Observation of Elusive CF$_2$Cl⋯Cl in Matrix Infrared Spectra and Density Functional Calculations

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CF$_2$Cl⋯Cl, an elusive photo-isomer of CF$_2$Cl$_2$, has been observed in matrix IR spectra from the precursors exposed to radiation from laser ablation of transition-metals. Other plausible products, CFCl$_2$⋯F and FCl⋯F, are not detected due to their considerably higher energies. Parallel to its previously reported analogues, the C-X bonds are considerably stronger than those of the reactant, and particularly the Cl atom that is weakly bound to the residual Cl atom forms an unusually strong carbon-halogen bond. NBO analysis reveals that the C-Cl bond is a true double bond, and the weak Cl⋯Cl bond is largely ionic. IRC computation reproduces smooth inter-conversion between the reactant and product, and the transition state is energetically close to the product, consistent with its prompt disappearance in the early stage of photolysis.

Key Words: iso-Halomethane, Infrared, DFT, Matrix, Laser-ablation

Introduction

Halomethanes not only cause ozone depletion in the stratosphere, but also are strong, long-lasting greenhouse gases. The fragments (radicals, ions) and isoformers of halomethanes are reaction intermediates of many atmospheric reactions. Therefore, the spectroscopic properties of these unstable species are important to understand the photo-reactions and other behaviors of the environmentally hazardous halogen-containing gases.

The unstable iso-tetrachloromethane CC$_3$⋯Cl was first identified by Maier and coworkers following selective irradiation in the photo-dissociation region (222 nm through 193 nm) for CC$_3$ in solid argon. Later work of Jacox et al. produced related chlorocarbon ions and the CC$_3$⋯Cl species in solid neon. The CH$_2$X⋯X (X = Cl, Br, I) species were also detected by Maier et al. via photo-isomerization of methylene halides, and the structures and vibrational frequencies were computed using MP2 methods. The infrared absorptions of these species with a weak X⋯X bond disappear on visible irradiation in the early stage of photolysis, indicating that they are shallow energy minima. The CHCl$_2$⋯Cl, CHFCl⋯Cl, CHBr$_2$⋯Br, and CFCl$_2$⋯Cl have recently been observed in the matrix IR spectra via photo-isomerization of their precursors during co-deposition of laser-ablated transition-metal atoms. CBr$_3$⋯Br was detected in radiolysis experiment. NBO analysis reveal that the C-X bond is a true double bond and the weak X⋯X bond is largely ionic, X=C=O⋯⋯O= (X = H, halogen). The fluorine-containing iso-halomethanes are rare. No iso-halomethanes with an F⋯F, F⋯Cl, or Cl⋯F bond have been identified, and moreover, no iso-halomethanes with two F atoms and an X⋯X bond have been reported to date.

Recently a new breed of small high oxidation-state transition-metal complexes are produced in reactions with halomethanes. Along with the metal containing products, photo-reaction products of the precursor (radicals, ions, and isomers) are also observed in the matrix spectra, due to the plume radiation from laser ablation. In this paper, we report observation of elusive CF$_2$Cl⋯Cl with $^{13}$C shifts for comparison. DFT and intrinsic reaction coordinate computations reveal smooth inter-conversion between the reactant and product, and the transition state is energetically close to the product, consistent with the disappearance of the product in the early stage of photolysis.

Experimental

The CF$_2$Cl⋯Cl photo-isomer spectra shown in this report were recorded from samples prepared by co-deposition of laser-ablated Hf atoms with CF$_2$Cl$_3$ and $^{13}$CF$_2$Cl$_2$ (Dupont) in excess argon at 10 K using a closed-cycle refrigerator (Air Products, Displex). While the product absorptions are strongest in the Hf spectra, other metals (groups 3-11 and actinides) also yield the same product absorptions although the intensities vary owing to different laser ablation plume radiation from specific metal surfaces. Hence, these metal independent absorptions do not arise from metal containing species.

In this study, Hf atoms and intense radiation from the laser ablation plume impinge on the depositing matrix sample. These methods have been described in detail elsewhere. Reagent gas mixtures are typically 0.50% in argon. The Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate, 10 ns pulse width) was focused onto the rotating metal target (Johnson-Matthey) using 5-10 mJ/pulse. After co-deposition, infrared spectra were recorded at 0.5 cm$^{-1}$ resolution using a Nicolet 550 spectrometer with a Hg-Cd-Te range B detector. Then samples were irradiated for 20 min periods by a mercury arc street lamp (175 W) with the globe removed using a combination of optical filters or annealed to allow further reagent diffusion.
Complementary density functional theory (DFT) calculations were carried out using the Gaussian 09 package, the B3LYP density functional, and 6-311++G(3df,3pd) basis sets for C, F, and Cl to provide a consistent set of vibrational frequencies and energies for the reaction products and their analogues. Geometries were fully relaxed during optimization, and the optimized geometry was confirmed by vibrational analysis. Additional BPW91 calculations were done to confirm the B3LYP results. The vibrational frequencies were calculated analytically, and the zero-point energy is included in the calculation of binding energy of a metal complex. Intrinsic reaction coordinate (IRC) calculations have been performed to link the transition state structures with the reactants and specific products.

Results and Discussion

**CF_2Cl····Cl Absorptions.** Figure 1 shows the CF_2Cl····Cl absorption region for CF_2Cl· co-deposited with laser-ablated Hf atoms. The product absorptions marked “t” are observed in the original deposition spectra, but do not reappear in the following full arc (λ > 220 nm) photolysis and annealing to 30 K. The early disappearance of these product absorptions in the process of photolysis is in line with those of the previously reported *iso*-halomethanes. The weak absorption intensities shown in Figure 1 are consistent with the rarity of F containing halomethane radicals of CF_2Cl·.

New product absorptions are observed at 1281 and 1256 cm\(^{-1}\) with intensity ratio of ~1:2.5 on the blue side of the CF_2 stretching absorptions of the precursor at 1150 and 1090 cm\(^{-1}\). The frequencies are also compared with the previously reported C-F stretching frequencies of 1199 and 1211 cm\(^{-1}\) for CHFClCl and CFCl_2. They shift to 1250 and 1219 cm\(^{-1}\) on \(^{13}\)C substitution (12/13 ratios of 1.025 and 1.030). No other considerable product absorptions are observed. The observed vibrational characteristics do not match with the previously reported values for the fragments (ions and radicals) of CF_2Cl_2. They are assigned to the anti-symmetric and symmetric CF_2 stretching modes of CF_2Cl····Cl on the basis of their frequencies, relatively large \(^{13}\)C shifts, and good correlation with the predicted values. The computed frequencies are 1302 and 1286 cm\(^{-1}\). \(^{13}\)C shifts both 36

**Table 1.** Observed and DFT Fundamental Frequencies of CF_2Cl····Cl Isotopomers in the Ground \(^{1}\)A' Electronic State

<table>
<thead>
<tr>
<th>Approximate Description</th>
<th>CF_2Cl····Cl</th>
<th>(^{13})CF_2Cl····Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Obs B3LYP</td>
<td>Int</td>
</tr>
<tr>
<td>A' as CF_2 str.</td>
<td>1281</td>
<td>1302</td>
</tr>
<tr>
<td>A' s CF_2 str.</td>
<td>1256</td>
<td>1286</td>
</tr>
<tr>
<td>A' C-Cl str.</td>
<td>734</td>
<td>35</td>
</tr>
<tr>
<td>A' CCl_3F deform</td>
<td>544</td>
<td>15</td>
</tr>
<tr>
<td>A' CF_2 scis.</td>
<td>446</td>
<td>93</td>
</tr>
<tr>
<td>A' CF_2 rock</td>
<td>411</td>
<td>1</td>
</tr>
<tr>
<td>A' Cl-Cl str.</td>
<td>256</td>
<td>87</td>
</tr>
<tr>
<td>A' CClCl oop bend</td>
<td>126</td>
<td>2</td>
</tr>
<tr>
<td>A' CClCl ip bend</td>
<td>85</td>
<td>9</td>
</tr>
</tbody>
</table>

*Frequencies observed in solid argon in recent laser ablation experiments; bold are stronger matrix sites. Harmonic frequencies (cm\(^{-1}\)) and intensities (km/mol) were computed with 6-311++G(3df,3pd). *Computed with B3LYP. **Computed with BPW91.
The strongest C-F and C-Cl stretching absorptions are not observed. CFCl2 is the first isomer of FClC=Cl, and the other bands are too weak to observe. The observed stretching absorptions at ~1200 and 1020 cm⁻¹, and intensity ratio between the two bands 1:2.3 (Table 1). These two are the strongest bands of the photo-isomer, suggesting that the iso-tetrahalomethane containing two F atoms (CF2Cl⋯Cl).

CFCl2⋯F and FCIC⋯F-Cl, other plausible products, are not detected. CFCl1⋯F would show its strong C-F and C-Cl stretching absorptions at ~1200 and 1020 cm⁻¹, which are not observed. The strongest C-F and C-Cl stretching absorptions of FCIC⋯F-Cl expected at ~1140 and 710 cm⁻¹ are also not observed. CFCl1⋯Cl, CFCl1⋯F, and FCIC⋯F-Cl are 251, 321, and 446 kJ/mol higher than the precursor. On the contrary, the attempts to optimize the geometry of Cl2C⋯F-F all ended up with the structure of CF2Cl2, suggesting that the iso-tetrahalomethane with an F-F bond is not a meaningful energy minimum. Clearly, the observed photo-isomer of CF2Cl2 with a Cl⋯Cl bond is the most stable.

Molecular Structures and Bonding. Figure 2 shows the B3LYP structures of the precursor (CF2Cl2), transition states, and plausible three iso-tetrahalomethanes (CFCl⋯Cl and CFCl⋯F, and FCIC⋯F-Cl). The C and three atoms bonded to C form a near planar structure with a bridging halogen atom in the transition state. The product structure is in fact similar to that of the transition state, other than the larger <CXX, indicating that the transition state is energetically closer to the product than the reactant. The C-X bond lengths of the products are considerably shorter than those of the precursor. The C-F and C-Cl bond lengths of 1.296 and 1.638 Å for CF2Cl⋯Cl and 1.308 and 1.696 and 1.612 Å for CFCl⋯F are compared with those of 1.332 and 1.772 Å for the CF2Cl2. Particularly the Cl atom bonded to the residual X atom forms an exceptionally strong bond with carbon (C-Cl bond lengths of 1.638 and 1.612 Å in CF2Cl⋯Cl and CFCl⋯F). On the other hand, The Cl⋯Cl and Cl⋯F bondlengths (2.429 and 1.948 Å) are significantly longer than those of Cl⋯Cl and FC1 (2.011 and 1.643 Å) computed at the same level of theory.

The Natural atomic charges, bond lengths, occupancies, bond orders, and structural parameters of CF2Cl⋯Cl and CFCl⋯F are listed in Table 2 with those of several previously reported iso-halomethanes. The unusually short C-X bonds have considerable double bond character (natural atomic charges of 0.339 and −0.477 for CF2Cl⋯Cl and those of 0.548 and −0.618 for FCIC⋯F). Hence, these photo-isomers are better represented as X2C=X⋯X⋯X°. Similarly, in the structure of transition state, the bridging X carries a substantial amount of negative charge, indicating that it is largely ionically bonded to the planar CX2 subunit. The bridging Cl and F in the transition states in the CF2Cl2 ↔ CFCl⋯Cl and CFCl2 ↔ FCIC⋯F conversions own natural atomic charges of −0.681 and −0.728, [CF2Cl]°−0.681⋯Cl°−0.681 and [CFCl]°−0.728⋯F°−0.728.

The structure of CFIC⋯F-Cl, which is much higher in energy than CF2Cl⋯Cl and CFCl⋯F, is also shown in Figure 2. F cannot expand its valency unlike Cl, which can

![Figure 2](image-url)
utilize its 3d-orbitals. During geometry optimization, the initial geometry of CFCl\textsubscript{2}ÍF\textsubscript{2}ÍCl converges to the structure of FCIC\textsubscript{2}Í-F. The F-Cl bondlength of 1.644 Å in CFCl\textsubscript{2}Í-F is essentially the same as that of 1.643 Å for F-Cl calculated at the same level of theory, and the interatomic distance between C and F is 3.124 Å as shown in Figure 2.

**Reactions.** Intrinsic reaction coordinate\textsuperscript{13} (IRC) calculations are carried out for the isomerization reactions between CF\textsubscript{2}Cl\textsubscript{2} and the plausible products. Figure 3 shows the IRC results for the CF\textsubscript{2}Cl\textsubscript{2}↔ CFCl\textsubscript{2}ÍCl and CF\textsubscript{2}Cl\textsubscript{2}↔ CFCl\textsubscript{2}Í-F systems. Due to the large energy difference between the reactant and product, the transition state is energetically much closer to the product. The activation energies from the reactant to CF\textsubscript{2}Cl\textsubscript{2}-Cl and CFCl\textsubscript{2}Í-F (294 and 365 kJ/mol) are noticeably higher than those for previously introduced CHCl\textsubscript{2}Í-Cl, CHFCl\textsubscript{2}Í-Cl, CFCI\textsubscript{2}Í-Cl, and CCl\textsubscript{3}-Cl (248, 274, 254, and 220 kJ/mol, respectively).\textsuperscript{8} Fluorine evidently increases the activation energy from the precursor to the iso-halomethane, and the high activation energy is consistent with the observed weak product absorptions (the low yield) of CF\textsubscript{2}Cl\textsubscript{2}-Cl. The activation energy from CF\textsubscript{2}Cl to CF\textsubscript{2}Cl\textsubscript{2}-F is even higher (406 kJ/mol), consistent with its absence in the CF\textsubscript{2}Cl spectra.\textsuperscript{18}

In contrast, the activation energies in the reverse reactions are considerably smaller (43 and 44 kJ/mol, respectively), consistent with the disappearance of the product in the early stage of photolysis. Separate IRC computation has also been carried out for production of FCIC\textsubscript{2}Í-F, showing that its transition state, which is 555 kJ/mol higher than the reactant, is also linked smoothly to the reactant and product. Evidently the high energy barrier prohibits production of FCIC\textsubscript{2}Í-F.

**Conclusion**

CF\textsubscript{2}Cl\textsubscript{2}-Cl, the first iso-halomethane with two F atoms, is produced from CF\textsubscript{2}Cl\textsubscript{2} during co-deposition with laser-ablated metal atoms and the associated laser plume irradiation and identified in the matrix IR spectra with isotopic substitution and DFT computational results. The absorptions of this photo-isomer are relatively weak, and they disappear in the early stage of photolysis, parallel to those of its analogues from di-, tri-, and tetra-halomethanes. The other plausible products, CFCl\textsubscript{2}Í-F and FCIC\textsubscript{2}Í-F, are not identified due to their considerably higher energies. Cl\textsubscript{2}C\textsubscript{2}Í-F is probably not a meaningful energy minimum.

CF\textsubscript{2}Cl\textsubscript{2}-Cl has a near planar structure of the C and three atoms bonded to Cl, and the residual X atom is bonded to the Cl atom. The product structure is similar to the structure of the transition state except for the larger <C-X. The C-X bonds of the product are considerably stronger than those of the precursor. Particularly the Cl atom that is bonded to the residual X atom forms an unusually strong C-Cl bond. NBO analysis reveals that the strong carbon-chlorine bond has considerable double bond character (natural bond order >1.5). The weak Cl--X bond is largely ionic on the basis of the large atomic charges, X=C=Cl\textsubscript{2}Í-X\textsuperscript{16}.

The IRC calculations reproduce smooth conversion between the reactant and product. The transition state is much closer in energy to the product, consistent with the disappearance of the product in the early stage of photolysis and the similarity in the structures of the transition state and product. The previous and present results show that the activation energy to the iso-halomethane increases substantially with the number of F, making formation of the photo-isomer increasingly difficult.

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**References**


