J. Chem Soc. Nigeria, Vol. 43, No. 2, pp 42 - 49 [2018]

Computational Studies of Sulphur Trioxide (SO_3) and its Protonated Analogues

Etim, E. E[1*].,Oko, G. E[1], Onen, A. I[1]., Ushie, O. A[1]., Andrew, C[1]., Lawal., U[1]., Khanal, G. P[2]

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

[2]Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore

Corresponding Author's Email: emmaetim@gmail.com

Received 22 September 2017; accepted 23 December 2017, published online 10 February 2018

Abstract

This article reports quantum chemical calculations on sulphur trioxide (SO_3) and its protonated analogues (HSO_3^+ and $HOSO_2^+$) by employing six different computational methods. This covers the simple Hatree Fock (HF) method, coupled cluster method, the Gaussian-4 (G4) compound method amongst others with two different basis sets (6-311++G** and cc-pVDZ). Optimized geometries, bond distance, rotational spectroscopy, dipole moment, proton affinity, vibrational spectroscopy and vibrational zero-point energy are among the parameters that have been effectively and successfully computed for the three molecular species under investigation. From the result obtained, there is a perfect agreement between the different parameters investigated and the available experimental values. The high accuracy of the calculated results gives a good image of the protonated analogues (HSO_3^+ and $HOSO_2^+$) which are deficient in experimental data. The optimized geometry reveals that two of the three molecular species (i.e. SO_3 and $HOSO_2^+$) have a trigonal geometry in all the computational methods employed while HSO_3^+ analogue was discovered to have a square planar geometry for MP2/6-311++G**, MP2/cc-pVDZ, CCSD/cc-pVDZ and G4 methods. We found that the proton affinities (PA) of SO_3 was between 139.6 – 151.1 kcal/mol with B3LYP/6-311++G** method predicting the best result and that S-protonation was by far the most favoured site for proton attachment. Thus, the present quantum chemical studies have helped in bridging the gap existing in the literature regarding this species since they are less studied experimentally due to their unstable nature.

Keywords: Protonation, Silicon trioxide, Quantum chemistry, Spectroscopy

Introduction

Computational methods are rapidly becoming a mainstay in the field of chemistry. Advances in computational methods, increasing availability of computational resources and the advancement of parallel computing are some of the major forces driving this trend. The application of quantum mechanics in computational chemistry is its ability to describe effectively the behaviors of relatively small systems (e.g. electrons) and finding solutions to chemical problems. As such, quantum mechanics is the basis in which most computational chemistry is built upon. Computational chemistry today has been applied in the field of IR spectroscopy to elucidate the chemical structure of some molecules [1-6]. It is based upon the fundamental laws of quantum mechanics and uses variety of mathematical transformation and approximation techniques to solve the fundamental equations. Thus, one of the main goals of computational chemistry is to calculate macroscopic chemical quantities that we observe in the laboratory. In other words, the model chemistry has the capability to predict some experimental properties to a certain degree of accuracy. With computational chemistry, physical properties and quantities that are difficult or even impossible to observe experimentally for chemical systems can be predicted.

Sulfur trioxide is a colourless to white solid crystals which is always shipped with inhibitor for polymerization prevention. The molecule SO_3 is of environmental and industrial importance and has been the subject of a number of infrared studies [7-9]. It is an intermediate in the oxidation of numerous sulphur containing compounds [10]. As an acidic oxide, it reacts violently with water to produce tetraoxosulphate (VI) acid with the release of heat and play a significant role in atmospheric chemistry since it contributes to the formation of acid rain [7]. In the gaseous form, it is significantly a pollutant. It is prepared by reversible and exothermic conversion of sulfur (IV) oxide (SO_2) to sulfur trioxide (SO_3) in the presence of a catalyst usually vanadium (V) oxide (V_2O_5) during the contact process.

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{V_2O_5} 2SO_{3(g)} \ldots\ldots(1)$$

Protonation is the addition of proton (usually hydrogen) to either an atom or a molecule and results in the formation of molecular ion. Protonated species are known to play a key role for ion-molecule reactions in gas phase interstellar chemistry [11]. The protonation products formed in many molecules remain a "controversial" as regards to which particular atom in the molecule the H-atom is attached to. This is because the mass spectrometry is so silent on the actual atom the protonation usually takes place. However, using computational method, it is possible to indicate which atom in the molecule is more favoured for the protonation process.

In this paper, we have utilized a highly sophisticated quantum chemistry program; the Gaussian-09 suite of program to perform a complete geometry optimizations for sulphur trioxide and its protonated analogues. Protonated molecules are less studied experimentally due to their reactive nature even with standard spectroscopic techniques. Therefore, using computational methods, it is possible to provide valuable information that would aid their experimental study. Thus, in this research work, different computational methods have been used to predict some properties (e.g. IR frequency, bond distance, rotational constant, proton affinity, dipole moment etc.) with the view to compare the result with experimental data where available for these species of molecules.

Computational Methods

All computational study in this work was carried out using the Gaussian 09 suite of programs [12] with Hartree Fock (HF), Hybrid functional (Becke, 3-parameter, Lee-Yang-Parr, B3LYP), Møller–Plesset perturbation theory (MP2), Gaussian 04 (G4) compound and Coupled Cluster Single-double (CCSD) methodologies [13-17]. We have employed two basis sets in this research; triple size basis set (6-311++G**) and Dunning's correlation-consistent polarized valence double zeta (cc-pVDZ) [18-20]. The choice of these methods is based on experience as some methods perform well for some properties than other methods. Thus there is need for comparison of methods to determine which is better to predict well a particular parameter. In each case, care was taken that all the reported optimized structures are for stable molecules with no imaginary (negative) vibrational frequencies. The vibrational frequencies were used without scaling

Results and Discussion

The various parameters obtained from the quantum chemical calculations carried out in this study for silicon trioxide (SO_3) and two of its possible protonated analogues; (HSO_3^+ and $HOSO_2^+$) using the different computational methods are discussed under separate sub-headings as follows. In some section of the discussion, we have used 1=HF/6-311++G**; 2=B3LYP/6-311++G**; 3=MP2/6-311++G**; 4=MP2/cc-pVDZ; 5=G4; 6= CCSD/cc-pVDZ to represent the computational methods. Error have been determined as Δ = Cal. value – Expt. value.

Optimized geometries of sulphur trioxide and its protonated analogues: Figures 1 to 3 respectively displays the optimized structures at the B3LYP/6-311++G** level for SO_3, HSO_3^+ and $HOSO_2^+$.

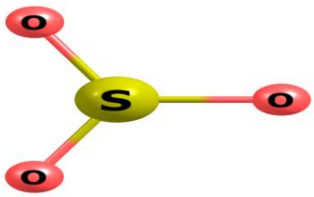


Figure 1: Optimized Geometry of SO_3

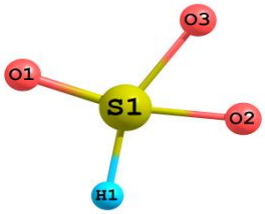


Figure 2: Optimized geometry of HSO_3^+

Figure 3: Optimized geometry of $HOSO_2^+$

Furthermore, other optimized geometries for SO_3, HSO_3^+ and $HOSO_2^+$ at different computational methods are presented in the appendix. All tetra atomic molecular species with three atoms bonded to a central atom have a trigonal geometry as can be observed for SO_3 in all the six methods (figures 1a to 1f in the appendix). It is quite amazing that, the two protonated analogues are not the same for all the computational methods which described the neutral molecule as trigonal. The $HOSO_2^+$ protonated analogue was found to be trigonal for all the six methods while HSO_3^+ analogue was discovered to have a square planar geometry for MP2/6-311++G**, MP2/cc-pVDZ, CCSD/cc-pVDZ and G4 methods (figures 2c to 2f in the appendix). Since these methods have been able to describe and predict correctly the molecular geometry of the neutral molecule (SO_3) with known experimental values, it therefore suggest that the molecular description and calculation for its protonated analogues ($HOSO_2^+$, HSO_3^+) are also correct and acceptable at the determined levels of theory.

Bond Distance: The S-O bond distances obtained for sulphur trioxide with the six different computational methods are presented in table 1. In the present study, the difference between the experimental and calculated S-O bond distances in SO_3 molecule range from 0.014 to 0.242 Å. It is clear from table 1 that the methods used fairly predicted the S-O bond distance in the SO_3 molecule. However, the G4 level of theory gave the best prediction for the bond length and the calculated value agrees well with the experimental value of 1.418 Å [21]. Furthermore, table 1contains the corresponding H-S and S-O bond distances for the two protonated analogues. The accuracy obtained in the calculated S-O bond length in the neutral molecule with known experimental data suggest that the values for the calculated corresponding H-S and S-O bond distances for the two protonated analogues are accruate.

Rotational Spectroscopy: Rotational spectroscopy has a restricted but unique application unlike other spectroscopic techniques. It is employed in the chemical examination of interstellar medium (the matter that exists in the space between stars) as majority of the known interstellar molecular species are astronomically observed via their rotational transitions [22].

Table 1: Bond length (Å) for SO_3 and its protonated analogues

Molecule	Bond length	Methods					
		1	2	3	4	5	6
SO_3	S-O	1.397	1.447	1.449	1.471	1.432	1.660
	Error	0.021	0.029	0.031	0.053	0.014	0.242
HSO_3^+	H-S	1.353	1.387	1.372	1.380	1.381	1.378

$HOSO_2^+$	H-O	0.965	0.987	0.985	0.992	0.987	0.960

Table 2a contains the rotational constants of SO_3. Its experimental rotational constants are less compared to the calculated values but the MP2/cc-pVDZ gave the best prediction for the A rotational constant, this is followed by the CCSD/cc-pVDZ method for the B and C rotational constants. To the best of our knowledge, there are no scientific reports on the experimental spectra/rotational constants for HSO_3^+ and $HOSO_2^+$ because of the unstable nature of these ions [23]. The rotational constants for HSO_3^+ and $HOSO_2^+$ obtained from the six different computational methods employed in this study are presented in table 2b. The MP2/cc-pVDZ method is expected to produce the best prediction for the two protonated analogues. Since this same method (MP2/ cc-pVDZ) was able to give a good prediction for the neutral molecule with known experimental rotational constants, suggesting that the calculated values obtained from this computational methods are accurate enough to guide the laboratory studies and possible astronomical searches for this unstable molecular species.

Table 2a: Rotational Constants (GHz) for SO_3

Rot. Const. (GHz)	Methods					
	1	2	3	4	5	6
A	10.79426	10.06480	10.03521	9.74194	10.27325	14.43296
Δ	0.34519	-0.38427	-0.41386	-0.70713	-0.17582	3.98389
B	10.78685	10.06008	10.02987	9.73837	10.27116	5.71734
Δ	0.33778	-0.38899	-0.4192	-0.7107	-0.17791	-4.73173
C	5.39528	5.03122	5.01627	4.87008	5.13610	4.09513
Δ	0.17925	-0.18481	-0.19976	-0.34595	-0.07993	-1.1209

Expt. values; A=10.44907 GHz, B=10.44907 GHz, C=5.21603 GHz [21]

Table 2b: Rotational Constants (GHz) for HSO_3^+ and $HOSO_2^+$ protonated analogue

Molecule	Rot. Const.	Methods					
		1	2	3	4	5	6
HSO_3^+	A	21.71000	19.60232	18.76992	18.39668	19.99894	19.15755
	B	6.84656	6.29331	6.28217	6.04891	6.44027	6.18672
	C	5.20507	4.76387	4.70683	4.55214	4.87150	4.67650
$HOSO_2^+$	A	10.41571	9.71350	9.80638	9.54735	9.92452	-
	B	9.94238	9.21887	9.09824	8.79418	9.38816	-
	C	5.08677	4.72986	4.71952	4.57765	4.82444	-

Dipole Moment: Dipole moment plays a central role in rotational spectroscopy. Molecules that are IR active must be associated with a change in the dipole moment [24]. Provided there is a dipole moment change during a normal molecular vibration, molecular rotation, and or from combinations of the latter, chemical compounds that absorb IR and are said to be IR active. The dipole moment as presented in table 3 for SO_3, the neutral molecule has no experimental dipole value because it has D_{3h} symmetry. In this study, the G4 method calculated the dipole moment with a value of 0.0009 D which agrees well with the experimental value of zero conforming to a molecule with D_{3h} symmetry. There are also no experimental information regarding the dipole moments of the protonated analogues because of their instability. Table 3 also contains the dipole moment for these ions (HSO_3^+ and $HOSO_2^+$). Since the G4 method gives the best prediction for the neutral molecule and still gives the best values or the least values for the protonated

analogues, the values from the G4 method are believed to be very accurate [24-26].

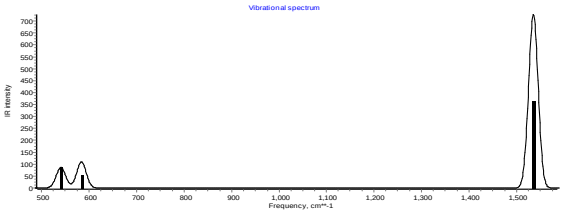
Table 3: Dipole moment (Debye) of SO_3 and its protonated analogues

Mol	Methods					
	HF/6-311++G**	B3LYP/6-311++G**	MP2/6-311++G**	MP2/cc-pVDZ	G4	CCSD/cc-pVDZ
SO_3	0.0049	0.0011	0.0028	0.0028	0.0009	
HSO_3^+	3.6401	3.3757	3.7434	3.7564	3.2682	3.2431
$HOSO_2^+$	3.4693	3.1806	3.3584	3.2191	3.3826	

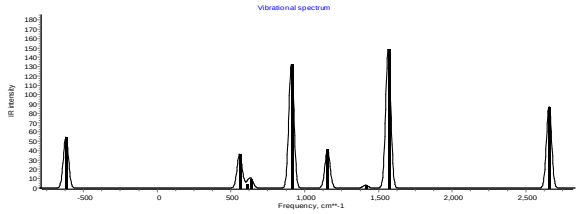
Vibrational Spectroscopy: According to the NIST Website, SO_3 is a non-linear molecular specie with expected six vibrational modes with only four of these detected experimentally as shown in table 4 which also contains the calculated values. For the neutral molecule the error between the experimental and calculated values are given in bracket. The values predicted by the B3LYP/6-311++G** is in excellent agreement with the experimental values which is closely followed by the MP2/cc-pVDZ method [27]**.** This means that the protonated analogue with no experimentally determined vibrational frequencies can be effectively predicted by this method. Table 4 contains the vibrational frequencies of HSO_3^+ and $HOSO_2^+$ using the six different methods employed in this study. They all have nine vibrational modes as expected and the B3LYP/6-311++G** method is suggested to be more accurate since it predicted the experimental values with a high degree of accuracy [28]. Figures 4a, 4b and 4c depict the infrared spectra of SO_3, HSO_3^+ and $HOSO_2^+$ respectively. From the NIST website, the vibrational zero-point energy (VZPE) has been experimentally measured as 7.72143 kcal/mol. As presented in table 5, the G4 method gave a more accurate prediction with a value of 7.68436 kcal/mol which is in good agreement with the experimental value. As would be expected, no experimental data involving vibrational zero-point energy is available for the protonated analogues (HSO_3^+ and $HOSO_2^+$) but the computed values are also shown in table 5. The values predicted by the G4 method are assumed to be accurate since it gave a better prediction of the neutral specie [29-30].

Table 4: Vibrational frequencies (cm^{-1}) for So_3 and its protonated analogues

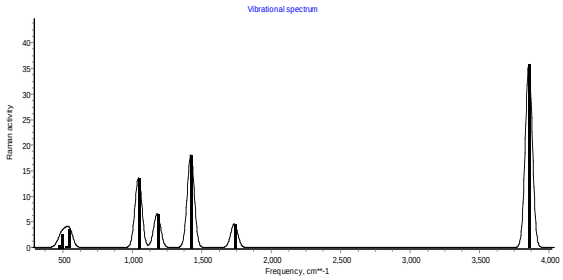
Molecule	Methods	Frequency (cm^{-1})								
SO_3	HF/6311++G**	541()		584	584		1212	1535		1536
	B3LYP/6311++G**	442		496	496		1016	1328		1328
	MP2/6311++G**	421		495	495		1015	1373		1374
	MP2/cc-pVDZ	464		488	488		1004	1370		1371
	G4	489		517	518		1063	1394		1395
	Expt. [31]	498		530	530		1065	1391		1391
HSO_3^+	HF/6311++G**	619	559	607	634	910	1155	1413	1567	2659
	B3LYP/6311++G**	513	471	489	557	744	926	1203	1298	2358
	MP2/6311++G**	455	470	516	683	843	915	1276	1276	2494
	MP2/cc-pVDZ	379	460	616	690	873	953	1185	1257	2532
	G4	495	506	540	630	770	983	1227	1356	2394
	CCSD/cc-pVDZ	484	493	547	621	709	926	1239	1288	2533
$HOSO_2^+$	HF/6311++G**	471	499	527	548	1046	1181	1423	1735	3855
	B3LYP/6311++G**	377	423	459	477	863	1092	1213	1497	3549
	MP2/6311++G**	358	427	455	469	890	1101	1219	1541	3608
	MP2/cc-pVDZ	412	414	443	498	887	1131	1209	1510	3565
	G4	432	437	474	511	918	1119	1263	1542	3559



IR spectrum of SO_3



IR Spectrum of HSO_3^+



IR spectrum of $HOSO_2^+$

Figure 4: IR spectrum of SO_3 and its protonated analogues at HF/6-311++G** level

Table 5: Zero-point vibrational energy (ZPVE) (kcal/mol) for SO_3 and its protonated analogues

molecule	Methods	HF/6-311++G**	B3LYP/6-311++G**	MP2/6-311++G**	MP2/cc-pVDZ	CCSD/cc-pVDZ	G4
SO_3	ZPVE	8.56543	7.30037	7.39491	7.41118	-	7.68436
	Error	0.84400	0.42106	0.32652	0.31025	-	0.03707
HSO_3^+	ZPVE	13.58346	11.50259	12.04354	12.24496	11.94559	12.01350
$HOSO_2^+$	ZPVE	16.13013	14.22428	14.39391	14.39426	-	14.65941

Protonation of sulphur trioxide

The protonation of sulphur trioxide in principle can either be through sulphur atom (figure 2) or oxygen atom (figure 3). Table 6 reports the proton affinities (PA) at two different sites calculated using different levels of theory and the deviation from experimental value. Firstly, a comparison between the two different sites of protonation (i.e. sulphur and oxygen atom) reveals that the S-protonation is most favoured process. This can be deduced from the results of the calculated PA values at two different sites using the different computational methods. It is clear that the PA for S-protonation is higher than O-protonation hence the most favoured site for proton attachment. In other words, PA corresponds to the most stable protonated analogue with proton attached to the site of highest electron density and in this case sulphur atom. A comparison of the methods used with experimentally observed value (140.6 kcal/mol, NIST data base) reveals that the B3LYP/6-311++G** method predicted the best PA value (140.2 kcal/mol) for the protonation of SO_3 while the HF/6-311++G** underestimated the PA value and CCSD/6-311++G** overestimated the PA value by about 0.98 and 10 kcal/mol respectively.

Table 6: 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. [31]	140.6		140.6	

Conclusion: The present study investigated the efficiency and accuracy of quantum chemical calculations in comparism to experimentally established data on sulphur trioxide (SO_3) and its two possible protonated analogues; HSO_3^+ and $HOSO_2^+$ using the Gaussian 09 suite of programs. Different computational methods; HF, B3LYP, MP2, CCSD and G4 have been employed with the 6-311++G** and cc-pVDZ basis sets. Different parameters such as bond distance, rotational constants, dipole moment, infrared frequency, zero point vibrational energy and proton affinity have been computed for the three molecular species investigated in this work. For the neutral species in which some of the parameters have been experimentally measured, the calculated values at the MP2 level of theory with the cc-pVDZ, basis set are in good concordant than other levels of theory as seen in the discussion. We have calculated the proton affinity for the protonation of SO_3 and have established that S-protonation was the most favoured site for the attachment of proton. The accuracy of the obtained results for the neutral SO_3 suggests that the predicted values for the protonated analogues (HSO_3^+ and $HOSO_2^+$) whose experimental data are lacking are accurate. From the results, optimized geometries show that two of the three molecular species (i.e. SO_3 and $HOSO_2^+$) have a trigonal geometry in all the computational methods employed while HSO_3^+ analogue was discovered to have a square planar geometry for MP2/6-311++G**, MP2/cc-pVDZ, CCSD/cc-pVDZ and G4 methods.

Acknowledgement: EEE acknowledges a research fellowship from the Indian Institute of Science, Bangalore.

References

1. A. Barth and W. Mantele (1998). ATP-Induced phosphorylation of the sarcoplasmic reticulum Ca^{2+} ATPase: molecular interpretation of infrared difference spectra. Biophys. J., 75, 538–544.
2. E. E. Etim, P. Gorai, A. Das, and E. Arunan (2017). Interstellar Protonated Molecular Species. Advances in Space Science, 60: 709-721.
3. C.J Cramer (2014). Essentials of computational chemistry: theories and models. 2nd edition, Chichester, West Sussex, England; Hoboken, NJ: Wiley.
4. K. Gerwert (1999). Molecular reaction mechanisms of proteins monitored by time-resolved FTIR-spectroscopy. Biol.Chem. 380, 931–935.
5. L.V Gurvich, I,V Veyts and C.B Alcock (1989). Thermodynamic Properties of Individual Substances, Fouth Edition, Hemisphere Pub. Co., New York.
6. Heberle, J., Recent Res. Dev. Appl. Spectrosc. 1999, 2,147–159.
7. P. L. Anto, R.J. Anto, H.T. Varghese, C.Y. Panicker, D. Philip, G.F.S. Andrade and A.G. Brolo (2011). Spectroscopic investigations and computational study of sulfur trioxide– pyridine complex, J. Raman Spectrosc., 42, 1812-1819.
8. N. F. Henfrey, B. A. Thrush (1983). The ν_3 band of SO_3 at high resolution, Chem. Phys. Lett., *102*, 135-138.
9. J. Ortigoso, R. Escribano, A. G. Maki (1989). The ν_2 and ν_4 IR bands of SO_3, J. Mol. Spectrosc. *138*, 602.
10. J. G. Calvert, A. Lazrus, G. L. Kok, B. G. Heikes, J. G. Walege, J. Lind, C. A. Cantrell (1985). Chemical mechanisms of acid generation in the troposphere, Nature, 317, 27.
11. B. Pascal *et al*. (1999). Theoretical Study of Interstellar Hydroxylamine Chemistry: Protonation and Proton Transfer Mediated by H3+. In: *Chemical Physics*, 1999, vol. 244, 2-3, p. 163-174.

12. M.J Frisch, G.W Trucks, H.B Schlegel, G.E Scuseria, M.A Robb, J.R Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A Petersson, (2009). Gaussian 09, revision D.01; Gaussian, Inc., Wallingford, CT.
13. E.E. Etim and E. Arunan (2015). Rotational Spectroscopy and Interstellar Molecules: Mini-review. Planex News letter, 5 (2): 16-21.
14. Etim, E. E and Arunan, E. (2016). Interstellar isomeric species: Energy, stability and abundance relationship. European Phys. J. Plus., 131: 448.
15. E.E. Etim and E. Arunan (2017). Accurate Rotational Constants for linear Interstellar Carbon Chains: Achieving Experimental Accuracy. Astrophysics and Space Science, 362.
16. E.E. Etim, P. Gorai, A. Das, S. Charabati and E. Arunan (2016). Systematic Theoretical Study on the Interstellar Carbon Chain Molecules. The Astrophysical Journal, 832, 144.
17. E.E. Etim, P. Gorai, A. Das, and E. Arunan (2017). C_5H_9N Isomers: Pointers to Possible Branched Chain Interstellar Molecules. European Physical Journal D, 71:86.
18. R. Krishnan, J.S. Binkley, R. Seeger, J.A. Pople (1980). Self- consistent molecular orbital methods. XX. A basis set for correlated wave functions, J. Chem. Phys., 72, 650.
19. R.A. Kendall, T.H. Dunning Jr, R.J. Harrison (1992). Electron affinities of the first- row atoms revisited. Systematic basis sets and wave functions, J. Chem. Phys., 96, 6796.
20. D.E. Woon and T.H. Dunning Jr. (1993). Gaussian basis sets for use in correlated molecular calculations. III. The atoms aluminum through argon, J. Chem. Phys., 98, 1358.
21. V. Meyer, D. Sutter, H. Dreizler (1991). "The Centrifugally Induced Pure Rotational Spectrum and the Structure of Sulfur Trioxide. A Microwave Fourier Transform Study of a Non-polar Molecule." Z. Naturforsch. 46a, 710-714
22. M. E. Jacox (1994). Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules, Monograph 3, J. Phys. Chem. Ref. Data, p. 461
23. P.R Davies, W.J Orville-Thomas (1969). "Infrared Band Intensities and Bond polaritites Part1. Bond Moment constants in CO2, OCS, CS2, CSe2, and SCSe" J. Mol. Structure. 4, 163
24. R.L Pecsok, L.D Shields and A.T Schwartz (1994). Chemistry in Context, Wiley, New York, American Chemical Society, Washington, DC.
25. A. Villar, E. Gorritxategi, E. Aranzabe, S. Fernandez, D. Otaduy and L.A Fernandez (2012). "Low-cost visible–near infrared sensor for on-line monitoring of fat and fatty acids content during the manufacturing process of the milk". Food Chemistry. **135** (4): 2756–2760.
26. W.B Person and G. Zerbi (1982). Vibrational intensities in infrared and Raman spectroscopy. Amsterdam: Elsevier Scientific Pub. Co.
27. W.G Golden, A.C Jeannotte II, C.C Blackburn, J. Overend (1977). "Intensities of binary overtone and combination bands in the IR spectrum of NF3" Spectrochimica Acta 33A, 901
28. Etim**,** E.E., Ashu, H. A, Mbakara, I.E, Inyang, E. J., Ukafia, O. P, Sambo, I. F, 2017. Quantum Chemical Calculations on Oxygen Monofluoride (OF) and its Protonated Analogues: Comparison of Methods. Elixir Computational Chemistry, 111: 48823-48827.
29. Etim, E. E., Mbakara, I. E., Khana, G. P., Inyang, E. J., Ukafia, O. P., Sambo, I. F, 2017. Coupled Cluster Predictions of Spectroscopic Parameters for (Potential) Interstellar Protonated Species. Elixir Computational Chemistry, 111: 48818-48822.
30. Etim, E.E. , Mbakara, I.E., Inyang, E.J., Ushie, O.A., Lawal, U., Andrew, C. 2017. Spectroscopy of Linear Interstellar Carbon Chain Isotopologues: Meeting Experimental Accuracy. Trop. J. Appl. Nat. Sci., 2(1): 11-16.
31. NIST data base. Retrieved on 26/12/2017