The Absorption Spectrum of Chlorine Fluoride

in the Region $\lambda\lambda$4650-5200;

The Electron Diffraction Investigation

of Chlorine Fluoride and Chlorine Trifluoride

. Thesis by

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Table of Contents

Illustrations

Tables

Tables

The Absorption Spectrum of Chlorine Fluoride
in the Region $\lambda\lambda$ 4650 - 5200

I. Introduction

Fluorine is the strongest oxidizing agent known[1], so its properties are of very great interest to the chemist. Yet, there is very little accurate information available as to its thermodynamic constants. All attempts to obtain the absorption spectrum of fluorine have yielded only a continuum[2], while the bands obtained in emission surely do not involve the ground state[3]. Hence, it was decided to investigate the absorption spectrum of chlorine fluoride, itself a very interesting molecule, in the hope of obtaining more information about fluorine. As all the halogens except fluorine have a relatively simple band system near the blue region of the spectrum, there seemed to be an excellent chance that resolvable structure might be obtained.

In the preparation of chlorine fluoride, chlorine trifluoride is also obtained. This also was investigated spectroscopically, but nothing of interest was found.

II. Preparation of Chlorine Fluoride and
Chlorine Trifluoride

Chlorine fluoride was prepared by the method of Ruff[4], direct combination of chlorine and fluorine. The method is simple--chlorine and fluorine are passed into a reaction vessel at 250°C., using an excess of fluorine, so that all the chlorine reacts to give chlorine fluoride and chlorine trifluoride. The products and the excess fluorine are then separated by fractional condensation. There are, however, certain experimental difficulties. The great reactivity of the fluorine and the even greater reactivity of the chlorine fluoride and chlorine trifluoride

require that the apparatus be made entirely from copper and quartz, with no wax or grease in immediate contact with the products; and the impurities in the fluorine, carbon and silicon tetrafluorides, are difficult to remove.

In these experiments, the fluorine was obtained by the electrolysis of molten potassium hydrogen fluoride in a generator which was kindly made available by Professor Yost. Several different preparations of the chlorine fluoride were made, in between which it was necessary to regenerate the charge in the generator, replacing the hydrogen fluoride decomposed by the electrolysis. It was found that a method much faster and cheaper than putting in a new charge or regenerating the old by the method of Simons[5] is to distil anhydrous hydrogen fluoride into the melt. Anhydrous hydrogen fluoride of quite good purity can now be obtained commercially, and to carry out the distillation it is necessary only to lead a tube from the tank to near the bottom of the melt, the hydrogen fluoride being absorbed very rapidly and smoothly, without excessive evolution of heat. In this manner a regeneration can be carried out in a few hours instead of a day or more. Another advantage is that more hydrogen fluoride can be distilled in than corresponds to the formula KHF_2, and so a greater quantity of fluorine can be obtained before regeneration is again necessary. After treatment in this way, fluorine is obtained within fifteen minutes of the start of the electrolysis. However, the electrolysis was always allowed to proceed for at least two hours before the start of the reaction, in order to eliminate silicon and oxygen compounds from the melt.

The apparatus used to prepare the chlorine fluoride is diagramed in Figure 1. From the fluorine generator A, the gas flows through the traps B, C, and D into the furnace E. Trap B, of copper, is filled with fused potassium fluoride to remove hydrogen fluoride from the fluorine.
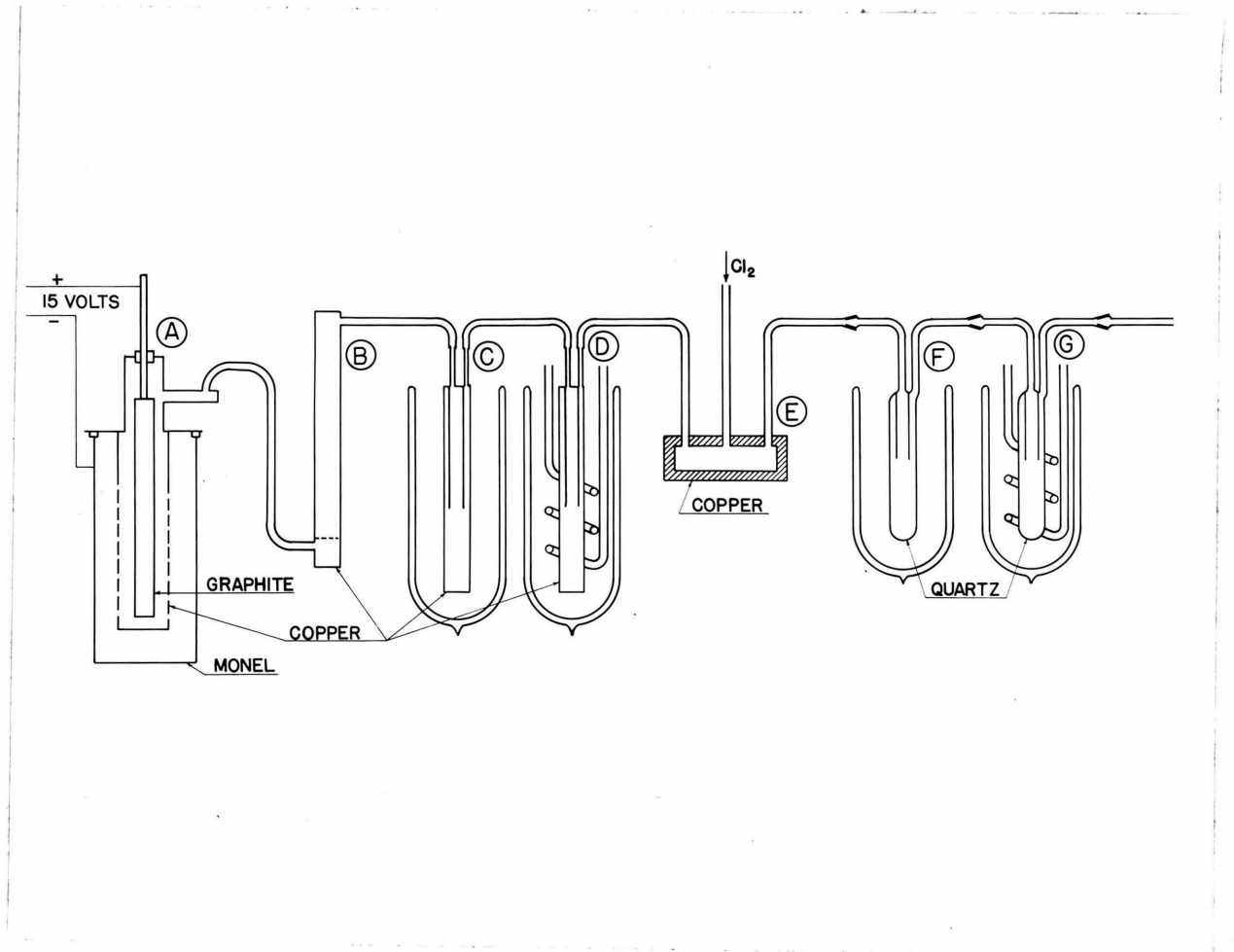
Figure 1.

Apparatus for the Preparation

of Chlorine Fluoride and Chlorine Trifluoride

Traps C and D, of copper with thin-walled monel tubing leads are cooled to about -75° and -150°C, respectively, trap C by a dry-ice alcohol bath, trap D by a liquid propane bath. The temperature of the latter, determined by means of a five-junction copper-constantin thermocouple, was held in the range -140° to -150° by blowing liquid air through a spiral of copper tubing immersed in the liquid propane. The reaction vessel E, a copper block bored out, with copper tubes silver soldered in place as indicated in Figure 1, was heated electrically by a heater wound about it. The temperature, measured by a thermometer, was held between 250° and 275° during all preparations.

The chlorine used was commercial tank chlorine which is believed to be reasonably pure. It was bubbled twice through concentrated C.P. sulfuric acid, passed through a column containing tightly packed glass wool, and then led into the reaction vessel through a copper tube. The rate of flow of the chlorine was determined by its rate of bubbling through one of the sulfuric acid traps.

For ease in disassembling, the reaction vessel outlet was fitted with a copper standard taper ($\mathfrak{F}$ 7/25), and the next two traps, F and G, were constructed of fused quartz with similar tapers. Trap F was cooled in a dry-ice alcohol bath to about -75°; trap G was kept at about -150° in the same manner as trap D. It was found necessary to use a small amount of lubricant on the tapered joints. Nothing that was tried was very satisfactory, but graphite bound together with apiezon grease and applied to the slightly warmed taper was found to hold up for a week or so.

The freezing points and boiling points of the substances which need to be considered in this preparation are listed in Table 1.

Table 1

	Melting point, °C	Boiling point, °C
HF	−92	19.4
ClF_3	−83	13
ClO_2	−59	9.9 731
Cl_2	−102	−34
SiF_4	−−	−95 760 (subl.)
ClF	−154	−100
CF_4	−−	−130
F_2	−223	−188

It is seen that the impurities present in the fluorine are largely re-moved in traps A, B, and C. Thus, provided a sufficient excess of fluor-ine is present, the only substances issuing from the reaction vessel are chlorine trifluoride, chlorine fluoride, and fluorine. The first of these is condensed in trap F, the second in trap G, and the last is not condensed.

The fluorine generator current was held at about 10.5 amperes, which at 100% efficiency corresponds to 4.9 liters of fluorine per hour. The efficiency of the generator is unknown, but Ruff has reported 60% to 83%. The rate of flow of reactants, the length of the run, and the est-imated amount of products collected are given in Table 2.

Table 2

Prep.	Rate F_2 flow 100% eff. l. gas/hr.	Rate Cl_2 flow l. gas/hr.	Time prod. collected, hrs	Amount of ClF coll. ml. liq	Amount of ClF_3 coll. ml. liq.
I	4.9	1 1/2	6 3/4		15
			5	7	
II	4.9	2 1/4	4	not estimated, but ClF $<$ ClF_3	
III	4.9	2 3/4	4	12	16

At the conclusion of a preparation, the quartz traps were dis-
assembled from the apparatus and their outlets closed ~~off~~ with sealed
off quartz tapers. The traps containing the chlorine fluoride and the
chlorine trifluoride were kept in liquid air and dry-ice alcohol baths,
respectively, until completion of the experiments.

Before being used, the products were distilled in an all-quartz
system, approximately the first and last 15% of the distillate being dis-
carded.

It is believed that the purity of the products was reasonably
good. The most likely impurities in the chlorine fluoride are the carbon
and silicon tetrafluorides. Both of these are present in the fluorine as
it comes from the generator, but should be largely removed in trap D, as
previously mentioned. Also, carbon tetrafluoride could be obtained by the
action of the chlorine fluoride on the lubricant on the tapered joints,
and silicon tetrafluoride could be obtained by the action of the chlorine
fluoride on the quartz. The rate of both these reactions was observed
to be very slow. In any case, no trouble from any unknown absorption was
experienced in photographing the spectrum. Also, the electron diffraction
investigation (discussed in a later section of this thesis) gave no in-
dication of the presence of silicon tetrafluoride, which would show up
plainly if present in large amount, more than fifteen percent.

In the course of the spectroscopic investigation, chlorine diox-
ide was found to be present in both the chlorine fluoride and the chlorine
trifluoride. This will be discussed later. Any other impurities which
might have gotten into the chlorine trifluoride have boiling points suf-
ficiently different from the boiling point of the chlorine trifluoride to
be removed by the simple distillation.

III. The Chlorine Fluoride Spectrum

Experimental Procedure

Description of Bands

The absorption spectrum of chlorine fluoride was studied under both low and high dispersion. The absorption cell, used for all photographs, was a three meter length of brass tubing, of twelve millimeter internal diameter. The windows of fused quartz were clamped onto the ends of the tube using copper gaskets.

The apparatus used to evacuate the cell and to introduce the chlorine fluoride is shown in Figure 2. Valve A is a special needle valve, designed primarily for use on the electron diffraction machine. It is so constructed that nothing but copper comes into contact with the gas. The needle of copper with a spherical end of 3/16" radius is forced against a narrow seat about 3/16" in diameter by a strong spring. A 0.006" copper diaphram 1 1/2" in diameter permits a 1/16" motion of the needle.

The pressure gauge B, also constructed so that nothing but copper comes in contact with the gas, has a 0.0015" copper diaphram 3 3/4" in diameter on which rests a steel needle, the upper part of which is visible through a glass tube. The gauge was used as a null indicator, the air pressure above the diaphram being adjusted to balance the chlorine fluoride pressure below. The sensitivity of the gauge is low; also the diaphram showed considerable hysteresis, but it was adequate for adjusting the pressure in the cell to within half a centimeter of the desired value.

The valve C is a commercial stainless steel needle valve, placed so the packing gland is on the pump side of the line. It was entirely satisfactory, save that the packing had to be replaced once. The solid sodium hydroxide in the trap D, placed there to protect the pump and the mercury manometer F, was not very satisfactory, as the rate of reaction
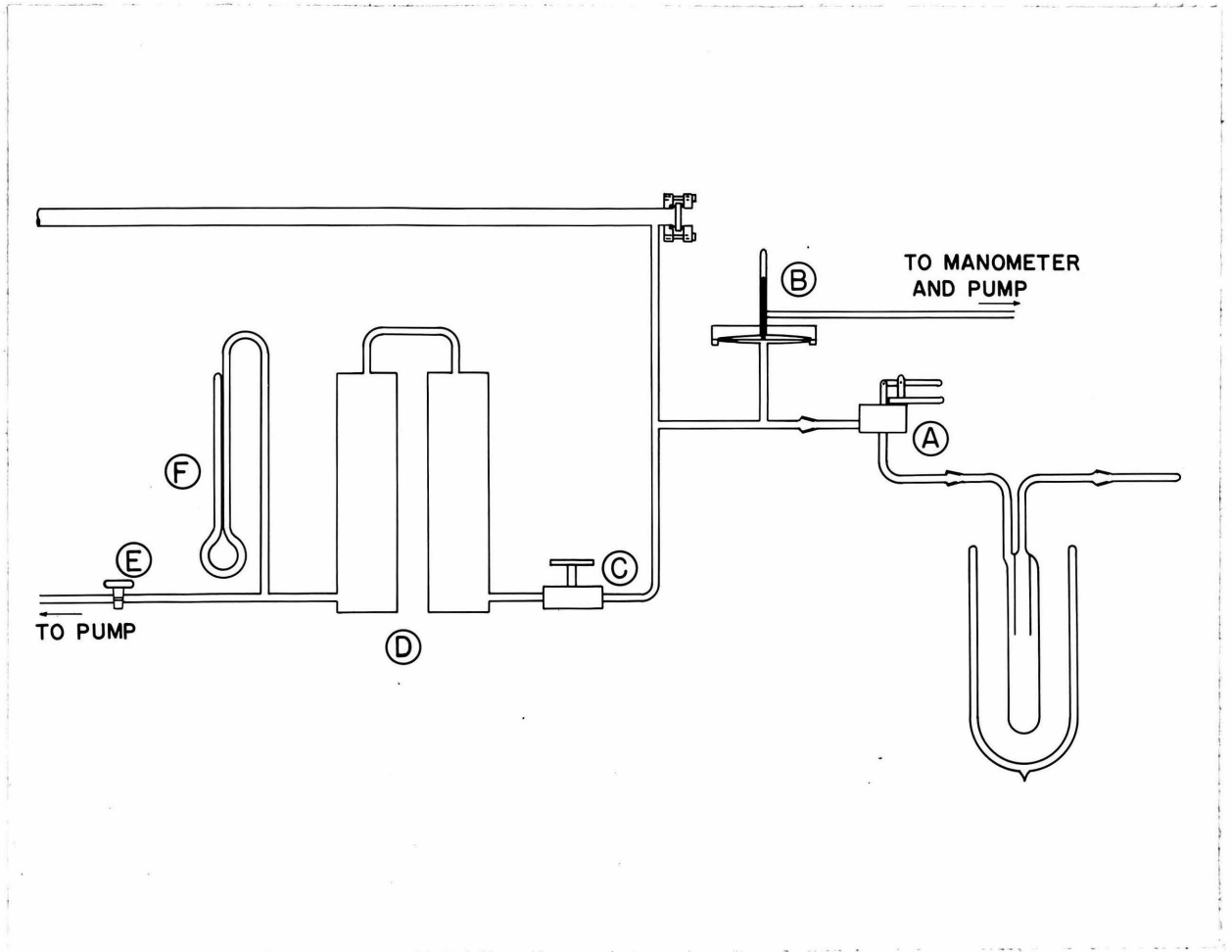
Figure 2

Absorption Cell and Associated Apparatus

of the solid dry sodium hydroxide with the chlorine fluoride was slow.
The chlorine fluoride that did get through the sodium hydroxide reacted
with the pump oil. This was no doubt rather hard on the pump, but did
keep the chlorine fluoride out of the laboratory, where it could have caused
far more damage.

The entire system was reasonably vacuum tight, considering the
fact that most of the connections were made by standard brass couplings.
When evacuated to the limit of the rather old mechanical pump used, a
pressure of about two millimeters, the pressure would rise to perhaps one
and one-half centimeters in an hour. As the exposure times never ran
much longer than this, and as only the moisture in the air could cause
trouble, such a leak was of no consequence.

The experimental procedure was to evacuate the system completely
with the chlorine fluoride cooled in liquid air. Then, valve C was closed
and the liquid air removed until the pressure had reached the desired
value, when valve A was closed and the liquid air again placed around the
chlorine fluoride. The exposures were then taken as quickly as possible,
after which valve E was closed and valve C opened, allowing the chlorine
fluoride to come into contact with the sodium hydroxide in trap D. Then,
after ten or fifteen minutes, valve E was opened and the system pumped
out.

The light source used was a five hundred watt projection lamp
focused into the tube by a short focus lense. At the exit end of the cell
a lens and plane mirror served to focus the light on the slit of the low
dispersion prism instrument, while a lens only was needed to focus the
light on the slit of the grating. With unfogged windows, exposure times
of two minutes and thirty minutes were needed on the prism and grating
instruments, respectively, at λ 4800. However, the quartz windows were
attacked fairly rapidly, the light by causing dissociation of the chlor-

ine fluoride greatly increasing the rate of the reaction. The window at the exit end of the absorption cell remained in a usable condition for perhaps ten hours, but the window at the source end became badly fogged after only two or three hours. During several of the exposures a filter consisting of a ten centimeter layer of a ten percent solution of potassium ferrocyanide was placed before the cell to cut out radiation of wave lengths shorter than λ 4400, but this had very little if any effect on the fogging of the windows.

The low dispersion studies were made on a Littrow quartz spectrograph with Eastman 40 and Eastman 1F plates. The dispersion obtained was about 64 cm^{-1} per mm. at λ 4000; the slit width was 0.02mm. for most plates, 0.01mm. for several. An iron spectrum was placed below and above the absorption spectra on each plate. The region $\lambda\lambda$ 3500-7000 was investigated and in the region $\lambda\lambda$ 3500-4830 a large number of band heads* were observed. The long wave length heads were weak with an atmosphere pressure of chlorine fluoride in the cell, but the strength of the absorption increased rapidly on going to shorter wave lengths, so that in the shortest wave length region examined a fraction of a millimeter pressure was sufficient. Largely due to the decrease in output of the source at shorter wave lengths, the exposures time had to be increased from one-half minute at λ 6000 to fifteen minutes at λ 3500.

Measurements were made on one low dispersion plate on which four spectra had been taken, the first with a chlorine fluoride pressure of 50 cm. and an exposure of 1 minute, the others at 50 cm. and 4 minutes, 3 mm. and 4 minutes, and 0.3 mm. and 13 minutes, respectively. Fifty eight band heads were measured. With a few exceptions, four measurements from at least two of the above spectra were made on each band head.

*On pp. 13-16 of this thesis a short description of some of the spectroscopic nomenclature is given.

Similar measurements were made on thirty-one selected iron lines. The wave lengths of the iron lines were obtained from the M.I.T. Wavelength Tables[6]. The reciprocals of the wave lengths were calculated, the correction to vacuum as given by the International Critical Tables[7] applied, a linear interpolation formula obtained, and a correction curve plotted in the usual way.

On plotting the positions of the band heads on a wave number scale it was seen that there were at least four progressions, and the general appearance was that of a polyatomic rather than a diatomic molecule. At the suggestion of Dr. Eyster, the above bands were compared with the chlorine dioxide bands in this region, the vibrational structure of which has been thoroughly investigated by Urey and Johnston[8]. It was found that fifty-seven of the fifty-eight bands measured were reported by them, the mean deviation between their results and the results of this investigation being about seven wave numbers. The remaining band head, at 21,140 cm^{-1} (λ4729), was later found to be of chlorine fluoride.

As reported by Urey and Johnston, the chlorine dioxide absorption is very strong in the near ultra-violet but becomes weak as one goes into the blue region of the spectrum. They found it necessary to use pressures ranging from 0.2 to 600 mm. in absorption cells 30 and 60 cm. in length. As the difference in boiling points of chlorine dioxide and chlorine fluoride is very large (see Table 1), it seems impossible that a large concentration of the former could be present in the latter after distillation. It seems more likely that the amount of chlorine dioxide was very small, probably less than one percent, this percentage being more than enough to account for the observed absorption. The presence of chlorine dioxide causes no trouble in the spectroscopic investigation, as the bands due to it are easily identified on the high dispersion plates, but the appearance of the low dispersion bands has been treated

in some detail here for use later in regard to the investigation of chlorine fluoride and chlorine trifluoride by the electron diffraction method, in which it is not usually possible to determine the presence of or the effect of impurities.

The high dispersion studies were made in the second order of a twenty-one foot concave grating, using Eastman 40 plates. The absorption cell was used exactly as in the low dispersion work. A very large number of bands were found, most of them with very complicated, only partially resolved, fine structure, and hence due to chlorine dioxide; also several bands obviously resulting from a diatomic molecule of low moment of inertia were observed. The region about these, $\lambda\lambda$ 3990-5380, was then intensively studied. The pressure of gas used varied from 60 to 80 cm. It would have been advantageous to use a higher pressure or a longer path length, but neither was feasible. Exposure times varied from one-half to two hours, depending principally on the condition of the windows. The slit width used was 0.035 or 0.040 mm., and the dispersion obtained was approximately 5 cm^{-1} per mm. An iron arc comparison spectrum was placed on either side of each chlorine fluoride spectrum.

A beautiful progression of five bands, degraded to the red, was found, with sharp heads at 4901, 4868, 4812, 4761 and 4728 Å. The fine structure in these bands is clearly resolved. The bands at 4901, 4868 and 4761 Å seem to consist of doublets whose separation increases as one goes further away from the band heads. The bands at λ 4812 and λ 4728 consist of single lines having a spacing uniformly increasing with distance from the origin, but the spacing in the λ 4812 band is twice that in the λ 4728 band.

Between the head at λ 4728 and λ 4680 there is a region of broad diffuse lines in which there are faintly visible three diffuse band heads but no corresponding fine structure. Then at about 4662, 4654, 4649 and

and 4647 Å there are four more band heads which plainly converge to a limit very near the last mentioned head. The first three of these last mentioned heads have plainly resolved fine structure, but it was possible to measure the lines of the first two only. A contact print of the above region is given in Figure 3; a microphotometer trace of part of the region is given in Figure 4.

The region beyond λ4647 was carefully examined for more diatomic bands, but none could be found. A large number of bands of chlorine dioxide were found to the violet of λ4600, but their intensity decreases rapidly with increasing wave length, so that no bands arising from chlorine dioxide could be detected to the red of λ4620. It can be definitely said that there are no bands of chlorine fluoride in the region $\lambda\lambda$4600-4647 of intensity at all comparable to the bands in the region 4901-4728.

On the long wave side of λ4901 the bands soon become indistinct. The intensity of absorption rapidly decreases and the bands begin to overlap badly. Beyond λ5250 the absorption lines fade out completely with the path length and pressure used. Two bands were analysed in this region, their heads being at λ4907 and λ4987.

IV. The Chlorine Fluoride Spectrum

Analysis of the Rotational Structure

The first step in the analysis was to make high-contrast enlargements of the chlorine fluorine bands and to pick out the obvious branches. This was very easy in the bands shown in Figure 3. It can easily be seen that the bands consist of single P and R branches, which give the bands at λ4868 and 4761 a doublet appearance and which overlap in the band at λ4812.

After picking out the branches of several bands, the positions of all the lines on the plates in the vicinity of the bands so treated were

11a

17 ← 0   λ 4647
16 ← 0   4649
15 ← 0   4654
14 ← 0   4662
13 ← 0
12 ← 0
11 ← 0
10 ← 0   4728
9 ← 0   4761
8 ← 0   4812
7 ← 0   4868
6 ← 0   4901

Figure 3

17 ← 0
16 ← 0
15 ← 0
14 ← 0
13 ← 0
12 ← 0
11 ← 0
10 ← 0
9 ← 0
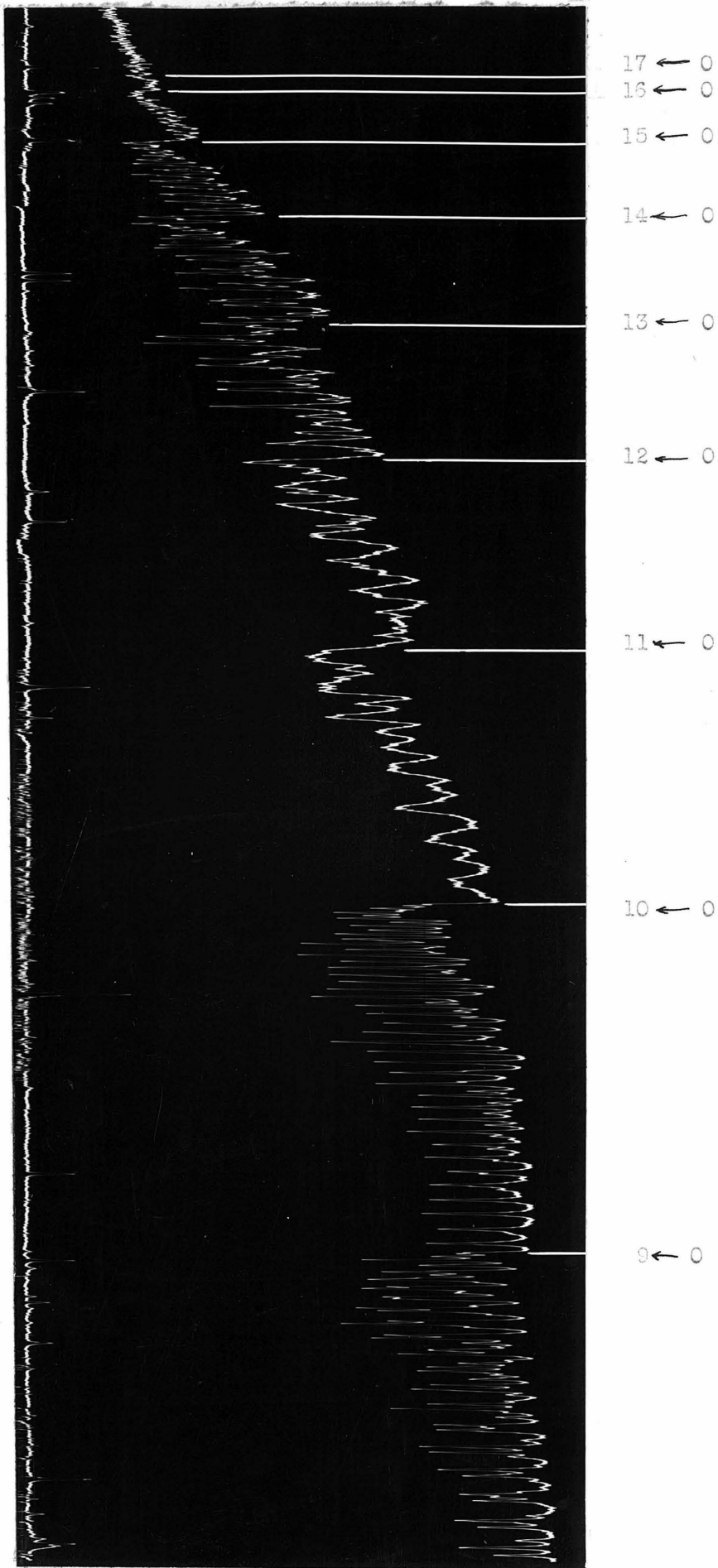
Figure 4

measured. Measurements were made on two plates, the region $\lambda 4654$ to $\lambda 4900$ being measured on one (the plate shown in Figure 3) and the region $\lambda 4900$ to $\lambda 5032$ on the other. Three settings were made on each line of the absorption spectrum and the iron arc spectrum.

The accuracy of these measurements varied greatly. On most strong sharp absorption lines and on the the iron arc comparison lines the maximum difference between any two of the three measurements made on each line was 0.002cm. corresponding to a probable error of less than 0.1 cm^{-1}. But very few of the lines measured were both strong and sharp, so that differences between successive measurements of two and three times the above figure were not uncommon. The calculations of the frequencies from the comparator readings were made in the way described for the low dispersion plates. The deviation curves were smooth and had a probable error less than 0.05cm^{-1}. Hence, it is believed that the probable error in measurement of strong sharp lines is 0.1cm^{-1}, of most of the remaining lines 0.2cm^{-1}, while for some of the weakest lines (Principally from the "isotope" bands) and for overlapping lines there may be errors of 0.5 cm^{-1}. It might be noted here that the slit width corresponds to 0.2cm^{-1} and that the theoretical resolving power of the grating in this region for an infinitely narrow slit is 0.11cm^{-1}.

The rotational analysis was now carried out in the usual way. For convenience in the description to follow, the numbering of the bands as finally decided upon will be used, the reasons for this choice of numbering being given later. The connection between this numbering and the wave lengths previously given for certain band heads may be seen by a glance at Figure 4. It is evident that this being the absorption spectrum of a cold gas, the *set* ~~series~~ of bands $6 \leftarrow 0$, $7 \leftarrow 0$, $8 \leftarrow 0$, $9 \leftarrow 0$, and $10 \leftarrow 0$ must be a progression arising from a common initial state and hence there must be a numbering for each of these bands such that the $\Delta_2 F''_{(J)}$'s are the same for all bands.

Throughout this paper the standard spectroscopic nomenclature is used [9,10,9]. We will here digress to summarize the more important definitions and formulas used in the following discussion.

$$T = T_e + G + F, \qquad T_e \gg G \gg F, \qquad (1)$$

where T is the total energy of the molecule expressed in wave number units, and T_e, G, and F are the electronic, vibrational, and rotational energies, respectively, of the molecule. Then for a diatomic molecule, $G = G_{(v)}$ is a function of a vibrational quantum number v, and $F = F_{v(J)}$ is a function of a rotational quantum number J, and also of the value of v. Both $F_{v(J)}$ and $G_{(v)}$ depend on the electronic state of the molecule. The two states involved in any given transition, in this case two electronic levels, are designated by applying primes to all quantities referring to the upper or higher energy state, double primes to all quantities referring to the lower state.

It is in general found that:-

$$G_{(v)} = \omega_e(v + \tfrac{1}{2}) - \omega_e x_e(v + \tfrac{1}{2})^2 + \omega_e y_e(v + \tfrac{1}{2})^3 + \ldots\ldots\ldots \quad (2)$$

$$\omega_e \gg \omega_e x_e \gg \omega_e y_e$$

$$F_{v(J)} = B_v J(J + 1) - D_v J^2(J + 1)^2 + \ldots\ldots\ldots \quad (3)$$

$$B_v \gg D_v$$

$$B_v = B_e - \alpha_e(v + \tfrac{1}{2}) + \ldots\ldots\ldots\ldots\ldots$$

$$B_e \gg \alpha_e$$

$$D_v = D_e + \beta_e(v + \tfrac{1}{2}) + \ldots\ldots\ldots\ldots\ldots \quad (4)$$

$$D_e \gg \beta_e$$

For the frequencies emitted or absorbed,

$$\nu = T' - T'' = T_e' - T_e'' + G_{(v')}' - G_{(v'')}'' + F_{v'(J')}' - F_{v''(J'')}'' \ldots\ldots \quad (5)$$

where the selection rules are that $\Delta v = v' - v'' = $ any integer and $\Delta J = J' - J'' = \pm 1$, or 0 in general, but in certain special cases $\Delta J = \pm 1$ only.

Thus a given band system arises from the totality of transitions between two electronic levels of the molecule. Each band of the band system consists of all the transitions involving a single vibrational levels in the upper and lower electronic states and so can be denoted by two quantum numbers, v' and v'', the transition giving rise to an absorption band being represented by $v' \leftarrow v''$. Each line of a given band then involves a definite rotational levels in the initial and final states, but because of the selection rule on J it is more convenient to give only the quantum number of the lower state together with the value of ΔJ.

It is usual to consider the rotational structure, resulting from $F'_{v'(J')} - F''_{v''(J'')}$ as superimposed upon the vibrational structure. The latter is described by

$$\nu_o = \nu_e + \omega'_e(v' + \tfrac{1}{2}) - \omega'_e x'_e(v' + \tfrac{1}{2})^2 + \omega'_e y'_e(v' + \tfrac{1}{2})^3 + \ldots\ldots$$

$$-\left[\omega''_e(v'' + \tfrac{1}{2}) - \omega''_e x''_e(v'' + \tfrac{1}{2})^2 + \ldots\ldots\ldots\ldots\right] \qquad (6)$$

where $\nu_e = T'_e - T''_e$ is the origin of the band system and the values of ν_o given by the equation are the band origins, the positions of lines resulting from an imaginary transition ($v' \leftarrow v''$) in which $F'_{(J')} = F''_{(J'')}$.

The rotational structure of a band is then given by $\nu = \nu_0 + F'_{v'(J')} - F''_{v''(J'')}$. A set of lines in which $\Delta J = J' - J'' = +1$ is called an R branch, a set in which $\Delta J = 0$ a Q branch, and a set in which $\Delta J = -1$ a P branch. As no Q branch was observed in these experiments no more consideration will be given here to the case $\Delta J = 0$. Thus, we can write:-

R branch:- $\nu = \nu_0 + F'_{(J + 1)} - F''_{(J)} = R_{(J)}$

P branch:- $\nu = \nu_0 + F'_{(J + 1)} - F''_{(J)} = P_{(J)}$ $\quad\ldots\ldots\ldots$ (7)

The quantities obtained by direct measurement of the spectrographic plate are $R_{(J)}$ and $P_{(J)}$. To obtain from these information about

the rotational constants of the molecule one calculates the quantity

$\Delta_2 F_{v(J)} = F_{v(J+1)} - F_{v(J-1)}$. It is at once evident from equation (7) that

$$\Delta_2 F''_{v(J)} = F''_{v(J+1)} - F''_{v(J-1)} = P_{(J+1)} - R_{(J-1)}$$

$$\Delta_2 F'_{v(J)} = F'_{v(J+1)} - F'_{v(J-1)} = P_{(J)} - R_{(J)} \quad \cdots\cdots\cdots (8)$$

As the values of the $\Delta_2 F_{v(J)}$ vary quite appreciably with **v**, it is apparent that if the same $\Delta_2 F_{v(J)}$'s are obtained by the analysis of several different bands, these bands must have one state in common.

Using equation (3) but neglecting D_v, we may write more explicit expressions for $R_{(J)}$ and $P_{(J)}$:-

$$R_{(J)} = \nu_0 + 2B' + (3B' - B'')J + (B' - B'')J^2$$

$$P_{(J)} = \nu_0 - (B' + B'')J + (B' - B'')J^2 \quad \cdots\cdots\cdots (9)$$

If $B' - B''$ is appreciably different from zero, it will be observed that there exists either a minimum in the values for $P_{(J)}$ or a maximum in the values for $R_{(J)}$, the former signifying that $B' - B''$ is greater than zero and giving a band described as shaded or degraded toward the violet, the latter signifying that $B' - B''$ is less than zero and giving a band described as shaded toward the red. This maximum or minimum is known as the band head and is the most prominent feature on a plate taken with low dispersion. The distance between the band origin and the band head is small if $B' - B''$ is greatly different from zero, as is the case in these bands, and can often be neglected in qualitative considerations of vibrational structure.

It is usual to arrange the band heads or band origins into progressions, a progression being a group of bands having a common upper or lower vibrational level. From equation (6) it is seen that the band origins for a progression having a common lower state (v" const.) must satisfy and equation:-

$$\mathcal{V} = \mathcal{V}_0 + w'_e(v' + \tfrac{1}{2}) - w'_e x'_e(v' + \tfrac{1}{2})^2 + w'_e y'_e(v' + \tfrac{1}{2})^3 + \ldots\ldots$$

where $\mathcal{V}_0$ is a constant for a given progression.

We have so far ignored the fact that chlorine has two isotopes, Cl^{35} and Cl^{37}, so that the spectrum observed actually arises from two molecules, $Cl^{35}F$ and $Cl^{37}F$. The electronic terms T'_e and T''_e, depending on the nuclear charges and the electron interactions are practically identical for the two molecules, but the vibrational and rotational energies, depending on the reduced masses of the molecules, will be different. To distinguish between the two sets of bands and the two sets of constants obtained therefrom, the usual convention is followed in applying the superscript i to every symbol having to do with the less abundant molecule. Since the ratio of $Cl^{37}F$ to $Cl^{35}F$ is 1 to 3, relatively few bands of the isotopic molecule were found.

To return to the ClF spectrum, it was found that the rotational *lines* of seven of the bands in the region studied could be numbered so as to give the same $\Delta_2 F''$'s. Since at room temperature the number of molecules in states having $v'' > 0$ decreases very rapidly as v'' increases, the state these seven bands have in common must be the lower state. The experimental values for $R_{(J)}$ and $P_{(J)}$ for these bands, called $7 \leftarrow 0$, $8 \leftarrow 0$, $9 \leftarrow 0$, $10 \leftarrow 0$, $14 \leftarrow 0$ and $15 \leftarrow 0$, are given in Tables 3 to 7 along with the values of $\Delta_2 F'_{(J)} = R_{(J)} - P_{(J)}$. In Table 8, are given the values of $\Delta_2 F''_{(J)}$ for these bands and their average. It is seen that the agreement is quite satisfactory for the middle range of J values. For small J, say $J < 4$ the lines involved come very near the band heads and so are difficult to measure because of the crowding together occurring there. Also the intensity becomes low as J approaches 0. For high J the intensity again approaches zero, so that the last lines measured in a branch are in accurate. In band $8 \leftarrow 0$ the overlapping of P and R branches give an additional error, which is discussed in some detail later.

Overlapping the $6 \leftarrow 0$ band is another band, the $10 \leftarrow 1$

band, having the same $\Delta_2 F'_{(J)}$ as the $10 \leftarrow 0$ band. At a slightly

longer wave length another band, the $8 \leftarrow 1$ band, was found having the

same $\Delta_2 F'_{(J)}$ as the $8 \leftarrow 0$ band. The $8 \leftarrow 1$ band is also like the

$8 \leftarrow 0$ band in having the lines of the P and R branches overlapping.

On comparing the $\Delta_2 F''_{(J)}$ for the bands $10 \leftarrow 1$ and $8 \leftarrow 1$ it is

found that they also agree within experimental error. The values for

$P_{(J)}$, $R_{(J)}$ and $\Delta_2 F'_{(J)}$ for the band $8 \leftarrow 1$ are given in Table 4

where the $\Delta_2 F'_{(J)}$ may be compared with those for the $8 \leftarrow 0$ band. The

$10 \leftarrow 1$ band is similarly treated in Table 6, and in Table 9 the $\Delta_2 F''_{(J)}$

are compared for these two bands.

Table 3

J	6←0				7←0			
	$R_{(J)}$	$P_{(J)}$	$\Delta_2 F'_{(J)}$	$\dfrac{\Delta_2 F'_{(J)}}{J + 1/2}$	$R_{(J)}$	$P_{(J)}$	$\Delta_2 F'_{(J)}$	$\dfrac{\Delta_2 F'_{(J)}}{J + 1/2}$
0								
1						20618.65		
2		20393.00			20620.02	617.06	2.96	1.184
3	20395.23	391.19	4.04	1.154	618.65	615.21	3.44	0.983
4	393.91	388.66	5.25	.167	617.06	612.37	4.69	1.042
5	392.15	386.03	6.12	.113	615.21	609.45	5.76	.047
6	390.02	382.46	7.56	.163	612.95	605.93	7.00	.076
7	387.16	378.93	8.23	.097	610.17	601.80	8.37	.116
8	384.01	374.67	9.34	.099	606.66	597.44	9.22	.085
9	380.50	369.71	10.79	.114	602.78	592.58	10.20	.073
10	376.33	364.62	11.71	.115	598.49	587.25	11.24	.070
11	371.78	358.87	12.91	.123	593.52	581.29	12.23	.063
12	366.61	352.80	13.81	.105	588.18	574.88	13.30	.064
13	361.25	345.87	15.38	.139	582.68	567.81	14.87	.101
14	355.26	338.84	16.36	.128	576.40	560.25	16.15	.114
15	348.78	331.21	17.57	.134	569.55	----	----	----
16	(342.47)	323.23	----	----	562.21	544.54	17.67	.070
17	334.37	(314.43)	----	----	554.42	535.60	18.82	.075
18	326.28	305.80	20.48	1.107	546.10	526.28	19.82	.071
19	318.15	296.46	21.69	.112	537.29	516.23	20.97	.075
20	309.39	286.54	22.85	.115	527.86	505.92	21.94	.070
21	300.24	275.99	24.25	.128	518.09	495.21	22.88	.064
22	390.47	265.18	25.29	.124	507.88	483.76	24.12	.072
23	280.32	254.29	26.03	.108	497.00	471.87	25.13	.069
24	269.33	242.16	27.17	.109	485.75	459.49	26.26	.071
25	258.05	229.83	28.22	.107	473.75	446.81	26.94	.056
26	248.38	----	----	----	461.58	433.28	28.30	.067
27	234.38	203.85	30.53	1.109	448.80	419.54	29.26	.064
28					435.68	405.41	30.27	.062
29					421.74			
30					407.70			

Table 4

J	8←0			8←1			$\Delta_2F'(J)$ Ave.	$\dfrac{\Delta_2F'(J)}{J + 1/2}$
	$R_{(J)}$	$F_{(J)}$	$\Delta_2F'(J)$	$R_{(J)}$	$P_{(J)}$	$\Delta_2F'(J)$		
0	20821.53							
1	20821.53	20819.36	2.17		20045.99		2.17	1.447
2	820.73	817.73	3.00	20047.11	20044.62	2.49	2.74	1.096
3	819.36	815.72	3.64	045.99	042.48	3.51	3.58	1.022
4	817.73	813.23	4.50	044.62	039.88	4.74	4.62	1.027
5	815.72	810.09	5.63	042.48	036.82	5.66	5.64	1.025
6	813.23	806.41	6.82	039.88	033.18	6.70	6.76	1.040
7	810.09	802.34	7.75	036.82	029.27	7.55	7.65	1.020
8	806.41	797.77	8.64	033.18	024.51	8.67	8.66	1.019
9	902.34	792.54	9.80	029.27	019.66	9.61	9.70	1.021
10	797.77	786.75	11.02	024.51	014.09	10.42	10.72	.021
11	792.54	780.66	11.88	019.66	008.13	11.53	11.70	.017
12	786.75	774.00	12.75	014.09	001.48	12.61	12.68	.014
13	780.66	766.81	13.85	008.13	19994.32	13.81	13.83	.024
14	774.00	759.04	14.96	001.48	986.78	14.70	14.83	.023
15	766.81	750.78	16.03	19994.32	978.58	15.74	15.89	.025
16	759.04	742.04	17.00	986.78	969.91	16.87	16.94	.027
17	750.78	732.53	18.25	978.58	960.79	17.79	18.02	.030
18	742.04	722.91	19.13	969.91	951.22	18.69	18.91	.022
19	732.53	712.52	20.03	960.79	940.85	19.94	19.98	.025
20	722.91	701.71	21.20	951.22	930.30	20.92	21.06	.027
21	712.52	690.26	22.26	940.85	919.23	21.62	21.89	.018
22	701.71	678.42	23.29	930.30	907.50	22.80	23.04	.024
23	690.26	665.91	24.35	919.23	895.02	24.21	24.28	.033
24	678.42	653.29	25.13	907.50	882.51	24.99	25.06	.023
25	665.91	639.51	26.40	895.02			26.40	.035
26	653.29	625.45	27.84	882.51			27.84	.050
27	639.51	611.09	28.42				28.42	.033
28	625.45	596.53	28.92				28.92	.015
29	611.09							
30	596.53	564.18	32.35				32.35	.061
31		547.63						
32	564.18	530.53	33.65				33.65	.035
33	547.63	512.82	34.81				34.81	.039
34	530.53	494.27	36.26				36.26	.051
35	512.82	475.27	37.55				37.55	.058
36	494.27	455.99	38.28				38.28	.049

Table 5

J	$R_{(J)}$	$P_{(J)}$	$\Delta_2 F'_{(J)}$	$\dfrac{\Delta_2 F'_{(J)}}{J + 1/2}$
		9 ← 0		
0				
1	20997.53	20995.69	1.85	1.233
2	996.85	20993.92	2.93	1.172
3	995.69	991.84	3.85	1.100
4	993.92	989.49	4.43	0.984
5	991.84	986.41	5.43	.987
6	988.92	982.70	6.22	.956
7	985.67	978.37	7.30	.973
8	981.73	973.67	8.06	.948
9	977.38	968.22	9.16	.964
10	972.48	962.16	10.32	.982
11	966.78	955.86	10.92	.949
12	960.89	948.87	12.02	.961
13	954.30	941.17	13.13	.972
14	947.09	933.13	13.96	.962
15	939.35	924.39	14.96	.965
16	931.09	915.16	15.93	.965
17	922.38	905.46	16.92	.966
18	912.87	895.13	17.74	.958
19	902.85	884.28	18.57	.952
20	892.45	872.79	19.66	.959
21	881.41	860.91	20.50	.953
22	869.77	848.30	21.47	.954
23	857.53	835.22	22.31	.949
24	844.71			
25	831.51	807.44	24.07	0.944
26				
27		777.13		
28	788.05	761.06	26.99	0.947
29	772.38	744.55	27.83	0.943
30	756.20	727.41	28.79	0.944
31	739.34	709.77	29.57	0.939
32				
33	703.39	671.88	31.51	0.941

Table 6

J	10 ← 0			10 ← 1			$\Delta_2F'(J)$ Ave	$\dfrac{\Delta_2F'(J)}{J + 1/2}$
	$R_{(J)}$	$P_{(J)}$	$\Delta_2F'(J)$	$R_{(J)}$	$P_{(J)}$	$\Delta_2F'(J)$		
0								
1	21146.05							
2	145.23	21142.96	2.27				2.27	0.908
3	143.85	140.69	3.16				3.16	0.903
4	141.92	138.07	3.85	20368.58			3.85	0.856
5	139.53	134.60	4.93	365.86			4.93	0.896
6	136.53	130.78	5.75	362.62	20357.50	5.12	5.75	0.885
7	132.96	126.29	6.67		352.80		6.67	0.889
8	128.65	121.20	7.47	355.20	347.66	7.54	7.50	0.882
9	123.92	115.46	8.46	351.05	342.47	8.58	8.51	0.896
10	118.54	109.30	9.24		336.08		9.24	0.880
11	112.57	102.40	10.17	339.49	329.12	10.37	10.27	0.893
12	106.01	094.99	11.02	333.13	321.86	11.27	11.14	0.891
13	098.91	086.79	12.12	326.28	314.43	11.85	11.99	0.888
14	091.18	078.31	12.87	(20318.15)	20305.80	(12.35)	12.87	0.887
15	082.90	069.07	13.83	310.25	296.46	13.79	13.81	0.891
16	073.87	059.19	14.68	301.52	(286.54)	(14.98)	14.68	0.890
17	064.32	048.82	15.50	292.10	(276.99)	(15.11)	15.50	0.886
18	054.00	037.82	16.18	282.12			16.18	0.874
19	043.32	026.30	17.02	271.65	(254.29)	(17.36)	17.02	0.873
20	031.97	013.90	18.07	260.38	(242.16)	(18.22)	18.07	0.881
21	019.78	001.15	18.63	248.34	(229.83)	18.51	18.57	0.864
22	007.22	20987.59	19.63	235.80	218.11	19.69	19.66	0.874
23				222.75			----	
24	20980.04	958.86	21.18	209.55	188.23	21.32	21.25	0.867
25	965.41	943.68	21.73	195.22	173.22	22.00	21.87	0.858
26	950.32	927.68	22.64	179.94	157.32	22.62	22.63	0.854
27	934.36	910.87	23.51		140.93		23.51	0.855
28	917.93	893.98	23.95				23.95	0.840
29	900.88	875.68	25.20				25.20	0.854
30								
31	864.41	837.66	26.75				26.75	0.849

Table 7

J	$R_{(J)}$	$P_{(J)}$	$\Delta_2 F'_{(J)}$	$\dfrac{\Delta_2 F'_{(J)}}{J + 1/2}$	$R_{(J)}$	$P_{(J)}$	$\Delta_2 F'_{(J)}$	$\dfrac{\Delta_2 F'_{(J)}}{J + 1/2}$
		14 ← 0				15 ← 0		
0								
1								
2	21444.15							
3	442.35	21440.42	1.93	0.551	21475.86	21474.27	1.59	0.454
4	439.48	21437.10	2.33	0.529	472.83	470.85	1.98	0.440
5	21435.90	433.03	2.87	0.522	469.08	466.57	2.51	0.456
6	431.62	428.39	3.23	0.497	464.48	461.55	2.93	0.451
7	426.49	422.51	3.98	0.531	458.86	455.74	3.12	0.416
8	420.58	416.15	4.43	0.521	452.52	448.91	3.61	0.425
9	414.05	408.60	5.45	(0.574)	445.57	441.38	4.29	0.452
10	406.25	401.20	5.05	(0.481)				
11	398.45	392.36	6.09	0.530		423.88		
12	398.37	383.03	6.34	0.507				
13	379.64	372.78	6.86	0.508				
14	369.44	361.83	7.61	0.525				
15	357.76	350.15	7.61	0.491				
16	345.35	337.35	8.00	0.485				
17	332.50	323.79	8.71	0.498				
18	319.21	309.60	9.61	0.519				
19	305.11	294.62	10.49	0.538				
20		278.71						
21		262.19						

Table 8

				$\Delta_2 F''(J)$					$\dfrac{\Delta_2 F''(J)}{J + 1/2}$
J	6 ← 0	7 ← 0	8 ← 0	9 ← 0	10 ← 0	14 ← 0	15 ← 0	Ave	
1			3.80					3.80	2.5333
2			5.81	5.69	5.36			5.620	2.2480
3		7.65	7.50	7.36	7.16	7.05		7.344	2.0982
4	9.20	9.20	9.27	9.28	9.25	9.32	9.29	9.258	2.0573
5	11.45	11.13	11.32	11.22	11.14	11.09	11.28	11.232	2.0421
6	13.22	13.41	13.38	13.47	13.24	13.39	13.34	13.350	2.0538
7	15.35	15.49	15.46	15.25	15.33	15.47	15.57	15.417	2.0556
8	17.45	17.59	17.55	17.45	17.50	17.89	17.48	17.558	2.0656
9	19.39	19.41	19.66	19.57	19.35	19.38	----	19.460	2.0484
10	21.63	21.49	21.68	21.52	21.52	21.69	21.69	21.602	2.0573
11	23.53	23.61	23.77	23.61	23.55	23.22	----	23.548	2.0476
12	25.91	25.71	25.73	25.61	25.78	25.67		25.735	2.0588
13	27.77	27.93	27.71	27.76	27.70	(27.54)		27.774	2.0573
14	30.04	----	29.88	29.91	29.84	(29.49)		29.917	2.0623
15	31.97	31.86	31.96	31.93	31.99	(32.09)		31.942	2.0607
16	----	33.95	34.28	33.89	34.08	(33.97)		34.050	2.0636
17	----	35.93	36.13	35.96	36.05	(35.75)		36.017	2.0581
18	37.91	38.10	38.26	38.10	38.02	(37.88)		38.078	2.0582
19	39.74	40.18	40.33	40.08	40.10	(40.50)		40.086	2.0556
20	42.16	42.08	42.27	41.94	42.17	(42.92)		42.129	2.0548
21	44.21	44.10	44.49	44.15	44.38	----		44.266	2.0588
22	45.95	46.22	46.61	46.19	----			46.242	2.0552
23	48.31	48.39	48.42	----	48.36			48.370	2.0583
24	50.49	50.19	50.75	50.09	----			50.380	2.0563
25	----	52.47	52.97	----	52.36			52.600	2.0627
26	54.25	54.21	54.82	54.38	54.54			54.440	2.0543
27	----	56.17	56.76	----	56.34			56.423	2.0517
28		----	----	----	58.70			58.700	2.0596
29			61.27	60.64	----			60.955	2.0662
30			63.46	62.61	63.22			63.096	2.0687
31			66.00	----				66.00	2.0952
32			----					----	----
33			69.91					69.91	2.0868
34			72.36					72.36	2.0973
35			74.54					74.54	2.0997

*In the (8 ← 0) band, the P and R branches overlap almost perfectly for small J, but give band lines for J.

Table 9

J	$\Delta_2{}^{F''}(J)$			$\dfrac{\Delta_2{}^{F'}(J)}{J + 1/2}$
	8 ← 1	10 ← 1	Ave.	
1	.			
2				
3	7.23	.	7.23	2.066
4	9.17	.	9.17	2.038
5	11.44	11.08	11.26	2.047
6	13.21	13.06	13.14	2.022
7	15.37	14.96	15.16	2.021
8	17.16	---	17.16	2.019
9	19.09	19.12	19.10	2.010
10	21.14	(21.93)	21.14	2.013
11	23.03	---	23.03	2.003
12	25.34	25.06	25.20	2.016
13	27.31	27.33	27.32	2.024
14	29.55	29.82	29.68	2.047
15	31.57	(31.61)	31.57	2.037
16	33.53	(33.26)	33.53	2.032
17	35.56	---	35.56	2.032
18	37.73	---	37.73	2.039
19	39.55	(39.96)	39.55	2.028
20	41.56	(41.82)	41.56	2.027
21	43.72	44.27	44.00	2.056
22	45.83	---	45.83	2.037
23	47.85	47.57	47.71	2.030
24		49.53	49.53	2.022
25		52.23	52.23	2.048
26		54.29	54.29	2.049

Table 10

J	(8 ← 0)^i				(10 ← 0)^i			
	$R_{(J)}$	$P_{(J)}$	$\Delta_2 F'_{(J)}$	$\dfrac{\Delta_2 F'_{(J)}}{J + 1/2}$	$R_{(J)}$	$P_{(J)}$	$\Delta_2 F'_{(J)}$	$\dfrac{\Delta_2 F'_{(J)}}{J + 1/2}$
1								
2								
3		20804.10						
4		801.61						
5	20804.10	798.44	5.66	1.029				
6	801.61	795.05	6.56	1.009		21119.54		
7	798.44	790.88	7.56	1.008				
8	795.05				21116.98			
9	790.88	781.44	9.44	0.994		103.93		
10		775.86				097.59		
11	781.44	769.85	11.59	1.008	100.49	090.66	9.83	0.855
12	775.86	763.34	12.52	1.002	21093.88			
13	769.85				086.45	074.80	11.65	0.863
14	763.34	748.84	14.50	1.000		066.24		
15		740.61			070.42	056.94	13.48	0.870
16	748.84				061.38	047.18	14.20	0.861
17	740.61				051.69	036.51	15.18	0.867
18					041.53			
19					030.98			

Table 11

J	$\Delta_2 F''(J)^i$			$\dfrac{\Delta_2 F''(J)^i}{J + 1/2}$
	$(8 \leftarrow 0)^i$	$(10 \leftarrow 0)^i$	Ave.	
0				
1				
2				
3				
4				
5				
6	13.22		13.22	2.034
7			-----	
8	17.00		17.00	2.000
9	19.19	19.39	19.29	2.030
10	21.03	----	21.03	2.003
11	----	----	----	---
12	----	25.69	25.69	2.055
13	27.02	27.64	27.33	2.024
14	29.24	29.51	29.38	2.026
15	----	----	------	---
16		33.91	33.91	2.055

The above bands account for all the strong lines and some of the weaker ones in the region studied, but leave unexplained the vast majority of weak lines. However, so far only the molecule $Cl^{35}F$ has been considered; the $Cl^{37}F$ molecule will also give rise to a band system, identical in appearance with the $Cl^{35}F$ system and describable in the same manner but with slightly different constants.

We consider here the change in the rotational constants. The value for B_e is given by[11]:-

$$B_e = \frac{h}{8\pi^2 c \mathcal{M} r_e^2} \qquad \dots\dots\dots\dots\dots (10)$$

It is convenient to define a quantity ρ :-

$$\rho = \sqrt{\frac{\mathcal{M}}{\mathcal{M}^i}} \qquad \dots\dots\dots\dots\dots (11)$$

Then, it is seen that $B_e^i = \rho^2 B_e$. A more complete treatment[12] indicates that $\alpha_e^i = \rho^3 \alpha_e$, $D_e^i = \rho^4 D_e$, and $\mathcal{B}_e^i = \rho^5 \mathcal{B}_e$. We so obtain:

$$B_v^i = B_e^i - \alpha_e^i (v + \tfrac{1}{2}) = \rho^2 B_e - \rho^3 \alpha_e (v + \tfrac{1}{2})$$

$$= \rho^2 B_v - \rho^2 (\rho - 1) \alpha_e (v + \tfrac{1}{2})$$

In the next section of this thesis it is calculated that $\rho = 0.99055$. Hence the second term on the right in the above equation is very small compared to the first and we can say $B_v^i = \rho^2 B_v$, or

$$\Delta_2 F^i (J) = \rho^2 \Delta_2 F(J) \qquad \dots\dots\dots\dots\dots (12)$$

Using the values of $\Delta_2 F^i$ calculated in this manner as an aid, it was possible to pick out the isotope bands corresponding to two of the bands previously found, namely, the $10 \leftarrow 0$ and $8 \leftarrow 0$ bands. The lines belonging to these isotope bands, labeled $(10 \leftarrow 0)^i$ and $(8 \leftarrow 0)^i$, are listed in Table 10 along with the values of $\Delta_2 F'(J)$.

In Table 11 the values for $\Delta_2 F''(J)$ obtained from the two bands are compared.

Next the positions of the band origins were determined. It is seen from Equation 9 that

$$R_{(J-1)} + P_{(J)} = 2\nu_0 + 2(B' - B'')J^2 \quad \ldots\ldots\ldots (13).$$

Hence if one picks out an approximate value for $B' - B''$, say $\overline{B' - B''}$, and plots the quantity $R_{(J-1)} + P_{(J)} - 2\overline{(B' - B'')}J^2$ against J^2, one will obtain a straight line whose intercept on the ordinate axis is $2\nu_0$ while the slope of the line will give the correction which must be applied to the approximate value of $B' - B''$ to obtain the true value of $B' - B''$. The terms involving D have been neglected in the above. They cause the line obtained to be slightly curved and introduce a slight correction into the values for $B' - B''$, but do not affect the extrapolated value of $2\nu_0$. As it was only desired here to obtain ν_0 accurately, the terms in D were ignored.

The results of such calculations are given in Table 12. In the third column of the table is listed ν_0, the band origin, as found by extrapolation of $R_{(J-1)} + P_{(J)} - 2\overline{(B' - B'')}J^2$ to $J = 0$; in the fourth and fifth columns are listed the approximate value of $\overline{B' - B''}$ used in the calculation and the actual value of $B' - B''$ when corrected for the slope of the resulting curve. When measured, the value of ν (band head) is given for later reference. It is estimated that the probable error in ν_0 in the bands listed is $\pm 0.05 \text{cm}^{-1}$, except for the $15 \leftarrow 0$ and $10 \leftarrow 1$ bands and the isotope bands where the number of points available for the extrapolation was very small, so that the probable error is perhaps four times the above figure. Similarly, the probable error in $B' - B''$ is estimated to be 0.002 cm^{-1}, save for the bands listed above where it is several times larger.

Table 12

Band	ν band head	ν band origin	$\overline{B' - B''}$ (assumed)	$B' - B''$ (corrected)
6 ← 0	20396.45	20395.82	0.24	0.233
7 ← 0	620.02	619.32	.245	.243
8 ← 0	821.53	820.37	.26	.258
9 ← 0	997.53	996.94	.275	.272
10 ← 0	21146.05	21145.54	.30	.288
14 ← 0	---	445.87	.40	.384
15 ← 0	---	479.95	.40	.407
8 ← 1	20047.1	20047.04	.25	.259
10 ← 1	---	372.07	.29	.287
$(8 ← 0)^i$	---	803.60	.25	.248
$(10 ← 0)^i$	---	134.31	.30	.295

It has been mentioned that in between bands 10 ← 0 and 14 ← 0 there is a region of broad diffuse lines. Some of these lines come from the band 14 ← 0, in which the lines are sharp near the head (or origin) but begin to become diffuse in both branches at about $J'' = 14$. However, it is seen from Table 7 that the perturbation causing this broadening does not cause any great displacements of line position. There are three more band heads in this region which have not been mentioned yet; those designated 11 ← 0, 12 ← 0, and 13 ← 0. These can be seen in Figures 3 and 4. In two of the bands, 12 ← 0 and 13 ← 0, there is not a trace of observable structure, even the heads being **too** diffuse to measure on the comparator. The band 11 ← 0 has a little structure for as can be seen from Figure 3 and 4, there is a branch of very diffuse lines converging to a head. On a four-fold enlargement these lines have a definite doublet structure, indicating they consist of smeared together P and R branch lines. The centers of these as determined by measurement on the comparator are given in Table 13. It is seen that in the band 11 ← 0 there is some regularity, but there is considerable perturbation in the positions of several of the lines.

The positions of the band heads of these three diffuse bands were found from measurements on a microphotometer plate containing traces of chlorine fluoride spectrum and of the adjoining iron arc spectrum. The plate microphotometered having previously been measured on the comparator, the interpolation formula and correction curve then obtained **were** used to calculate the frequencies from the measurements on the trace.

Table 13

m^*	ν	$\Delta\nu$
1	21236.9	4.6
2	232.3	6.2
3	226.1	5.9
4	220.3	7.2
5	213.1	8.6
6	204.5	
7	---	
8	187.1	13.3
9	173.8	9.1
10	164.7	9.3
11	155.4	

*This numbering is arbitrary.

Table 14

Band	$\nu_{\text{band head}}$
11 ← 0	21255.5
12 ← 0	338.3
13 ← 0	398.4
16 ← 0	499.8
17 ← 0	507.8

Also measured in the same way were two bands, $16 \leftarrow 0$ and $17 \leftarrow 0$, to the high-frequency side of the $15 \leftarrow 0$ band. The positions of these last five bands heads are given in Table 14. The probable error in these values is $\pm 2 \text{cm}^{-1}$, the error coming almost entirely from the possible error in the choice of the point on the trace to be taken as the band head. It is of course impossible to find the band origins for these bands, but it is seen from Table 12 that the separation of band head and band origin is of the order of one wave number for the other bands of the progression. Hence, within experimental error, the band origin and band head may be taken as coincident for the bands listed in Table 14.

V.   The Chlorine Fluoride Spectrum
Analysis of the Vibrational Structure
Determination of the Vibrational Constants.

An analysis of the vibrational structure of the band system may now be carried out, using the accurate values for the band origins previously obtained. It is at once apparent from the values of ν_0 and from the rotational analysis that the bands can be arranged into two V' progressions, one consisting of 12 bands, the other of two bands. There are also two isotopic bands which belong to the first of these progressions. Then the Deslandres table for the bands must be as given in Table 15, where for the present the numbering of the bands is to be taken as tentative.

Table 15

V' \ V''	0	ΔG	Δ²G	1
6	20395.82			
		223.5		
7	619.32		22.45	
		201.05		
8	820.37		24.48	20047.04
		176.37		(773.33)
9	996.94		27.97	
		148.60		
10	21145.54		38.6	20372.07
		110.0		(773.47)
11	255.5		27.2	
		82.8		
12	338.3		22.7	
		60.1		
13	398.4		12.6	
		47.5		
14	445.87		13.4	
		34.08		
15	479.95		14.3	
		19.9		
16	499.8		11.8	
		8.0		
17	507.8			

Isotope bands

V' \ V''	0
8	20808.60
9	----
10	21134.31

Since most of the molecules in a gas are in their lowest vibrational level, it is expected that the lowest level observed has $v'' = 0$. This is found to be the case in almost all studies of the absorption spectra of other molecules. Since a rather long v' progression is observed for chlorine fluoride, the Condon parabola[13] must be of the open type. This in turn requires that if the lowest vibrational level in the ground state does not give rise to the strong observed v' progressions, it must give rise to a continuum at shorter wave lengths.

Because of the chlorine dioxide bands, it is impossible to say that such continuum is absent. However, it can be said that there are no bands of chlorine fluoride to the short wave length side of λ 4650 with intensity as much as one-tenth the intensity of the $10 \leftarrow 0$ band. From the approximate value of $\omega_e = G_{(1)} - G_{(0)} = 773.40$ cm^{-1}, it is calculated from the Boltzman expression that the ratio of the number of molecules in a given level to the number in the next higher level is for low v'' roughly forty to one. The intensity of an electronic band is the product of two factors, the population of the initial state and the transition probability between the initial and final states. Therefore, it is necessary that if a level exists corresponding to $v'' = -1$, the transition probability for the band $10 \leftarrow -1$ must be only one-four hundredth of the transition probability for the band $10 \leftarrow 0$. This is a very large ratio for adjacent bands in the Deslandres table, especially as the vibrational frequency in the ground state is fairly high so that the amplitude of oscillation does not change much with v'' for v'' small. Hence it may be concluded that although the numbering in the ground state might possibly be wrong, the chance that such is the case is negligibly small. Additional evidence in favor of the conclusion

that the selected numbering in the lower state is correct is obtained
from the potential curves for the chlorine fluoride molecule which
are discussed in a later section of this thesis.

The bands $v' \leftarrow 1$ are perhaps one-fifth as strong as the bands
$v' \leftarrow 0$. This indicates that the transition probabilities for the
former bands are eight times as large as the transition probabilities
for the latter bands, a not unreasonable factor. Very weak lines were
observed in the region in which bands having $v'' = 2$ would appear, but
these lines might equally well arise from transitions $v' \leftarrow 1$ with
v' equal to or less than six.

With the numbering of the lower state fixed, the isotopic shift
can now be used to determine the absolute numbering of levels in the
upper state. It is first necessary to fit an equation of the form of
equation 7 to the progression $v'' = 0$. It is clear from the first and
second differences given in Table 15 that no simple quadratic or cubic
in $(v' + 1/2)$ will fit all the bands of this progression. This is to
be expected, for the perturbation which destroys the rotational struct-
ure for the bands $11 \leftarrow 0$, $12 \leftarrow 0$ and $13 \leftarrow 0$ surely also affects the
vibrational levels. Such a perturbation usually requires that the levels
above the perturbation region be fitted by an equation appreciably dif-
ferent from the equation fitting the levels below the perturbed region.
It is evident from Table 15 that only the *bands* $6 \leftarrow 0$ to $10 \leftarrow 0$ can
be fitted by a simple equation.

It is necessary here to write the equations for the vibrational
isotope effect. We start with Equation 7:-

$$\nu = \nu_e + \omega_e'(v' + 1/2) - \omega_e'x_e(v' + 1/2)^2 + \omega_e'y_e'(v' + 1/2)^3 + \ldots\ldots$$

$$-\left[\omega_e''(v'' + 1/2) - \omega_e''x_e''(v'' + 1/2)^2 + \ldots\ldots\ldots\right]. \quad (14)$$

It is well known that

$$\omega_e = \frac{1}{2\pi c}\sqrt{\frac{k_e}{\mu}} \quad \dots\dots\dots\dots\dots\dots \quad (15)$$

where k_e is the bond force constant. Hence it is seen that for the isotopic molecule, $\omega_e^i = \rho\omega_e$, where ρ is as defined before; it can also be shown that the dependance of the other vibrational constants on ρ is: $\omega_e^i x_e^i = \rho^2 \omega_e x_e$ and $\omega_e^i y_e^i = \rho^3 \omega_e y_e$. The positions of the band origins for the isotopic molecules will then be given by :

$$\nu^i = \nu_e + \rho\omega_e'(v' + 1/2) - \rho^2\omega_e'x_e'(v' + 1/2)^2 + \rho^3\omega_e'y_e'(v' + 1/2)^3 +$$
$$- \left[\rho\omega_e''(v'' + 1/2) - \rho^2\omega_e''x_e''(v''+ 1/2)^2 + \dots\dots\dots\right](16)$$

The isotopic displacement is :

$$\nu - \nu^i = (1 - \rho)\omega_e'(v' + 1/2) - (1 - \rho^2)\omega_e'x_e'(v' + 1/2)^2$$
$$+ (1 - \rho^3)\omega_e'y_e'(v' + 1/2)^3 + \dots\dots$$
$$- \left[(1 - \rho)\omega_e''(v'' + 1/2) - (1 - \rho^2)\omega_e''x_e''(v'' + 1/2)^2 + \dots\right]\dots (17)$$

As ρ is usually very nearly equal to one, the only **exceptions** being the molecules containing hydrogen or deuterium, the approximation may be made that :

$$1 - \rho^2 = (1 - \rho)(1 + \rho) = 2(1 - \rho)$$
$$1 - \rho^3 = (1 - \rho)(1 + \rho + \rho^2) = 3(1 - \rho) \quad \dots\dots\dots\dots \quad (18)$$

Equation 17 can then be simplified:-

$$\nu - \nu^i = (1 - \rho)\left\{\omega_e'(v' + 1/2) - 2\omega_e'x_e'(v' + 1/2)^2\right.$$
$$+ 3\omega_e'y_e'(v' + 1/2)^3 + \dots\dots$$
$$\left. - \left[\omega_e''(v'' + 1/2) - 2\omega_e''x_e''(v'' + 1/2)^2 + \dots\right]\right\}\dots\dots(19)$$

As bands were found involving only two vibration levels in the lower electronic state, the values of $\omega_e'' x_e''$ cannot be obtained, but only $G''_{(1)} - G''_{(0)} = \omega_e'' - 2\omega_e'' x_e''$. We wish to examine the isotope shift in the progression $v'' = 0$, so that the quantity desired is as seen from equation 19, $1/2\,\omega_e'' - 1/2\,\omega_e'' x_e''$. As $\omega_e x_e$ is only about one percent of ω_e, the approximation can evidently be made that

$$1/2\,\omega_e'' - 1/2\,\omega_e'' x_e'' = 1/2(\,G''_{(1)} - G''_{(0)}) + 1/2\,\omega_e'' x_e''$$

$$\approx 1/2\left[G''_{(1)} - G''_{(0)}\right] = 386.70\,\text{cm}^{-1}.$$

The error in $v - v^i$ arising from this assumption is at most $0.1\,\text{cm}^{-1}$.

We might now calculate ρ. From a summary by Hahn[14] we have for the atomic weights:- $F^{19} = 19.0045$, $Cl^{35} = 34.9803$, $Cl^{37} = 36.9779$, (Aston scale, $O^{16} = 16.0000$). Thus, in atomic weight units,

$$\mu_A = \frac{(34.9803)(19.0045)}{53.9848} = 12.3140, \quad \mu_A^{\,i} = 12.5529$$

and $\rho = \sqrt{\dfrac{\mu}{\mu^i}} = 0.99045$. Substituting the numerical values just obtained in equation 19, we have

$$v - v^i = 0.00955\left\{\omega_e'(\,v' + 1/2) - 2\,\omega_e' x_e'(\,v' + 1/2)^2 + \right.$$

$$\left. 3\,\omega_e' y_e'(\,v' + 1/2)^3 - 386.70\right\}.$$

It was found that no quadratic in $(v' + 1/2)$ would fit the progression of bands $6 \leftarrow 0$ to $10 \leftarrow 0$ in a satisfactory manner, but that with the addition of a cubic term the experimental data could be fitted fairly well over a considerable range of $\omega_e' x_e'$ and $\omega_e' y_e'$. As the isotope shift calculated might depend on the choice made, three different equations were fitted to the band origins. The isotope shifts were then calculated, using each equation with several choices for the v' numbering. The three equations, the equations for the isotopic shift

obtained therefrom, and a comparison of the values calculated from the several equations with the experimental values are given in Table 16. The isotopic shifts are given not only for the V' numbering finally chosen but also for the cases where the number assigned a given band is **increased** or decreased by one. It is to be noted that the change of variable required for such a new choice of V' ($V' = \overline{V}' - 1$ in order to increase the number on each band by one) must be made in equation 14, the equation for the band origins, and then a new equation 20 for the isotope shift calculated; the change of variable cannot be made directly in equation 20.

Equation 21 is the best quadratic in ($V' + 1/2$) through the experimental points, and equation 21a is the corresponding equation for the isotope shift. It is seen that there are deviations from the experimental values of over a wave number, many times any possible experimental error. Equation 22, with a large negative value for $\omega'_e y'_e$, fits the data very well, but has a negative value for $\omega'_e x'_e$. This last means that the spacing of the vibrational levels for low V' would be contrary to the spacing generally observed. As one purpose of this equation is to give reasonable extrapolation to $V' = -1/2$, a third equation, equation 23, was arbitrarily selected as a compromise between equations 21 and 22. This equation fits the data in a satisfactory manner and also has a value for $\omega'_e x'_e$ of the same order of magnitude as is usually found.

It is seen by an inspection of the isotope shifts as given in Table 16 that all three equations give essentially the same result. The numbering chosen yields very satisfactory agreement with experiment for $V' = 8$, but poor agreement for $V' = 10$. If the number assigned to each band is increased by one, then satisfactory agreement is obtained

Table 16

$$\nu = 18336.11 + 396.80(V' + 1/2) - 12.300(V' + 1/2)^2 \qquad \ldots\ldots\ldots (21)$$

$$\nu = 18618.48 + 292.604(V' + 1/2) + 0.304(V' + 1/2)^2 - 0.500(V' + 1/2)^3 \quad (22)$$

$$\nu = 18561.65 + 313.484(V' + 1/2) - 2.217(V' + 1/2)^2 - 0.400(V' + 1/2)^3 \ldots (23)$$

V'	$\nu_{expt.}$	ν_{calc}, eq.21	ν_{calc}, eq.22	ν_{calc}, eq.23
6	20395.82	20395.64	20395.93	20395.78
7	20619.32	620.24	619.17	619.32
8	20820.37	820.24	820.51	820.44
9	20996.94	995.64	996.96	996.71
10	21145.54	21146.44	21145.52	21145.76
11	(21255.5)	272.64	263.19	265.17
12	(21338.3)	374.24	346.96	352.54
13	(21398.4)	451.24	393.85	405.49
14	21445.87	503.64	400.84	421.59
15	21479.95	531.44	364.94	398.47
16	(21499.8)			----
17	(21507.8)			224.91

$$\nu - \nu^i = \Delta\nu = 0.00955 \quad 396.80(V' + 1/2) - 24.600(V' + 1/2)^2 - 386.70 \qquad \ldots\ldots (21a)$$

$$\Delta\nu = 0.00955 \quad 292.604(V' + 1/2) + 0.608(V' + 1/2)^2 - 0.500(V' + 1/2)^3$$
$$- 386.70 \qquad \ldots\ldots (22a)$$

$$\Delta\nu = 0.00955 \quad 313.484(V' + 1/2) - 4.434(V' + 1/2)^2 - 0.400(V' + 1/2)^3$$
$$-386.70 \ldots (23a)$$

V'	$\Delta\nu_{expt.}$	Eq.21a		Eq.22a		Eq.23a	
		$\Delta\nu_{calc}$	$\Delta\nu_{exp.} - \Delta\nu_{calc}$	$\Delta\nu_{calc}$	$\Delta\nu_{exp.} - \Delta\nu_{calc}$	$\Delta\nu_{calc}$	$\Delta\nu_{expt.} - \Delta\nu_{calc}$
8	11.77	11.55	0.22	11.68	0.09	11.65	0.12
10	11.23	10.20	1.03	9.70	1.53	9.81	1.42
If V' is decreased by one							
7	11.77	9.75	2.02	9.87	1.90	9.84	1.93
9	11.23	8.88	2.35	8.43	2.80	8.51	2.72
If V' is increased by one							
9	11.77	13.34	−1.57	13.49	−1.72	13.46	−1.69
11	11.23	11.52	−0.29	10.98	+0.25	11.09	+0.14

for v' = 11 but very poor agreement for v' = 9. If v' is decreased by one, the agreement is entirely unsatisfactory; similarly if v' is increased by two the agreement is not satisfactory.

There are two reasons for choosing the v' given rather than v' increased by one. First, the numbering chosen does give slightly better agreement than the alternative given. Second, and more important, the data on the $(8 \leftarrow 0)^{i}$ band *are* more complete and *are* believed to be more reliable than the data on the $(10 \leftarrow 0)^{i}$ band. Hence, the numbering giving *best* agreement with the data on the $(8 \leftarrow 0)^{i}$ band was sellected.

It might be pointed out that although the v' numbering is uncertain by 1, the quantities useful in thermodynamic calculations and hence of interest to the chemist, the dissociation energy D_o'', ω_e'', $\omega_e''x_e''$, B_e'', all relate to the lower state and are independent of the numbering in the upper state.

VI. The Chlorine Fluoride Spectrum

Determination of the Rotational Constants.

The rotational constants of chlorine fluoride can now be obtained. Substituting Equation 3 in Equation 8 it is found that

$$\Delta_2 F_v(J) \equiv F_v(J + 1) - F_v(J - 1)$$

$$= (4B_v - 6D_v)(J + 1/2) - 8D_v(J + 1/2)^3$$

Hence, if the values of $\Delta_2 F_v(J)$ are known, $\dfrac{\Delta 2F_v(J)}{(J + 1/2)}$ can be calculated and plotted against $(J + 1/2)^2$, and a straight line fitted to the points. Then, the value of the ordinate at $(J + 1/2)^2 = -3/4$ gives $4B_v$ and the slope of the line gives $8D_v$. Actually, in these experiments the ex-

trapolation was made to $(J + 1/2)^2 = 0$, $6D_v$ being negligible in comparison with $4B_v$.

The $\Delta_2F''_{v(J)}$ and $\Delta_2F'_{v(J)}$ values obtained from the analysis of the various bands have already been tabulated in Tables 3 through 11. From these, or from the average Δ_2F where several bands have a common state, the $\dfrac{\Delta_2F_{(J)}}{J + 1/2}$ values were calculated. The results of these calculated are also given in Tables 3 through 11. On plotting the $\dfrac{\Delta_2F_{(J)}}{J + 1/2}$ it was found that the data in general were too scattered and were not available for sufficiently high values of J to permit the determination of D_v with any accuracy.

Data is available for only two levels of the lower state $v'' = 0$ and 1. Here, as suggested by Herzberg[15], a theoretical value for D_v from the equation $D_e = \dfrac{4B_e^3}{\omega_e^2} \ldots$ was used in calculating B_v. While ω_e''

$$\cdots (26)$$

is not known, the error introduced by using $G_{(1)} - G_{(0)}$ in its place is small, as is also the error introduced by neglecting β_e and so assuming $D_v = D_e$. A preliminary estimate of B_e, made by a very rough extrapolation of $\Delta_2F''_{0(J)}$ and $\Delta_2F''_{1(J)}$, yielding $B_e'' = 0.52$, we have

$$D'' = \frac{4(0.52)^3}{(773)^2} = 0.94 . 10^{-6}$$

Using $8D''$ as the slope, the best straight line through the experimental Δ_2F'' values was then drawn. The intercepts on the $\dfrac{\Delta_2F''}{J + 1/2}$ axis were $4B_0'' = 2.061$, $4B_1'' = 2.036$. From these, making an estimate of the probable error, we obtain:-

$$B_0'' = 0.5152 \pm 0.0005 \text{ cm}^{-1}$$

$$B_1'' = 0.5090 \pm 0.0015 \text{ cm}^{-1}$$

The rotational constants in the ground state of ClF are therefore

$$B_e{}'' = 0.5183 \pm 0.0010 \text{ cm}^{-1}$$

$$\alpha_e{}'' = 0.0062 \pm 0.0017 \text{ cm}^{-1}$$

From these the internuclear distance can be determined by the use of equation 10. We find

$$r_e{}'' = 1.6255 \pm 0.002 \quad 10^{-8} \text{ cm}$$

$$r_o{}'' = \quad 1.6304 \pm 0.001 \quad 10^{-8} \text{ cm.}$$

The data for the isotopic bands are too few to permit a very accurate determination of $B_o{}''{}^i$. However, taking

$$D_o{}''{}^i = \rho^4 D_o{}'' = 0.90 \cdot 10^{-6}, \text{ we obtain from the}$$

experimental data $4B_o{}''{}^i = 2.03$,

$$B_o{}''{}^i = 0.5075 \pm 0.005 \text{ cm}^{-1}, \text{ in satisfactory agree-}$$

ment with $\rho^2 B_o{}'' = 0.5050 \text{ cm}^{-1}$.

To obtain the rotational constants in the upper state, the values of $\dfrac{\Delta_2 F_v{}'(J)}{J + 1/2}$ were plotted against $(J + 1/2)^2$. Let us first consider those levels with $v' = 6$, to 10. These levels are in the region of large anharmonicity of the potential function, as is evidenced by the equation necessary to fit the band origins, Equation 23. Hence it is not to be expected that the values for D_v will be even approximately equal to $D_e \simeq \dfrac{4B_e{}^3}{\omega_e{}^2}$. The method used to obtain D_v' and B_v' was to first draw through the experimental value for $\dfrac{\Delta_2 F'}{J + 1/2}$ a straight line that seemed reasonable and determine a tentative B_v and D_v. From these B_v and B_e was calculated and then a D_e, using Equation 26 and ω_e' from Equation 23. The values for D_v were then plotted against V and a smooth curve taken.

It was found that the sign of D_8' was opposite to the sign for

D_v' for $v' \neq 8$; this arises from the overlapping of the P and R branches in this band, so that a mean value was measured on the comparator. Enough data is available on this band to make quite a good determination of B_8' without assuming a D_8' and it is seen that this value agrees well with the B_v's for the other bands

The curve taken appears quite arbitrary, as an attempt was made to weight the various points on a basis of how definitely the $\dfrac{\Delta_2 F(J)}{J + 1/2}$ values determined the slope of the line through them. Using the smoothed values of D_v, the final values of B_v were obtained. These calculations are summarized in Table 17. In the second and third columns are the tentative values of B_v and D_v selected, in the fourth column the smoothed value of D_v, and in the fifth column the final values of B_v. Also listed are the values of B_v and D_v as calculated for $v = -1/2$, that is, B_e and D_e. From B_e', we calculate $r_e' = 1.92$ Å. There is no method of estimating the departure from linearity of the dependence of B_v' on $v' + 1/2$, so no estimate can be made as to the accuracy of B_e' and r_e'. In fact, all that can be said is that the B_e' and r_e' given represent the experimental data over the limited range $6 \leqslant v' \leqslant 10$. The estimated probable error in the B_v values is ± 0.001 cm^{-1}, except for $v' = 8$, where the error might be larger.

Taking $D_v'^{i} = \rho^4 D_v'$, it is found that $B_8'^{i} = 0.253$, $B_{10}'^{i} = 0.219$. From the B_v' of Table 17 we have $\rho^2 B_8' = 0.250$ and $\rho^2 B_{10}' = 0.222$, which is satisfactory agreement.

There is no simple way of predicting D_v' for the levels with $v' = 14$ and 15. From the few values of $\dfrac{\Delta_2 F'}{J + 1/2}$, available for these bands it is estimated that

Table 17

v'	$4B_v'$ cm^{-1} tentative	$8D_v'$ cm^{-1} tentative	$8D_v'$ cm^{-1} smoothed	B_v' cm^{-1} final value	$\neq B_v'$ calc. cm^{-1}
6	1.122	2.10^{-5}	$1.7 \cdot 10^{-5}$	0.280	0.282
7	1.076	$1.5.10^{-5}$	2.0	.270	0.268
8*	(1.018)	$(-2.4 \cdot 10^{-5})$	----	(0.254)	0.255
9	0.968	$2.8 \cdot 10^{-5}$	3.4	0.243	0.241
10	0.899	$5.6 \cdot 10^{-5}$	5.2	0.224	0.227
$-1/2$	1.493	$1.7 \cdot 10^{-5}$		0.372	
	$4\alpha_e' = 0.056$			$\alpha_e' = 0.0138$	
14	0.530			0.132	
15	0.450			0.112	

*See discussion in text on pg. *45*.

$\neq B_v'$ calc $= 0.372 - 0.0138(v' + 1/2)$

$$B_{14}' = 0.132 \pm 0.003 \text{ cm}^{-1}$$

$$B_{15}' = 0.112 \pm 0.005 \text{ cm}^{-1}$$

For convenience, these also are listed in Table 17. One sees that B_v' is now very rapidly approaching zero. This can be explained classically as resulting from the vibrational energy of the molecule being very near the dissociation limit, so that the particle spends a large part of its time at large r where the potential energy changes very slowly with r.

The results of these calculations of B_v values are in agreement with the values for $B' - B''$ obtained in the determination of the band origins. The values of $B' - B''$ found in this manner, tabulated in Table 12 are given again in Table 18, where they are compared with the difference of B' and B'' as obtained from the extrapolation of $\dfrac{\Delta_2^F}{J + 1/2}$. In view of the probable error previously assigned to the quantities listed, the agreement is entirely satisfactory.

It has been mentioned several **times** previously that in the bands $8 \leftarrow 0$, $(8 \leftarrow 0)^i$ and $8 \leftarrow 1$ the P and R branch lines overlap. The reasons for and results of this overlapping are here described. Let us calculate the separation of the lines $R_{(J + n)}$ and $P_{(J)}$. From Equations 9 we obtain

$$R_{(J + n)} - P_{(J)} = 2B' + (3B' - B'')(J+n) + (B'-B'')(J+n)^2 + (B'+B'')J - (B'-B'')J^2$$

$$= (2J+n+1)\left[2B'+n(B'-B'')\right] \quad \ldots\ldots\ldots\ldots (27)$$

If these lines of the P and R branches exactly coincide, it is evident that we must have $B' = \dfrac{n}{n+2} B$. When this relationship is approximately satisfied, say

$$B'' = \frac{n+2}{n} B' - \alpha, \quad \text{then}$$

$$R_{(J+n)} - P_{(J)} = n\alpha(2J + n + 1) \quad \ldots\ldots\ldots\ldots (28).$$

From the rotational analysis it is found that $B' \approx \frac{1}{2}B''$ and n = 2 for the

Table 18

Band	From the $\Delta_2 F/(J+1/2)$ Values			From ν_0 calc.
	B''	B'	$B'' - B'$	$B'' - B'$
$6 \leftarrow 0$	0.515	0.280	0.235	0.233
$7 \leftarrow 0$	.515	.270	.245	.243
$8 \leftarrow 0$	.515	.254	.261	.258
$9 \leftarrow 0$	.515	.243	.272	.272
$10 \leftarrow 0$	.515	.224	.291	.288
$14 \leftarrow 0$	.515	.132	.383	.384
$15 \leftarrow 0$	.515	.112	.403	.407
$8 \leftarrow 1$	0.509	.254	.255	.254
$10 \leftarrow 1$	.509	.224	.285	.287
$(8 \leftarrow 0)^i$	.508	0.253	.255	.248
$(10 \leftarrow 0)^i$	.508	.219	.289	.295

bands mentioned above. It is obvious that this relation cannot hold exactly for both the bands $8 \leftarrow 0$ and $8 \leftarrow 1$, for they have the same B' and different B''. On examining the photographic plates it was observed that the lines of the band $8 \leftarrow 1$ were quite narrow, only slightly broader than normal single lines of the same intensity, but that the lines of the band $8 \leftarrow 0$ were very much broadened, of the lines for high J $(J > 30)$ having a width of about one wave number. This is exactly what one calculates from the values of B found. We have

$$B_8{}' = 0.254 \text{ cm}^{-1}$$

$$B_0{}'' = 0.515$$

$$B_1{}'' = 0.509$$

It is seen that $B_1{}''$ is exactly twice $B_8{}'$ within less than experimental error. For the $8 \leftarrow 0$ band we calculate from Equation 28, putting $n = 2$ and $J = 30$,

$$R_{(J+2)} - P_{(J)} = 2 \alpha (2J + 3) = 2(-.007)(63) = -0.9$$

If $R_{(J + 1)} - P_{(J)}$ is calculated from Equation 3 without neglecting the terms involving D' and D'', it is found that even if $B' = \dfrac{n}{n + 2} B$, $R_{(J + n)} - P_{(J)}$ is not equal to zero but is a function of D', D'' and terms in J up to J^3. This separation is negligible for small J and need not be considered here, but if it would cause the coinciding lines to be separated if the bands could be followed out to $J = 40$.

It is evident that the quantity determined by measurement on a band with overlapping P and R branch lines is actually $\dfrac{R_{(J+n)} + P_{(J)}}{2}$.

From Equation 28, we see that for $n = 2$, $R_{(J + n)} - P_{(J)}$ approaches zero as J approaches $-3/2$, and will be very small at $J = 0$. Hence it is expected that any quantity involving $R_{(J)}$ or $P_{(J)}$ which is extrapolated to $J = 0$ will give very nearly the true value. However, any quantity

determined from the rate of change of the $R_{(J)}$ or $P_{(J)}$, that is, any quantity derived from the slope of a curve of a function of $R_{(J)}$ and $P_{(J)}$ plotted against J is likely to be in great error. Thus it was found that the values of B', and B'' and ν_o obtained for the bands mentioned were consistent with the results on the other bands, but the values for D', obtained from the slopes of curves were meaningless. In calculating $\Delta_2 F''_o$ values, where data is available from seven bands, it is seen from Table 8 that the $\Delta_2 F''_o$ obtained from band 8 ← 0 do not deviate systematically for low J from the $\Delta_2 F_o''$ obtained from the other bands, but that for high J there is a considerable deviation. Hence, the $\Delta_2 F_o''(J)$ obtained from the band 8 ← 0 for J greater than 28 were ignored in calculating B_o''.

As a check on the correctness of the analysis we might see how well Badger's rule on the relation of internuclear distance for frequency holds in this molecule.[15] The rule states that

$$r_e = \left(\frac{C_{ij}}{k_e}\right)^{1/3} + d_{ij} ,$$

where for ClF, a molecule composed of one atom from the first row and one atom from the second row of the periodic table, $(C_{ij})^{1/3} = 0.535$ and $d_{ij} = 0.94$. It has been shown earlier in this paper that

$$\omega_e'' \approx 773.40 \text{ cm}^{-1} \qquad \omega_e' = 313.5$$

$$r_e'' \approx 1.63 \qquad r_e' = 1.92$$

From Equation 15, we obtain, introducing appropriate values for the constants and the reduced mass

$$k_e = 4\pi^2 \mu c^2 \nu_e^2 = .725 \omega_e^2$$

$$k_e'' = 0.433 \cdot 10^{+6} \text{ dynes cm.}, \quad k_e' = 0.0712 \cdot 10^6$$

and hence we calculate

$$r_e'' \text{calc.} = 1.64_5 \qquad r_e' \text{ calc.} = 2.23$$

The agreement is very good in the ground state. In the excited state, the agreement is very poor, but as has been remarked previously, no real significance can be given to the values of ω_e' and B_e' (or r_e'), as there is no reason to believe that the extrapolations from v' = 6 to v' = -1/2 are the correct one. The large difference between r_e' and r_e'calc. leads one to believe that at least one of the extrapolations is badly off. It would surely be possible to find values for ω_e' and B_e' consistant with the spectroscopic data and satisfying Badger's rule, but for such values to have meaning it would be necessary to show the solution unique. As there is no great interest in the values of B_e' and ω_e', it was not thought worthwhile to attempt this.

VII. The Chlorine Fluoride Spectrum.

Determination of the Dissociation Energy and Potential Curve.

The dissociation energy of a molecule, a quantity of very great interest to the chemist, can under favorable circumstances be determined with very great accuracy spectroscopically. The dissociation energy D_o is defined to be the energy required to separate into two normal atoms a molecule in its lowest vibrational level. If a (v' ← 0) progression is observed which permits a reasonable extrapolation to a convergence limit, at which the molecule in the excited state dissociates into atoms, it is seen that if the energies relative to the normal atoms of the products of this dissociation are known the dissociation limit can be directly obtained.

In ClF, the convergence limit is easily obtained. Following the usual proceedure, $\Delta G_{v+\frac{1}{2}}' \equiv G_{v+1}' - G_v'$ for the (v' ← 0) progression is plotted against v'. A plot of the values of the $\Delta G_{v+1/2}'$ obtained from Table 15 against v'

is given in Figure **5**. The experimental points are represented by **circles**, the size of the larger circles representing the probable error in those points, the smaller circles representing a probable error of 0.1 cm^{-1}. The curve drawn for $v' < 9$ is the one calculated from Equation 23. For $9 < v' < 12$, the perturbations in the vibrational levels are too large to permit any reasonable curve to be drawn, but for $v' > 12$ a straight line fits all the points within experimental error. It is seen that this line cuts the axis $\Delta G = 0$ at $v' = 16.6$. From this it will be concluded that the $17 \leftarrow 0$ band is the last band of the progression. Allowing for the rather large possible error in the measurement of the band head on the microphotometer trace and for the distance between band origin and band head, it may be written

$$\nu_{conv.\ lim.} = 21,507.8 \pm 2\ cm^{-1}.$$

The positions of the band origins of the $v' \leftarrow 0$ progression plotted against v' are also given in Figure **5**. Here the curve was drawn to correspond to Equation 23 for $v' < 10$, and to fit the experimental points for $v' > 10$.

There appears to be a very faint narrow region of absorption immediately to the violet, of the $17 \leftarrow 0$ band which might possibly correspond to another band. It is too weak to say definitely ~~but~~ *that* it is real, so the evidence given by the $\Delta G_{v+1\ 2}$ plot is taken and this possible band is neglected. In any case, it is separated from the $17 \leftarrow 0$ band by less than 2 cm^{-1}, the probable error given for the convergence limit.

We can immediately obtain D_o' and also D_e', the latter being the dissociation energy in the upper state measured from the minimum of the potential curve. Using Equation 23 to obtain the value of ν extrapolated to $v' = -1/2$ we obtain
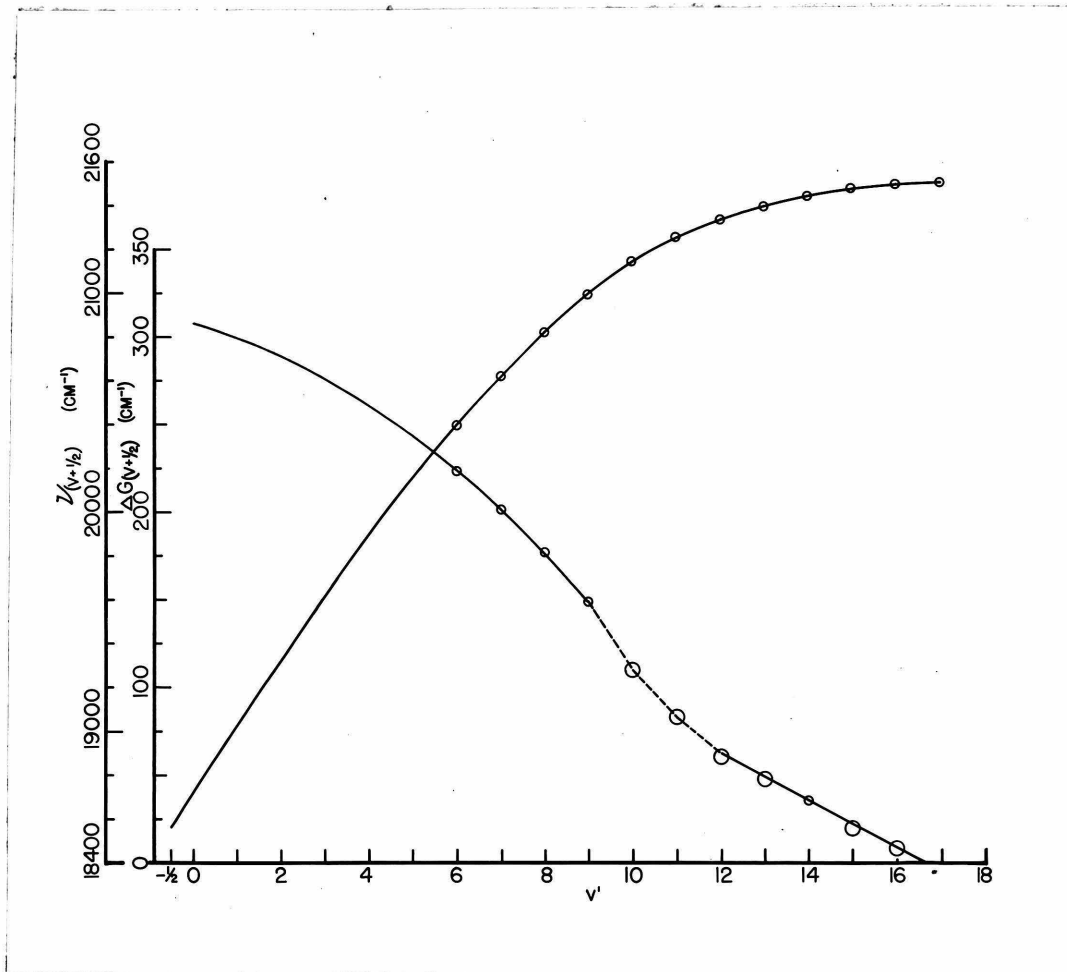
$$D_e' = 21\ 507.8 - 18561.6 = 2946\ cm^{-1}.$$

Figure 5.

Determination of the Convergence Limit

$D_0' = 21507.8 - 18561.6 + 1/2(313.5) - 1/4(2.2 - 1/8 (.4) = 2790 \text{ cm}^{-1}$.
As has been mentioned before, the extrapolation to $v' = -1/2$ is quite arbitrary, so that the above figure might be greatly in error. A reasonable value for the probable error in D' is 50 cm^{-1}.

To obtain D_0'' (and D_e'') it is necessary to know the products of the dissociation at the convergence limit. No attempt will be made in this thesis to discuss the electronic levels and their dissociation products, for that in itself is a subject for an entire thesis. The assumption will be made that chlorine fluoride electronic states resemble the iodine chloride states and, less closely, the chlorine, bromine and iodine states. Mulliken[16] has given a general discussion of the halogen spectra, in which he concludes that the absorption in the visible region is due to a $^3\Pi_0{}^+ \leftarrow {}^1\Sigma^+$ transition, with the $^3\Pi_0{}^+$ level an example of Hund's case C coupling. The $^1\Sigma^+$ ground state is formed from two normal atoms, both in the $2P_{3/2}$ state, while the $^3\Pi_0{}^+$ is formed from one normal atom in the $2P_{3/2}$ state, and one excited atom in the $2P_{1/2}$ state. There also exists a $^3\Pi_1$ state which lies below the $^3\Pi_0{}^+$ state and which is formed from two normal atoms in the $2P_{3/2}$ state. The transition $^3\Pi_1 \leftarrow {}^1\Sigma^+$ gives bands having P, Q and R branches while the transition $^3\Pi_0{}^+ \leftarrow {}^1\Sigma^+$ gives bands having only P and R branches.

In all visible and infra-red halogen spectra, the only states of the halogen atoms which need be considered are the two parts of the ^2P ground states, all other states having far too high term values. All the halogen atom doublets are inverted ($^2P_{3/2}$ lower than $^2P_{1/2}$), with separations I - 7598, Br - 3685, Cl - 881 and F - 407 cm^{-1}.

The spectra of all interhalogen compounds studied, are quite similar to the halogen spectra. Here again, in ICl, Brown and Gibson[17] find two

band systems corresponding to a $^3\Pi_1 \leftarrow {}^1\Sigma^+$ and to a $^3\Pi_0{}^+ \leftarrow {}^1\Sigma^+$ transition, the former having P, Q and R branches, the latter only P and R branches. Also there is very good evidence that the dissociation products of the $^3\Pi_0{}^+$ excited state are a normal $^2P_{3/2}$ iodine atom and an excited $^2P_{1/2}$ chlorine atom. It is observed in the ICl spectrum that the bands in the $^3\Pi_0{}^+ \leftarrow {}^1\Sigma^+$ system become very diffuse for $v' \geqslant 4$. This Brown and Gibson ascribe to the intersection of the potential curve of the $^3\Pi_0{}^+$ state by a repulsive 0^+ state arising from two normal $^2P_{3/2}$ atoms. Van Vleck[18] concurs with this explanation of the experimental observations, both as to the general nature of the states of the halogen and interhalogen molecules and as to the nature of the perturbation in the $^3\Pi_0{}^+$ state. The spectrum of iodine bromide has also been investigated by Brown,[19] who reports the spectrum to be similar in all particulars including the perturbation of certain levels in the $^3\Pi_0{}^+$ state, to the iodine chloride spectrum. As in the halogen and iodine chloride spectra, the two upper states have different convergence limits, their separation in IBr corresponding to the $^2P_{3/2} - {}^2P_{1/2}$ separation in bromine.

It is evident that the chlorine fluoride transition reported in this thesis resembles closely the $^3\Pi_0{}^+ \leftarrow {}^1\Sigma^+$ transitions in the halogen and interhalogen molecules. If a second band system had been observed in ClF with a convergence limit separated from the observed convergence limit by the $^2P_{3/2} - {}^2P_{1/2}$ separation in either chlorine or fluorine, the above assignment could be made with certainty. Although this was not observed (unfortunately, no serious attempt was made to locate it), the following points of similarity between the chlorine fluoride states and spectrum and the halogen states and spectra can be made:-

(1) The chlorine fluoride bands have only P and R branches, as do the halogen and other interhalogen $^3\Pi_0{}^+ \leftarrow$ $^1\Sigma$ bands. If one only assumes the ground state of ClF to be $^1\Sigma^+$ the lack of a Q branch requires that the upper state be an 0^+ state.

(2) In the chlorine fluoride spectrum, as in the $^3\Pi_0{}^+ \leftarrow$ $^1\Sigma$ band spectrum of iodine chloride and iodine bromide there is a perturbation of certain of the vibrational levels of the upper state.

(3) In the upper state of chlorine fluoride as in the $^3\Pi_0{}^+$ state of of the halogen and other interhalogen molecules, the energy of dissociation ~~of it~~ is low compared to the energy of dissociation of the ground state. There is a corresponding large increase of $r_e{}'$ over $r_e{}''$.

Since there is no reason to believe chlorine fluoride different from the other molecules mentioned, there is surely no doubt but that the chlorine fluoride upper state is a $^3\Pi_0{}^+$ state, which dissociates into one $^2P_{3/2}$ and one $^2P_{1/2}$ atom.

It is still necessary to decide which of the two atoms in chlorine fluoride goes into the $^2P_{1/2}$ state on the dissociation of the upper state. It seems reasonable to assume the products are $Cl(^3P_{3/2})$ and $F(^2P_{1/2})$ for the following two reasons:-

(1) In iodine chloride and iodine bromide the dissociation of the $^3\Pi_0{}'$ state gives the lowest possible energy state for the divided system with one atom excited, namely, $I(^2P_{3/2})$ and Cl or $Br(^2P_{1/2})$. In ClF the energy of the divided system is lowest with $Cl(^2P_{3/2})$ and $F(^2P_{1/2})$.

(2) The two $^3\Pi_0{}^+$ states of ClF formed from $^2P_{1/2}$ + $^2P_{3/2}$ will have the same symmetry. For large internuclear distance the separation is the difference in the doublet separations of chlorine and

fluorine, 474 cm^{-1}. This is quite small, so that as the atoms
approach one another there will be resonance between the states
resulting in first approximation from $Cl(^2P_{3/2})$ + $F(^2P_{1/2})$ and
$Cl(^2P_{1/2})$ + $F(^2P_{3/2})$. This resonance will cause a separation of
these states, causing the former (the lower) to be deepened and
the latter to be raised. It has been observed by Mulliken that
in halogens the dissociation energy of the $^3\Pi_0{}^+$ state (where,
of course, this resonance cannot exist, there being only one
state) is of the same order of magnitude as the doublet splitting
in the halogen atom. So we find:-

	F	Cl	Br	I
$D_0{}'$ =	---	3150	3730	6850
$^2P_{1/2} - {}^2P_{3/2}$ =	407	881	3685	7598

In chlorine fluoride $D_0{}'$ = 2790, just slightly smaller than in chlor-
ine. If the chlorine fluoride state observed rises from excited chlor-
ine, this D_0 corresponds to the upper of the two possible states, for
which the potential curve has been raised by its interaction with the
other chlorine fluoride state so decreasing the depth of the minimum.
But then, the observed D_0 is much larger than one would expect from
the above data on the halogens. On the other hand, if the chlorine
fluoride state observed arises from excited fluorine, this $D_0{}'$ is for
the lower of the two possible states. Here, neglecting resonance, a
$D_0{}'$ somewhat less than 3000 cm^{-1} would be expected, while the re-
sonance would increase this depth somewhat. This could easily give a
dissociation energy comparable to the observed one. In iodine chloride,
D' is only 1060 cm^{-1} for the $^3\Pi_0{}^+$ state, only one-**fourth** the expected
value, so the validity of the quantitative comparison just made is

very doubtful. On the other hand, iodine chloride is known to give excited chlorine on dissociation. Hence, as the depth of the minimum in chlorine fluoride is as deep *as* or deeper than expected it seems certain that the upper state involved in the observed transitions is the lower of the two states postulated.

Having decided on the dissociation products of the upper state as being $Cl(^2P_{3/2}) + F(^2P_{1/2})$, the dissociation energy of the ground state, measured from the first vibrational level, $v'' = 0$, is easily obtained:-

$$D_o'' = \nu_{conv.\ lin.} - (^2P_{1/2} - {}^2P_{3/2})\ in\ F.$$

$$D_o'' = 21101 \pm 2\ cm^{-1}.$$

Also of interest is the dissociation energy D_e'' of the ground state as measured from the minimum of the potential curve. It is evident that it is obtained from D_o'' by adding to the latter the zero point energy. Hence, *from* Equation 2 we have

$$D_e'' = D_o'' + 1/2\ \omega_e'' - 1/4\ \omega_e''x_e'' + 1/8\ \omega_e''y_e'' + \ldots ;$$

all that is obtained by the analysis of the spectrum is $G_{(1)} - G_{(0)} = \omega_e'' - 2\ \omega_e''x_e''$ (neglecting higher terms). To obtain ω_e'' and $\omega_e''x_e''$, an empirical equation of Birge[20] is used $\dfrac{a_e}{B_e} = 1.4\ \dfrac{\omega_e x_e}{\omega_e}$

On calculating the values of the constant in the expression for the halogens it is found to *be* appreciably smaller than 1.4, namely 0.98 for Cl_2, 1.01 for Br_2, 1.15 for ICl, and 1.16 for I_2. As a reasonable extrapolation for ClF the value 0.95 is taken. Taking α_e'' and B_e'' from the rotational analysis, it is found that $\omega_e''/\omega_e''x_e'' = 80$. Substituting in the equation for $G_{(1)} - G_{(0)}$ we obtain

$$\omega_e''x_e'' = 9.9\ cm^{-1}$$

$$\omega_e'' = 793.2\ cm^{-1},$$

and the dissociation energy is:-

$$D_e'' = 21495 \pm 3 \text{ cm}^{-1}$$

It is now possible to draw a reasonable approximation to the potential curves of the chlorine fluoride molecule. These are given in Figure 6. The curves for $^1\Sigma^+$ and $^3\Pi_0^+$ states are obtained using the Morse function calculated from the values of B_e, ω_e and D_e. The repulsive 0^+ state, ~~shown dotted~~, is arbitrarily drawn as all that is known for it is its horizontal asymptote and the approximate location of its intersection with the $^3\Pi_0^+$ curve. The first two vibrational levels are drawn in the lower state, and the vibrational levels $v' = 6$ and $v' = 10$ are indicated in the upper state. It is seen by application of the Franck-Condon principle that the most intense transitions from $v'' = 0$ should be to around $v' = 5$, and from $v'' = 1$ to about $v' = 3$. From the observed spectrum the bands $(10 \leftarrow 0)$ and $(8 \leftarrow 1)$ are estimated to be the most intense bands of their respective v' progressions. This deviation is not surprising in view of the large deviations of the upper state $G_{(v)}$ from the simple quadratic in $v + 1/2$ given by the Morse potential curve. It is seen that if the vibrational quantum numbers assigned to the lower state bands are increased by one this deviation of the expected intensities from the observed intensities would be increased, for the effect of the new numbering would be to increase the internuclear distance at which transitions would be most likely to take place.

While the postulated perturbation of the $^3\Pi_0^+$ state gives a quite reasonable explanation of the diffuseness of the bands $11 \leftarrow 0$, $12 \leftarrow 0$ and $13 \leftarrow 0$, it does not explain why the lines of $14 \leftarrow 0$, sharp near the origin, become diffuse for J greater than 14. The
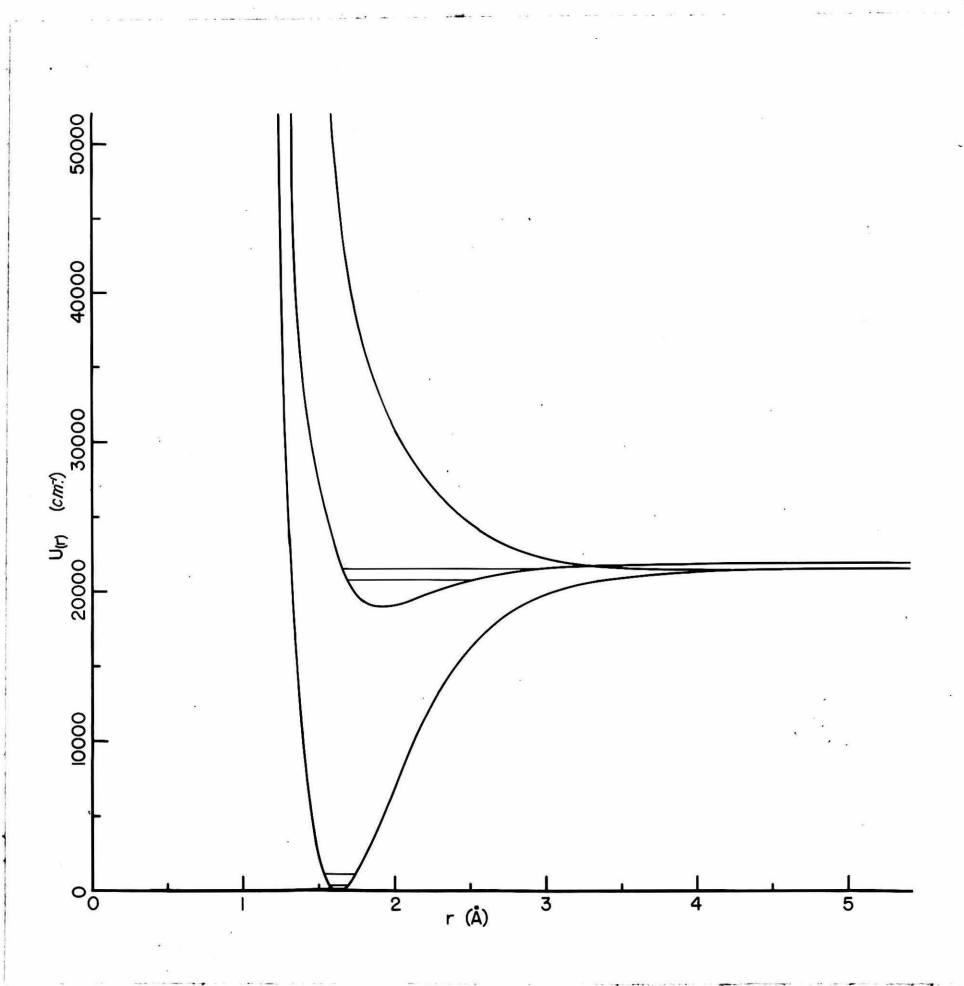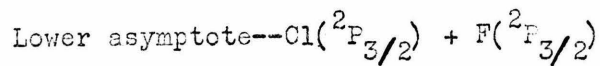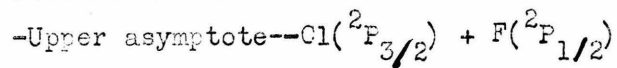
Figure 6

The Potential Curves of Chlorine Fluoride

Dissociation Products

  -Upper asymptote--$Cl(^2P_{3/2})$ + $F(^2P_{1/2})$

  Lower asymptote--$Cl(^2P_{3/2})$ + $F(^2P_{3/2})$

Vibrational levels indicated are

  Lower state--$v'' = 0, 1$

  Upper state--$v' = 6, 10$

diffuseness cannot be caused by dissociation by rotation[21] for the rotational energy levels affected start thirty wave numbers below the dissociation limit. On the other hand, the effect of rotation on the effective potential curve for vibration is such that on the high energy side of a region of perturbation one expects the levels with low J, not those with high J, to be perturbed. No other explanation has been found for this observation which is in any way satisfactory. This completes the discussion of the ClF spectrum To summarize the conclusions:-

(1) The band system observed results from a $^3\Pi_0{}^+ \leftarrow {}^1\Sigma^+$ transition, the upper state belonging to Hund's case c. The upper state is perturbed by a repulsive 0^+ state.

(2) The dissociation products are:-

$^1\Sigma^+$ ground state and the 0^+ repulsive state:-

$$Cl(^2P_{3/2}) + F(^2P_{3/2}) \quad ,$$

$^3\Pi_0{}^+$ state:- $Cl(^2P_{3/2}) + F(^2P_{1/2})$
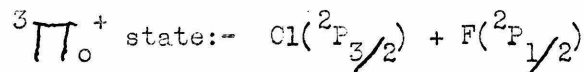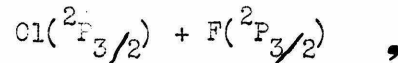
(3) The constants for the ground state, determined from the levels $v'' = 0, 1$, are:-

$$D_0{}'' = 21101 \pm 2 \text{ cm}^{-1} = 2.616 \text{ volts}$$

$$D_e{}'' = 21495 \pm 3 \text{ cm}^{-1} = 2.665 \text{ volts}$$

$$B_e{}'' = 0.5183 \pm 0.001 \text{ cm}^{-1}$$

$$\alpha_e{}'' = 0.0062 \pm 0.002 \text{ cm}^{-1}$$

$$G''_{(1)} - G''_{(0)} = 773.4 \text{ cm}^{-1}$$

$$\omega_e{}'' \approx 793.2 \text{ cm}^{-1} \qquad \omega_e x_e{}'' \approx 9.9 \text{ cm}^{-1}$$

$$r_e{}'' = 1.6255 \pm 0.002 \text{Å}$$

$$r_0 = 1.6304 \pm 0.001 \text{Å}$$

(4) The constants for the excited state below the perturbation region, determined from the bands ($v' \leftarrow 0$) with $6 \leq v' \leq 10$, ($8 \leftarrow 1$), ($10 \leftarrow 1$), ($8 \leftarrow 0$)^i, and ($10 \leftarrow 0$)^i are:-

$$B_e = 0.372 \text{ cm}^{-1} \qquad\qquad r_e = 1.92 \text{ cm}^{-1}.$$

$$\alpha_e = 0.0138 \text{ cm}^{-1}$$

For the progression $v' \leftarrow 0$,

$$\nu = 18561.65 + 313.484(v'+1/2) - 2.217(v'+1/2)^2 - 0.400(v'+1/2)^3$$

$$\omega_e' = 313.484 \text{ cm}^{-1}, \quad \omega_e' x_e' = 2.217 \text{ cm}^{-1}, \quad \omega_e' y_e' = -0.400 \text{ cm}^{-1}$$

$$\nu_e = 18956 \text{ cm}^{-1}$$

(5) The remaining constants for the upper state, determined from the bands of (4) and also the bands ($v' \leftarrow 0$) with $11 \leq v' \leq 17$ are:-

$$\nu_{\text{conv. lim.}} = 21507.8 \pm 2 \text{ cm}^{-1}$$

$$D_0' = 2790 \pm 50 \text{ cm}^{-1} = 0.346 \text{ volts}$$

$$'D_e' = 2946 \pm 50 \text{ cm} = 0.365 \text{ volts}$$

$$B_{14}' = 0.132 \text{ cm}^{-1}, \qquad B_{15}' = 0.112 \text{ cm}^{-1}$$

VIII. The Chlorine Fluoride Spectrum

Some Applications

It is of interest to compare the constants of the chlorine fluoride molecule with the constants for the other halogen and interhalogen molecules. In Table 19 are listed the values of the dissociation energy, D_0'', the vibrational constant, ω_e'', the force constant, k_e'', and the internuclear distance r_e'', for the several molecules. Also given are the molecular weights and the reduced masses in atomic weight units. In Figure 7, k_e'', r_e'' and D_0'' are plotted against the molecular weight.
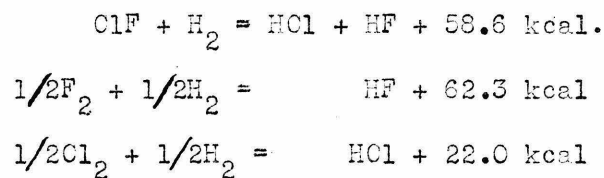
Table 19.

	$D_o''(\text{volts})$	$\omega_e''(\text{cm}^{-1})$	$k_e 10^{-7}$ dynes cm.	$r_e''(\overset{\circ}{A})$	Molecular Wt.	μ
F_2	———————			1.44	38	9.5
ClF	2.616	793.2	4.59	1.625	54.5	12.4
Cl_2	2.481	564.9	3.32	1.989	71	17.7
BrCl	2.26	(430)	2.68	————	115.5	24.6
Br_2	1.971	323.2	2.45	2.284	160	40.0
ICl	2.153	384.2	2.36	2.321	162.5	27.8
IBr	1.818	268.4	2.00	—————	207	49.0
I_2	1.542	214.4	1.74	2.667	254	63.5

57 b.

58.
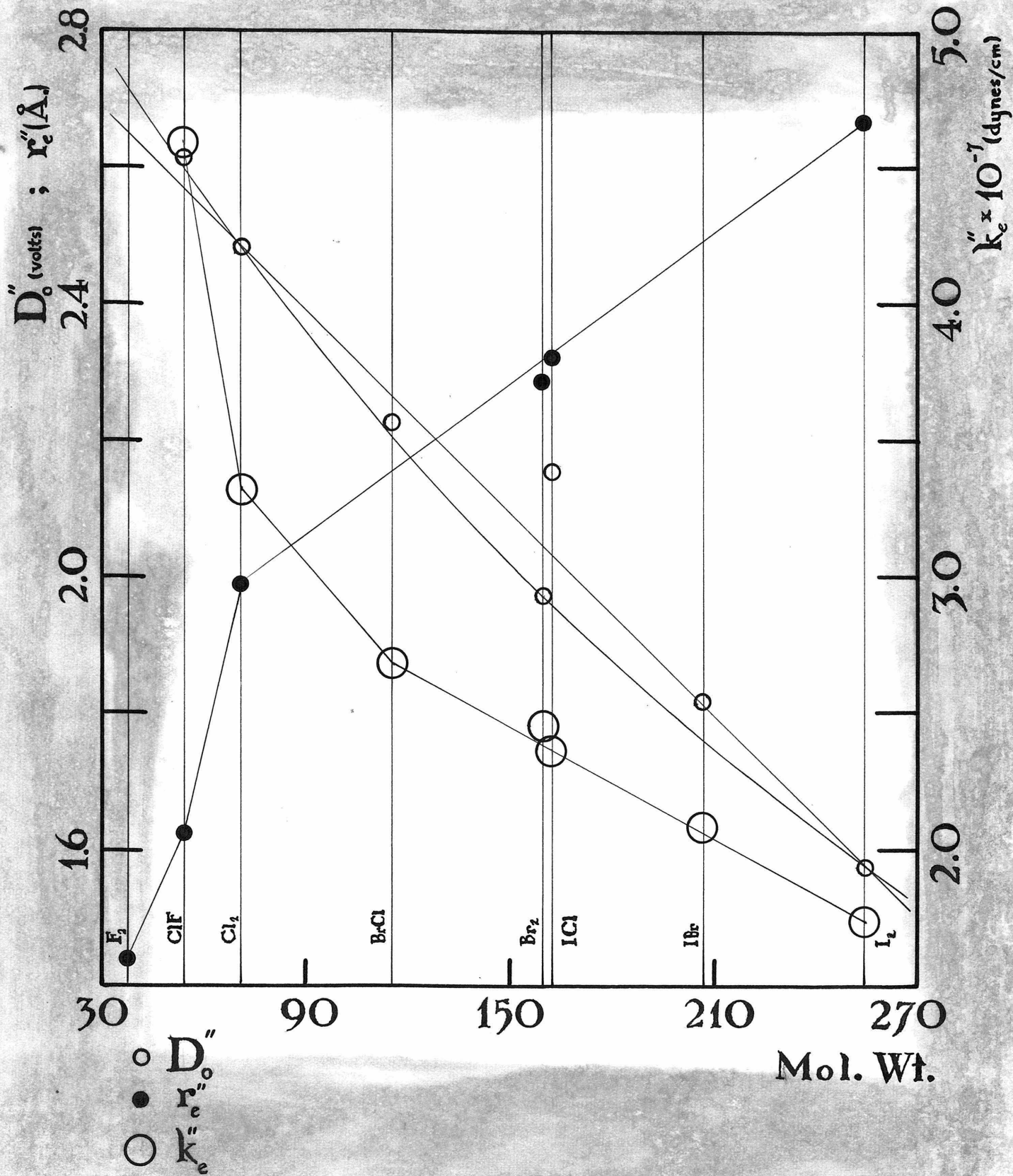
Some regularity is seen in the values for k_e, but the values for r_e appear to be rather erratic. No attempt has been made to determine possible explanations for the observed values.

It is seen that all the values for D_o'' lie fairly near a straight line. However, it is probably more reasonable to draw a smooth curve through the points for iodine, bromine, and chlorine. Then, the deviations from this curve for the interhalogen compounds can be interpreted in terms of difference in electronegativity of the two halogen atoms. So, in iodine bromide and bromine chloride, this difference is small, while in iodine chloride it is much larger, in agreement with prediction. However, the point for chlorine fluoride deviates only slightly from the curve, decidedly not in accordance with former ideas[22].

It has been reported by Ruff and Laass[23] that the heat of formation of chlorine fluoride is 25.7k cal. per mole. This they determined from the heats of the reactions of chlorine fluoride, fluorine, and chlorine with hydrogen. They report:-

$$ClF + H_2 = HCl + HF + 58.6 \text{ kcal.}$$
$$1/2F_2 + 1/2H_2 = HF + 62.3 \text{ kcal}$$
$$1/2Cl_2 + 1/2H_2 = HCl + 22.0 \text{ kcal}$$

Hence, $1/2F_2 + 1/2Cl_2 = ClF + 25.7 \text{ kcal.}$

In a later paper, Ruff and Menzel[24] reporting a more accurate determination of the above heats of reaction calculate $\Delta H = -27.4$ kcal. for the formation of chlorine fluoride. Since this heat of reaction will be practically independent of temperature, it may be combined with the spectroscopic values for the energy of dissociation of chlorine and chlorine fluoride to obtain the energy of dissociation of fluorine. From Herzberg[25], we obtain

$$Cl_2 = 2Cl, \qquad D_o = 57190 \text{ cal.}$$

From this research,

$$ClF = Cl + F, \qquad D_o = 60307 \text{ cal}$$
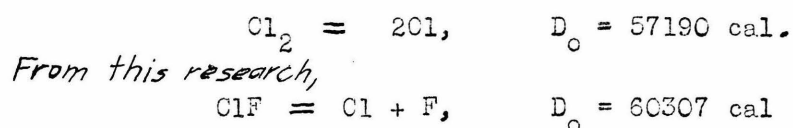
Combining these last three equations with the proper factors we obtain:-

$$F_2 = 2F, \qquad D_o = 8.6 \text{ kcal.} \qquad (0.37 \text{ volts})$$
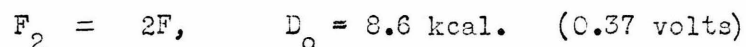
This is of a different order of magnitude from all values previously reported. From the continuum observed in the absorption spectrum of fluorine it has been calculated that D_o is 2.8 volts[26], or 64.6 kcal. It is seen from Figure 7 that any reasonable extrapolation of the D_o curve will give a value between 2.5 and 2.9 volts.

The work of Ruff and his collaborators on chlorine fluoride appears to be well done. Their work on the heat of reaction of hydrogen and fluorine agrees well with other determinations. The spectroscopic value for the dissociation energy of chlorine is certainly correct, the chlorine spectrum having been thoroughly studied. The dissociation energy of chlorine fluoride obtained in this investigation can at most be high by the doublet separation in chlorine, or low by the doublet separation in fluorine. These possible corrections are far too small to account for the discrepancy, being only 2.52 and 1.16 kcal., respectively.

It is true that there is no definite reason why one should be able to extrapolate from the other halogens to obtain a dissociation energy for fluorine; it is also true that one cannot usually make an entirely definite calculation of the dissociation limit from measurements on a continuum, but it is difficult to believe that either of these methods could be off by the extent indicated by the difference between 2.8 volts and 0.37 volts. Hence, the conclusion is reached

that the value of Ruff for the heat of formation of chlorine fluoride
is far too large, the error probably being caused by too low a value
for the heat of the reaction:-

$$H_2 + ClF = HCl + HF.$$
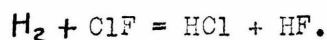
This conclusion is also reached by an examination of the heats of form-
ation of iodine chloride, iodine bromide and iodine chloride, resp-
ectively 4.0, 1.7 and 0.7 kcal. per mole.

There seems to be no other way of obtaining a reasonable value
for the heat of formation of chlorine fluoride. There is no other
chemical evidence available to permit a simple determination of this
quantity. The electronegativity of fluorine was selected by Pauling[27]
to fit the previous values for the heat of formation of chlorine fluor-
ide and the dissociation energy of fluorine; the electronegativity
values as presently assigned cannot be used. It perhaps would be pos-
sible to find unique solutions for the electronegativity of fluorine
and the heat of formation of chlorine fluoride consistent with the
data on other fluorine compounds.

If the value for the heat of formation of chlorine fluoride is
calculated using the dissociation energy of fluorine obtained from the
absorption continuum, it is found that $\Delta H_{ClF} = +0.6$ kcal. This too
is certainly incorrect, for chlorine and fluorine form an explosive
mixture.

Hence, it appears that the value reported by Ruff for the heat of
formation of chlorine fluoride is too high by a rather large amount,
and the value given by Wartenberg[26] for the dissociation energy of
fluorine is also at least slightly too high. It can be definitely
said only that

$$\Delta H_{ClF} = \frac{D_{oCl_2} + D_{oF_2} - 2D_{oClF}}{2}$$

$$1/2D_{oF_2} + (-\Delta H_{ClF}) = 31.712$$

where $-\Delta H_{ClF}$ = the heat of formation of chlorine fluoride in kcal. per mole (at $0^{\circ}K$, but also at room temperature with very little error). D_{oF_2} = the dissociation energy of fluorine.

IX. The Chlorine Trifluoride Spectrum

An attempt to find some absorption bands of chlorine trifluoride was made. The chlorine trifluoride was prepared as described in the Section II of this thesis. The quartz prism spectrometer was used with Eastman 40 plates. The 3 meter absorption cell and auxiliary system was exactly as described for chlorine fluoride.

Pressures from five to seventy centimeters were used; the necessary exposure times varied from one-half to ten minutes.

Under these conditions, no bands were found in the region $\lambda 4800$ to $\lambda 5550$. To the red side of $\lambda 5550$ the sensitivity of the Eastman 40 plates used dropped off rapidly. As the color of the gas was very pale yellow, it was not thought worth while to look for absorption in this latter region.

To the violet of $\lambda 4800$ the chlorine dioxide bands described in Section III of this thesis were found. The intensity of these bands was too great to permit decision as to the presence or absence of absorption by chlorine trifluoride.

It is found on comparing low dispersion plates of chlorine fluoride and chlorine trifluoride taken under similar conditions that the intensity of the chlorine dioxide bands are approximately the same on each.

Thus it may be concluded that the amount of chlorine dioxide in the chlorine trifluoride is the same as the amount of the chlorine dioxide in chlorine fluoride, namely, one percent or less as decided in Section III of this thesis.

While it would be interesting to determine the frequencies and, if possible, the moments of inertia of chlorine trifluoride, to do so would be quite difficult. It would be necessary to eliminate all quartz from the system. Lithium fluoride could probably be used for windows on the absorption cell. It is possible that all the observed yellow color of the chlorine trifluoride arose from the chlorine dioxide, so that the former compound might not absorb in the near ultraviolet. In that case the Raman spectrum of the chlorine trifluoride might be obtainable, provided only it did not react with the quartz of the Raman tube too rapidly.

X. The Electron Diffraction Investigation of Chlorine Fluoride
and Chlorine Trifluoride*

The internuclear distance in chlorine fluoride as determined spectroscopically has been given earlier in this thesis (Section VI). In chlorine trifluoride, it is expected that the chlorine-fluorine distance will be appreciably greater than in chlorine fluoride, but there is no method of predicting the amount of lengthening or the bond angles to be expected. Here is described an independent determination of the chlorine-fluorine distance in chlorine fluoride and an examination of the possible structures of chlorine trifluoride by the electron diffraction method.

----

*With Dr. Verner F. H. Schomaker.

The electron diffraction apparatus used in this investigation has been described by Brockway[28]. The camera distance was about 11 cm. and the wave length of the electrons, determined in the usual way[28] from transmission photographs of gold foil (a_o = 4.070), was approximately 0.06Å.

The chlorine fluoride and chlorine trifluoride samples used were portions of these compounds prepared for the spectroscopic investigation as described in Section II of this thesis. The samples were distilled shortly before use in a quartz system and kept in quartz traps. The valve described in Section II as value A of Figure 2 was used to control the introduction of the gas into the electron diffraction machine.

Photographs of chlorine fluoride were taken with the temperature of the liquid sample ranging from the temperature of liquid air to -105°C; the photographs of chlorine trifluoride were taken with the temperature of the liquid sample ranging from -75°C to +12°C. The boiling points and freezing points of these substances are listed in Table 1. Immediately before each set of photographs was taken a small amount of the sample was distilled off in order to remove any highly volatile substances formed as the result of reaction of the sample with the quartz of the trap or the lubricant on the tapers. It is believed that neither sample contained a large amount of impurity. Both the chlorine fluoride and the chlorine trifluoride contained some chlorine dioxide, but the amount of this latter substance, as stated earlier in this thesis, is believed to have been present to the extent of one percent or less, a negligible amount. The photographs of chlorine fluoride have a simple diatomic pattern, indicating the absence of large amounts of the tetrafluorides of carbon and

silicon. These latter impurities are surely not present in the chlorine trifluoride because of the very large differences in boiling points.

Chlorine Fluoride.

The photographs of chlorine fluoride, as has been mentioned, show the simple diatomic pattern. Seven measureble rings were observed, for which the measured s_0 values corresponding to the maxima and minima are given in Table 20. Two sets of measurements are listed, set A the average of measurements on three photographs, set B the average of measurements on nine photographs. The measurements of set B were made nine months after those of set A. In the last column of Table 20 are given the values of r, the internuclear distance in chlorine fluoride, as obtained by comparing the observed s with the s values calculated for $r = 1$. The values for r determined from the innermost and outermost features in an electron diffraction photograph are often unreliable. Neglecting these extreme values, one obtains the averages given in Table 20 for each of the sets of measurements, or combining the two,

$$r_0 = 1.63 \pm 0.01\text{Å}$$

This is to be compared with the result of the spectroscopic investigation, where it was found for the lowest vibrational level in the ground state, $r_0 = 1.6304 \pm 0.001$. The agreement is excellent.

Chlorine Trifluoride.

The photographs of chlorine trifluoride are quite satisfactory, having seven measureable rings. The measured q_0 values $(q = \frac{10}{\pi} s)$ are given in Table 21. The estimated intensities of the various maxima and minima are given in the column headed I, and the corresponding

Table 20

Max	Min	s_o	r
Set A			
	3	----	----
3		8.43	(1.669)
	4	10.40	(1.656)
4		12.32	(1.653)
	5	14.36	1.638
5		16.27	1.639
	6	18.15	1.642
6		20.17	1.634
	7	---	---
7		---	---
		Average	1.638 ± 0.002
Set B			
	2	2.99	(1.501)
2		4.55	(1.698)
	3	6.53	(1.670)
3		8.60	1.635
	4	10.47	1.645
4		12.62	1.614
	.5	14.36	1.638
5		16.47	1.619
	6	18.30	1.629
6		20.47	1.610
	7	22.20	1.627
7		24.23	1.621
	8	26.3	(1.61)
8		28.2	(1.62)
		Average =	1.626 ± 0.009

Table 21

Max	Min	q_0	I	C_k	q/q_0
	2a	7.46	−20	20	---
2a		12.9	19	18	---
	2b	14.8	−2	2	---
2b		17.2	4	4	---
	3	21.4	−20	17	(1.029)
3		27.0	20	15	1.007
	4	32.5	−20	+14	1.000
4		38.1	23	14	0.992
	5	44.2	−13	(6)	---
5		50.7	15	(6)	---
	6	57.4	−20	6	0.994
6		62.5	20	5	0.998
	7	67.7	−18	3	0.997
7		73.3	19	3	0.996
	8	78.8	−16	2	---
8		83.8	+16	1	---
				Average =	0.998

Max	Min	q_0	I	C_k	q/q_0
1*		2.40	30	30	
	5*	43.4		−3	
		45.0		−3	
5*		49.6		2	
		51.4		4	

*Values used in calculating the radial distribution function.

coefficients of the radial distribution function[29] are listed in the column headed c_k. In the lower part of the table are given the values of q_o and I assumed for the first maximum as used in the radial distribution function. The fifth minimum and maximum were each represented by the two peaks listed in the lower section of the table as it was possible thereby to better represent the nature of the observed features of the photographs. The calculated radial distribution curve, R.D. of Figure 8, has strong peaks at r equal to 1.69 and 2.31 Å, and small peaks, which may or may not have significance, at 2.69, 3.36 and 3.66 Å. The last peak listed cannot have significance for any structure having the three fluorine atoms about a central chlorine atom.

It is obvious that the distances 1.69 and 2.31 must correspond to a chlorine-fluorine and fluorine-fluorine distances, respectively, giving a bond angle of 87°. Reduced theoretical curves were calculated for symmetrical pyramidal structures with F-Cl-F bond angles of 84°, 85.5°, 87°, 88.5° and 90°. These are the curves marked A in Figure 8. The curves were calculated using the equation

$$I_{(q)} = \frac{Z_{Cl}}{l_{Cl-F}} \sin \frac{\pi}{10} q l_{ClF} + \frac{Z_F}{l_{F-F}} \frac{\frac{Z_F - f_F}{Z_F}}{\frac{Z_{Cl} - f_{Cl}}{Z_{Cl}}} \sin \frac{\pi}{10} q \, l_{FF}$$

where l_{ij} is the distance between the ith and jth atoms, Z_i is the atomic number of the ith atom, f_i is the X-ray scattering factor as calculated by Pauling and Sherman, and $q = \frac{10}{\pi} s = \frac{40}{\lambda} \sin \varphi/2$, φ = scattering angle.

The appearance of the photographs is best represented by the cuve A-87, with A-85.5 only slightly less satisfactory. The doublet appearance of the second maximum, represented by measurements 2a and 2b in
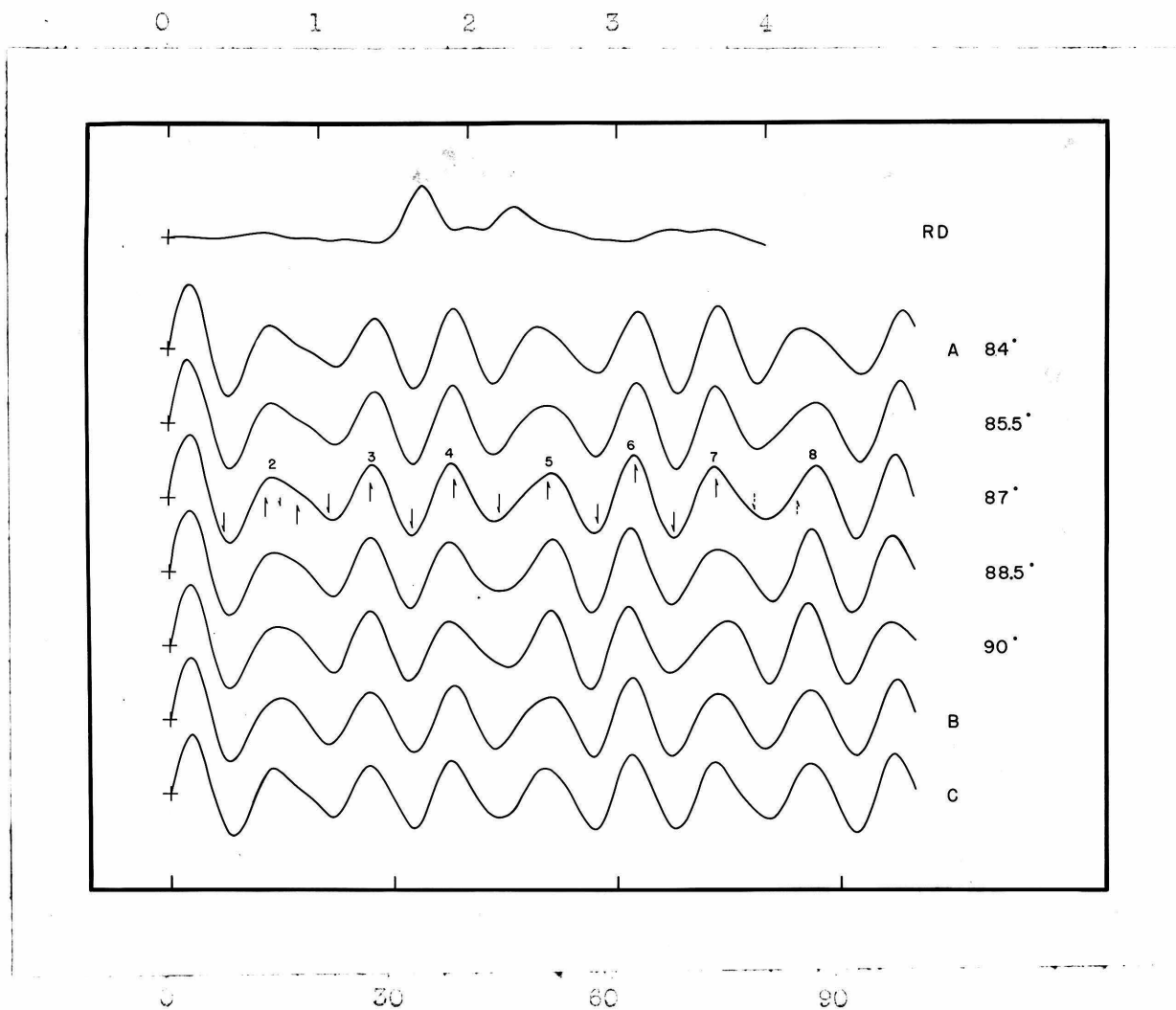
Figure 8

Curve RD — The radial distribution function for ClF_3

Curves A, B, C — Reduced theoretical intensity curves for ClF

    A--Symmetrical pyramidal model with indicated F-Cl-F
       bond angle.

    B--Asymmetrical pyramidal model--
       two F-Cl-F bond angles = $87°$
       one F-Cl-F bond angle = $105°$

    C--Planar model--two F-Cl-F bond angles = $87°$.

Table 21, is definitely not indicated by the curves A-90° or A-88.5° curve. The appearance of the fifth maximum on the photographs indicates this feature is broad, with the peak displaced to large q. This excludes the A-84° structure.

From these and other less obvious deviations of observed and calculated curves, it can be said that if chlorine trifluoride has the symmetrical pyramidal structure, the F-Cl-F bond angle is 86.5° ± 1.5°.

However, there is no simple theoretical reason which requires that the structure of chlorine trifluoride have the above symmetry. It might be assumed that one of the two subsidiary peaks in the radial distribution function, at 2.69 or 3.36Å, has meaning. Thus one obtains the unsymmetrical pyramidal structure (B) having two F-Cl-F angles of 87°, giving a 174° angle between the outer fluorines. In both these structures the Cl-F distances are all assumed to be 1.69Å The reduced theoretical curves for these structures, labeled B and C are given in Figure 7. The second maximum on curve B does not agree with the photographs, nor does the fifth minimum and maximum on curve C. However, the deviations are small and it is not possible at present to exclude all the non-symmetrical structures which might be obtained by slight modification of models B or C.

In the last column of Table 21 are given the values for q/q_o; as it is equal to one within experimental error, the radial distribution function peaks give the correct internuclear distances.

The final result then is:-

If the chlorine trifluoride molecule has a three-fold axis, the Cl-F distance is 1.69 ± 0.01Å and the F-Cl-F bond angle is 86.5 ±1.5°.

If the chlorine trifluoride molecule does not have a three-fold axis, the mean of the Cl-F distances is $1.69\overset{\circ}{A}$, and there are at least two F-F distances of approximately $2.31\overset{\circ}{A}$.

It is seen that the effect of having three fluorine atoms bonded to one chlorine atom is to increase the Cl-F distance from 1.63 to $1.69\overset{\circ}{A}$, or $0.06\overset{\circ}{A}$, which is a reasonable amount. The bond angle, only 87°, is rather surprising. However, the bond orbitals for this case have not been studied sufficiently for one to say what is a reasonable value for the bond angle.

Acknowledgements

The Absorption Spectra of Liquid HF and of its Aqueous Solution in the Region λλ8000–11,000

The absorption spectra of liquid HF and of HF in aqueous solution have been photographed in the region λλ8000–11,000 with a dispersion of about 60A per mm. In the case of the anhydrous HF a copper cell was used, with windows of MgO (artificial crystal) clamped directly onto the ends of the tube. The MgO is not attacked by anhydrous HF and appears to have greater mechanical strength than glass.

The absorption band of anhydrous HF in the liquid state is very similar to the band of liquid water at λ9722 as reported by Badger and Bauer,[1] though it is somewhat broader. The position of the band maximum determined at several temperatures is given in the following table. The large probable error indicated arises from the difficulty in estimating the maximum of a broad band in this region where the trend in plate sensitivity is large.

TABLE I. *The maximum of the band of liquid HF as a function of temperature.*

$t(°C)$	$\lambda_{max}(A)$
19	9940 ±75
0	9990
−30	10140
−60	10300
−75	10380

Salant and Kirkpatrick[2] have found that the third harmonic band of unassociated HF gas is located at λ8790. From the data just given it is evident that the frequency decrease in going from the gas to the liquid is very large

even at the boiling point, namely about 1320 cm⁻¹. This shift in the HF frequency, which must be due mainly to the formation of hydrogen bonds of the type $F-H\cdots F$, is large in comparison with the shift in OH frequency on the formation of the $O-H\cdots O$ linkage. The third harmonic OH band of methyl alcohol, for example, is found at λ9490 in the vapor[3] and at λ10,070 in the liquid,[1] so that the frequency shift is about 600 cm⁻¹.

The large difference in the magnitudes of the frequency shifts just mentioned is very interesting in view of the fact that the energies of the hydrogen bonds in associated HF and CH_3OH are so nearly the same, being 6.7 and 6.2 kcal. per mole,[4] respectively.

The absorption spectrum of HF in aqueous solution has also been examined at HF concentrations of 25 and 50 percent and at 0° and at 25°C. In no case does a cursory examination reveal any significant difference between the solution band and the λ9722 band of water in either position or shape.

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March 11, 1940.

[1] Badger and Bauer, J. Chem. Phys. 5, 840 (1937).
[2] Salant and Kirkpatrick, Phys. Rev. 48, 945 (1935).
[3] Badger and Bauer, J. Chem. Phys. 4, 469 (1936).
[4] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, 1939), p. 313.

Summary

Chlorine fluoride and chlorine trifluoride have been prepared, their absorption spectra in the region $\lambda\lambda$ 4500 - 5500 examined, and their molecular structures investigated by the electron diffraction method.

Chlorine fluoride gives a band system with single P and R branches resulting from a $^3\Pi_0^+ \leftarrow\ ^1\Sigma^+$ transition with the convergence limit for the progression $v' \leftarrow 0$ at 21507.8 ± 2 cm^{-1}. The dissociation products are probably $Cl(^2P_{3/2}) + F(^2P_{1/2})$. The values of the various spectroscopic constants are:-

$D_0'' = 21101 \pm 2$ cm $= 2.616$ volts, $\qquad D_0' = 2946 \pm 50$ cm$^{-1} = 0.365$ volts

$D_e'' = 21495 \pm 3$cm$^{-1} = 2.665$ volts, $\qquad D_e' = 2790 \pm 50$ cm$^{-1} = 0.346$ volts

$B_e'' = 0.5183 \pm 0.001$ cm^{-1}, $\qquad B_e' = 0.372$ cm^{-1}

$\alpha_e'' = 0.0062 \pm 0.002$ cm^{-1}, $\qquad \alpha_e' = 0.0138$ cm^{-1}

$r_e'' = 1.6255 \pm 0.002$Å, $\qquad r_e' = 1.92$ cm^{-1}

$r_0'' = 1.6304 \pm 0.001$Å

$\omega_e'' = 793.2$ cm^{-1}, $\qquad \omega_e' = 313.484$ cm^{-1}

$\omega_e x_e'' = 9.9$ cm^{-1}, $\qquad \omega_e' x_e' = 2.217$ cm^{-1}

$\qquad\qquad\qquad\qquad\qquad\qquad \omega_e' y_e' = -0.400$ cm^{-1}

Chlorine trifluoride has no absorption bands of appreciable intensity in the region $\lambda\lambda$ 4800 - 5550.

The electron diffraction investigation of chlorine fluoride yields r $= 1.63 \pm 0.01$Å, in excellent agreement with the spectroscopic value.

The electron diffraction investigation of chlorine trifluoride indicates that if the structure of the molecule is symmetrical pyram-

idal, the Cl-F distance is 1.69 ± 0.01Å and the F-Cl-F angle is 86.5° ± 1.5°. If the structure does not have the above symmetry, the mean of the Cl-F distance is 1.69Å and there are at least two F-F distances equal to about 2.31Å.

The absorption spectrum of liquid hydrogen fluoride and of its aqueous solution have been investigated in the region $\lambda\lambda$ 8000 - 11000.

Physical Constants

The values for the physical constants used in this thesis were taken from Herzberg[9]. He gives:-

Electronic charge	e	$4.8029.10^{-10}$ e.s.u.
Planck's constant	h	$6.626.10^{-27}$ erg. sec.
Velocity of light	c	$2.99776.10^{+10}$ cm. sec.
1/16 mass of the O^{16} atom	M_1	$1.6600.10^{-24}$ gm.
Boltzmann's constant	k	$1.3807.10^{-16}$ erg. degree.

Conversion factors:-

Unit	cm^{-1}	erg molecule	cal mole	electron-volt
Cm^{-1}	1	$1.9863.10^{-16}$	2.8581	$1.2398.10^{-4}$
1 erg per molecule	$5.0344.10^{15}$	1	$1.4389.10^{16}$	$6.2416.10^{11}$
1 cal per mole	0.34988	$6.9498.10^{-17}$	1	$4.3378.10^{-5}$
1 electron volt	8066.0	$1.6022.10^{-12}$	23,053	1

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \qquad \text{reduced mass.}$$

μ_A = reduced mass in atomic weight units.

$$k_e = 4\pi^2 \mu c^2 \omega_e^2 = 5.8894.10^{-2} \mu_A \omega_e^2 \text{ dyne cm.}$$

$$B_e = \frac{h}{8\pi^2 c \mu r_e^2} = \frac{27.994.10^{-40}}{I_e}$$

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11. Reference 9, page 114.

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20. Reference 9, page 114; reference 10, page 29.

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24. O. Ruff and W. Menzel, Zeit. f. anorg. u. allgem. Chemie., 198, 375 (1931).

25. Reference 9, page 485.

26. Wartenberg, Sprenger and Taylor, Zeit. f. Physik. Chem., Bodenstein-Festband, p. 61 (1931).

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28. L. O. Brockway, Rev. Mod. Phys., 8, 231 (1936).

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Propositions

1. It is much simpler to regenerate the charge in a fluorine generator by distilling in anhydrous hydrogen fluoride than to use the methods previously suggested.

2. Using the electron diffraction value for the F–F distance in chlorine trifluoride, it can be argued that the structure of this molecule is very likely not symmetrical **pyra**midal.

3. The application of the Franck-Condon principle to values of $r' - r''$ calculated from B_v' values as is done by W. S. Brown and G. E. Gibson[1] in their discussion of the iodine chloride spectrum is without meaning. Their interpretation of the system III bands as a separate system is unnecessary and surely incorrect.

    1. Phys. Rev. 40, 529 (1932).

4. A consideration of the work of Badger on the spectrum of methyl alcohol vapor in the photographic infra-red[1] and the work of Borden and Barker[2] on the far infra-red absorption indicate that it would be of interest to reexamine the spectrum in the photographic region with the gas at various temperatures, and also perhaps with a longer absorption path.

    1. J. Chem. Phys., 4, 8 (1936)
    2. J. Chem. Phys., 6, 553 (1932).

5. A simple mechanism can be postulated for the polymerization of cyclopropene.

6. A vacuum tube amplifier can be designed to operate a mechanical recorder directly from a thermocouple without the use of any galvanometer. It should be possible to obtain just as great sensitivity as is possible with any other method.

7. The absorption spectrum of cyclopropene in the photographic infra-red is interesting in that the "ethylene band" does not appear, but

two strong bands are observed at longer wave lengths.

1. E. H. Eyster. J. Chem. Phys., 6,10 (1938).

8. A consideration of the relative rates of the forward and reverse reactions in the equilibrium

M(with internal H bond) = M(no internal H bond)
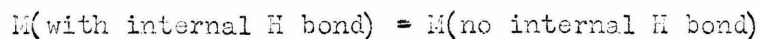
leads to an explanation of the observation that five-membered rings containing a hydrogen bond are more stable than six membered rings containing a hydrogen bond.

9. One should not be surprised, as are Buswell, Maycock, and Rodebush[1], at the lack of an association bond in the absorption spectrum of hydrogen fluoride in carbon tetrachloride solution.

13X Chlorine Trifluoride, the perfect oxidant for rocket engines.

9-1. J. Chem. Phys. 8, 362 (1940)