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Research Article

Protonation of Carbonyl Sulfide: *Ab initio* Study

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Abstract

Background and Objectives: Computational studies have gained popularity nowadays as a means of studying simple and complex chemical systems with a view to complement experimental techniques. Hence the objective of this work was to use different computational methods to study the protonation of carbonyl sulphide, its possible protonated analogues and determine the best site for its protonation which will correspond with the experimentally determined proton affinity. **Materials and Methods:** In this study, quantum chemical calculations were carried out using GAUSSIAN 09 suite of programs using 5 different levels of theory and two basis sets. Bond lengths and angles, vibrational frequencies, dipole moments and proton affinity (PA) are among parameters of interest that have been calculated for OCS and its protonated analogues. In other to evaluate the best computational method, the difference between the calculated value and the reported experimental data is used as a benchmark. **Results:** CCSD method along with 6-311++G** gives the best prediction for the bond length in the neutral molecule. G4 predicts best the rotational constants and dipole moments for HOCS⁺ and OCS respectively. The proton affinity values calculated in this work reveals that the protonation of OCS is more favoured via sulphur atom than via oxygen atom. Thus proton affinity corresponds to the most stable protonated analogue with the proton attached to the site of less electron density hence electronegativity is not a good criterion for predicting the protonation site of a molecule. **Conclusion:** Optimization of OCS molecule and its protonated analogues was performed. We have shown that the protonation of a molecule can be determined by considering electron density rather than electronegativity.

Key words: Interstellar medium, protonation, quantum chemical calculations, level of theory, basis sets, electron density

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

A substantial (>200) number of molecular species have been observed from the interstellar and circumstellar media with about 10% being cations and almost 80% of these cations are protonated molecules¹⁻⁸. Of all the known interstellar molecules, hydrogen predominates the interstellar medium and this implies that all the neutral molecular species present in the ISM are susceptible to protonation. Studies have shown that both the protonated species and their neutral analogues consist part of the interstellar media where the protonated species form as the natural precursors to the neutral species⁹⁻¹⁰ and this implies that for every neutral species existing in the ISM, there also exist its protonated analogue¹¹⁻¹². Carbonyl sulfide (OCS) is a well known interstellar molecule that was first detected within the giant molecular Sagittarius B2 by Jefferts *et al.*¹³ and was further confirmed in about ten interstellar sources¹⁴⁻¹⁶. OCS is among the 15 sulfur-containing compounds that have been known from interstellar observations¹⁷. This interstellar molecule OCS plays an important role in the global cycling of sulphur¹⁸ and due to its high abundance (about 500 ppt) in the troposphere; it forms the major source of stratospheric aerosol¹⁹.

Protonations are key constituents of interstellar molecules and are essential to many chemical processes occurring in the ISM. The protonation of a neutral molecule can occur in more than one position and can affect electronic, molecular structure and proton binding energies. The presence of protonated OCS has been postulated in the interstellar clouds^{15,20}. In principle, the OCS molecule has three possible protonation sites (either through O, C or S) which could result in three isomers namely, HOCS⁺, OC(H)S⁺ and HSCO⁺ respectively. Two of these isomers (HOCS⁺ and HSCO⁺) are more stable and have been a subject of study²¹. The HOCS⁺ isomer was first reported by Nakanaga and Amano²² using a high-resolution infrared spectrum and the authors reported that the vibrational frequency of the O-H stretching mode was 3435.16 cm⁻¹. For the HSCO⁺ corresponding isomer, these authors were unable to identify the S-H stretching mode. In another experimental study, the rotational spectrum of HOCS⁺ was observed by Ohshima and Endo²³ and the values of their rotational constants were in excellent agreement with the previous work of Nakanaga and Amano²². Though, Ohshima and Endo²³ failed to measure the spectrum of HSCO⁺. Another theoretical and experimental study was conducted by Saebø *et al.*²⁴, in order to resolve the disagreement between *ab Initio* and experimental studies of the HSCO⁺ isomer. Theoretical studies predicted the S-H stretching mode of HSCO⁺ at 2496 cm⁻¹ and the spectroscopic study was only

able to observe HOCS⁺ but failed to detect the IR absorption of HSCO⁺. Though, these authors suggested that the reason for not observing HSCO⁺ was attributed to the low amount which was below the detection limit. Further work from Xia *et al.*²⁵ with that of McCarthy and Thaddeus²⁶ could not locate the S-H stretching band for the HSCO⁺. However, in a recent study by Tsuge and Lee²¹, the IR spectrum of HSCO⁺ was studied together with HOCS⁺ and t-HOCS through electron bombardment of a mixture of OCS and para-hydrogen. For the first time, the conflict between theoretical and experimental study for the IR spectra of HSCO⁺ ($\nu_1 = 2506.9$, $\nu_2 = 2074.2$ cm⁻¹) was resolved and new modes (ν_2 and ν_3) for HOCS⁺ was reported.

Motivated by the recent advancement in quantum chemical calculation methods, the present work is focused at determining the proton affinity (PA), vibrational frequencies, rotational constants and dipole moments for OCS and all its possible protonated analogues using five different theoretical methods (HF, B3LYP, MP2, CCSD, G4) with two basis sets (6-311++G** and cc-pVDZ). The differences between the calculated parameters of interest and the corresponding experimental data (where available) have been used to ascertain the efficiency and accuracy of the different computational methods applied. Specifically, the purpose this work was to use results of the different computational method to determine the best site for the protonation of OCS which will correspond with the experimentally determined proton affinity.

MATERIALS AND METHODS

Study area: This research project was conducted from August, 2015 to September, 2016 at the Indian Institute of Science (IISc) Bangalore.

Computational procedure: All the quantum chemical calculations reported in this study have been carried out using the GAUSSIAN 09 suit of programs²⁷. In order to obtain highly accurate values for all the parameters investigated in this study for all the molecular species considered, different high-level *ab initio* methods have been employed. These include the Hartree-Fock (HF), B3LYP, second-order Møller-Plesset perturbation theory (MP2) and coupled-cluster theory (CCSD) with 6-311++G** basis set. Besides this basis set, the Dunning correlation-consistent polarized valence double zeta (cc-pVDZ) basis set which is designed to converge smoothly towards the complete basis set limit is also used with the MP2 method. In addition to the above methods, the Gaussian 4 theory (G4) compound model is also utilized in

predicting accurate parameters for all the systems under consideration in this study. This compound model offers high accuracy results at a less computational cost. It consists of different component calculations whose results are then combined in a predefined manner²⁸⁻³⁶. The choice of these methods and basis sets is based on our previous studies by Etim and Arunan⁶⁻⁷ and Etim *et al.*⁸. The OCS molecular species and its possible protonated analogues were optimized with the different methods mentioned above. For the calculation of the proton affinity, 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. Proton affinity 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.

Statistical analysis: Standard deviation analysis was used to estimate the error difference between our computational results and the reported experimental values.

RESULTS AND DISCUSSION

To get the best computational method, the difference between the computed parameters of interest and the observed experimental values where available was used as standard. The smaller the error is, the more accurate the computational method would be in predicting the experimental data.

Optimized geometry: Optimized geometries of the neutral OCS and its protonated analogues calculated using 5 different computational methods are presented in Table 1. The geometrical parameters for the bond length and angles for the neutral molecule at the levels of theory used agree well with the observed experimental data reported by Callomon *et al.*³⁷. A close look at Table 1 reveals that at the same level of theory, the HOC bond angle in HOCS⁺ is greater than the HSC bond angle in HSCO⁺. In the HOCS⁺ analogue, hydrogen is bound to sp²-hybridized oxygen while in the HSCO⁺ system, hydrogen is bound to a sulfur atom which undergoes hybridization to a lesser degree than in oxygen. In addition, the H-O and H-S bond lengths in the two protonated analogues are quite different with the former been smaller than the later; this can be explained based on hybridization. Upon protonation, it is clear that the C-S bond distance is generally much longer than in the neutral molecule while the C-O distance in the HSCO⁺ is shorter. Thus, there is a contraction of C-O and elongation of C-S bond lengths in HSCO⁺ compared to that in the neutral molecule (OCS). On the other hand, the C-S distance in HOCS⁺ is shorter whereas the C-O bond distance is longer when compared to the neutral molecule. In general, our geometrical calculated values compare favourably with that reported by Saebo *et al.*²⁴. Furthermore, the protonation of OCS through the oxygen atom results in HOC bond angles of about 120° and through sulfur atom the HSC bond angle is about 90°. The rotational constants for the optimized structures of OCS and two of its protonated analogues at different computational methods used are listed in Table 2. Based on the different levels of

Table 1: Equilibrium geometries of OCS and its protonated analogues

Molecules	Methods						Experimental values
	HF/6-311++G**	B3LYP/6-311++G**	MP2/6-311++G**	MP2/cc-pVDZ	CCSD/6-311++G**	G4	
OCS							
C-O	1.2432	1.1572	1.1703	1.176	1.1619	1.1578	1.160 ^a
C-S	1.5668	1.5685	1.5627	1.5804	1.5861	1.5671	1.56
S-C-O	180	179.89	179.96	179.98	180	179.99	180
HOCS⁺							
r(SC)	1.4779	1.5046	1.5098	1.5267	1.5175	1.5027	
r(CO)	1.2563	1.2322	1.2445	1.2511	1.2495	1.233	
r(HO)	0.962	0.9827	0.9801	0.9885	0.9847	0.9822	
<(HOC)	119.45	120.14	116.17	115.15	114.81	119.75	
HSCO⁺							
r(SC)	1.6792	1.6589	1.6539	1.6699	1.6885	1.6553	
r(CO)	1.0914	1.1238	1.1383	1.1454	1.1299	1.1267	
r(HS)	1.3442	1.3667	1.3512	1.3646	1.3655	1.3643	
<(HSC)	90.54	90.94	89.86	90.34	90.36	91.11	

^aCallomon *et al.*³⁷, HF: Hartree-Fock, B3LYP: Becke, 3-parameter, Lee-Yang-Parr, MP2: Second-order Møller-Plesset perturbation theory, CCSD: Coupled-cluster theory, G4: Gaussian 4 theory

Table 2: Rotational constants (GHz) for protonated OCS

Molecules	Methods						Experimental values
	HF/6-311++G**	B3LYP/6-311++G**	MP2/6-311++G**	MP2/cc-pVDZ	CCSD/6-311++G**	G4	
HOCS⁺							
A _e	811.665	793.939	695.194	706.461	707.052	786.371	782.696 ^a
B _e	5.925	5.739	5.687	5.592	5.638	5.755	5.751
C _e	5.882	5.698	5.641	5.548	5.593	5.703	5.703
HSCO⁺							
A _e	286.767	276.329	282.146	276.921	277.04	277.843	
B _e	5.707	5.687	5.661	5.565	5.537	5.691	
C _e	5.595	5.572	5.551	5.455	5.429	5.578	

^aSaebø *et al.*²⁴, HF: Hartree-Fock, B3LYP: Becke, 3-parameter, Lee-Yang-Parr, MP2: Second-order Møller-Plesset perturbation theory, CCSD: Coupled-cluster theory, G4: Gaussian 4 theory, A_e, B_e, C_e: Rotational constants

Table 3: Dipole moments for OCS and its protonated analogues

Molecules	Methods						Experimental values
	HF/6-311++G**	B3LYP/6-311++G**	MP2/6-311++G**	MP2/cc-pVDZ	CCSD/6-311++G**	G4	
OCS	0.355	0.779	0.879	0.636	0.308	0.767	0.7152 ^a
HOCS ⁺	2.316	2.368	2.260	2.405	2.148	2.285	
HSCO ⁺	1.918	2.160	2.270	2.281	1.733	2.216	

^aLahaye *et al.*³⁹, HF: Hartree-Fock, B3LYP: Becke, 3-parameter, Lee-Yang-Parr, MP2: Second-order Møller-Plesset perturbation theory, CCSD: Coupled-cluster theory, G4: Gaussian 4 theory

theory used, the G4 level agrees excellently well with a difference of about 3.675 GHz from the experimental values of HOCS⁺ reported by Nakanaga and Amano²². The largest deviation between the *ab initio* used and the observed experimental rotational constants is found at the Hartree-Fock level of theory.

A general look at the rotational constants for HOCS⁺ in this work indicates that the values are well predicted even though the results of the computational methods used are based on equilibrium structures while the experimental data are obtained from vibrationally averaged structures. The rotational constants of HSCO⁺ have not been determined experimentally and we have compared our results with other theoretical results. Our rotational constants using MP2 at 6-311++G** basis set and G4 methods are in excellent agreement with the theoretical values reported by Saebø *et al.*²⁴ and Wheeler *et al.*³⁸. A comparison of the different computational methods used in calculating the dipole moments (Table 3) indicates that the dipole moment of OCS is well predicted using G4 level with a difference of only 0.05 from the experimental value of Lahaye *et al.*³⁹.

IR spectra: The vibrational wave-numbers of the two protonated carbonyl sulfide (HSCO⁺ and HOCS⁺) have been widely studied both experimentally and with different computational techniques. The results of the predicted harmonic vibrational frequencies of OCS and its protonated analogues (HSCO⁺ and HOCS⁺) using different *ab initio*

methods are presented in Table 4. Figure 1a-f depicts the IR spectra of the OCS at different levels of theories and Fig. 2a-f represents the corresponding IR spectra of the protonated analogues. For OCS which is a linear molecule, there will be 3N-5 modes of vibrations⁴⁰. Hence only four vibrational modes are possible which include; symmetrical stretching (ν₁), asymmetrical stretching (ν₃) and two of the degenerated bending modes (ν₂). Comparing the five computational methods used in this work reveals that the HF method gave a larger average error (8.5%) between the calculated and experimental frequencies and MP2 at 6-311++G** basis set predicted the best frequencies with an average percentage error of 1.66%. Generally, the HF method is known with the fact that it does not take into account electron correlation which often overestimates the vibrational frequencies by about 10%⁴¹. On the basis of a specific frequency, the CCSD method predicted the best bending vibrational frequency followed by MP2 and B3LYP were the differences between the calculated frequencies and the observed experimental value is very small. On the other hand, the two protonated analogues (HOCS⁺ and HSCO⁺) are all non-linear and will have 3N - 6 vibrations giving rise to six vibrational frequencies. For the HOCS⁺, only three of these frequencies (O-H stretch, C-O stretch, HOC bend) have been observed experimentally²¹⁻²². Our predicted vibrational frequency for the O-H stretch (3582 cm⁻¹) at the G4 level of theory (without empirical corrections or scaling) was the method with the least error (147 cm⁻¹) when compared with the experimental data of Nakanaga and Amano²² and other computational methods.

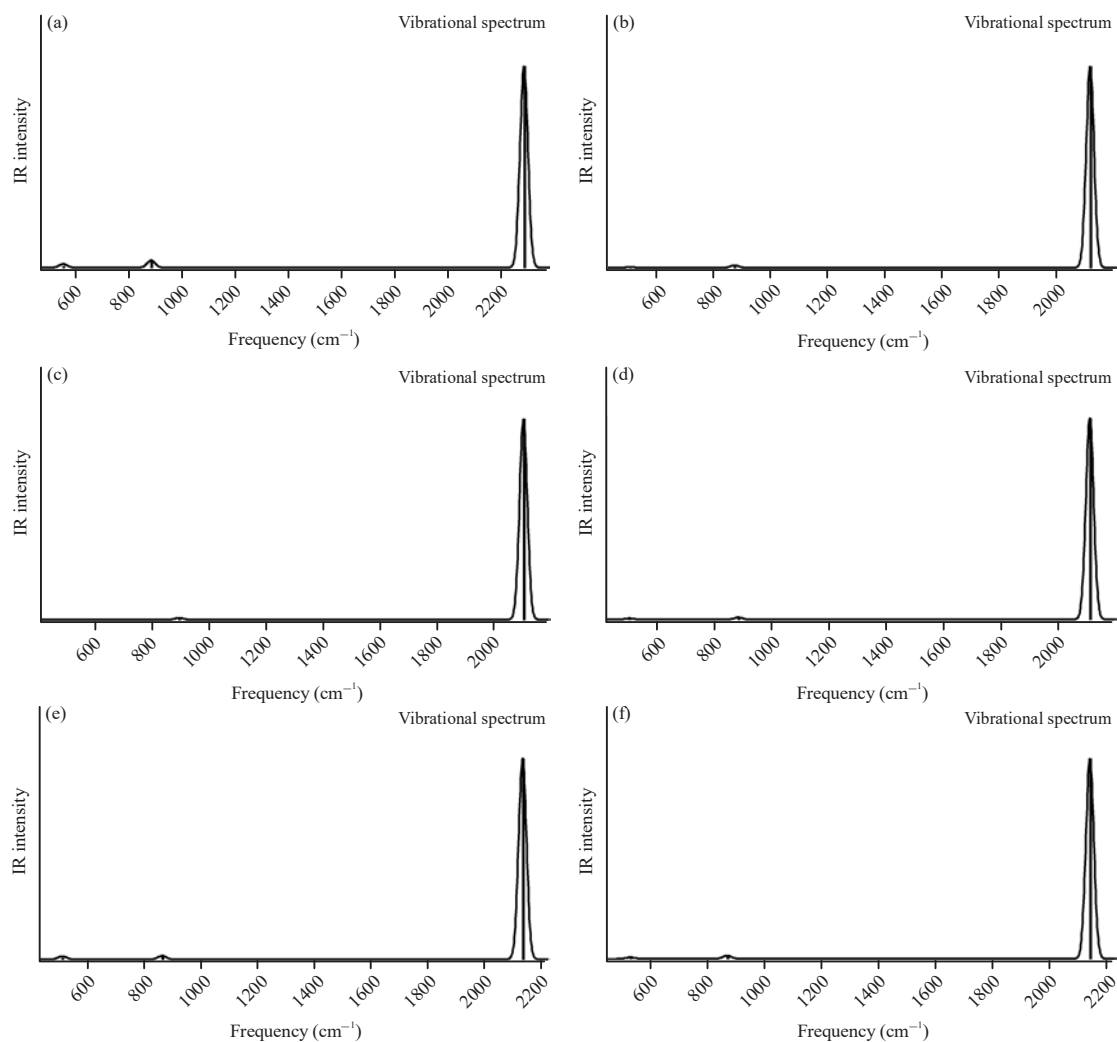


Fig. 1(a-f): IR spectra of SCO at (a) HF/6-311++G**, (b) B3LYP/6-311++G**, (c) MP2/6-311++G**, (d) MP2/cc-pVDZ, (e) CCSD//6-311++G** and (f) G4 level

Table 4: Vibrational frequencies (cm⁻¹) for OCS and its protonated analogues

Methods								Experimental
Molecules	Mode	HF/6-311++G**	B3LYP/6-311++G**	MP2/6-311++G**	MP2/cc-pVDZ	CCSD/6-311++G**	G4	values
OCS	Bend	568	512	495	513	523	540	520 ^a
	Asymmetrical	568	512	495	513	523	540	
	Stretch	898	876	902	890	874	876	859 ^a
HOCS ⁺	Symmetrical stretch	2295	2115	2102	2106	2135	2139	2062 ^a
	Torsion	482	433	415	422	422	450	-
	SCO bend	526	469	434	457	466	488	-
	CS stretch	1001	919	904	895	913	920	-
	COH bend	1108	997	1028	1068	1115	1021	1042 ^b
HSCO ⁺	CO stretch	2018	1931	1953	1937	1903	1938	1875 ^b
	OH stretch	3876	3586	3654	3598	3646	3582	3435 ^c
	OCS bend	428	389	381	384	386	406	-
	OCS bend	477	445	427	448	449	474	-
	CS stretch	683	713	738	730	686	719	-
HSCO ⁺	CSH bend	1087	976	987	962	985	975	-
	CO stretch	2554	2278	2184	2168	2290	2278	2074 ^b
	SH stretch	2776	2563	2698	2672	2657	2577	2507 ^b

^aSaebo *et al.*²⁴, ^bTsuge and Lee²¹, ^cNakanaga and Amano²², HF: Hartree-Fock, B3LYP: Becke, 3-parameter, Lee-Yang-Parr, MP2: Second-order Møller-Plesset perturbation theory, CCSD: Coupled-cluster theory, G4: Gaussian 4 theory

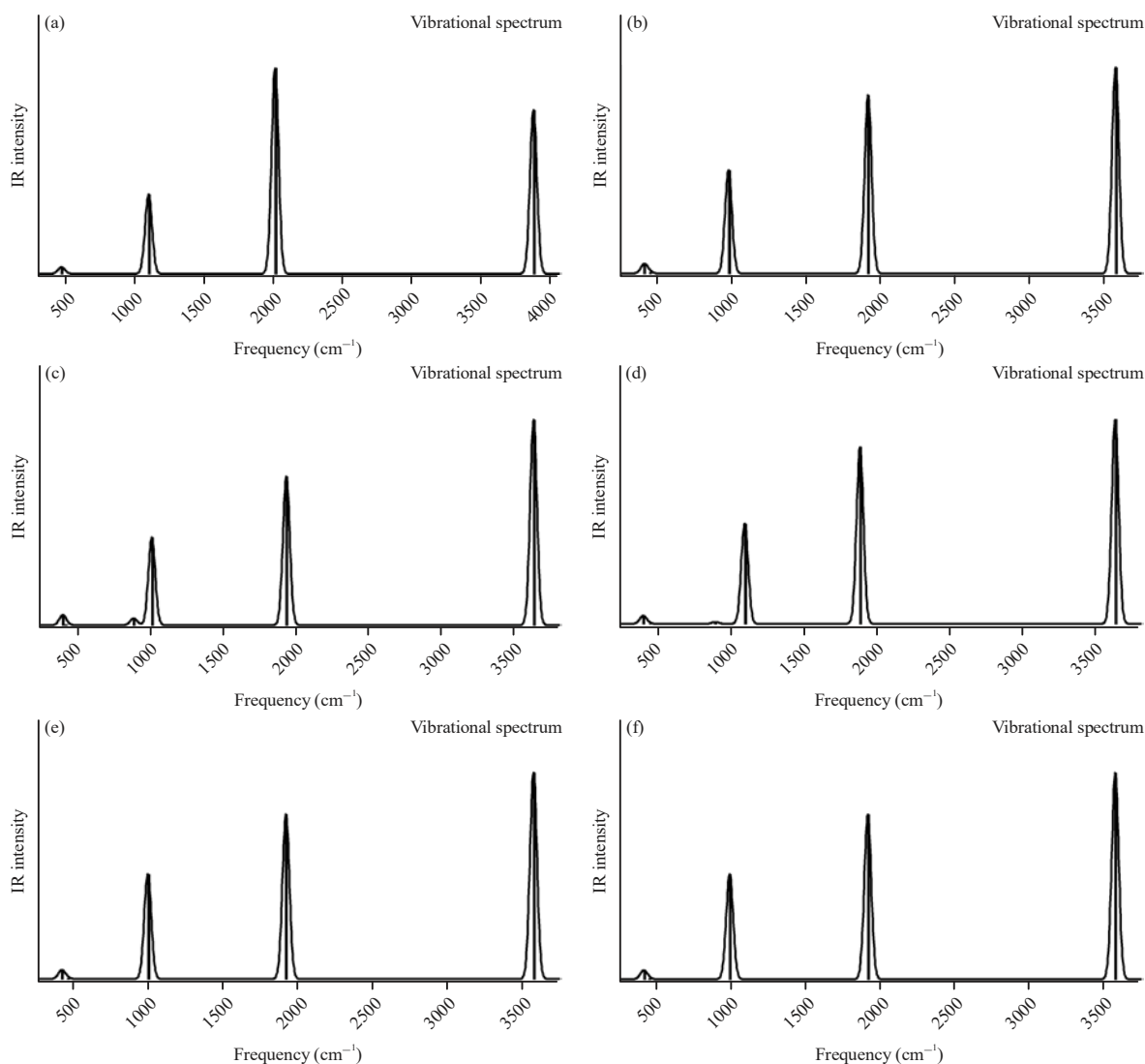


Fig. 2(a-f): IR spectra of protonated SCO at (a) HF/6-311++G**, (b) B3LYP/6-311++G**, (c) MP2/6-311++G**, (d) MP2/cc-pVDZ, (e) CCSD/6-311++G** and (f) G4 level

The G4 method also produced the best result for the predicted HOC bend frequency for the HOCS⁺ isomer. The C-O stretch frequency was much accurately predicted at the CCSD level of theory. The H-S vibrational frequency for HSCO⁺ protonated analogue has been a subject of experimental observation not until recently where Tsuge and Lee²¹ observed the S-H frequency at 2507 cm⁻¹. For the H-S vibrational frequency, 2 methods; B3LYP and G4 computed the accurate frequency with an error of 56 and 70 cm⁻¹ respectively when compared with other methods. The C-O stretch frequency was better predicted at the MP2 level with the cc-pVDZ basis set.

Proton affinity (PA): Table 5 reports the proton affinities for the protonation of OCS calculated at different levels of theory together with the corresponding errors. Figure 3 shows the corresponding optimized structures of protonated analogues for OCS. It is clear from Table 5 that the results of the five computational methods used in calculating the PA indicates that the PA is better predicted when protonation occurs via sulfur atom (i.e., a site with less electron density) than at oxygen atom (a site with high electron density) even though oxygen is more electronegative than sulfur. Therefore, PA corresponds to the most stable protonated analogue with the proton attached to the site of less electron density.

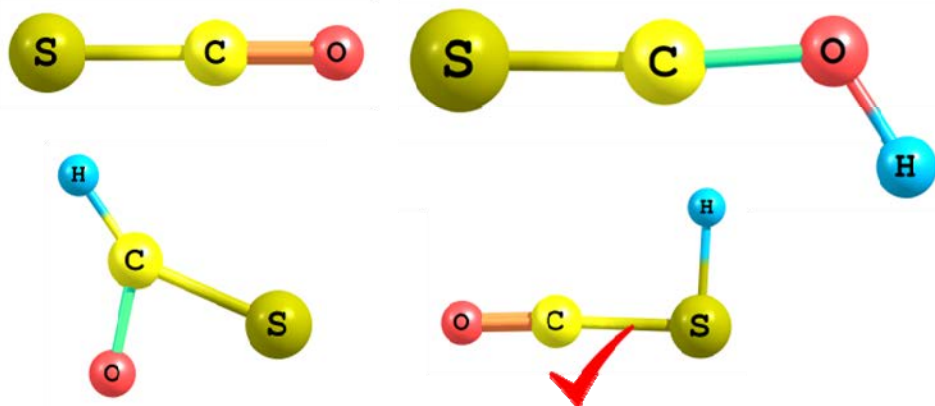


Fig. 3: Optimized structures of protonated analogues of OCS

Source: Gaussian-09 suit program

Table 5: Proton affinity (PA) of OCS at different sites of protonation

Methods	Proton attached to O atom		Proton attached to C atom		Proton attached to S atom	
	PA (kcal mol ⁻¹)	Error	PA (kcal mol ⁻¹)	Error	PA (kcal mol ⁻¹)	Error
HF/6-311++G**	141.1532	-9.04677	79.78595	-70.4141	150.7309	0.530912
B3LYP/6-311++G**	141.2398	-8.96017	85.832	-64.368	144.7037	-5.49632
MP2/6-311++G**	143.8528	-6.34722	86.05602	-64.144	149.1979	-1.00209
MP2/cc-pVDZ	141.9608	-8.23916	85.19194	-65.0081	148.3087	-1.89127
CCSD//6-311++G**	146.0553	-4.14466	92.84944	-57.3506	154.6692	4.469161
G4	144.8593	-5.34069	90.71967	-59.4803	148.1556	-2.04439
Experimental values	150.2	NA	150.2	NA	150.2	NA

HF: Hartree-Fock, B3LYP: Becke, 3-parameter, Lee-Yang-Parr, MP2: Second-order Møller-Plesset perturbation theory, CCSD: Coupled-cluster theory, G4: Gaussian 4 theory, NA: Not applicable

Hence, electro-negativity of an atom is not a good criterion for deciding the site of protonation. Thus, from the calculated PA in this work, S-protonation is more favoured than O-protonation which indicates that HSCO⁺ is more stable than HOCS⁺. This also confirms the previously reported *ab initio* studies that HSCO⁺ protonated form is more stable than HOCS⁺^{24,38,42-45}.

CONCLUSION

Protonation of carbonyl sulfide was studied through *ab initio* methods to ascertain the best computational method by determining the difference between the computed and experimental values. The five computational methods used in calculating the PA indicate that the PA is better predicted when protonation occurs via sulfur atom i.e., a site with less electron density than at oxygen atom, a site with high electron density even though oxygen is more electronegative than sulfur. Generally, CCSD and G4 methods give the best prediction of the parameters of interest calculated. This study has shown that electronegativity is not the only criterion when predicting the protonation of a molecule.

SIGNIFICANCE STATEMENT

This study discovered that the protonation of OCS is more favoured via sulphur atom than via oxygen atom. Thus proton affinity corresponds to the most stable protonated analogue with the proton attached to the site of less electron density hence electronegativity is not a good criterion for predicting the protonation site of a molecule.

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