

Ab Initio Study of the Weakly Bonded CO–Cl₂ Complex†

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Ab initio structure and vibrational frequency calculations have been performed on the weakly bonded CO–Cl₂ complex at the SCF and MP2 levels of approximation. Minima were found for the two linear structures, specifically CO–Cl₂ and OC–Cl₂, with the latter being slightly more stable than the former. In addition, minima were found for two nonlinear structures, one T-shaped and the other essentially parallel. In the T-shaped structure, the oxygen is very weakly bonded to the chlorines (C_{2v} symmetry). The parallel isomer is slightly lower in energy than the T-shaped structure; however, both of the nonlinear isomers are less stable than either of the linear isomers. The calculated properties of the OC–Cl₂ isomer are in excellent agreement with experimental results reported earlier, lending further support to the conclusion that the structure of the experimentally observed isomer is OC–Cl₂ rather than CO–Cl₂.

Introduction

We recently reported the results of an experimental study on the weakly bonded CO–Cl₂ complex.¹ Using a tunable diode laser to probe the CO chromophore, we found the complex to have a linear geometry with a 6.228-cm⁻¹ blue shift in the CO vibrational frequency relative to uncomplexed CO. Whether the carbon atom or the oxygen atom lies closest to the chlorine atom was not determined experimentally. We proposed, however, that the structure of the complex we observed was OC–Cl₂.

Our objective in initiating this theoretical study was twofold. First, ab initio calculations can be used to help determine the orientation of the CO in this complex. A comparison of the experimental results along with the theoretical calculations should allow us to corroborate our conclusions presented in the experimental paper. Second, we should be able to determine whether additional minima exist on the potential energy surface corresponding to other geometries, i.e., T-shaped and/or slipped parallel. In this paper, we present results from ab initio calculations on the CO–Cl₂ complex at the SCF and MP2 levels of approximation, utilizing two atomic orbital (AO) basis sets: double- ζ plus single polarization (DZP) and triple- ζ plus double polarization (TZ2P).

Theory

Closed-shell Hartree–Fock SCF and MP2 calculations² were performed using two AO basis sets. The smaller DZP basis for carbon and oxygen is the Dunning³ contraction of the (9s5p) to [4s2p] plus a single primitive d function ($\alpha_C = 0.80$, $\alpha_O = 0.90$)⁴ for carbon and oxygen. The chlorine DZP basis is the Dunning⁵ (11s,7p) contracted to [6s,4p] plus one d polarization function with $\alpha_{Cl} = 0.75$.⁶ The TZ2P basis sets for carbon and oxygen are also contracted Dunning^{7a} basis sets consisting of (10s,6p) \rightarrow [5s,4p] plus two d polarization functions with $\alpha_C = (1.2, 0.4)$ and $\alpha_O = (1.35, 0.45)$. The chlorine was described by the Huzinaga^{7b} (12s9p) \rightarrow [9s,6p] augmented by two d polarization functions with $\alpha_{Cl} = (1.50, 0.375)$. These chlorine α values were determined by splitting the single d ($\alpha_{Cl} = 0.75$) according to the “even scaling rule”.⁸ The calculations were performed using the CADPAC⁹ (version 4.1) quantum chemistry codes running on a Cray XMP located at the U.S. Army Research Laboratory.

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The two monomers were optimized separately at both the SCF and MP2 levels using both basis sets. This was followed, at each level of theory, by a geometry optimization of the complex starting with the two linear isomers. All degrees of freedom were allowed to vary with no symmetry constraints imposed upon the calculations. For each run, the two monomers were set at an initial separation of approximately 3.0–3.5 Å, typical van der Waals bond lengths. The optimizations were considered converged when all gradients were $\leq 1 \times 10^{-5}$ hartree/bohr. Harmonic vibrational frequencies were obtained at the optimized geometries using analytic second derivatives of the gradients except at the highest level of theory (MP2/TZ2P), where machine storage capabilities necessitated the calculation of the force constant matrix by taking finite differences of the gradients using center differencing with steps sizes of ± 0.002 bohr. To check for stable nonlinear CO–Cl₂ structures, we ran additional optimizations at the highest level of theory used in this work (MP2/TZ2P) starting with the Cl–Cl–C bond angle at 90° and 135° and the Cl–C–O bond angle at 180° (structures 1 and 2 in Figure 1). This process was then repeated with the CO orientation reversed, that is, with the oxygen lying closer to the chlorine (structures 3 and 4 in Figure 1). These calculations were then followed by a second set of calculations where the C–O–Cl and the O–C–Cl angles were each started at 90° and 135°, and the O–Cl–Cl and C–Cl–Cl bond angles were started at 180° (structures 5–8 in Figure 1).

Results

Linear Complexes. Both linear isomers of CO–Cl₂ were found to be minima and are shown schematically in Figure 2. Linear OC–Cl₂ structures resulted from initial starting structures 2, 5, 7, and 8 shown in Figure 1. Linear CO–Cl₂ structures were obtained when starting from structures 4 and 6 in Figure 1. Tables I and II summarize the structural parameters of the stable linear complexes and the monomers, respectively. As one might expect, the calculated bond lengths of the monomers change very little (i.e., $\sim 10^{-3}$ Å) when reoptimized in the complex. However, the calculated CO bond length is always shorter in the OC–Cl₂ (carbon bonded to the chlorine) complex and remains essentially constant in the CO–Cl₂ complex when compared to uncomplexed CO. In addition, the Cl₂ bond length has increased slightly in both of the linear isomers of the complex when compared to “free” chlorine. Jager et al. have observed a shortening of the CO bond length and a lengthening of the Cl₂ bond length in a microwave study

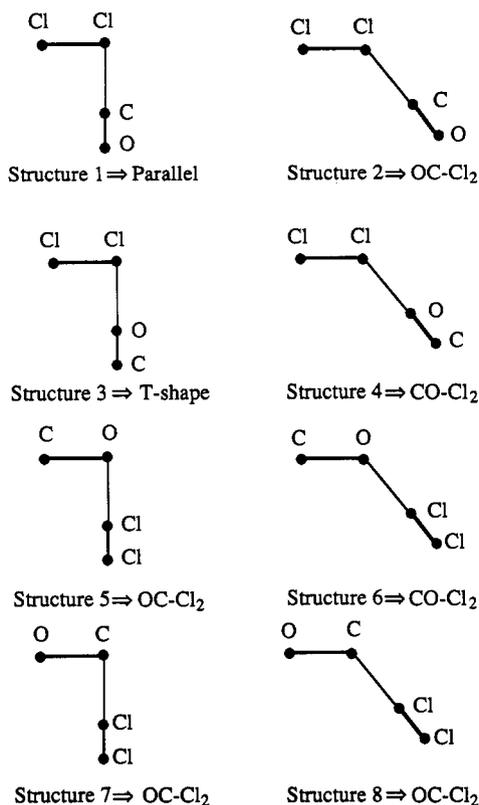


Figure 1. Initial structures for the optimizations and their converged geometry.

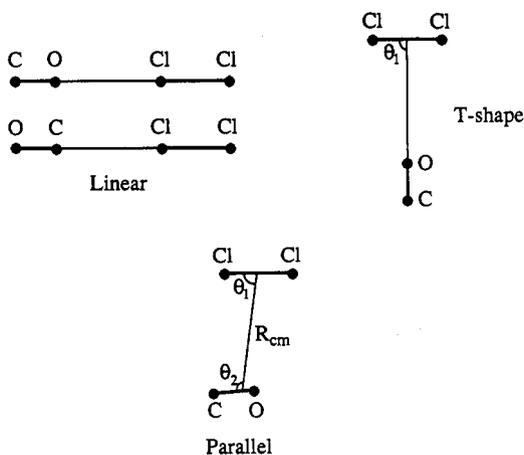


Figure 2. Optimized structures of the four isomers of the CO-Cl₂ van der Waals complex.

of OC-Cl₂.¹⁰ Two other trends can also be observed in the linear structures. First, the OC-Cl₂ complex is consistently lower in energy than the CO-Cl₂ isomer at all levels of theory. At the MP2/TZ2P level, the OC-Cl₂ isomer has an energy of $-1032.765\,025$ hartrees and the CO-Cl₂ isomer has an energy of $-1032.764\,068$ hartrees, a difference of $0.000\,957$ hartree (210 cm^{-1}). Subtracting the energies of the monomers from the energy of each complex yields D_e , the binding energies of the complexes. The binding energy is found to be 554 cm^{-1} for the OC-Cl₂ complex and 337 cm^{-1} for the CO-Cl₂ complex. After correcting for basis set superposition errors (BSSE) using the counterpoise method of Boys and Bernardi,¹¹ these values become 432 and 232 cm^{-1} , respectively. In making comparisons between the binding energies of the two isomers, it is meaningful to compare the energy difference between the zero-point levels (D_0) as well as the D_e values. Using the frequency data presented in Tables III and IV, the zero-point energies of OC-Cl₂ and CO-Cl₂ are calculated to be 397 and 232 cm^{-1} , respectively. Again, the BSSE-corrected

values are 275 and 120 cm^{-1} , a difference of 155 cm^{-1} . While the calculations consistently predict the formation of OC-Cl₂ over CO-Cl₂, the two minima are close enough in energy that both isomers may exist as long as the barrier between them is sufficiently high.

An additional trend observed in the data of Table I can be seen in $\Delta\nu_0$, the shift in the CO vibrational frequency upon forming the complex. The frequency shifts were obtained by taking the difference between the vibrational frequency of the CO monomer (found in Table II) and the binary complex using the same basis set at the same level of theory. All of the shifts are seen to be very small, i.e., $\Delta\nu_0 \leq 9\text{ cm}^{-1}$. The CO-Cl₂ isomer exhibited a very small blue shift ($+0.6\text{ cm}^{-1}$) for the MP2/DZP calculations and small red shifts for the SCF/DZP (-2.9 cm^{-1}) and MP2/TZ2P (-2.0 cm^{-1}). The red shifts contradict the observed experimental blue shift of $+6.2\text{ cm}^{-1}$. In contrast, the more stable OC-Cl₂ isomer is predicted to have a blue shift in the CO stretch at all levels of theory. The SCF/DZP calculation results in a shift of $+7.9\text{ cm}^{-1}$, and at the MP2/DZP level, a shift of $+8.6\text{ cm}^{-1}$ is predicted. At the MP2/TZ2P level, the shift is calculated to be $+6.3\text{ cm}^{-1}$, in excellent agreement with experiment. Such quantitative agreement is most likely fortuitous. The significance of these frequency shifts lies not in their absolute magnitudes but in the consistency with which they predict a blue shift in the CO frequency upon formation of the OC-Cl₂ complex. This consistent blue shift is absent in the CO-Cl₂ isomer calculations, lending further support that the OC-Cl₂ complex was observed experimentally.

The dipole moments μ of the complexes are listed in Table I. The orientation of the dipole moment is not shown for the complexes computed at the SCF level because SCF calculations on CO give erroneous values for the polarity. At the MP2 level, however, the computed polarity of the CO dipole moment is $\delta\text{-CO}^{\delta+}$, in agreement with experiment. The MP2 polarities of the dipole moments of the complexes have the positive end of the dipole pointing in the direction of the chlorine atoms in CO-Cl₂ and reversed in the OC-Cl₂ complex.

Nonlinear Complexes. Our search for a nonlinear CO-Cl₂ complex produced two minima corresponding to nonlinear van der Waals complexes. These structures are less well defined than their linear counterparts due to the very shallow potentials in which they reside. Nevertheless, they do correspond to minima on the potential energy surface. The optimized geometries of these complexes are shown in Figure 2. The T-shaped minimum was found when starting from structure 3 in Figure 1. In this isomer, the oxygen is very weakly bonded midway between the two chlorine atoms, as can be seen in Figure 2. It is interesting to note that the corresponding T-shaped isomer with the carbon atom perpendicular to the Cl₂ internuclear axis does not have a minimum. Optimizations starting at this geometry resulted in a parallel structure. This will be discussed in more detail below. The structural characteristics of the T-shaped isomer are shown in Table V. The average distance between the centers of mass of the CO and Cl₂ is $R_{\text{cm}} = 3.89\text{ \AA}$, and the average bond angle between R_{cm} and the Cl₂ is found to be 90° . The intermolecular bending motions of this complex exhibited very soft potentials as witnessed by the very low frequencies associated with these motions (8.1 and 17.8 cm^{-1}), as seen in Table VI. The vibrational modes were assigned by constraining the complex to C_{2v} symmetry and calculating the vibrational frequencies. The calculated energy of this complex is $-1032.763\,442$ hartrees, which is 347 and 137 cm^{-1} higher in energy than the linear OC-Cl₂ and CO-Cl₂ complexes, respectively. The binding energy of the T-shaped isomer is calculated to be 207 cm^{-1} (99 cm^{-1} after correction for BSSE). Calculated values of D_0 for this complex are 151 cm^{-1} (44 cm^{-1} including BSSE), indicating that this isomer may be very difficult to observe experimentally since it may dissociate rapidly due to the very weak bonding energy. Frequency

TABLE I: Summary of the Results of *ab Initio* Calculations on the Linear Isomers of CO-Cl₂

exp	SCF//DZP		MP2//DZP		MP2//TZ2P	
	CO-Cl ₂	OC-Cl ₂	CO-Cl ₂	OC-Cl ₂	CO-Cl ₂	OC-Cl ₂
R_{CO} (Å)	1.128 ^a	1.116	1.115	1.154	1.137	1.136
R_{Cl_2} (Å)	1.987 ^a	1.995	1.995	2.012	2.031	2.034
R_{vdw} (Å)	3.12	3.34	3.38	3.02	3.10	3.10
R_{cm} ^b (Å)	4.78	4.82	5.02	4.52	4.77	4.77
ν_0 (cm ⁻¹)	2149.542	2426.465	2437.239	2106.468	2114.302	2129.035
$\Delta\nu_0$ ^c (cm ⁻¹)	+6.228	-2.914	+7.860	+0.621	+8.455	-2.003
μ ^d (D)	-	-	-	+0.080	-0.6723	+0.0704
E (hartree)	-	-1031.656390	-1031.656941	-1032.379621	-1032.380938	-1032.764068
D_e (cm ⁻¹)	-	117	238	345	634	337 (232) ^e
D_0 (cm ⁻¹)	-	45	96	271	506	232 (120) ^e

^a Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure*; Van Nostrand Reinhold: New York, 1979; Vol. 4. ^b Separation between the CO and Cl₂ centers of mass. ^c Shift relative to uncomplexed CO. ^d μ is the electric dipole moment vector defined as pointing from the net negative toward the net positive charge. In this table, a positive dipole moment will then point from CO toward Cl₂. ^e Includes correction for BSSE.

TABLE II: Summary of the Monomer Properties Determined from *ab Initio* Calculations

	SCF//DZP	MP2//DZP	MP2//TZ2P
CO			
R_{CO} (Å)	1.116	1.154	1.137
ν_0 (cm ⁻¹)	2429.379	2105.847	2122.782
E	-112.759732	-113.070186	-113.161461
BSSE E^a CO-Cl ₂	-	-	-113.161525
BSSE E^a OC-Cl ₂	-	-	-113.161664
BSSE E^a T shape	-	-	-113.161523
BSSE E^a parallel	-	-	-113.161604
Cl ₂			
R_{Cl_2} (Å)	1.994	2.011	2.030
ν (cm ⁻¹)	578.286	536.024	562.905
E	-918.896125	-919.307864	-919.601037
BSSE E^a CO-Cl ₂	-	-	-919.601484
BSSE E^a OC-Cl ₂	-	-	-919.601392
BSSE E^a T shape	-	-	-919.601466
BSSE E^a parallel	-	-	-919.601399

^a Energies in hartrees.

TABLE III: Summary of the *ab Initio* Vibrational Frequencies Calculated for the Linear OC-Cl₂ Complex at the MP2/TZ2P Level of Approximation

symmetry	ν (cm ⁻¹)	mode
Π	29.1	Cl ₂ intermolecular bend
Π	29.2	
Σ^+	61.9	intermolecular stretch
Π	97.8	CO intermolecular bend
Π	97.8	
Σ^+	555.4	Cl ₂ stretch
Σ^+	2129.0	CO stretch

TABLE IV: Summary of the *ab Initio* Vibrational Frequencies Calculated for the Linear CO-Cl₂ Complex at the MP2/TZ2P Level of Approximation

symmetry	ν (cm ⁻¹)	mode
Π	25.5	Cl ₂ intermolecular bend
Π	25.5	
Σ^+	58.6	intermolecular stretch
Π	59.2	CO intermolecular bend
Π	59.2	
Σ^+	562.3	Cl ₂ stretch
Σ^+	2120.8	CO stretch

calculations indicate a slight (1.1-cm⁻¹) red shift in the CO vibrational frequency in this complex.

The second nonlinear minimum, a parallel structure, is shown in Figure 2. In this complex, the CO axis is nearly parallel to the Cl₂ internuclear axis, with the average separation between the Cl₂ and the CO centers of mass, R_{cm} , equal to 3.63 Å and the average angle between the Cl₂ axis and R_{cm} equal to 67.4°. This complex stabilized after starting from structure 1 in Figure 1. The structural parameters of this isomer are summarized in Table V, and the vibrational frequencies are given in Table VII. The

TABLE V: Summary of the Results of *ab Initio* MP2/TZ2P Calculations on the Nonlinear Isomers of CO-Cl₂

	T-shaped	parallel
R_{CO} (Å)	1.136	1.137
R_{Cl_2} (Å)	2.030	2.030
R_{cm} (Å)	3.89	3.63
θ_1	90.0°	67.4°
θ_2	-	99.2°
ν_0 (cm ⁻¹)	2121.656	2121.665
$\Delta\nu_0$ ^a (cm ⁻¹)	-1.126	-1.117
μ (D)	0.2600	0.2859
E (hartree)	-1032.763442	-1032.763687
D_e (cm ⁻¹)	207 (99) ^b	261 (150) ^b
D_0 (cm ⁻¹)	151 (44) ^b	189 (79) ^b

^a Shift relative to uncomplexed CO. ^b Includes correction for BSSE.

TABLE VI: Summary of the *ab Initio* Vibrational Frequencies Calculated for the T-Shaped CO-Cl₂ Complex at the MP2/TZ2P Level of Approximation

symmetry	ν (cm ⁻¹)	mode
B ₂	8.1	in-plane intermolecular bend
B ₁	17.8	out-of-plane intermolecular bend
B ₂	42.2	intermolecular rock
A ₁	43.4	intermolecular stretch
A ₁	563.4	Cl ₂ stretch
A ₁	2121.6	CO stretch

TABLE VII: Summary of the *ab Initio* Vibrational Frequencies Calculated for the Parallel CO-Cl₂ Complex at the MP2/TZ2P Level of Approximation

symmetry	ν (cm ⁻¹)	mode
A'	17.9	out-of-plane intermolecular bend
A'	31.9	in-plane intermolecular bend
A'	41.4	intermolecular rock
A''	52.6	intermolecular stretch
A''	562.8	Cl ₂ stretch
A''	2121.7	CO stretch

parallel isomer is calculated to be slightly more stable than the T-shaped isomer, but only by 51 cm⁻¹ (after correction for BSSE), indicating that it too may be difficult to observe experimentally. Both the parallel isomer and the T-shaped isomer have red shifts of equal magnitude in their CO vibrational frequencies. Of course, whether these isomers are observable experimentally also depends upon the energies of the transition states connecting the stable forms and the energies of the transition states connecting the stable forms with the dissociated diatomics. Our suspicion, though we have not calculated the energies of the transition states, is that well depths of the nonlinear species are not large enough to support a stable structure.

Conclusions

The results of this theoretical study support the conclusion that the OC-Cl₂ isomer was observed in our earlier experimental

work. The very small change in the CO bond length and the CO stretching frequency upon forming the complex suggests that electron distribution in the CO is essentially unperturbed by the Cl₂. The calculated binding energy of the other linear isomer, CO-Cl₂, suggests that it too might be observed experimentally. Plans are under way to search for this isomer. In addition to the two linear isomers, our calculations indicate that two nonlinear complexes, one T-shaped and the other parallel, are also predicted to have minima. The calculations, however, predict that these complexes are so weakly bound that they could be difficult to observe experimentally. Finally, the qualitative and quantitative agreement between theory and experiment presented in this work is quite encouraging. While these results are quite promising for predicting the qualitative trends in the structure of and vibrational frequency shifts in weakly bound systems, a more statistical set of comparisons between theory and experiment is needed to validate the quantitative accuracy of this type of calculation.

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