

THE ABSORPTION SPECTRUM OF NITRYL CHLORIDE

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by

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## THE ABSORPTION SPECTRUM OF NITRIL CHLORIDE

Approved:

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## THE ABSORPTION SPECTRUM OF NITRYL CHLORIDE

### SUMMARY

The absorption spectrum of nitryl chloride,  $\text{NO}_2\text{Cl}$ , has been investigated photographically in the visible and ultraviolet regions with a Genco replica grating spectrograph. A continuum was found which extends from 3300Å to a region beyond the 2200Å limit of the apparatus. No band structure was observed. This strongly indicates that, while the ground state potential function possesses a minimum, that of the excited state does not.

The absorption coefficients from 3000Å to 2200Å have been measured using a Beckman Model DU spectrophotometer adapted to a recording instrument. The absorption was found to follow the Beer-Lambert Law. Sample values for the absorption coefficients are 1.32 at 3000Å, 7.4 at 2500Å, and 15.0 at 2300Å, in units of  $\text{atm}^{-1}\text{cm}^{-1}$  at 300°K. A plot was made of the absorption coefficient vs wavelength, and the rapidity with which the coefficient is rising with decreasing wavelength indicates that the maximum lies beyond the 2200Å limit of the equipment.

The infrared absorption spectrum has been measured throughout the range of 1-15 $\mu$ , using a Beckman Model IR-2 spectrophotometer. Eight comparatively strong bands were found, with indications that a ninth lay just beyond the 15 $\mu$  limit of the instrument.

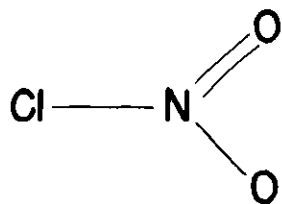
It is assumed that  $\text{NO}_2\text{Cl}$  is an asymmetric top molecule of symmetry  $C_{2v}$ . Such a molecule possesses six fundamental vibrations,

all active in the infrared. Three of these yield type A bands, two yield type B bands, and one yields type C bands. Only one type B band was found and it was assumed that the other band lay just outside the range of the instrument.

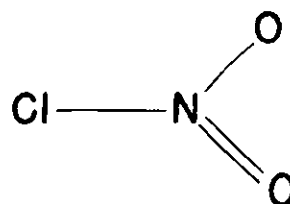
Fundamental frequency assignments have been made on this basis as follows:

$\nu_1$	1322 $\text{cm}^{-1}$	7.56 $\mu$	Type A
$\nu_2$	1170	8.65	Type A
$\nu_3$	798	12.51	Type A
$\nu_4$	1695	5.90	Type B
$\nu_5$	(643)	(15.5)	Type B
$\nu_6$	733	13.65	Type C

This assignment is consistent with the envelopes expected for a planar molecule with resonating structures:



and



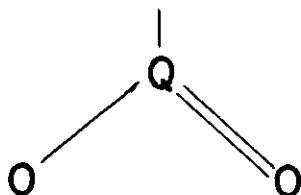
No thermodynamic data were found for  $\text{NO}_2\text{Cl}$ . The following constants have been approximated from spectrum analysis and statistical theory for 300, 500, and 1000°K., and a pressure of one atmosphere:



	300°K.	500°K.	1000°K.
$S^\circ$	63.3	69.6	80.6 cal./deg.mol.
$C_V^\circ$	8.7	11.9	15.7 cal./deg.mol.
$E^\circ - E_0^\circ$	2000	5100	13,200 cal./mol.

## INTRODUCTION

Spectrographic investigations in the School of Chemistry are concerned, in part, with the class of molecules containing the grouping



where Q is any atom capable of forming such a grouping, such as N, O, S, Cl, etc.

Nitryl chloride was chosen for investigation since it falls into the above classification, and since no mention of its spectrum can be found in the chemical literature.

In addition,  $\text{NO}_2\text{Cl}$  contains a large percentage of oxygen, is a powerful oxidizing agent, quite stable at  $100^\circ\text{C}.$ , and, with its boiling point of  $-16^\circ\text{C}.$ , might well find usage as an oxidizing agent in rocket propellants.

Although a slight amount of information has been reported on  $\text{NO}_2\text{Cl}$ , no thermodynamic data were found. If such data were known, the nature of its various reactions could be determined.

Spectrographic data are of great value, since they can be used to estimate thermodynamic quantities, with high accuracy.

## PREPARATION OF NITRYL CHLORIDE

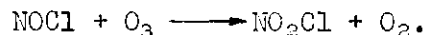
Little work has been done with nitryl chloride, although several preparations have been reported in the literature, and some studies have been made of its physical properties. Most of these preparations, however, have features which make the sample produced unsuitable for spectrographic investigations.

Muller,<sup>(1)</sup> in 1862, produced  $\text{NO}_2\text{Cl}$  by the reaction of gaseous  $\text{HCl}$  and  $\text{NO}_2$ . This process also produces  $\text{NOCl}$  and  $\text{H}_2\text{O}$ , which are serious contaminants and difficult to remove.

Hassenbach<sup>(2)</sup> passed gaseous  $\text{NO}_2$  and  $\text{Cl}_2$  through a heated tube and isolated a product which was principally  $\text{NO}_2\text{Cl}$ . Oxides of nitrogen interfere because of their absorption spectrum and are hard to remove.

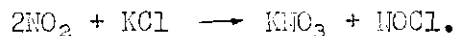
Other methods based on standard chlorination techniques have been reported. Odet and Vignon<sup>(3)</sup> reacted cold  $\text{PCl}_5$  and  $\text{N}_2\text{O}_4$ ; Zuskind<sup>(8)</sup> used  $\text{PCl}_5$  and  $\text{HNO}_3$ ; and an I. G. Farben patent<sup>(9)</sup> used  $\text{HNO}_3$  and  $\text{ClHSO}_3$ . All of these methods also yield contaminants which are hard to remove.

Schumacher and Sprenger<sup>(5)</sup> have reported a method which appears satisfactory for the preparation of samples pure enough for spectrographic work, and it was adopted in this investigation. It consists of the oxidation of  $\text{NOCl}$  with concentrated ozone gas to form nitryl chloride:



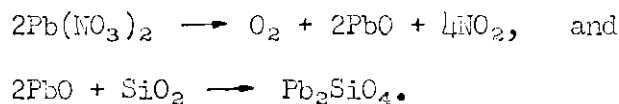
The only impurities are the oxygen and excess ozone, both of which are easily removed by pumping on the sample, cooled to  $-145^\circ\text{C}$ . Schumacher prepared  $\text{NOCl}$  by the direct reaction of  $\text{NO}$  and  $\text{Cl}_2$ . A simpler method has been reported by Whittaker,<sup>(10)</sup> in which gaseous  $\text{NO}_2$  is passed

through moist KCl:



The preparation of nitryl chloride finally adopted consists of four steps: preparation and purification of  $\text{NO}_2$ , reaction of  $\text{NO}_2$  and KCl to form HOCl, the preparation and purification of ozone, and the oxidation of HOCl with ozone to give  $\text{NO}_2\text{Cl}$ . Since the steps are essentially separate processes, each will be described separately in the following sections.

Nitrogen dioxide was prepared by heating a mixture of 70% C. P. lead nitrate and 30% clean, dry sand to 450-500°C. The reaction may be described by the equations:



The sand forms a matrix which reacts with the PbO formed and prevents the destruction of the glass tube containing the mixture. The apparatus is presented schematically in Figure 1. The tube containing the lead nitrate was made from Pyrex tubing and was attached to the condensing system by means of a 10/30 "no lube" standard taper joint.

The electric heater was made from 2 inch copper pipe, closed at the bottom and wrapped successively with a layer of asbestos paper for electrical insulation, 17 feet of No. 22 nichrome wire, and several layers of asbestos paper for thermal insulation. The voltage on the wiring was controlled by a Variac or Powerstat, 60 volts being optimum. Any voltage much higher than this value caused the lead oxide and sand

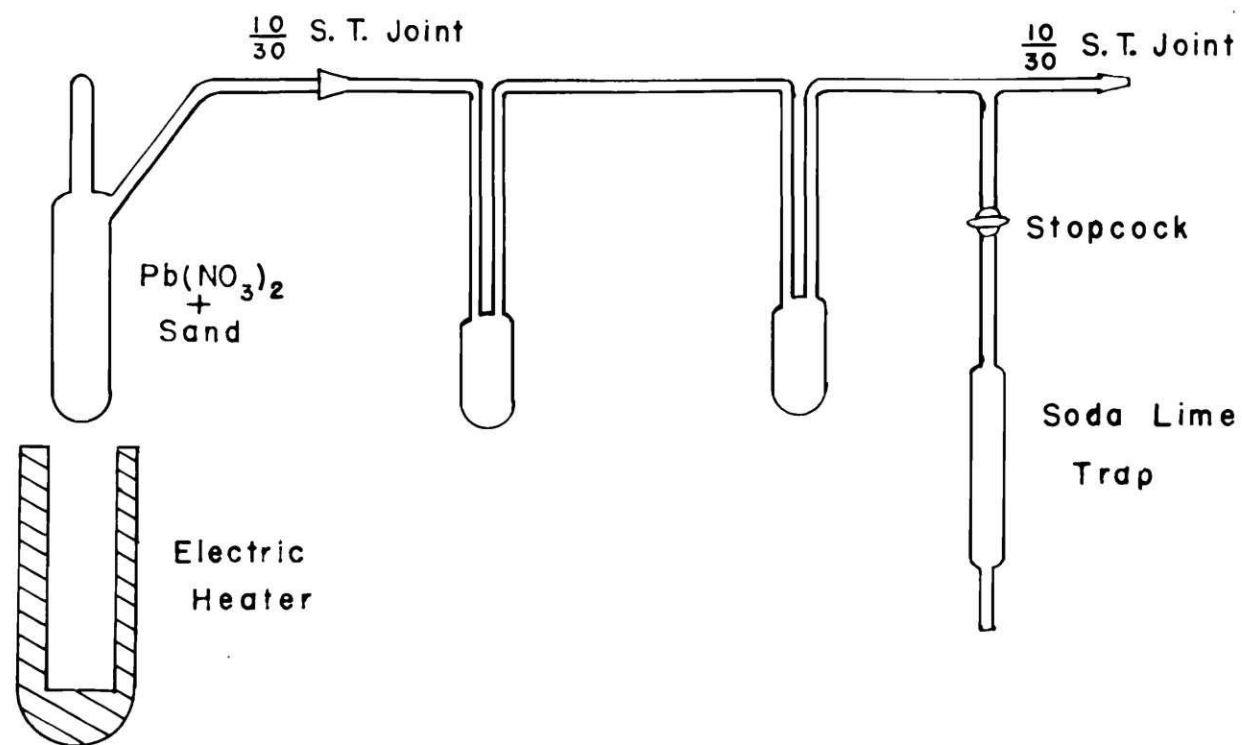


Fig. 1  $\text{NO}_2$  Generator and System

to fuse with the Pyrex tube, and destroyed it.

The condensing cell was fitted with a 10/30 standard taper joint on each end so that the lead nitrate tube and the NOCl assembly could be attached.

The NO<sub>2</sub> was collected in a trap cooled by a dry ice-acetone mixture, and the oxygen was allowed to escape into the atmosphere through the soda lime trap. The NO<sub>2</sub> produced was relatively dry and pure, but was redistilled into the second trap to eliminate small amounts of nitric acid that may have been formed.

The NOCl reaction assembly was composed of eight vertical tubes, 22 mm in diameter and 30 cm long, arranged so that the gas flowed from one to the next in succession. The first six were filled with moist KCl (2.4% water as recommended by Whittaker), the seventh with CaCl<sub>2</sub>, and the eighth with P<sub>2</sub>O<sub>5</sub>. The last tube was fitted with a 10/30 standard taper joint so that a condensing bulb could be attached.

The NO<sub>2</sub> was vaporized directly into the KCl tubes, where the reaction to form NOCl occurred essentially instantaneously. The boundary of the reaction could easily be followed since the NO<sub>2</sub> is reddish-brown, while the NOCl is greenish-yellow. This boundary provided a simple indication of the exhaustion of the reagents. When the reaction reached the end of the fourth tube, all the tubes were refilled with the moist KCl. In this manner, never less than two tubes, the fifth and sixth, acted as "purge" units, insuring that no NO<sub>2</sub> could be collected with the NOCl. The NOCl was collected in a trap cooled with a dry ice-acetone mixture. This trap was fitted with a 10/30 standard taper joint so that it could be detached from the NOCl train, and

transferred to the ozonizing apparatus. The trap had an outlet of capillary tubing to allow free passage of uncondensable gases, such as air, through the system during collection of the NOCl. When sufficient NOCl had been collected, the outlet was sealed with a torch, and the trap was disconnected from the reaction system and capped with a 10/30 standard taper plug. It was stored over dry ice until needed.

Spectrographic examination of this material showed no trace of NO<sub>2</sub> lines in the visible or ultraviolet regions.

Because of the extreme explosion sensitivity of liquid ozone, it was felt desirable to try to prepare NO<sub>2</sub>Cl from NOCl and dilute ozone, which would remove the necessity for having liquid ozone. This was first attempted by maintaining the temperature of the NOCl such that its vapor pressure was approximately equal to the partial pressure of the ozone. Dilute ozone, directly from the ozonizer, was passed over the liquid NOCl, and the resulting gas condensed with liquid nitrogen. Considerable time was expended with this process, but the difficulties of trying to maintain the optimum conditions ruled it out as a good method.

It was then thought to condense NOCl in a tube, and to condense the O<sub>2</sub>-O<sub>3</sub> mixture over it, using a liquid nitrogen bath. This also bore no fruit, since the two molecules apparently react only in the concentrated gaseous state.

Because of the failure of these attempts, it was necessary to resort to the use of concentrated ozone as suggested in the initial work of Schumacher and Sprenger.

The concentrated ozone was prepared in the same manner as

reported by Wilson,<sup>(11)</sup> using a duplicate apparatus.

The ozonizing train consisted of a safety trap, a sulfuric acid bubbler and  $P_2O_5$  tube to remove water, a fritted glass disc to remove dust and  $P_2O_5$  particles, the ozonizer, and the condensing bulb.

The ozonizer (diagrammed by Robinson<sup>(12)</sup>) consisted of three concentric glass tubes. The inner tube was sealed to hold water, and the outer tubes formed a water jacket. The oxygen passed between the two inner tubes, where it was partially converted to ozone by the action of the high voltage discharge. The water jacket and one side of the transformer secondary were grounded to a water pipe, while the other side of the transformer secondary winding was connected to the central water tube. The conductivity of the water was quite sufficient to produce an even discharge. The water jacket also served to keep the unit cool, improving its efficiency.

The transformer was a General Electric X-ray transformer, the primary of which was controlled with an autotransformer.

Nitrogen in the system was converted quantitatively to  $N_2O_5$  in the ozonizer, and, since  $N_2O_5$  has a spectrum of its own, it had to be removed. There are indications also that it catalyzes the decomposition of ozone. The dry ice-acetone mixture attained a low enough temperature that the  $N_2O_5$  was adequately removed.

The ozone was condensed in the condensing bulb (diagrammed by Wilson<sup>(11)</sup>) immersed in liquid nitrogen. Because of the extreme shock sensitivity of liquid ozone, the Dewar flask containing the liquid nitrogen was placed on an elevator, driven by a small reversible electric motor, and the elevator and condensing bulb were placed in a wooden case



with a door of safety glass. In this way, the liquid nitrogen could be raised or lowered at will with complete safety to the operator.

The large, bulbous "weak spots" at the top of the condensing bulb, and the 2 mm capillary tubing attached to them, are for the purpose of protecting the rest of the apparatus from the shock of an ozone explosion. The capillary tubing offers a relatively unhampered path to the slow flow of the gases, but acts as a "brake" to the shock wave. The "weak spots" were made from 12 mm tubing on which spots had been heated, and blown out. Their purpose was to further relieve the force of the shock wave by releasing it to the atmosphere. In practice, this arrangement has worked very well to protect the remainder of the equipment from damage. All glassware within the case was usually demolished.

Ozone was prepared by passing the oxygen through the system at a rate of 5-7 bubbles per second for a period of two hours, and condensing the partially ozonized gas with liquid nitrogen. Oxygen condensed with the ozone was removed by pumping on the sample cooled in liquid nitrogen for a period of four hours.

Figure 2 illustrates the system used to prepare the  $\text{NO}_2\text{Cl}$ . The volume of the reaction flask was about one liter. A Bourdon gauge, used as the null cell, is of the type described by Barr and Anhorn.<sup>(13)</sup> In order to protect the gauge from undesirable pressure differentials, which might destroy it, a stopcock was placed across it, and left open at all times, except when actually measuring the pressure of the  $\text{NO}_2\text{Cl}$ , when the stopcock was closed.

The soda lime trap was wrapped with asbestos paper and 5 feet of No. 22 nichrome wire, similar to the  $\text{NO}_2$  heater. It was run at 20 volts,

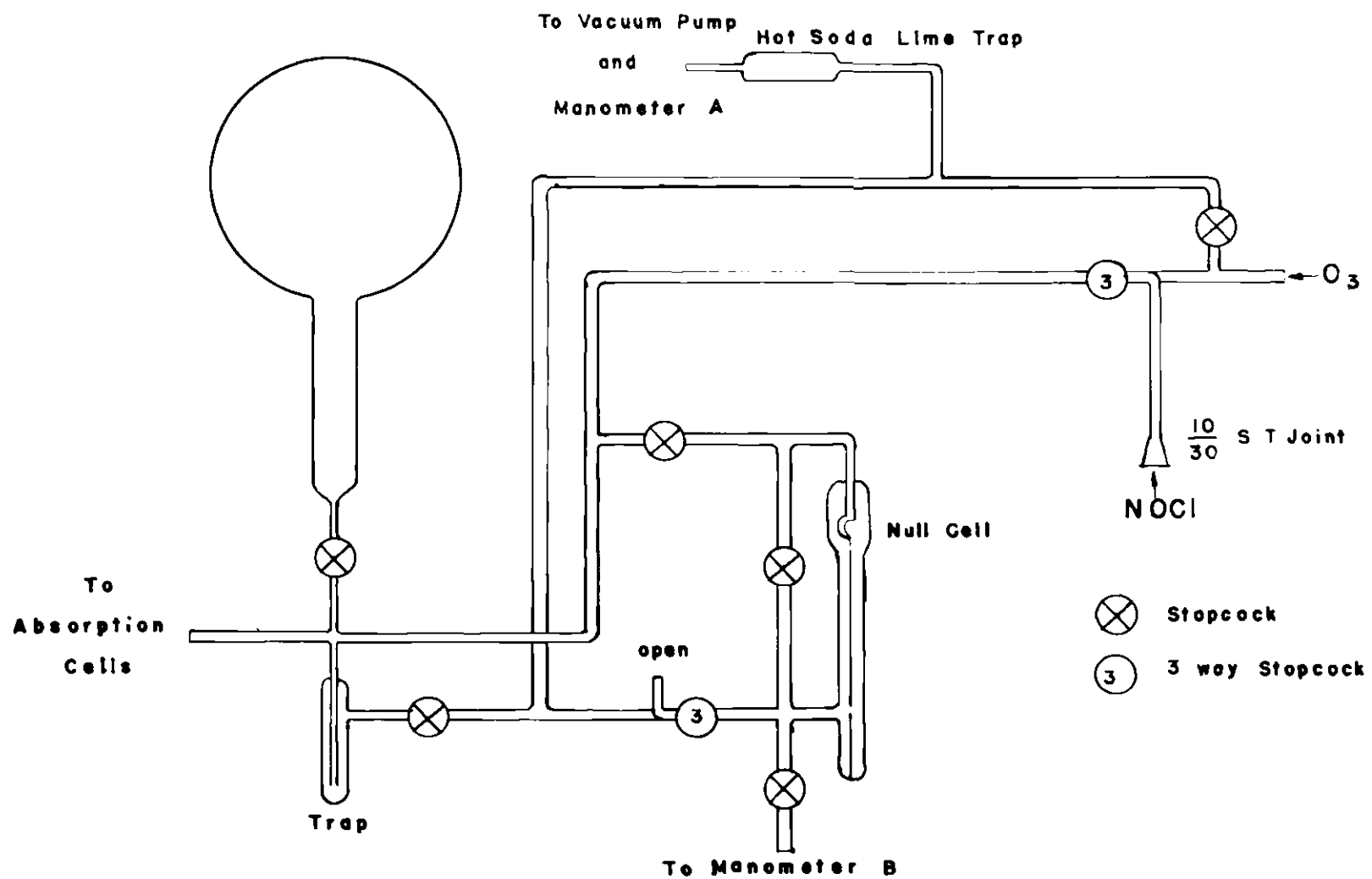


Fig. 2  $NO_2Cl$  Reaction System

and operated hot enough to decompose the ozone effectively, and to absorb the  $\text{NOCl}$  and  $\text{NO}_2\text{Cl}$ , thus protecting the pump and connecting rubber tubing.

Nitrosyl chloride was introduced into the evacuated system to a pressure of 200 mm as measured by manometer A. The ozone was allowed to build up to the same pressure by lowering the liquid nitrogen, and was then introduced into the  $\text{NOCl}$  where the oxidation took place. The reaction mixture was frozen down into the trap with liquid nitrogen and the system evacuated. The excess ozone and oxygen were pumped off, after which the temperature of the  $\text{NO}_2\text{Cl}$  was raised to  $-78^\circ\text{C}$ . Further pumping removed carbon dioxide which had formed from the oxidation of the stopcock lubricants (described later). Carbon dioxide did not interfere in the ultraviolet absorption measurements except as a diluent, since the first absorption band does not extend to wavelength longer than  $1700\text{\AA}$ . However, as a diluent, it caused great error in determining the absorption coefficients of  $\text{NO}_2\text{Cl}$ , and it had to be removed. The  $\text{NO}_2\text{Cl}$  was then allowed to vaporize into the absorption cell assembly.

Nitryl chloride has a strong corrosive action on mercury, and special precautions had to be taken to measure the pressure. No decomposition traps could be used, because of the danger of decomposition products finding their way into the absorption cell. The null cell, which gives a deflection with pressure differential, was used, with the  $\text{NO}_2\text{Cl}$  on one side, and the manometer B and air on the other, with excellent results.

The various absorption cells were then removed from the reaction system, and transferred to the optical system for the absorption measure-

ments.

Silicone grease and Apiezon N were used as stopcock lubricants with about equal resistance to oxidation. The Apiezon N did seem to lose its lubricating efficiency a little quicker, however.

## ULTRAVIOLET AND VISIBLE INVESTIGATIONS

The first absorption work was largely of a qualitative nature and had a two-fold purpose:

- 1) To test the purity of the product,
- 2) To get a general indication of the nature of the spectrum.

This was first undertaken by using an absorption cell of Pyrex tubing 25 mm in diameter and 120 cm long, with optically flat Pyrex windows fused onto the ends. This cell was attached through a stopcock to the  $\text{NO}_2\text{Cl}$  reaction system. When the cell was full of gas, the stopcock was closed, and the cell was transferred to the optical system. The light source was a 500 watt projection lamp operated at 90 volts, and the recording device was a Cenco replica grating spectrograph, adapted to use 35 mm spectrographic film, type 103-F.

Close examination of the spectrum photographs showed no trace of any sort of absorption bands or structure at pressures up to 200 mm throughout the visible range to 3500Å, the limit of the apparatus. This indicated that  $\text{NO}_2\text{Cl}$  exhibited no absorption in the visible and the near ultraviolet regions, and that the samples contained no  $\text{NO}_2$  or  $\text{NOCl}$ , both of which have strong visible spectra.

For the ultraviolet investigation, a similar cell was made from 20 mm tubing also 120 cm long, with optically flat silica windows sealed onto the ends. The ends of the tube were ground flat with 600 mesh carborundum, and annealed with a bunsen flame. The windows were 25 mm squares of 96% silica (Corning filter number 791) having good transmission down to 2200Å. Since the Pyrex and silica could not be fused directly, they were sealed together with fused silver chloride. A layer of

Sauereisen cement was placed over the silver chloride to lend physical strength to the seal, and this in turn was covered with a layer of paraffin to insure vacuum tightness. In use, this cell held a vacuum very well, and did not seem to be noticeably attacked by the nitryl chloride.

The light source was a hydrogen discharge lamp, furnished with the Beckman model DU spectrophotometer. Its only disadvantage was its low intensity, necessitating long exposures.

The spectrum photographs showed no trace of any band or fine structure, but exhibited only a continuum from 3300Å to a region beyond the 2200Å limit of the equipment. This region of absorption was narrowed by reduction of the gas pressure, but the continuum at each pressure still extended beyond the 2200Å limit, although the upper limit was reduced from 3300Å to 2600Å. Slit settings varied from 0.01-.03 mm, quite sufficient to resolve the fine structure of  $\text{NO}_2$ .

These data strongly indicate that, while the potential function of the ground electronic state has a minimum, that of the excited state does not. Hence, any transition results in dissociation.

In order to interpret the data better, it was desired to know the absorption coefficients for the range 3000-2200Å. This was accomplished by the use of a shorter absorption cell (Figure 3), with silica windows sealed onto the ends as described earlier. The cell was made from 20 mm Pyrex tubing, and was 15.2 cm long. A dummy cell completely of Pyrex, and of similar volume, was connected to the absorption cell through a three way stopcock, and a vacuum line was attached to the third leg of the stopcock. The stopcock was arranged so that the dummy cell could be

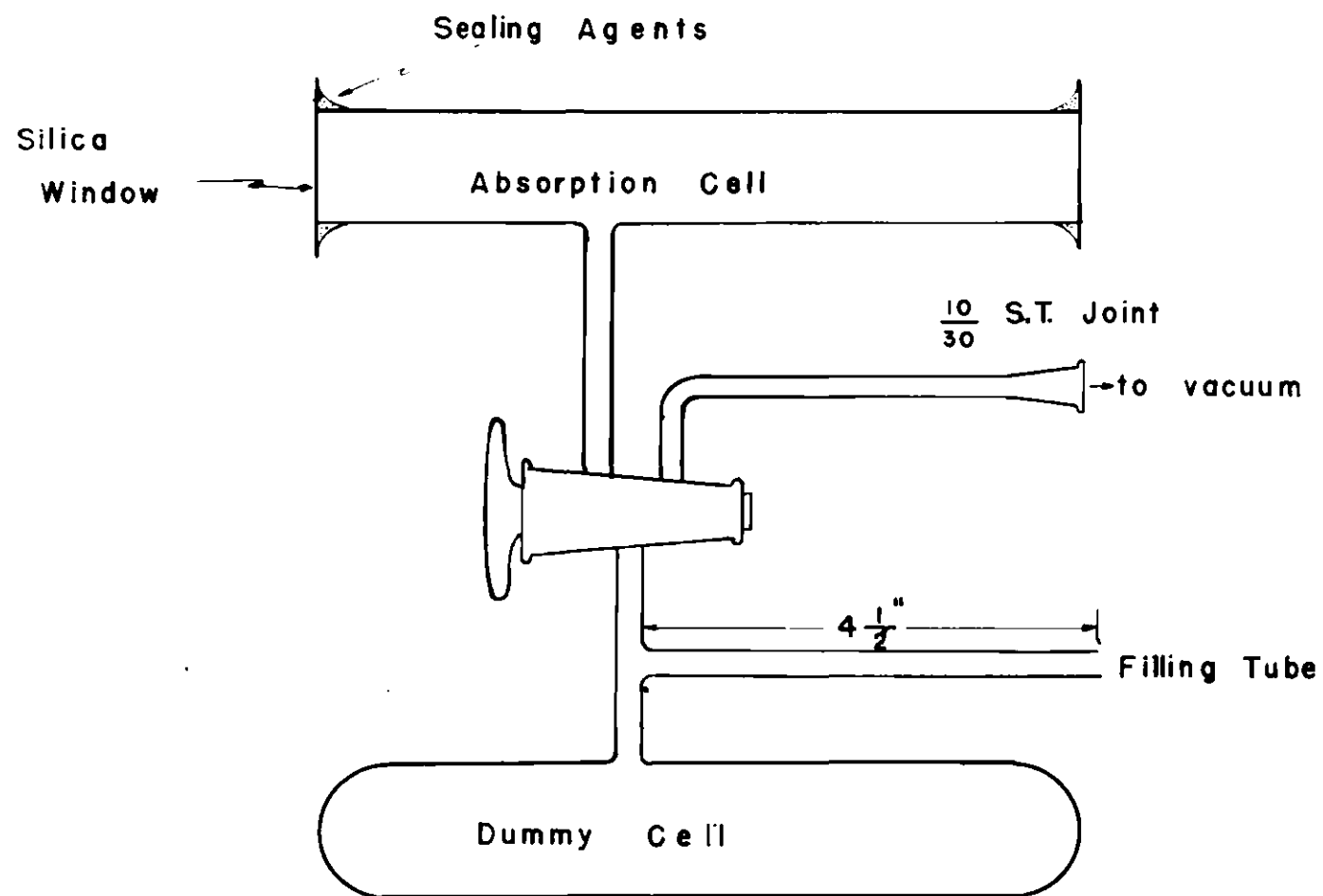


Fig. 3 Ultraviolet Absorption Cell

connected alternately to the absorption cell and to the vacuum line. In this way, the dummy was evacuated while an absorption measurement was being made, the stopcock was turned, connecting the dummy to the absorption cell and cutting its pressure by a factor depending upon the volumes. A new absorption measurement was made while the dummy was again being evacuated, and the whole procedure repeated. In this manner, several readings of transmission could be made at different pressures, with only one initial pressure measurement, that made with the null cell. Another stopcock, not shown, was connected directly from the absorption cell to the vacuum line to enable readings of cell transmission alone to be made.

The cell was attached to the  $\text{NO}_2\text{Cl}$  assembly by a tube leading from the dummy. In order to keep a constant volume, this tube was always sealed off 4 1/2 inches long, after the cell had been filled and the stopcock closed.

It was necessary to know the fraction that the pressure was cut by this scheme. This was accomplished by attaching the cell, by means of the filling tube, to the top of an open tube manometer, using a short piece of Tygon tubing. (The tube pointed down and the cells were horizontal). A short piece of glass tubing was sealed onto the bottom of the U of the manometer, and a bulb of mercury was attached at this point through a long piece of rubber tubing. By raising or lowering the bulb of mercury, the mercury level in the manometer could be brought to any given level. When a reading of pressure in the cell was to be made, the bulb was raised until the mercury level was at the 4 1/2 inch point on the filling tube of the cell assembly. The vacuum line was attached to the third leg of the stopcock as in normal operation.



The pressure in the cell was reduced stepwise as described earlier, and the pressure read each time after bringing the mercury level to the 4 1/2 inch point. In this manner, the pressures were read at constant volume, and the ratios of the pressures gave the cutting fraction, which was found to be 0.458. Thus, each time the evacuated dummy was connected to the absorption cell, the pressure was reduced to .458 its original value.

The cell was filled with  $\text{NO}_2\text{Cl}$  and the pressure measured by means of the null cell. It was then removed from the reaction assembly, the filling tube sealed at 4 1/2 inches, and the cell placed in the optical system.

For this series of readings, quantitative values of transmission were necessary; hence, a Beckman model DU quartz spectrophotometer was used, and was adapted to a chart recording instrument for permanent records. This adaptation is described by Wilson.<sup>(11)</sup> The cell was placed on an optical bench between the hydrogen discharge lamp and the spectrophotometer, and the various readings of transmission vs pressure and wavelength made.

In order to try to find any fine structure that might have escaped photographic analysis, the wavelength mechanism was driven by a synchronous motor. Since the chart recorder was also driven by a synchronous motor, calibration was an easy matter. Traces were made of transmission vs wavelength for various pressures. Again, no fine structure was found, only a continuum. The absorption coefficients were found and plotted as a function of wavelength. This was rechecked, using a point-to-point trace for accuracy and speed.

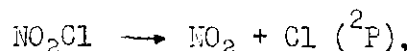
It was also necessary to find the absolute absorption coefficient at 3000Å since the other coefficients were based on the assumption that this was zero, and are relative coefficients. Traces were made of transmission vs pressure at 3000Å, and the optical density was plotted against the pressure. The absorption coefficient was found from the slope of this line, and the absolute magnitude of the coefficients at other wavelengths were found from this value.

These coefficients are shown in Table I, and a plot of the coefficients against wavelength is given in Graph 1. The calculations are derived from the Beer-Lambert Law.

It is noticed that the coefficient rises slowly to about 2700Å, then rises much more quickly to the 2200Å limit.

It was desired to try to determine the dissociation products from this excited state. No thermodynamic data were found for  $\text{NO}_2\text{Cl}$  so approximations were used.

In the reaction



it was assumed that the heat of reaction was the same as the heat of formation of the N - Cl bond, which is 38.4 Kcal/mol.<sup>(14)</sup> This is not a bad assumption since the heat of dissociation for the reaction



is given as 38 Kcal/mol.<sup>(15)</sup> Actually, 38.4 is probably a little high since the N - O bond is strengthened in going from  $\text{NO}_2\text{Cl}$  to  $\text{NO}_2$ , while it remains essentially unchanged in going from  $\text{NOCl}$  to  $\text{NO}$ .

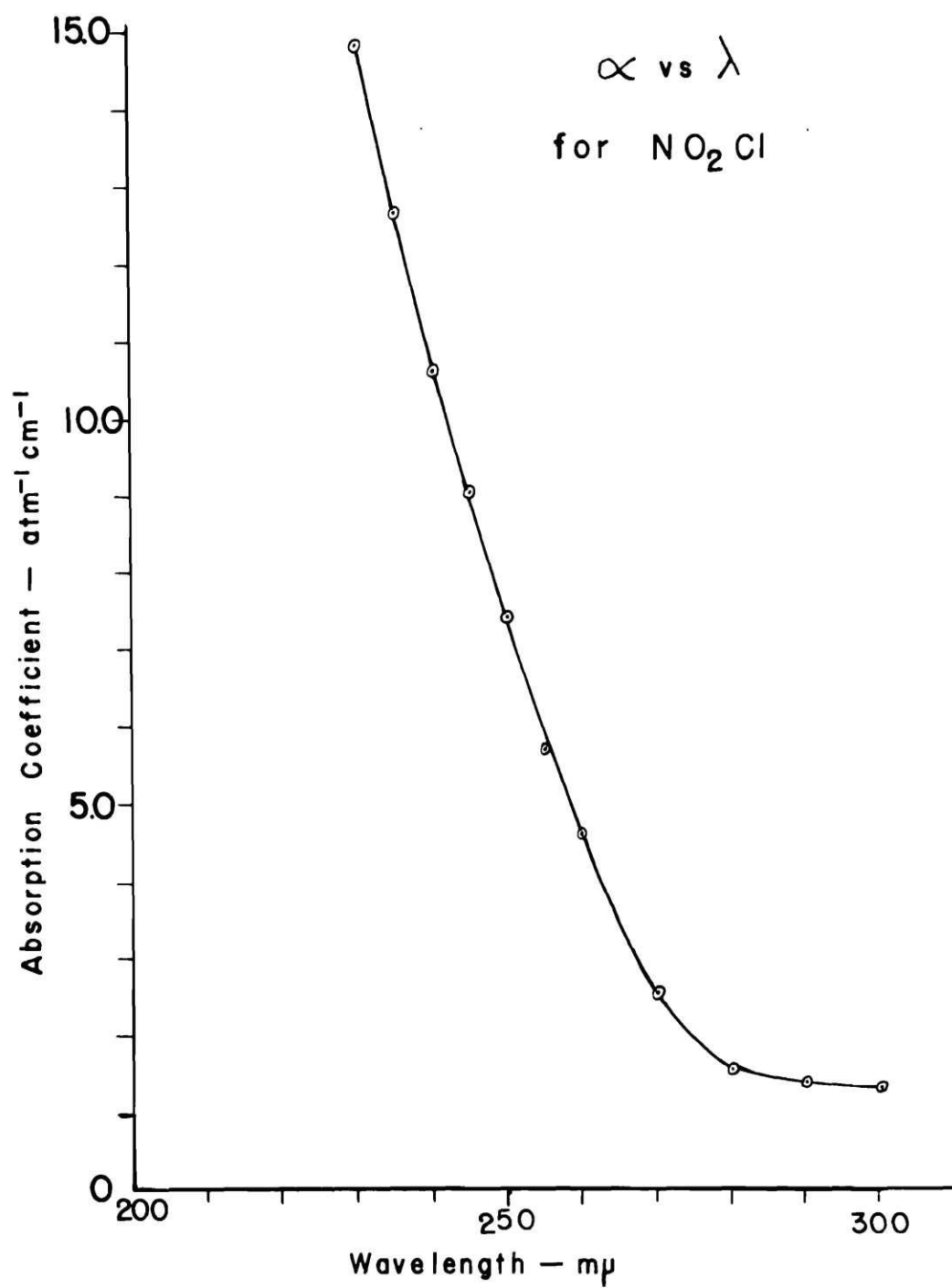
Assuming 38.4 Kcal/mol to be correct, the heat of formation of

TABLE I

## ABSORPTION COEFFICIENT VERSUS WAVELENGTH

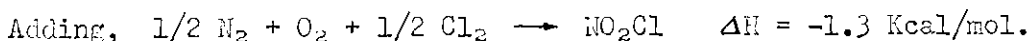
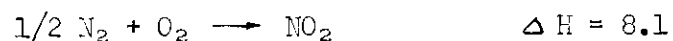
3000 A	1.32 atm <sup>-1</sup> cm <sup>-1</sup>
2900	1.41
2800	1.59
2700	2.54
2600	4.63
2550	5.75
2500	7.47
2450	9.08
2400	10.65
2350	12.70
2300	14.9
2250	High*
2200	High*

\*Experimental error here was much larger than the actual coefficients, and accurate values could not be found.

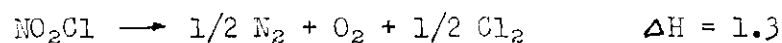


Graph 1 Absorption Coefficient vs Wavelength

$\text{NO}_2\text{Cl}$  at  $300^\circ\text{K}$ . can be calculated as follows:



Using this value, the heat of dissociation into  $\text{NOCl}$  and oxygen atoms may be calculated:



These values, when converted to electron-volts, become 1.66 ev for 38.4 Kcal/mol, and 3.17 for 73.1 Kcal/mol.

The various excited states for chlorine and oxygen atoms, and the  $\text{NOCl}$  and  $\text{NO}_2$  molecules were found, and are listed in Table II.

The excited states of the  $\text{NO}_2$  molecule are not clearly known. A spectrophotograph of  $\text{NO}_2$  reveals a broad absorption band extending from about 5300Å to 4000Å. A thorough search of the literature<sup>(18-32)</sup> reveals that the bands of  $\text{NO}_2$  in this region are too complex for analysis, while that at 8900Å is comparatively simple. It is not clearly known whether the band at 8900Å is the band head for the whole system or whether the band at 5300Å is another system. In view of the extent of the spectral range, it seems hardly likely that a single band could encompass 6400Å. Therefore, the assumption of another

TABLE II

## EXCITED STATES AND ENERGIES

State	Energy over the Ground State		Source
O ( $^1D$ )	15867 $\text{cm}^{-1}$	1.97 ev.	17
O ( $^1S$ )	33793	4.19	17
Cl ( $^4P$ )	71954	8.92	17
NOCl*	16240	2.02	15
NO <sub>2</sub> *	8900 A	1.39	18
NO <sub>2</sub> **	5300 A	2.34	--

$$\begin{aligned}
 1 \text{ ev} &= 23055 \text{ cm}^{-1} \\
 &= 22.8 \text{ Kcal/mol}
 \end{aligned}$$

electronic band starting at 5300Å does not seem at all unlikely.

Using the energy values from Table II, the energy required for several dissociation schemes have been calculated, and are listed in Table III.

The wavelength at which  $\text{NO}_2\text{Cl}$  begins to absorb is around 3300Å, or 3.76 ev. This, plus the fact that the energies shown in Table III may be slightly large, seems to indicate strongly that reaction 4) is the proper dissociation. The nature of the second excited state of  $\text{NO}_2$  is unknown, however.

The change in the slope of the curve of absorption coefficient vs wavelength is best explained by the Franck-Condon Principle: Transitions are most probable when the nuclei do not change positions appreciably. This means that a transition "straight up" on the potential function curves is most probable, as illustrated by lines A and B on Graph 2. Line A would be an intense transition, because of the large population of the lower vibrational levels of the lower electronic state. Line B, of longer wavelength, would be considerably weaker, since, although the transition is quite probable, the population of the higher excited vibrational states is low. Line C would also be weak, because of the Franck-Condon Principle, although the population of the lower vibrational states is large.

The fact that the absorption coefficient is still increasing at 2200Å indicates that the transition from the lowest state of the molecule consumes more energy than 2200Å can supply. Part of the upper state potential curve is dotted for this reason.

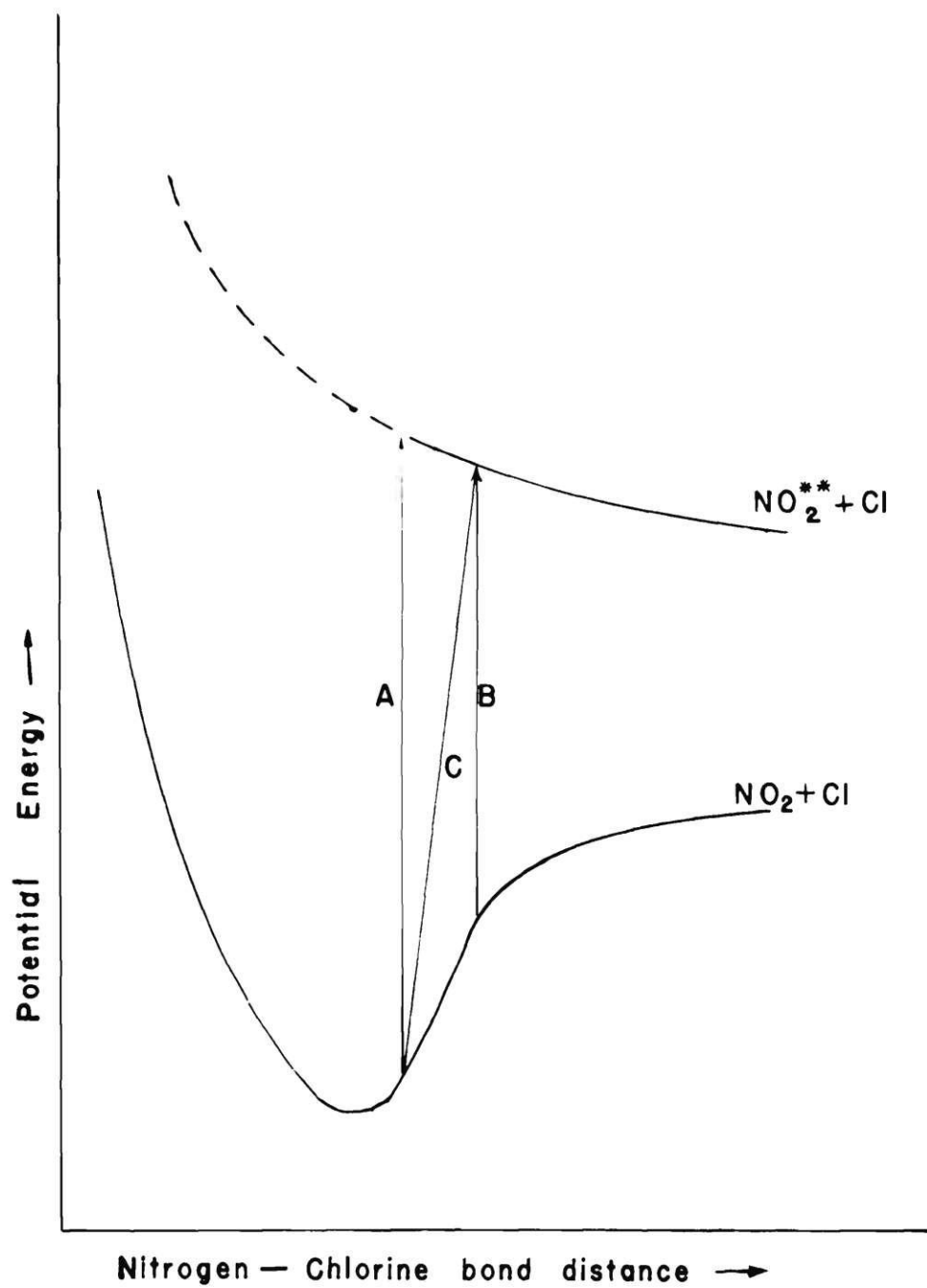
In summary,  $\text{NO}_2\text{Cl}$  exhibits no electronic absorption above 3300Å,

TABLE III

## ENERGIES OF DISSOCIATION FOR SEVERAL MECHANISMS

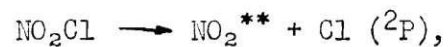
	Mechanism	Energy
1)	$\text{NO}_2\text{Cl} \longrightarrow \text{NO}_2 + \text{Cl } ({}^2\text{P})$	1.66 ev
2)	$\longrightarrow \text{NO}_2 + \text{Cl } ({}^2\text{P})$	10.58
3)	$\longrightarrow \text{NO}_2^* + \text{Cl } ({}^2\text{P})$	3.05
4)	$\longrightarrow \text{NO}_2^{**} + \text{Cl } ({}^2\text{P})$	4.00
5)	$\longrightarrow \text{NOCl} + \text{O } ({}^3\text{P})$	3.17
6)	$\longrightarrow \text{NOCl} + \text{O } ({}^1\text{D})$	5.14
7)	$\longrightarrow \text{NOCl}^* + (\text{O}^3\text{P})$	5.19





Graph 2 Potential Energy Curve

and it is continuous from this value to a point beyond the 2200A limit of the apparatus. No fine structure or band system was found. The first electronically excited state is unstable, the molecule probably dissociating according to the equation:



with dissociation limit at approximately 4.0 ev or 3100A.

## INFRARED INVESTIGATIONS

In order to determine the fundamental vibrational frequencies in the infrared region, the Beckman model IR-2 infrared spectrophotometer was used. However, the gas cells built into the machine could not be used since they are put together with lead amalgam seals. The spectrum obtained would have been principally that of decomposition products, since  $\text{NO}_2\text{Cl}$  attacks the lead.

The spectrophotometer is built so that the light source compartment can be removed a short distance from the monochromator unit to allow the insertion of special absorption cells. A lucite box one foot in length and with a 4 inch square cross section was made. One and one-half inch diameter holes were cut in the ends to allow free passage of the infrared light, and the box was placed between the light compartment and the monochromator unit, which were joined with one foot extension screws. The lucite box was held in place simply by the frictional force on the ends. A pan of silica gel was placed on the floor of the box, and the cell, described later, was placed in the box. The weight of the cell was supported by two V-blocks, also on the floor of the box. The holes through which the glass leads to the cell entered the box were sealed with paraffin, insuring a comparatively dry atmosphere in the box.

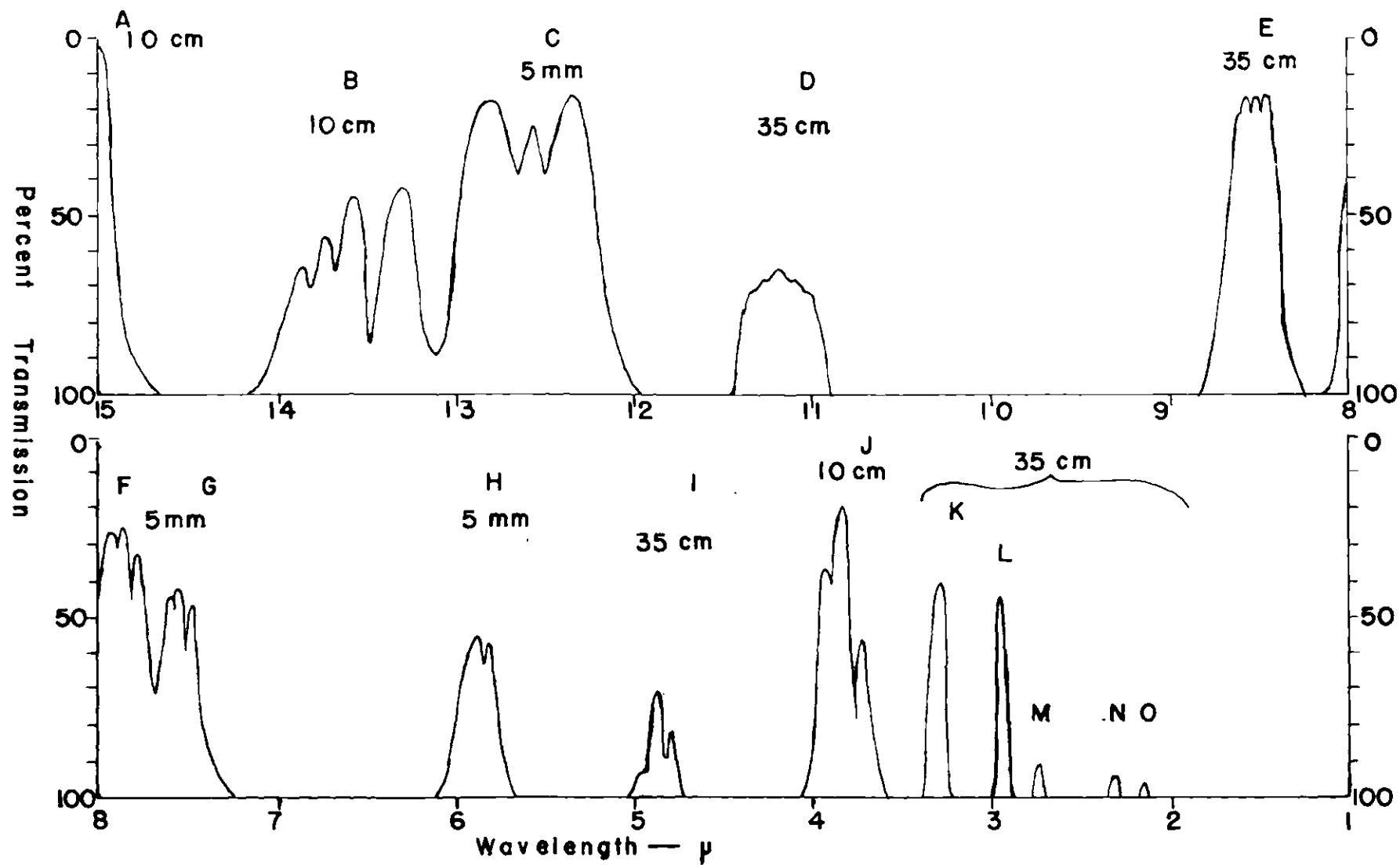
The absorption cell was made from 25mm Pyrex tubing, 24 cm long, with threaded steel flanges sealed onto the ends with Sauereisen cement. The ends of the cell were ground with carborundum and jewelers rouge until both the glass and the metal were flush and smooth. Sodium chloride windows were placed on the ends, and caps screwed on to hold them in place. Apiezon N was used as a sealing medium, but it was found that a

good vacuum could not be maintained. When Apiezon Q was substituted, however, the cell held a good vacuum. It did not seem to be attacked by the  $\text{NO}_2\text{Cl}$ , and no trace of  $\text{NO}_2$  bands could be found in the spectra. The windows were 1 1/2 inch in diameter, 1/4 inch thick, and were furnished by the National Technical Laboratories.

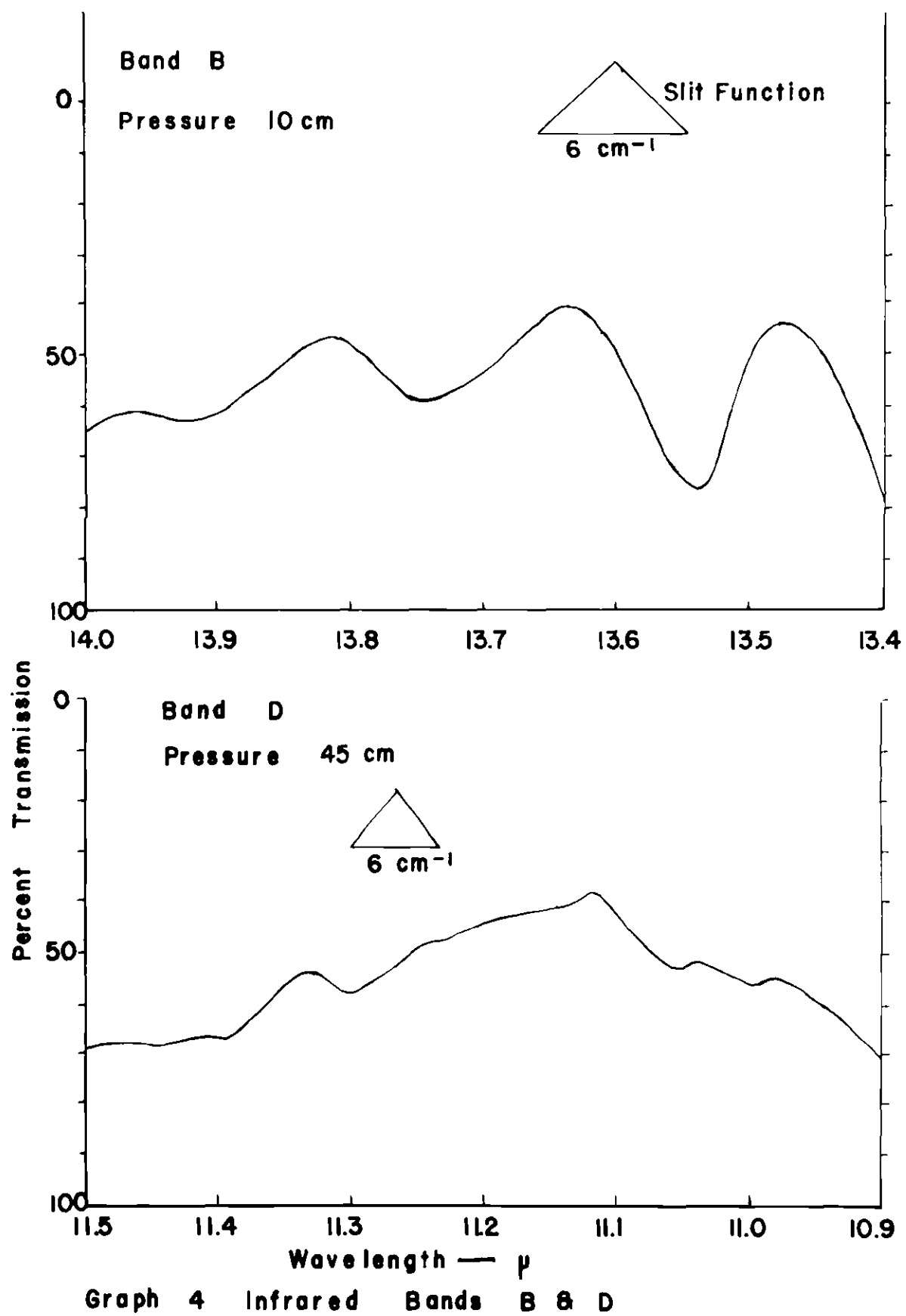
In order to get an indication of the spectrum as a whole, a trace was made at high speed, and low damping, 20 minutes being required for the complete range from 1-15 $\mu$ . Graph 3 illustrates the spectrum obtained. The several strong lettered bands were retraced using a low speed and high damping, and are shown on the succeeding Graphs. Only the envelopes are shown, since the resolution of the instrument is, at best, 6  $\text{cm}^{-1}$ , while the rotational structure is of the order of one  $\text{cm}^{-1}$ . (See section on structure.) The intensities of the various bands are indicated by the pressures required to give a reasonable amount of transmission through the 24cm cell. These pressures are entered over the center of each band. The amount of the spectrum covered by the slit in each case is entered near the pressure entry as a triangle representing the slit function, with the resolution just below it.

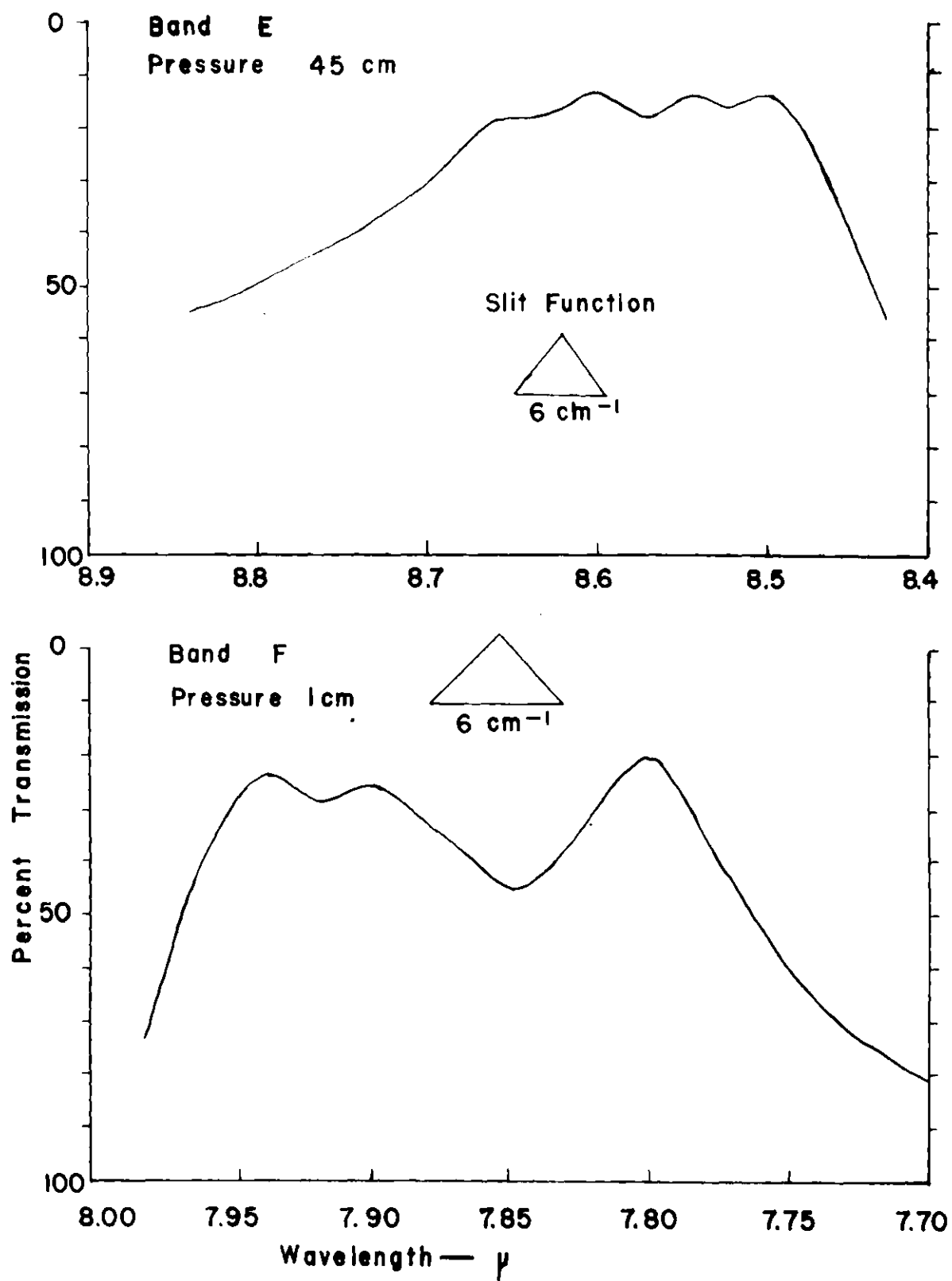
These traces were made with the smallest possible slits and greatest possible gain of the amplifier, but the resolution still was of the order of 6  $\text{cm}^{-1}$ , insufficient to resolve fine structure.

Graph 3 shows that at the 15 $\mu$  edge of the spectrum, there is strong absorption which decreases with decreasing pressure of gas. This strongly indicates the presence of another band just beyond 15 $\mu$ . The exact location of this band cannot be determined with the present

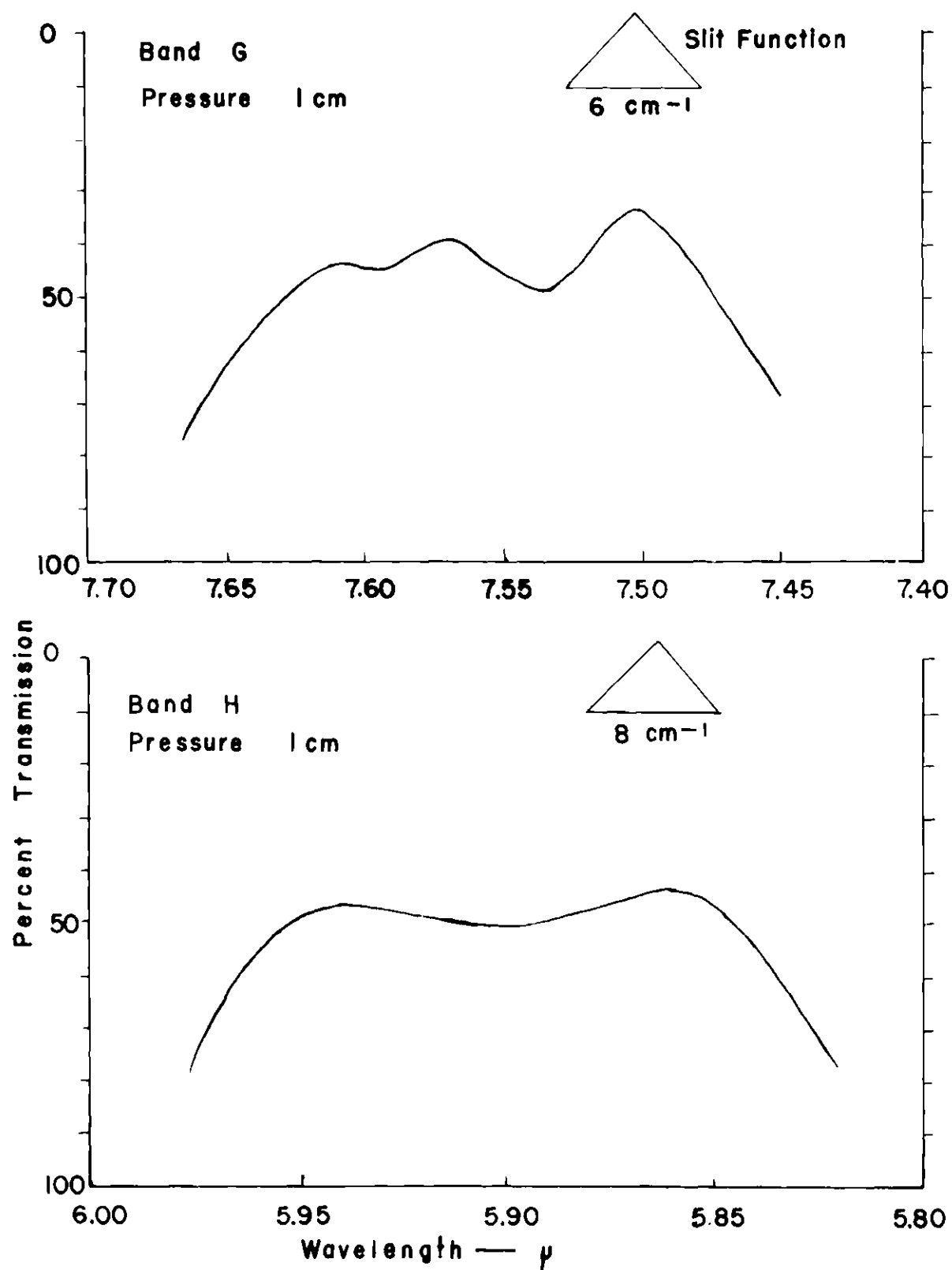


Graph 3 Infrared Absorption Spectrum of  $\text{NO}_2\text{Cl}$





Graph 5 Infrared Bands E &amp; F



Graph 6 Infrared Bands G &amp; H

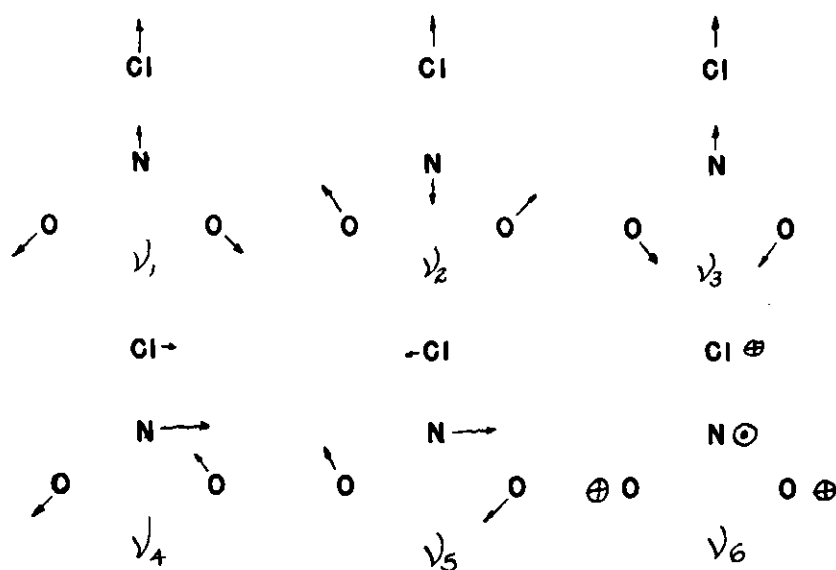


equipment.

The intensity of bands A, B, C, E, F, G, and H indicates that they are probably fundamentals. Band D is weak and complex, and is assigned as a combination band. The remainder of the bands are also weak, and high in energy, and they are assigned as combination and overtone bands.

It is to be noted that seven bands were intense, while there can be only six fundamentals. One of these is, therefore, a combination or overtone band.

It is assumed that nitryl chloride is a planar asymmetric top molecule of symmetry  $C_{2v}$ . The six fundamental vibrations are as shown: (19)



Two of these vibrations,  $\nu_4$  and  $\nu_5$ , give rise to Type B bands. Herzberg<sup>(19)</sup> describes these bands as possessing no Q branches, only P and R branches. Only one band of this type was found, band H at  $5.9\mu$ , and it was assumed that the other B band was the band just outside the range at around  $15.5\mu$ . Since  $\nu_4$  involves stretching of the bonds,

while  $\nu_5$  involves primarily bending, the higher frequency band was assigned to  $\nu_4$  and the lower to  $\nu_5$ . Band B at  $13.6\mu$  is the most complex, possessing several maxima. Because of its complexity, it was assigned as a Type C band, and, hence,  $\nu_6$ , the only vibration yielding this type band.

This left four Type A bands, which are described by Herzberg as possessing clear, simple P, Q, and R branches.  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  give rise to Type A bands, and since  $\nu_3$  involves only bending, while the others involve stretching of the bonds, it was assigned to the lowest band at  $12.5\mu$ .

Of the three remaining bands, it was noticed that the band at  $7.8\mu$  was almost exactly twice the band at  $15.5\mu$ . A study of the symmetry properties<sup>(19)</sup> shows that the second harmonic of  $\nu_5$  would be a Type A band, and this was assigned to  $2\nu_5$ .

$\nu_2$  involves bending and some stretching of the bonds, while  $\nu_1$  involves primarily stretching. Therefore, band G was assigned to  $\nu_1$ , and band E to  $\nu_2$ .

Using these values for the fundamental vibrations, the remainder of the bands were assigned as shown in Table IV.

Bands M, N, and O were of such high frequency and so weak that several assignments could be made within the experimental error. Hence, no assignment was attempted.

Much more information can be gotten from further resolution of the several bands, and from extension of the analysis beyond  $15\mu$ .

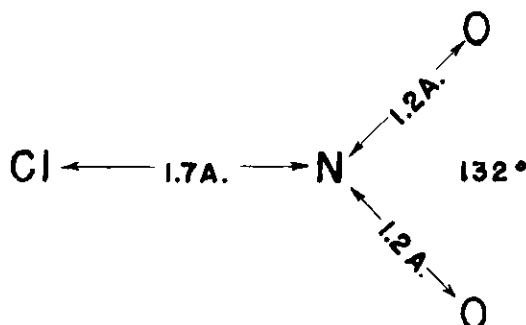
TABLE IV

## ASSIGNMENT OF INFRARED BANDS

Band	Frequency	Wavelength	Assignment
A	(643) $\text{cm}^{-1}$	(15.5) $\mu$	$\nu_5$
B	733	13.56	$\nu_6$
C	798	12.58	$\nu_3$
D	897	11.23	$\nu_4 - \nu_3$
E	1170	8.58	$\nu_2$
F	1272	7.87	$2 \nu_5$
G	1322	7.56	$\nu_1$
H	1695	5.91	$\nu_4$
I	2058	4.86	$\nu_1 + \nu_6$
J	2600	3.85	$2 \nu_1$
K	3014	3.32	$\nu_1 + \nu_4$
L	3390	2.95	$2 \nu_4$
M	3657	2.75	?
N	4255	2.35	?
O	4610	2.17	?

## MOLECULAR STRUCTURE AND THERMODYNAMIC DATA

The resolution of the Beckman model IR-2 spectrophotometer is insufficient to determine the rotational structure of the infrared bands, and the moments of inertia cannot be accurately determined. In order to calculate the entropy of  $\text{NO}_2\text{Cl}$ , its three moments of inertia must be known. From the work of Donohue,<sup>(34)</sup> the N - O bond distance in  $\text{NO}_2$  is found to be 1.20Å, and the angle between the oxygens,  $132^\circ$ . The N - Cl bond distance of 1.7Å has been taken from Pauling.<sup>(14)</sup>  $\text{NO}_2\text{Cl}$  probably exists, then, as shown:



The center of mass is easily found to be 0.55Å from the nitrogen to the chlorine.

Since the molecule uses all the valence electrons to form bonds, and there are none remaining, it is assumed to be planar. The three moments of inertia are defined:

$I_a$  is the least moment of inertia,

$I_b$  is the middle moment, and

$I_c$  is the largest moment.

The three moments have been calculated:

$$I_a = 64 \times 10^{-40} \text{ gm.cm.}^2 \quad (\text{through the N - Cl axis})$$

$$I_b = 144 \times 10^{-40}$$

$$I_c = 208 \times 10^{-40} \quad (\text{perpendicular to the plane of the molecule}).$$

The separation between the rotational lines in the infrared region is given by the expression: (19)

$$B = \frac{h}{8\pi^2 c I_a}$$

$0.44 \text{ cm}^{-1}$ , where  $I_a = 64 \times 10^{-40}$

The spectrophotometer would have to have a resolution better than  $.4 \text{ cm}^{-1}$  in order to resolve these lines.

Statistical Mechanics(34) yields expressions for entropy, internal energy, and heat capacity as follows:

1) Translational case,

$$E = 3/2 RT$$

$$C_v = 3/2 R$$

$$S = R(3/2 \ln M + 5/2 \ln T + \ln P + 1.157)$$

2) Vibrational case,

$$E = RTu(e^u - 1)^{-1} + E_0$$

$$S = R \left[ u(e^u - 1)^{-1} - \ln(1 - e^{-u}) \right]$$

$$C_v = Ru^2 e^u (e^u - 1)^{-2}$$

This is repeated for each fundamental vibration.

3) Rotational case,

$$E = 3/2 RT$$

$$S = R \left[ 3/2 \ln T + 1/2 \ln(I_a I_b I_c \times 10^{120}) - 3.446 \right]$$

$$C_v = 3/2 R$$

- 4) Symmetry number; since  $\text{NO}_2\text{Cl}$  has a symmetry number of two, the total entropy must be reduced by a factor  $R\ln 2$ .
- 5) Nuclear Spin, Mixing, Isotope, and Anharmonicity corrections have not been made, since they are, for the most part, small.

The symbols are conventional and are defined as follows:

$$u = \frac{hc\omega}{kT},$$

$M$  = molecular weight,  
 $T$  = absolute temperature,  
 $P$  = pressure in atmospheres,  
 $h$  = Plancks constant,  
 $c$  = velocity of light,  
 $k$  = Boltzmans constant,  
 $\omega$  = vibrational frequency in  $\text{cm}^{-1}$ .

By substitution of the proper values in the various formulae, heat capacity, internal energy, and entropy have been calculated for a pressure of one atmosphere. The internal energy, as derived from spectrographic data, is actually not the total energy, but the energy above a "zero point" energy, which can be found only from chemical data. The energies are, therefore, expressed as differences as shown.

The thermodynamic constants are listed as follows:

	300°K.	500°K.	1000°K.
$S^\circ =$	63.3	69.6	80.6 cal./deg.mol.
$C_v =$	8.7	12.0	15.7 cal./deg.mol.
$E^\circ - E_0^\circ =$	2000	5100	13,200 cal./mol.

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