

6-1978

# CO<sub>2</sub> laser induced decomposition of freon 113

Richard S. Herrick

*Union College - Schenectady, NY*

Follow this and additional works at: <https://digitalworks.union.edu/theses>

 Part of the [Chemistry Commons](#)

---

## Recommended Citation

Herrick, Richard S., "CO<sub>2</sub> laser induced decomposition of freon 113" (1978). *Honors Theses*. 1863.  
<https://digitalworks.union.edu/theses/1863>

This Open Access is brought to you for free and open access by the Student Work at Union | Digital Works. It has been accepted for inclusion in Honors Theses by an authorized administrator of Union | Digital Works. For more information, please contact [digitalworks@union.edu](mailto:digitalworks@union.edu).

CO<sub>2</sub> Laser Induced Decomposition of Freon 113

Richard S. <sup>del</sup>Herrick  
///

Submitted in partial fulfillment  
of the requirements for  
Honors in the Department of Chemistry

UNION COLLEGE

April 18, 1978

2  
11/18/82  
H 566 C  
1978

ABSTRACT

Irradiations were made on  $\text{CCl}_2\text{FCClF}_2$ , Freon 113, to see if the resulting decomposition was photochemical in nature. The irradiation source was a Molelectron 250, continuous wave, infrared laser operating in the single line mode. The wavelength of irradiation was varied over the range 9.473  $\mu$  to 9.734  $\mu$ . The pressure of Freon 113 was 20 torr for all reactions discussed except one (in which the cell window broke).

Relative rates of reaction were calculated for a constant power absorbed by the sample of 7.8 $\pm$ .4W. These relative rates were plotted against the irradiation wavelength. This was superimposed on a plot of the IR band for Freon 113 which was irradiated in this project. A difference in wavelength of 0.11  $\mu$  in the maximum of absorption of the IR band for Freon 113 and the maximum relative rate of reaction was found. This indicates that the fastest reaction occurs when the laser is tuned to a vibrational level transition other than the  $v = 0$  to  $v = 1$  transition.

Thermal and photochemical models are discussed, but are rejected as possible mechanisms for the reaction observed in this project. A model combining thermal excitation and photochemical reaction is discussed. Despite some assumptions made, it is shown that this model explains the data well.

#### ACKNOWLEDGEMENT

I would like to thank Dr. Sam Waits of R.P.I. for making the expanded scale infrared spectrum of Freon 113 which is found in Figures 3 and 7.

I would like to thank Dr. Thomas Galantowicz for allowing our research team the use of this CO<sub>2</sub> laser, as well as for his help with problems we had with the laser.

I would like to thank Dr. Herb Sutter for his help and for his insight into the problem. Without him as part of the project we might never have solved the mystery of the off-resonance.

Finally, I would like to thank Dr. Les Hull who, as part of the research team and as my research advisor, was invaluable to my understanding of this project, and who, also, greatly increased my general education in the field of chemistry.

TABLE OF CONTENTS

Abstract - p.1  
Acknowledgement - p. ii  
Table of Contents - p. iii  
Introduction - p. 1  
Experimental - p. 15  
Results - p. 22  
Discussion - p. 44  
Suggestions for Further Work - p. 60  
Appendix - p. 61  
References - p. 68

## Introduction

Laser is an acronym for light amplification by stimulated emission of radiation. The theory of a laser's operation is fairly simple. A substance which might be a gas, liquid or solid is excited to an excited state. The excited molecules or atoms fall back to a metastable excited state. This is called optical pumping. The non-Boltzman distribution of molecules with an excess in an excited state is called an inverted population. Quanta, whose energy is equal to the energy difference between the ground and metastable excited state, are fed into the system. The collision of quanta with excited molecules causes stimulated emission of light which is coherent with respect to both space and time. An inverted population is necessary for stimulated emission since the stimulated emission of radiation must predominate over the absorption of radiation. Since the two processes are of equal probability, there must be an excess of molecules in the excited state.

After the photons, which are in phase, are emitted they travel from one end of the resonating chamber to the other many thousands of times. As the photons collide with excited molecules, they induce more stimulated emission. Through repetition of this process, a coherent wave builds in intensity. When the beam of light reaches a threshold intensity, it is able to pass through a semi-

transparent mirror at one end of the resonating cavity. The light comes out coherent spatially since only the quanta which have been reflected thousands of times are now travelling along the axis of the resonator. Radiation not travelling along the axis of the resonator is absorbed by the walls of the resonator.

Stimulated emission is a resonant phenomenon which takes place with the highest probability at the frequency of the photon which hits it. Hence the light is coherent in frequency. An infrared laser can be tuned to many different frequencies over a small range, since vibrational-rotational levels in molecules are coupled. The vibrational transition is always the same. The rotational transition can take place with varying probability from numerous rotational levels. This accounts for the large number of frequencies to which the laser can be tuned.

A vibration-rotation band in the IR contains 2 or 3 branches. These are the P,Q,R branches. They correspond to a change in the rotational quantum number,  $J$ , of  $-1$ ,  $0$ ,  $+1$  respectively. The Q branch does not occur in the spectrum of some molecules. Each branch has numerous narrow peaks which correspond to a rotational level and a type of rotational transition (i.e.  $\Delta J = -1, 0$ , or  $+1$ ).<sup>1,2</sup>

The characteristics of a laser are determined by the frequency of the beam, the power of the beam and

whether the beam is pulsed or continuous wave. A pulsed laser can emit thousands of bursts of coherent light per second. Each burst lasts approximately  $10^{-9}$  seconds. A continuous wave or CW laser puts out energy continuously, so the pulse length is infinite. The power of a pulse in a pulsed laser is on the order of  $10^6$ W, while a CW laser has a maximum power on the order of  $10^2$ W.

The laser used in this project was a Molelectron 250 CO<sub>2</sub> infrared continuous wave laser operating on the single line mode. The maximum power output was about 30W. The beam diameter was 0.4cm. The laser could be tuned to many lines in the region between 9 and 11 $\mu$ .

The CO<sub>2</sub> laser puts out infrared radiation. If an IR photon hits a molecule which has a vibrational transition in resonance with the photon, the molecule goes into an excited vibrational state by absorbing the photon. If the molecule absorbs enough quanta, ( $m$ ), such that  $m h \nu$  equals the dissociation energy, the molecule would instantaneously dissociate. Planck's constant is represented by  $h$  and  $\nu$  is the frequency of the quanta. However, due to the anharmonicity of the potential well, the difference between vibrational levels becomes smaller as you ascend the potential well.

The problem is that the laser is too monochromatic to tolerate these small changes in frequency. An optimum situation would be a molecule whose vibrational level



differences are large while the energy of dissociation is small. Only a few quanta of energy would need to be absorbed, and the anharmonicity might not be a problem.<sup>3</sup>

Theoretically, it is not necessary to absorb an amount of energy equal to the dissociation energy. The dissociation energy corresponds to the energy of activation. By absorbing one quantum of energy equal to  $h\nu$ , the rate of reaction (dissociation) can be increased.<sup>3</sup>

$$E_a = E_{\text{diss}} - h\nu \quad (1)$$

$$k = A [\exp(-E_a/RT)] \quad (2)$$

$k$  is the rate constant

$A$  is a constant

Initially:

$$k = A [\exp(-E_{\text{diss}}/RT)] .$$

After excitation:

$$k = A [\exp(-E_{\text{diss}}/RT)] [\exp(N_0 h\nu/RT)] \quad (3)$$

where  $N_0 h\nu$  is the average increase in energy of the system.

So, if  $h\nu > kT$ , the effect of absorbing one quantum has an effect on the rate of bond breaking. An unsolved aspect of this explanation is the value of  $T$  to be used in finding  $k$ . In lasing a sample, the "temperature" of one mode is increased tremendously while the other modes remain temporarily at the same temperature. Plugging in the temperature of the non-affected modes gives a value of  $k$  that is too small. Using the temperature of the

excited mode yields a rate constant that is too large.<sup>3</sup> In the discussion above, the definition of temperature is the average energy in a mode.

The discovery of the laser process has led to many uses of the laser in today's society. Communications, surveying and delicate eye surgery are just a few of the applications which have been found for the laser process. The application of lasers in the field of chemistry is presently being examined to determine if lasers can solve practical chemical problems. Two examples of possible uses are isotope enrichment and the use of laser induced photochemical reactions. Both processes involve absorption of laser energy leading to selective breaking of a chemical bond.

Isotopic enrichment has uses in medicine where radioactive isotopes are used as tracers in the body. Another example of isotopic enrichment is the separation of  $U^{235}$  from  $U^{238}$ . Isotopic enrichment is an important use for lasers since separation of isotopes is a difficult process. Isotopes are chemically similar and can not be separated by thermal reactions. Their physical properties differ so little that separation by methods such as diffusion are time consuming, expensive processes.

Separation by laser stimulation is possible due to the differences in frequency of the maximum absorption of light by the two isotopes. For a suitable compound

this difference in frequency may be within the range in which the laser can be tuned. When tuned, one isotope will preferentially absorb more radiation than the other isotope. The excited molecules will be more liable to undergo dissociation as discussed before. If enough energy is absorbed, the molecules will dissociate instantaneously. The molecules containing the other isotope will be mostly unexcited. The starting material is enriched in the unexcited isotope, and the product is enriched in the excited isotope.<sup>4</sup> Enrichment of an isotope is a useful means of determining if photochemical reaction is occurring.

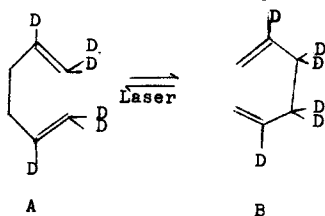
The work of Ambartzumian and Letokhov<sup>5</sup> is an example of laser induced isotope enrichment. An intense IR laser pulse was directed at a sample of gaseous  $\text{BCl}_3$ . The laser was tuned so the  $^{10}\text{BCl}_3$  molecules dissociated were mostly undissociated. The enrichment factor for  $\text{B}^{10}$  was 20 or less for all runs.

A photochemical reaction can be defined as a reaction that occurs at non-thermal equilibrium. Photodissociation is included in this discussion with photochemistry by considering bond breaking a chemical reaction. Isotope enrichment is being considered separately although it is a photochemical reaction.

Laser induced photochemical reactions could be important as a new route to chemical synthesis, since

it may be possible to control the bond breaking by controlling the wavelength of energy absorbed by the molecules. The  $\text{CO}_2$  laser is ideal for examining photochemistry. Its high energy output and high monochromaticity allow it to put energy into a vibrational level in resonance with the laser. Therefore there may be a difference in temperature between degrees of freedom. This situation is a non-thermal equilibrium.<sup>3</sup> A reaction occurring during such a non-thermal equilibrium would be a photochemical reaction.

An example of a photochemical reaction occurring due to IR lasing is the Cope reaction given below.<sup>6</sup> It was found by Glatt and Yogev that B preferentially absorbed



the IR radiation and photoisomerized. A acted as a window to radiation of this frequency and did not react. The isomerization involves a (3S,3S) sigmatropic shift and is therefore allowed in the electronic ground state. The reaction was decidedly photochemical, making this an example of photochemistry in the electronic ground state. Photochemistry has previously been considered

to occur only in an electronically excited state.<sup>7</sup> This shows that it is possible to have photochemical reactions in the electronic ground state (under the condition that a vibrational mode is excited).

In general the size of an infrared photon is small compared to the energy needed for dissociation. Therefore several photons (10 - 20 might be considered an average number) must be absorbed to dissociate the molecule.

As noted before, an increase in the vibrational energy increases the rate of reaction by a factor of  $\exp(N_0 h\nu/RT)$ . To absorb  $n$  photons consecutively, which increases the chemical energy and the chance of reaction, the laser power must be increased according to equation (4).<sup>8</sup>

$$\text{Reaction rate} \propto \text{laser power}^n \quad (4)$$

Here  $n$  is an integral number which is less than or equal to the number of photons which must be absorbed to reach the dissociation energy.

The discussion above concerned a collisionless model. If collisions occur before  $n$  photons can be consecutively absorbed by a molecule, vibrational-vibrational relaxation, vibrational-translational relaxation, or vibrational-rotational relaxation can occur. If any of these processes happen, they funnel energy out of the high temperature mode into another mode. All would hinder increased reac-

tivity except possibly V-V (vibrational-vibrational) relaxation. If the V-V relaxation transferred energy exclusively into another vibrational degree of freedom, this bond would now be caused to break at an accelerated rate.

A possible example of V-V relaxation leading to reaction was given by Zitter and Koster.<sup>9</sup> In two separate experiments, energy was pumped into two different vibrational modes of  $\text{CF}_2\text{ClCF}_2\text{Cl}$  by tuning the laser to the appropriate absorption band in the IR. Both experiments apparently gave the same reaction but at different rates. The rates were the reverse of what would be seen for a thermal reaction, since the band with the larger absorption coefficient led to the reaction with the smaller rate constant. It was suggested that the absorbed laser energy was transferred by collisional interactions into a vibrational mode for which the dissociation energy was less. There had to be some kind of collisional interaction since the 2.5W - 4.0W put out by the laser is far smaller than what is needed for multiphoton absorption.

A laser induced reaction is either photochemical or thermal depending upon whether the energy is removed from a vibrational mode before there is enough for the bond to break. Hence, low pressure and high laser power favors photochemical reaction, since few molecular

collisions and a high photon density speeds collection of energy in a mode and slows down the removal of energy from the mode.

An example of higher pressures leading to increased thermalization is suggested by the work of Glatt and Yogev,<sup>6</sup> which was discussed on page 7. A mixture of compounds A and B was irradiated by a CO<sub>2</sub> laser which resulted in the enrichment of A. Enrichment of A was found to be a maximum at 5 torr. Apparently as the pressure is increased beyond that, too many collisions occur and the photochemical reaction becomes less predominant.

Up to this point it has been assumed that the laser must be set for the transition  $v = 0 \rightarrow v = 1$ . Keeping in mind that  $\Delta v = \pm 1, \pm 3, \pm 5, \dots$  is the selection rule for vibrational transitions (normally only  $\Delta v = \pm 1$  is seen), it is worthwhile to see if some other setting would be more efficient.<sup>3</sup> Since the laser is of high energy, it may be more economical to effect the transition  $v = 0 \rightarrow v = m$  using one large quanta instead of  $m$  small quanta. For  $m$  quanta absorbed consecutively:

$$E_{1p} = mh\nu_{10}(t_R/t_{VV})^{\frac{1}{2}} \quad (5)$$

where  $E_{1p}$  is the average energy absorbed per molecule from a long duration laser pulse,  $\nu_{10}$  is the frequency for a transition from the  $v = 0 \rightarrow v = 1$  level,  $t_R$  is the rotational relaxation time, and  $t_{VV}$  is the V-V relaxation time. For the absorption of 1 large quantum:

$$E_{1p} = hv_{10}(t_r/S_m t_{vv})^{1/2} \quad (6)$$

where  $S_m = \frac{h\nu}{k}(1/k)$ . Therefore it is more efficient to tune the laser to the frequency  $\nu_{10}$  instead of the frequency  $\nu_{m0}$ . The same result is found for pulsed lasers.

After exposing a sample to the laser, the next step is to determine whether a photochemical reaction has occurred. Probably the simplest way of analyzing the reaction is to examine the products. If the products are significantly different from those of hot tube pyrolysis, a photochemical reaction took place in a sample at a non-thermal equilibrium. The methods of determining product composition would be gas chromatography, mass spectrometry or IR. Despite the ease of analysis, this method is quite difficult to use as proof. This is illustrated in the paper by Bailey et al.<sup>10</sup> Analysis of the products of the irradiation of ethyl chloride was used as the test for determining if a photochemical reaction had occurred. The authors were unable to prove whether the reaction was photochemical since the reaction conditions were quite different from those of the hot tube pyrolysis.

A second method which can be used is isotope analysis. If the reaction is photochemical there should be some selective isotopic enrichment as explained earlier. If the reaction is thermal in nature, there will be no isotopic selectivity with respect to the products formed. A mass spectrometer should be sufficient in determining



whether isotopic enrichment occurred.

There are difficulties with this method, however. The isotope of one molecule must have a fairly low absorption coefficient at the lasing frequency, while the other isotope should have a fairly high absorption coefficient at this frequency. Otherwise the enrichment might not be large enough to be detected.<sup>3</sup> It is easier to work with isotopes whose atomic weights are small. The frequency maxima of these isotopes are farther apart since the relative difference in their masses is fairly large.

Another problem of isotopic separation is that the small difference of frequency maxima of the different isotopic molecules can cause energy exchange between excited molecules and non-excited molecules of the other isotope. In order to separate the two isotopes, the average temperature ( $T_1$ ) of the resonance excited first isotope must be greater than the average temperature ( $T_2$ ) of the second isotope. Thus with the first isotope present in concentration  $c$ , separation takes place under the condition that:<sup>3</sup>

$$c [\exp(-E_a/T_1)] > [\exp(-E_a/T_2)] \quad (7)$$

$$\ln(c) - E_a/T_1 > -E_a/T_2 \quad (8)$$

$$-E_a/T_1 + E_a/T_2 > \ln(1/c) \quad (9)$$

$$(1/T_2 - 1/T_1) > 1/E_a \ln(1/c) \quad (10)$$

Therefore a large energy of activation is desired since

this requires only a small temperature difference for separation. Since the rate of reaction decreases as activation energy increases, there is an activation energy which is optimal for the separation of isotopes.

A mixture of gases can be used to determine if a non-thermal reaction occurred. This can be accomplished with several trials run with the gases in different proportions. Freeman and Travis<sup>8</sup> used this setup with a mixture of  $\text{CF}_2\text{Cl}_2/\text{Ar}/\text{SF}_6$ . The test was intended to analyze the decomposition of  $\text{CF}_2\text{Cl}_2$ . Its partial pressure was kept constant throughout the trials at .5atm. The reason for using argon was that it does not absorb infrared radiation since it has no vibrational mode.  $\text{SF}_6$  was chosen since it is a strong absorber of  $\text{CO}_2$  laser radiation, and it does not decompose until very high temperatures. The ratio of  $\text{SF}_6/\text{Ar}$  was the only variable, since the power absorbed by  $\text{CF}_2\text{Cl}_2$  was constant.

The calculation that the amount of power absorbed by  $\text{CF}_2\text{Cl}_2$  is constant is made on the assumption that all energy absorbed is instantaneously distributed evenly to all modes of freedom. Therefore, if instant thermalization takes place, the results should be the same for all runs. It was found that the fraction of  $\text{CF}_2\text{Cl}_2$  dissociated depended on the  $\text{SF}_6$  added with the percentage of  $\text{CF}_2\text{Cl}_2$  decreasing with increased  $\text{SF}_6$ . Therefore, it appears that there is a non-thermal component to this

reaction.

The research project which is the subject of this paper was concerned with the decomposition of  $\text{CF}_2\text{ClCCl}_2\text{F}$  following laser irradiation. The purpose was to see whether the dissociation was photochemical in nature. In the following pages of this paper data accumulated from this project are presented. Several model reaction mechanisms are discussed in an attempt to find one that fits the data observed.

EXPERIMENTAL

Two different irradiation cells were used in this project. Each had four orifices to which windows could be attached. Two of the windows were for the laser beam to enter and exit. The other two windows were perpendicular to the laser windows and allowed infrared spectra to be taken during the laser irradiation. The smaller pair of windows was used for the laser beam. They had an inside diameter of 1.9 cm. The larger pair of windows had an inside diameter of 3.5 cm. The path length between the larger pair of windows was 10 cm, the path length between the smaller pair of windows was 5 cm in one cell and 10 cm in the other cell (Figure 1).

The cell with the short path length between the small windows was used for the first six runs. The windows were then removed to be polished. Upon replacing the windows it was noticed that the cell would no longer hold a vacuum well. The other cell was used after this run.

Initially, the window the laser beam entered was a CsBr window. The laser beam burned a hole through the window in an early run. Since each CsBr window costs approximately \$150, it was decided to use a much cheaper KCl window as the entry window for the laser beam. The other three windows were also KCl.

The adhesive used to cement the windows to the lens joint was GE Clear Silicone Glue and Seal. After a

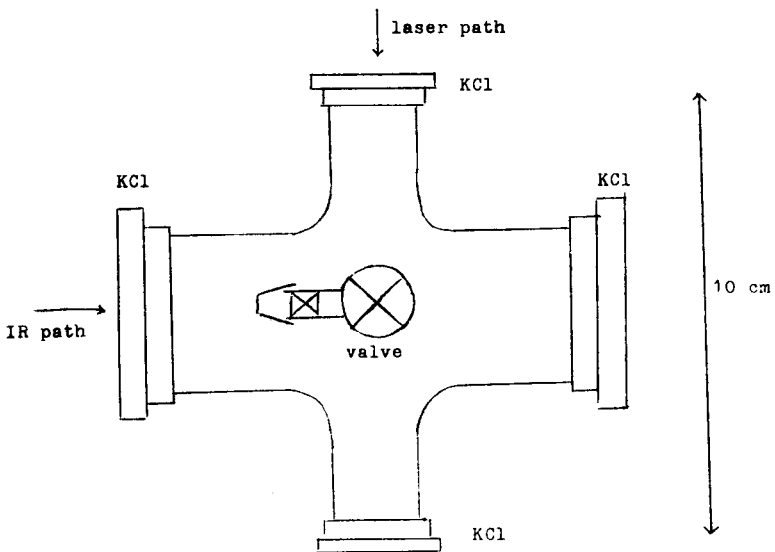
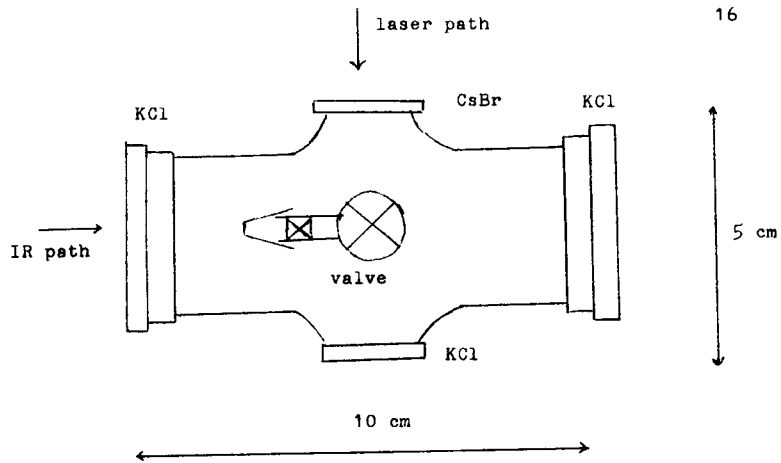


FIGURE 1 - IRRADIATION CELLS

number of runs the windows would no longer be clear because of the attack of water on the surfaces. The cells were then removed to be polished. The cell was placed in a toluene bath overnight to loosen the glue so the windows could be removed the next day by gentle twisting. Occasionally, this loosening of the glue took more than 24 hours. This may be explained by the fact that benzene was used as the solvent instead of toluene. In these cases a scalpel was inserted between the window and lens joint, and the window was "cut" off. After polishing the windows, they were reglued to the cell. The glue was allowed at least 24 hours to dry.

A glass vacuum line was used to evacuate the cell. The vacuum line could be pumped down to approximately 10  $\mu$  with the cell attached. Near vacuum pressures were measured by a manometer. Freon 113 (also referred to as  $\text{CF}_2\text{ClCFCl}_2$  or 1,1,2 trichlorotrifluoroethane) was kept in a trap in the vacuum system in its liquid form. Before expanding the Freon 113 into a closed off portion of the line, the line was first evacuated, then the reactant degassed.

Degassing removes dissolved gases from a liquid. A Dewar flask filled with liquid nitrogen is placed around the trap until the sample is frozen. The trap is opened and all volatiles in the trap are pulled out of the vacuum line by a vacuum pump. The trap is then

closed, and the compound is allowed to melt. This degassing was done at least twice before every run.

The cells were attached to the vacuum line at ground glass joints lubricated with high vacuum silicone grease. To place the compound in the cell, a portion of the vacuum line was closed off. The trap was now opened so the gas could expand into the system. When the pressure reached the desired value, the trap was closed. After the pressure in the vacuum line was allowed to come to equilibrium, the stopcock of the cell was closed, and the cell was removed from the system. The pressure of the sample in the line was measured by a mercury column. The pressure of the gas in the cell could be determined to  $\pm 0.4$  Torr.

The irradiation source was a continuous wave Molelectron Model C-250 Infrared Gas Laser. Irradiations were done with the laser in the single line mode. The procedure for turning on, tuning, and changing the laser line can be found in the Appendix.

The cell was placed on a wooden block in such a way that spectra could be taken with a Perkin Elmer Model 21 Spectrophotometer during the irradiation. The laser beam was directed into the cell by a silver-coated mirror held in a clamp attached to a ringstand (Figure 2).

A Helium-Neon laser was used to align the mirror. This laser was placed so the beam passed through the

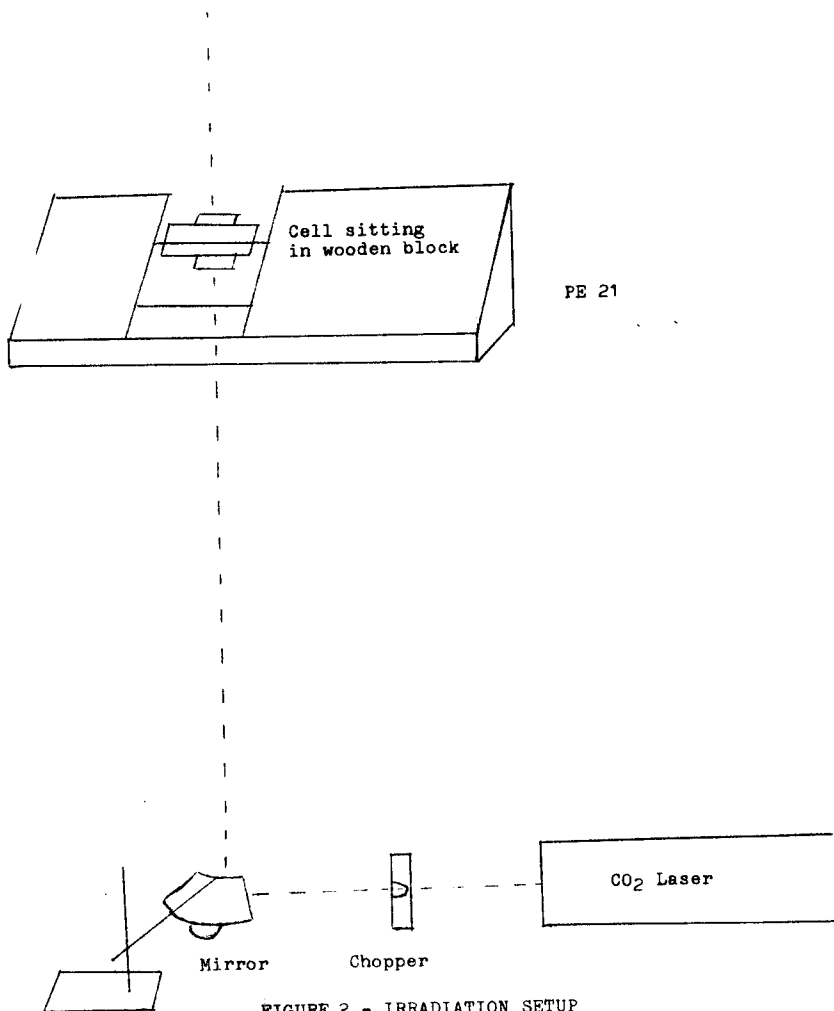


FIGURE 2 - IRRADIATION SETUP



center of the small windows of the cell as it sat on its wooden block. The cell was removed, since its windows diffused the laser beam. The mirror was placed so the beam was reflected into the center of the front CO<sub>2</sub> laser lens. The reflection which came off this lens (which was a partially reflecting mirror) was directed back to the lens of the He-Ne laser by manipulation of the silvered mirror.

The cell was replaced in its block and bricks were placed in front of and behind the cell. The CO<sub>2</sub> laser was turned on. A piece of wood was placed behind the front brick and the brick was removed. If the burn spot did not line up with the center of the front window, the mirror could be moved slowly with the bricks in place. The process was repeated until the mirror was correctly aligned.

Several runs were made using the chopper. This was a disk rotating at 15 Hz. with holes cut so that the beam was blocked half the time. After the CsBr window was broken, several runs were made in which a blocking brick was used. After one or five minutes of lasing, a brick was placed in front of the cell for one or five minutes. This process was repeated throughout the run. In Table 1 there is a column indicating whether the chopper or blocking bricks were used.

The laser power was measured by means of a power

detector connected to a Coherent Radiation power meter. The power detector was placed in front of the cell before the start of the run so the beam went into the center of the detector. The power into the cell could then be read off the meter. The power out of the cell was measured similarly with the power detector placed behind the cell.

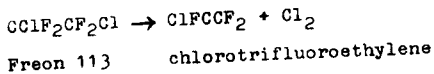
Before starting a run, the power was watched for half an hour to make sure it would remain constant for the run. During many runs, the power was checked often. Before measuring the power out of the back of the cell it was necessary to make sure the beam was not being obstructed by striking the sides of the cell. This was done by getting a burn spot on a piece of tissue paper.

Infrared spectroscopy was the only method of analysis used in this project. A mass spectrometer was being calibrated to help with the analysis, but the filament burned out. The infrared spectrometer used to monitor the reaction was a Perkin Elmer 21 spectrophotometer.

Infrared scans were taken over the range  $2500\text{ cm}^{-1}$  to  $600\text{ cm}^{-1}$  both before and after every run. During the run, spectra were taken periodically over the  $1400\text{ cm}^{-1}$  to  $1300\text{ cm}^{-1}$  range to monitor the growth of the  $13300\text{ cm}^{-1}$  peak due to  $\text{C}_2\text{ClF}_3$  (also referred to as chlorotrifluoroethylene and ethylene product).

### RESULTS

Except for the first reaction, all spectra taken after a reaction showed peaks at  $1330\text{ cm}^{-1}$  and  $1795\text{ cm}^{-1}$ . According to a literature spectrum<sup>11</sup>, these peaks were due to chlorotrifluoroethylene. It was proposed by Curt Brown<sup>12</sup> that the chlorotrifluoroethylene was formed by the following reaction:



It was decided to monitor the breakdown of the Freon 113 by following the appearance of the  $1330\text{ cm}^{-1}$  peak of the ethylene product. The  $1330\text{ cm}^{-1}$  peak had a higher extinction coefficient than the  $1795\text{ cm}^{-1}$  peak, and its size and shape were unaffected by neighboring peaks.

Other irradiation product peaks not characteristic of  $\text{C}_2\text{ClF}_3$  were found. A peak at  $845\text{ cm}^{-1}$  was often found after a reaction. It was identified by comparison with a literature spectrum<sup>13</sup> as probably due to  $\text{CCl}_3\text{F}$ . C. Brown identified  $\text{CCl}_2\text{F}_2$ ,  $\text{CClF}_3$  and  $\text{CCl}_3\text{F}$  as reaction products by GC analysis.<sup>12</sup> The identification of  $\text{CCl}_3\text{F}$  was ambiguous. Table 1 summarizes the results of irradiations made in this project.

The first reaction occurred in run 3 when 28 torr of  $\text{C}_2\text{Cl}_3\text{F}_3$  were irradiated at  $21.4 \pm 1.4$  watts at  $9.665\text{ u}^*$

TABLE I - RESULTS OF IRRADIATIONS

23

Run # <sup>a</sup>	Pressure ( $\pm$ .4 Torr)	$\lambda(\mu)$	Lasing Time(min)	Power (watts)	Reaction
1	52.0	9.604	6	10.5	-
2	49.5	9.520	28	11.2	-
3	28.0	9.665	11	21.4	rxn; window cracked
4	11.5	9.695	40	4.2	-
5	11.4	9.714	35	6.3	-
6	20.4	9.714	35	11.6	rxn
7I	21.0	9.520	35	10.0	-
7II	21.0	9.540	10	11.5	-
8	42.0	9.458	25	6.5	-
9I	20.0	9.520	10	7.1	-
9II	20.0	9.639	10	8.3	-
10I	21.0	9.604	20	1.5	-
10II	21.0	9.604	15	3.1	-
10III	21.0	9.604	15	5.6	-
11	25.0	9.552	20	7.0	-
12I	40.0	9.552	25	4.45	-
12II	40.0	9.552	10	6.5	-
12III	40.0	9.552	25	8.35	-
13I	20.4	9.714	15	6.0	-
13II	20.4	9.714	15	8.65	-
13III	20.4	9.714	10	12.0	-
13IV	20.4	9.714	8	17.3	rxn
14I	20.0	9.552	10	12.0	-
14II	20.0	9.552	10	14.5	-

TABLE I - (cont.)

24

Run #	Pressure ( $\pm 0.4$ Torr)	$\lambda$ ( $\mu$ )	Lasing Time(min)	Power (watts)	Reaction
14III	20.0	9.552	10	16.0	-
14IV	20.0	9.552	10	17.5	-
14V	20.0	9.552	10	20.5	-
14VI	20.0	9.552	10	21.3	-
15I	20.0	9.552	10	15.3	14.5 <sup>c</sup> -
15II	20.0	9.552	10	17.1	17.5 <sup>c</sup> -
15III	20.0	9.552	10	20.6	-
16I	20.0	9.714	20	16.3	rxn
16II	20.0	9.714	5	20.0	rxn
17	20.0	9.645	b	d	rxn
18I	20.0	9.552	b	d	-
18II	20.0	9.714	b	d	rxn
19I	20.0	9.604	b	d	ambiguous
19II	20.0	9.694	b	d	rxn
20I	20.0	9.476	b	d	-
20II	20.0	9.734	b	d	rxn
21	20.0	9.552	30	17.1	-
22	20.0	9.695	7	17.2	rxn
23	20.0	9.714	15	17.0	rxn
24	20.0	9.734	25	17.3	rxn
25	20.0	9.654	30	17.3	-

Peaks Other Than Freon 113 Peaks Found After ReactionRun

- 3 - 1880  $\text{cm}^{-1}$  strong; 1255  $\text{cm}^{-1}$  strong; 775  $\text{cm}^{-1}$  moderate;  
725  $\text{cm}^{-1}$  strong; (no Freon 113 peaks in spectrum);  
window broke
- 6 - 840  $\text{cm}^{-1}$  moderate
- 13 - 840  $\text{cm}^{-1}$  moderate
- 16 - 740  $\text{cm}^{-1}$  weak; 710  $\text{cm}^{-1}$  weak; 840  $\text{cm}^{-1}$  strong; 990  $\text{cm}^{-1}$   
strong; 1730  $\text{cm}^{-1}$  strong; 1650  $\text{cm}^{-1}$  weak
- 17 - 845  $\text{cm}^{-1}$  moderate
- 18 - no other peaks
- 19 - no other peaks
- 20 - 1730  $\text{cm}^{-1}$  weak; 845  $\text{cm}^{-1}$  strong
- 21 - 845  $\text{cm}^{-1}$  moderate; 780  $\text{cm}^{-1}$  moderate
- 22 - 845  $\text{cm}^{-1}$  moderate
- 23 - 845  $\text{cm}^{-1}$  moderate
- 24 - 845  $\text{cm}^{-1}$  moderate; 1590  $\text{cm}^{-1}$  weak

<sup>a</sup> - Runs that have Roman numerals indicate that the same sample was used through all parts of the run. The wavelength or power level was changed marking a different part of same run.

<sup>b</sup> - The runs were done to get absorbance measurements, so the lasing time was not recorded.

<sup>c</sup> - power varied over range as indicated.

<sup>d</sup> - many power readings taken, since absorbances were being measured.

Runs 1-8 and 10-13II used the chopper. The other runs did not use the chopper.

Runs 4-8 and 10-13II alternated 5 minutes of blocking and 5 minutes of irradiation. Runs 13III-15III alternated one minute of blocking with one minute of irradiation. All other runs did not use blocking.

for 17 minutes. Reaction was first detected after four minutes of irradiation. The CsBr window had a hole burned through it at between 8 and 11 minutes into the run. The hole burned through the inside of the window. There was a black film in the crater formed and a brown film around the edges of the hole. After the hole appeared, a white powder was deposited on the inside of the cell.

An IR spectrum was taken of the powder (as a KBr pellet) on a Perkin Elmer 237 infrared spectrophotometer. The spectrum had no identifiable peaks. It was found that the powder dissolved easily in water and was insoluble in benzene.

An IR spectrum taken of the cell after the run did not contain the characteristic ethylene product peaks at  $1795\text{ cm}^{-1}$  and  $1330\text{ cm}^{-1}$ . Four other peaks were found after irradiation - strong absorption bands at  $1880\text{ cm}^{-1}$ ,  $1255\text{ cm}^{-1}$  and  $1725\text{ cm}^{-1}$  and a band of moderate absorption at  $875\text{ cm}^{-1}$ . During the irradiation, both before and after the breaking of the window, the  $1330\text{ cm}^{-1}$  product peak was present and growing. After stopping the irradiation, the  $1330\text{ cm}^{-1}$  peak disappeared.

\*In this paper wavelengths will be used when referring to the laser line or to the band which was irradiated. Conversion of wavelength to wavenumbers is made with the formula  $\lambda = 1/\bar{\nu}$ .  $\lambda$  is wavelength,  $\bar{\nu}$  is energy in wavenumbers.

The purpose of Runs 1-18 was to characterize the reaction as a function of different frequencies. Several irradiations were made with the laser at  $9.552 \mu$ . No reaction was ever detected at this wavelength at any power, including powers absorbed by the sample of  $7.6 \pm .4 W$ . Reaction occurred at  $9.714 \mu$  at powers absorbed by the sample as low as  $5.1 \pm .4 W$  with laser power, sample pressure and irradiation time unchanged.

Reaction at  $9.714 \mu$  in runs 13, 16, and 18 and no reaction at  $9.552 \mu$  in runs 11, 12, 14, and 15 was unexpected since  $9.552 \mu$  was near the absorption maximum of the Freon 113 peak in the IR spectrum, while  $9.714 \mu$  was on the side of the peak. The IR absorption at  $9.714 \mu$  was seen to be about half the absorption at  $9.552 \mu$  for a sample of 20 torr.

At first it was thought that this anomaly might be caused by oxygen acting as an inhibitor in the the cell. Run 18 disproved this since reaction occurred at a power absorbed by the sample of  $5.1 \pm .4 W$  at  $9.714 \mu$  after irradiating the same sample for 20 minutes at powers absorbed by the sample greater than  $7.6 \pm .4 W$  at  $9.552 \mu$ .

The calibration of the maximum of absorption of the Freon 113 and of the polystyrene peak at  $1028.0 \pm .3 \text{ cm}^{-1}$  was performed with a 621 Perkin Elmer infrared spectro-photometer set on the x10 expanded scale. According to



the calibration (Figure 3) the Fraun 113 being irradiated was actually three peaks superimposed on one another. Their absorption maxima are  $9.601 \pm .005 \mu$  ( $1041.6 \pm .5 \text{ cm}^{-1}$ ),  $9.548 \pm .005 \mu$  ( $1047.3 \pm .5 \text{ cm}^{-1}$ ) and  $9.487 \pm .005 \mu$  ( $1054 \pm .5 \text{ cm}^{-1}$ ).

To find out more about the reason for reaction at unexpected wavelengths, absorbance measurements were taken of the power into the cell and the power out of the cell for various powers and laser wavelengths (Tables 2-5 and Figures 4-6). The power absorbed by the sample was calculated by using absorbance measurements to find the power absorbed by the cell plus the windows. From this was subtracted the amount of power absorbed or reflected by the cell windows with the cell holding a vacuum (taken from the top plot in Figure 4).

An interesting trend was noticed. At the frequency where the maximum of absorption in the IR was, the sample absorbed less power than it did at lower frequency (Table 6) for a given entering power of 20W.

Relative rates were computed by comparing the absorbance/time for a series of runs carried out at various wavelengths in which  $7.8 \pm .4 \text{ W}$  was absorbed by the sample. The values for absorbance versus time were calculated by taking the absorbance of the  $1330 \text{ cm}^{-1}$  peak and dividing by the minutes of sample irradiation. The maximum reaction rate was at  $9.714 \mu$ .

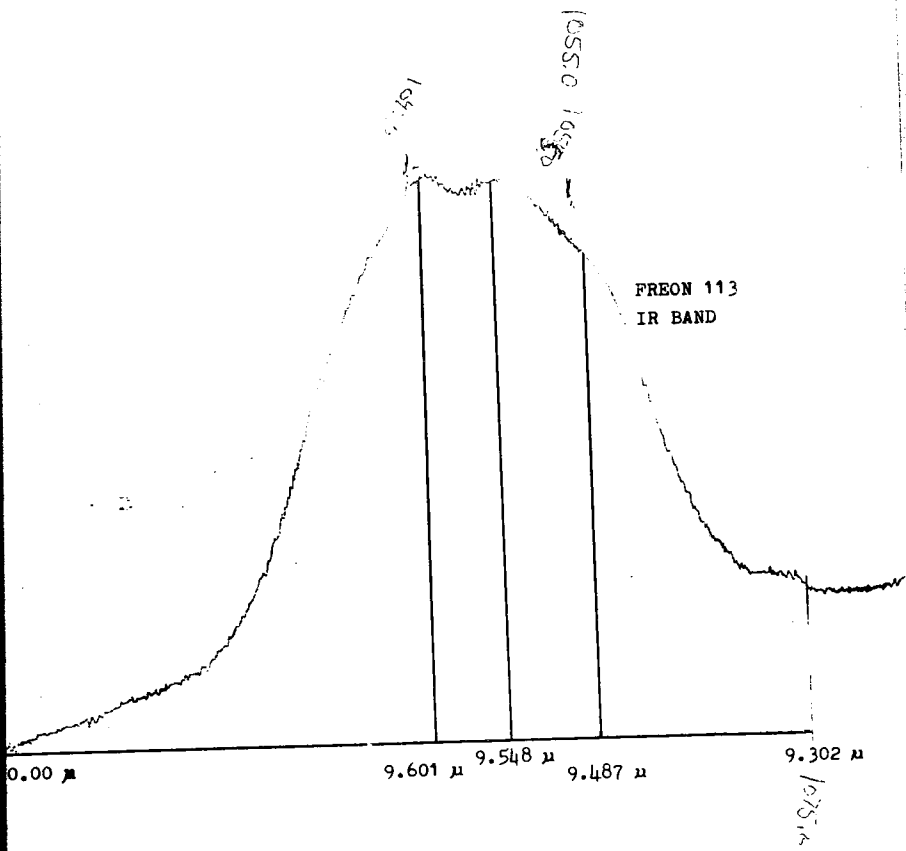


FIGURE 3 - CALIBRATION SPECTRUM FOR FREON 113 IR BAND

TABLE 2 - NET POWER FOR RUNS 14 and 15

Run	$\lambda(\mu)$	Pressure/Reaction	Power( $\pm 0.2W$ ) <sup>*</sup>		Net Power( $\pm 0.4W$ )
			Into Cell	Out Of Cell	
14	9.552	20.0torr/no rxn	12.0	3.0	9.0
14	9.552	20.0torr/no rxn	14.5	3.2	11.3
14	9.552	20.0torr/no rxn	16.0	5.4	10.6
14	9.552	20.0torr/no rxn	17.5	6.4	11.1
14	9.552	20.0torr/no rxn	20.5	7.5	13.0
14	9.552	20.0torr/no rxn	21.3	8.2	13.1
14	9.552	vacuum	17.5	10.0	7.5
14	9.552	vacuum	10.1	6.0	4.1
15	9.552	vacuum	5.0	3.0	2.0
15	9.552	vacuum	10.0	5.6	4.4
15	9.552	20.0torr/no rxn	15.5 $\pm$ .8	5.4 $\pm$ .6	10.1 $\pm$ 1.4
15	9.552	20.0torr/no rxn	17.0 $\pm$ .6	5.7 $\pm$ .2	11.3 $\pm$ .8
15	9.552	20.0torr/no rxn	20.9	7.2	13.7

\*Power measurements made over short periods of time (approximately 30 seconds) allowing for more precise measurements.

Net power is the power absorbed by cell not the power absorbed by the sample.

Vacuum readings from the plot in Figure 4 were used in calculating the power absorbed by the sample.

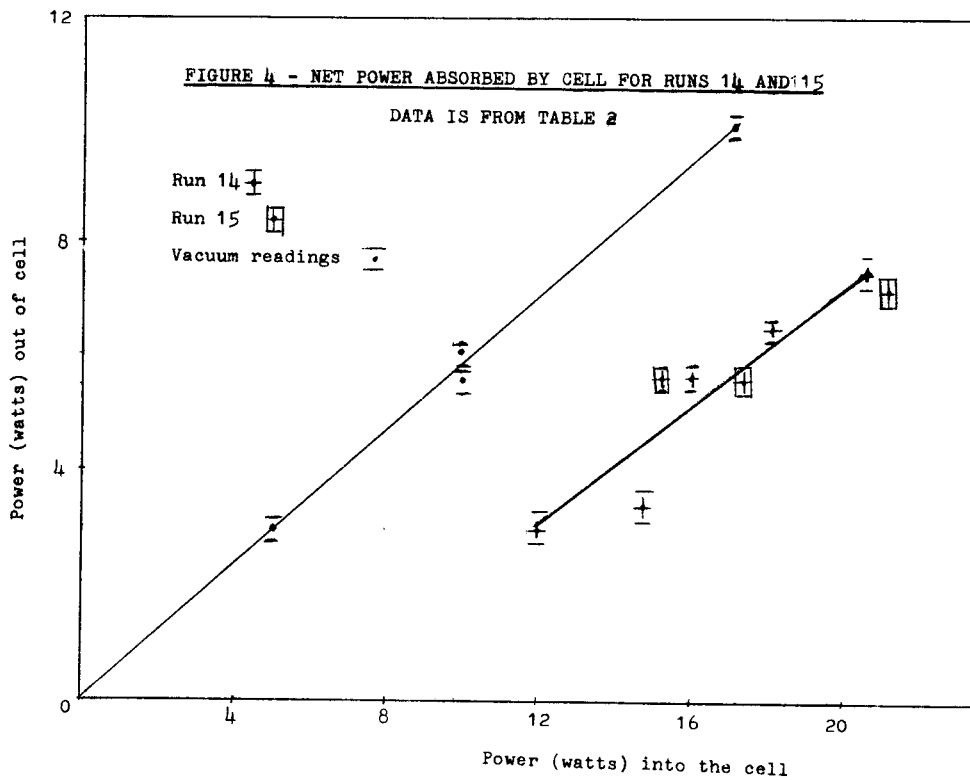


TABLE 3 - NET POWER IN RUN 18

<u>Part I</u>	<u>Power in(<math>\pm</math>.2W)</u>	<u>Power out(<math>\pm</math>W)</u>	<u>Net Power(<math>\pm</math>.4W)</u>	<u>Minutes*</u>
9.552 u	7.8	.70	7.1	5
20.0torr	10.4	1.34	9.1	1
	9.9	1.31	8.6	5
	13.1	1.70	11.4	1
	12.7	1.65	11.1	5
	14.9	2.4	12.5	1
	14.5	2.3	12.2	5
	17.3	3.4	13.9	1
	17.5	3.1	14.4	5
	20.0	4.0	16.0	1
	20.6	-	-	5
<u>Part II</u>				
9.714 u	9.0	1.15	7.9	1
20.0torr	12.1	1.18	10.9	1
	10.5	.95	9.5	1
	13.1	1.32	11.8	5
	11.4	1.20	10.2	1
	18.4	2.40	16.0	1
	20.6	3.4	17.2	5
	-	3.7	-	5

\* - Number of minutes the laser was at that power level.

There was no reaction in Part I. Reaction during Part II first occurred at 12.1W

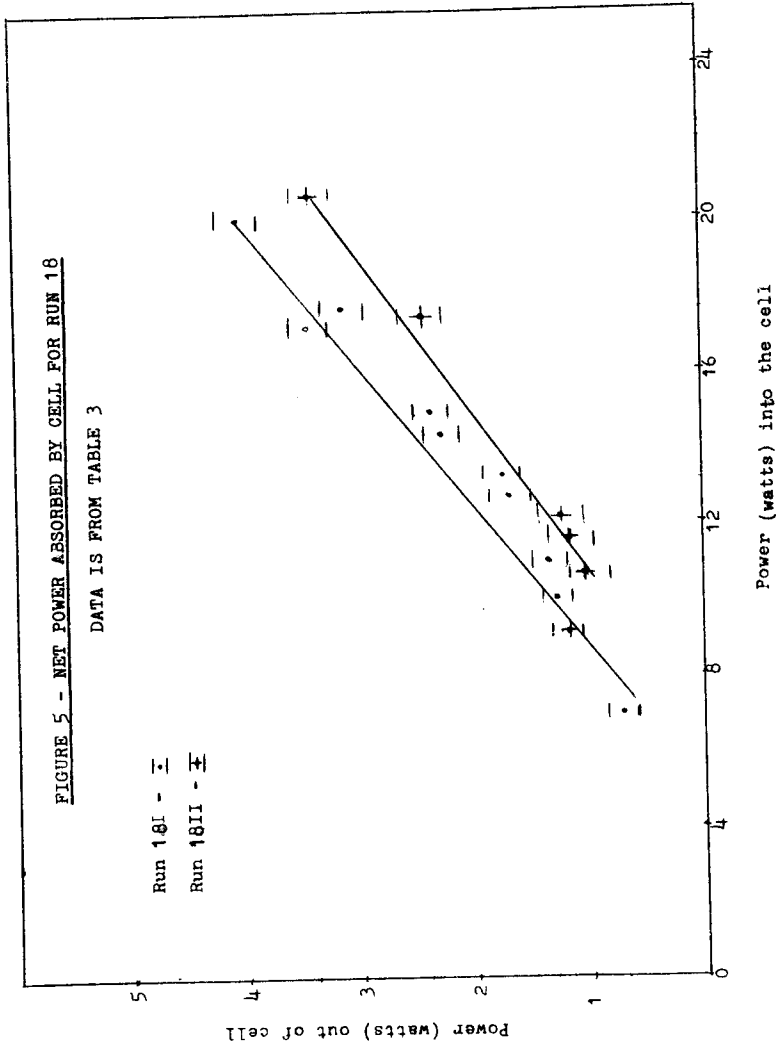


TABLE 4 - NET POWER IN RUN 19

Part I		Power in( $\pm 0.2W$ )	Power out( $\pm 0.2W$ )	Net Power( $\pm 0.4W$ )	Minutes*
9.604 u	10.9		1.18	8.7	-
20.0torr	15.7		1.55	14.1	2
	15.7		1.80	13.9	5
	20.5		3.6	16.9	1
	19.2		3.5	15.7	10
Part II					
9.694 u	11.0		.82	10.2	1
20.0torr	9.9		.74	9.2	5
	17.5		2.15	15.4	1
	17.6		2.1	15.5	5
	20.5		2.9	17.6	1
	20.2		3.2	17.0	5

\* - Number of minutes the laser was at that power level.

No reaction in Part I. Reaction in Part II occurred beginning with 17.5W.

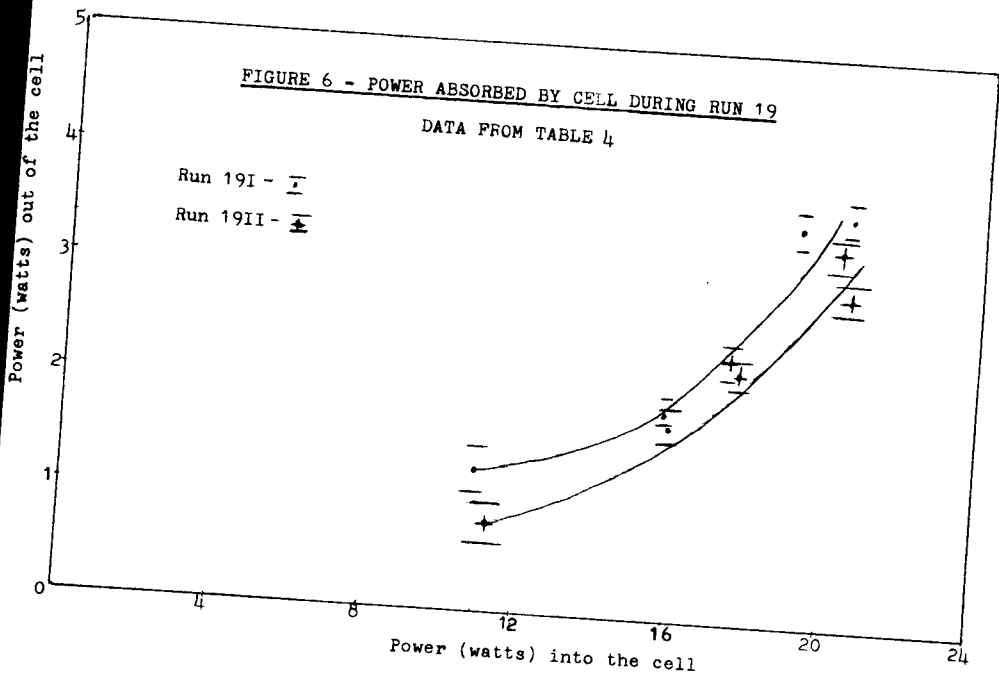




TABLE 5 NET POWER IN RUN 20

<u>Part I</u>	<u>Power in(±.2W)</u>	<u>Power out(±.2W)</u>	<u>Net Power(±.4W)</u>	<u>Minutes*</u>
9.618 u	20.0	6.2	13.8	1
20.0torr	20.4	6.0	14.4	28
<u>Part II</u>				
9.734 u	18.5	2.7	15.8	1
20.0torr	-	2.65	-	6
	20.0	3.2	16.8	30
<u>vacuum measurements</u>				
9.618 u	10.0	5.8	4.2	-
	20.2	12.1	8.1	-

\* - Number of minutes the laser was at that power level.

No reaction in Part I. Reaction in Part II after 3 minutes.

TABLE 6 - POWER ABSORPTION AT DIFFERENT FREQUENCIES FOR  
A GIVEN ENTERING POWER OF 20W

<u>Run</u>	<u>Power entering cell (<math>\pm 2W</math>)</u>	<u>Power absorbed by sample (<math>\pm .4W</math>)</u>	<u>wavelength (<math>\pm .002 \mu</math>)</u>
20	20	5.4	9.480
18	20	7.6	9.552
19	20	8.0	9.604
19	20	8.6	9.694
18	20	8.5	9.714
20	20	8.4	9.734

No reaction was observed at 9.840  $\mu$  or 9.552  $\mu$ . A maximum relative rate of reaction was calculated for those wavelengths by using a maximum absorbance level at which reaction could be detected. The value used was 0.025. Some of the runs had net powers absorbed by the sample less than 7.8 $\pm$ .4W, and their corresponding relative rates of reaction for 7.8 $\pm$ .4W should be higher, (Table 7). Figure 7 plots relative rates as a function of wavelength. This plot is superimposed on the PE 621 plot of the Freon 113 band which was irradiated.

During Run #16 the growth of the 1330  $\text{cm}^{-1}$  peak was recorded every minute for 25 minutes. The absorbances were calculated and used in zero and first order kinetic plots (Table 8, Figures 8 and 9).

TABLE 7 - RELATIVE RATES OF REACTION

Run	$\lambda$ ( $\pm 0.002 \mu$ )	Net Power ( $\pm .4W$ ) <sup>a</sup>	Absorbance ( $\pm .005$ )	Abs/time
20	9.743	5.9 <sup>b</sup>	.025 <sup>c</sup>	.0008 $\pm$ .0002
14	9.552	7.6	.025 <sup>c</sup>	.0013 $\pm$ .0010
19I	9.604	7.7	.025	.0025 $\pm$ .0005
19II	9.694	7.7	.156 $\pm$ .010	.0156 $\pm$ .0010
22	9.694	7.9	.210 $\pm$ .010	.030 $\pm$ .001
23	9.714	7.7	.239 $\pm$ .010	.016 $\pm$ .001
13	9.714	7.7	.257 $\pm$ .010	.032 $\pm$ .001
24	9.734	7.9	.256 $\pm$ .010	.010 $\pm$ .001
18	9.714	6.4	.02 $\pm$ .01	.004 $\pm$ .001
6	9.714	5.7 <sup>d</sup>	.065 $\pm$ .010	.0020 $\pm$ .0005

The Abs/time measurements were averaged for readings in the table taken at the same wavelength. Run 18 and Run 19 were not averaged in for runs at 9.714  $\mu$  since they both had a much lower power.

wavelength ( $\mu$ )	relative rate ( $\pm .1$ )
9.473	.03
9.552	.05
9.604	.1
9.694	.9
9.714	1.000
9.734	.4
9.714	.2 (Run 18)
9.714	.1 (Run 6)

TABLE 7 - (cont.)

- a - The power absorbed by the sample was calculated by using absorbance measurements to find the power absorbed by the cell. From this was subtracted the amount of power absorbed by the cell windows with the cell holding a vacuum (Figure 4).
- b - Power absorbed by the sample slightly low.
- c - No sign of any reaction. Assigned limit of detection of Absorbance = .025 and calculated a maximum possible relative rate.
- d - This was the lowest power at which reaction was detected in this project.

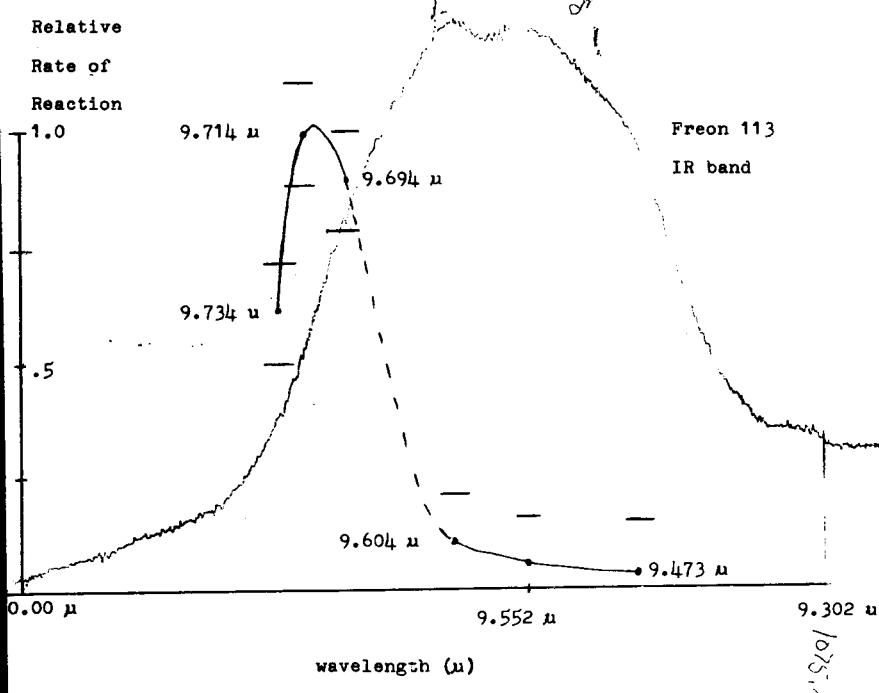


FIGURE 7 - RELATIVE RATES OF REACTION FOR VARIOUS WAVELENGTHS

TABLE 8 - ABSORBANCE AND TIME DATA FOR RUN 16

<u>Time</u>	<u>Transmittance (%)</u>	<u>Absorbance</u>	<u>ln Absorbance</u>
1	100	0	-
2	90.6±5	.043±.002	-1.37±.06
3	86.0±5	.065±.004	-1.19±.07
4	84.2±3	.075±.003	-1.12±.04
5	81.3±3	.090±.003	-1.05±.03
6	78.1±2	.107±.003	-.971±.020
7	75.0±2	.125±.003	-.903±.020
8	70.8±2	.150±.004	-.824±.020
9	68.4±2	.165±.003	-.783±.020
10	67.4±2	.171±.003	-.767±.010
11	64.7±2	.189±.003	-.724±.010
12	61.5±2	.211±.003	-.676±.010
13	61.0±2	.215±.003	-.668±.010
14	60.0±2	.222±.004	-.654±.010
15	59.8±2	.223±.004	-.652±.010
16	59.2±2	.228±.004	-.642±.010
17	54.8±2	.261±.004	-.583±.010
18	53.3±2	.273±.005	-.564±.010
19	54.2±2	.268±.005	-.572±.010
20	52.9±2	.277±.005	-.558±.010

FIGURE 8 - ZERO ORDER KINETIC PLOT FOR RUN 16

DATA FROM TABLE 8

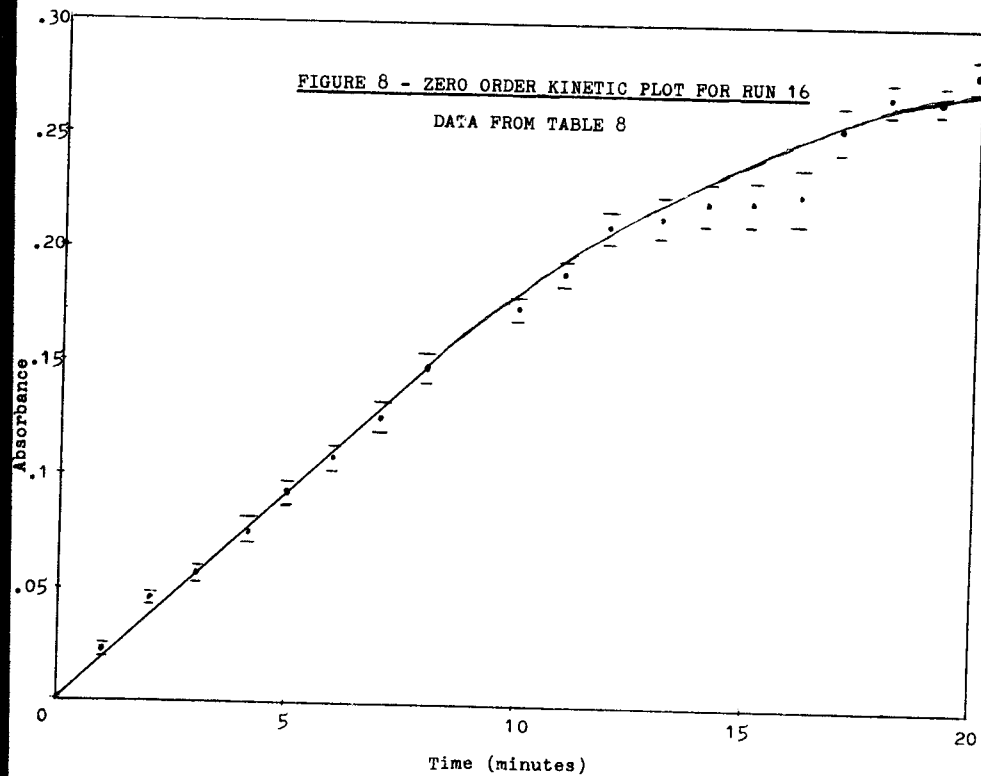
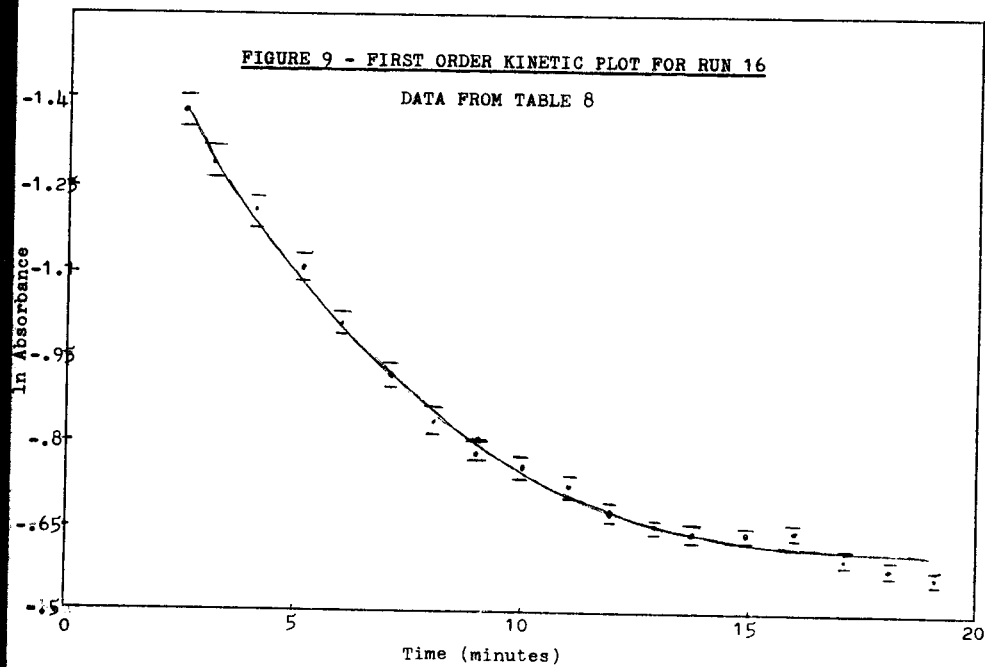




FIGURE 9 - FIRST ORDER KINETIC PLOT FOR RUN 16

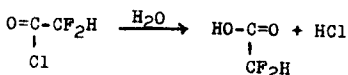
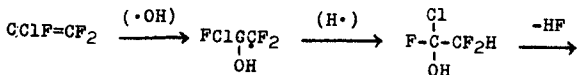
DATA FROM TABLE 8



DISCUSSION

The film formed on the inside of the CsBr window at 28 torr suggests that a polymer was formed as the beam first entered the cell. This polymer coated the window. Absorption of radiation on the inside of the cell window creating a substantial temperature increase at that point, is believed to be the cause of the hole in the cell window. Polymer buildup was not observed on the exit window since much of the beam's power had been absorbed travelling through the cell. Polymer buildup was never noticed after irradiation at similar power levels at 20 torr.

Curt Brown had a similar run during which a NaCl window was cracked. He put forward the following mechanism to explain the phenomena observed:<sup>12</sup>



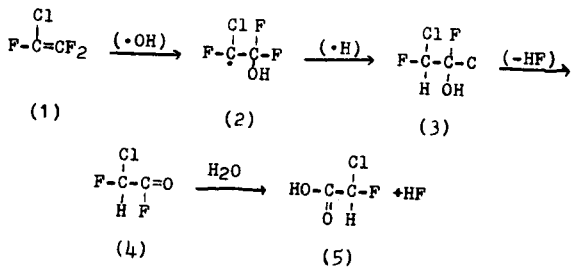
Due to the existence of the resonance structure below:



attack of the hydroxyl radical seems more likely at the difluorocarbon. A similar resonance structure for the

analogous compound in the mechanism is impossible since fluorine lacks d orbitals.

By analogy we propose a similar mechanism arising from the different first step.



Results from run #3 in which the window cracked were checked for agreement with the proposed mechanism.

The ethylene product was formed after the hole appeared and oxygen entered the cell, but it was absent in the final spectrum taken. The attack of hydroxyl radicals on the ethylene product would account for the disappearance of the  $1330 \text{ cm}^{-1}$  peak in the final spectrum. A literature spectrum<sup>15</sup> of dichloroacetyl chloride was compared with the spectrum taken after irradiation to see if compound (4) was in the cell (Table 9).

TABLE 9 - COMPARISON OF IR ABSORPTION PEAKS

<u>dichloroacetylchloride (<math>\text{cm}^{-1}</math>)</u>	<u>experimental values</u>
1820	1870±15
1250	1255±10
719	723±5

Referring to Nakanishi,<sup>16</sup> the effects of substituting two fluorines for chlorine in dichloroacetyl chloride were determined. The carbonyl peak in the acetyl fluoride is shifted to higher energy. A shift of the carbonyl peak of about  $30\text{ cm}^{-1}$  is expected for an alpha fluorine substituted for an alpha chlorine. A shift of  $50\pm 15\text{ cm}^{-1}$  for the carbonyl peak is not unexpected. The peak at  $910\text{ cm}^{-1}$  to  $1000\text{ cm}^{-1}$ , which is predicted for acid halides, may be covered up by Freon 113's strong band centered at  $910\text{ cm}^{-1}$ . The other two major peaks observed are in agreement with the similar acid chloride peaks.

Alpha-halo acid halides are very soluble in water and often insoluble in benzene. They often have melting points lower than room temperature. The white powder formed on the inside of the cell could be the carboxylic acid, (5), formed by the hydrolysis of (4). The suggestion of an acetyl fluoride with hydrolysis to the acid agrees with the experimental evidence.

The plot of  $\ln$  Absorbance vs. time, (Figure 9), shows that the reaction is not first order. The plot of Absorbance vs. time, (Figure 8), is linear up to absorbance = .1. Above .1, the plot curves. It should be noticed, that upon sufficient formation of chloro-trifluoroethylene, absorption of radiation and reaction

by the product may occur. This would account for the non-linearity of the plot at higher absorbances.

If the product reacts, some of the absorbance values used in the calculation of relative rates are inaccurate. Hence the relative rates calculated from absorbances of around .2 may be smaller than the actual values. This can be seen by observing the non-linearity of Figure 8 at absorbances of about .2.

The relative rates of reaction as a function of wavelength of irradiation for a constant power absorbed by the sample of  $7.8 \pm .4 W$  does not coincide with the maximum of absorption in the IR spectrum. This is shown in Figure 3. The relative rates of reaction are plotted on an infrared spectrum of the peak centered around  $9.601 \pm .005 \mu$ . The maximum relative rate is at  $9.714 \pm .005 \mu$ .

The frequency ( $\nu$ ) of maximum absorption in the IR spectrum is higher than the frequency of the maximum relative rate of reaction. Due to the inherent anharmonicity of a molecule's potential well,  $h\nu_0 > h\nu_1 > h\nu_2 \dots$ . Here  $\nu_0$  is the  $v = 0$  to  $v = 1$  transition,  $\nu_1$  is the  $v = 1$  to  $v = 2$  transition, etc. Hence the vibrational levels tend to converge as the vibrational energy increases (Figure 10).

The spectroscopic interpretation of Figure 10 is shown in Figure 11. An  $h\nu_0$  transition gives the band of the vibrational-rotational envelope shown in

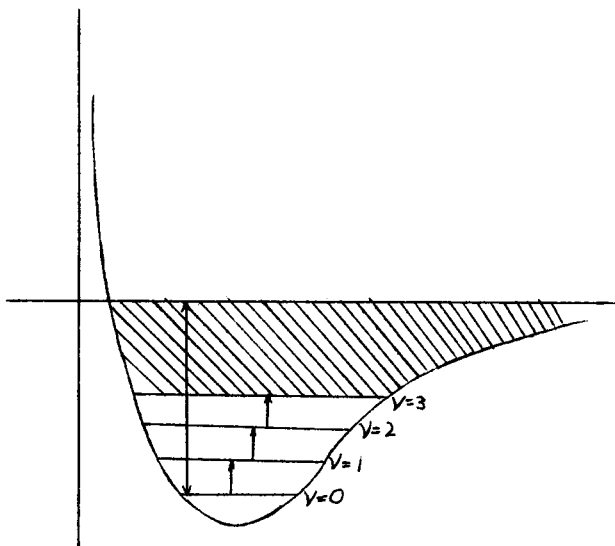


FIGURE 10 - POLYATOMIC POTENTIAL WELL

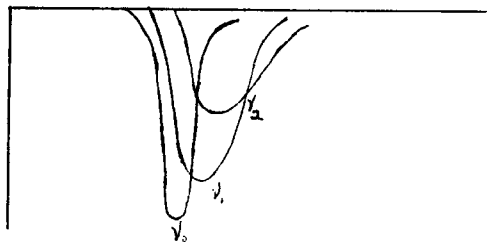


FIGURE 11 - VIBRATIONAL TRANSITIONS IN THE IR

Figure 11. This is the peak seen in normal infrared spectroscopy. Since  $h\nu_1 < h\nu_0$  it is seen as occurring at a higher wavelength. It is broader since at higher temperatures more rotational states are occupied. Similar reasoning is applied to other peaks. This discussion, when applied to the discrepancy explained earlier, implies that the laser is in resonance with a vibrational transition other than the  $v = 0$  to  $v = 1$  transition.

Three models will be considered in an attempt to explain the anomaly observed experimentally. These are complete thermal reaction, complete photochemical reaction, and a combination of these two models.

In the model of complete thermal heating, the laser is acting as a source of thermal energy. All energy absorbed by the molecule is evenly distributed among all modes. For a particular net power absorbed by the molecule, the relative rate of reaction should be independent of laser wavelength. Table 7 gives evidence to the contrary, since there is a factor of about 25 difference for the relative rates obtained in runs 13 and 14. The run with the slower rate had the higher net power absorbed by the molecule. Hence a thermal heating model is incorrect.

The second model involves completely photochemical reaction. Two types of photochemical reaction can be considered: collisionless reaction or reaction with the

help of collisions. Collisionless photochemical reaction, also called multi-photon absorption, requires the absorption of at least as many photons as are required to reach the dissociation energy. This minimum number can be calculated for Freon 113 using 70 kcal/mole as the bond strength of the C-Cl bond which breaks in this reaction (a similar calculation could be performed for the C-C bond since that appears to cleave also). The energy of the photon for the  $v = 0$  to  $v = 1$  transition can be calculated, since it is given by the wavelength of the IR absorption band. Using  $9.60 \pm 0.01 \mu$ , the photon size is  $2.98 \pm 0.01$  kcal/mole. The photon energy giving the maximum relative rate of reaction is  $2.94 \pm 0.01$  kcal/mole (calculated for the irradiation wavelength of  $9.71 \pm 0.01 \mu$ ). If multi-photon absorption is to occur at the frequency of maximum relative reaction, this means that  $\sim 24$  photons must be absorbed for the molecule to reach the dissociation energy.

In the first step of the mechanism, a process called "triple vibrational-rotational resonance" occurs to carry the molecule up to  $v = 3$ . The laser is tuned to the Q branch ( $\Delta J = 0$ ) of the transition  $v = 1 \rightarrow v = 2$  to carry out this process. Molecular anharmonicity is overcome by "rotational compensation" (the reason for the compensation is not dealt with by the authors).



The compensation is that for  $v = 0$  to  $v = 1$ ,  $\Delta J = -1$ ;  
for  $v = 1$  to  $v = 2$ ,  $\Delta J = 0$ ; for  $v = 2$  to  $v = 3$ ,  $\Delta J = 1$ .

The intensity necessary for such a transition to possible is given by:

$$I = c\pi/2(\hbar c B/2TP_{v,v+1})^2 \quad (11)$$

where  $I$  is the laser intensity,  $c$  is the speed of light,  $B$  is the rotational constant and  $P_{v,v+1}$  is the transition dipole moment. Ambartzumian<sup>5</sup> gives  $P_{v,v+1} = .3D$  and  $B = .05 \text{ cm}^{-1}$  as typical values for a polyatomic molecule. Under these conditions, laser intensity of  $I_{\text{exc}} = 10^5 \text{ W/cm}^2$  is necessary for population of the  $v = 3$  level. The intensities involved in this project were on the order of  $60 \text{ W/cm}^2$ , where a power of  $7.8 \text{ W}$  and a beam diameter of  $.4 \text{ cm}$  were assumed. This is clearly much less than the intensity required.

The second step of this collisionless photocnemical reaction requires multi-photon absorption from the  $v = 3$  level to the dissociation level. Despite molecular anharmonicity, this process is possible because of the existence of a pseudo-continuum region in polyatomic molecules (see Figure 10). In the pseudo-continuum region, photon size does not matter because of the large density of vibrational-rotational energy levels arising from the many degrees of freedom in a polyatomic molecule. In some molecules, for example  $\text{SF}_6$ <sup>5</sup>, the pseudo-continuum starts as low as just above the  $v = 3$  level.

The laser intensity required to get this effect is larger than the intensity needed to get triple vibrational-rotational resonance.

A hard spheres calculation for the molecular collision frequency of Freon 113 at 20 torr was made (Appendix A). There are  $\cong 10^9$  collisions  $\text{sec}^{-1}$  molecule $^{-1}$ . Basov gives some typical relaxation rates<sup>3</sup> which can be applied to a situation like this one.

TABLE 10 - TYPICAL RELAXATION RATES

<u>Relaxation</u>	<u>Rates</u>
V-V (vibrational-vibrational)	$\cong 10^{-6}$ sec*
V-R (vibrational-rotational)	$\cong 10^{-4}$ sec#
V-T (vibrational-translational)	$\gg$ V-V

\* - For a 100 torr sample

# -  $V-R/V-V \cong 10^2 - 10^3$

The total number of collisional deactivations that can possibly occur in one second for one molecule is the sum of the reciprocals of the relaxation rates. Since there are  $10^9$  molecular collisions per second, there is the full number of  $10^6$  collisional deactivations occurring per second per molecule.

The average number of photons absorbed by a molecule in a beam of 7.8W, in which all 7.8W are absorbed by the cell, is about  $10^2 - 10^3$  photons molecule $^{-1}$  second $^{-1}$  (Appendix B). Since there are  $10^2-10^3$

photon collisions per molecule per second, and  $10^6$  collisional deactivations per second per molecule, there are  $10^3 - 10^4$  collisional deactivations for every photon absorbed. Since collisional deactivation occurs much faster than photon absorption, and since our power level was not enough to get either triple vibrational-rotational resonance or multiphoton absorption in the continuum, collisionless photochemical reaction can not occur in this system.

Photochemical reaction induced by energy transfer following collision is another process that could be occurring. In this mechanism some low lying vibrational level is photochemically populated. Collisions transfer energy into the molecules in these low lying states which then move up the continuum and out of the well. A possible explanation for why vibrational energy transfer would give energy to a molecule with higher energy is that the higher energy molecule is in the pseudo-continuum. Since the molecule is in the pseudo-continuum, it would be able to accept any size photon while the molecule outside of the pseudo-continuum could only accept photons of a certain size. This has been referred to in the literature as vibrational up-conversion of energy.<sup>8</sup>

The place where the pseudo-continuum starts depends on the number of degrees of freedom available

in a molecule. As stated before,  $SF_6$  has a pseudo-continuum that starts just above  $v = 3$ . Since  $C_2Cl_3F_3$  would be expected to have more degrees of freedom, it would be expected to have a higher density of vibrational states than  $SF_6$ . For the purpose of exploring this feature, it will be assumed that the pseudo-continuum for Freon 113 likewise begins just above the  $v = 3$  level. Therefore, it takes 4 photons to get Freon 113 into the continuum.

To dissociate the molecule, at least 24 photons must be absorbed. Since only 4 photons are absorbed directly to get the molecule into the continuum, at least 20 vibrational transfers are needed to dissociate the molecule.

The rotational relaxation time is about  $10^2 - 10^3$  times slower than the vibrational relaxation time. Hence there will be  $10^2 - 10^3$  vibrational relaxations per rotational relaxation. Twenty vibrational energy transfers is well within this range. If it is assumed that the translational relaxation time is 10 to 100 times as slow as the vibrational energy transfer, there will still often be twenty vibrational energy transfers before a translational energy transfer.

Thus, although unfavorable vibrational energy transfers such as transfer to a molecule with lower energy or transfer to a different vibrational mode were

not considered, the possibility of collisional transfer of vibration energy pushing a molecule out of the well seems reasonable. But there still remains the problem of how to get the molecules into the pseudo-continuum with the low power of this laser. As stated before,  $10^5 \text{W/cm}^2$  is needed for consecutive absorption of the 4 photons needed to get the molecule into the pseudo-continuum. Hence this model doesn't give a satisfactory explanation of the facts in this project.

The third model to be considered entails a combination of thermal and photochemical reaction. The laser beam was turned on for several minutes during each run. Energy absorbed by the sample could be converted to thermal energy raising the temperature. If there were a thermal equilibrium at some raised temperature, it is possible that enough levels just below the pseudo-continuum would be populated that the laser could selectively excite the molecules in these levels into the pseudo-continuum. To get any kind of wavelength selectivity from this reaction, the level below the pseudo-continuum must not be significantly populated, since any size photon would excite the molecule into it.

A Boltzmann distribution was assumed in order to calculate the percentage of molecules in the  $v = 2$  and  $v = 3$  levels. The Boltzmann function,  $e^{-E/RT}$ , was used

with 2(2.98 kcal/mole) and 3(2.98 kcal/mole) as the vibrational spacing and  $0.001987 \text{ kcal mole}^{-1} \text{ deg}^{-1}$  as R. Results are listed in Table 11.

TABLE 11 - RELATIVE POPULATION OF VIBRATIONAL LEVELS  
AT DIFFERENT TEMPERATURES

<u>% in v = 2 level</u>	<u>% in v = 3 level</u>	<u>Temperature(°K)</u>
.004	0	298
.25	.01	500
1.4	.16	700
3.6	.67	900

At room temperature there is almost no population of the  $v = 2$  or  $v = 3$  level. At  $700^\circ\text{K}$  there begins to be a moderate population of these levels.

From these calculations, it is seen to be possible to get molecules in the  $v = 2$  level by thermal excitation. However temperatures higher than room temperature are needed for this to begin to be significant. To dissociate these molecules, according to this model, the laser is tuned to the  $v = 2$  to  $v = 3$  transition ( $\nu_2$ ). Absorption of two photons from the laser gets the molecule into the pseudo-continuum. From that point the vibrational transfer of energy to molecules in the pseudo-continuum can occur to carry the molecules to the dissociation energy in the way discussed earlier.

The difference between this hybrid model and the

collisional photochemical model is the process of getting the molecule into the pseudo-continuum. In the hybrid model there is two photon absorption, whereas in the photochemical model there is four photon absorption.

According to Freeman and Davis,<sup>8</sup> consecutive absorption of  $n$  photons requires laser intensities to the  $n$ th power. Ambartzumian and Letokhov estimate that about  $10^5 \text{W/cm}^2$  is required to add four photons to an average polyatomic molecule. Assuming Freon 113 is average, it requires about  $10^3 \text{W/cm}^2$  for two photon absorption.

The standard to determine whether a molecule is average is the transition dipole moment. If this is large, then the laser intensity will have to be about  $10^5 \text{W/cm}^2$  to absorb 4 photons. The transition dipole moment is related to the extinction coefficient at the particular wavelength. The moment of Freon 113 is large since the peak irradiated was intense. Therefore it requires about  $10^3 \text{W/cm}^2$  for two photon absorption.

The laser beam was calculated to have a power density of about  $60 \text{W/cm}^2$ . However the beam power was not constant throughout the cross section, since the power absorbed by the sample is greater in the region where the beam first enters the cell. Also, there was a hole in the center of the beam since it was often in the "doughnut mode." So the power density was higher than  $60 \text{W/cm}^2$  in some parts of the cell.

There were several assumptions made in the explanation of the thermally enhanced photochemical reaction model. A Boltzmann distribution was assumed in calculating the populations of Table 11. But, there is clearly a non-Boltzmann distribution, since the laser is exciting a vibrational mode. Another assumption was that when two molecules collide, and one is in the pseudo-continuum and the other is in some low lying excited state, the molecule in the pseudo-continuum always gets the vibrational energy transferred. This is probably only approximately true. Another assumption was that the vibrational energy transferred remains in the same mode.

Despite the assumptions made, the model of thermally enhanced photochemical reaction fits the data best for several reasons. The power involved was not sufficient to excite the molecule into the pseudo-continuum by multi-photon absorption of 4 photons, yet the reaction could not be explained by a thermal model. In fact it is apparent that the laser was in resonance with some other than the  $v = 0$  to  $v = 1$  transition. These facts, plus the fact that the cell does get hot during a run, imply that thermal population of low lying vibrational levels is the first step in the mechanism.

This was not the first observation of a photochemical reaction induced by a laser tuned to an energy less than  $h\nu_0$ . Ambartzumian<sup>5</sup> noticed a similar effect with  $SF_6$ ,



in which the maximum relative rate was  $9 \text{ cm}^{-1}$  less than the IR absorption maximum. The experimental conditions were such that heating and collisions were not significant factors due to the short pulse time and low pressures used.

The significance of the results of this project is that results similar to those reported in the literature were found, but under the vastly different conditions of low power and continuous wave radiation. Hence a different model had to be proposed as the best way to explain these results. This is the first time, to this writer's knowledge, that thermal excitation has been incorporated in a proposed model in order to explain the mechanism of a photochemical reaction.

### SUGGESTIONS FOR FURTHER WORK

The conclusions about this reaction, though they agree with the data, are based on very little data. More data, such as relative rates of reaction for other frequencies, should be obtained. Other variables which could be varied to observe their effect are pressure and temperature. Most of the runs were at pressures of 20 torr. Therefore, it is unknown how pressure affects this reaction.

An interesting way to see if our theory holds would be to use a heating element to heat the cell during the run. According to the model proposed, there would be more molecules thermally excited to a low lying state. Thus, it would be expected that the rate would increase significantly at lower laser power levels.

The reaction has not yet been fully characterized. The reaction products and their relative quantities should be determined. This could then be compared with the pyrolytic decomposition of Freon 113.

A second problem which should be answered is whether isotopic enrichment occurs. As stated in the introduction, significant enrichment is evidence that photochemical reaction has occurred. The chlorine isotopes could be examined because there is a large percentage of each isotope. Each molecule of Freon 113 has three chlorines. The reaction product has two chlorines. This could potentially yield a lot of information as to whether the reaction is photochemical.

APPENDIX AMolecular Collision Frequency with the Hard Spheres Model

$$Z = 4(2r)^2(\pi RT/M)^{1/2}C$$

Z is the molecular collision frequency

r is the hard sphere radius of the molecule

R =  $8.314 \times 10^7$  erg  $^{\circ}\text{K mole}^{-1}$  is the Real Gas constant

T is the temperature in  $^{\circ}\text{K}$

M is the molecular weight

C is the concentration in moles/cm<sup>3</sup>

a) calculation of r

The molecule is assumed to be a hard sphere whose radius is the distance (following the bonds) between chlorine atoms at opposite ends of the molecule, plus the atomic radius of both chlorine atoms.

$$r = (1.45\text{\AA}) + 2(1.74\text{\AA}) + 2(0.9\text{\AA}) / 2$$

1.45Å is the carbon carbon bond distance

1.74Å is the carbon chlorine bond distance

0.9Å is the chlorine atomic radius

$$r = 3.375\text{\AA}$$

$$2r = 7\text{\AA}$$

b) calculation of concentration

$$c = n/v$$

n is the number of moles

v is the volume in cm<sup>3</sup>

$$c = n/v = p/RT$$

$p = 2/76$  atm is the pressure.

$$c = 1.08 \times 10^{-6} \text{ moles/cm}^3$$

c) calculation of  $Z$  for  $T = 298^\circ\text{K}$

$$Z = 2(14 \times 10^{-8})^2 (\pi RT/M)^{1/2} (1.08 \times 10^{-6})$$

$$Z = 8.60 \times 10^{-16} \text{ moles/sec}$$

$$Z = 5.2 \times 10^8 \text{ collisions/sec}$$

d) calculation of  $Z$  for  $T = 1000^\circ\text{K}$

$$Z = 2(14 \times 10^{-8})^2 (\pi RT/M)^{1/2} (1.08 \times 10^{-6})$$

$$Z = 1.58 \times 10^{-16} \text{ moles of collisions/sec}$$

$$Z = 9.5 \times 10^8 \text{ collisions/sec}$$

Since this a rough model, the figure  $10^9 \text{ sec}^{-1}$  will be used as the molecular collision frequency. Notice the value is nearly independent of temperature for a difference of  $700^\circ\text{K}$ .

APPENDIX BCalculation of Photon Collision Frequency

a) calculation of the number of photons per second entering the sample.

$$\text{photons/sec} = p/h\nu$$

p is the power in watts

$h\nu$  is the energy of each photon.

$$\text{photons/sec} = (7.8\text{J})(6.023 \times 10^{23}) / 1.25 \times 10^4 \text{J}$$

$$\text{photons/sec} = 3.77 \times 10^{20} \text{ photons/sec}$$

b) volume of cell that beam passes through

$$v = r^2 d$$

v is the volume

r is the beam radius

d is the path length

$$v = (.2 \text{ cm})^2 (10 \text{ cm})$$

$$v = 1.26 \text{ cm}^3$$

c) calculation of the number of molecules in  $1.26 \text{ cm}^3$

$$Pv/RT = n$$

P = 2/76 atm is the pressure

R =  $82.06 \text{ cm}^3 \text{ atm } ^\circ\text{K}^{-1} \text{ mole}^{-1}$  is the Real Gas constant

T is the temperature in  $^\circ\text{K}$

$$n = Pv/RT = 1.36 \times 10^{-6} \text{ moles}$$

$$n = (1.36 \times 10^{-6} \text{ moles})(6.023 \times 10^{23}) = 8.19 \times 10^{17} \text{ molecules}$$

d) calculation of photon/(sec molecule) absorbed (assuming that all photons are absorbed.

$$3.77 \times 10^{20} / 8.19 \times 10^{17} = 4.6 \times 10^2 \text{ photons/(sec molecule)}$$

UN82 HERRICK, R. CO2 LASER INDUCED DECOMPOSITION, ETC.  
H566c/1978 Chemistry HRS. 4/78 2 of 2



APPENDIX CUse of the Laser

Turning the laser on

- 1) Make sure all blocking bricks are in place.
- 2) Turn on the external vacuum pump behind the laser.
- 3) Turn on Power and Refrigeration switches of the RTE-4 circulator, located under the main power control panel.
- 4) Turn on the Main, Primary, and Control switches of the Molectron Corporation Power System Model CPS control system.
- 5) Open the internal vacuum valve all the way and pump down to about 5 torr. Pressures are read off the pressure dial next to the gas toggle switches.
- 6) Open the CO<sub>2</sub> and He toggle switches and partially close internal vacuum pump to obtain 12 torr of pressure.
- 7) Open N<sub>2</sub> toggle switch.
- 8) Set voltage control to 0.
- 9) Press H.V. on.
- 10) Turn Voltage Control Dial until a reading is obtained on the milliamperes dial.
- 11) Turn Voltage Control down to value just above the value where milliamperes goes back to zero. The beam is now on.
- 12) Make sure all portions of the beam are accounted for.

### Power maximizing

- 1) Adjust the two knobs at the front of the laser which control the front end mirrors. One mirror covers vertical direction and the other covers the horizontal direction. Therefore maximize the power first with one knob, then with the other. Do not use both mirrors at once.  
Below are other ways of maximizing the power that are usually done only by Professor Galantowicz or one of his students.
- 2) Maximization of power by adjusting rear end mirrors (similar to 1)).
- 3) Change of relative pressures of  $\text{CO}_2/\text{He}$  or  $\text{N}_2/\text{CO}_2, \text{He}$  can be performed by using dials under toggle switches.
- 4) Sometimes 12 torr of  $\text{CO}_2, \text{He}$  is too low or too high for maximum power. The internal vacuum is opened or closed the appropriate amount to get this pressure. Professor Galantowicz or his students will know what the best pressure is.
- 5) Changing the current can sometimes change the power.  
The power maximum is about 25W coming directly out of the laser (unchopped) at 9.552  $\mu$  (P(20)).



### Changing the laser line

- 1) The piezoelectric detector (a green cylinder next to the monochromator) is connected to the "input" terminal of the Ithaco Dynatrac 391 Lock In Amplifier (LIA).
- 2) The aluminum switch box is connected to the "Ref In" terminal of the LIA. The switch to the left of "Ref In" should be at "Ext."
- 3) Turn on the CO<sub>2</sub> laser and the LIA, piezoelectric detector, power meter and the aluminum switch box.
- 4) Allow the laser and the LIA a few minutes to warm up. After warming up, the "Ref Unlock" and "Overload" lights should go off.
- 5) The LIA should be at the following settings: time constant = 0.125 seconds, mode = low drift, and sensitivity = 30 microvolts.
- 6) Adjust the phase angle such that the deflection is maximized. If there is no reading, increase the sensitivity. If there is still no reading, the laser and monochromator are not set to the same values.
- 7) After the reading is maximized, change the monochromator setting to the setting of the line desired. Never change by more than one branch at a time. Changing by more than one branch can be done by changing in two or three steps.
- 8) Change the laser setting until a deflection on the LIA is obtained. Note: the dial on the laser is wrong.

Turning the laser off

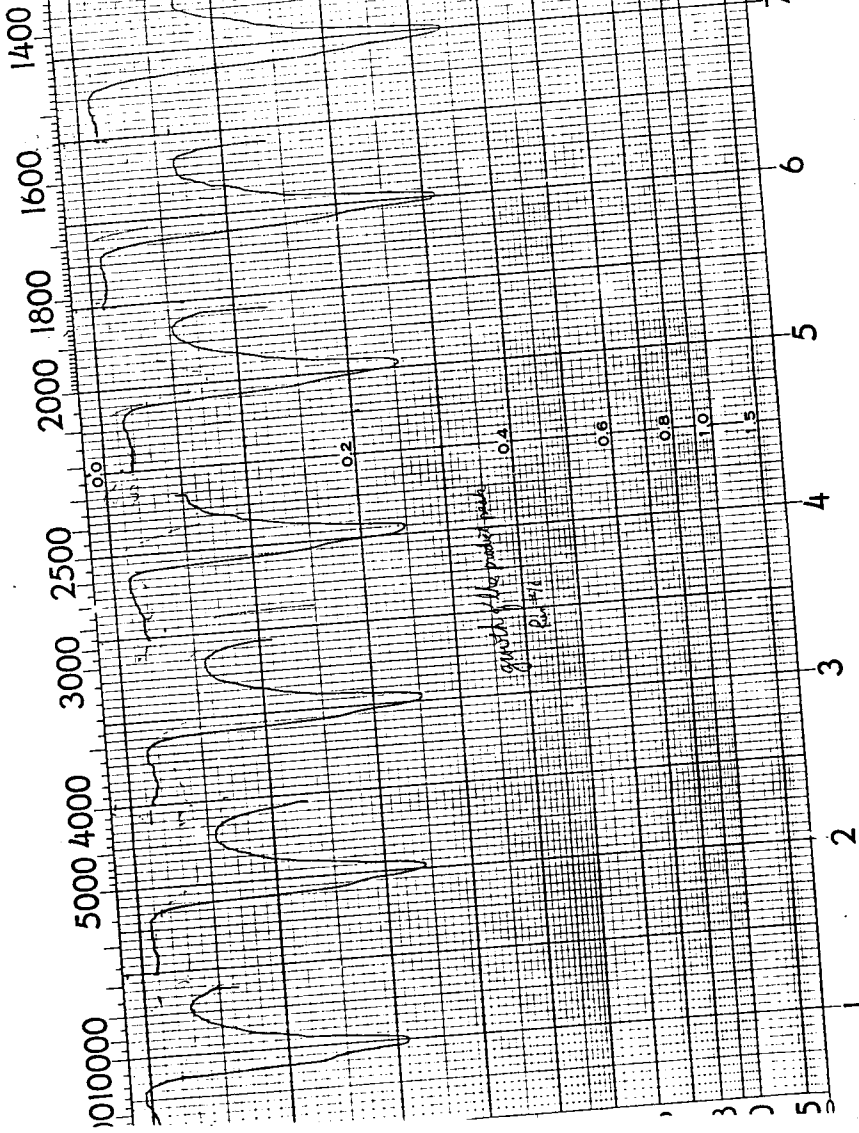
- 1) Press H.V. off
- 2) Turn off the Main, Primary, Control, Water and Refrigeration switches. Turn off Gas switches.
- 3) Close off internal vacuum.
- 4) Shut off external vacuum.
- 5) Make sure the LIA, Power meter, piezoelectric detector, aluminum switch box, and anything you might have used is turned off.

Note: the order of steps 1) and 2) is unimportant. However, step 3) must be done before step 4).

On the following pages are some spectra which are representative of this research project.

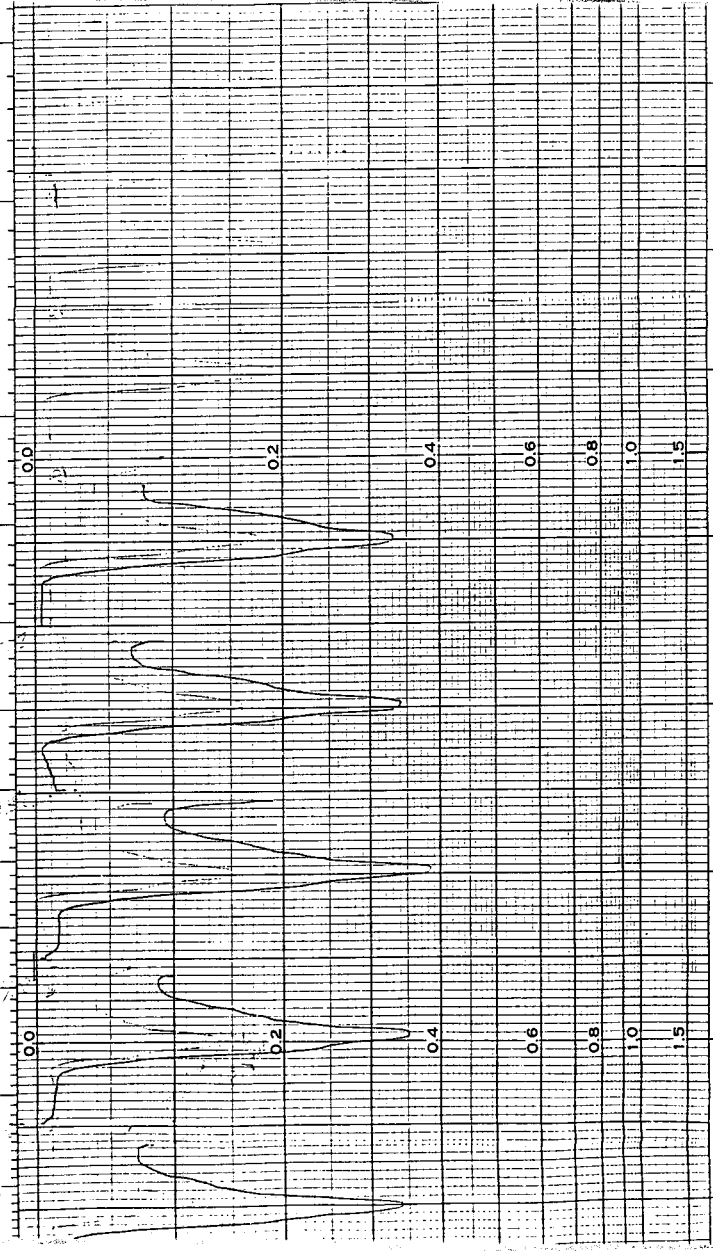
FREQUENCY

WAVELENGTH



FREQUENCY (CM<sup>-1</sup>)

1400 1200 1100 1000 950 900 850 800 750 700

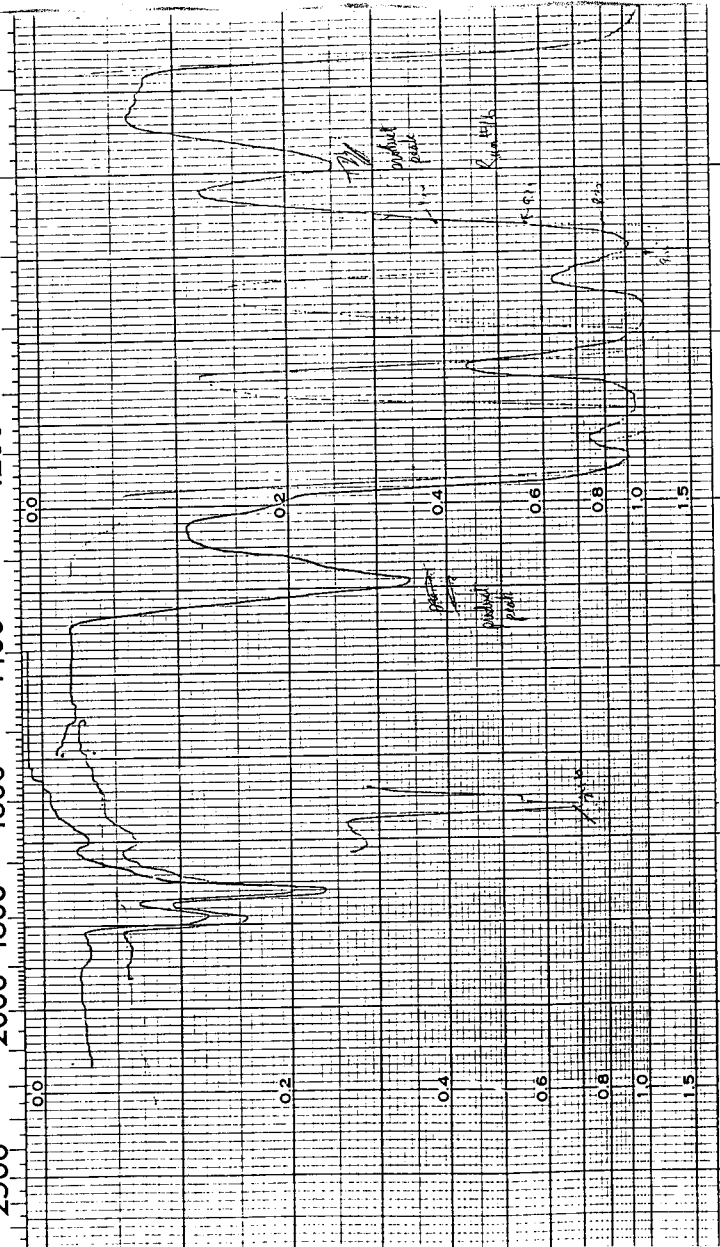


WAVELENGTH (MICRONS)

7 8 9 10 11 12 13 14

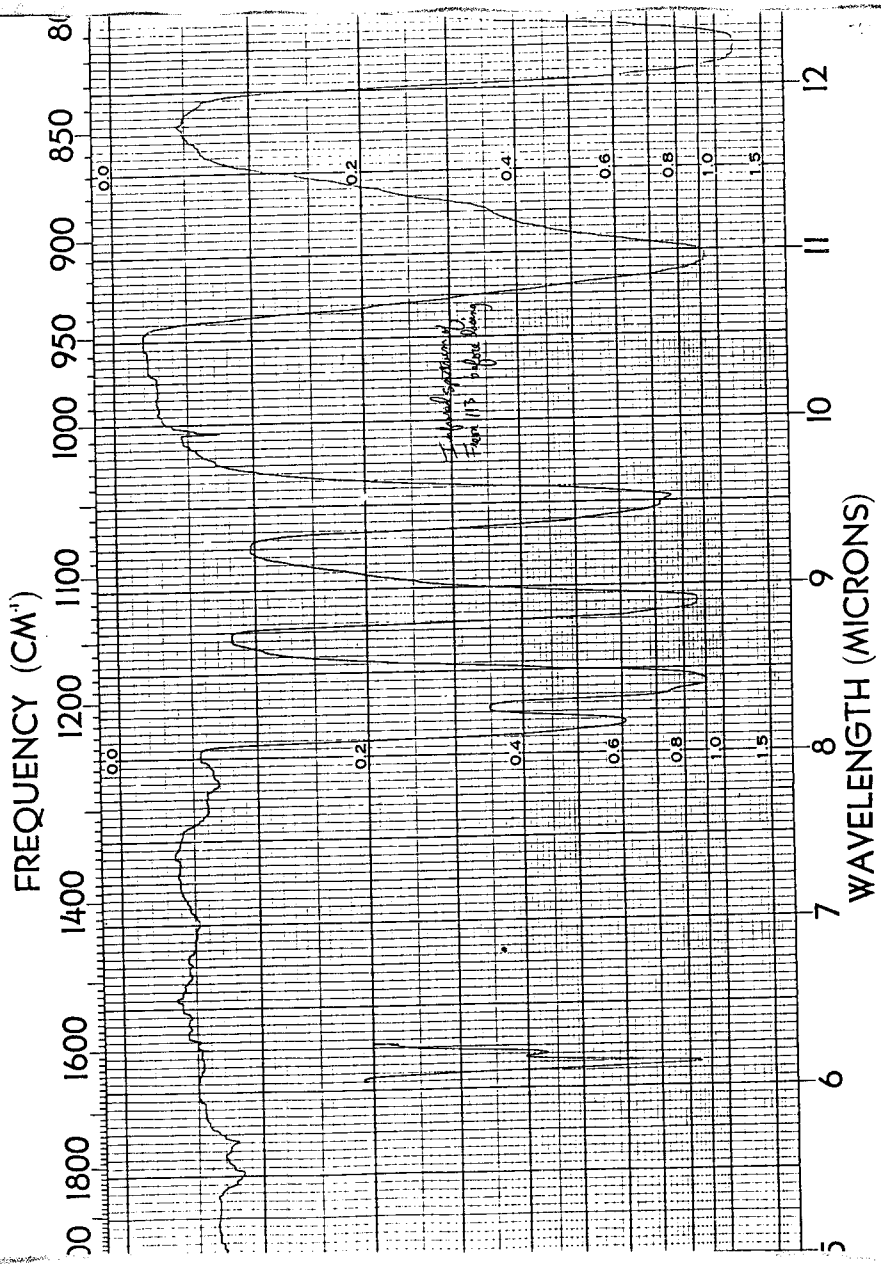
FREQUENCY (CM<sup>-1</sup>)

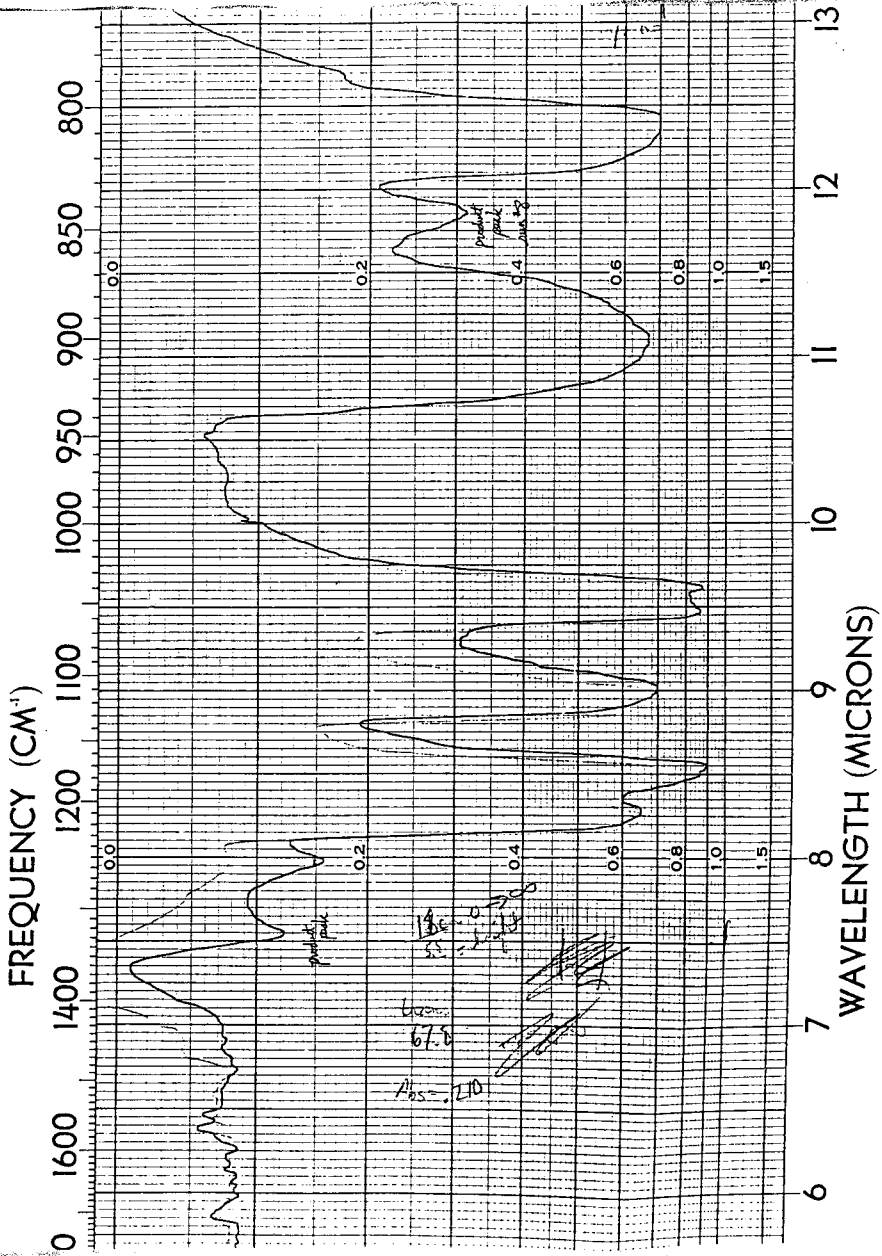
2500 2000 1800 1600 1400 1200 1100 1000 950



WAVELENGTH (MICRONS)

4 5 6 7 8 9 10





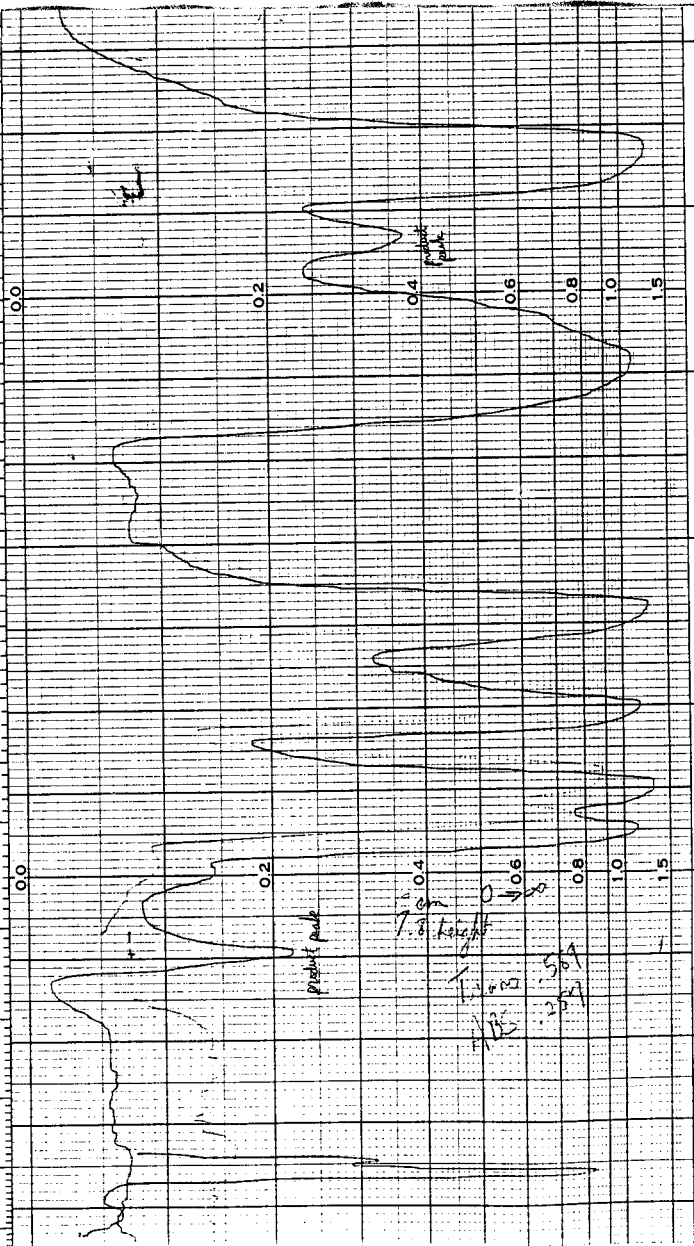


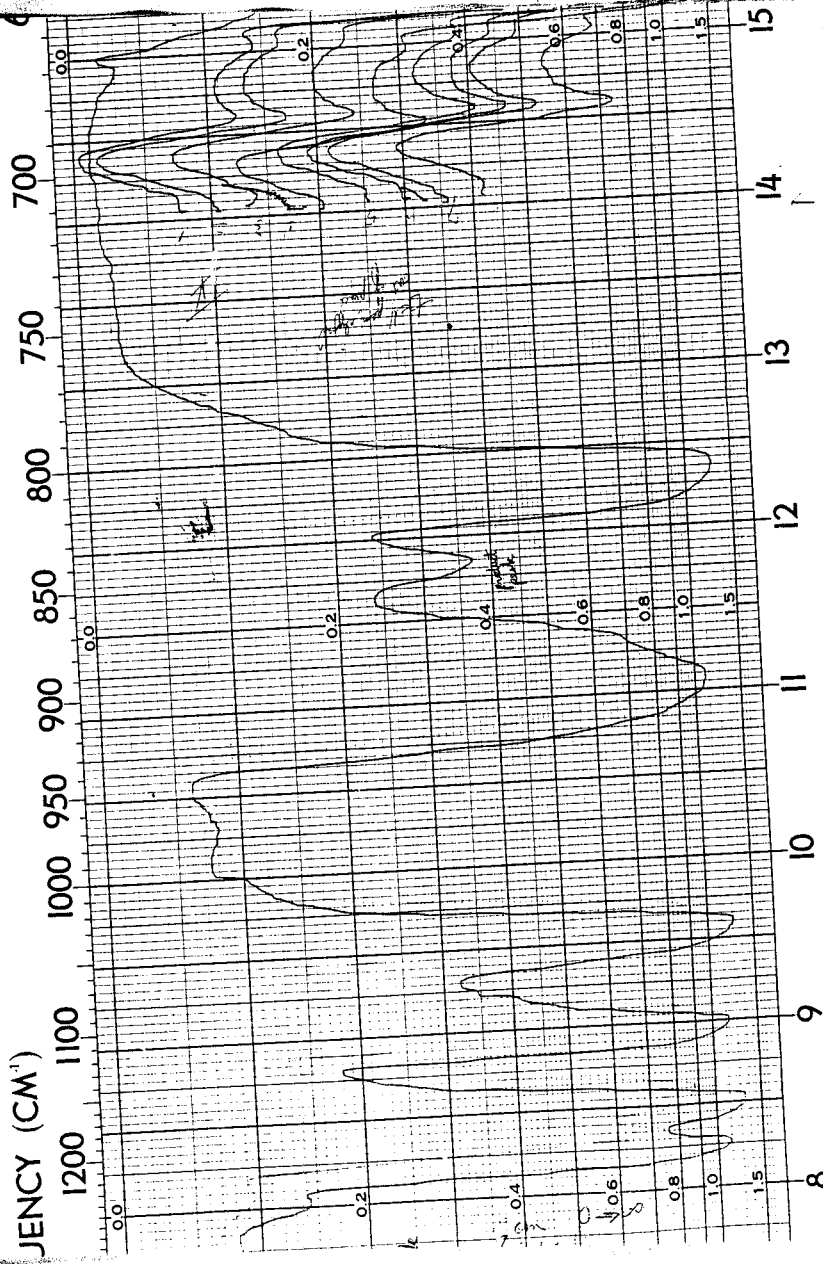
FREQUENCY (CM<sup>-1</sup>)

1600 1400 1200 1100 1000 950 900 850 800 7

WAVELENGTH (MICRONS)

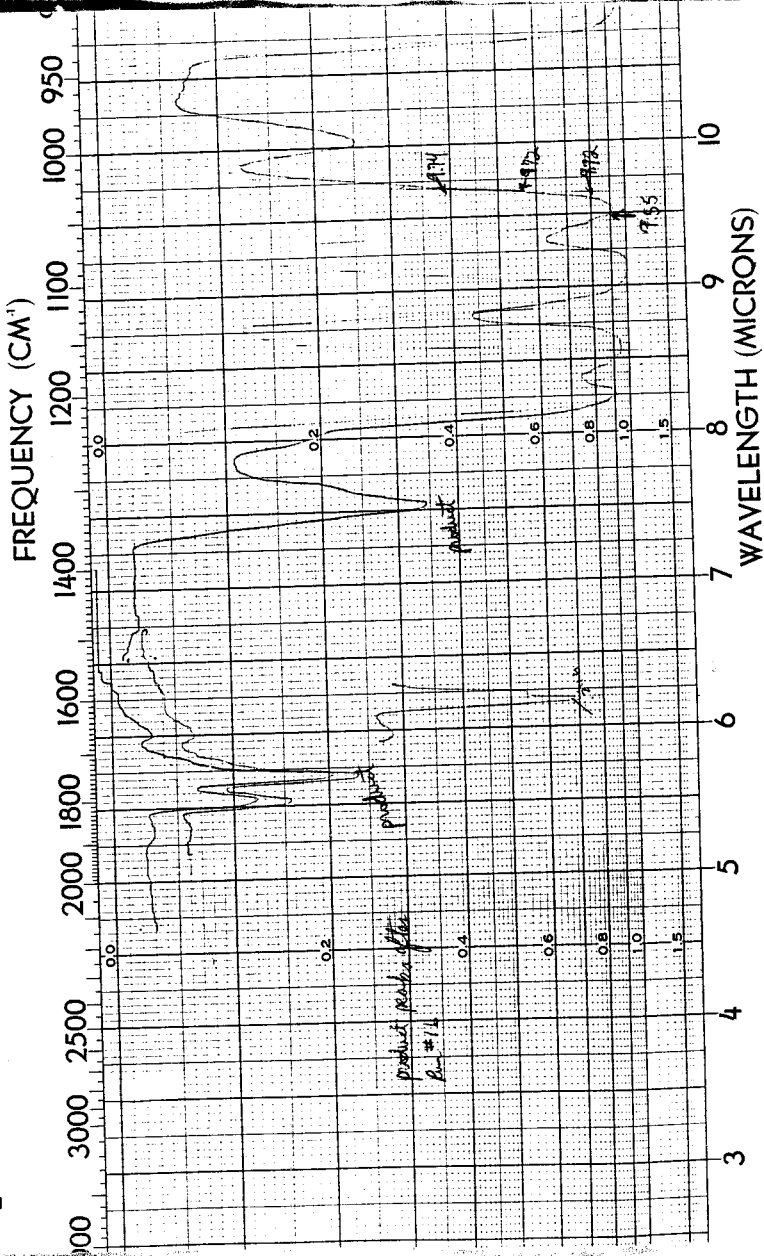
6 7 8 9 10 11 12 13

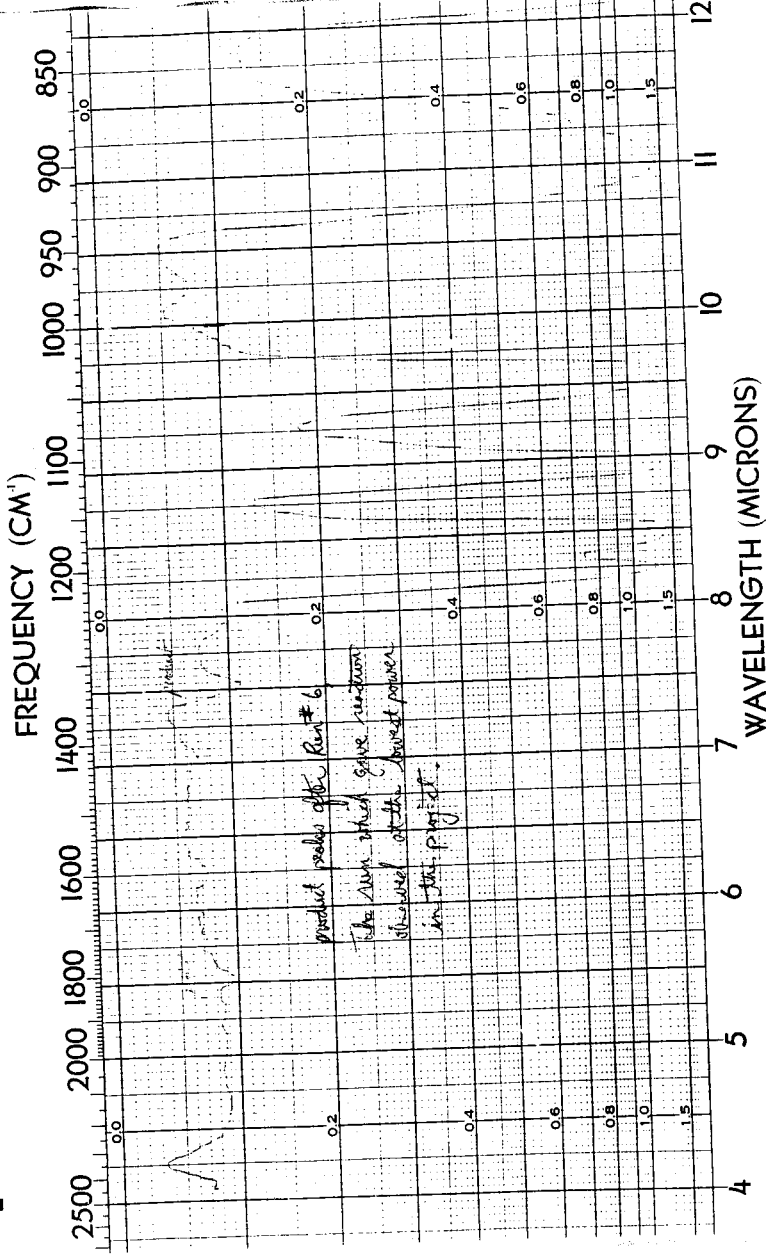




LENGTH (MICRONS)

78





product peaks after Run # 6  
 The Run which gave maximum  
 observed at the lowest power  
 in the plot.



REFERENCES

1. Schlalaw, Sci. Am., June 1961, 52.
2. Encyclopedia Americana, vol. 16, 763, 1973.
3. Basov, N.G., Biological and Chemical Applications of Lasers, C. Moore, Editor, Academic Press, 203, 1974.
4. Zare, Richard, Sci. Am., Feb. 1977, 89.
5. Ambartzumian, R. V. and Letokhov, V. S., Acc. of Chem. Res., 10, 61, (1977).
6. Yogev., A., J. Am. Chem. Soc., 98, 7077, (1976).
7. Farneth, Flynn, Slater, and Turro, J. Am. Chem. Soc., 98, 7877, (1976).
8. Freeman, M. P., and Travis, D.N., J. Chem. Phys., 60, 231, (1974).
9. Zitter, R.N., and Koster, D. F., J. Amer. Chem. Soc., 98, 1613, (1976).
10. Bailey, R.T., Cruickshank, F.R., Farrell, J., Herne, D. S., North, A. M., Wilmot, P.B., and Win, T., J. Chem. Phys., 60, 1699 (1974).
11. Mann, D.E., Acquista, N., and Plyer, E. K., J. Chem. Phys., 21, 1949 (1953).
12. Brown, C. Undergraduate Thesis - Union College, 1977.
13. Bernstein, R. B., Zietlow, J. P. and Cleveland, F. F., J. Chem. Phys., 21, 1778, (1953).
14. Cole, A. R., Tables of Wavenumbers for the Calibration of Infrared Spectrometers, Pergamon Press, New York, 1960, p. 189.

80  
69

15. Pouchert, C., The Aldrich Library of Infrared Spectra,  
Aldrich Chemical Co., p. 322.
16. Nakanishi, Infrared Absorption Spectroscopy, Holden-Day,  
Inc., San Francisco, 1962, pp. 42-43.