

气相中 O₃ 与 HSO 自由基间的氢键复合物袁焜^{1,*} 刘艳芝¹ 朱元成¹ 张继^{1,2}¹天水师范学院生命科学与化学学院, 甘肃 天水 741000; ²西北师范大学化学化工学院, 兰州 730070

摘要: 气相中 O₃ 与 HSO 自由基之间的相互作用及其反应在大气化学中非常重要. 在 DFT-B3LYP/6-311++G** 和 MP2/6-311++G** 水平上求得 O₃+HSO 复合物势能面上的稳定构型, B3LYP 方法得到了三种构型(复合物 I, II 和 III), 而 MP2 方法只能得到一种构型(复合物 II). 在复合物 I 和 III 中, HSO 单元中的 1H 原子作为质子供体, 与 O₃ 分子中的端基 O 原子作为质子受体相互作用, 形成红移氢键复合物; 而在复合物 II 中, 虽与复合物 I 和 III 中具有相同的质子供体和质子受体, 却形成了蓝移氢键复合物. B3LYP/6-311++G** 水平上计算的单体间相互作用能的计算考虑了基组重叠误差(BSSE)和零点振动能(ZPVE)校正, 其值在-3.37 到-4.55 kJ·mol⁻¹ 之间. 采用自然键轨道理论(NBO)对单体间相互作用的本质进行了考查, 并通过分子中原子理论(AIM)分析了三种复合物中氢键的电子密度拓扑性质.

关键词: HSO 自由基; 臭氧; 氢键相互作用; 自然键轨道理论; 分子中原子理论

中图分类号: O641

Hydrogen-Bonded Complex between Ozone and Thioperoxy Radical in Gas-Phase

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Abstract: B3LYP/6-311++G** and MP2/6-311++G** calculations were used to analyze the interaction between thioperoxy radical (HSO) and ozone (O₃) in gas-phase, which are of interest in atmospheric chemistry. The results showed that there were three equilibrium geometries (complexes I, II, and III) at the B3LYP/6-311++G** level, but only one stable configuration (complexes II) at MP2/6-311++G** level. And all the equilibrium geometries were confirmed to be stable states by analytical frequency computations. Complexes I and III use the 1H atom of HSO as proton donor and the terminal 4O atom of O₃ as acceptor to form red shift hydrogen bond systems. However, complex II uses the same proton donor and acceptor to form a blue shift hydrogen bond system. Interaction energies of the complexes corrected with basis set superposition error (BSSE) and zero point vibrational energy (ZPVE) lie in the range from -3.37 to -4.55 kJ·mol⁻¹ at B3LYP/6-311++G** level. The natural bond orbital (NBO) and atoms in molecules (AIM) theories were also applied to explain the structures and the electron density topology properties of the three hydrogen bond complexes.

Key Words: Thioperoxy radical; Ozone; Hydrogen bond interaction; NBO theory; AIM theory

In recent years, non-covalent intermolecular interaction has been implicated as an important type of interactions in many systems^[1-7], especially in atmospheric chemistry^[8-10]. Not long ago,

Mansergas *et al.*^[11] reported a theoretical study on the hydrogen-bonded complexes formed between O₃ and HOO, and provided information that can be very useful in their possible experimental

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characterization. The chemistry of atmospheric sulfur is of great interest due to its significant role in environmental problems as acid rain, air pollution, and global climate change. The thioperoxy radical, HSO, analogous to HOO, is of particular interest as a potential reactive intermediate and can play a catalytic role in ozone destruction. The reaction of thioperoxy radical with ozone (Eqs.(1–2)) is of great importance in both the troposphere and the stratosphere, as it participates in the ozone-destruction process^[12]. In addition, there have been numerous experimental and theoretical studies on the structure of HSO radical^[13–16], but there was few reports about HSO complex. So it is important to perform a further theoretical study on these reactions, and we have considered that the first stage of the reaction would involve the formation of pre-reactive hydrogen-bonded complex between ozone and thioperoxy radical, in a similar way as a pre-reactive hydrogen-bonded complex has been recently measured and characterized among O₃, HOO or HO radicals^[11,17]. The existence of pre-reactive complexes has proven to be very useful to the understanding of the kinetic behavior of many gas-phase atmospheric reactions^[18], and we report in this work a theoretical study on the hydrogen-bonded complexes formed between O₃ and HSO, which is part of an ongoing *ab initio* study on these reactions. We have employed high-level *ab initio* calculations to locate and characterize these hydrogen-bonded complexes, to estimate its energetic stability, and to calculate the IR spectrum and the electron density topological property. By comparing the changes in the vibrational spectrum originated by the formation of the complexes, we aim to provide information that can be very useful in their possible experimental characterization.



1 Calculation details

The geometries of the isolated O₃ and HSO moieties and their complexes were fully optimized using B3LYP^[19]/6-311++G** and

MP2^[20]/6-311++G** computational levels. These methods and basis set adequately describe O₃···HOC^[21] and HO···H_nX (n=1, 2, 3; X=F, O, N)^[22] non-covalent interaction systems, so they are reliable for the purpose of our study. Harmonic vibrational frequency calculations confirmed the structures as a minimum or transition state and enabled the evaluation of zero-point vibrational energies (ZPVE). Counterpoise procedure (CP) was used to correct the interaction energy for basis set superposition error (BSSE). In the scheme of the CP method, the binding energy of two molecules (A and B) can be expressed as follows^[23]:

$$\Delta E^{\text{CP}} = E_{\text{AB}}(\text{AB}) - [E_{\text{Aeq}}(\text{A}) + E_{\text{Beq}}(\text{B})] - [E_{\text{A}}(\text{AB}) + E_{\text{B}}(\text{AB})] + [E_{\text{A}}(\text{A}) + E_{\text{B}}(\text{B})]$$

where $E_{\text{AB}}(\text{AB})$ is the total energy of the complex, $E_{\text{Yeq}}(\text{Y})$ (Y=A or B) is the total energy of monomer Y with equilibrium geometry but without extended basis sets, and $E_{\text{Y}}(\text{AB})$ and $E_{\text{Y}}(\text{Y})$ are the total energy of monomer Y based on the same geometry as that in the complex with and without extended basis sets, respectively. At the same time, zero-point vibrational energy corrections are also considered. Natural bond orbital (NBO)^[24] analysis and atoms in molecules (AIM) theory analysis^[25] are featured wholly through a series of intermolecular interactions under the HSO···O₃ system. NBO analysis was performed *via* NBO 5.0 program^[26], and the other calculations were performed using Gaussian 03 program^[27].

2 Results and discussion

2.1 Geometric configuration

All possible stable geometries (named as complex I, II, and III) obtained by a full optimization on the surface of O₃+HSO are depicted in Fig.1. It is easy to find that complexes I, II, and III all use the 1H atom of HSO radical as proton donor and the terminal 4O atom of O₃ as acceptor. And the three structures all can be regarded as conventional open-shell hydrogen bond complexes. Guo *et al.*^[22] pointed out that the DFT methods performed significantly worse than the unrestricted second order

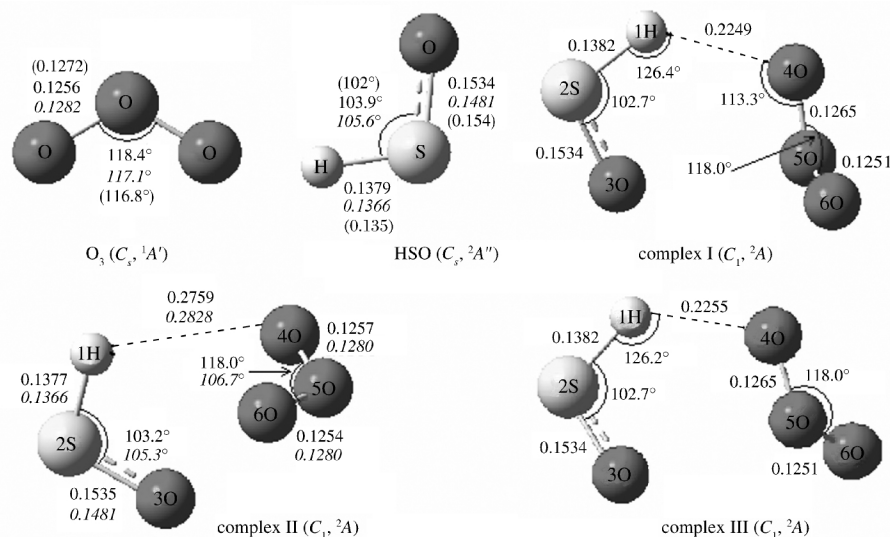


Fig.1 Geometries of the monomers and complexes calculated at B3LYP/6-311++G and MP2/6-311++G** (in italics) levels**
Bond length is in nm, bond angle is in degree, and the experimental values^[11] are given in parentheses.

Table 1 Computed harmonic vibrational frequencies (f/cm^{-1}) and intensities ($I/(\text{km}\cdot\text{mol}^{-1})$) for reactants (O_3 , HSO) and complexes calculated at B3LYP/6-311++G** level

Mode	Approximate description	reactants ^a		complex I		complex II		complex III	
		f	I	f	I	f	I	f	I
ν_1	scissoring bending (O_3)	746.5(705)	8.3	746.3	6.6	752.2	5.1	746.4	6.6
ν_2	O—S stretching (HSO)	955.7	14.6	962.6	5.7	955.8	11.3	962.6	5.7
ν_3	symmetrical stretching (O_3)	1183.1(1042)	238.9	1160.9	179.2	1187.4	211.9	1161.3	179.6
ν_4	asymmetrical stretching (O_3)	1245.4(1110)	0.1	1239.1	70.8	1242.7	6.5	1239.4	69.8
ν_5	scissoring bending (HSO)	1068.9	6.5	1060.9	32.0	1071.5	7.4	1061.2	31.5
ν_6	H—S stretching (HSO)	2426.6	69.5	2401.2	81.8	2451.8	30.8	2401.5	80.9

^a The experimental values^[11] are in parentheses.

Møller-Plesset perturbation (MP2) method in geometry optimization calculations for the open-shell hydrogen bonds and the B3LYP method seriously underestimated the donor-acceptor distances for the open-shell hydrogen bonds with radical proton donors. Here, complex I and complex III are the two interesting structures whose existence is predicted only in calculation with DFT-B3LYP/6-311++G** level, and they would go to the geometry of complex II when the optimization was carried out at MP2/6-311++G** level. This indicates that the complex II is probably the most stable configuration among the three complexes. In addition, as for complex II, the donor-acceptor distance (1H—4O) calculated *via* B3LYP method, is 0.2759 nm, which is shorter than that obtained by MP2 method (0.2828 nm). These results consist well with Guo's opinion^[22]. The relatively large errors of the DFT-B3LYP method in predicting the donor-acceptor distance are possibly due to the fact that the DFT methods are incapable of properly describing London dispersion forces^[23]. Some of the other key geometrical parameters optimized for these complexes using B3LYP and MP2 methods are also displayed in Fig.1. Comparing the data, we can find that the 2S—1H distances increased obviously after formed complexes I and III. For example, 2S—1H distances in complex I obtained *via* B3LYP method increased 0.0003 nm. However, 2S—1H distance in complex II obtained *via* the same method decreased 0.0002 nm. Bondi^[29] reported that van der Waals radius of O atom was 0.152 nm, and Taylor *et al.*^[30] reported that van der Waals radius of H atom was 0.109 nm. Here, under B3LYP method calculation, 4O \cdots 1H distances in complexes I and III are 0.2249 and 0.2255 nm, respectively. It is clear that these non-covalent interaction distances are both less than the sum of the relevant atoms' van der Waals radii. As for in complex II, the distance of 4O \cdots 1H is longer than the sum of the relevant atoms' van der Waals radii. Furthermore, it should be noticed that the three complexes all have nonplanar configurations. For example, in complex I, the O_3 and HSO moieties are near perpendicular to each other with an angle between the OOO and HSO planes of 103.6°, and the hydrogen of the HSO points at one of the terminal oxygen atoms of ozone forming a 4O5O6O1H dihedral angle of 49.6°.

2.2 Vibrational frequencies, rotational constants and interaction energies

To help the possible experimental identification of the hydrogen bond complexes described in this work, we report in Table 1 the computed harmonic vibrational frequencies of complex I,

complex II, and complex III along with the ones corresponding to the reactants O_3 and HSO. The change in the IR spectra originated by the formation of the hydrogen bond as well as the change of the corresponding intensity is a useful tool to identify experimentally or theoretically hydrogen bond complexes, as has been done recently for the $\text{O}_3\cdots\text{HOO}$ and $\text{O}_3\cdots\text{HO}$ complexes^[11,31]. The results from Table 1 predict that the 1H—2S stretching mode is red-shifted by 25.4 and 25.1 cm^{-1} for complex I and complex III, respectively, whereas for complex II, the 1H—2S stretching frequency is blue-shifted by 25.2 cm^{-1} . It is reported that the increase and decrease of IR strength of X—H are the typical character of red shift and blue shift hydrogen bond system, respectively^[32]. In present study, it should be noticed that the intensities of 1H—2S stretching in complex I and complex III (red-shifted complexes) are enhanced obviously, but in complex II (blue-shifted complex), it is weakened by 1.2 times. For the remaining vibrational modes, our results predict a tiny red shift for the O_3 asymmetric stretching and a tiny blue shift for the 2S—3O stretching of the HSO moiety.

For the reason of completeness, the rotational constants for monomers and the complexes calculated at B3LYP/6-311++G** level are also listed in Table 2. The three complexes are asymmetric rotors and behave like prolate rotors, with $A > B \approx C$. The computed rotational constants for O_3 agree well with the experimental values^[21].

Table 3 presents the total interaction energies (ΔE^{tot}) and the BSSE corrected interaction energies (ΔE^{CP}) for each complex. It is necessary to use sufficiently flexible basis sets to get reliable interaction energies of the open-shell hydrogen bonds^[22]. The basis set, 6-311++G**, is advantageous to the decrease of BSSE error, but obviously, it is necessary to perform CP and ZPVE corrections. Both the BSSE and ZPVE corrected interaction energies range between -3.37 and $-4.55 \text{ kJ}\cdot\text{mol}^{-1}$ at B3LYP/6-311++G** level. Complex II is clearly the most strongly bound of

Table 2 Rotational constants (in GHz) for O_3 , HSO, and the three complexes computed at B3LYP/6-311++G** level

Species	A	B	C
O_3	114.757(106.531)	13.561(13.384)	12.128(11.835)
HSO	294.019	19.560	18.340
complex I	9.217	1.762	1.568
complex II	8.797	1.797	1.688
complex III	9.233	1.759	1.565

Experimental values^[21] are in parentheses.

Table 3 Interaction energies in the three complexes^a

Complex	$\Delta E^{tot}/(\text{kJ}\cdot\text{mol}^{-1})$	BSSE($\text{kJ}\cdot\text{mol}^{-1}$)	$\Delta E^{CP}/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta E^{CP+ZPVE}/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta E^{tot}/(\text{kJ}\cdot\text{mol}^{-1})$	BSSE($\text{kJ}\cdot\text{mol}^{-1}$)	$\Delta E^{CP}/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta E^{CP+ZPVE}/(\text{kJ}\cdot\text{mol}^{-1})$
	B3LYP/6-311++G**				MP2/6-311++G** ^b			
I	-10.93	3.81	-7.12	-3.37	-6.92	10.64	3.72	7.14
II	-10.85	2.62	-8.23	-4.55	-21.71	9.62	-12.09	-8.79
III	-10.93	3.82	-7.11	-3.37	-6.95	10.63	3.68	7.08

^a ΔE^{tot} is the total interaction energy, ΔE^{CP} is the interaction energy with BSSE correction, and $\Delta E^{CP+ZPVE}$ is the interaction energy with both BSSE and ZPVE corrections.

^b For complex I and complex III, single-point calculations were used based on the geometry optimized at B3LYP/6-311++G** level.

the various complexes, with a binding energy of $-8.23 \text{ kJ}\cdot\text{mol}^{-1}$ after correction of BSSE, the other two hydrogen bond complexes (I and III) have approximate equivalent interaction energies. Guo *et al.*^[22] also pointed out that the DFT methods performed significantly worse than the unrestricted second order Møller-Plesset perturbation (MP2) method in interaction energy calculations for the open-shell hydrogen bonds and the DFT-B3LYP method seriously overestimated interaction energies for the open-shell hydrogen bonds with radical proton donors. In the present study, compared to the DFT-B3LYP method, the MP2 method leads to much lower (more positive) interaction energy. For instance, the both BSSE and ZPVE corrected interaction energies of complex I and complex III are both positive values (7.14 and $7.08 \text{ kJ}\cdot\text{mol}^{-1}$, respectively) *via* single-point calculation at MP2/6-311++G** level based on the geometry optimized at B3LYP/6-311++G** level. In other words, the system's energy would increase after complexation of complex I or III. So the complex I and complex III are the two interesting configurations which are not obtained *via* MP2 optimization method. It is clear at this moment that the complex II is the most reliable structure among the three theoretical configurations, and the performances of MP2 method are acceptable for those hydrogen bonds with radical proton donors.

Taking one with another, hydrogen bond interaction energy, similar to the binding energy of $\text{O}_3\cdots\text{HOO}$ system^[11], is weak in the present studied system. According to the BSSE and ZPVE corrected interaction energies listed in Table 3, we can conclude that the three complexes' stabilities increase in the order of complex I \approx complex III < complex II.

2.3 NBO analysis

The analyses for the combining interaction between O_3 and HSO with the natural bond orbital (NBO) method have been performed at MP2/6-311++G** level, and the corresponding results are listed in Table 4. The NBO analysis results for the monomers suggest that the 1H atom in HSO carries significant amount of positive charge ($0.026e$). On the other hand, the 4O atom in O_3 carries certain amount of negative charge ($-0.160e$). Therefore, intermolecular interaction should take place in the $2\text{S}-1\text{H}\cdots 4\text{O}$. This means that the non-covalent interaction involved in $2\text{S}-1\text{H}\cdots 4\text{O}$ can be defined as hydrogen bond.

The interaction strength between monomers could be clarified according to second-order stabilization energy ($E^{(2)}$) between proton donor and acceptor obtained from the NBO analysis. As NBO theory indicates, the larger the stabilization energy $E^{(2)}$ is, the stronger the interaction of donor and acceptor orbitals is. In

addition, the importance of the orbital hyperconjugation and electron density transfer (EDT) from electron donor orbital to electron acceptor orbital in non-covalent interaction systems is well known, which leads to an increase in population of electron acceptor antibonding orbital. This weakens the filled orbital bond and leads to itself elongation and concomitant stretching frequency red shift. The above theory is applicable for $\text{O}_3\cdots\text{HOO}$ system. In complex I, the second-order stabilization energies ($E^{(2)}$) of $n^{1,2,\text{and}3}(4\text{O})\rightarrow\sigma^*(1\text{H}-2\text{S})$ are 1.34, 0.59, and $3.89 \text{ kJ}\cdot\text{mol}^{-1}$, respectively. 3D images of the orbital interaction between $n^{1,2,\text{and}3}(1\text{O})$ and $\sigma^*(1\text{H}-2\text{S})$ are given in Fig.2(a, b, c). And the electron density of $\sigma^*(1\text{H}-2\text{S})$ increases by 1.08 me . In complex III, similar to that of complex I, an obvious overlap can be seen between the related orbitals (Fig.2(f, g, h)), and electron density of $\sigma^*(1\text{H}-2\text{S})$ increases by 1.04 me . As for complex II, $n^1(4\text{O})\rightarrow\sigma^*(1\text{H}-2\text{S})$ and $n^3(4\text{O})\rightarrow\sigma^*(1\text{H}-2\text{S})$ are the two main orbital interactions, but their $E^{(2)}$ values are very small, so the overlaps of the related orbital are very restricted, even can be ignored, as shown in Fig.2(d-e). Different from redshifted hydrogen bond in complex I or III, we notice that the electron density of $\sigma^*(1\text{H}-2\text{S})$ in complex II decreases by 0.59 me rather than increases by some amounts, since there is electron density redistribution effect of HSO moiety in complex II (especially the electron density transfer of $n^3(3\text{O})\rightarrow\sigma^*(1\text{H}-2\text{S})$ is weakened compared to the monomer of HSO, and the related data are not given in Table 4). On the other hand, it can be seen from Table 4 that, *s* character of 2S in $1\text{H}-2\text{S}$ of HSO moiety increases after formation of complex II. So we can conclude that the total of electron density redistribution and atom rehybridization effect exceed orbital hyperconjugation. Thus, $1\text{H}-2\text{S}$ bond length obtained by B3LYP method decreases by 0.0002 nm , and its stretching frequency represents blue shift after complexation.

2.4 AIM analysis

Table 4 NBO analysis of HSO and the three complexes at MP2/6-311++G** level

Species	HSO	Complex I	Complex II	Complex III
$E^{(2)}[n^i(4\text{O})\rightarrow\sigma^*(1\text{H}-2\text{S})]/(\text{kJ}\cdot\text{mol}^{-1})$	-	1.34	0.13	1.38
$E^{(2)}[n^i(4\text{O})\rightarrow\sigma^*(1\text{H}-2\text{S})]/(\text{kJ}\cdot\text{mol}^{-1})$	-	0.59	0.46	0.63
$E^{(2)}[n^i(4\text{O})\rightarrow\sigma^*(1\text{H}-2\text{S})]/(\text{kJ}\cdot\text{mol}^{-1})$	-	3.89	-	3.93
$\Delta\sigma^*(1\text{H}-2\text{S})/\text{me}$	-	1.08	-0.59	1.04
$\Delta q(1\text{H})/\text{me}$	-	18.58	11.45	18.47
sp^n of 2S in $\sigma(1\text{H}-2\text{S})$	$sp^{7.17}$	$sp^{6.00}$	$sp^{7.01}$	$sp^{6.90}$
$\Delta s(2\text{S})$ in $\sigma(1\text{H}-2\text{S})^a$ (%)	-	0.42	0.24	0.41
pol(1H) in $\sigma(1\text{H}-2\text{S})^b$ (%)	47.71	46.89	54.44	45.14

^a *s*-character increasing of 2S atom hybrid orbital in $\sigma(1\text{H}-2\text{S})$ on the complexation; ^b polarization percentage of 1H atom in $\sigma(1\text{H}-2\text{S})$

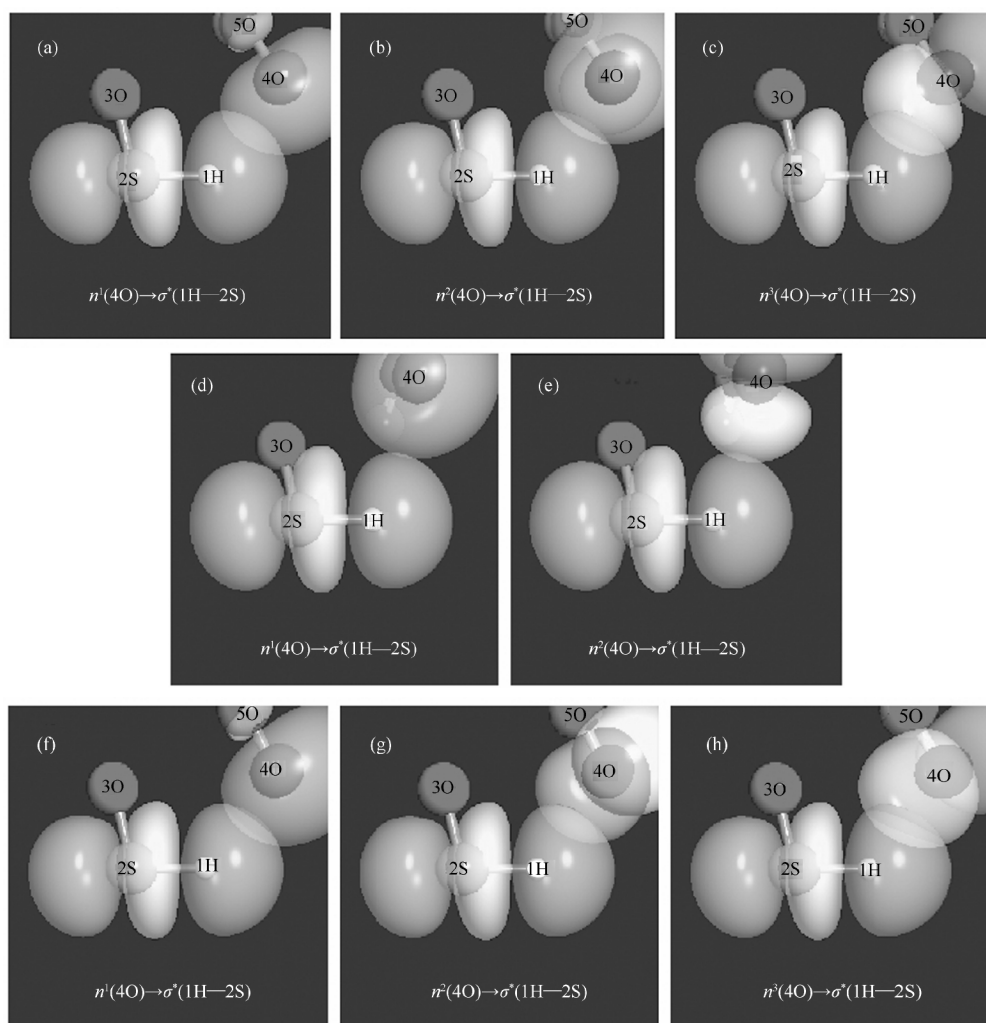


Fig.2 3D images of the main interactions between natural bond orbitals in $O_3 \cdots HSO$ systems

(a–c): complex I; (d, e): complex II; (f–h): complex III

A topological analysis of the electron density was performed using Bader's theory of atoms in molecules (AIM). This analysis has been applied to study the properties of a variety of interaction between atoms^[33]. Especially, the properties of the electron density at bond critical points (BCP) for the binding interaction between O_3 and HSO were analyzed in the present study. Table 5 lists the electron density (ρ) at BCP and its Laplacian of electron density ($\nabla^2\rho$) and ellipticities (ε). λ_1 , λ_2 , λ_3 listed in Table 5 are the eigenvalues of the electron density Hessian matrix, and $\nabla^2\rho = \lambda_1 + \lambda_2 + \lambda_3$. From Table 5, we can see $\lambda_1 < 0$, $\lambda_2 < 0$, $\lambda_3 > 0$ in each complex, according to Bader's theory^[21], they can be labeled as (3, -1) critical points, and christened BCP, which can indicate the

presence of the hydrogen bond interaction in the three complexes. For example, for the $1H \cdots 4O$ hydrogen bond in complex I, its ρ is 0.0147 a.u., and its $\nabla^2\rho$ is 0.0505 a.u., for complex II, they are 0.0059 a.u. and 0.0241 a.u. for complex III, they are 0.0145 a.u., 0.0498 a.u., respectively and the $\nabla^2\rho$ are all above zero, this indicates that the charge density is in radiation at BCP and the hydrogen bond has more ionic property. In addition, Lipkowski *et al.*^[34] pointed out that the electron density and positive values of the Laplacian in hydrogen bond system should be in the range of 0.002–0.04 and 0.02–0.15 a.u., respectively. Here, in the hydrogen-bonded complex I, complex II, and complex III, ρ and $\nabla^2\rho$ of $1H \cdots 4O$ all lie in the range of what Lip-

Table 5 The electron density topological properties at the hydrogen bonds' critical points of the three complexes at MP2/6-311++G** level

Complex	Atom pair	ρ	λ_1	λ_2	λ_3	$\nabla^2\rho$	ε	Interaction distance
I	$1H \cdots 4O$	0.0147	-0.0157	-0.0145	0.0808	0.0505	0.0862	0.2249
II	$1H \cdots 4O$	0.0059	-0.0055	-0.0031	0.0327	0.0241	0.7700	0.2759
III	$1H \cdots 4O$	0.0145	-0.0155	-0.0143	0.0797	0.0498	0.0850	0.2255

for atomic number, see Fig.1; ρ is electron density of critical point; λ_1 , λ_2 , λ_3 are Hessian eigenvalues; $\nabla^2\rho$ is density Laplacian; ε is ellipticity; ρ and $\nabla^2\rho$ in atom unit (a.u.); interaction distance in nm

kowski suggested. What's more, the smaller value of ellipticity (ε), the stronger the σ property is, and otherwise the stronger the π property is. In the present study, the value of ε of hydrogen bond in the three complexes are all in the range of 0.0850–0.7700 a.u.. These ε values are all smallness. According to AIM theory, the covalent content of the hydrogen bond in the three complexes would mainly represent σ property.

3 Conclusions

A theoretical study of the 1:1 complexes formed by O_3 and HSO has been carried out at B3LYP/6-311++G** and MP2/6-311++G** computational levels. Three stable configurations have been found at B3LYP/6-311++G** level, but only one stable configuration has been found at MP2/6-311++G** level. The theoretical analysis shows that the three complexes are held together by one hydrogen bond (S—H \cdots O) that is formed between the hydrogen of HSO moiety and one of the terminal oxygen atoms of ozone. Interaction energies of the three complexes corrected with basis set superposition error (BSSE) and zero point vibrational energy (ZPVE) lie in the range from -3.37 to -4.55 $\text{kJ}\cdot\text{mol}^{-1}$ at B3LYP/6-311++G** level. We also report computed harmonic vibrational frequencies and rotational constants to help for a possible experimental identification of these complexes. AIM analysis shows that a hydrogen bond interaction is presented unquestionably in $O_3\cdots\text{HSO}$ system.

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