ORIGINAL PAPER

Theoretical study on the properties and stabilities of complexes formed between SO$_4$ (C2v) and isostructure species of CO$_2$, CS$_2$, and SCO

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Abstract In this work ab initio calculations at MP2 level in conjugation with aug-cc-pVXZ (X=D and T) basis set were performed in order to examine complexes formed between SO$_4$ and each of linear molecules of CO$_2$, CS$_2$, and SCO. The results have been discussed on real minima located on singlet potential energy surface (PES). Single-point energy calculations at the MP2/aug–cc–pVTZ level uphold results obtained at the MP2/aug–cc–pVDZ level. The atom in molecules theory (AIM) was utilized to analyze the nature of intermolecular interactions. Also, natural bond orbital (NBO) analysis has been used in order to get charge transfer quota in complexes. The results show that the atmospheric role of SO$_4$–CS$_2$ system is more important than those followed by SO$_4$–SCO and SO$_4$-CO$_2$, respectively.

Keywords AIM · Atmospheric chemistry · Linear species · MP2 · SO$_4$ (C2v)

Introduction

The importance of non-covalent intermolecular interactions in many areas of current chemistry has been illustrated in numerous pamphlets of systems that are retained together by forces ranging from weak van der Waals forces to much stronger covalent and ionic interactions [1, 2]. Due to its importance, the investigation of complexes formed by these interactions is in order per se.

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With this fact in mind that sulfur chemistry plays an important role in the atmosphere of earth [3, 4], undoubtedly, SO$_4$ is one of potentially present species in atmosphere. This species was supplied by Kugel and Taube [5] in the 1970s. One of the interesting characteristics of SO$_4$ is the existence of two very strong bands at 1434 and 1267cm^{-1} allocated to the symmetric and asymmetric stretches of an SO$_2$ unit. McKee [6, 7] considered several structures for SO$_4$ neutral molecule and predicted the most stable structure has a three-membered OSO ring which causes the C2v symmetry for SO$_4$.

Goodarzi et al. [8] displayed the mechanism of OSO ring formation in sulfur tetroxide molecule. The existence and instability of monomeric SO$_4$ relative to polymerization has been theoretically discussed [9]. Also the formation of acid rain based on the sulfur tetroxide (SO4 (C2v)) with OH radical reaction has been studied [10]. Sulfur tetroxide has previously been proposed as an intermediate in a variety of sulfur oxide reaction systems, as an atmospheric intermediate in the photo induced oxidation of sulfur dioxide by the molecular oxygen [11–14].

The environmental effects of carbon dioxide (CO$_2$) are of significant interest. CO$_2$ is an important greenhouse gas, absorbing heat radiation from Earth's surface which otherwise would leave the atmosphere. From a geometrical point of view, it is interesting to mention that CO$_2$ is isostructure with carbon disulphide (CS$_2$) and carbonyl sulphide (SCO), two of the major pollutants in the atmosphere [15, 16]. The pollutants derived from CS$_2$ by photolysis, are great menaces to the global environment and human health. The SCO molecule, a substantial compound in the global sulfur cycle, is the most abundant sulfur compound naturally present in the atmosphere. Its long atmospheric lifetime begets it the major source of stratospheric sulfate, through sulfur from volcanic activity [17].

With the mentioned importance of the present species in mind, let us inquire the properties and stabilities of the

possible complexes formed between SO_4 and present linear triatomic molecules for the first time, from the viewpoint of microscopic. It is hoped that our results lead to useful information for atmospheric chemistry.

Computational details

The geometries of the isolated SO_4, CO_2, CS_2, and SCO moieties and their dimers were fully optimized at the MP2 [18] level in conjunction with the aug-cc-pVDZ basis set [19, 20] within the frozen core (FC) approximation on the singlet potential energy surface (PES). To achieve reliable relative energies of each dimer, single–point energy calculations at the MP2/aug-cc-pVTZ level were carried out on the optimized geometries of MP2/aug-cc-pVDZ level. Harmonic vibrational frequency calculations were performed at the MP2/aug-cc-pVDZ computational level to confirm the nature of all dimers as real minima (NIMAG =0) and empower the benchmark of the zero–point energies (ZPEs). In the present work, the binding energies were calculated as the difference between the energy of the complexes and the sum of the energies of the isolated monomers in their minimum configurations. The counterpoise (CP) method [21] was used to take into account the basis set superposition error (BSSE) in the calculation of the binding energies and present the energies with more validity. All calculations were performed with the GAMESS quantum chemical package [22].

The molecular electrostatic potential on the electron density isosurface of 0.001 a.u. has been calculated and represented using the WFA program [23]. This isosurface has been shown to be like the van der Waals surface [24]. The atoms in molecules (AIM) methodology [25] was utilized to examine the electron density of the systems with the AIM2000 program [26]. The natural bond orbital (NBO) method has been employed to assay atomic charges using the NBO-3 program [8–30], and to analyze charge-transfer interactions between occupied and unoccupied orbitals.

Results and discussion

To optimize the complexes, between SO_4 and each of the linear triatomic molecules, different orientations of them toward SO_4 were considered. After optimization of all complexes, with respect to the number of imaginary frequencies (NIMAG =0), those complexes with the real nature of minima (NIMAG =0) were discussed. One, one, and two real minima have been located on the singlet PES of SO_4-CO_2, SO_4-CS_2, and SO_4-SCO systems, respectively. Our results were expounded on three main sections. In the first, a succinctly electrostatic potential analysis of the present monomers has been performed. The second section has been allocated to

geometrical and energetic discussions of all studied complexes in three subsections. The third section describes the nature of intermolecular interactions in the studied complexes and charge transfer between moieties.

Monomers

To identify the electronic feature of the studied monomers and for better insight into basic and acidic sites, in the possible intermolecular interactions, the molecular electrostatic potential (MEP) analysis was used. A molecule's electrostatic potential, $V(r)$, has proven to be an effective index to its reactive behavior. $V(r)$ is the potential that is emerged at any point r by the molecule's nuclei and electrons, and is given by:

$$V(r) = \sum_A \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r')dr'}{|r' - r|}, \qquad (1)$$

in which Z_A is the charge on nucleus A, located at R_A, and $\rho(r)$ is the molecule's electronic density. $V(r)$ is a physical quantity and can be obtained experimentally, or computationally. Also $V(r)$ will be positive or negative in a given region depending upon whether the contribution of the nucleus or that of the electrons is dominant there.

The electrostatic potential profiles of all monomers are shown in Fig. 1. Note that the represented colors in this figure indicate the strength of basic and acidic sites of interacting monomers in interaction. It is mentionable that red and blue colors show the most positive and the most negative regions of MEP on the surface of monomers. It is obvious that there are four minima for SO_4 monomer on the MEP, each of them belongs to one oxygen atom.

Moreover we can see that only around S atom, the central atom of SO_4, is a positive region in this molecule. This figure also describes many important points in the electrostatic profiles of linear triatomic species present in this study.

Considering other monomers, the positive region in all species is located on central atoms. The values of this deficiency of charge are listed in Fig. 1. The inflation of this deficiency can be organized in the order of CO_2 > SCO > CS_2. It should be noted that the negative region of these molecules shifts to the oxygen atoms, in linear species of CO_2 and SCO. It can be related to the larger value of electronegativity of O atom compared to S atom. Thus, the head of oxygen is more negative than that of the S atom.

Geometries and energies

SO_4-CO_2 system

Only one complex, A1, is found on the PES of SO_4-CO_2 system. From Fig. 2, it can be seen that the S atom from

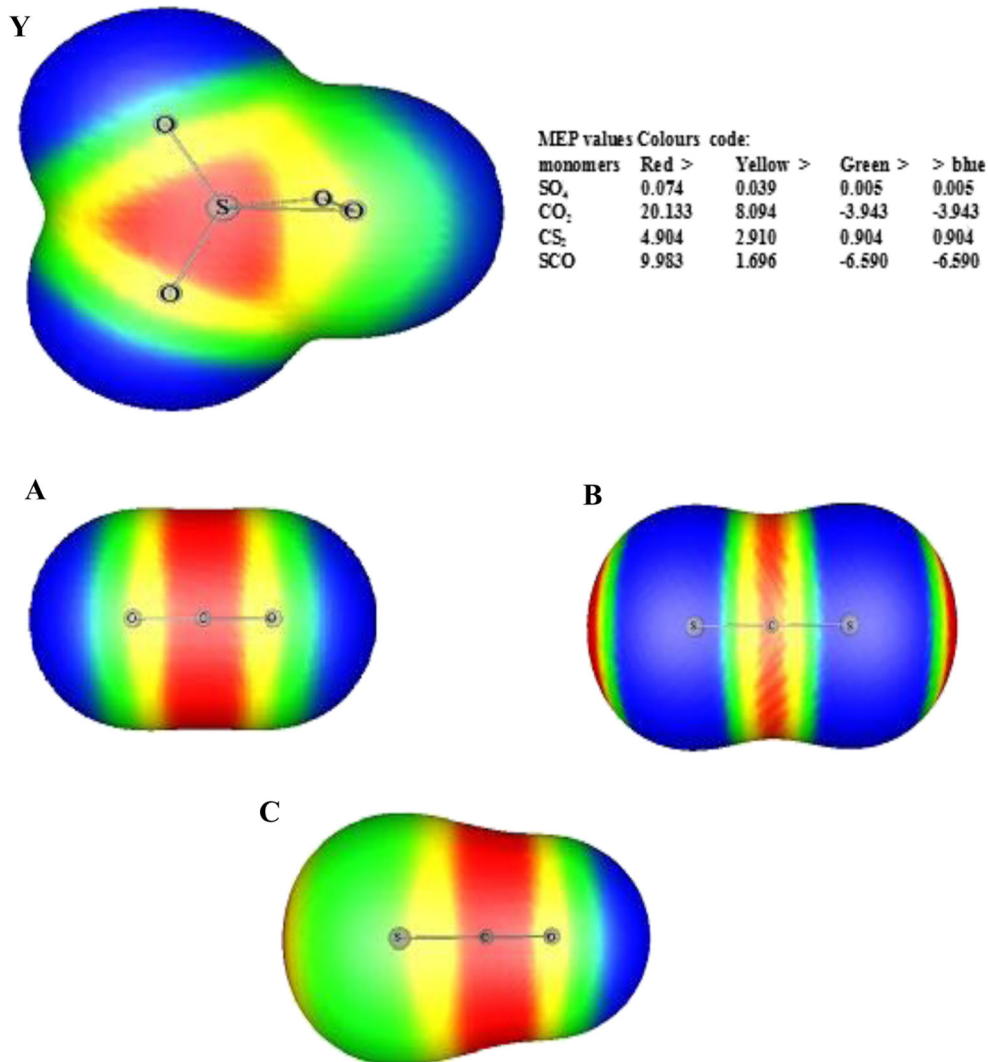**Fig. 1** Molecular electrostatic potential (MEP) at 0.001 a.u electron density isosurface of the monomers: Y:SO_4 A:CO_2 B:CS_2, and C:SCO

MEP values monomers	Colours code: Red >	Yellow >	Green >	> blue
SO_4	0.074	0.039	0.005	0.005
CO_2	20.133	8.094	-3.943	-3.943
CS_2	4.904	2.910	0.904	0.904
SCO	9.983	1.696	-6.590	-6.590

Fig. 2 Molecular graphs of the minima obtained at the MP2/aug-cc-pVDZ level; **a** SO_4-CO_2, **b** SO_4-CS_2, and **c** SO_4-SCO systems. The red and yellow dots display the position of the bond and ring critical points, respectively
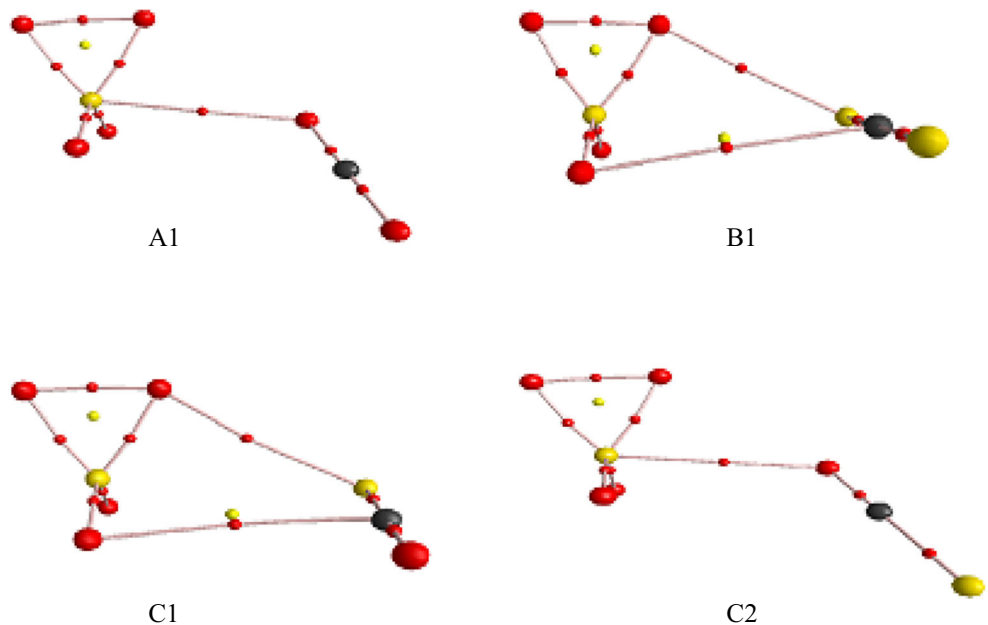
Table 1 Stabilization energies (kJ mol^{-1}) of SO$_4$–CO$_2$, SO$_4$–CS$_2$, and SO$_4$–SCO and systems at the MP2 level

| | MP2 /aug-cc-pVDZ | | | MP2/aug–cc–pVTZ// | |
| | | | | MP2/aug–cc–pVDZ | |
Complexes	E$_I$	E$_I$ + BSSE	E$_I$ + BSSE + ZPE	E$_I$	E$_I$ + BSSE
A1	−17.66	−10.03	−4.12	−15.55	−12.25
B1	−22.03	−13.54	−10.04	−21.34	−18.01
C1	−18.76	−10.86	−6.26	−17.73	−14.01
C2	−18.63	−10.62	−5.71	−16.89	−13.38

SO$_4$ has an interaction with the O atom from CO$_2$ moiety, (S…O), with intermolecular interaction distance of 2.89 Å. Regarding what was mentioned in a prior section, that S and O atoms are positive and negative, it seems that for A1complex the electrostatic nature for the mentioned interaction is in top order. The binding energy of this complex (BSSE-corrected) is 12.25 kJ mol^{-1} at the MP2/aug-cc-pVTZ//MP2/aug-cc-pVDZ level, see Table 1.

SO$_4$-CS$_2$ system

Similar to the prior system, only one real minima on the PES of SO$_4$-CS$_2$ system, B1, was located. Two intermolecular interactions stabilize this complex. One of them is formed by the interaction between hooped-oxygen atom from SO$_4$ and sulfur atom of CS$_2$. The other is formed by the interaction between the non hooped-oxygen atom from SO$_4$ with the C atom from CS$_2$. The interaction distances for these intermolecular interactions are 2.93 Å and 3.28 Å, respectively. The binding energy of this complex (BSSE-corrected) is 18 kJ mol^{-1} at the MP2/aug-cc-pVTZ//MP2/aug-cc-pVDZ level. It should be noted that B1 complex is the most stable complex studied in this work.

SO$_4$-SCO system

C1 and C2 complexes are two real minima located on the PES of the SO$_4$-SCO system. The more stable complex, C1, is very similar to B1 complex. As can be seen from Fig. 1, two intermolecular interactions, O…S with 3.06 Å and O…C with 3.14 Å, formed this complex. Also it is mentionable that C2 complex is similar to A1 complex. The interatomic distances of S…O and O…C are 3.06 Å and 3.14 Å, respectively, Fig. 1.

The binding energies (BSSE- corrected) of C1 and C2 complexes are 14 and 13.38 kJ mol^{-1} at the MP2/aug-cc-pVTZ//MP2/aug-cc-pVDZ level, respectively. With respect to binding energies, the stability of studied systems can be organized in the order of SO$_4$–CS$_2$ > SO$_4$–SCO > SO$_4$-CO$_2$. Recently, a similar trend has been shown in complexes between ozone and isostructure species of CO$_2$, CS$_2$, and SCO [31].

AIM and NBO analysis

The atoms in molecules (AIMs) methodology was performed to analyze the characteristics of the intermolecular critical points (BCP) in the present complexes. The parameters (the electron density, ρ, the Laplacian of electron density, $\nabla^2\rho$, and the electronic energy density, H_C, at BCP and the sum of the kinetic electron energy density, G_C, and the potential electron density, V_C, that $H_C = G_C + V_C$) derived from the Bader theory also indicate the type of interactions.

The positive value of the Laplacian of the electron density at BCP ($\nabla^2\rho>0$) shows the depletion of the electron charge in the region between the nuclei of the interacting atoms and is a typical interaction of closed-shell systems like ions, van der Waals interactions, or H-bonds. Inversely, in the case of the negative value of Laplacian, there is a concentration of the electron charge in the region between the nuclei of the interacting atoms and is typical of covalent bonds-shared interactions.

Table 2 Interatomic distances (Å) and bond critical point data (a.u.) calculated at the MP2/aug–cc–pVDZ level

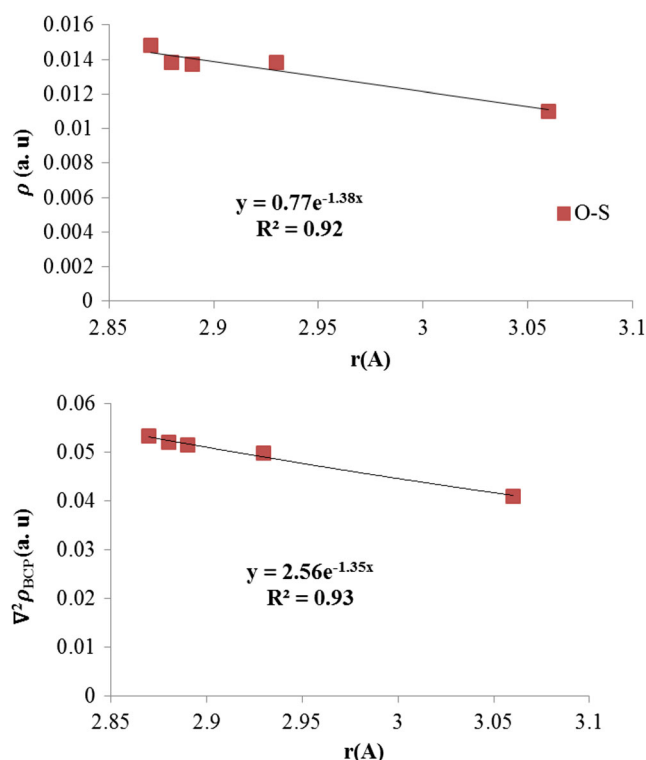| Complexes	Interaction	Interaction distance	ρ	$\nabla^2\rho$	H$_r$	–Gc/Vc
A1	S….O	2.89	0.0137	0.0514	−0.0010	1.0925
B1	O….S	2.93	0.0138	0.0497	−0.0015	1.1595
	O….C	3.28	0.0062	0.0216	−0.0008	1.2245
C1	O….S	3.06	0.0110	0.0409	−0.0014	1.1939
	O….C	3.14	0.0070	0.0262	−0.0010	1.2370
C2	S….O	2.88	0.0138	0.0519	−0.0010	1.0941

Fig. 3 Exponential relationships between the interatomic distances (Å) and the (**a**) ρ_{BCP}, (**b**) $\nabla^2\rho_{BCP}$ (a.u.) . The more abundant intermolecular interaction, O⋯S, is considered here

The total electronic energy density at the BCP (H_{BCP}), so-called Hamiltonian kinetic energy, is negative for interactions with significant sharing of electrons, its magnitude reflects the covalence of the interaction.

The -Gc/Vc ratio was computed to measure the covalency in non-covalent interactions. Values greater than 1 generally imply a non-covalent interaction without covalent character while ratios smaller than unity are indicative of the covalent nature of the interaction [32].

Here, for the four systems, small value of ρ and positive value of Laplacian in intermolecular interactions were observed, see Table 2. As illustrated in this table, BCPs present electron density values between 0.0053 and 0.0148 a.u. and also Laplacians between 0.0204 and 0.0519. Moreover, the -Gc/Vc ratio is greater than 1 for all intermolecular interactions. All our evidence shows that the present intermolecular interactions are weak interactions and have non-covalent nature.

Table 3 The resultant and value of charge transfers (|e|) and dipole momentum (Debye) of SO_4–CO_2, SO_4–CS_2, and SO_4–SCO systems

Complexes	Donor → acceptor	CT	Dipole momentum
A1	$CO_2 \rightarrow SO_4$	0.005	0.6014
B1	$CS_2 \rightarrow SO_4$	0.019	0.8904
C1	$SCO \rightarrow SO_4$	0.013	0.0942
C2	$SCO \rightarrow SO_4$	0.006	1.1834

Exponential relationships can be obtained between the intermolecular distances and the values of ρ and $\nabla^2\rho$ at BCP [33], see Fig. 3. According to this figure, as the intermolecular distance of the interacting atoms decreases, the values of ρ and $\nabla^2\rho$ increase.

The results of NBO analysis are gathered in Table 3. From this table, it is found that SO_4 monomer plays an acceptor role of charge in the present complexes. Also the maximum value of charge transfer, by 0.019 |e|, belongs to the most stable complex of B1. Table 3 also shows the value of dipole momentum of complexes. These values are in the range of 0.17–1.18 D.

Conclusions

Details of the intermolecular interactions of the SO_4 with isostructure species CO_2, CS_2, and SCO on the singlet PES have been characterized at the MP2 level, theoretically. The results show that the attack of SO_4 to CO_2, CS_2, and SCO monomers leads to the formation of one, one, and two real minima on singlet potential energy surfaces (PES) of SO_4-CO_2, SO_4-CS_2, and SO_4-SCO systems, respectively, at the MP2/aug-cc-pVDZ level. The stability of the three systems can be ranged in the order of SO_4–CS_2 > SO_4–SCO > SO_4-CO_2, indicating the more important role of the SO_4–CS_2 system in atmospheric chemistry. Based on AIM analysis, the small electron density, positive values of $\nabla^2\rho$ and -G_C/V_C >1 indicate that all intermolecular interactions present in these systems are weak interactions of non-covalent with no covalent nature. Also the maximum value of charge transfer is occurred in the most stable complex of B1. Also in all complexes, the resultant of charge transfers is from linear molecules to the SO_4 monomer.

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