

# Transient Resonance Raman and Density Functional Theory Investigation of the Chlorine Atom/Carbon Disulfide Molecular Complex Involved in Selective Alkane Photochlorination Reactions

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The structure and bonding of the chlorine atom/carbon disulfide ( $\text{CS}_2/\text{Cl}$ ) complex involved in selective photochlorination reactions with alkanes was directly probed using transient resonance Raman spectroscopy. The experimental Raman vibrational frequencies were compared to those computed from density functional theory calculations for probable structures of the  $\text{CS}_2/\text{Cl}$  complex. Our results indicate that the  $\text{S}=\text{C}=\text{S}\cdots\text{Cl}$  complex species is responsible for the  $\sim 370$  nm transient absorption band observed after ultraviolet photolysis of  $\text{CCl}_4$  in the presence of  $\text{CS}_2$ . We discuss the structure and properties of the  $\text{S}=\text{C}=\text{S}\cdots\text{Cl}$  complex and compare them with those for the related benzene/Cl and pyridine/Cl complexes.

## Introduction

The selectivity for alkane photochlorination reactions can be increased greatly when done in a range of aromatic solvents or carbon disulfide solvent.<sup>1–18</sup> This important and intriguing solvent effect is usually investigated using 2,3-dimethylbutane (DMB) as the substrate and then measuring the selectivity ( $S^m$ ) for its chlorination.  $S^m$  is defined as  $[2\text{-chloro-2,3-dimethylbutane}]/[1\text{-chloro-2,3-dimethylbutane}] = [2\text{-CIDMB}]/[1\text{-CIDMB}]$ . The increased selectivity of the chlorination reactions done in aromatic or  $\text{CS}_2$  solvent has been explained in terms of an equilibrium between free Cl atoms and those bound to a solvent complex (either an arene/Cl  $\pi$  complex or a  $\text{CS}_2/\text{Cl}$  complex).<sup>1–18</sup> The solvent/Cl complexes were ex-

pected to have a larger propensity to react at the tertiary position of DMB. The overall selectivity of the chlorination could be increased by either increasing the concentration of the aromatic or  $\text{CS}_2$  solvent or decreasing the concentration of the DMB substrate.<sup>1–18</sup>

The chlorine atom/benzene  $\pi$  complex (benzene/Cl) electronic absorption spectrum was first observed by Bühler and Ebert after pulse radiolysis of carbon tetrachloride in benzene.<sup>19</sup> Laser flash photolysis techniques have also been used to observe and characterize the benzene/Cl complex<sup>5,7,16–18</sup> and the related pyridine/Cl<sup>11</sup> and dimethyl sulfoxide/Cl (DMSO/Cl) complexes.<sup>20–24</sup> A similar study examined the  $\text{CS}_2/\text{Cl}$  complex and compared its electronic absorption, kinetics of formation, and chemical reactivity toward DMB with those of the benzene/Cl and pyridine/Cl complexes.<sup>25</sup> This study found the  $\text{CS}_2/\text{Cl}$  complex had an intense electronic absorption band with a maximum around  $\sim 370$  nm with a shoulder at  $\sim 490$  nm.<sup>25</sup> The gas-phase reaction of chlorine atom with  $\text{CS}_2$  is also of interest in atmospheric chemistry, and a reversible adduct complex has been observed.<sup>26–28</sup> Several theoretical studies have been done to examine the possible structures of the  $\text{CS}_2/\text{Cl}$  complex or adduct species, and potential structures were found for either the chlorine atom attached to the carbon atom of  $\text{CS}_2$  or the chlorine atom attached to the S atom of  $\text{CS}_2$ .<sup>29,30</sup>

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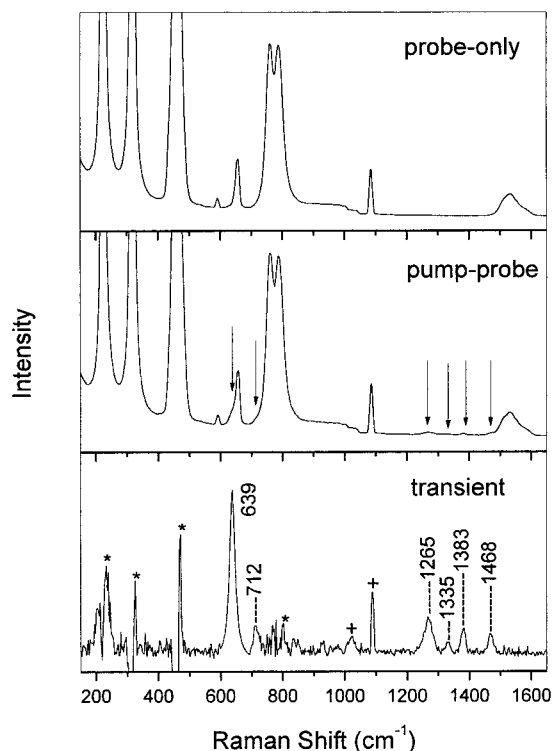
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In this paper, we report a transient resonance Raman experiment done to directly probe the structure and bonding of the CS<sub>2</sub>/Cl complex associated with the ~370 nm transient absorption band. Comparison of the experimental vibrational frequencies to those predicted from density functional theory calculations of the probable CS<sub>2</sub>/Cl complex structures indicates that the CS<sub>2</sub>/Cl complex has a structure with the chlorine atom attached to the S atom of CS<sub>2</sub>. We discuss the structure and properties of the CS<sub>2</sub>/Cl complex and compare them to the related chlorine atom/benzene and chlorine atom/pyridine complexes.

## Results and Discussion

The 218 nm pump wavelength in the transient resonance Raman experiments is expected to lead to photodissociation of the CCl<sub>4</sub> solvent to produce Cl atoms that may then form complexes with the CS<sub>2</sub> molecule. The 369 nm probe wavelength used in the transient resonance Raman experiments is resonant near the maximum of the intense transient electronic absorption band previously observed and assigned to the CS<sub>2</sub>/Cl complex.<sup>25</sup> Therefore, the transient resonance Raman spectrum should directly probe the species responsible for the intense ~370 nm transient electronic absorption band observed after ultraviolet photolysis of CCl<sub>4</sub> in the presence of CS<sub>2</sub>.<sup>25</sup> Figure 1 presents probe-only (top) and a pump-probe (middle) resonance Raman spectra of the CS<sub>2</sub>/Cl complex and the CCl<sub>4</sub> solvent and CS<sub>2</sub> parent compound. Several new Raman band features (indicated by arrows in Figure 1) appear in the pump-probe spectrum but are not observed in the probe-only spectrum. These new Raman band features are at about 639 (shoulder of the parent 658 cm<sup>-1</sup> band), 712 (small shoulder of the very large nearby parent band), 1265, 1335, 1383, and 1468 cm<sup>-1</sup>. These transient Raman bands are more clearly seen in the transient resonance Raman spectrum shown in Figure 1 (bottom). They are assigned to the CS<sub>2</sub>/Cl complex responsible for the strong ~370 nm transient absorption band previously observed after ultraviolet photolysis of CCl<sub>4</sub> in the presence of CS<sub>2</sub>.<sup>25</sup> Table 1 lists the transient resonance Raman bands and their tentative assignments as fundamentals, overtones, or combination bands. Most of the Raman intensity in the transient spectrum of Figure 1 appears in the fundamental and overtone of the 639 cm<sup>-1</sup> mode and their combination bands with two low-frequency modes. There is also moderate intensity in a 1468 cm<sup>-1</sup> fundamental band.

We have performed density functional theory computations to find the optimized geometry and vibrational frequencies for the two most probable structures for the CS<sub>2</sub>/Cl complex (either the Cl atom attached to the carbon atom or the Cl atom attached to a sulfur atom). Table 2A presents the parameters for the optimized geometry of the two most probable structures of the CS<sub>2</sub>/Cl complex (S-C(Cl)-S or S=C=S...Cl) obtained from density functional theory calculations (UB3LYP/cc-pVDZ, UB3LYP/aug-cc-pVTZ, and UBPW91/aug-cc-pVTZ). Table 2B lists the corresponding computed vibrational frequencies from the density functional theory calculations and compares them to the experimental transient resonance Raman



**Figure 1.** Probe-only (top), pump-probe (middle), and transient (bottom) resonance Raman spectra of the CS<sub>2</sub>/Cl complex. The pump and probe excitation wavelengths are 218 and 369 nm, respectively. The transient resonance Raman spectrum (bottom) was obtained by subtracting the probe-only spectrum from the pump-probe spectrum to remove CCl<sub>4</sub> solvent and parent CS<sub>2</sub> Raman bands. Asterisks mark solvent subtraction artifacts, and plus signs label stray light or ambient light artifacts. Raman band features that appear in the pump-probe spectrum (middle) and are not observed in the probe-only spectrum (top) are indicated by arrows above the pump-probe spectrum (middle). The larger Raman band features in the transient resonance Raman spectrum are marked with their Raman shift position (cm<sup>-1</sup>). See Tables 1 and 2 and the text for details of the assignments of the transient Raman bands.

**Table 1. Transient Resonance Raman Vibrational Frequencies (cm<sup>-1</sup>) Observed for the CS<sub>2</sub>/Cl Complex (See Figure 1)**

Raman band vibrational frequency	tentative assignment
639	fundamental
712	combination band (639 + 73 cm <sup>-1</sup> )
1265	overtone (~2 × 639 cm <sup>-1</sup> )
1335	combination band (1265 + 70 cm <sup>-1</sup> )
1383	combination band (1265 + 118 cm <sup>-1</sup> )
1468	fundamental

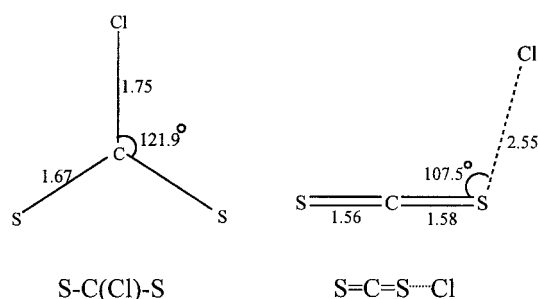
vibrational frequencies. Inspection of Table 2 shows that the transient resonance Raman fundamental bands at 639 and 1468 cm<sup>-1</sup> exhibit good agreement with the DFT-computed values for the nominal C-S symmetric stretch mode ( $\nu_2$ ) and C-S asymmetric stretch mode ( $\nu_1$ ) for the S=C=S...Cl species. However, the S-C(Cl)-S species has no computed vibrational fundamental modes near these bands in the 550–800 cm<sup>-1</sup> region or above 1200 cm<sup>-1</sup>. Similarly, the two low-frequency modes (~118 and ~70–73 cm<sup>-1</sup>) that appear as combination bands with the fundamental and overtone of the main 639 cm<sup>-1</sup> progression of the experimental transient Raman spectrum of Figure 1 show reasonable agreement with two

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**Table 2. (A) Optimized Geometry for the Two Isomers of CS<sub>2</sub>/Cl Complexes Obtained from the Density Functional Theory Calculations and (B) Vibrational Frequencies Computed for the Two CS<sub>2</sub>/Cl Complexes from the Density Functional Theory Computations<sup>a</sup>**

A. Optimized Geometry for the Two CS <sub>2</sub> /Cl Complexes <sup>b</sup>				
structural param	UB3LYP/cc-PVDZ	UB3LYP/aug-cc-PVTZ	UBPW91/aug-cc-PVTZ	
		S-C(Cl)-S		
C-S	1.670	1.658	1.666	
C-Cl	1.752	1.742	1.747	
S-C-Cl	121.9	122.1	121.7	
D(S-C(Cl)-S)	180.0	180.0	180.0	
		S=C=S...Cl		
C-S <sub>1</sub>	1.564	1.553	1.565	
C-S <sub>2</sub>	1.579	1.567	1.578	
S <sub>2</sub> -Cl	2.554	2.437	2.357	
S <sub>2</sub> -C-S <sub>1</sub>	178.8	177.6	176.3	
C-S <sub>2</sub> -Cl	107.5	108.5	110.6	
D(Cl-S <sub>2</sub> -C-S <sub>1</sub> )	0.0	0.1	0.0	
B. Vibrational Frequencies (cm <sup>-1</sup> ) Computed for the Two CS <sub>2</sub> /Cl Complexes				
description	UB3LYP/cc-PVDZ	UB3LYP/aug-cc-PVTZ	UBPW91/aug-cc-PVTZ	expt
		S-C(Cl)-S		
$\nu_1$ , C-S asym stretch	967	962	996	
$\nu_2$ , C-S sym stretch	932	922	892	
$\nu_3$ , C-Cl stretch	500	497	486	
$\nu_4$ , S-C-S bend and Cl-C-S bend (op)	453	459	449	
$\nu_5$ , S-C-Cl bend	269	267	257	
$\nu_6$ , S-C-S bend	252	249	231	
		S=C=S...Cl		
$\nu_1$ , C-S asym stretch	1520	1501	1467	1468
$\nu_2$ , C-S sym stretch	663	660	637	639
$\nu_3$ , S-C-S bend (op)	382	387	368	
$\nu_4$ , S-C-S bend	363	363	338	
$\nu_5$ , S-Cl stretch	149	181	232	~118 <sup>c</sup>
$\nu_6$ , C-S-Cl bend	71	82	87	~70-73 <sup>c</sup>

<sup>a</sup> The experimental Raman band frequencies are compared to the computed frequencies. <sup>b</sup> Bond lengths are in angstroms, and bond angles are in degrees. <sup>c</sup> These fundamental frequencies are extracted from combination bands of these modes with the intense 639 fundamental and its overtone at 1265 cm<sup>-1</sup> (see Table 1).



**Figure 2.** Simple schematic for the optimized geometry computed for the two most probable CS<sub>2</sub>/Cl complex structures (S-C(Cl)-S and S=C=S...Cl) from UB3LYP/cc-PVDZ density functional theory calculations. Selected bond lengths (Å) and bond angles (deg) are shown.

vibrational frequencies of the S=C=S...Cl species but not the S-C(Cl)-S species, which has no computed vibrational frequencies below 200 cm<sup>-1</sup>. Our results indicate that the S=C=S...Cl species is responsible for the ~370 nm transient absorption band observed after ultraviolet photolysis of CCl<sub>4</sub> in the presence of CS<sub>2</sub>.<sup>25</sup>

Figure 2 shows a simple schematic of the optimized geometry for the S=C=S...Cl and S-C(Cl)-S obtained from the UB3LYP/cc-pVDZ calculations. Addition of the Cl atom to the sulfur atom of CS<sub>2</sub> leads to formation of the weakly bound S=C=S...Cl complex, while addition of the Cl atom to the carbon atom of CS<sub>2</sub> may lead to formation of the more strongly bound S-C(Cl)-S complex. The S=C=S...Cl complex has a weak S...Cl bond (~2.35-2.56 Å in length), and this bond appears to

slightly weaken the nearest C=S bond by ~0.015 Å compared to the C=S bond further from the S...Cl bond (see Table 2A). The somewhat weaker C=S bond in the S=C=S...Cl complex leads the nominal symmetric S=C=S stretch and asymmetric S=C=S stretch modes to shift down in frequency to ~639 and 1468 cm<sup>-1</sup>, respectively, in the complex species compared to the corresponding modes at ~658 and 1535 cm<sup>-1</sup>, respectively, in the parent CS<sub>2</sub> molecule.<sup>31</sup> The formation of the relatively weak  $\sigma$  bond between S and Cl appears to also perturb the  $\pi$ -bonding of the C=S group to which the Cl atom is attached. This suggests that the S=C=S...Cl complex has some of both  $\sigma$ - and  $\pi$ -bonding character for the Cl atom interaction with the CS<sub>2</sub> moiety. The two highest occupied a'' molecular orbitals in the S=C=S...Cl complex can be approximately represented as 0.71 3p<sub>z</sub>(Cl) + 0.60 3p<sub>z</sub>(S<sub>2</sub>) - 0.13 2p<sub>z</sub>(C) - 0.60 3p<sub>z</sub>(S<sub>1</sub>) and 0.90 3p<sub>z</sub>(Cl) - 0.59 3p<sub>z</sub>(S<sub>2</sub>) - 0.10 2p<sub>z</sub>(C) + 0.59 3p<sub>z</sub>(S<sub>1</sub>), where the xy plane is the molecular plane and the S<sub>2</sub> atom is weakly bonded to the Cl atom. It is evident that there exists considerable  $\pi$  conjugation interaction between the Cl atom and the CS<sub>2</sub> molecule in the complex species. There is one singly occupied molecular orbital with a' symmetry in the S=C=S...Cl complex, which can be approximately represented as 0.80 3p<sub>y</sub>(Cl) + 0.45 3p<sub>y</sub>(S<sub>2</sub>) + 0.24 2p<sub>y</sub>(C) - 0.45 3p<sub>y</sub>(S<sub>1</sub>) - 0.24 3p<sub>x</sub>(Cl) - 0.32 3p<sub>x</sub>(S<sub>2</sub>) - 0.32 2p<sub>x</sub>(C) + 0.50 3p<sub>x</sub>(S<sub>2</sub>). This indicates that the unpaired electron is mainly distributed in the Cl region but with considerable prob-

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ability in the S=C=S region, and thus, a weak  $\sigma$  interaction also exists between the Cl atom and the CS<sub>2</sub> molecule in the S=C=S...Cl complex.

We note that a two-center three-electron bonded system is one in which a bonding  $\sigma$  molecular orbital between two atoms is doubly occupied while the complementary  $\sigma^*$ -antibonding orbital is singly occupied. Such a bond exists in two homonuclear atoms of a dimer cation such as (H<sub>2</sub>O)<sub>2</sub><sup>+</sup> and X<sub>2</sub><sup>+</sup> (where X = He, Ne, HF, NH<sub>3</sub>, Ar, HCl, H<sub>2</sub>S, and PH<sub>3</sub>).<sup>32,33</sup> Unlike these dimer cations, the singly occupied orbital in the S=C=S...Cl complex has  $\sigma$ -bonding character, and its symmetry ( $a'$ ) is different from that ( $a''$ ) of the bonding  $\pi$  orbital. Although the  $\sigma$  and  $\pi$  interactions exist in the complex, the three  $\sigma$  and  $\pi$  electrons are mainly distributed in the Cl atom, and hence a formal three-electron bond is not formed in the S=C=S...Cl complex. Braida, Savin, and Hiberty<sup>33</sup> have previously found that density functional theory methods can describe X<sub>2</sub><sup>+</sup> weakly bonded complexes reasonably well.

The stabilization energies of the S=C=S...Cl and the S-C(Cl)-S species are estimated to be 15.3 and 14.3 kcal/mol, respectively, using the UBPW91/aug-cc-pVTZ calculations and 10.5 and 8.2 kcal/mol, respectively, using the UB3LYP/aug-cc-pVTZ computations. While density functional theory methods have become increasingly popular to use and apply to a wide variety of chemical systems including hydrogen-bonded systems, charge-transfer complexes, transition-metal complexes, and other complexes, there are some limitations in the ability of DFT methods in dealing with some special systems. For example, DFT methods can moderately overestimate the bonding energies of two-center three-electron bonds and underestimate barrier heights for some reactions.<sup>32,33</sup> The N-Cl bond enthalpy of the related pyridine/Cl complex was calculated to be about 11.3 kcal/mol using the G2(MP2,SVP) method.<sup>34</sup> We performed UB3LYP/Aug-cc-PVTZ calculations and obtained a value of 14.5 kcal/mol for the N-Cl bond enthalpy of the pyridine/Cl complex. Thus, the values we have obtained using density functional theory methods for the stabilization energies of the S=C=S...Cl and the S-C(Cl)-S species may be modestly overestimated by several kilocalories per mole. We note that for the same level of theory (UB3LYP/Aug-cc-PVTZ) the stabilization energy of the pyridine/Cl complex (14.5 kcal/mol) is noticeably larger than that for the S=C=S...Cl complex (10.5 kcal/mol). The two structures for the CS<sub>2</sub>/Cl system, S-C(Cl)-S and S=C=S...Cl, are reported in the present work. The C-Cl distance is 1.73 Å in the S-C(Cl)-S species and is in the range of a normal C-Cl single bond. The UBPW91-calculated molecular orbitals show that the C-Cl  $\sigma$  bond is formed with one unpaired electron mainly localized in the S-C-S region. It appears that no two-center three-electron bond exists in the S-C(Cl)-S structure.

Our DFT computational results in Table 2A for the structure of the S-C(Cl)-S species are in reasonable agreement with previous MP2/6-31G(d) results of McKee<sup>29</sup> (C-Cl bond length of 1.733 Å, C-S bond length of 1.657 Å, and S-C-S angle of 116.0°) and UMP2(full)/

6-311G\*\* results of Wilson and Hirst<sup>30</sup> (C-Cl bond length of 1.73 Å, C-S bond length of 1.65 Å, and S-C-S angle of 116.1°). However, our DFT-computed vibrational frequencies are significantly different from those previously reported for MP2 calculations especially for the C-S antisymmetric stretch vibrational mode, which is calculated to be at 1652 cm<sup>-1</sup> by McKee<sup>29</sup> or at 1685.6 cm<sup>-1</sup> by Wilson and Hirst.<sup>30</sup> McKee<sup>29</sup> previously noted that these vibrational frequencies are even higher than that found for the parent CS<sub>2</sub> molecule and were physically unrealistic in light of the significantly longer C-S bond lengths and corresponding lower C-S bond order in the S-C(Cl)-S species. McKee<sup>29</sup> indicated that to obtain reasonable vibrational frequencies from the C<sub>2v</sub> structure of the S-C(Cl)-S species one would likely need to use a MCSCF treatment or a method other than the MP2 level of theory.<sup>29</sup> The formation of the C-Cl bond leads to the S-C-S angle changing from 180° in the ground state of CS<sub>2</sub> to about 116.2° in the S-C(Cl)-S species as well as the C=S bond changing from 1.566 Å in the ground state of CS<sub>2</sub> to about 1.666 Å in the S-C(Cl)-S species. The large angle change disrupts any  $\pi$  bond conjugation interaction between the two C=S bonds, and the significant increase in the C-S bond length indicates the C-S bond order is significantly weaker in the S-C(Cl)-S species. Thus, one would reasonably expect that the C-S symmetric stretch and asymmetric stretch vibrational modes are significantly lower in the S-C(Cl)-S species compared to the ground-state CS<sub>2</sub> molecule. Similar changes in the S=C=S moiety are observed in some electronic excited states of CS<sub>2</sub>. For example, the b<sup>3</sup>A<sub>2</sub> (R) state has an experimentally measured C-S bond length of 1.64 Å<sup>35</sup> and a S-C-S angle of 135.8°.<sup>36</sup> Its experimental vibrational frequencies are 691.5 cm<sup>-1</sup> for the symmetric C-S stretch mode, 310.8 cm<sup>-1</sup> for the S-C-S bend mode, and ~940 cm<sup>-1</sup> for the C-S antisymmetric stretch mode.<sup>35</sup> These structural parameters and vibrational frequencies are similar and consistent with those observed for the DFT computational results given in Table 2 for the S-C(Cl)-S species. We also note that CIS-MP2 computational results for the b<sup>3</sup>A<sub>2</sub> state<sup>37</sup> of CS<sub>2</sub> show reasonable agreement with the experimental values and are also close to those computed for the similar A<sup>1</sup>A<sub>2</sub> state.<sup>37</sup> This suggests that vibrational frequencies found from our DFT computations are physically realistic and consistent with those of similar CS<sub>2</sub> structures found in several electronic excited states of CS<sub>2</sub>.

One would expect that the interaction between solvent and solute only perturbs the intramolecular vibrational modes by a small amount. Thus, the DFT-calculated frequencies of the intramolecular vibration for the complexes in the gas phase are likely to be comparable with the experimental values in the solution phase. Solvent effects can make noticeably larger perturbations on lower frequency intermolecular vibrational modes, and this may be the reason for the relatively larger difference observed between the S...Cl stretch and C-S...Cl bend computed and experimental vibrational frequencies for the S=C=S...Cl complex in Table 2B.

An absolute rate constant for formation of the CS<sub>2</sub>/Cl complex from the reaction of Cl atoms with CS<sub>2</sub> was

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measured to be  $1.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  by following the decay of the charge-transfer band of Cl atoms in CCl<sub>4</sub> (~330 nm transient absorption band) and the growth of the ~370 nm transient absorption band attributed to the CS<sub>2</sub>/Cl complex.<sup>25</sup> This is consistent with our observation of the CS<sub>2</sub>/Cl complex transient Raman spectrum (see Figure 1) on the order of 5–10 ns after ultraviolet photolysis of CCl<sub>4</sub> in the presence of CS<sub>2</sub>. The reactivity of the CS<sub>2</sub>/Cl complex toward DMB was previously examined by Chateaufneuf using transient absorption spectroscopy of the ~370 nm band and Cl<sub>2</sub> photolysis as the Cl atom source.<sup>25</sup> He found rate constants ranging from  $2.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  (in N<sub>2</sub> saturated solution), to  $6.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  (in air), and to  $1.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  (O<sub>2</sub>-saturated solution) for the reaction of the CS<sub>2</sub>/Cl complex with DMB.<sup>25</sup> This oxygen-dependent behavior was noted to be similar to that previously observed for the benzene/Cl  $\pi$  complex reactions with DMB and was explained as being due to formation of more Cl atoms within the decay time of the complex through a radical chain process.<sup>7,17</sup> Similar experiments using pulse radiolysis showed that after completion of the primary processes there was very little possibility for regeneration of Cl atoms, and the rate constant for reaction of the CS<sub>2</sub>/Cl complex with DMB was measured to be  $1.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  (in N<sub>2</sub>-saturated solution).<sup>25</sup> Similar experiments using 266 nm flash photolysis of CCl<sub>4</sub> as the Cl atom source found similar rate constants,  $2.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  (in N<sub>2</sub>-saturated solution),  $2.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  (in air-saturated solution), and  $1.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  (in O<sub>2</sub>-saturated solution) and little dependence on oxygen,<sup>25</sup> similar to results previously found for the pyridine/Cl complex in the presence of O<sub>2</sub>.<sup>11</sup> Thus, the CS<sub>2</sub>/Cl complex appears to behave in a manner similar to that of both benzene/Cl  $\pi$  complexes and pyridine/Cl  $\sigma$  complexes. This is consistent with the assignment of the CS<sub>2</sub>/Cl complex to the S=C=S...Cl complex species observed in our transient resonance Raman experiment and density functional theory computations which indicate that the Cl atom interacts with both the C=S  $\pi$  bond and also forms a weak S–Cl  $\sigma$  bond.

The equilibrium constants for the benzene/Cl, CS<sub>2</sub>/Cl, and pyridine/Cl complexes have been determined to be  $K = 200, 1900,$  and  $123000 \text{ M}^{-1}$ .<sup>7,11,17,18,25</sup> The CS<sub>2</sub>/Cl complex has an equilibrium constant more similar to that of the weakly bound benzene/Cl  $\pi$  complex than that of the more strongly bound pyridine/Cl complex, which indicates that the CS<sub>2</sub>/Cl complex is a relatively loosely bound species. This is consistent with our present transient resonance Raman and density functional theory results that indicate the loosely bound S=C=S...Cl species (with a weak S...Cl bond) is associated with the ~370 nm transient absorption band of the CS<sub>2</sub>/Cl complex. For example, UB3LYP/Aug-cc-PVTZ calculations indicate the stabilization energy of the pyridine/Cl complex (14.5 kcal/mol) is significantly larger than that for the S=C=S...Cl complex (10.5 kcal/mol). However, proposed CS<sub>2</sub>/Cl complex structures with formation of a much stronger C–Cl bond would be expected to have a relatively large equilibrium constant closer to that found for the pyridine/Cl complex.

Chateaufneuf previously noted the close similarity of the benzene/Cl complex transient absorption spectrum (intense sharp band at ~310 nm with a broader weaker band at ~500 nm) with that found for the CS<sub>2</sub>/Cl complex (intense sharp band at ~370 nm with a broad weaker

band at ~490 nm).<sup>25</sup> However, the pyridine/Cl complex transient absorption band was noticeably different with only one relatively broad feature at ~320 nm with no weaker band in the 500 nm region (see Figure 7 of ref 25 for comparison of the benzene/Cl, CS<sub>2</sub>/Cl, and pyridine/Cl transient absorption spectra). This provides further support for our assignment of the S=C=S...Cl complex to be responsible for the ~370 nm transient absorption band and is consistent with the relative intensity pattern observed in our transient resonance Raman spectrum of Figure 1. Most of the resonance Raman intensity in the transient Raman spectrum of Figure 1 is in the fundamental and overtone of the nominal symmetric C=S mode progression ( $m\nu_2$ ). This progression has noticeable combination bands with the two low-frequency modes associated with the S...Cl stretch and C=S...Cl bend modes. The resonance Raman intensity pattern recently observed for several I<sub>2</sub>/alkene  $\pi$  complex species<sup>38</sup> is similar to that found here for the S=C=S...Cl complex. The I<sub>2</sub>/alkene  $\pi$  complex species had most of the resonance Raman intensity in the fundamental and overtones of the C=C stretch and I–I stretch modes and their combination bands with each other.<sup>38</sup> The C=C stretch and I–I vibrational frequencies were also lower in the I<sub>2</sub>/alkene  $\pi$  complex compared to their separated species, and this indicates that their bond order decreases moderately in the ground-state complex.<sup>38</sup> This is similar to the lower C=S symmetric stretch and C=S asymmetric stretch fundamental frequencies (~639 and ~1468 cm<sup>-1</sup>, respectively) found for the S=C=S...Cl species compared to the free CS<sub>2</sub> molecule (658 and 1535 cm<sup>-1</sup>, respectively). The charge-transfer nature of the ~270 nm electronic absorption spectrum of the I<sub>2</sub>/alkene  $\pi$  complex species is between two molecules, results in a large change in bond order for both of them, and accounts for the large resonance Raman intensity enhancement of both the C=C and I–I stretch modes and their combination bands with each other.<sup>38</sup> The CS<sub>2</sub>/Cl complex is somewhat different in that it appears the charge-transfer nature (probably via movement of charge from the  $\pi$  bond of C=S to an orbital of the Cl atom) of the ~370 nm absorption band occurs between the CS<sub>2</sub> molecule and a Cl atom. Thus, the bond order change is mostly in the C=S bonds of the CS<sub>2</sub> molecule, which results in mainly resonance Raman enhancement of the C=S stretch modes. The transient Raman spectrum also displays some moderate combination bands with the S...Cl stretch and C=S...Cl bend modes since these are also likely affected by the charge transfer between the C=S bond(s) and the Cl atom. This can help explain the close similarity between the transient absorption spectra of the benzene/Cl complex and the CS<sub>2</sub>/Cl complex observed in previous studies.<sup>5,7,16–18,25</sup>

The tertiary/primary selectivity observed for the photochlorination of DMB was measured to be 50/1 for the benzene/Cl complex,<sup>5</sup> 100/1 for the CS<sub>2</sub>/Cl complex,<sup>25</sup> and 200/1 for the pyridine/Cl complex<sup>11</sup> at low DMB concentration (<0.1 M) in the presence of 4 M complexing agent. The weak S...Cl  $\sigma$  bond of the CS<sub>2</sub>/Cl complex and the Cl atom interaction with the C=S  $\pi$ -bonding of CS<sub>2</sub> provide the CS<sub>2</sub>/Cl complex with both  $\sigma$ - and  $\pi$ -bonding interactions of the Cl atom with the CS<sub>2</sub> moiety. This is consistent with its selectivity being intermediate between

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the  $\pi$ -bonded benzene/Cl complex and the  $\sigma$ -bonded pyridine/Cl complex.

### Conclusion

We have obtained a transient resonance Raman spectrum of the CS<sub>2</sub>/Cl complex associated with the  $\sim$ 370 nm transient absorption band observed after ultraviolet photolysis of CCl<sub>4</sub> in the presence of CS<sub>2</sub>. Comparison of the Raman band vibrational frequencies to those computed for probable structures of the CS<sub>2</sub>/Cl complex from density functional theory calculations indicates the S=C=S $\cdots$ Cl species with a weak S $\cdots$ Cl bond is mainly responsible for the  $\sim$ 370 nm transient absorption band of the CS<sub>2</sub>/Cl complex. The transient Raman spectra and density functional theory calculations suggest that the S=C=S $\cdots$ Cl species has both  $\sigma$ -bonding and  $\pi$ -bonding interactions between the Cl atom and the S=C=S moiety via formation of a weak S $\cdots$ Cl bond and perturbation of the C=S bonds, respectively. This dual  $\sigma$ - and  $\pi$ -bonding character appears to be related to the intriguing chemical reactivity and spectroscopic properties of the CS<sub>2</sub>/Cl complex compared to the  $\pi$ -bonded benzene/Cl complex and the  $\sigma$ -bonded pyridine/Cl complex. Previously measured equilibrium constants for the CS<sub>2</sub>/Cl complex,<sup>25</sup> its tertiary/primary selectivity for reaction with DMB,<sup>25</sup> and the close similarity between the benzene/Cl and CS<sub>2</sub>/Cl transient absorption spectra<sup>5,7,16–18,25</sup> are consistent with our present results and assignment of the CS<sub>2</sub>/Cl complex to the S=C=S $\cdots$ Cl species.

### Experiment and Computational Methods

Spectroscopic grade carbon tetrachloride (CCl<sub>4</sub>) and carbon disulfide (CS<sub>2</sub>) were used to prepare samples of CS<sub>2</sub> in CCl<sub>4</sub> with  $\sim$ 1 M concentration. The transient resonance Raman spectra were obtained using an experimental apparatus and methods described previously, so only a short description will be given here.<sup>39–45</sup> The pump (218 nm) and probe (369 nm) excitation wavelengths for the transient resonance Raman experiments were generated from the hydrogen Raman shifted laser lines of the harmonics of a Nd:YAG laser. An optical delay of about 5–10 ns was used between the pump and probe laser beams, which were loosely focused onto a flowing liquid

stream of sample via a near collinear and backscattering geometry. The Raman scattered light was collected by reflective optics and directed through a depolarizer and entrance slit of a 0.5 m spectrograph. The grating of the spectrograph dispersed the Raman light onto a liquid nitrogen cooled CCD that accumulated the signal for about 300–600 s before being read out to an interfaced PC computer. Between 10 and 20 of these readouts were added together to get a resonance Raman spectrum. Pump-only, probe-only, and pump–probe spectra as well as a background scan were acquired. The known Raman bands of the CCl<sub>4</sub> solvent and parent CS<sub>2</sub> molecule were used to calibrate the Raman shifts of the spectra. The parent CS<sub>2</sub> and CCl<sub>4</sub> solvent bands were removed from the pump–probe spectrum by subtracting a probe-only spectrum. The pump-only spectrum was also subtracted to remove stray light or ambient light artifacts to obtain the transient resonance Raman spectrum of the CS<sub>2</sub>/Cl complex.

All of the density functional theory calculations reported here made use of the Gaussian 98W program suite.<sup>46</sup> Complete geometry optimization and vibrational frequency computations were done analytically using the UB3LYP and UBPW91 methods<sup>47,48</sup> for the C-isomer and S-isomer of the CS<sub>2</sub>/Cl complex. The Aug-cc-PVTZ and cc-PVDZ basis sets were used in the computations.<sup>49</sup>

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**Supporting Information Available:** Selected output from the UBPW91/aug-cc-pVTZ and UB3LYP/aug-cc-pVTZ density functional theory calculations showing the Cartesian coordinates, total energies, and vibrational zero-point energies of the S–C(Cl)–S, S=C=S $\cdots$ Cl, and pyridine/Cl complexes and the CS<sub>2</sub> molecule. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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