

Ab initio Study of the Transition State of Direct Isomerization from *CIOCl* to *CICIO* on the S_0 and S_1 State

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There have been many experimental studies of the photolysis of dichlorine monoxide (Cl_2O),¹⁻⁸ partially because it is the anhydride of $HOCl$, an important chlorine reservoir species in the stratosphere. A rather unusual chemical species, *CICIO*, was detected in even the very earliest studies of *CIOCl*. After the detection of two of the vibration modes (962 - 952 cm^{-1} and 368 - 377 cm^{-1}) of *CICIO* in 1967,¹ the third vibration mode (241 cm^{-1}) was also reported in 1973.² In 1995, Johnsson *et al.* investigated the properties of *CICIO* by using irradiation of light between 320 and 428 nm, refined all three of the vibrational properties,³ and suggested that the geminate recombination of *CIO* and *Cl*, which are the products of the initial dissociation of *CIOCl*, is the main photoisomerization pathway to *CICIO*.³ This proposal seems to be further supported in 1999 by a resonance Raman study of *CICIO* photochemistry in solution with radiation with a wavelength of 282.4 nm (4.39 eV).⁴

Meanwhile, the direct isomerization from *CIOCl* into *CICIO* through a transition state (TS_{S_0}) of S_0 was also suggested in 1998,⁵ as another possible explanation for the isomer, but the role of TS_{S_0} in actual dynamical process has not yet been clearly studied theoretically. A later theoretical study in 2001 with reduced two-dimensional space at fixed bond angle showed that the initial dynamics of excited electronic states is the direct dissociation of *CIOCl* to *CIO* and *Cl*,⁶ but the possibility of isomerization through angular motion in either the ground or the excited electronic state was not explicitly studied there. Neither the validity of the TS_{S_0} nor the possibility of the direct isomerization has been explicitly examined yet.

In addition, Nickolaisen *et al.* observed unknown vibrational series in their absorption spectrum in the energy region of 20,000 - 22,000 cm^{-1} ; 'We have identified fragmentary series having 110, 325, and 786 cm^{-1} spacing in this region ... but we have been unable to establish a unique origin for the bands in this region.'⁷ No theoretical result has been reported yet about the state responsible to this observation.

Since the energies of the light sources (irradiation of light 320 - 428 nm corresponds to 3.9 - 2.9 eV) used in the detection of *CICIO* correspond to the first excited singlet state, S_1 (1B_1), of *CIOCl*,^{2,7} the detailed dynamical behavior of the S_1 state of *CIOCl* and *CICIO* deserves to be studied too. In other word, the possibility of direct isomerization through the potential energy surface (PES) of not only the S_0 state but also the S_1 state deserve to be explored further. However, no reliable theoretical study of the stability, stationary structure, and vibration pro-

erties of the S_1 electronic states of *CIOCl* and *CICIO* has previously been explicitly reported yet. Because the photolysis with higher photon energies opens up more complicated and distinct pathways,^{4,7-9} a clearer understanding of the characteristics of S_1 is an indispensable prerequisite of further rigorous dynamical study of the higher excited states of Cl_2O systems.

To provide additional insights on the matters, i.e., the validity and role of the transition state structure involved in the direct isomerization along S_0 PES from *CIOCl* to *CICIO* isomer is re-examined in the present work by using highest level of theory applied so far. The stability of the first excited singlet state, S_1 , of both *CIOCl* and *CICIO* are also studied here, at first.

Details of Computations. The coupled-cluster singles and doubles (CCSD) method¹⁰ and its extended CCSD(T) method¹¹ including non-iterative triples were used for the study of the ground singlet state (S_0), whereas the equation-of-motion coupled-cluster singles and doubles (EOM-CCSD) method¹² was used for the first excited singlet states (S_1). The molecular orbitals (MOs) corresponding to the core atomic orbitals of O (1s) and Cl (1s, 2s, and 2p) atoms were frozen (dropped) in the post Hartree-Fock calculations. The analytic gradient method for the CCSD and EOM-CCSD energies with the dropped MO space not only for the ground state¹³ but also for excited states,¹⁴ as implemented in the ACES-2 suit of programs,¹⁵ was used in the present study.

To make direct comparisons with previous theoretical works, exactly the same two basis sets (Basis-1 and Basis-2) of them were used in the present study too. Basis-1 is the TZV2d sets, consisted of 5s3p2d and 5s4p2d contracted GTO for oxygen and chlorine, respectively, as used by Chaquin and colleagues for their B3LYP calculations.^{5,16} Basis-2 is the TZ2P sets having 5s3p2d and 6s5p2d contracted GTO for oxygen and chlorine, respectively, and was used by Lee with the CCSD(T) method.¹⁷ All six components of the Cartesian d-functions were included in Basis-1 and -2. In order to get nearest result to the one-electron basis set limit, the aug-cc-pVQZ sets (Basis-3) is used for the B3LYP-DFT method while the aug-cc-pVTZ sets for the CCSD and CCSD(T) methods. Only five pure spherical d-type functions were used in Basis-3 and -4.

The Ground State, S_0 (X^1A_1 , X^1A'). The vibrational properties of the ground states of *CIOCl* and *CICIO* are relatively well established,³ with reliable theoretical results.^{16,18} The theoretical results for *CIOCl* and *CICIO* with various functional forms (BLYP, BP86, BPW91, B3LYP, and SVWN) of DFT

Table 1. Bond lengths (γ in Å), angles (\angle in degrees), vibrational frequencies (ω in cm^{-1}), and total energies (E_{tot} in a.u.) of the ground electronic states (S_0) of *CIOCl*, *CICIO*, and the transition state (TS_{S_0}) connecting the S_0 states of the two isomers. The structures of the isomers and TS_{S_0} are depicted in Figure 1

Method-	1	2	3	4	5	
Theory	B3LYP		CCSD	CCSD(T)		Exp. ^b
Basis ^a	Basis-1	Basis-2	Basis-3	Basis-4	Basis-3	
<i>CIOCl</i> (S_0, X^1A_1)						
γ_{Cl-O}	1.724	1.709	1.699	1.731	1.715	1.696
$\angle_{Cl-O-Cl}$	112.4	112.8	111.3	110.7	110.9	110.9
ω_1 (asym. str.)	651	669	763	667(4)	699(1.4)	686
ω_2 (sym. str.)	649	657	674	624(1)	642(1.1)	640
ω_3 (bend)	290	294	305	288(0.1)	293(0.1)	300
E_{tot}^c (a.u.)	-1.5711	-1.6095	-0.4466	-0.3569	-0.4791	
ΔE_{bind}^d (eV)	1.25	1.38	1.23	1.26	1.44	1.40
<i>CICIO</i> (S_0, X^1A')						
γ_{Cl-Cl}	2.186	2.147	2.108	2.232	2.167	
γ_{Cl-O}	1.533	1.517	1.518	1.545	1.532	
$\angle_{Cl-O-Cl}$	114.0	113.4	112.2	114.2	113.2	
ω_1 (<i>Cl-O</i> str.)	949	976	970	918(38)	957(56.2)	962
ω_2 (<i>Cl-Cl</i> str.)	393	403	431	336(33)	371(45.1)	375
ω_3 (bend)	240	250	256	214(5)	231(5.1)	239
ΔE_{iso}^e (eV)	0.68	0.56	0.90	0.82	0.74	
TS_{S_0} <i>CIOCl</i>						
γ_{Cl-O}	1.552	1.535	1.550	1.618	1.598	
γ_{O-Cl}	2.603	2.574	2.604	2.821	2.886	
$\angle_{Cl-O-Cl}$	76.8	77.6	76.3	114.6	113.6	
ω_1 (str.)	925	948	899	753	786	
ω_2 (str.)	227	229	211	80	64	
ω_3 (bend)	566 i	583 i	683 i	192 i	193 i	
ΔE_{iso}^e (eV)	2.11	2.12	2.46	1.16	1.36	
ΔE_{bind}^d (eV)	+0.86	+0.73	+1.23	-0.10	-0.08	

^aBasis-1, Basis-2, Basis-3, and Basis-4 are the TZV2d, aug-cc-pVQZ, aug-cc-pVTZ, and TZ2P sets, respectively. ^bRef. 19 for bond lengths and angles, Ref. 22 for ΔE_{bind} , and Ref. 3 for vibration frequencies. ^cThe total energies are given with respect to -994.0 Hartrees. ^dThe binding energy (in eV) with respect to the dissociation limit of $\text{Cl}(\text{P})$ and $\text{ClO}(\text{P})$. ^eThe relative energy (in eV) with respect to the S_0 of *CIOCl*.

theory as well as various levels (SCF, MP2, and CCSD[T]) of *ab initio* theory have been compared there.¹⁸ The transition state (TS_{S_0}) connecting the two ground states, S_0 (1A_1) of *CIOCl* and S_0 ($^1A'$) of *CICIO* has been investigated with a DFT method only, and the possibility of isomerization through TS_{S_0} was suggested and discussed there with the DFT results for the TS_{S_0} .⁵

In order to verify the validity of the previous results, especially for the reliability of the TS_{S_0} , we have applied five different methodologies, and the results are shown with some available experimental values and previous theoretical results in Table 1. The results by Method-1 (B3LYP/TZV2d) are included here because the method is what used in the previous work by Chaquin *et al.*,^{5,16} whereas the results by Method-4 (CCSD(T)/TZ2P) are shown here because they are used as the most reliable theoretical values at the time.¹⁷ We have tested many different combinations of DFT methods and basis sets, and the results by B3LYP/aug-cc-pVQZ (Method-2) are included in Table 1

as typical basis set-limit results of DFT methods. Method-3 and Method-5 correspond to the CCSD/aug-cc-pVTZ and the CCSD(T)/aug-cc-pVTZ method, respectively.

The calculated bond lengths and angles as well as vibrational frequencies of our five methodologies are all in excellent agreement with experiment values.^{3,19} Especially, the vibration frequencies by CCSD(T)/aug-cc-pVTZ method are almost in perfect agreement with experimental values. Therefore, the results by Method-2 (B3LYP/aug-cc-pVQZ) and Method-5 (CCSD(T)/aug-cc-pVTZ) correspond to the ones obtained with one of the highest levels of theory applied so far to these systems. The calculated isomerization energies (ΔE_{iso}) shown in the middle part of Table 1 – 0.56 and 0.74 eV by Method-2 and Method-5, respectively – are all comparable to the most reliable value provided previously, 0.685 eV, which was obtained with the CCSD(T)/ANO4 method.²⁰ The positive values of the isomerization energies correspond to the fact that *CIOCl* isomer structure is more stable than the *CICIO* isomer. The binding energy (ΔE_{bind}) with respect to the dissociation limit of $\text{Cl}(\text{P})$ and $\text{ClO}(\text{P})$ is 1.44 [1.38] eV according to the CCSD(T)/aug-cc-pVTZ [B3LYP/aug-cc-pVQZ] method, whereas the experimental value is 1.40 eV.²¹ The previous theoretical study by the CAS-PT2-Cl/cc-pVTZ+2s2p method produced 1.44 eV.²² The results by the DFT calculations are reasonably good so far, not only for the spectroscopic properties but also energetic properties, E_{bind} and ΔE_{iso} .

The question about the reliability of the transition state (TS_{S_0}) structure connecting the stationary S_0 structures of *CIOCl* and *CICIO* is one of the main motivations of the present work. The results by our five methodologies are given in the lowest part of Table 1. Two important facts can be noticed from the results. First, the structure and vibration frequencies by Method-1, Method-2, and Method-3 are basically all alike. The bond angles ($\angle_{Cl-O-Cl}$) are around 77° , and the magnitudes of the imaginary frequency are around 600 cm^{-1} . The results by the CCSD(T) method (Method-4 and Method-5), however, disclose a rather different structure ($\angle_{Cl-O-Cl} \approx 114^\circ$) and the magnitude of the imaginary frequency ($\sim 190 \text{ cm}^{-1}$). The second important difference is the binding energy (E_{bind}) of the TS_{S_0} structure with respect to the dissociation limit of ' $\text{Cl}(\text{P}) + \text{ClO}(\text{P})$ ' fragments. Method-1, -2, and -3 produced negative binding energies, and it imply that the TS_{S_0} structure has higher energy than the dissociation limit. The length of one *Cl-O* bond of TS_{S_0} structure is about 2.6 Å, about 150% of equilibrium bond length. It seems unreliable result, due to the limitation of DFT methods (Method-1 and Method-2) and the limitation of the single-reference CCSD method (Method-3). The CCSD(T) seems to remedy the problem, and the binding energy by Method-4/Method-5 is just around 0.1 eV. If we consider the possible basis-set-superposition-error (BSSE) effect, the binding energy would become zero. The large *Cl-O* bond distance (~ 2.9 Å) also implies that the TS_{S_0} structure by the CCSD(T) method is nothing but a kind of van der Waals complex between the dissociated fragments, $\text{Cl}(\text{P})$ and $\text{ClO}(\text{P})$. More detailed study on the van der Waals complex should include much higher theoretical levels for electron correlation with even larger basis sets and relativistic spin-orbit coupling, but the study is out of the scope of the present work.

Table 2. Bond lengths (γ in Å), angles (\angle in degrees), vibrational frequencies (ω in cm^{-1}), and relative energies (ΔE in eV)^a of the first excited singlet electronic state (S_1) of *CIOCl*, *CICIO*, and the transition state (TS_{S_1}) connecting the S_1 states of the two isomers by the EOM-CCSD/aug-cc-pVTZ method.

	<i>CIOCl</i> (S_1)	TS_{S_1}	<i>CICIO</i> (S_1)
$\gamma_{\text{Cl-O}}$	1.597	1.563	1.544
$\gamma_{\text{O-Cl}}$	2.206	2.904	
$\gamma_{\text{Cl-Cl}}$		2.993	2.395
$\angle_{\text{Cl-O-Cl}}$	115.5	77.8	
$\angle_{\text{Cl-Cl-O}}$		71.5	137.1
ω_1	822	768 ^b	859
ω_2	326	325 ^b	270
ω_3	140	110 ^b	118
ΔE^a (eV)	2.286	2.944	2.291

^aRelative energy is defined with respect to the S_0 state energy of *CIOCl* by the CCSD/aug-cc-pVTZ method. ^bExperimentally observed values (Ref. 7), which were not explained before.

It is now clear that the transition state structure, suggested in previous work,¹² is just a false result due to the limitation of B3LYP-DFT method, and therefore, the possibility of direct isomerization through TS_{S_0} , suggested in earlier work,¹² has to be dismissed. Then, the possibility of direct isomerization within the first excited electronic state is the next question to be explored.

The Excited Singlet States S_1 . The equilibrium geometry and vibrational properties of the first excited singlet state, S_1 (1B_1 , in C_{2v} , $^1A''$ in C_s), of *CIOCl* and *CICIO* were studied by using the EOM-CCSD/aug-cc-pVTZ method. The transition state structure (TS_{S_1}) connecting the S_1 of *CIOCl* and *CICIO* is also obtained by the same method, as shown in Table 2.

One of the most important fact disclosed from the results in Table 2 is the fact that the calculated vibration frequencies (822, 326, 140 cm^{-1}) of S_1 of *CIOCl* are well comparable to the experimental values (768, 325, 110 cm^{-1}),⁷ which were not explained yet. Considering the fact that calculated vibration frequencies with single reference CCSD method tends to slightly larger than experimental values, our results well match the experimental observation. Moreover, the calculated vertical excitation energy of the S_1 state is 2.68 eV (21615 cm^{-1})²¹ and our calculated adiabatic excitation energy is 2.286 eV (18438 cm^{-1}). The values are comparable to the experimental energy region of 20,000 - 22,000 cm^{-1} , and we believe that the S_1 state of *CIOCl* is responsible to the experimental observation.⁷

According to the results in Table 2, S_1 of *CICIO* has almost the same energy as S_1 of *CIOCl*, and TS_{S_1} locates at 2.944 eV above the S_0 stationary structure of *CIOCl*, as depicted in Figure 1. Though the energy of the irradiation light 320 - 428 nm, used in previous experiment, corresponds to 3.9 - 2.9 eV range, the calculated results (especially the relative energy of TS_{S_1} , 2.944 eV) should not be regarded as a suggestion of direct isomerization on the PES of S_1 state. The reason is that the dissociation limit of '*Cl + OCl*' locates only 1.44 eV above the S_0 stationary structure of *CIOCl*, as shown in Figure 1. Our separate calculations with full CCSDT method indicate that the barrier of S_1 PES towards the dissociation limit is just around

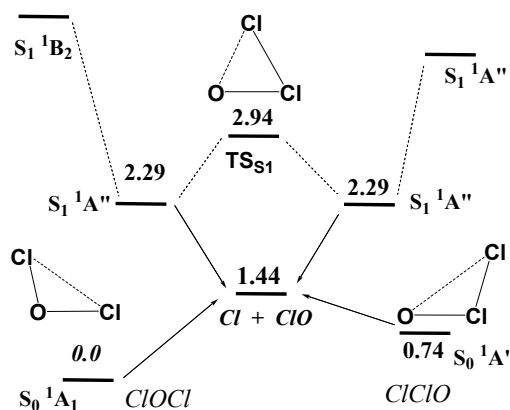


Figure 1. The relative energies (in eV) among stationary structures and transition states of the *CIOCl* and *CICIO* isomerization.

0.3 eV.

Summary and Conclusions. This work was motivated by the unclear situation concerning to the possibility of the direct isomerization^{5,6} from *CIOCl* to *CICIO*. According to our study, however, the transition structure (TS_{S_0}) for the direct isomerization on S_0 PES, suggested in previous work by DFT methods, is a false, and has to be dismissed. The CCSD(T)/aug-cc-pVTZ results show that the TS_{S_0} structure is nothing but a weakly bound complex of *Cl* atom and *ClO* radical. The stationary structure of S_1 state is obtained for both *CIOCl* and *CICIO* isomers, at first in this work. The calculated vibration frequencies of *CIOCl* in S_1 state are very close to previously reported experimental observation, which was not properly explained before. Though the transition structure (TS_{S_1}) for the direct isomerization on S_1 PES is found in this work at first, the energy barrier of the *Cl-O* bond dissociation on S_1 PES is just around 0.3 eV. In other word, the S_1 stationary state of *CIOCl* corresponds to vibrationally predissociative state. The possibility of direct isomerization on both S_0 and S_1 PES, therefore, has to be neglected completely, and the recombination of the fragments is the only remaining possibility for the formation of the *CICIO* isomer. More rigorous study by using multi-reference methods for the electron correlation with the larger basis sets are under progress now.

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