TEMPERATURE DEPENDENCE OF 
CCI4 INFRARED ABSORPTION CROSS-SECTIONS

by

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TEMPERATURE DEPENDENCE
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CCL₄ INFRARED ABSORPTION CROSS-SECTIONS

1. Abstract
In this experiment I determined infrared absorption cross-sections of pure CCl₄ at 223, 248, 273, and 298 K. All absorption spectra were taken at high resolution (0.05 cm⁻¹) and in the 700-830 cm⁻¹ interval. Spectral files, organized by temperature, were entered into a computer program that performed a linear least-squares fitting of absorbance versus sample concentration. From these fittings, plots of cross-section vs. frequency were generated for each of the four temperatures, and variation with temperature could then be observed by superimposing the plots.

I found that decreases in temperature produce narrowing and heightening of absorption bands. I also took spectra of CCl₄ with approximately 100, 200, 300, and 400 torr of nitrogen added at 223 and 298 K, and I concluded that only slight broadening of the Q branches of the 796 cm⁻¹ band occurred at these conditions; no significant structural changes could be seen from 700 to 830 cm⁻¹. Possible applications of my results to improving the vertical mixing profile of CCl₄ are also discussed.

2. Introduction
The class of anthropogenic compounds known as chlorofluorocarbons, or CFCs, has in recent years made its presence widely known.
Because of the high reactivity of chlorine free radicals with ozone, CFCs are largely responsible for the gradual catalytic destruction of the Earth's stratospheric ozone layer. Carbon tetrachloride, which consists of four chlorine atoms bound to a single carbon atom, has a chemical composition similar to the CFCs and thus has similar effects on ozone.

The first step in CFC-based ozone destruction is photolysis of the CFCs that reach the stratosphere. Solar ultraviolet radiation penetrates the CFC bonds, thus yielding the reactive chlorine radicals. In the case of CCl₄, two chlorines are able to be released from one CCl₄ molecule, as shown in Figure 1. The first reaction cycle shown in Figure 1 dominates depletion of ozone and atomic oxygen (the two "odd-oxygen" species) at high altitudes. At lower altitudes the other two cycles, which involve nitrogen oxides and hydrogen oxides, become more important. The free chlorines that arise from CFCs initiate all three cycles, and furthermore, they function catalytically by being recycled following the conversion of odd oxygen to oxygen molecules. Cl radicals, then, are doubly dangerous because they not only deplete ozone, but can do so repetitively.

The efficiency of a molecule in destroying ozone can be understood in terms of Ozone Depletion Potential, or ODP, which is the ability of a molecule to destroy ozone, relative to CFCl₃ (see Table 1). For example, if a gaseous species has an ODP > 1.0, then it can react with and hence destroy a correspondingly greater amount of ozone than can the same mass of CFCl₃. Because CCl₄ has the maximum amount of chlorine that a mono-carbon halocarbon can bear, and because the more chlorines a molecule contains, the more
ozone molecules it can potentially destroy, CCl₄ consequently has the largest ODP of any non-brominated halocarbon.

Although CCl₄ has a low release rate and a short lifetime relative to other chlorinated halocarbons, some of it does reach the upper troposphere as well as the lower stratosphere (about 10 to 25 km up), where it is photolyzed to reactive chlorine and also where the ozone layer starts to build up (see Figures 2 and 3). In this way, it does contribute a fair amount to ozone depletion. This condition makes it necessary for us to know as much about atmospheric CCl₄ as we can.

The group at NCAR that produces and analyzes atmospheric spectra is ACD's Global Remote Observations (GRO) group. The data that I have produced regarding temperature dependence and nitrogen dependence of CCl₄ cross-sections will be utilized by this group, perhaps to obtain a vertical concentration profile of CCl₄ in the atmosphere and thereby quantitatively predict its various effects more accurately.

In order to obtain a vertical profile of CCl₄, GRO must be able to identify CCl₄ in atmospheric spectra and in precise amounts. In this way it is similar to the Atmospheric Trace Molecule Spectroscopy (ATMOS) project of 1985. This project was held aboard Spacelab 3 and utilized remote sensing using Fourier transform infrared solar absorption spectroscopy. In Figure 4, we see that the observed spectra that actually contained CCl₄ were compared with synthetic (computed) spectra that contained only major atmospheric components (CO₂, H₂O, O₃, etc.). When CCl₄ contributions were added to the synthetic spectra, a dip appeared that made them look
identical to the observed spectra. Thus, CCl₄ spectra at the proper atmospheric conditions, which I have produced, are needed to identify CCl₄ in complicated atmospheric spectra. To see how much CCl₄ there is in a given spectrum, I have calculated IR cross-sections, which are absolute numbers that show IR-absorbing ability per molecule.

The power of knowing CCl₄ cross-sections can be seen by contrasting occultation measurements with laboratory measurements. These occultations, performed in the ATMOS study, measure "the amount of energy absorbed by molecules along the line of sight of a satellite" (Zander et al., 1987). Although the satellite occultations measure a minute concentration of CCl₄ along a path length of many miles, they can still be used to determine gas density by using laboratory cross-sections that are obtained from experiments using a relatively high concentration of CCl₄ at a low path length of a few centimeters. Cross-sections, then, because they are constants, can be used to proportion absorbance with concentration in two totally different environments, such as the stratosphere and the laboratory.

Laboratory data, then, interrelate with observational data, and both of these interrelate with atmospheric models. Laboratory cross-sections are combined with satellite measurements to obtain a vertical mixing profile of CCl₄. Models are continuously tuned to match these profiles and to ultimately show where CCl₄ is being destroyed, or, in other words, where Cl is being released. The rates of photolysis and transport of CCl₄, when known precisely, will show where and how fast CCl₄ is depleting O₃.
3. Theory

The way in which IR absorption cross-sections are determined depends on the way in which the sample absorbs IR radiation, the wavelengths of which range from approximately 800 nm to 50 μm. When compounds absorb IR radiation, their atoms vibrate faster about their bonds. However, only radiation of certain frequencies will bring about the vibration changes. The reason for this is that the vibrations actually correspond to certain quantized vibrational energy levels, denoted by \( v \), and it takes radiation of certain frequencies to excite the molecules from one level to another. It is these energy level transitions that correspond to absorption of IR energy, and their occurrences are always accompanied by a change in the molecule's dipole moment.

Once a sample absorbs IR radiation, a spectrum can be produced, which shows absorbed bands in certain frequency regions. In the case of CCl\(_4\), the broad absorptions around 796 cm\(^{-1}\) and 768 cm\(^{-1}\) correspond to \( v_3 \) and \( (v_1 + v_4) \) transitions, respectively. The \( v_3 \) transition corresponds to asymmetric combinations of C-Cl bond stretches; the \( v_1 \) transition results from the expanding and contracting of the entire CCl\(_4\) molecule; and the \( v_4 \) transition results from the "wagging" of a pair of Cl atoms. The 796 cm\(^{-1}\) band, then, results from stretching vibrations, and the 768 cm\(^{-1}\) band arises from the wagging plus the expanding and contracting (see figure 5).

An absorption spectrum of a particular compound is effectively a "fingerprint" of that molecule, since there are so many different combinations of and structures of absorption bands that no two
spectra of different compounds look exactly the same. However, a spectrum does not tell how much of a given sample is responsible for a given amount of observed absorption. That value is obtained with the cross-section.

The Beer-Lambert Law, shown in Figure 6, states that absorbance, which is unitless, equals the cross-section, in cm$^2$/molecule, times the sample concentration, in molecules/cm$^3$, times the radiation path length, in cm. The advantage of the Beer-Lambert Law is that with it, cross-sections can be calculated at each frequency, and, unlike absorbances, these cross-sections take sample concentration into account, as they are simply constants of proportionality between absorbance and concentration. With a plot of cross-section versus frequency, then, we can see the true absorbing efficiency of the sample compound, molecule for molecule (see Figure 7).

4. Materials and Methods
In the laboratory I used a BOMEM model Fourier transform spectrometer interfaced to a short path absorption cell, a BOMEM vector processor, a Digital VAXstation 3100, and a Neslab refrigerated circulating bath (see Figure 8).

Typically, I would first take a reference spectrum of an empty cell. The intensity of the IR beam coming from the lamp is designated as $I_0$. Then I passed the sample into the cell, where it was irradiated with an IR beam. After some of the radiation was absorbed, the beam, now with intensity $I$, was converted into an interferogram, and then into a spectrum by the vector processor.
The data were then ratioed to the reference data and transferred to the VAXstation, where a plot of absorbance versus frequency was displayed. The absorbance, then, equals the ln of the quotient of the reference beam intensity \( I_0 \) and the sample beam intensity \( I \) (see Figure 6); the smaller \( I \) is, the more of the radiation the sample has absorbed, and thus the higher the absorbance is.

I then simulated stratospheric conditions in two ways:

1. For low temperature measurements, which were done at -50°C, -25°C, and 0°C, I simply hooked up the cooling bath to the cell and adjusted it to the proper temperature before scanning the sample.
2. I also did some runs with up to 400 torr of nitrogen added to the CCl₄ at 25°C and at -50°C to see if there was any pressure broadening effect.

Upon completion of all the data-taking, I entered the spectral files, organized by temperature, into a computer program. The program then performed a linear least-squares fit of absorbance versus concentration at each wavelength. The slope of these fits divided by the path length equals the cross-section (as indicated by Figure 9, Beer-Lambert linearity was also confirmed by inspection for the 796 cm\(^{-1}\) band). At the end, the program listed the cross-sections at frequencies between 715 cm\(^{-1}\) and 825 cm\(^{-1}\). I transferred the data files at the four different temperatures to a personal computer, and plots of cross-section versus frequency were compiled.
5. Results

What I found from my study was that successive decreases in temperature yield successively narrower and higher absorption bands for CCl₄ (see Figure 10). The reason for this can be related to the Boltzmann distribution of molecules, which changes according to temperature. At a given temperature there is a set distribution of molecules in certain vibrational and rotational energy levels. At lower temperatures, however, the population of molecules in lower-energy states increases. Because high-energy molecules are responsible for absorption in the "wings" of a band and low-energy molecules account for absorption in the center of a band, the absorption at lower temperatures becomes sharper accordingly in the middle of the band and in the Q branches too, which in this way act like mini absorption bands. The narrowing on the left side of the 796 cm⁻¹ band and the sharpening of the peak are both noticeable, but on the right side, the narrowing is not as apparent because its effect is partially obscured by the sharpening of the Q branches.

Nitrogen pressure broadening was also observed to a small degree at both 25°C and -50°C. The Q branches of the 796 cm⁻¹ band were found to be shorter and broader, but the overall structure of the band remained essentially constant.

From Table 2, we can see that the peak cross-sections increase with decreasing temperature. In addition, the Denver University peak cross-section value at room temperature agrees well with mine. Neither the integrated band intensity between 740 cm⁻¹ and 820 cm⁻¹ nor the one between 773 cm⁻¹ and 802 cm⁻¹ fluctuates by more than 5%. This integrated intensity is a calculation of the area under
the cross-section versus frequency curve at a specified frequency interval. The intensities should theoretically remain the same, since the dipole moment derivative should not change with temperature, meaning that the total absorption remains the same. Only the distribution of molecules changes along the curve.

6. Conclusions
The integrated intensities in the 773 cm\(^{-1}\) - 802 cm\(^{-1}\) range will perhaps play a part in improving calculations of CCl\(_4\) volume mixing ratios (VMRs). In this range, my intensity at each temperature approximated 4.67 x 10\(^{-17}\) (cm\(^{-1}\) x cm\(^2\)/molecule) -- about 27% higher than the band strength shown in the ATMOS study. As stated previously, this study involved occultations, which measure the amount of absorption along the line of sight of a satellite. This absorption, which can be found for CCl\(_4\), is directly proportional to the gas density. Density is then combined with atmospheric density to yield the VMR, which, when plotted against altitude, gives a vertical mixing ratio (see Figure 11).

The vertical mixing ratio that ATMOS and GRO are concerned with is precisely what my data can be used to determine. By comparing my band intensities with the one used by ATMOS, I can see approximately where my VMR profile will stand. Because my band intensities are higher than that used by ATMOS, my cross-sections will likewise be bigger. According to the Beer-Lambert Law, \(A = \sigma CL\). Since my \(\sigma\) is larger and \(L\) is constant, my concentration is smaller. Since change in \(C\) is proportional to change in VMR, my VMRs will be smaller as well. Therefore, my hypothetical Altitude
versus VMR curve will be shifted to the left relative to the ATMOS curve. In effect, my curve will approach that of the in situ measurements, which were accomplished by chromatography and mass spectroscopy of atmospheric samples collected by aircraft and balloon payloads. Finally, what this means for the model calculations done by Guy Brasseur and Anne de Rudder is that, with my VMR values, the lower stratospheric part of their curve will remain approximately the same, but at 20-30 km, the curve will grow farther and farther apart. Although I have not resolved the discrepancy between the model curve and the ATMOS curve, I believe that my data, with their revised values for integrated band strength, can be used to help GRO establish an improved vertical mixing profile of CCl₄.

7. Acknowledgements

I thank John Orlando and Geoff Tyndall for guiding me through my first experiences in scientific research and for having the patience to bear with me in my work. I also thank Guy Brasseur, Anne de Rudder, and Claire Granier for furnishing some of the data I used in my discussion, and Steve Massie for suggesting my project topic. Finally, thanks to NCAR and to Jack Calvert and Chris Cantrell of the Atmospheric Kinetics and Photochemistry group for hosting my stay here this summer.
8. References


CCL$_4$ PHOTOLYSIS

CCL$_4$ + h$_v$ --> CCl$_2$ + 2Cl

ATMOSPHERIC ODD-OXYGEN LOSS CYCLES

**Cycle 1:**

Cl + O$_3$ --> ClO + O$_2$

ClO + O --> Cl + O$_2$

---

Net: O + O$_3$ --> O$_2$ + O$_2$

**Cycle 2:**

Cl + O$_3$ --> ClO + O$_2$

OH + O$_3$ --> HO$_2$ + O$_2$

ClO + HO$_2$ --> HOCl + O$_2$

HOCl + h$_v$ --> OH + Cl

---

Net: O$_3$ + O$_3$ --> O$_2$ + O$_2$ + O$_2$

**Cycle 3:**

Cl + O$_3$ --> ClO + O$_2$

ClO + NO --> Cl + NO$_2$

NO$_2$ + O --> NO + O$_2$

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Net: O + O$_3$ --> O$_2$ + O$_2$

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Fig. 1. Photolysis reaction and odd-oxygen loss reactions.
From Table I, R. P. Chemistry of Atmospheres, 2nd ed.

To ozone loss contribution potential 10^6 KEP yr^{-1}p

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<th>Com pound</th>
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<th>Contribution</th>
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<td>Ozone Release Rate</td>
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<th>Ozone depletion Lifetime (yr)</th>
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<td>CF_2Cl_CF_2Cl</td>
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<td>CFC_1</td>
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Table I: Effect of different halocarbons on stratospheric ozone

From Zander et al., 1987.

From Wayne, R. P., Chemistry of Atmospheres, 2nd ed.
Fig. 4. Synthetic spectra calculations over the 786–806 cm\(^{-1}\) region, when including CCl\(_4\) (middle trace) compare well with an observed run (lower trace). The upper trace shows all absorptions excluding CCl\(_4\).

From Zander et al., 1987.
Fig. 5. Sample absorption spectrum of CCl₄.
THE BEER-LAMBERT LAW

\[ A = \sigma CL \]

where \( A \) = Absorbance, \( \sigma \) = Cross-section (cm\(^2\)/molecule),
\( C \) = sample concentration (molecules/cm\(^3\)),
and \( L \) = radiation path length (cm)

\[ A = \ln \left( \frac{I_0}{I} \right) \]

where \( I_0 \) = reference beam intensity
and \( I \) = sample beam intensity

Fig. 6. The Beer-Lambert Law of absorbance in terms of cross-sections and in terms of beam intensities.
Fig. 7. Sample plot of cross-section versus frequency for CCl₄.
Fig. 9. Linearity of absorbance versus concentration plot for CCl₄, obtained by spectral inspection.
ABSORPTION CROSS SECTION

\((\text{cm}^2 \text{ molecule}^{-1})\)

Fig. 10. CCL\(_4\) ABSORPTION CROSS SECTIONS AS A FUNCTION OF TEMPERATURE.
Table 2 Summary of measured $\text{CCl}_4$ infrared absorption cross-sections.

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<th>273 K</th>
<th>298 K</th>
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<td>(10^{-18} cm² molecule⁻¹)</td>
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<td>(10^{-17} cm⁻¹ cm²</td>
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<tr>
<td>molecule⁻¹)</td>
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<tr>
<td>BAND INTENSITY BETWEEN</td>
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<td>4.71</td>
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<td>3.68</td>
<td>3.68</td>
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Fig. II. Retrieved 30°N-Zonal VMR profile of CCL\textsubscript{4} compared to in situ mean results [Pabian and Gœmèr, 1984] and model calculations [Brasseur and de Visscher, 1986].