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An *Ab Initio* Study of the Weakly Bonded CO-Cl_2 Complex

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13. ABSTRACT *(Maximum 200 words)*

Ab initio structure and vibrational frequency calculations have been performed on the weakly bonded CO-Cl_2 complex at the SCF and MP2 levels of approximation. Minima were found for the two linear structures, specifically CO-Cl_2 and OC-Cl_2, 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-Cl_2 isomer are in excellent agreement with the experimental results reported earlier, lending further support to the conclusion that the structure of the experimentally observed isomer is OC-Cl_2 rather than CO-Cl_2.

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TABLE OF CONTENTS

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LIST OF TABLES

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1. INTRODUCTION

The results of an experimental study on the weakly bonded CO-Cl_2 complex were recently reported (Bunte et al. 1992). Using a tunable diode laser to probe the CO chromophore, the complex was found 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. It was proposed, however, that the structure of the complex that was observed was OC-Cl_2.

The 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 for corroboration of the conclusions presented in the experimental paper. Secondly, it should be possible to determine if additional minima exist on the potential energy surface corresponding to other geometries (i.e., T-shaped and/or slipped parallel). In this report, the results from *ab initio* calculations on the CO-Cl_2 complex at the SCF and MP2 levels of approximation, utilizing two atomic orbital (AO) basis sets (double-zeta plus single polarization [DZP] and triple-zeta plus double polarization [TZ2P]) are presented.

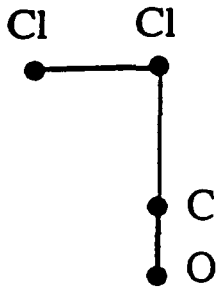
2. THEORY

Closed shell Hartree-Fock SCF and MP2 calculations (Amos 1980 and Moller and Plesset 1934) were performed using two AO basis sets. The smaller DZP basis for carbon and oxygen is the Dunning (1970) contraction of the (9s,5p) to [4s,2p] plus a single primitive d function (α_C = 0.80, α_O = 0.90) (Hariharan and Pople 1973) for carbon and oxygen. The chlorine DZP basis is the Dunning (Dunning and Hay 1977) (11s,7p) contracted to [6s,4p] plus one d polarization function with α_{Cl} = 0.75 (Francl et al. 1982). The TZ2P basis for carbon and oxygen are also contracted Dunning (1971) basis sets consisting of (10s,6p) → [5s,4p] plus two d polarization functions with α_C = (1.2, 0.4) and α_O = (1.35, 0.45). The chlorine was described by the Huzinaga (1971) (12s,9p) → [9s,6p] augmented by two d polarization functions with α_{Cl} = (1.50, 0.375). These chlorine α-values were determined by splitting the single d (α_{Cl} = 0.75) according to the "even scaling rule" (Rafenetti 1973). The calculations were performed using the CADPAC (Amos and Rice 1987) (Version 4.1) quantum chemistry codes running on a CRAY XMP located at the U.S. Army Research Laboratory.

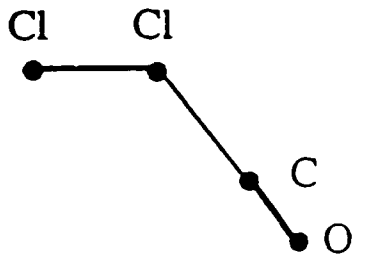
The two monomers were optimized separately at both the SCF and MP2 levels using both basis sets. This was followed, at each level of theory, by a geometry optimization of the complex starting with the two linear isomers. All degrees of freedom were allowed to vary with no symmetry constraints imposed upon the calculations. For each run, the two monomers were set at an initial separation of approximately 3.0 to 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 stepsizes of ±0.002 bohr. In order to check for stable nonlinear CO-Cl_2 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 (i.e., 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).

3. RESULTS

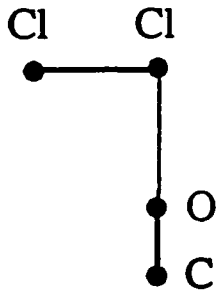
3.1 Linear Complexes. Both linear isomers of CO-Cl_2 were found to be minima, and are shown schematically in Figure 2. Linear OC-Cl_2 structures resulted from initial starting structures 2, 5, 7, and 8 shown in Figure 1. Linear CO-Cl_2 structures were obtained when starting from structures 4 and 6 in Figure 1. Tables 1 and 2 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-Cl_2 (carbon bonded to the chlorine) complex and remains essentially constant in the CO-Cl_2 complex when compared to uncomplexed CO. In addition, the Cl_2 bond length has increased slightly in both of the linear isomers of the complex when compared to "free" chlorine. Jäger, Xu, and Gerry (1992) have observed a shortening of the CO bond length and a lengthening of the Cl_2 bond length in a microwave study of OC-Cl_2. Two other trends can also be observed in the linear structures. First, the OC-Cl_2 complex is consistently lower in energy than the CO-Cl_2 isomer at all levels of theory. At the MP2/TZ2P level, the OC-Cl_2 isomer has an energy of −1032.765025 H and the CO-Cl_2



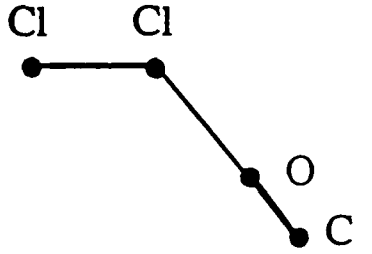
Structure 1 ⇒ Parallel



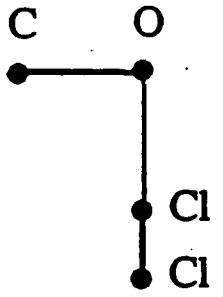
Structure 2 ⇒ $OC\text{-}Cl_2$



Structure 3 ⇒ T-shape



Structure 4 ⇒ $CO\text{-}Cl_2$



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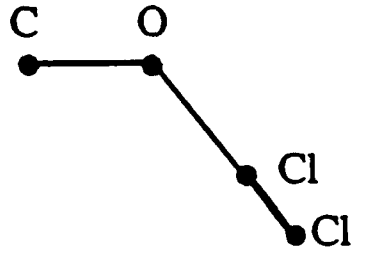

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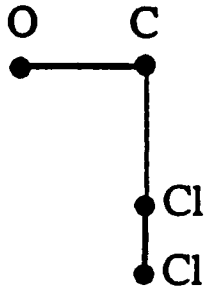

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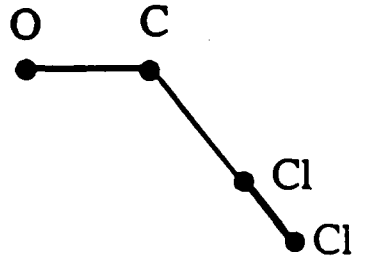

Structure 8 ⇒ $OC\text{-}Cl_2$

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

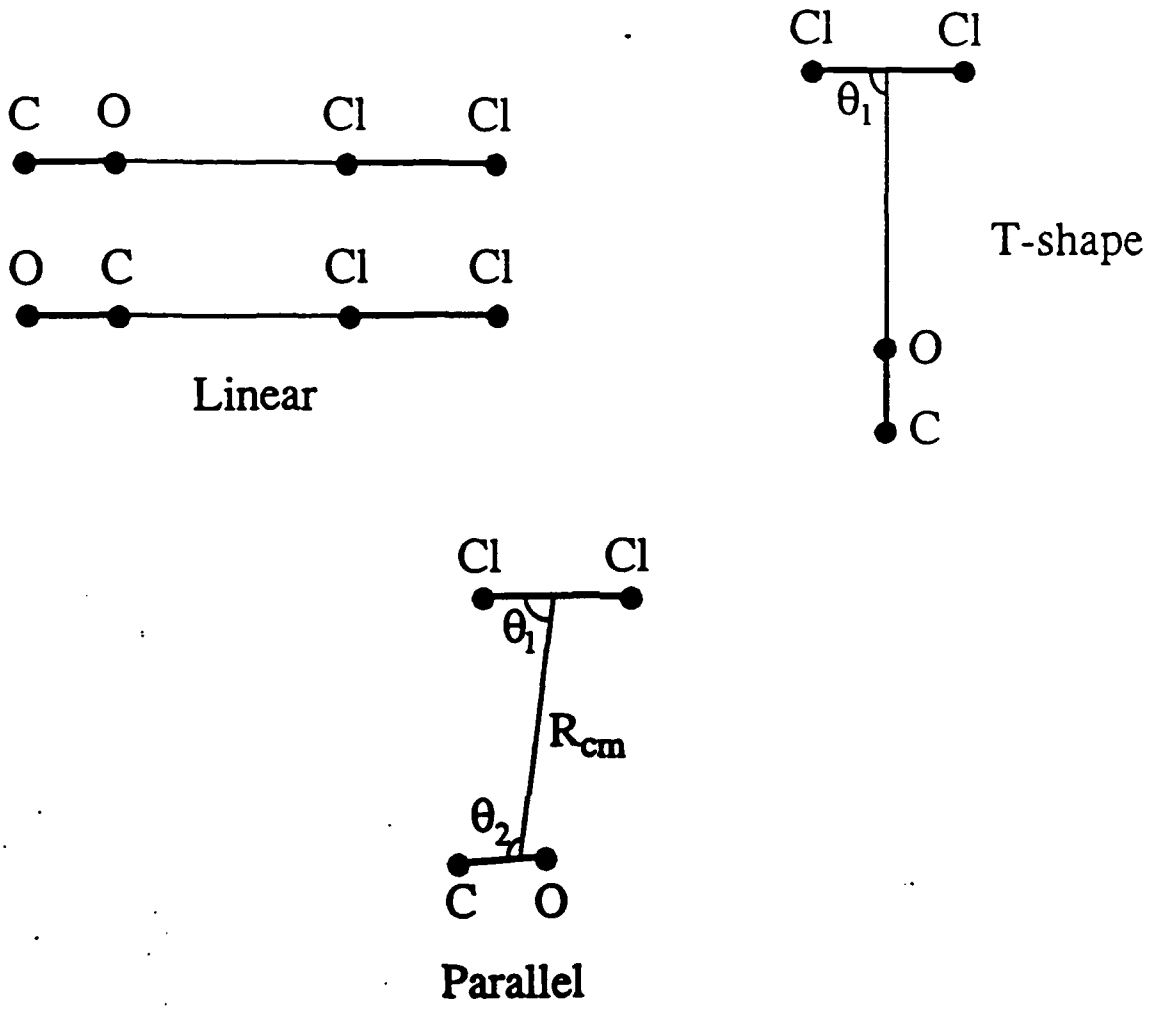

Figure 2. Optimized structures of the four isomers of $CO\text{-}Cl_2$ van der Waals complex.

Table 1. Summary of the Results of *Ab Initio* Calculations on the Linear Isomers of $CO\text{-}Cl_2$

	Experiment	SCF/DZP		MP2/DZP		MP2/TZ2P	
		$CO\text{-}Cl_2$	$OC\text{-}Cl_2$	$CO\text{-}Cl_2$	$OC\text{-}Cl_2$	$CO\text{-}Cl_2$	$OC\text{-}Cl_2$
R_{CO} (Å)	1.128[a]	1.116	1.115	1.154	1.153	1.137	1.136
R_{Cl_2} (Å)	1.987[a]	1.995	1.995	2.012	2.016	2.031	2.034
R_{vdw} (Å)	3.12	3.34	3.38	3.02	3.10	3.06	3.10
R_{cm}[b] (Å)	4.78	4.82	5.02	4.52	4.77	4.56	4.77
ν_0 (cm^{-1})	2149.542	2426.465	2437.239	2106.468	2114.302	2120.779	2129.035
$\Delta\nu_0$[c] (cm^{-1})	+6.228	−2.914	+7.860	+0.621	+8.455	−2.003	+6.253
μ[d] (D)	—	—	—	+0.080	−0.6723	+0.0704	−0.6825
E (H)	—	−1031.656 390	−1031.656 941	−1032.379 621	−1032.380 938	−1032.764 068	−1032.765 025
D_e (cm^{-1})	—	117	238	345	634	337 232[e]	554 432[e]
D_0 (cm^{-1})	-	45	96	271	506	232 120[e]	397 275[e]

[a] Huber and Herzberg (1979).

[b] Separation between the CO and Cl_2 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 Cl_2.

[e] Includes correction for BSSE.

Table 2. Summary of the Monomer Properties Determined From *Ab Initio* Calculations

	CO		
	SCF/DZP	MP2/DZP	MP2/TZ2P
R_{CO} (Å)	1.116	1.154	1.137
ν_0 (cm^{-1})	2429.379	2105.847	2122.782
E (H)	−112.759 732	−113.070 186	−113.161 461
BSSE E(H) CO-Cl_2	—	—	−113.161 525
BSSE E(H) OC-Cl_2	—	—	−113.161 664
BSSE E(H) T-shape	—	—	−113.161 523
BSSE E(H) Parallel	—	—	−113.161 604
	Cl_2		
	SCF/DZP	MP2/DZP	MP2/TZ2P
R_{Cl_2} (Å)	1.994	2.011	2.030
ν (cm^{-1})	578.286	536.024	562.905
E(H)	−918.896 125	−919.307 864	−919.601 037
BSSE E(H) CO-Cl_2	—	—	−919.601 484
BSSE E(H) OC-Cl_2	—	—	−919.601 392
BSSE E(H) T-shape	—	—	−919.601 466
BSSE E(H) Parallel	—	—	−919.601 399

isomer has an energy of −1032.764068 H, a difference of 0.000957 H (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-Cl_2 complex and 337 cm^{-1} for the CO-Cl_2 complex. After correcting for basis set superposition errors (BSSE) using the counterpoise method of Boys and Bernardi (1970), 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 3 and 4, the zero-point energies of OC-Cl_2 and CO-Cl_2 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}.

Table 3. Summary of the *Ab Initio* Vibrational Frequencies Calculated for the Linear OC-Cl_2 Complex at the MP2/TZ2P Level of Approximation

Symmetry	Vibrational Frequency (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 4. Summary of the *Ab Initio* Vibrational Frequencies Calculated for the Linear CO-Cl_2 Complex at the MP2/TZ2P Level of Approximation

Symmetry	Vibrational Frequency (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

While the calculations consistently predict the formation of OC-Cl_2 over CO-Cl_2, 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 1 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 2) 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., $\Delta\nu_0 \leq 9$ cm^{-1}. The CO-Cl_2 isomer exhibited a very small blue shift (+0.6 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}) calculations. The red shifts contradict the observed experimental blue shift of +6.2 cm^{-1}. In contrast, the more stable OC-Cl_2 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 cm^{-1}, and, at the MPD/DZP level, a shift of +8.6 cm^{-1} is predicted. At the MP2/TZ2P level, the shift is calculated to be +6.3 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-Cl_2 complex. This consistent blue shift is absent in the CO-Cl_2 isomer calculations, lending further support that the OC-Cl_2 complex was observed experimentally.

The dipole moments, μ, of the complexes are listed in Table 1. 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 $^{\delta-}CO^{\delta+}$, 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-Cl_2 and reversed in OC-Cl_2 complex.

3.2 Nonlinear Complexes. Our search for a nonlinear CO-Cl_2 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 Cl_2 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 5. The average distance between the centers of mass of the CO and Cl_2 is R_{cm} = 3.89 Å, and the average bond angle between R_{cm} and the Cl_2 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 6. 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 −1032.763442 H, which is 347 cm^{-1} and 137 cm^{-1} higher in energy than the linear OC-Cl_2 and CO-Cl_2 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 calculations indicate a slight (1.1 cm^{-1}) red shift in the CO vibrational frequency in this complex.

Table 5. Summary of the Results of *Ab Initio* Calculations on the Nonlinear Isomers of CO-Cl_2

	MP2/TZ2P	
	T-shape	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(H)	−1032.763 442	−1032.763 687
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 6. Summary of the *Ab Initio* Vibrational Frequencies Calculated for the T-Shaped CO-Cl_2 Complex at the MP2/TZ2P Level of Approximation

Symmetry	Vibrational Frequency (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

The second nonlinear minimum, a parallel structure, is shown in Figure 2. In this complex, the CO axis is nearly parallel to the Cl_2 internuclear axis, with the average separation between the Cl_2 and the CO centers of mass R_{cm} = 3.63 Å and the average angle between the Cl_2 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 5 and the vibrational frequencies are given in Table 7. The 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 transitions states, is that well depths of the nonlinear species are not large enough to support a stable structure.

4. CONCLUSIONS

The results of this theoretical study support the conclusion that the OC-Cl_2 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 suggest that electron distribution in the CO is essentially unperturbed by the Cl_2. The calculated binding energy of the other linear isomer, CO-Cl_2, suggests that it too might be observed experimentally. Plans are underway to search for this isomer. In addition to the two linear isomers, our calculations indicate that two nonlinear complexes (one T-shaped, the other parallel) are also

Table 7. Summary of the *Ab Initio* Vibrational Frequencies Calculated for the Parallel CO-Cl_2 Complex at the MP2/TZ2P Level of Approximation

Symmetry	Vibrational Frequency (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

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 are needed to validate the quantitative accuracy of this type of calculation.

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