimental works and investigations in all aspects of chemistry and physics (Bell *et al*., 2007), (Casella-Ventura *et al*., 2000). An insight into quantum chemical calculations reveals that it has find many applications such asin pharmaceutical industries in the development of drugs, polymer chemistry, chemical process industry in the computation of thermodynamic and spectroscopic properties, calculating heat of formation for both ideal and non-ideal systems (Sadler *et al*.,2001), (Ruiperez, 2019).

Different methods have been introduced for implementing and computing quantum chemical calculations such as the semi-empirical methods, Ab-initio methods, molecular mechanics, quantum mechanics and QM/MM methods, Urich and Allinger (1982), Szabo and Ostund (1989), (Bartlett 1989), Hobenberg and Koln (1964), (Johnson *et al*., 1993) and (Leach, 2001). In obtaining useful information such as energy or proton affinity of a specie, the ab-initio quantum chemical calculation has always been employed due to its experimental independent nature (uses only physical quantities) and high performance nature (Accuracy and Consistency) (Parr, 1990). The most common ab-initio methods usually used in electronic structure calculations include; Gaussian 04 compound method (G4), Moller-Plesset perturbation theory (MP2), the coupled cluster method Becke, three-parameter, Lee-Yang-Parr (B3LYP), and the Hartree-Fock (HF) methods (Jensen, 2007).

Over the years, computational techniques have become sophisticated, even though acceptability of any computational method has been based on comparison with experimental observations (Yaoquan Tu and AattoLaaksoner, 2010), (Sperger *et al*., 2016). There is an obvious possibility that experiments and experimental procedure may be shrouded in uncertain errors (either random or systematic) (Kuselman *et al*., 2013), (Weigman, 2005) Edminston and Williams (2000). This forms the basis of this work. Thus, the aim of this research is to point out molecules whose reported experimentally observed proton affinity (PA) are suspected to be wrong from the round of quantum chemical calculations.

2. Materials and Methods

Gaussian 09 suite of programs was applied with six Ab-initio computational methods ranging from the Gaussian 04 theory compound method (G4), Moller-Plesset perturbation theory (MP2) at cc-

pVDZ basis set, Becke, three-parameter, Lee-Yang-Parr (B3LYP) at 6-311++G** basis set, Moller-Plesset perturbation theory (MP2) at 6-311++G** bais set, the coupled cluster method including singles and doubles terms (CCSD) and the Hartree-Fock (HF) at 6-311++G** were implemented (Frisch *et al*., 2009)

These methods were carefully chosen based on the accuracy of the methods and experience from our previous researches, having shown an outstanding performances in the computation of PA values and other parameters of interest (Etim *et al*., 2020a), (Etim *et al*.,2015), (Etim *et al*., 2017), (Etim *et al*., 2016), (Etim *et al*., 2018). The error values reported in this work corresponds to the difference between the computational PA values and the experimentally observed PA values.

3. Results and Discussion

3.1. NO

Table 1 presents the results of the PA of NO and Fig 1a-c depicts their geometries as obtained using five different Ab-initio computational methods and an experimental value of 127.10 kcal/mol reported in the NIST chemical web book. There occurs no good agreement between the computational and experimental value as they are wide apart at both site of protonation. The least error was recorded when proton is attached to N with an error of 13.51kcal/mol using MP2/CC-PVD2. This value is still quite large making the experimental value suspicious of errors. This could be the reason why a related study by kazazic and his team (Kazazic *et al*., 2006) even though the determinations were done via a semi- empirical procedure obtained a quite different PA value of NO as 123.9kcal/mol, as a result, we suspect that the experimental value of 127.10kcal/mol may be wrong. Predictably, the value should be lower.

Fig. 1a: Optimized geometry for NO

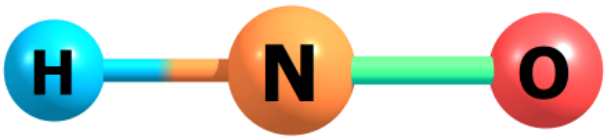

Fig. 1b: Geometry for the protonated analogue

Fig. 1c: Geometry for the protonation of NO

Table 1. PA values for NO

Method	Proton attached to N atom		Proton attached to O atom	
	PA (kcal/mol)	Error	PA (kcal/mol)	Error
HF/6-311++G**	**101.18**	**25.92**	**92.27**	**34.83**
B3LYP/6-311++G**	**104.77**	**22.33**	**88.59**	**38.50**
MP2/6-311++G**	**111.02**	**16.08**	**87.52**	**39.57**
MP2/cc-pVDZ	**113.59**	**13.51**	**89.86**	**37.24**
CCSD/6-311++G**	**109.20**	**17.90**	**91.19**	**35.90**
G4	**109.26**	**17.84**	**92.66**	**34.44**
Expt	**127.10**	**NA**	**127.10**	**NA**

3.2. OF

In table 2, the computed PA values for NO is shown and its geometries shown in Fig 2a-c The least error observed for the PA value of in all the methods here is 42.42 kcal/mol. This value is higher than the least error observed in all of the diatomic species reported in a related study (Etim *et al*., 2020a). Thus, we suspect that there could be an error in the experimentally reported PA value of 121.6 kcal/mol for OF.

Table 2. PA values for OF

Method	Proton attached to O atom		Proton attached to F atom	
	PA (kcal/mol)	Error	PA (kcal/mol)	Error
HF/6-311++G**	**58.35**	**63.26**	**79.18**	**42.42**
B3LYP/6-311++G**	**60.41**	**61.19**	**65.66**	**55.94**
MP2/6-311++G**	**55.95**	**65.65**	**66.18**	**55.42**
MP2/cc-pVDZ	**58.14**	**63.46**	**69.07**	**52.53**
CCSD//6-311++G**	**62.21**	**59.39**	**70.65**	**50.95**
G4	**68.30**	**53.30**	**70.92**	**50.68**
Expt	**121.6**	**NA**	**121.6**	**NA**

Fig. 2a: Optimized geometry for OF

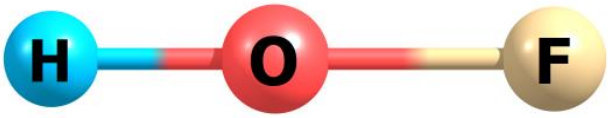

Fig.2b: Geometry for the protonation at O

Fig. 2c: Geometry for protonation at F

3.3. SF6

As compared to other similar studies (Etim *et al*., 2020a), (Etim *et al*., 2018) errors recorded for SiF_6 seems quite high for most similar studies, PA values are usually closer to the experimental value especially at the site were protonation is more favoured, but in this case, the least error on this site is -34.3236 kcal/mol as presented in table 3sand geometries in Fig 3a-c making it suspicious of error, other error values are still wide apart thereby placing suspicion that the experimentally reported value of 137.5kcal/mol reported by Hunter and Lias and present on the NIST chemical web book might be wrong. This could be as a result of random error or systematic error as Latimer and Smith, Bohme and his co-workers obtained a value of 139.4 kcal/mol and 138 kcal/mol using a semi-empirical and experimental approach respectively, Latimer and Smith (1994), (Bohme *et al*., 1992). Having observed some form of variations between the computated values and those reported experimental PA values, we suspect and error.

Table 3. PA values for SF6

Method	Proton attached to S atom		Proton attached to F atom	
	PA (kcal/mol)	Error	PA (kcal/mol)	Error
HF/6-311++G**	**195.126**	**57.62595**	**270.6304**	**133.1304**
B3LYP/6-311++G**	**35.39844**	**-102.102**	**102.4271**	**-35.0729**
MP2/6-311++G**	**28.09548**	**-109.405**	**98.84843**	**-38.6516**
MP2/cc-pVDZ	**28.08105**	**-109.419**	**91.50092**	**-45.9991**
CCSD//6-311++G**	**35.92805**	**-101.572**	**103.1764**	**-34.3236**
G4	**35.71282**	**-101.787**	**84.91144**	**-52.5886**
Expt	**137.5**	**NA**	**137.5**	**NA**

3.4. FCN

The difference between the computed and the experimental values for FCN is presented in table 4, with geometries as shown in Fig 4a-d for the neutral molecule and protonated species. Considering the consistency and accuracy of the computational method, errors recorded by FCN is way higher compared to other similar tri-atomic species reported by (Etim *et al*., 2018) such a large difference could possibly be pointing out that experimental values shrouded some errors

Table 4. PA values for FCN

Method	Proton attached to F atom		Proton attached to C atom		Proton attached to N atom	
	PA (kcal/mol)	Error	PA (kcal/mol)	Error	PA (kcal/mol)	Error
HF/6-311++G**	65.08026	-86.0197	93.22469	-57.8753	93.22469	-57.8753
B3LYP/6-311++G**	69.37619	-81.7238	163.6093	12.50929	163.5873	12.48733
MP2/6-311++G**	73.36778	-77.7322	161.5065	10.4065	162.2595	11.15952
MP2/cc-pVDZ	76.48901	-74.611	164.5248	13.42483	164.5248	13.42483
CCSD//6-311++G**	77.08954	-74.0105	-118.01	-269.11	-118.055	-269.155
G4	75.51449	-75.5855	170.1059	19.00589	170.0306	18.93059
Expt	151.1	NA	151.1	NA	151.1	NA

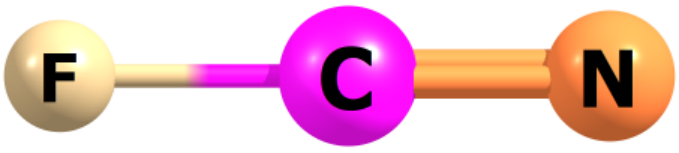

Fig. 4a: Optimized geometry for FCN

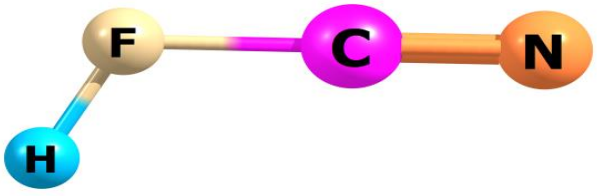

Fig. 4b: Geometry for protonation at F

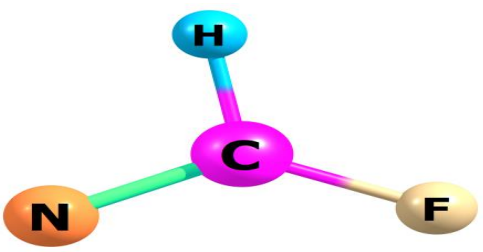

Fig. 4c: Geometry for protonation at C

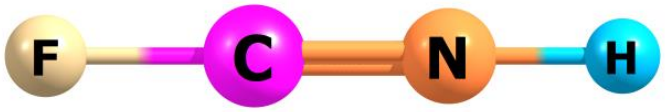

Fig. 4d: Geometry for protonation at N

3.5. CH_3Cl

Insight into results obtained from the quantum chemical calculations carried out on CH_3Cl as shown in table 5 and fig. 5a-c reveals that the experimental value must probably accommodate some form of error. As shown in the table, most of the computed values are within the same range while the experimental value seems quite high. The value with the least error differs by a magnitude of 20.7261 kcal/mol and so do others.

Table 5. *PA values for CH_3Cl*

Method	Proton attached to Cl atom		Proton attached to C atom	
	PA (kcal/mol)	Error	PA (kcal/mol)	Error
HF/6-311++G**	**133.9739**	**-20.7261**	**109.0825**	**-45.6175**
B3LYP/6-311++G**	**118.9833**	**-35.7167**	**114.2939**	**-40.4061**
MP2/6-311++G**	**115.3318**	**-39.3682**	**114.3517**	**-40.3483**
MP2/cc-pVDZ	**117.4133**	**-37.2867**	**114.2814**	**-40.4186**
CCSD/6-311++G**	**123.0352**	**-31.6648**	**114.9591**	**-39.7409**
G4	**120.7429**	**-33.9571**	**116.6226**	**-38.0774**
Expt	**154.7**	**NA**	**154.7**	**NA**

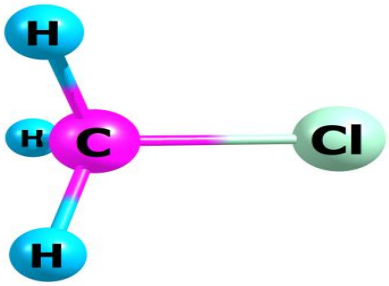

Fig. 5a: Optimized geometry for CH_3Cl

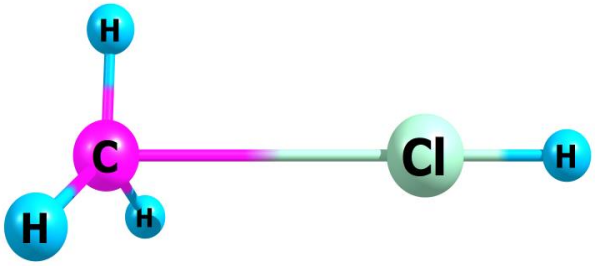

Fig. 5b: Geometry for protonation at Cl

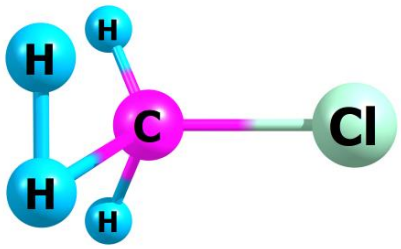

Fig. 5c: Geometry for protonation at C

3.6. CH3Br

A supporting statement that the experiment shrouded some errors (either random or systematic) is as evident in table 6. All computed values lie within a close range (110-130 kcal/mol) while the experimental value of 158 kcal/mol is higher. The PA value for CH3Br and CH_3Cl is within the range than does their experimental value. This could possibly be pointing towards error as the experimental value is higher while computed values are lower and even though obtained from six different computational methods still show a great level of agreement.

Table 6. PA values for CH3Br

Method	Proton attached to Br atom		Proton attached to C atom	
	PA (kcal/mol)	Error	PA (kcal/mol)	Error
HF/6-311++G**	**130.1423**	**-28.5577**	**110.6481**	**-48.0519**
B3LYP/6-311++G**	**115.5295**	**-43.1705**	**116.6019**	**-42.0981**
MP2/6-311++G**	**111.2662**	**-47.4338**	**115.9995**	**-42.7005**
MP2/cc-pVDZ	**113.406**	**-45.294**	**116.1727**	**-42.5273**
CCSD/6-311++G**	**119.3743**	**-39.3257**	**116.8667**	**-41.8333**
G4	**117.8218**	**-40.8782**	**118.5234**	**-40.1766**
Expt	**158.7**	**NA**	**158.7**	**NA**

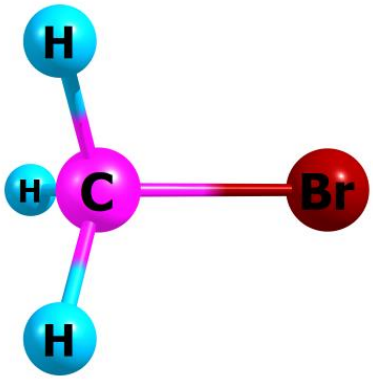

Fig. 6a: Optimized geometry for CH_3Br

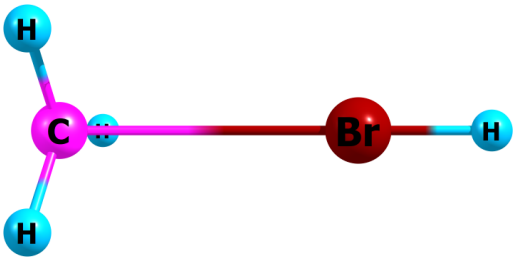

Fig. 6b: Geometry for protonation at Br

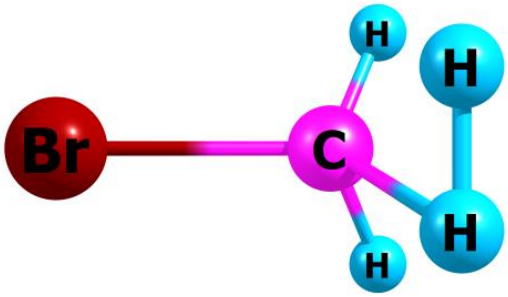

Fig. 6c: Geometry for protonation at C

3.7. Methanethiol (CH_3SH)

Table 7 contains the computational and experimental value of CH_3SH, its geometries are as shown in fig. 7a-c for both the neutral and protonated analogues. A critical look at the table reveals that a higher precision is observed amongst the six different computational methods (158-160kcal/mol) and (149-152kcal/mol) at both site of protonation while experimental values of 184.8 is too high, pointing out a possible error in the experiment.

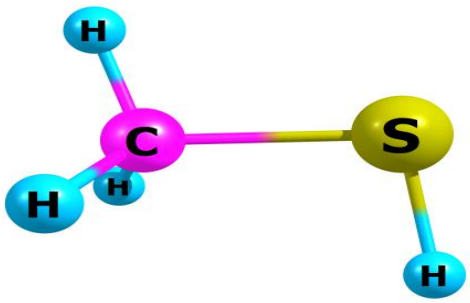

Fig. 7a: Optimized geometry for CH_3SH

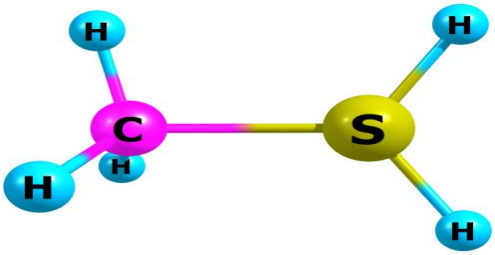

Fig. 7b: Geometry for Protonation at S

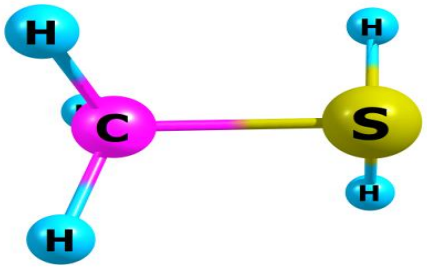

Fig. 7c Geometry for protonation at C

Table 7. PA values for CH_3SH

Method	Proton attached to S atom		Proton attached to O atom	
	PA (kcal/mol)	Error	PA (kcal/mol)	Error
HF/6-311++G**	**159.0109**	**-25.7891**	**150.0915**	**-34.7085**
B3LYP/6-311++G**	**158.0301**	**-26.7699**	**149.72**	**-35.08**
MP2/6-311++G**	**157.9768**	**-26.8232**	**151.1269**	**-33.6731**
MP2/cc-pVDZ	**157.855**	**-26.945**	**149.437**	**-35.363**
CCSD/6-311++G**	**159.8235**	**-24.9765**	**153.3232**	**-31.4768**
G4	**160.3582**	**-24.4418**	**152.215**	**-32.585**
Expt	**184.8**	**NA**	**184.8**	**NA**

Cases where the Computational methods have accurately calculated the PA values

Having shown errors in some experimentally measured proton affinity (PA) values of some molecules, it is pertinent at this point to show cases where our computational methods have been able to accurately calculate the PA values thus, the following are molecules whose computed PA values corresponds with the experimentally measured PA and also provides insight towards validating our earlier conjectures:

3.8. Carbon (ii) Oxide (CO)

In this new study on the protonation of carbon (ii) oxide (CO) using the computational method gave PA values that corresponds more to the experimentally determined value when proton is attached to the Carbon atom of the molecule as shown in table 8 and the optimized geometries in Figure 8a-c. The values ranges from 136 kcal/mol – 144 kcal/mol with the G4 composite method giving a near perfect value of 142.9303 kcal/mol while the experimentally measured value is 142.0 kcal/mol. This means this method can be employed in the determination of PAs of other molecules generally having given a perfect prediction; this finding has further given insights for suspecting errors in the PA of the above listed molecules.

Table 8: Proton Affinity values for CO

Method	Proton attached to O atom		Proton attached to C atom	
	PA (kcal/mol)	**Error**	**PA (kcal/mol)**	**Error**
HF/6-311++G**	106.1652	35.83481	136.2034	5.79656
B3LYP/6-311++G**	101.9784	40.02155	140.1423	1.857683
MP2/6-311++G**	97.63483	44.36517	144.6089	-2.60893
MP2/cc-pVDZ	98.9984	43.0016	144.6842	-2.68423
CCSD//6-311++G**	104.9516	37.04841	142.6536	-0.65361
G4	107.9655	34.03449	142.9303	-0.93034
Expt	142.0	NA	142.0	NA

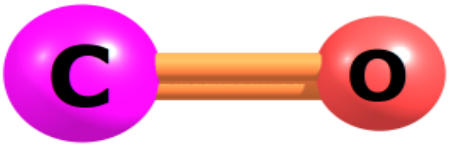

Fig. 8(a): Optimized geometry for CO

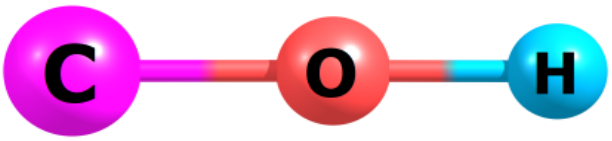

Fig. 8(b): Geometry for protonation at O

Fig. 8(c): Geometry for protonation at C

3.9. Silicon Tetraflourde (SiF_4)

In a related study by (Etim *et al*., 2020b), quantum chemical studies was carried out on SiF_4 and its protonated analogues, table 9 contains the results obtained for this studies with the geometries as shown by figure 9a-c. The experimentally measured PA for SiF_4 as recorded by the NIST chemical web book is 120.2 kcal/mol when proton was attached to F atom and the values obtained computationally has a good match with the right range of 113.181 – 122.563 kcal/mol. Six ab-initio composite methods were employed in the studies and the G4 level of theory stand out as the best method with the least error of -2.363 kcal/mol. If these methods can be so accurate in computation, it means the values obtained and presented in the above suspected molecules are actually wrong in the experimental determination and calls for in-depth reconsideration by the experimental analysts or adopting the computationally obtained values.

Table 9: Proton affinity values for SiF_4 (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

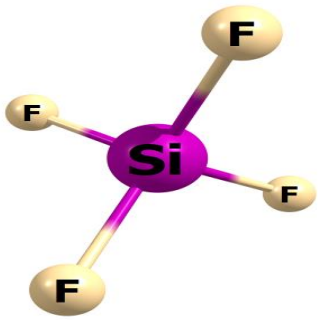

Fig. 9a: Optimized structure of SiF_4.

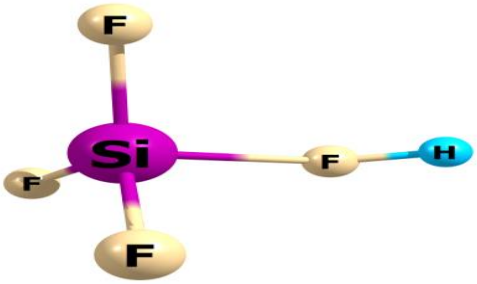

Fig. 9b: Optimized structure of $HSiF_4^+$.

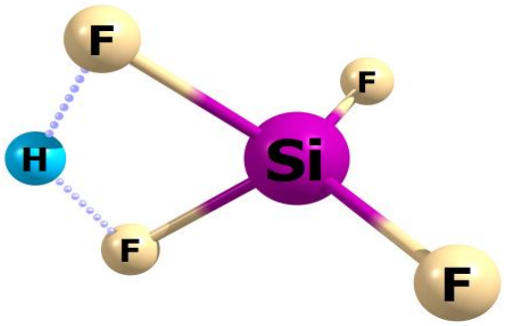

Fig. 9c: Optimized structure of HF_4Si^+.

3.10. Sulphur Trioxide (SO_3)

Another studies carried out on SiF_3 as presented in table 10, (Etim *et al*., 2018), obtained values very much in good agreement with the experimental value. The experimental value for SiF_3 from NIST is 140.6 kcal/mol while the computed values from six different computational methods ranges from 139.6 – 151.1 kcal/mol when proton was attached to O atom with the best method being the B3LYP/6-311++G** giving a value of 140.2 kcal/mol with the least error of 0.4 kcal/mol. The outstanding accuracy of the computational methods in this studies contributes towards affirming the authenticity of such computational methods in measuring the PA of molecules and serves as a basis for suspecting errors in experimental values that are too wide away from the computational methods

Table 10: Calculated proton affinities (PA) (kcal/mol) of sulphur trioxide

Method	Proton attached to O atom		Proton attached to S atom	
	PA	Error	PA	Error
HF/6-311++G**	139.6	1.0	-16.3	156.9
B3LYP/6-311++G**	140.2	0.4	11.7	128.9
MP2/6-311++G**	143.4	-2.8	13.7	126.9
MP2/cc-Pvdz	149.7	-9.1	25.3	115.3
CCSD/6-311++G**	151.1	-10.5	24.2	116.4
G4	146.4	-5.8	18.5	122.1
Expt. [29]	140.6		140.6	

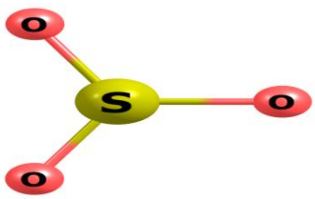

Fig. 10a: Optimized Geometry of SO_3

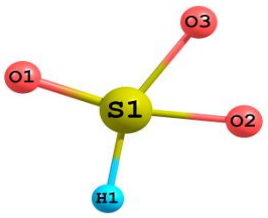

Fig. 10b: Optimized geometry of HSO_3^+

Fig. 10c: Optimized geometry of $HOSO_2^+$

3.11. 1, 2-Butadiene, C_4H_6

A similar scenario is observed in Table 11, figure 11a-c which contains the PA values and geometries of 1, 2-Butadiene, C_4H_6 respectively, the values obtained during the studies were quite closer to the experimental value especially the HF/6-311++G** method which gave a value of 185. 9078 kcal/mol as against the experimental value of 186.2 kcal/mol, the error recorded here was just 0.29216 kcal/mol. The calculation was also approximately accurate, meaning computational methods can serve as substitute for the measurement of PA of molecules.

Table 11: PA values for 1, 2-Butadiene, C_4H_6

Method	Proton attached to C4 atom		Proton attached to C3 atom		Proton attached to C1 atom		Proton attached to C2 atom	
	PA (kcal/mol)	Error	PA (kcal/mol)	Error	PA (kcal/mol)	Error	PA (kcal/mol)	Error
HF/6-311++G**	191.6226	5.422567	208.4128	22.21284	185.9078	-0.29216	166.5812	-19.6188
B3LYP/6-311++G**	184.8423	-1.35767	198.5572	12.35717	179.6127	-6.58734	159.7915	-26.4085
MP2/6-311++G**	183.4907	-2.70933	194.7676	8.567644	174.9754	-11.2246	153.9714	-32.2286
MP2/cc-pVDZ	184.6547	-1.5453	197.1898	10.98983	176.3502	-9.84976	154.5631	-31.6369
CCSD/6-311++G**	184.9553	-1.24472	199.6365	13.43649	180.35	-5.85001	157.8952	-28.3048
G4	189.8197	3.619732	203.2051	17.00514	184.3435	-1.85654	164.351	-21.849
Expt	186.2	NA	186.2	NA	186.2	NA	186.2	NA

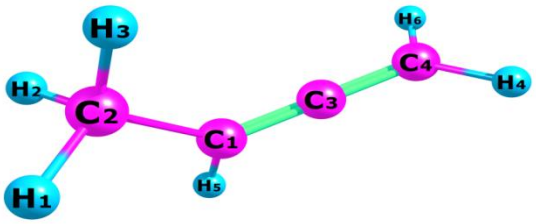

Fig. 11a: Optimized geometry for 1, 2-Butadiene

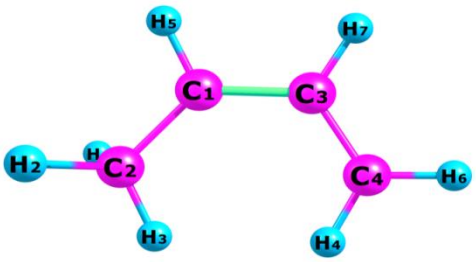

Fig.11b: Geometry for the protonation at C3

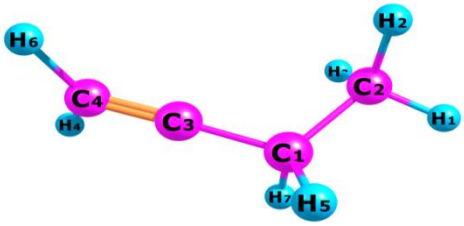

Fig.11c: Geometry for the protonation at C1

4. Conclusions

Based on insights and deductions from quantum chemical calculations carried out using six different high level Ab-initio computational methods, proton affinities (PA) were calculated, we have reported a suspected error in the experimentally determined PA for the following: FCN, OF, NO, CH3Br, CH3Cl, SF6. The experiment could have shrouded the error randomly or systematically and such calls for an in-depth look into the experiment. To buttress this assertion, cases were the same computational methods have accurately estimated the PA values of other molecules like CO, SiF_4, SiF_3, 1, 2-Butadiene, C_4H_6 have also been shown. The ability of the computational methods to provide opportunity to attached proton to a specific site during protonation is an added advantage over experimental procedures which is not possible but is rather randomly open to any site whether suitable or not and as such predisposes some determinations to error, such cases have been recorded using the computatioinal methods were protonoation at some sites is not suitable as seen on the various tables.

References

[1] B. Ulrich and N.L. Allinger, *molecular mechanics,* American Chemical Society, Washington D.C., 1982, vol.177 of ACS monographs.

[2] Bartlett, R.J. Coupled-cluster approach to molecular structure and spectra: a step toward predictive quantum chemistry. *J. phys. chem*. 1989, 93: 1697-1708

[3] Bell S, Chowdhry B.Z., Dines T.J., Withnall R., Computational Chemistry Using Modern Electronic Structure Methods *J. Chem. Ed.*, 2007, 84: 1364-1368

[4] Bohme D.K.; Schiff H.I.; Mackay G.I.; On the protonation and proton affinity of SF_6 *International Journal of Mass Spectrometry and ion processes*, 1992, DOI: 10.1016/0168-1176 80104-9

[5] Castella-Ventura M., Kassab E., Buntinx G., Poizat O., Procedure for Quantum Chemical Calculations. *Phys. Chem. Chem. Phys.*, 2000, 2: 4682.

[6] Darin R. Latimer and Mark A. Smith, Direct observation of HSF^+_6 the bracketing of the SIF_6 proton affinity at 5K. *J. Chem. Phy.* 1994, 101: 3410 doi: 10.1063/1.467590

[7] Etim E. Emmanuel; Sulaiman Adeoye Olagboye; Oko Emmanuel Godwin; Irene Mfoniso Atiatah; Quantum Chemical studies on Silicon tetrafluoride and its protonated analogues. *Int. J. Modern Chem.*, 2020b, 12(1): 26-45 ISSN: 2165-0128.

[8] Etim Edet Emmanuel, Chrysanthus Andrew, Usman Lawal, Ifeoma Sandra Udegbunam and Etiowo George Ukpong. Protonatioin of Carbonyl Sulfide: Ab-initio study. *J. Applied Sci.*, 2020a, 20: 26-34

[9] Etim E.E and E. Arunan, Rotational Spectroscopy and Interstellar molecules. *Planex Newslett*., 2015, 5: 16-21

[10] Etim E.E., Oko, G.E., Onen, A.I., Ushie, O.A., Andrew, C., Lawal, U., Khanal, G.P., Computational studies of sulfur Trioxide (SO3) and its protonated analogues, *J. Chem. Soc. Nigeria*, 2018,. 43(2): 10-17

[11] Etim, E.E., Abah, B.S., Mbakara, I.E., Inyang, E.J. and Ukafia, O.P. Quantum Chemical Calculations on Silicon Monoxide (SiO) and its Protonated Analogues. *Tropical Journal of Applied Natural Sciences*, 2017, 2(1): 61-68. doi: https://doi.org/10.25240/TJANS.2017.2.1.10.

[12] Etim, E.E., Arunan, E. interstellar isomeric species, energy, stability and abundance relationship. *Eur. Phys. j. plus*, 2016, 131, 448 https://doi.org/10.1140/epje/i2016-16448-0

[13] Etim, E.E., Oko, G.E., Onen, A.I., Ushie O.A., Andrew, C., Lawal, U., Khanal, G.P., Computaational Studies of Sulphur trioxide (SO_3) and its protonated analogues. *J. Chem. Soc. Nigeria*, 2018, 43(2): 10-17

[14] Fernando Ruiperez. Application of quantum chemical methods in polymer chemistry. *International review in physical chemistry*. (2019),38 (3-4):343-403 DOI:10.1080/0144235X.2019.1677062

[15] Frisch, M.J., Toucks, G.W., Schlegel, H.B., Scuseria G.E., Robb, M.A., Cheeseman, J.R., Scalmani, G., Baron, V., Mennucci, B., Peterson, G.A., *Gaussian 09 revision D.01*; Gaussian, Inc., Wallingford, CT. 2009.

[16] Hohenberg, P. and Kohn, W. Inhomogenous electron Gas, *phys. Rev.* 1964, 136, B864-B871

[17] Ilya Kuselman, Pennecchi, Francesca, Fajgel, Ales, Karpov, Ywry. Human errors and reliability of test results in analytical chemistry. *Accreditation and quality assurance.* 2013, 18(1): 3-9 DOI:10.1007/S00769-012-0934-Y

[18] Jensen, frank. *Introduction to computational chemistry*. John Wiley and sons. Chichester, England: 2007, Pp. 98-149 ISBN 978-0-470-01187-4

[19] Johnson ,B.G., Gille, P.M.W and Pople, J.A the performance of a family of density functional methods *J. chem. Phys.* 1993, 98, 5612-5626

[20] KatrinWeigmann. The consequences of errors. The European Molecular Biology Organisation 2005, 6(4): 306-309 doi: 10.1035/sj.embor.7400389

[21] Kazazic, Snjezana; Klasinc, Sean; Pryor, W.A. proton affinity of nitrogen oxyradicals, *croticaChemicaActa* 2004, 77(3): 465-468

[22] Leach, Dr Andrew (2001). Molecular modelling: principle and application (2 ed). Harlow: Prentice Hall. ISBN 9780582382107

[23] Leach, Dr Andrew. *Molecular modelling: principle and application* (2 ed). Harlow: Prentice Hall. 2001, ISBN 9780582382107.

[24] NIST data base. Retrieved on 26/12/2017

[25] Parr, R.G. on the genesis of a theory, *int. J. Quantum Chem.* 1990, 37(4):327-347. Doi:10.1002/qua.560370407

[26] Paul L. Edmiston and Theodore R. Williams. An analytical laboratory experiment in error analysis: repeated determination of glucose using commercial glucometers. *J.chem.edu.* (2000) 77,3, 377 doi: 10.1021/ed077p377

[27] Stanley Sandler, Amadeu K. Sun, ShiangTailin, some chemical engineering application of quantum chemical calculations. *Advances in chemical engineering,* (2001), 28:313-351 DOI:10.1016/50065-2377()0128010-7.

[28] Szabo and N.S. Osttund. *Modern quantum chemistry: introduction to advance electronic structure theory*. McGrawttill, New York, 1989, pp 2-98.

[29] T. Helgaker. *High accuracy quantum chemistry LCT*, UPMC, Paris, France, (2012), pp 1-40.

[30] Theresa Sperger, Italo A. Sanhueza and Franziska Schoenebeck. Computation and experiment: a powerful combination to understand and predict reactivities. *Am. Chem. Soc.* 2016, 49(6): 1311 - 1319 htttps:// doi.org/10.1021/acs.accounts.6b00068

[31] Yaoquan Tu, AattoLaaksoner, "combining quantum mechanics molecular mechanics" some recent progress in QM/MM modelling methods. *Advance in quantum chemistry,* 2010.