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Ab Initio Theoretical Study of the Interactions Between $CFCl_3$ and SO_2

Kai Sheng Diao · Fang Wang · Hai Jun Wang

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Abstract Ab initio calculations have been performed on complexes of $CFCl_3$ with SO_2. Ten complexes were found stable, the interaction energies that reflect their stability were corrected by the basis set superposition error and the correction of zero-point energy. The natures of these interactions were investigated by the analysis of natural bond orbital and the atoms in molecules. The results from theoretical calculation indicated that there were the interactions of Cl···O, F···O, Cl···S and F···S between $CFCl_3$ and SO_2, furthermore, the non-covalent bonds of Cl···O and Cl···S were the major interaction forces, which provided some data and information for studying the environment problem such as greenhouse effect relevant to $CFCl_3$ and SO_2.

Keywords Trichlorofluoromethane · Sulfur Dioxide · Ab Initio calculations

Trichlorofluoromethane ($CFCl_3$), a chemical compound that has been produced in industry since the 1930s, is extensively used as propellants, solvents and refrigerants because of its chemical inertness and suitable physical properties. In 1974, Rowland and Molina (1974) were the first to publish a paper warning that $CFCl_3$ could be split apart by solar radiation to produce chlorine atoms, which could catalyze the destruction of the protective ozone layer in Earth's aerosphere. The role of $CFCl_3$ in ozone depletion in the upper aerosphere has been clearly established now. Furthermore, the disposal of these compounds in existing stocks was a major environmental problem (Rowland and Molina 1975; Saltzman and Cooper 1989). On the other hand, some countries have been suffered from SO_2 pollution since 1980s. As the main by-product of industry activities, SO_2 was considered to cause the majority of acid rain, accounting for more than 80% (Xu and Masui 2008). SO_2 was not only a common air pollutant, but also an oxidative agent to all organs tested from mice (including brain, lung, heart, liver, stomach, spleen, kidney and testis) (Davies 2005; Meng and Liu 2007).

As is known to all, the ozone hole and air pollution especially acid rain result in heavy economic loss over the world. Therefore, we are interested in the interaction of SO_2 gas molecules with $CFCl_3$, how the interaction takes place, whether the interaction impacts decomposition of $CFCl_3$, whether these environmental problems can be resolved, and so on. An interaction model is established between $CFCl_3$ and SO_2 in this paper. A number of possible stable geometries of $CFCl_3$–SO_2 complexes, properties of stabilities and bond characteristics etc. are investigated at reliable levels of ab initio method. Our work will provide some valuable information for studying the environmental problem relevant to $CFCl_3$ and SO_2 and other related fields such as the design and synthesis of specific supramolecular complexes concerning CFCs (Riley and Hobza 2008).

Materials and Methods

In order to balance the calculation accuracy and calculation expends, it is very important to select an appropriate calculation method for the interaction system involved. In this paper, the geometry optimization of monomers and complexes were fully performed with the Møller–Plesset second-order perturbation (MP2) method at basis sets of aug-cc-pVDZ and aug-cc-pVTZ level, all their stationary points as

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K. S. Diao · F. Wang · H. J. Wang (✉)
School of Chemistry and Ecological Engineering,
Guangxi University for Nationalities, 530006 Nanning, China
e-mail: wanghj329@hotmail.com

true minima were confirmed by calculating harmonic frequencies.

The interaction energies of complexes were corrected by the basis set superposition error (BSSE) with the Boys–Bernardi full counterpoise (CP) method (Boys and Bernardi 1970) at MP2/aug-cc-pVDZ and MP2/aug-cc-pVTZ levels, as well as the zero-point energy (ZPE) evaluation applied. The natural bond orbital (NBO) (Reed et al. 1988; Mohajeri and Karimi 2006; Frisch 2004) and atoms in molecules (AIM) theory analysis were done to provide more information for the interaction at the MP2/aug-cc-pVDZ level. The topological property and the charge density distribution at bond critical point (BCP) were performed by AIM2000 (Biegler-Konig and Bader 2002) package. All calculations were carried out with the Gaussian 03 suite of program (Frisch et al. 2003).

Results and Discussion

The $CFCl_3$–SO_2 binary system was optimized; ten stable configurations were obtained with no imaginary

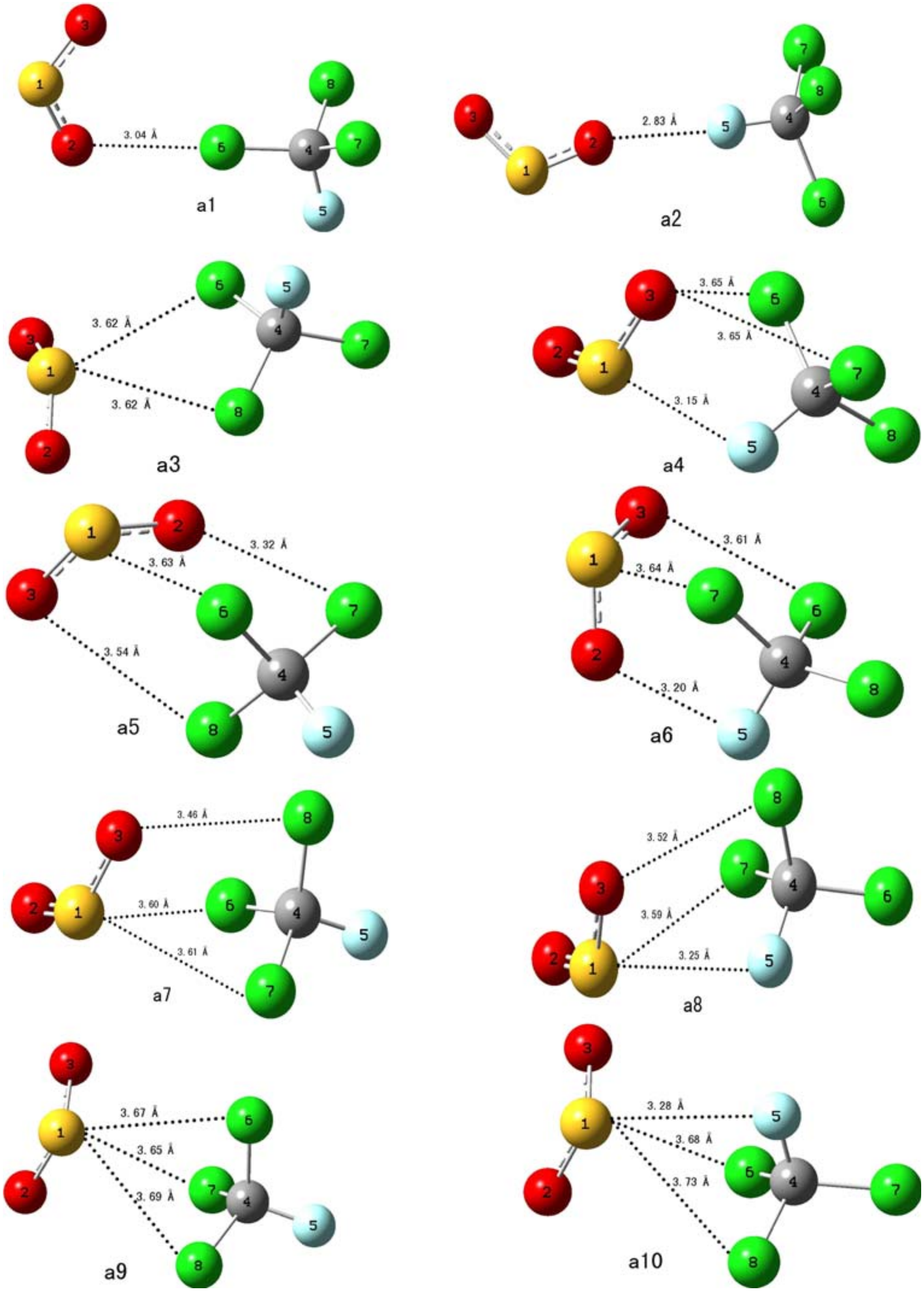

Fig. 1 Optimized structures of $CFCl_3$–SO_2 (MP2/aug-cc-pVDZ): a1, a2, a3, a4, a5, a6, a7, a8, a9, a10

frequencies. Their selected geometrical parameters are presented in Fig. 1.

There only one non-covalent bond is observed for a1 and a2 where distances of Cl···O and F···O are 3.04 and 2.83 Å, respectively, slightly less than the sum of corresponding distance in van der Waals radii (Bondi 1964). Two non-covalent bonds of Cl···S are found in a3, which length is 3.62 Å (Fig. 1).

The other seven configurations (a4, a5, a6, a7, a8, a9, a10) are established by three non-covalent bonds such as Cl···O, Cl···S, F···O or F···S. For configurations of a5, a7 and a9, SO_2 and Cl atom of $CFCl_3$ connects by Cl···O, Cl···S interactions. The distances of Cl···O are 3.32 Å, 3.54 Å for a5, and 3.46 Å for a7, respectively. Intermolecular Cl···S bonds are involved in a5, a7 and a9, with a range of 3.60–3.69 Å. Configurations of a4, a6, a8 and a10 have different non-covalent bonds from others, these configurations contain not only Cl···O or Cl···S bonds but also F···O or F···S bonds. The distances of Cl···O are in the range of 3.52–3.65 Å in a4, a6, a8, longer than the corresponding bonds in other configurations; The distances of Cl···S are in the range of 3.59–3.73 Å for a6, a8 and a10, close to the corresponding bonds in the other configurations. The length of F···O bond for a6 is 3.20 Å, longer than the corresponding bond in a2, the F···S bond lengths are 3.15, 3.25 and 3.28 Å for a4, a8 and a10, respectively.

Based on the above observations, it is suggested that the non-covalent bonds of Cl···O and Cl···S are the major interaction forces between SO_2 and $CFCl_3$.

Generally, the total energy from free $CFCl_3$ and SO_2 to corresponding binary complex will decrease when two molecules interact with each other. The decreased energy is called interaction energy, or binding energy, which is defined as the energy difference between complex and its free moieties. The stability of complex is closely related to the interaction energy (Shan et al. 2007). The BSSE is calculated with the counterpoise procedure method advanced by Boys and Bernardi (1970). Table 1 shows the interaction energies for a1–a10, including the BSSE, ZPE corrections and BSSE-corrected interaction energy ΔEcp.

Table 1 Interaction energies ΔE, BSSE, ZPE and ΔEcp for complexes (in kJ mol^{-1})

Complex	MP2/aug-cc-pVDZ				MP2/aug-cc-pVTZ
	ΔE	BSSE	ZPE	ΔE_{CP}	ΔE_{CP}
a1	−6.96	1.24	1.05	−5.72	−6.47
a2	−2.47	1.04	0.73	−1.43	−1.70
a3	−8.57	2.56	1.30	−6.01	−6.98
a4	−8.80	2.37	1.01	−6.43	−8.53
a5	−9.83	2.41	0.45	−7.42	−9.91
a6	−8.67	2.57	0.84	−6.1	−8.23
a7	−9.65	2.34	0.49	−7.31	−9.81
a8	−9.09	2.37	0.38	−6.72	−8.86
a9	−9.11	2.28	0.33	−6.83	−9.14
a10	−8.59	2.52	1.29	−6.07	−8.05

MP2/aug-cc-pVTZ method needs very long time to complete the calculation for the system studied, though the ΔE_{CP} of MP2/aug-cc-pVTZ are slightly larger than that of MP2/aug-cc-pVDZ. Therefore, the following calculations are performed at the MP2/aug-cc-pVDZ level because it spends little than MP2/aug-cc-pVDZ.

For all complexes, the BSSE corrections are approximately 20% of the uncorrected ΔE (Table 1), which indicates the BSSE correction is necessary for the interaction energies of these complexes using the MP2/aug-cc-pVDZ. The proportions of ZPE to the uncorrected ΔE are in the range of 3–13% (Table 1), indicating the effect of BSSE is larger than that of ZPE for the MP2/aug-cc-pVDZ calculations.

The values of interaction energy give two information: first, the stability of these complexes based on the number of non-covalent bonds decreases in the sequence: three non-covalent bonds pattern >two non-covalent bonds pattern >one non-covalent bond pattern; secondly, the stability of these complexes based on type of non-covalent bonds decreases in the order of Cl···O > Cl···S > F···S > F···O. The results show that complex a5 with two Cl···O bonds is the most stable because it offers the biggest binding energy, follows by a7 (Table 1).

NBO analysis provides a simple description of a chemical bond based on orbital interaction concepts. The ab initio wave functions transformed to the NBO form are in good agreement with the Lewis model of electronic structure concepts. The transformation produces both highly occupied and nearly empty localized orbitals. Consequently, they can be classified as core orbitals, lone pairs (*n*), bonding (σ, π). The orbitals with smaller occupations are considered as antibonding σ^*, π^*, which can be used to describe the effects of charge transfer or ''non covalence''. This is carried out by considering all possible interactions between filled donor NBO and empty acceptor NBO and estimating their energetic importance by second-order perturbation theory. For each donor NBO (i) and acceptor NBO (j), the stabilization energy $E^{(2)}$ associated with electron delocalization i→j is estimated as

$$E^{(2)} = -q_{\mathrm{i}}\frac{(F_{\mathrm{ij}})^2}{\varepsilon_{\mathrm{j}} - \varepsilon_{\mathrm{i}}}$$

where q_i is the orbital occupancy, ε_i and ε_j are diagonal elements (orbital energies), and F_{ij} is the off-diagonal NBO Fock matrix element. The stabilization energy is proportional to the NBO interacting intensity (Esrafili et al. 2008;

Foster and Weinhold 1980). In order to understand the nature of these complexes and the role of the unpaired orbital in the complexes, the NBO analysis was performed on complexes a5–a9 with wave functions calculated at the MP2/aug-cc-pVDZ level. The donor and the acceptor of NBO between two moieties, and their interacting stabiliztion energies estimated by second-order perturbation theory are listed in Table 2.

In NBO analysis, the orbital interaction of n(Cl)→σ*(S–O) is the main interaction between $CFCl_3$ and SO_2 in these complexes. For example, a5 offers the biggest stabilization energy of orbital interaction, which is 2.17 kJ mol^{-1}. There are two orbital interactions n(F)→RY*(O) and n(F)→RY*(S) in a6, a8, which are smaller than that of n(Cl)→σ*(S–O) (Table 2). The NBO analysis reveals that the n(Cl)→σ*(S–O) interactions give the strongest stabilization to these complexes and strengthen the intermolecular Cl···S and Cl···O interactions. The two orbital interactions of n(F)→RY*(O) and n(F)→RY*(S) in a6, a8 are weak interactions, though the RY*(O), RY*(S) also accept electrons from lone pairs of fluorin atom in $CFCl_3$.

The AIM Theory (Bader 1990) provides a powerful tool for the classification of the bonding interactions that take place in any molecular system, even inside a supermolecule (Bader 1998). Furthermore, this theory has been successfully used to characterize the nature of interaction. AIM calculations is based on a topological analysis of electron density (ρ_c) and Laplacian ($\nabla^2\rho_c$) at corresponding BCPs. ρ_c is used to describe the strength of a bond, a stronger bond associates with larger ρ_c value. $\nabla^2\rho_c$ describes the characteristic of the bond. As $\nabla^2\rho_c < 0$, it is named as the covalent bond. As $\nabla^2\rho_c > 0$, it refers to a closed-shell interaction and characteristic of ionic bond, hydrogen bond or van der Waals interaction (Ren et al. 2008). AIM calculations at the wave function of MP2/aug-cc-pVDZ level were performed to offer a deep insight into the nature of interactions. The values of ρ_c and $\nabla^2\rho_c$ at corresponding BCPs for these bonds are listed in Table 3.

These non-covalent bonds between two moieties in these complexes can be classified as closed-shell interactions because their values of $\nabla^2\rho_c$ are all positive, with a range of 0.0136–0.0356 e/au^{-5} (Table 3). On the basis of the AIM topological analysis, the Cl···O and Cl···S interactions occupy bigger proportion for these complexes because their ρ_c values are bigger than that of F···O and F···S interactions (Table 3), which means that the Cl···O and Cl···S interactions seems to be the main driving force influencing the arrangement of chlorine atom at $CFCl_3$ to a certain extent.

In this work, ab initio computations have been used to investigate the complexes of $CFCl_3$ with SO_2. There are seven complexes in which $CFCl_3$ and SO_2 are connected by

Table 2 NBO interacting and the corresponding stabilization energies (in kJ mol^{-1})

Complex	Donor NBO (i)	Acceptor NBO (j)	$E^{(2)}$
a5	LP (3) Cl_6	BD*(2) S_1–O_2	0.63
	LP (3) Cl_7	BD*(2) S_1–O_2	2.17
	LP (3) Cl_8	BD*(2) S_1–O_3	0.21
a6	LP (2) F_5	RY*(4) O_2	0.25
	LP (2) Cl_6	BD*(1)S_1–O_3	0.29
	LP (2) Cl_7	BD*(2) S_1–O_2	1.76
a7	LP (2) Cl_6	BD*(2) S_1–O_3	1.09
	LP (3) Cl_7	BD*(2) S_1–O_3	0.63
	LP (3) Cl_8	BD*(2) S_1–O_3	1.25
a8	LP (3) F_5	RY*(6) S_1	0.75
	LP (3) Cl_7	BD*(2) S_1–O_3	1.21
	LP (2) Cl_8	BD*(2) S1–O_3	0.38
a9	LP (3) Cl_6	BD*(2) S_1–O_2	0.54
	LP (3) Cl_7	BD*(1) S_1–O_2	1.67
	LP (3) Cl_8	BD*(2) S_1–O_2	0.42

BD*, antibonding orbital; LP, lone pair; RY* empty atomic orbital out of valance orbital

Table 3 Topological properties at the bond critical points for all complexes studied

Complex	Bond	$\lambda 1$	$\lambda 2$	$\lambda 3$	ρ_C (e/au^{-3})	$\nabla^2\rho_C$ (e/au^{-5})
a1	Cl_6···O_2	−0.0058	−0.0058	0.0472	0.0084	0.0356
a2	F_5···O_2	−0.0060	−0.0056	0.0442	0.0064	0.0326
a3	Cl_6···S_1	−0.0034	−0.0020	0.0238	0.0054	0.0184
	Cl_8···S_1	−0.0034	−0.0020	0.0238	0.0053	0.0184
a4	F_5···S_1	−0.0051	−0.0045	0.0372	0.0059	0.0277
	Cl_6···O_3	−0.0024	−0.0022	0.0182	0.0038	0.0136
	Cl_7···O_3	−0.0025	−0.0018	0.0189	0.0040	0.0146
a5	Cl_6···S_1	−0.0036	−0.0027	0.0248	0.0050	0.0184
	Cl_7···O_2	−0.0031	−0.0030	0.0234	0.0056	0.0173
	Cl_8···O_3	−0.0028	−0.0003	0.0210	0.0045	0.0179
a6	F_5···O_2	−0.0029	−0.0027	0.0253	0.0036	0.0197
	Cl_6···O_3	−0.0030	−0.0006	0.0216	0.0047	0.0180
	Cl_7···S_1	−0.0033	−0.0021	0.0226	0.0051	0.0172
a7	Cl_6···S_1	−0.0033	−0.0022	0.0228	0.0051	0.0173
	Cl_7···S_1	−0.0028	−0.0008	0.0237	0.0048	0.0200
	Cl_8···O_3	−0.0031	−0.0030	0.0234	0.0052	0.0173
a8	F_5···S_1	−0.0040	−0.0024	0.0312	0.0050	0.0248
	Cl_7···S_1	−0.0028	−0.0015	0.0234	0.0051	0.0190
	Cl_8···O_3	−0.0028	−0.0027	0.0209	0.0043	0.0155
a9	Cl_6···S_1	−0.0027	−0.0023	0.0203	0.0047	0.0153
	Cl_7···S_1	−0.0030	−0.0026	0.0219	0.0050	0.0163
	Cl_8···S_1	−0.0024	−0.0016	0.0212	0.0047	0.0173
a10	F_5···S_1	−0.0039	−0.0035	0.0302	0.0048	0.0228
	Cl_6···S_1	−0.0022	−0.0012	0.0190	0.0042	0.0156
	Cl_8···S_1	−0.0024	−0.0019	0.0180	0.0042	0.0137

three non-covalent bonds, such as Cl···O, F···O, Cl···S or F···S, one complex by two Cl···S non-covalent bonds, and the other two complexes contain only one non-covalent bond. The interaction energies of all complexes show the BSSE correction is absolutely necessary for the interaction system involved. Meanwhile, the complexes with three non-covalent bonds pattern are more stable. The NBO analysis reveals that the n(Cl) → σ*(S–O) interaction gives the strongest stabilization to these complexes and the lone pairs of fluorin atom in $CFCl_3$ play an weak role in the intermolecular interactions. The AIM analysis further approves the existence of four types of non-covalent bonds interactions and their roles in these complexes.

Obviously, the calculation results indicate that the non-covalent bonds of Cl···O and Cl···S are the major interaction forces in the Cl···O, F···O, Cl···S and F···S interactions between $CFCl_3$ and SO_2, which can provide some data and information for studying the environment problem.

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