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VIBRATIONAL SPECTRA OF COMPOUNDS IN THE GASEOUS STATE

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VIBRATIONAL SPECTRA OF COMPOUNDS

IN THE GASEOUS STATE

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ABBREVIATIONS USED IN TABLES

Symbol	Meaning
vvs	extremely strong
vs	very strong
s	strong
m	medium
w	weak
vw	very weak
vvw	extremely weak
vvvw	barely observable and questionable
d	diffuse
sh	sharp
b	broad
vb	very broad
db	doubled
sd	shoulder
e	Hg 4358 A
f	Hg 4347 A
g	Hg 4339 A
h	Hg 4108 A
i	Hg 4077 A
k	Hg 4046 A
H^o	heat content
E_o^o	internal energy
C_p^o	heat capacity
S^o	entropy
F^o	free energy (Gibbs)
R	Raman
I	infrared

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VIBRATIONAL SPECTRA OF COMPOUNDS IN THE GASEOUS STATE

CHAPTER I

INTRODUCTION

It is very desirable to obtain vibrational spectra of compounds in the gaseous state. Selection rules, based on the quantum-mechanical theory of the origin of such spectra, are derived on the assumption that the molecules are in the gaseous state. Moreover, contours of bands in the Raman spectrum of a gas may often yield more helpful information concerning the character of the vibrations than do polarization data. Also, the fundamental vibrational frequencies for the gaseous state are required to calculate the thermodynamic properties of compounds in the ideal gas state. In general, the differences between the vibrational frequencies in the liquid and gaseous states are not large. However, for the low frequencies the errors in the thermodynamical functions committed by using data for the liquid rather than for the gaseous state may be appreciable.

A summary of the early work on the Raman spectra of gases has been given by Welsh, et al.[1] Special attention was given by Welsh, et

[1]Welsh, Stansbury, Romanko, and Feldman, J. Opt. Soc. Am. 45, 338 (1955). Included were such workers as L. A. Ramdas, Indian J. Phys.

al., to the systematic and thorough work of Nielsen and Ward.[2]

Until recent years, the methods used to obtain vibrational Raman spectra of gases has been somewhat unsatisfactory. The usual irradiation apparatus has been essentially the same as that employed for liquids, but constructed on a larger scale. In order to obtain fairly complete spectral data, it was often necessary to use exposure times of the order of days or weeks. Even so, the spectra obtained were generally not as complete as desired. Furthermore, the index of refraction of the air inside the spectrograph will change because of atmospheric pressure variations occurring during long exposures. Raman bands will be broadened as a result of this effect. For these reasons, it is desirable to increase the intensity of the Raman bands in order to shorten the exposure times.

Three factors affect the Raman intensities; the number of molecules per unit volume, the intensity of irradiation falling on that volume, and the efficiency with which the scattered Raman radiation is gathered into the spectrograph.

The number of molecules per unit volume may be increased by raising the pressure within the Raman tube. However, the strength of the Raman tube and the effects of pressure broadening place an upper limit on

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3, 131 (1928); R. W. Wood, Phys. Rev. 33, 1097 (1929); idem, Phys. Rev. 35, 1355 (1930); idem, Phil. Mag. 7, 744 (1929); F. Rasetti, Phys. Rev. 34, 367 (1929); Dickenson, Dillon, and Rasetti, Phys. Rev. 34, 582 (1929); S. Bhagavantam, Nature 126, 995 (1930); A. Langseth and J. Rud Nielsen, Nature 130, 92 (1932); idem, Z. physik. Chem. B19, 427 (1932); idem, Phys. Rev. 46, 1057 (1934).

[2]J. Rud Nielsen and N. E. Ward, J. Chem. Phys. 10, 81 (1942).

the gas pressures that may be employed. The gas is usually contained in a glass tube which has a light trap at one end and a window and diaphragm system at the other end. Monochromatic radiation, usually provided by a Hg lamp, enters the tube perpendicular to its axis, and the scattered radiation passes through the window to the spectrograph. Few significant improvements have been made on the Raman tube, although the optical matching of this type of Raman tube with the spectrograph has been perfected.[3,4] Many modifications of Hg lamps have been made in order to increase the intensity of certain Hg lines (2537 A and 4358 A) without a simultaneous increase in intensity of the Hg continuum and broadening of the spectral lines. It is not the purpose of this work to investigate the properties of Hg lamps; however, certain improvements made in the last few years will be discussed later.

In 1951, Welsh, Cumming and Stansbury[5] increased the efficiency of a Raman tube by the use of spherical mirrors inside the tube. They based their design on a principle developed by J. U. White.[6] Welsh, et al., were able to increase the intensity, as compared to a similar tube without mirrors, by a factor of $1/(1 - R)$, where R is the reflective power of the mirrors. A detailed description of a similar Raman tube will be given in Chapter III.

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[3]J. Rud Nielsen, J. Opt. Soc. Am. 20, 701 (1930); 37, 494 (1947).

[4]G. Hansen, Optik. 6, 337 (1950).

[5]Welsh, Cumming, and Stansbury, J. Opt. Soc. Am. 41, 712 (1951).

[6]J. U. White, J. Opt. Soc. Am. 32, 285 (1942).

Welsh, et al., used air and water-cooled Hg lamps[7,8,9] at first, but later, following a design by B. P. Stoicheff,[10] completely water-cooled Hg lamps were employed as sources of illumination. The principal advantage of the Stoicheff lamp was that the lamp barrel could be maintained at approximately room temperature, thereby reducing the Hg continuum considerably. Also, an elaborate air-cooling system is made unnecessary. Kovar to glass electrodes were employed, and they appear to be more satisfactory for this purpose than tungsten to glass electrodes.

With the Raman tube and Hg lamps described above, Welsh and coworkers have been able to observe the Raman spectra of many compounds in the gaseous state; their primary interest being in the study of fine structure in rotational and rotation-vibrational spectra. They were able, for example, to obtain the rotational Raman bands of gaseous CO_2 at one atmosphere pressure, in a two minute exposure.[11] With such an apparatus it is possible to study the vibrational Raman bands of compounds in the gaseous state, and this, together with the study of vibrational infrared spectra, has been the purpose of the present work. The necessary infra-

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[7]D. H. Rank and J. S. McCartney, J. Opt. Soc. Am. 38, 279 (1948).

[8]H. H. Claassen and J. Rud Nielsen, J. Opt. Soc. Am. 43, 352 (1953).

[9]Welsh, Crawford, Thomas, and Love, Can. J. Phys. 30, 577 (1952).

[10]B. P. Stoicheff, Can. J. Phys. 32, 330 (1954).

[11]Welsh, Stansbury, Romanko, and Feldman, J. Opt. Soc. Am. 45 338 (1955).

red equipment, including a 1-m cell for gases, has been available to this laboratory for over two years.

CHAPTER II

STATEMENT OF THE PROBLEM

It was desired to design, construct and test the performance of a multiple-reflection Raman tube for gases and to observe the Raman spectra of selected compounds in the gaseous state. It was intended further to assign the fundamental vibrational frequencies and to make a detailed interpretation of the observed spectra. The following compounds were chosen for this study:

1. Vinyl Chloride, $CH_2 = CHCl$
2. Vinyl Bromide, $CH_2 = CHBr$
3. Trifluoroacetonitrile, CF_3CN

In addition, it was desired to calculate the thermodynamic functions of vinyl chloride and vinyl bromide from the assigned values of the fundamental frequencies.

Finally, the Raman spectra of several other compounds, which were studied by other workers in this laboratory, were to be observed in the gaseous state. These compounds were:

1. Dimethyl Ether, $(CH_3)_2O$
2. Sulphur Hexafluoride, SF_6
3. 1-Fluoro-1-chloroethylene, $CFCl = CH_2$
4. 1,1-Difluoro-bromoethylene, $CF_2 = CHBr$

5. Ethylene Oxide, $(CH_2)_2O$

CHAPTER III

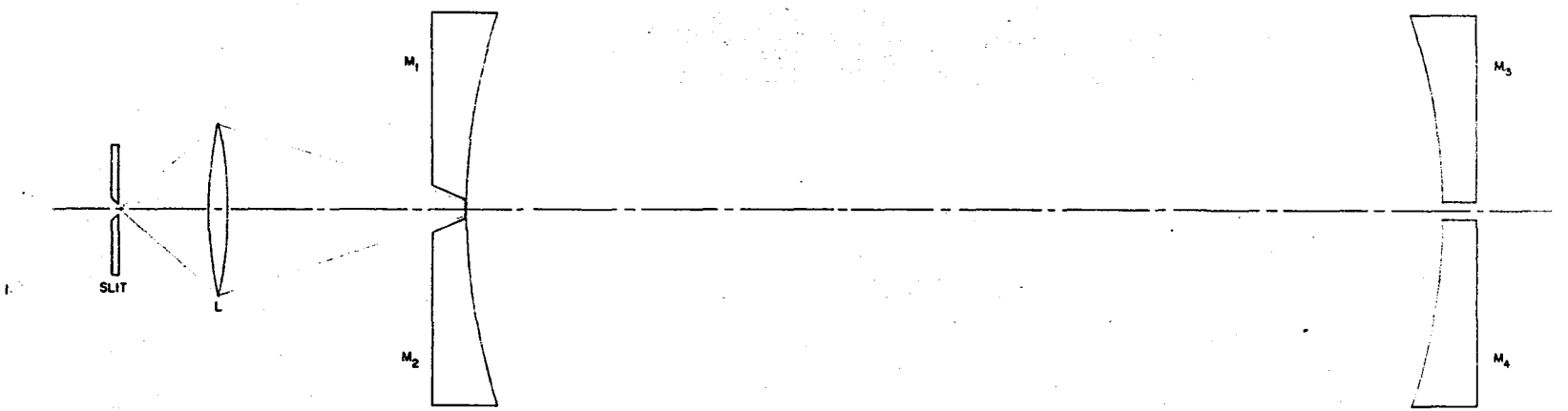
EXPERIMENTAL PROCEDURE

The Multiple-Reflection Raman Tube

Principle. The multiple-reflection Raman tube is similar to the tube designed by Welsh, *et al.*[1] Before proceeding to the details of its design, it seems advisable to give a brief explanation of the optical properties of the tube.

The optical system of the tube is shown in Figure 1. M_1, M_2, M_3 and M_4 are spherical front-surface mirrors of focal length 60 cm, cut along a diameter, and mounted 120 cm apart along the optical axis of the spectrograph. The diameter of each mirror is 6 cm. M_1 and M_2 are adjusted so that their reflecting surfaces are on one and the same sphere. Their mutual center of curvature is centered in the slot between M_3 and M_4. The center of curvature of M_3 is midway between the slit image, formed by the lens L, and the diametral edge of M_2, and the center of curvature of M_4 is midway between the slit image and the diametral edge of M_1. Instead of tracing the paths of light originating from a point source within the Raman tube, it is somewhat easier to understand the role of the mirrors by considering the reversed light path, i.e., by seeing what happens to light originating at the slit of the spectrograph.

[1] Welsh, Cumming and Stansbury, J. Opt. Soc. Am. 41, 712 (1951).



OPTICAL SYSTEM OF RAMAN TUBE FOR GASES

Figure 1

First of all, the lens L forms an image of the slit between M_1 and M_2. M_3 and M_4 see the slit image as an object. M_3 forms an image at the diametral edge of M_2, and M_4 forms an image at the diametral edge of M_1. These two images are again seen by M_3 and M_4 as objects and two more images are found on M_1 and M_2. This process is continued until the outer edges of M_1 and M_2 are reached, with the result that a series of images are formed all the way across M_1 and M_2. These images are parallel, equally spaced and decrease in intensity the farther they are from the slot. It may now be seen that light originating from any point within the Raman tube will eventually find its way to the exit cone of the Raman tube and therefore to the slit of the spectrograph. Welsh, et al., have shown that this arrangement of mirrors increases the intensity of the Raman radiation by the factor

$$1 + R + R^2 + \ldots + R^n = 1/(1 - R), \text{ for large } n, \quad (3.1)$$

where R is the reflecting power of the mirrors, and n is the number of images of the slit image. Limits on n are imposed by the width of the slit image, the width of the slot between M_1 and M_2 and the diameter of the mirrors. However, n is easily made large enough so that the series approximation holds, and if R is, say, 0.95, the intensity factor becomes equal to 20.

Dimensions. The two Hg lamps used for monochromatic irradiation, obtained through the courtesy of Dr. B. P. Stoicheff,[2] had a barrel length of 100 cm. It was desirable, therefore, that the illuminated section of the Raman tube be as close to 100 cm as feasible. If direct illumination from the lamps falls on the mirrors, the stray light becomes excessive.

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[2]Present address: National Research Council, Ottawa, Canada.

The radius of curvature of the mirrors was, therefore, chosen to be 120 cm, which allows the insertion of a system of diaphragms at each end of the Raman tube.

The minimum diameter of the Raman tube was determined in a calculation by Dr. C. A. Plint of The Department of Physics, The University of Oklahoma, Norman, Oklahoma. The necessary conditions that must be fulfilled are:

1. The condensing lens must image the slit of the spectrograph on the slot between the front mirrors.

2. The image of the cone defined by the collimator lens aperture and the spectrograph slit must be contained within the cross section of the Raman tube at the rear mirrors.

From these conditions one obtains the following formulae:

$$b_{min} = \frac{LS}{f} + 2\sqrt{\frac{LS(A + S)}{F}} \qquad (3.2)$$

$$x_{min} = f\left[\sqrt{\frac{SF}{L(A + S)}} + 1\right] \qquad (3.3)$$

where b_{min} = minimum Raman tube diameter

x_{min} = minimum distance of condensing lens from slit for given b_{min}

L = center of curvature of mirrors

S = slit height

f = focal length of condensing lens

A = diameter of (spectrograph) collimator lens

F = focal length of collimator lens

Certain of the above entities are constants, namely,

L = 120 cm

A = 8 cm

F = 90 cm

By substituting the values of the constants into (3.2) and (3.3), and choosing f and S to be 25.4 cm and 0.4 cm, respectively, it is found that

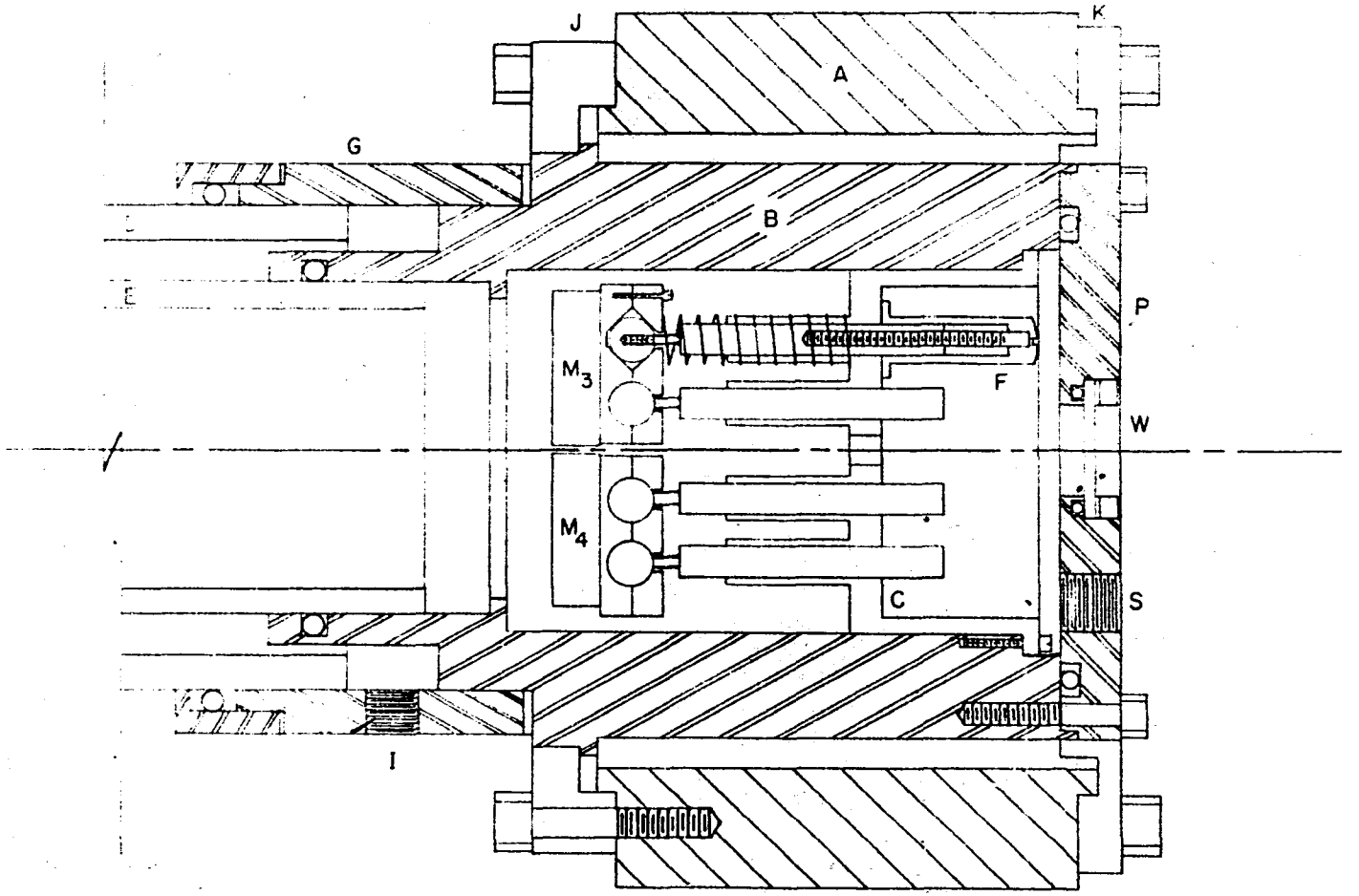
$$b_{min} = 6.1 \text{ cm}$$

and

$$x_{min} = 30.2 \text{ cm}$$

The above value of x_{min} determines the distance between the spectrograph slit and the exit slot of the Raman tube. This distance is found to be 190 cm. The effective height of the Raman tube aperture, at the slot between M_1 and M_2, is found to be 2.13 cm. The minimum diameter of the condensing lens aperture is 2.9 cm.

Description. The illuminated section of the Raman tube consists of a Pyrex glass tube of inside diameter 6 cm. Because it is sometimes necessary to remove or isolate certain Hg lines, the Raman tube is surrounded by a second Pyrex glass tube, which provides for a filter thickness of 1 cm. A 1/4-saturated $NaNO_2$ solution, having a thickness of 1 cm will satisfactorily absorb Hg 4047 A radiation, while transmitting 90% of the Hg 4358 A radiation. The glass tubes are held in position by two identical end-assemblies, which also hold the mirrors. A cross-sectional view of one end-assembly is shown in Figure 2. D and E are the glass tubes. A is an aluminum casting attached to a platform (not shown) which in turn rests on the optical bench and permits motion of the entire apparatus both parallel and transverse to the optical axis of the



END ASSEMBLY OF RAMAN TUBE FOR GASES

Figure 2

spectrograph. A also supports the inner steel cylinder B by means of two collars, J and K. B, and the removable threaded O-ring collar, G, support the glass tubes, and contain the mirror mount C. P is a removable end-plate having a window W and a sample inlet port S. I is the filter jacket inlet. M_3 and M_4 are the mirrors, each of which can be separately adjusted by means of three adjusting screws. One mirror adjusting screw, F, is shown in detail. All inner metallic surfaces are either of stainless steel or are chromium-plated to resist possible corrosion by the sample gases. O-rings are employed to provide vacuum seals at the glass tubes, the windows, and the end-plates. The volume of the Raman tube, including the volume of each end-assembly, is 4.1 l.

The Raman tube is irradiated by two 1500 watt Hg lamps. Each lamp has a straight barrel 100 cm long and 2 cm in diameter. Onto each end of the barrel is attached a 15 cm length of glass tubing of the same diameter, which is bent down at an angle of 30° to the horizontal to provide a reservoir for Hg. Kovar electrodes provide external contact with the Hg reservoirs. The entire lamp is enclosed by a water jacket of glass tubing.

Hg lamp barrels of ordinary Pyrex glass (Corning No. 7740) become darkened after a few hundred hours of operation reducing the transmission of light to a low level. It has been found[3] that Corning glass No. 1710 has a much higher resistance to coloration than No. 7740. The lamps employed in this research have barrels of No. 1710 and have shown no appreciable darkening after more than 1500 hours of operation.

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[3]Private communication from Dr. B. P. Stoicheff, National Research Council, Ottawa, Canada.

The Hg lamps are supported by an aluminum box which completely encloses the lamp barrels and the illuminated section of the Raman tube. The interior surfaces of the box, hereafter called the reflector housing, are coated with a diffuse reflecting paint. The reflective powers of various MgO surfaces have been investigated by Tellax and Waldron.[4] Initially, the reflector housing was coated with smoke from burning Mg wire, which was allowed to condense on tacky white paint. The resultant surface was found to be somewhat impractical, and was discarded in preference to a paint prepared by mixing equal volumes of MgO powder with a commercial white paint[5] containing 92.5% TiO_2.

A photograph of the completely assembled Raman tube and associated apparatus is shown in Figure 3. The two end-assemblies are joined at the top by a steel rod, which may be seen above the reflector housing. The reservoir ends of the Hg lamps are visible at either side of the rear end-assembly. The spectrograph is enclosed in a temperature-regulated box which rests on the table nearer the back wall. At the right may be seen part of a portable vacuum apparatus which was buit for the evacuation, filling and outgassing of the lamps.

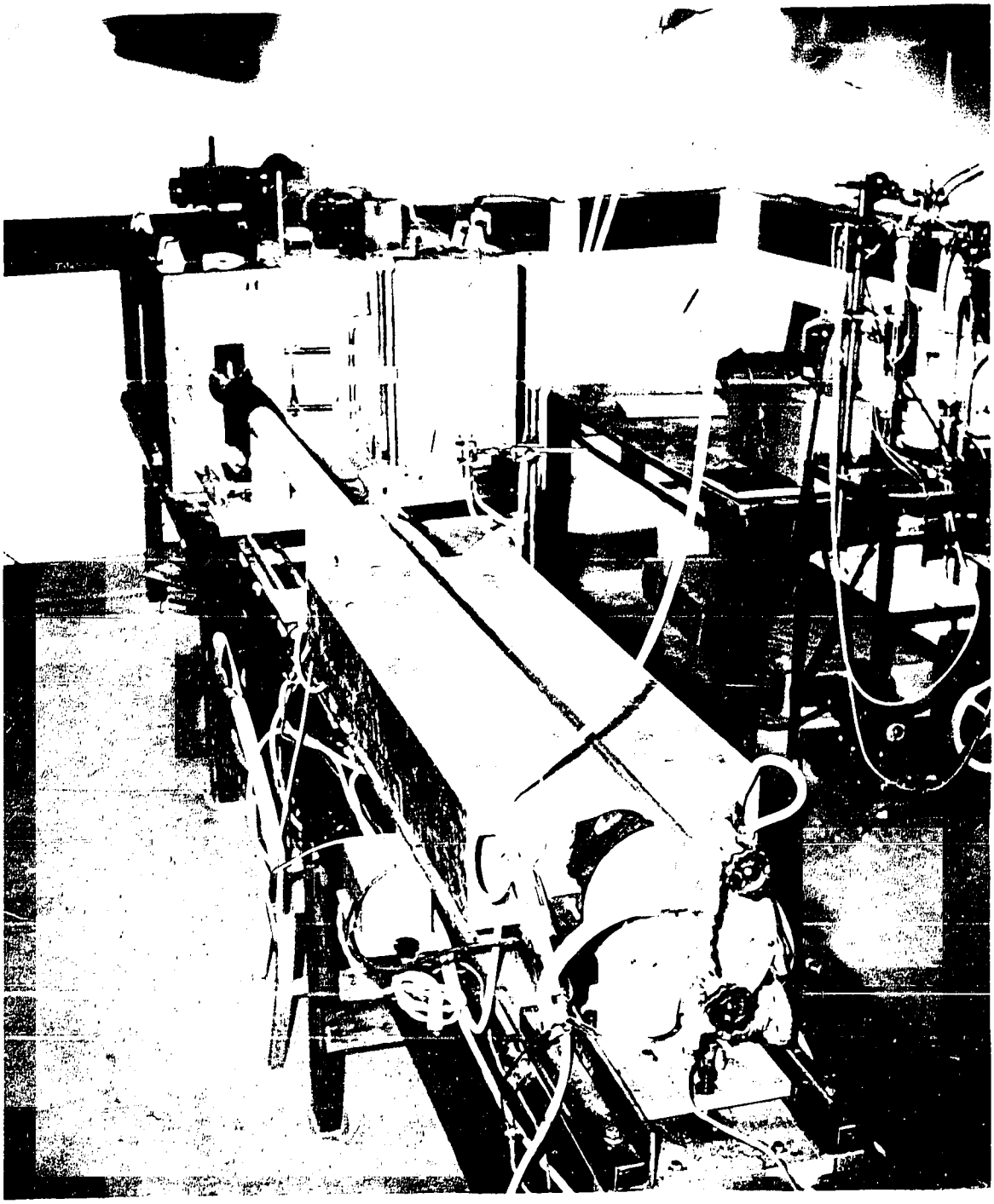
A control panel was designed and constructed to supply D.C. power to the Hg lamps. It will be more fully discussed later.

Mechanical Alignment. Each end-assembly has three adjustable legs which rest on the platform. In addition, the forward end-assembly, i.e., the assembly nearer the spectrograph, may be moved, upon the

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[4]P. A. Tellax and J. R. Waldron, J. Opt. Soc. Am. 45, 19 (1955).

[5]Glidden Japalac No. 1212, Ultra White Paint.



MULTIPLE-REFLECTION RAMAN TUBE

Figure 3

platform, parallel to the optic axis. This motion is necessary for the insertion of the glass tubes. The adjustable legs of the end-assemblies, and the transverse adjustment of the optical bench platform are sufficient to position the end-assemblies accurately on the optical axis of the spectrograph. After the leg adjustments are completed each end-assembly may be securely fastened to the platform by two bolts. Because the glass tubes, particularly the inner tube, are not straight, but are "bowed", it has been necessary to make very slight changes in the position of the end-assemblies. At present both end-assemblies are tilted up slightly to fit the inner tube. The procedure for installation of the glass tubes is as follows:

The inner tube is placed inside the outer tube, temporarily separated by two semicircular wooden rings. The inner tube is a few inches longer than the outer tube to facilitate installation. The forward end-assembly is moved away from the rear end-assembly so that the distance between the assemblies is slightly greater than the length of the inner glass tube. Both tubes are then allowed to rest on the lower half of the reflector housing. Each end of the inner tube is inserted into the end-assemblies up to the O-rings, and the wooden separators are removed. It is now necessary to push the forward end-assembly back to its former position. In doing so, the inner tube will be pushed past the O-rings. If the O-rings and the threaded retainers for the outer tube are loosened and placed around the outer tube a few inches from the ends of the tube, there will be no difficulty with the insertion of the outer tube. When the forward end-assembly is in position, both tubes will be in place, and

the O-rings and retainers for the outer tube may then be tightened. Two special wrenches have been designed for this purpose. Considerable caution must be exercised in the foregoing procedure in order to prevent glass breakage.

The glass tubes may be removed by reversing the above procedure.

Optical Alignment. The mirror halves must be gently but firmly clamped to the mirror mounts. The distance of separation of the rear mirror halves is not critical; therefore, a distance of 1 mm has been used. The front mirrors, as indicated earlier, should be separated by a distance somewhat greater than the width of the image of the slit (Figure 1), which is approximately 0.4 mm. Because it is imperative that the cone of light, lying between the condensing lens and the exit slot between the front mirrors, not be reduced, the original mirrors, which did not have their straight edges beveled, were separated by a distance of 1.0 mm. A second set of mirrors had their straight edges beveled to accommodate the cone of light, and were initially separated by a distance of 0.5 mm. Thus, it was possible to form many more reflections on the mirrors and formula (3.1) held more rigorously. However, the efficiency of this arrangement was less by a factor of 8, in comparison to the former arrangement. In consequence, the mirror separation was increased to 1.0 mm, and the efficiency increased to near its original value. The explanation of this is felt to be due in large part to the critical location of the condensing lens. With the wider mirror (exit) slot, the image of the slot at the slit is wider, and a slight movement of the condensing lens can be tolerated. With the narrower slot, and corresponding narrow

image, a very slight movement of the condensing lens is sufficient to throw the image an appreciable distance off the slit, resulting in a great loss in efficiency.

The radius of curvature of the mirrors may be determined in the following manner:

One set of mirrors is placed in its end-assembly. An object is placed in the other end-assembly. This object is in the form of a narrow pointed steel pin, mounted along a radius of a brass cylinder which has the same outside diameter as the mirror mount. The pin is located with its pointed end exactly on the optical axis, and is allowed to move parallel to the optical axis. By illuminating the pin from the side, and looking past the pin toward the mirrors, it is possible to see an inverted image of the pin. Observation of the pin and its image is more easily accomplished with the aid of a small telescope. The pin and image are made to coincide by moving the pin parallel to the optical axis, and the radii of curvature is then the distance between the pin and the mirrors. A mark has been filed into the top of each end-assembly which shows the position of the inside of the mirror mount flange. These marks are 139 cm apart. Knowing the center of curvature, and with the aid of the file marks, one may adjust the mirrors so that they are at equal distances from the file marks, and separated by a distance equal to their mutual radii of curvature. At this point, the mirrors should also be adjusted so that they are perpendicular to the optical axis. Care, exercised in this rough adjustment saves much time in making the finer adjustments later.

After positioning the mirrors in the above manner, the mounts are rotated until the slot between the halves is vertical. A plumb-bob may be used for this purpose. Then each set of mirrors may be adjusted so as to be "one" mirror having its center of curvature centered in the slot of the other set. This is done as follows:

A 6 V.A.C. lamp is placed before a diffusing screen at the outside end of one end-assembly. Light will then shine through the slot between the nearer mirrors. The opposite set of mirror halves will be under adjustment, separately, by first covering one, and then the other. A semicircular opaque disc is placed so that it covers the lower quadrants of the nearer mirrors. An image of the slot between the nearer mirrors will be formed, by the opposite mirror half under adjustment, on the disc. This image may be made to coincide with the slot. Each mirror half in both end-assemblies is adjusted in this fashion.

A small lamp, especially built for the purpose, fits into the camera aperture of the spectrograph, and will send light of any desired color back through the upper half of the slit of the spectrograph. The lower half of the slit is reserved for the Fe arc comparison spectrum. The condensing lens and the optical bench platform should be positioned so that an image of the slit falls symmetrically in the slot between the front mirrors, and in their plane. Using this slit image as an object, the final adjustment of the rear mirros may be completed as follows:

One rear mirror half is covered by an opaque semicircular disc. The other mirror half is rotated about a vertical axis until it forms an image of the slit image on the mirror diagonally in front of it. Another

semicircular opaque disc placed in front of the diagonally opposite front mirror half will help in locating this image. The image of the slit image should be made to lie as close as possible to the diametral edge of the diagonally opposite mirror half. The other rear mirror half is adjusted in a similar fashion. After both rear mirror halves have been adjusted in this manner, their optical axes will be crossed, and each axis will pass between the slit image and the edge of the mirror. Each rear mirror "sees" the slit image as an object and forms its image on the mirror diagonally in front of the rear mirror. These images again act as objects for the rear mirrors, giving rise to another pair of images on the front mirrors, etc., with the result that a series of equidistant slit images, gradually diminishing in brightness, are formed at the surfaces of the front mirrors. Each of these images and the diameter of the rear mirrors define a "cone" of light which contributes to the light-gathering power of the Raman tube.

It is seen from equation 3.1 that the reflectivity of the mirrors should be as high as possible to obtain maximum intensity from the Raman tube. Therefore, a few comments concerning the mirrors will be included in this section.

Two sets of mirrors have been in operation prior to this writing. The first set was not ground to specifications, and correct spacing of the mirrors caused the mirror adjustment screws to operate very close to their end-of-travel, resulting in poor control over the mirror adjustments. However this was no great difficulty in comparison to the trouble

encountered with the mirror surfaces, due to chemical reactions with the sample gases. Here a practical knowledge of organic chemistry would be most helpful, except that, in most cases, little is known about the chemical reactions of the sample gases which are studied. Several precautions should be taken in all cases to prevent loss of reflectivity. Moist gases should not be allowed contact with the mirrors; therefore, the sample gases should be dried either with a cold trap or a suitable drying agent. Also, room air should be dried before entry to the Raman tube by passing the air through a drying agent. Following an exposure and subsequent recovery of the sample gas, the tube may be flushed with dry air or N_2.

It is advantageous to have the mirrors coated with a material which gives high reflectivity in the region 4358-5000 A. However, because of the trouble which has been caused by chemical reactions of the sample gases with the mirrors, it is recommended that the mirrors be given a good, but less expensive aluminized coating first. Then, if the sample gas reacts with the aluminum to reduce the reflectivity, the mirrors may easily be recoated. This can be done in the laboratory here, and would save time and improve performance.

It is desirable to locate the condensing lens so that the Raman spectrum is located exactly adjacent to, or slightly overlapping the comparison spectrum on the film. One method which has been used to locate the Raman spectrum adjacent to the Fe arc spectrum is as follows:

A light source is placed at the focal plane of the spectrograph and allowed to pass through the lower half of the slit. It may be observed

on a piece of lens tissue placed at the slit. A second light source is placed at the rear window of the Raman tube. This light will also be observed on the lens tissue, and will be white as compared to the light coming from the spectrograph, which will be of one color, say green. Thus, the two images seen on the lens tissue may readily be identified. By moving the condensing lens up or down the two images may easily be located adjacent to each other, or slightly overlapping.

The distance from the condensing lens to the front mirrors (159.8 cm) is so great compared to its distance from the spectrograph slit (30.2 cm) that a very slight change in the position of the lens will throw light completely off the slit. For this reason, it is necessary to check the alignment of the condensing lens from time to time. This may be done in several ways. One method is to see that the light traveling back through the spectrograph falls symmetrically in the slot between the front mirrors. The inverse effect may also be used as a check.

This completes the optical adjustments of the Raman tube.

Operation. Following the mechanical and optical adjustments, the glass tubes and the end-plates may be replaced, and the gas inlet system connected. At present, the gas inlet system consists of several appropriate valves, a pressure gauge, and a glass-wool column for filtering out dust particles.

The Raman tube should be evacuated and checked against leakage. It may be necessary to pump overnight before a good vacuum is attained, especially if the tube has been open to the atmosphere for some time.

A control panel was designed and built to operate the Hg lamps.

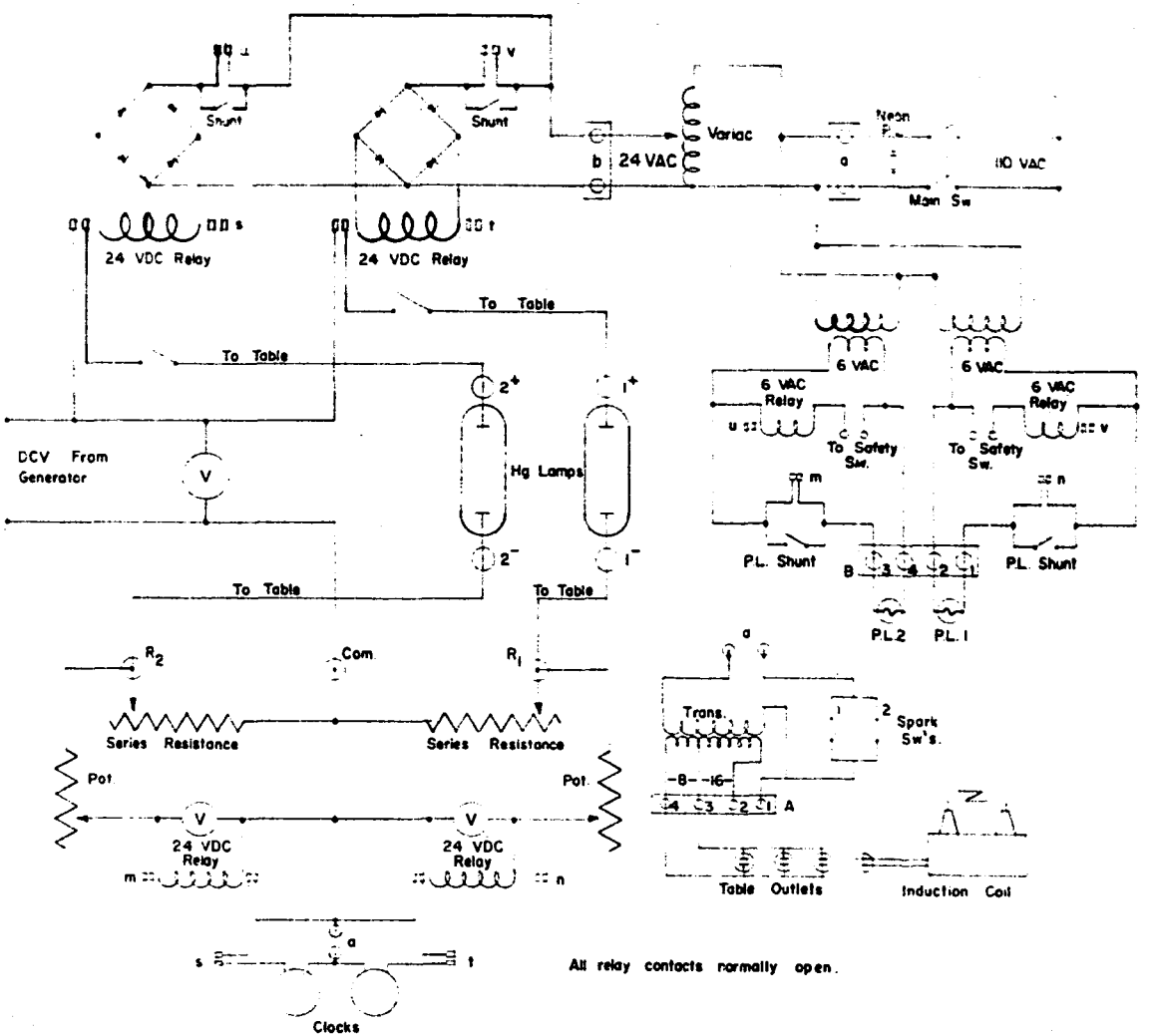
This is shown in Figure 4. There are two identical circuits, one for each lamp. Because the lamps are entirely water-cooled, a provision was made in the circuits to turn a lamp off if its water supply should fail or diminish appreciably.

Each series lamp resistance consists of six parallel 1000 watt Calrod heaters mounted in a laboratory sink. A continuous flow of water through the sink dissipates the heat from the heaters. Knife switches in series with the heaters provide for variation of the resistance. The exposures are timed by two clocks which operate indirectly from the voltage drop across the heaters.

Performance. The vibrational spectrum of oxygen, at one atmosphere pressure, has been obtained with a fifteen-minute exposure. The rotational structure shows up with an even shorter exposure. This is shown in Figure 5. The efficiency of the Raman tube, with and without the mirrors, however, has not been investigated; therefore, there is no quantitative data with which to evaluate the performance. Estimates of the efficiency have led to the belief that the mirrors increase the efficiency by a factor of 20 or more. This estimate was based on a comparison of the present tube with an earlier Raman tube for gases designed by H. H. Claassen and J. Rud Nielsen[6] which did not involve reflections. Two papers, reporting on the performance of the Raman tube and the spectra

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[6]H. H. Claassen and J. Rud Nielsen, J. Opt. Soc. Am. 43, 352 (1953).



D C. VOLTAGE CONTROL and SAFETY CIRCUIT for Hg LAMPS

Figure 4

RAMAN SPECTRUM OF O_2

Figure 5

of several compounds, have been given.[7,8]

Certain operating characteristics of the Hg lamps are shown in Figures 6, 7 and 8.

Possible Improvements. Experience with the Raman irradiation apparatus for gases has suggested the following improvements:

The inner cylinder B (Figure 2) might be altered to include several interchangeable O-ring seals to fit different diameters of the inner tube E.

Most of the inside corners of the cylinder B should be rounded-off slightly to facilitate chromium-plating.

The tolerances of the mirror mount and the cylinder B should be more carefully controlled, so that a smooth sliding fit is obtained.

The condensing lens holder should be redesigned to be more sturdy and capable of much finer adjustment.

The condensing lens and the front window of the Raman tube should be coated to reduce reflection losses.

The spectrograph and optical bench should be mounted on a concrete-slab table having legs of concrete blocks. This would give the necessary support to prevent loss of efficiency due to slight motions of the condensing lens.

A new design of a Hg lamp has been made and reported.[7] It has

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[7]Gullikson, Nielsen and Plint, "A Multiple-reflection Raman Tube for Gases". Paper delivered before the Ohio State Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, 1955.

[8]C. W. Gullikson and J. Rud Nielsen, "Vibrational Spectra and Calculated Thermodynamic Properties of Vinyl Chloride and Vinyl Bromide". Paper delivered before the American Physical Society, Houston, Texas, 1956.

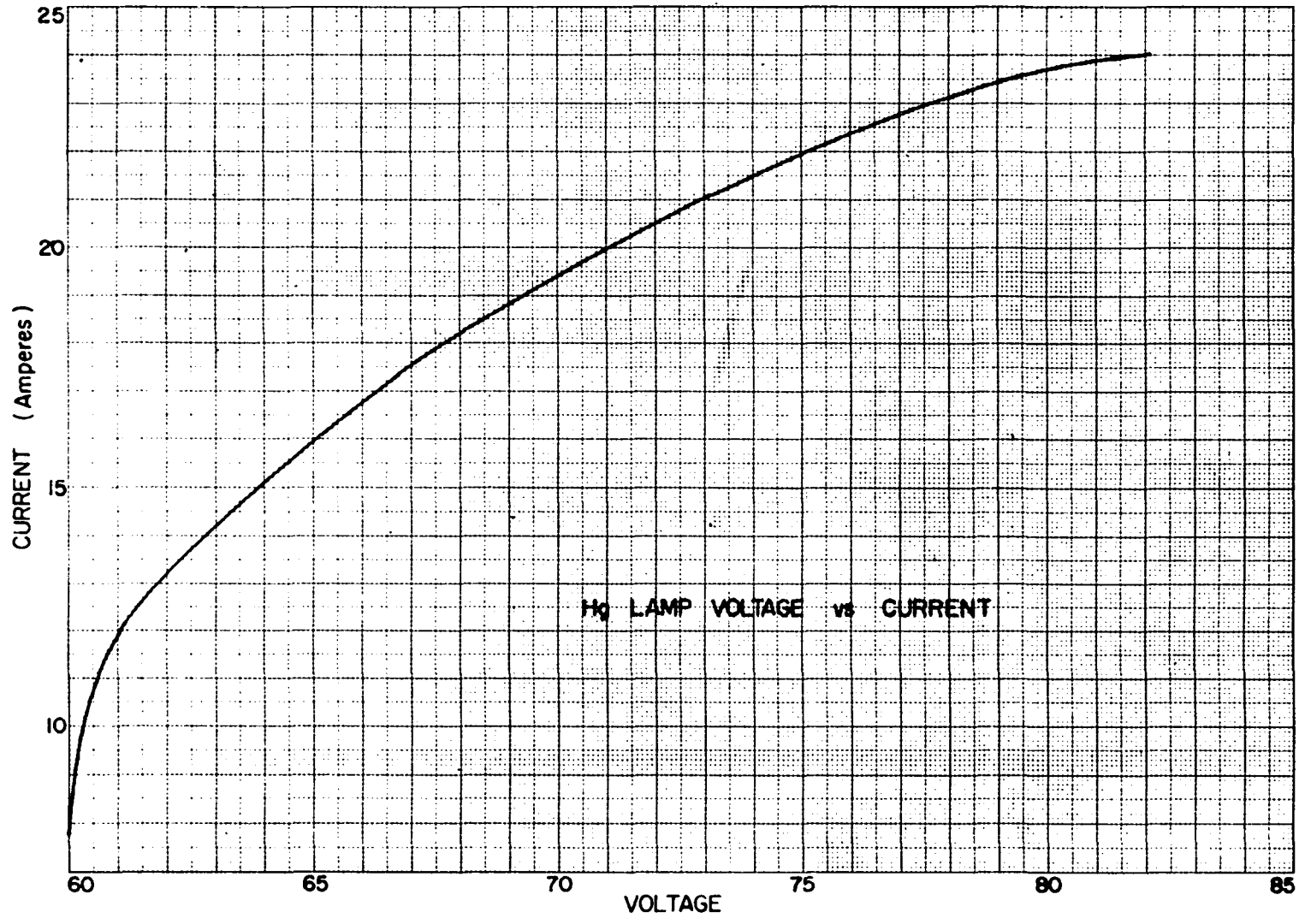

25
20
15
10
CURRENT (Amperes)
Hg LAMP VOLTAGE vs CURRENT
60
65
70
75
80
85
VOLTAGE

Figure 6

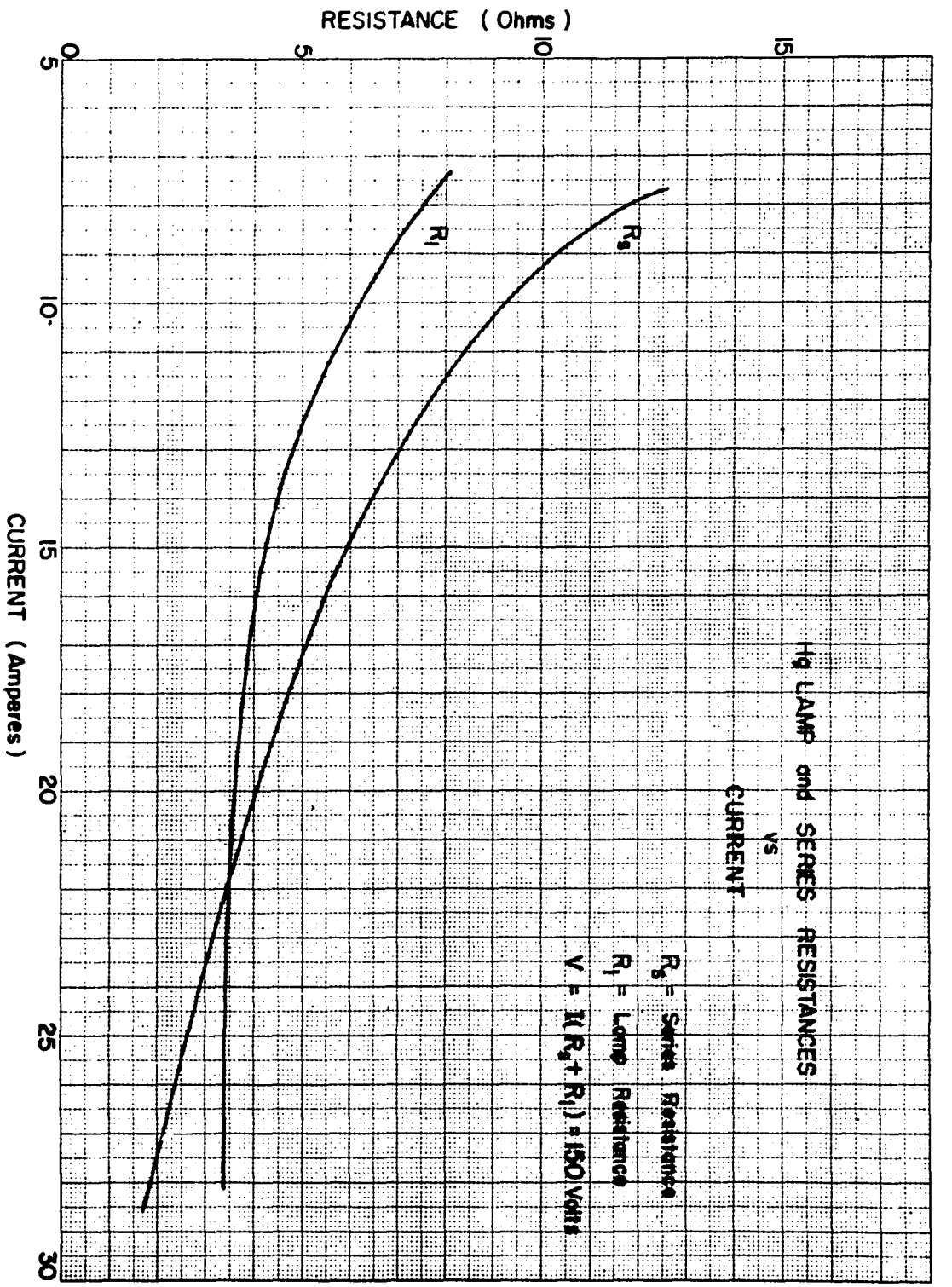

RESISTANCE (Ohms)
0
5
10
15
CURRENT (Amperes)
5
10
15
20
25
30
R_1
R_s
Hg LAMP and SERIES RESISTANCES
vs
CURRENT
R_s = Series Resistance
R_1 = Lamp Resistance
$V = I(R_s + R_1) = 150$ Volts

Figure 7

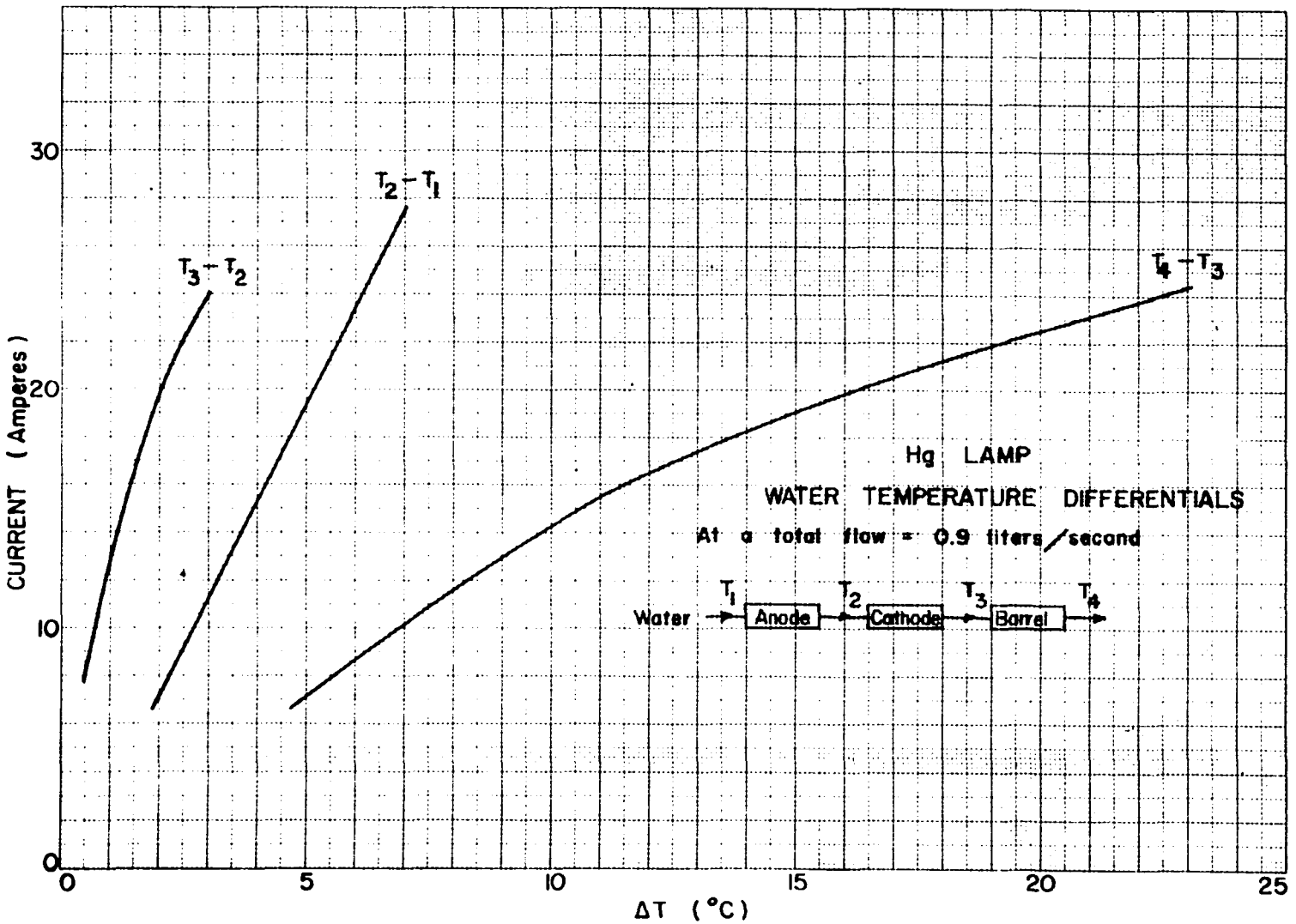
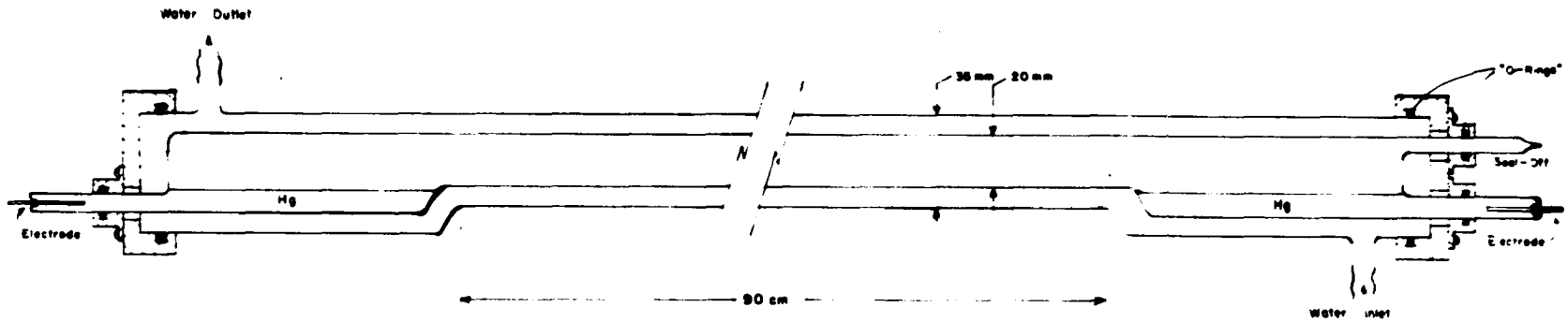

CURRENT (Amperes)
30
20
10
0
0
5
10
15
20
25
ΔT (°C)
T2 − T1
T3 − T2
T4 − T3
Hg LAMP
WATER TEMPERATURE DIFFERENTIALS
At a total flow = 0.9 liters / second
Water
T1
Anode
T2
Cathode
T3
Barrel
T4

Figure 8

the advantage, over the present lamps, of being inexpensive and of simpler construction. An additional advantage is that the lamp barrel may easily be replaced when it has become discolored after much use. The basic design of the lamp is shown in Figure 9. The dimensions are such that the lamp would fit into the present gas apparatus. The lamp is of Pyrex, except for two brass fittings at either end which provide a seal between the lamp and the water jacket. An experimental lamp of this type has been built and tested. The tests showed that the tungsten electrodes should project farther into the Hg reservoir; otherwise, the lamp gave satisfactory performance.



WATER-COOLED LOW PRESSURE Hg LAMP

Figure 9

CHAPTER IV

RESULTS

Vinyl Chloride

The sample of vinyl chloride was supplied by the Matheson Company.[1] The minimum purity of the sample was given as 99.8%.

The Raman spectrum, at room temperature and at 3.3 atmospheres pressure, was obtained with the aid of the multiple-reflection Raman irradiation apparatus and a 3-prism Lane-Wells spectrograph. The spectrograph has a reciprocal dispersion of 77 cm^{-1}/mm (15 A/mm) at 4358 A. Kodak Royal Pan film was used with a development time of 12 minutes at 20 °C. An iron comparison spectrum was placed on the film adjacent to the Raman spectrum. A 1/4-saturated $NaNO_2$ filter solution was placed in the filter jacket to reduce the Hg 4047 A radiation. Four exposures of 1, 5, 24 and 68 hours were obtained. The films were photographically enlarged by a factor of 20, and measurements of the Raman bands were made on the enlargements. The values of the Raman displacements, in wave numbers, together with their interpretations, are listed in Table I. Each value represents the average of several weighted measurements and may be considered correct to ± 1 cm^{-1}, except for certain bands, designated as

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[1]Address: The Matheson Company, Incorporated, East Rutherford, New Jersey.

TABLE I

RAMAN SPECTRUM OF GASEOUS VINYL CHLORIDE

Wave Number	Exciting Line	Description	Interpretation
394	e	m,sh	a' fundamental (396)[a]
719	e	m,b	a' fundamental (720)
1232	e	vvw,sh	2 x 620 = 1240 A'
1279	e	s,sh	a' fundamental (1280)
1368	e	s,sh	a' fundamental (1369)
1607	e,f,g	vs,sh	a' fundamental (1609)
2961	e	m,sh	1369 + 1609 = 2978 A'
3027	e	s,sh	a' fundamental (3030) } [b]
3033	e	s,sh	396 + 1030 + 1609 = 3035 A' } [b]
3086	e,k	s,sh	a' fundamental (3086)
3121	e	m,sh	a' fundamental (3121)
3214	e	vw,sh	2 x 1609 = 3218 A'

[a]The wave numbers in parentheses, in this and succeeding tables, are values of the fundamentals arrived at by averaging the observed Raman and infrared frequencies.

[b]Fermi resonance.

broad or extremely weak, which should be correct to ±2 cm^{-1}.

The infrared spectrum, at room temperature and at various pressures, was observed in the range 2 to 34 microns with a Perkin-Elmer Model 112 spectrometer, equipped with prisms of LiF, NaCl and CsBr, and a Perkin-Elmer gas cell of path length 1 m. The spectrometer and cell have been described by their manufacturer.[2] Dr. N. A. Narasimham[3] and Mr. J. C. Albright[4] calibrated the spectrometer, using bands of H_2O, CO_2, CO, NH_3, CH_4, HCl, HBr and polystyrene. Percentage transmission curves plotted from 2 to 34 microns are shown in Figures 10, 11 and 12. The measurements of the infrared bands, along with their interpretations, are given in Table II.

A discussion of the interpretations of Raman and infrared bands and the assignments of fundamentals will be given in Chapter V.

The entropy, free energy function, heat content function and heat capacity of vinyl chloride in the ideal gas state at one atmosphere were calculated by statistical methods from the assigned values of the fundamental frequencies over the temperature range 273.16 to 500 °K. The calculations were greatly simplified by the use of tables.[5] Values of certain physical constants, necessary for the calculations, were taken

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[2]The Perkin-Elmer Corporation, "Instruction Manual, Model 112, Single Beam, Double Pass, Recording Infrared Spectrometer", Volume 3A and Volume II. Also Bulletin 102 (Norwalk, Connecticut, 1953).

[3]Address: National Research Council, Division of Physics, Ottawa, Canada.

[4]Address: Continental Oil Company, Ponca City, Oklahoma.

[5]Miller, West and Bernstein, Tables of Functions for the Vibrational Contributions to Thermodynamic Quantities, N.R.C. Bulletin No. 1, National Research Council, Ottawa, Canada, 1951.

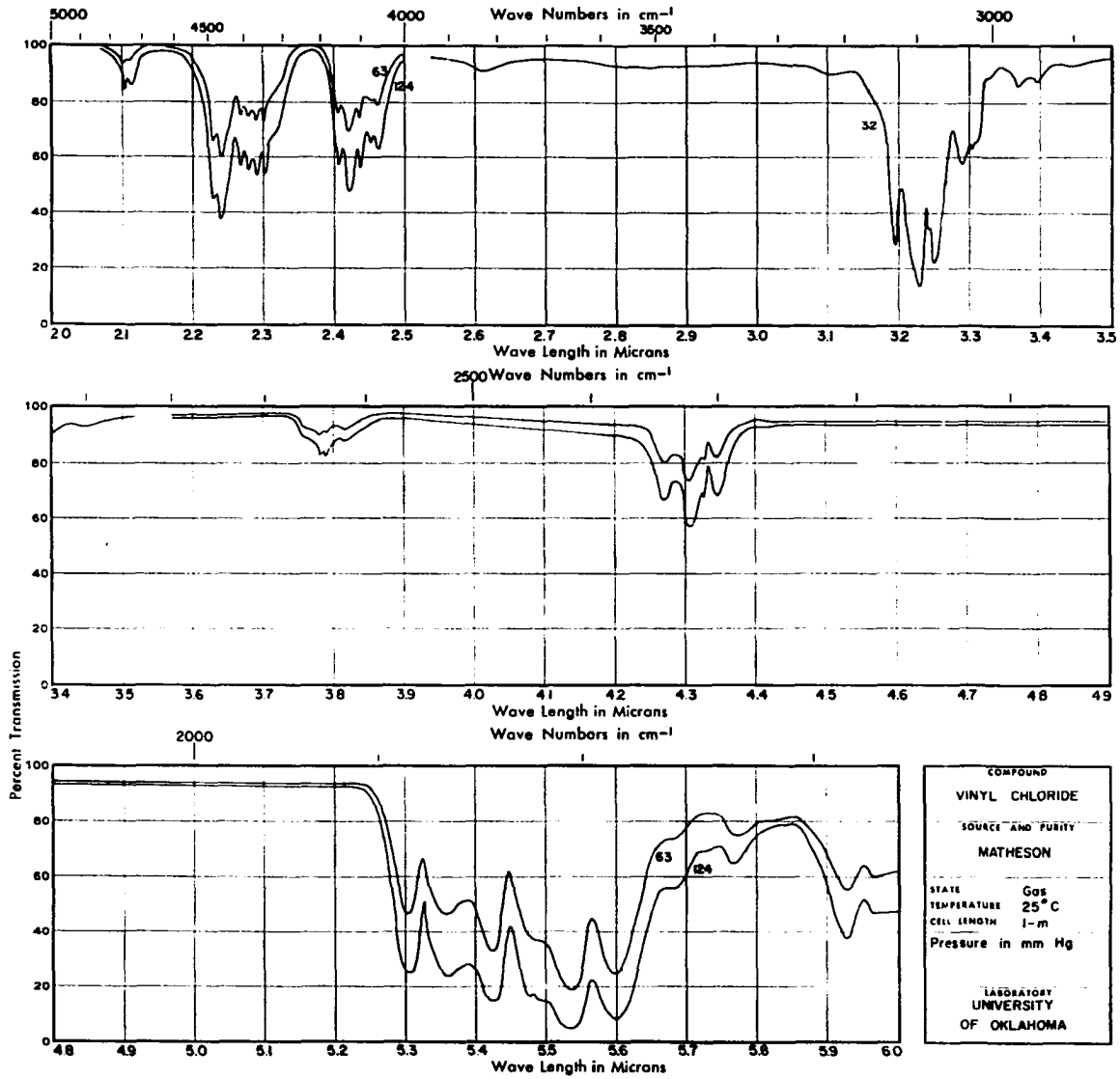

Wave Numbers in cm⁻¹
5000
4500
4000
3500
3000
Wave Length in Microns
2500
2000
Percent Transmission
63
124
32
COMPOUND
VINYL CHLORIDE
SOURCE AND PURITY
MATHESON
STATE Gas
TEMPERATURE 25°C
CELL LENGTH 1-m
Pressure in mm Hg
LABORATORY
UNIVERSITY
OF OKLAHOMA

Figure 10

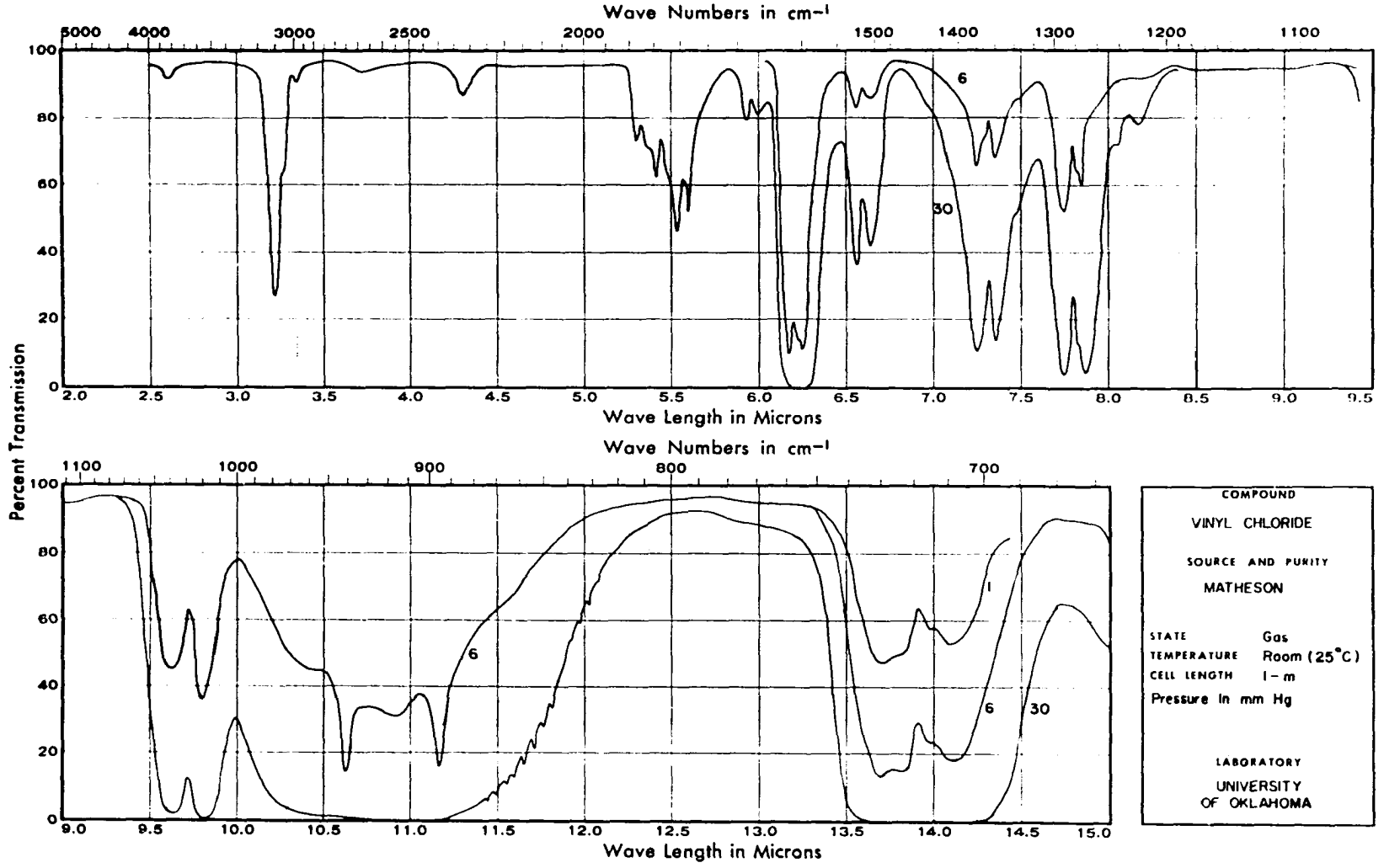

Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
100 80 60 40 20 0
Percent Transmission
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
6
30
Wave Numbers in cm⁻¹
1100 1000 900 800 700
100 80 60 40 20 0
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
6
1
6
30
COMPOUND
VINYL CHLORIDE
SOURCE AND PURITY
MATHESON
STATE Gas
TEMPERATURE Room (25°C)
CELL LENGTH 1 - m
Pressure in mm Hg
LABORATORY
UNIVERSITY OF OKLAHOMA

Figure 11

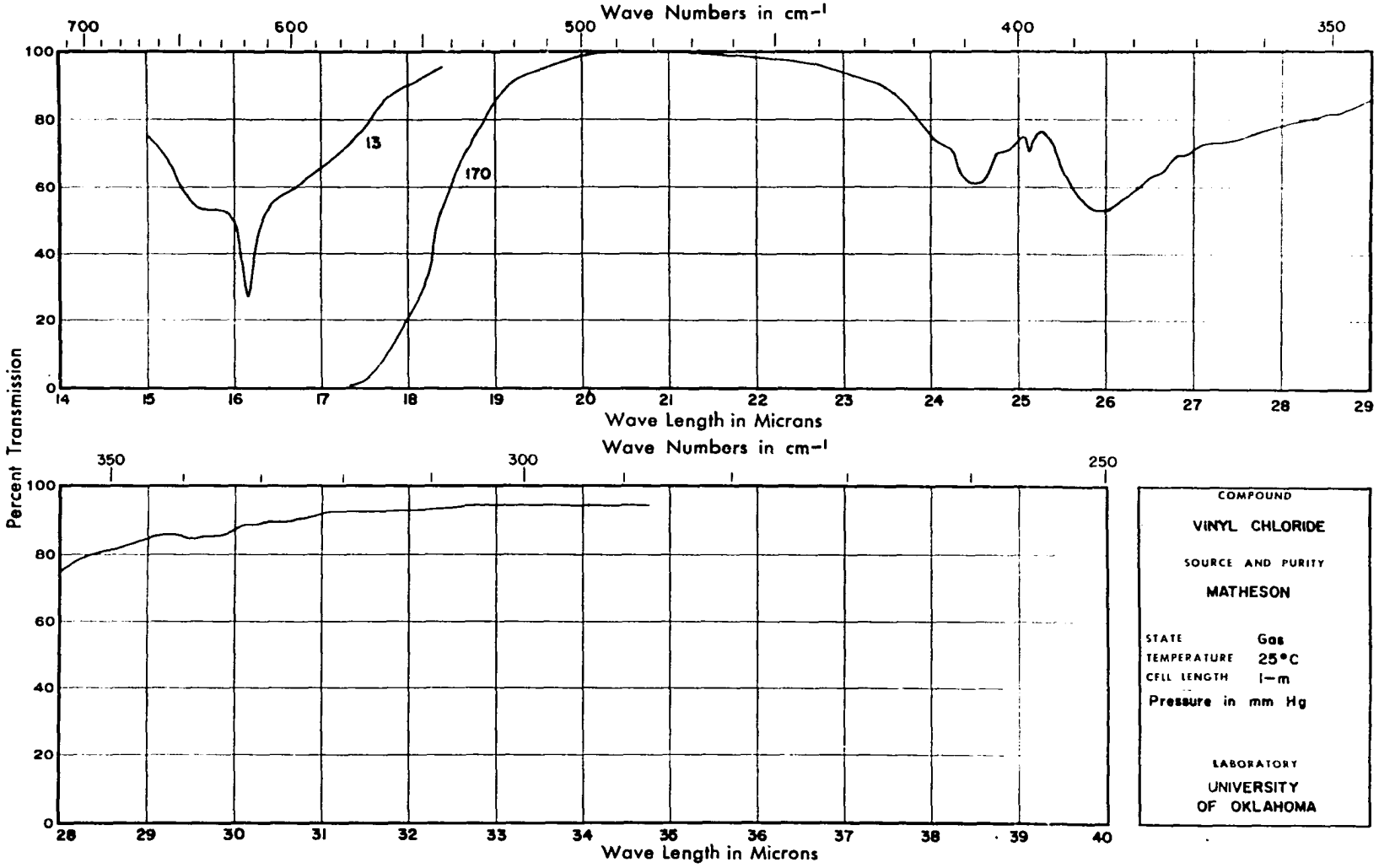

Wave Numbers in cm⁻¹
700
600
500
400
350
100
80
60
40
20
0
Percent Transmission
13
170
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
Wave Length in Microns
Wave Numbers in cm⁻¹
350
300
250
28
29
30
31
32
33
34
35
36
37
38
39
40
Wave Length in Microns
COMPOUND
VINYL CHLORIDE
SOURCE AND PURITY
MATHESON
STATE Gas
TEMPERATURE 25°C
CELL LENGTH 1-m
Pressure in mm Hg
LABORATORY
UNIVERSITY
OF OKLAHOMA

Figure 12

TABLE II

INFRARED SPECTRUM OF GASEOUS VINYL CHLORIDE

Wave Number	Description	Band Type	Interpretation
339	vvw		720 - 396 = 324 A'?
372	vvw		
376	vvw		
388	vw		
398	vw	B/A	a' fundamental (396)
406	sd		
410	vw		
~412	sd		
~590	sd		
620	vs	C	a" fundamental (620)
~635	sd		
710	vs		
716	sd	B/A	a' fundamental (720)
~725	vs		
731	vs		
828	vw		rotational fine structure
831	vw		rotational fine structure
835	vw		rotational fine structure
839	vw		rotational fine structure
~843	vvw		rotational fine structure
846	vw		rotational fine structure

TABLE II - Continued

Wave Number	Description	Band Type	Interpretation
850	vw		rotational fine structure
854	vw		rotational fine structure
858	vw		rotational fine structure
863	vw		rotational fine structure
866	vw		rotational fine structure
870	vw		rotational fine structure
874	vw		rotational fine structure
896	vs	C	a" fundamental (896)
~919	s		
941	vs	C	a" fundamental (941)
~960	sd		
1021	s	B/A	a' fundamental (1030)
1038	s		
1224	vw		2 x 620 = 1240 A'
1242	vw		
1271	m	B/A	a' fundamental (1280)
~1279	sd		
1292	m		
~1338	sd		396 + 941 = 1337 A'; 620 + 720 = 1340 A"
1360	m	B/A	a' fundamental (1369)
~1371	sd		
1381	m		

TABLE II - Continued

Wave Number	Description	Band Type	Interpretation
~1440	sd		2 x 720 = 1440 A'
1507	w		620 + 896 = 1516 A'
1526	w		
1601	vs		
1608	sd	B/A	a' fundamental (1609)
1621	vs		
1667	vw		620 + 1030 = 1650 A'; 720 + 941 = 1661 A"
1685	vw		396 + 1280 = 1676 A'
~1739	vw		720 + 1030 = 1750 A'
~1759	vw		396 + 1369 = 1765 A'
1787	m		2 x 896 = 1792 A'
1807	m		
1825	m		
~1830	sd		896 + 941 = 1837 A'
1846	w		
1868	w		2 x 941 = 1882 A'
1887	w		620 + 1280 = 1900 A"
2301	w		941 + 1369 = 2310 A"
2313	w		1030 + 1280 = 2310 A'
2322	w		720 + 1609 = 2329 A'
2341	w		

TABLE II - Continued

Wave Number	Description	Band Type	Interpretation
2621	vw		1030 + 1609 = 2639 A'
2639	vw		
2645	vw		1280 + 1369 = 2649
2655	vw		
2675	vw		
~2900	vvw		1280 + 1609 = 2889 A'
2950	vw		
2960	vw		1369 + 1609 = 2978 A'
2971	vw		
~3010	sd		spurious
3029	m	B/A	a' fundamental (3030) } a
3037	sd		396 + 1030 + 1609 = 3035 A' } a
3043	m		
3077	s		a' fundamental (3086)
3086	sd		
3098	s		a' fundamental (3121)
3109	sd		
3120	sd		
3131	s		
~3165	sd		2 x 896 + 1369 = 3161 A' ?
~3220	vvw		2 x 1609 = 3218 A'

TABLE II - Continued

Wave Number	Description	Band Type	Interpretation
~3820	vvw		720 + 3086 = 3806 A'; 720 + 3121 = 3841 A'
4062	w		1030 + 3030 = 4060 A'
4080	w		941 + 3121 = 4062 A"
4105	w		1030 + 3086 = 4116 A'
4130	m		1030 + 3121 = 4151 A'
4158	w		
~4310	sd		1280 + 3030 = 4310 A'
4346	w		1280 + 3086 = 4366 A'
4367	w		1369 + 3030 = 4399 A'
4388	w		1280 + 3121 = 4401 A'
4409	w		1369 + 3086 = 4455 A'
4466	m		1369 + 3121 = 4490 A'
4488	m		
~4632	vvw		1609 + 3030 = 4639 A'
4730	vw		1609 + 3086 = 4699 A'
4755	vw		1609 + 3121 = 4730 A'

[a]Fermi resonance.

from Cohen, et al.[6] The results are given in Table III.

Vinyl Bromide

The sample of vinyl bromide was supplied by the Matheson Company. Its purity was given as 99.0%.

The Raman and infrared spectra were obtained with the same experimental apparatus and procedure as was used for vinyl chloride, with the exception that the Raman spectrum of vinyl bromide was observed at a pressure of 1.3 atmospheres. A 1/4-saturated $NaNO_2$ filter was used. Four Raman exposures were made of duration 2, 20, 70 and 240 hours. The measured values of the Raman displacements, together with the interpretations, are given in Table IV. The values may be considered correct to ± 1 cm^{-1}, except for those bands, designated as very weak, extremely weak or broad, which should be correct to ± 2 cm^{-1}.

It was found necessary to extend the infrared calibration curve in the LiF region. The calibration curve was plotted from 1.75 to 0.5 microns, the Hg emission spectrum being used for a wavelength standard as suggested by Plyler and Peters.[7] The infrared percent transmission curves appear in Figures 13, 14, and 15. The measurements of the infrared bands, along with the interpretations, are given in Table V.

The same thermodynamic functions were calculated for vinyl bromide as for vinyl chloride in the range 273.16 to 500 °K. The results are given in Table VI.

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[6]Cohen, Dumond, Layton and Rollett, Revs. Modern Phys. 27, 363 (1955).

[7]E. K. Plyler and C. W. Peters, J. Research Natl. Bur. Standards 45, 462 (1950).

TABLE III

CALCULATED THERMODYNAMIC FUNCTIONS FOR VINYL CHLORIDE IN THE IDEAL GAS STATE AT ONE ATMOSPHERE (in cal deg^{-1} $mole^{-1}$)

T°K		$(H^\circ - E_o^\circ)/T$	C_p°	S°	$-(F^\circ - E_o^\circ)/T$
273.16	Tr. + Rot.	7.949	7.949	60.818	52.869
	Vib.	1.250	4.171	1.680	.430
	Total	9.20	12.12	62.50	53.30
298.16	Tr. + Rot.	7.949	7.949	61.514	53.565
	Vib.	1.525	4.882	2.078	.552
	Total	9.47	12.83	63.59	54.12
300	Tr. + Rot.	7.949	7.949	61.563	53.614
	Vib.	1.546	4.935	2.108	.562
	Total	9.49	12.88	63.67	54.18
400	Tr. + Rot.	7.949	7.949	63.850	55.901
	Vib.	2.735	7.609	3.906	1.171
	Total	10.68	15.56	67.76	57.07
500	Tr. + Rot.	7.949	7.949	65.624	57.675
	Vib.	3.941	9.844	5.851	1.910
	Total	11.89	17.79	71.48	59.58

TABLE IV

RAMAN SPECTRUM OF GASEOUS VINYL BROMIDE

Wave Number	Exciting Line	Description	Interpretation
344	e	s,sh	a' fundamental (344)
573	e	m	impurity?
611	e	s,sh	a' fundamental (614)
1258	e	s,sh	a' fundamental (1258)
1373	e	s,sh	a' fundamental (1373)
1601	e	vs	a' fundamental (1602)
2880	e	vw	1258 + 1602 = 2860 A' ?
2938	e	vw	1373 + 1602 = 2975 A' ?
2971	e	vvw	614 + 1005 + 1373 = 2992 A' ?
2990	e	vvw	3 x 1005 = 3015 A' ?
3027	e	s,sh	a' fundamental (3027)
3087	e	m,sh	a' fundamental (3087)
3112	e	m,sh	a' fundamental (3112)

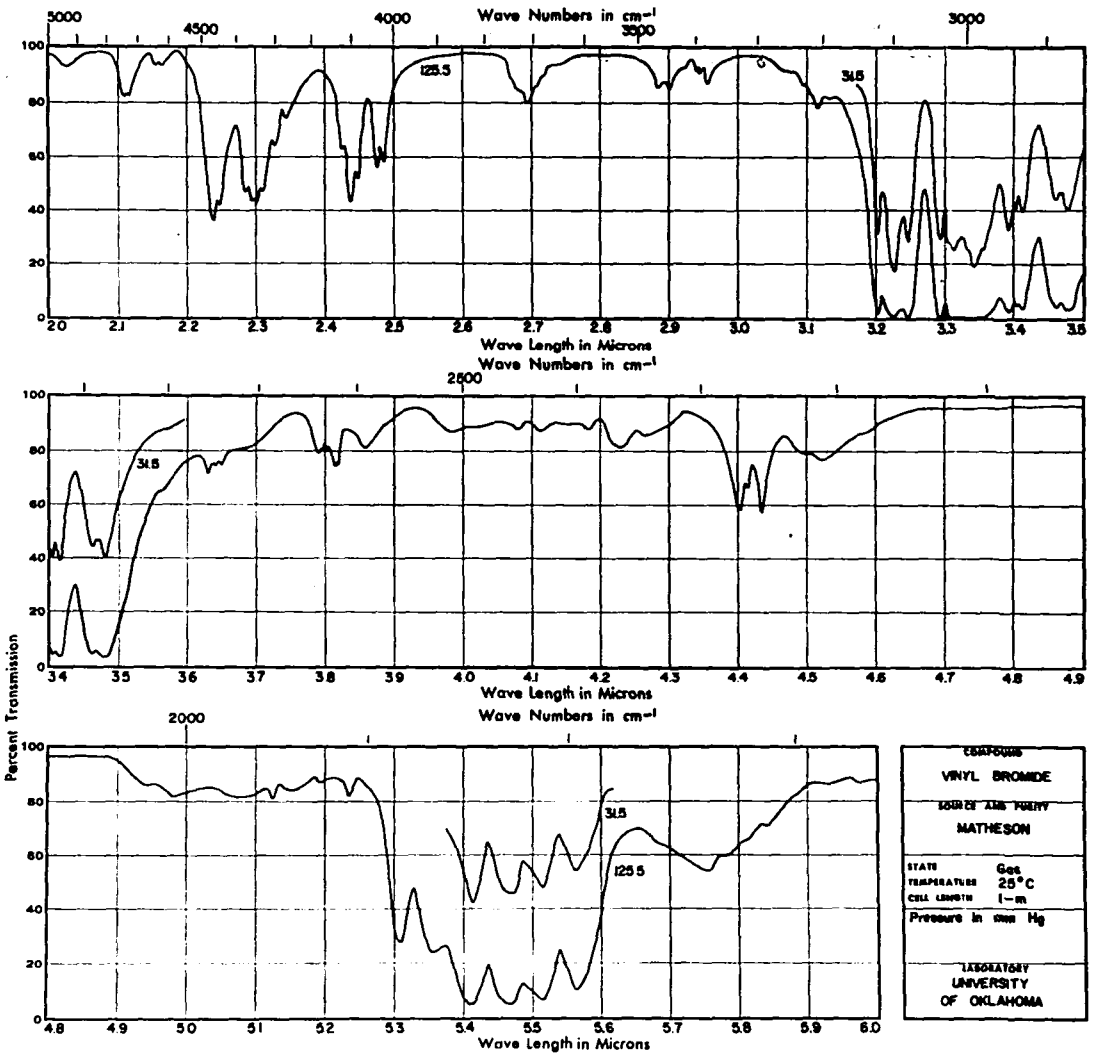

Wave Numbers in cm⁻¹
5000
4500
4000
3500
3000
Wave Length in Microns
2500
2000
Percent Transmission
VINYL BROMIDE
MATHESON
Gas
25°C
1-m
UNIVERSITY
OF OKLAHOMA

Figure 13

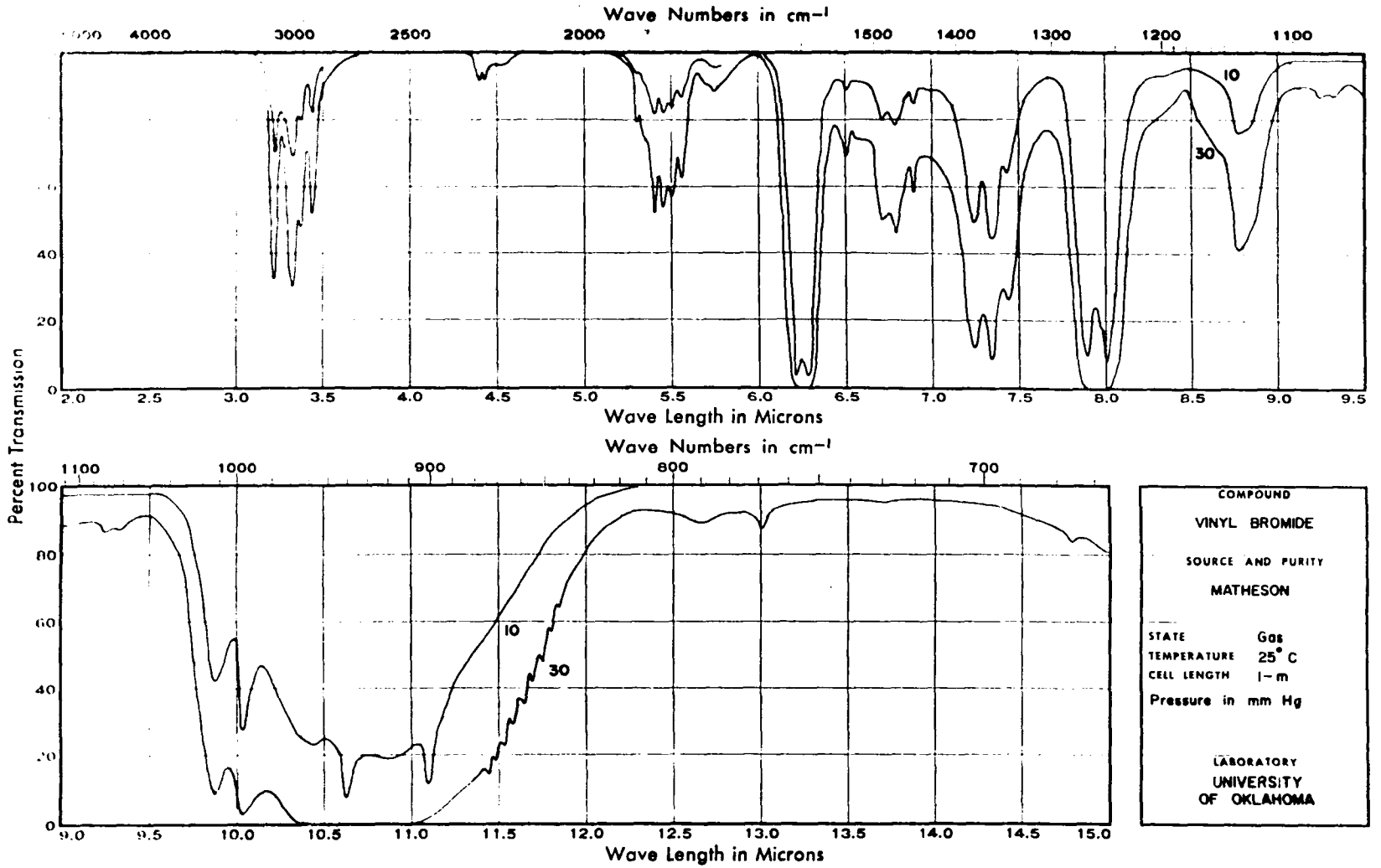

Wave Numbers in cm⁻¹
4000
3000
2500
2000
1500
1400
1300
1200
1100
10
30
Percent Transmission
0
20
40
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
Wave Length in Microns
Wave Numbers in cm⁻¹
1100
1000
900
800
700
100
80
60
40
20
0
10
30
9.0
9.5
10.0
10.5
11.0
11.5
12.0
12.5
13.0
13.5
14.0
14.5
15.0
Wave Length in Microns
COMPOUND
VINYL BROMIDE
SOURCE AND PURITY
MATHESON
STATE Gas
TEMPERATURE 25° C
CELL LENGTH 1-m
Pressure in mm Hg
LABORATORY
UNIVERSITY
OF OKLAHOMA

Figure 14

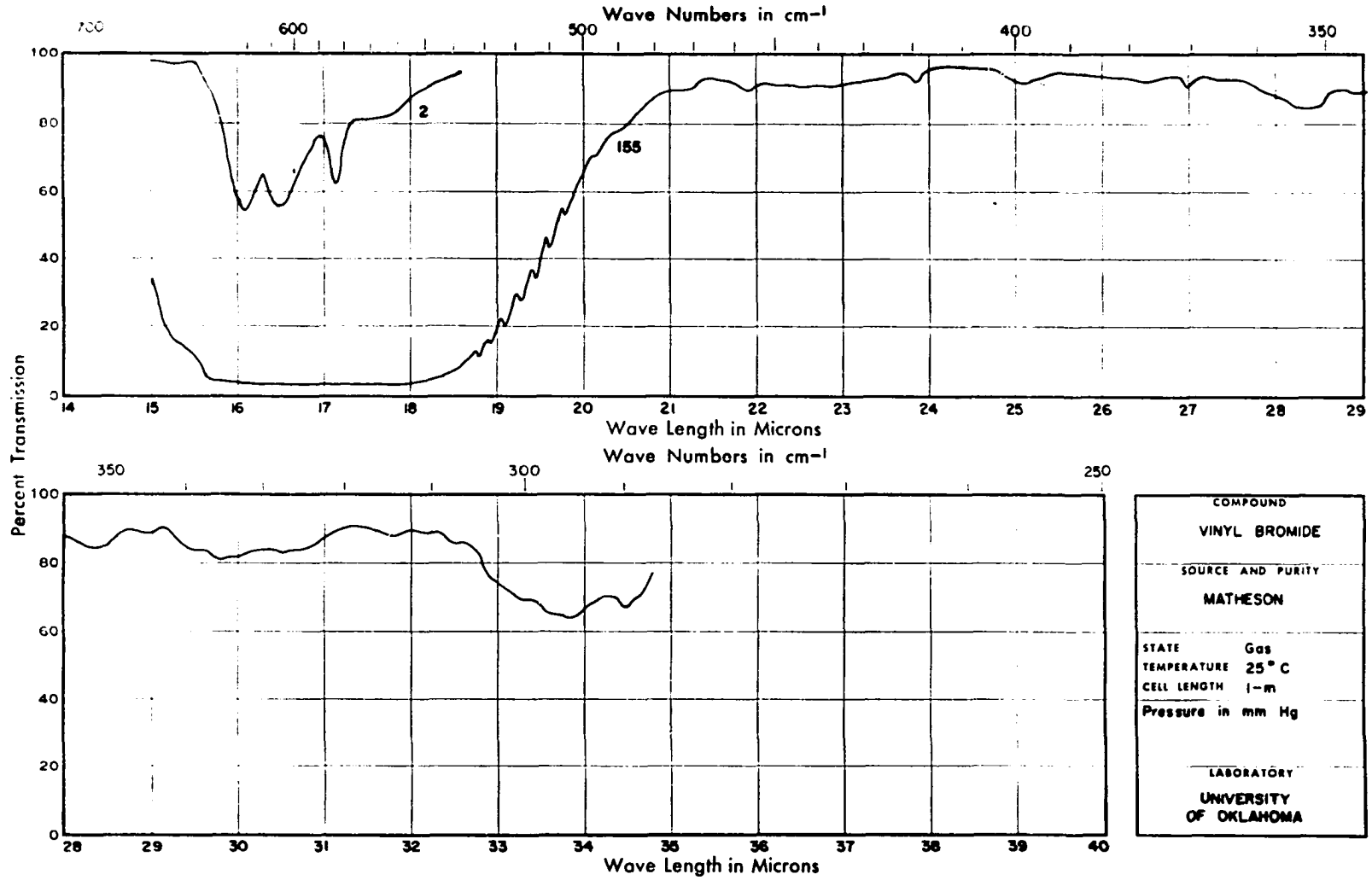

Wave Numbers in cm⁻¹
700
600
500
400
350
100
80
60
40
20
0
2
155
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
Wave Length in Microns
Percent Transmission
Wave Numbers in cm⁻¹
350
300
250
100
80
60
40
20
0
28
29
30
31
32
33
34
35
36
37
38
39
40
Wave Length in Microns
COMPOUND
VINYL BROMIDE
SOURCE AND PURITY
MATHESON
STATE Gas
TEMPERATURE 25° C
CELL LENGTH 1-m
Pressure in mm Hg
LABORATORY
UNIVERSITY OF OKLAHOMA

Figure 15

TABLE V

INFRARED SPECTRUM OF GASEOUS VINYL BROMIDE

Wave Number	Description	Band Type	Interpretation
289	sd		H_2O[a]
290	vw		impurity?
295	vw		H_2O
297	sd		H_2O
~300	sd		
310	vvvw		
315	vvw		H_2O?
328	vvvw		H_2O
336	vvw		H_2O
339	sd		
345	vvw		a' fundamental (344)
~352	vw		H_2O
~371	vvw		H_2O
377	vvvw		
398	vvw		H_2O
419	vvw		H_2O
456	vvw		H_2O
463	sd		
497	vvw		rotational fine structure
505	vvw		rotational fine structure

TABLE V - Continued

Wave Number	Description	Band Type	Interpretation
510	vvw		rotational fine structure
514	vvw		rotational fine structure
519	vvw		rotational fine structure
524	vvw		rotational fine structure
528	vvw		rotational fine structure
532	vvw		rotational fine structure
538	vvw		rotational fine structure
582	vs	C	a" fundamental (582)
606	vs	B/A	a' fundamental (614)
622	vs		
676	vw		2 x 344 = 688 A'
769	vw		1373 - 614 = 759 A'?
788	vw		1373 - 582 = 791 A'?
844	vw		rotational fine structure
847	vw		rotational fine structure
851	vw		rotational fine structure
856	vw		rotational fine structure
859	vw		rotational fine structure
864	vw		rotational fine structure
868	vw		rotational fine structure
871	vw		rotational fine structure

TABLE V - Continued

Wave Number	Description	Band Type	Interpretation
874	vw		rotational fine structure
879	vw		rotational fine structure
883	vw		rotational fine structure
887	vw		rotational fine structure
890	vw		rotational fine structure
893	vw		rotational fine structure
901	vs	C	a" fundamental (901)
~919	m		344 + 582 = 926 A"; 1258 - 344 = 914 A'
941	vs	C	a" fundamental (941)
~963	s		344 + 614 = 958 A'
996	s	B/A	a' fundamental (1005)
1013	s		
1072	vw		H_2O
1082	vw		H_2O
1141	m		impurity?
~1160	sd		2 x 582 = 1164 A'
~1200	sd		2 x 614 = 1228 A'; 582 + 614 = 1196 A"
1249	vs	B/A	a' fundamental (1258)
1266	vs		
1345	m		344 + 1005 = 1349 A'

TABLE V - Continued

Wave Number	Description	Band Type	Interpretation
1362	s	B/A	a' fundamental (1373)
1381	s		
1451	w		
1473	m		582 + 901 = 1483 A'
1490	m		
~1537	vw		614 + 941 = 1555 A"
1594	vs	B/A	a' fundamental (1602)
1613	vs		
1742	w		344 + 1373 = 1717 A'
1797	m		2 x 901 = 1802 A'
1814	m		
1832	m		582 + 1258 = 1840 A"
1847	m		901 + 941 = 1842 A'
~1867	w		614 + 1258 = 1872 A'
1884	w		2 x 941 = 1882 A'
1911	vw		901 + 1005 = 1906 A"
~1942	vw		941 + 1005 = 1946 A"; 344 + 1602 = 1946 A'
1951	vw		582 + 1373 = 1955 A"
~1977	vw		614 + 1373 = 1987 A'
~2009	vw		2 x 1005 = 2010 A'
~2023	vw		

TABLE V - Continued

Wave Number	Description	Band Type	Interpretation
~2180	vw		941 + 1258 = 2199 A"
~2212	w		641 + 1602 = 2216 A'
~2229	w		
2255	w		
2265	w		1005 + 1258 = 2263 A'
2271	w		
2275	sd		901 + 1373 = 2274 A"
2343	w		941 + 1373 = 2314 A"
2364	w		1005 + 1374 = 2379 A'
2390	vw		
2432	vw		582 + 901 + 941 = 2424 A"
~2451	vw		
~2481	vw		
~2511	vw		2 x 1258 = 2516 A'
~2592	w		1005 + 1602 = 2607 A'
2619	w		
2620	w		
2623	w		1258 + 1373 = 2631 A'
2631	w		
2634	w		
2639	w		
2739	w		

TABLE V - Continued

Wave Number	Description	Band Type	Interpretation
2749	w		2 x 1373 = 2746 A'
2755	w		
~2807	sd		
~2850	sd		
2876	s		
2883	s		1258 + 1602 = 2860 A'
2889	s		
2929	s		
2938	s		1373 + 1602 = 2975 A'
2946	s		
~2978	sd		
2990	s		3 x 1005 = 3015 A'
~2999	sd		
3008	sd		
3018	s		
3025	s	B/A	a' fundamental (3027)
3036	s		
~3039	sd		
3080	m	B/A	a' fundamental (3087)
3099	m		
3121	m	B/A	a' fundamental (3112)

TABLE V - Continued

Wave Number	Description	Band Type	Interpretation
3190	vw		
3208	vw		2 x 1602 = 3204 A'
~3220	sd		
3231	vw		614 + 1005 + 1602 = 3221 A'
3383	vw		344 + 3027 = 3371 A'
3397	vvw		
3404	vvw		
~3425	vw		344 + 3087 = 3431 A'
~3443	sd		
3450	vw		344 + 3112 = 3456 A'
3466	vw		
~3650	sd		614 + 3027 = 3641 A'
3678	vw		582 + 3087 = 3669 A'
3691	vw		582 + 3112 = 3694 A'
~3705	sd		614 + 3087 = 3701 A'
3713	vw		614 + 3112 = 3726 A'
3734	vw		
4022	m		941 + 3087 = 4028 A"; 1005 + 3027 = 4032 A'
4040	m		941 + 3112 = 4053 A"
4083	m		1005 + 3087 = 4092 A'

TABLE V - Continued

Wave Number	Description	Band Type	Interpretation
4103	m		1005 + 3112 = 4117 A'
4122	vw		
4275	vw		1258 + 3027 = 4285 A'
4297	vw		
4329	m		1258 + 3087 = 4345 A'
4354	m		1258 + 3112 = 4370 A'
4378	m		1373 + 3027 = 4400 A'
4448	m		1373 + 3087 = 4460 A'
4468	m		1373 + 3112 = 4485 A'
~4488	sd		
4623	vw		1602 + 3027 = 4629 A'
4639	vw		1602 + 3087 = 4689 A'
4721	w		1602 + 3112 = 4714 A'
4742	w		
4936	vw		582 + 1258 + 3087 = 4927 A"; 901 + 941 + 3087 = 4929 A'; 901 + 1005 + 3027 = 4933 A'
~5305	vw		614 + 1602 + 3087 = 5303 A'
~5848	sd		2 x 3027 = 6054 A'
5938	w		3027 + 3087 = 6114 A'
5995	w		3027 + 3112 = 6139 A'
6035	w		2 x 3087 = 6174 A'

TABLE V - Continued

Wave Number	Description	Band Type	Interpretation
6161	w		3087 + 3112 = 6199 A'; 2 x 3112 = 6224 A'

[a]Some H_2O bands have been included in this table because there yet remains some doubt of their interpretation.

TABLE VI

CALCULATED THERMODYNAMIC FUNCTIONS FOR VINYL BROMIDE IN THE IDEAL GAS STATE AT ONE ATMOSPHERE (in cal deg^{-1} $mole^{-1}$)

T^oK		$(H^o - E_o^o)/T$	C_p^o	S^o	$-(F^o - E_o^o)/T$
273.16	Tr. + Rot.	7.949	7.949	63.129	55.180
	Vib.	1.501	4.615	2.078	.577
	Total	9.45	12.56	65.21	55.76
298.16	Tr. + Rot.	7.949	7.949	63.825	55.876
	Vib.	1.791	5.314	2.510	.719
	Total	9.74	13.26	66.34	56.60
300	Tr. + Rot.	7.949	7.949	63.874	55.925
	Vib.	1.813	5.364	2.544	.731
	Total	9.76	13.31	66.42	56.66
400	Tr. + Rot.	7.949	7.949	66.161	58.212
	Vib.	3.033	7.961	4.450	1.416
	Total	10.98	15.91	70.61	59.63
500	Tr. + Rot.	7.949	7.949	67.935	59.986
	Vib.	4.243	10.122	6.466	2.223
	Total	12.19	18.07	74.40	62.21

A discussion of the interpretations of the Raman and infrared spectra and the assignment of fundamentals will be given in Chapter V.

Trifluoroacetonitrile

The sample of trifluoroacetonitrile was supplied by Peninsular Chemresearch, Incorporated.[8] No statement as to its purity was given.

The Raman spectrum of the gas, at room temperature and at a pressure of 2 atmospheres, was obtained with the aid of the multiple-reflection Raman irradiation apparatus. Three exposures were made of duration 1, 4 and 16 hours. A water filter was used. The Raman spectrum contains very striking band contours. For this reason, it is shown, along with a microphotometer trace, in Figure 16.

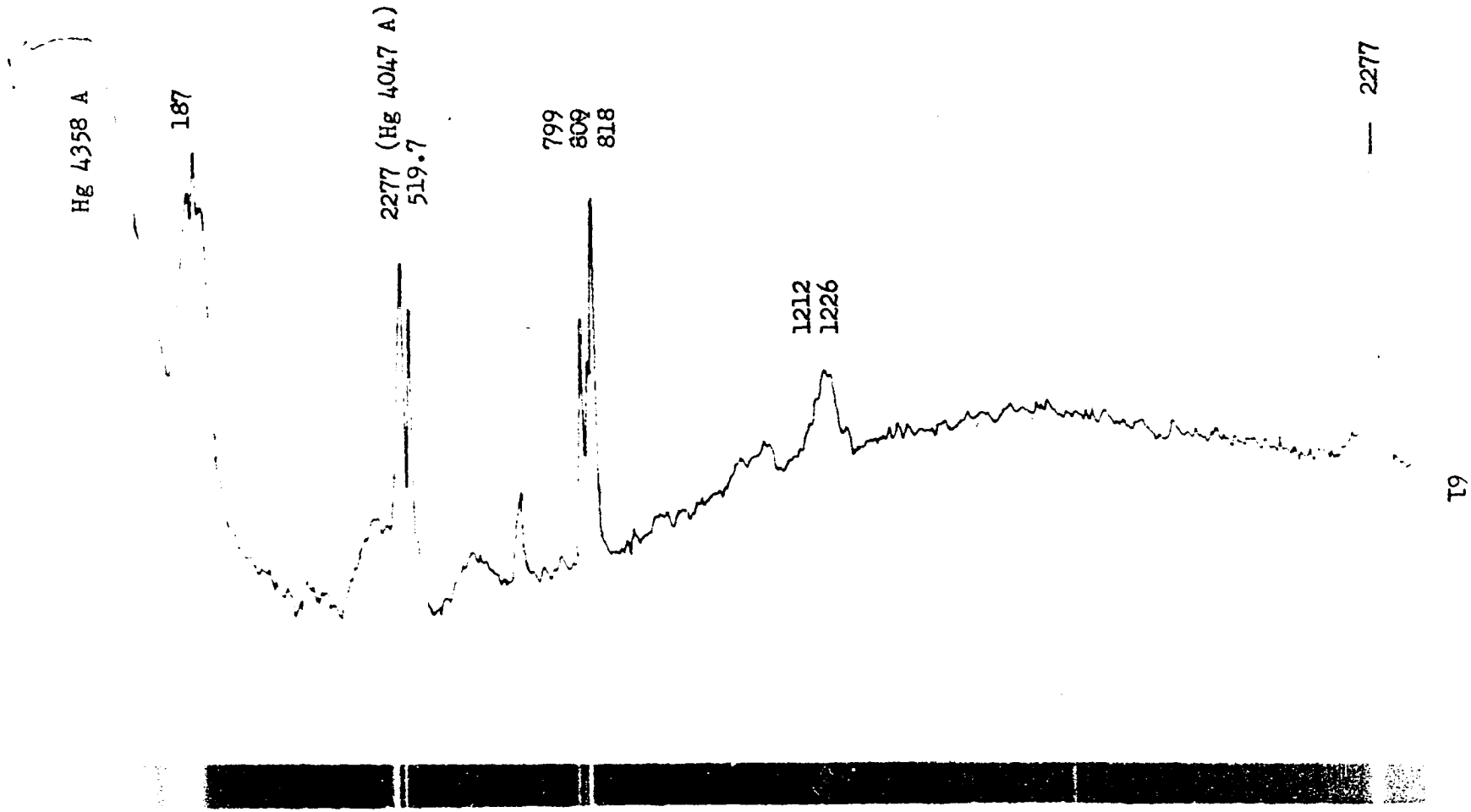
The measured values of the Raman displacements, in wave numbers, are given in Table VII. The values may be taken as correct to ± 1 cm^{-1}, except for those bands, designated as weak or broad, which should be correct to ± 2 cm^{-1}.

The infrared spectrum of the gas in the CsBr region was observed by Dr. N. A. Narasimham. The infrared spectrum of the gas in the NaCl region was observed as a part of this work, and the measurements of bands in both regions were taken. The percent transmission curves are shown in Figures 17 and 18. The infrared frequencies are given, together with their interpretations, in Table VIII.

A discussion of the interpretations and the assignment of fundamentals will be given in Chapter V.

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[8]Address: The Peninsular Chemresearch, Inc., Gainesville, Florida.



RAMAN SPECTRUM OF GASEOUS TRIFLUOROACETONITRILE

Figure 16

TABLE VII

RAMAN SPECTRUM OF GASEOUS TRIFLUOROACETONITRILE

Wave Number	Exciting Line	Description	Interpretation
177	±e	m,b	e fundamental (187)
187	±e	s,sh	
197	±e	m,b	
~460	e	vvw,vb	e fundamental (464)
519.7	e,k	m,sh	a_1 fundamental (520)
799	±e,k	m,sh	a_1 fundamental (~810) [a]
809	±e,k	w,sh	187 + 624 = 811 ($A_1 + A_2 + E$) [a]
818	±e,k	s,sh	
~1048	e	vvw,b	2 x 520 = 1040 A_1
~1085	e	vvw,b	464 + 624 = 1088 ($A_1 + A_2 + E$)
~1212	e	vw,b	e fundamental (1213)
~1226	e	vw,b	a_1 fundamental (1225)
2277	e,k,i	s,b	a_1 fundamental (2273)

[a] Fermi resonance.

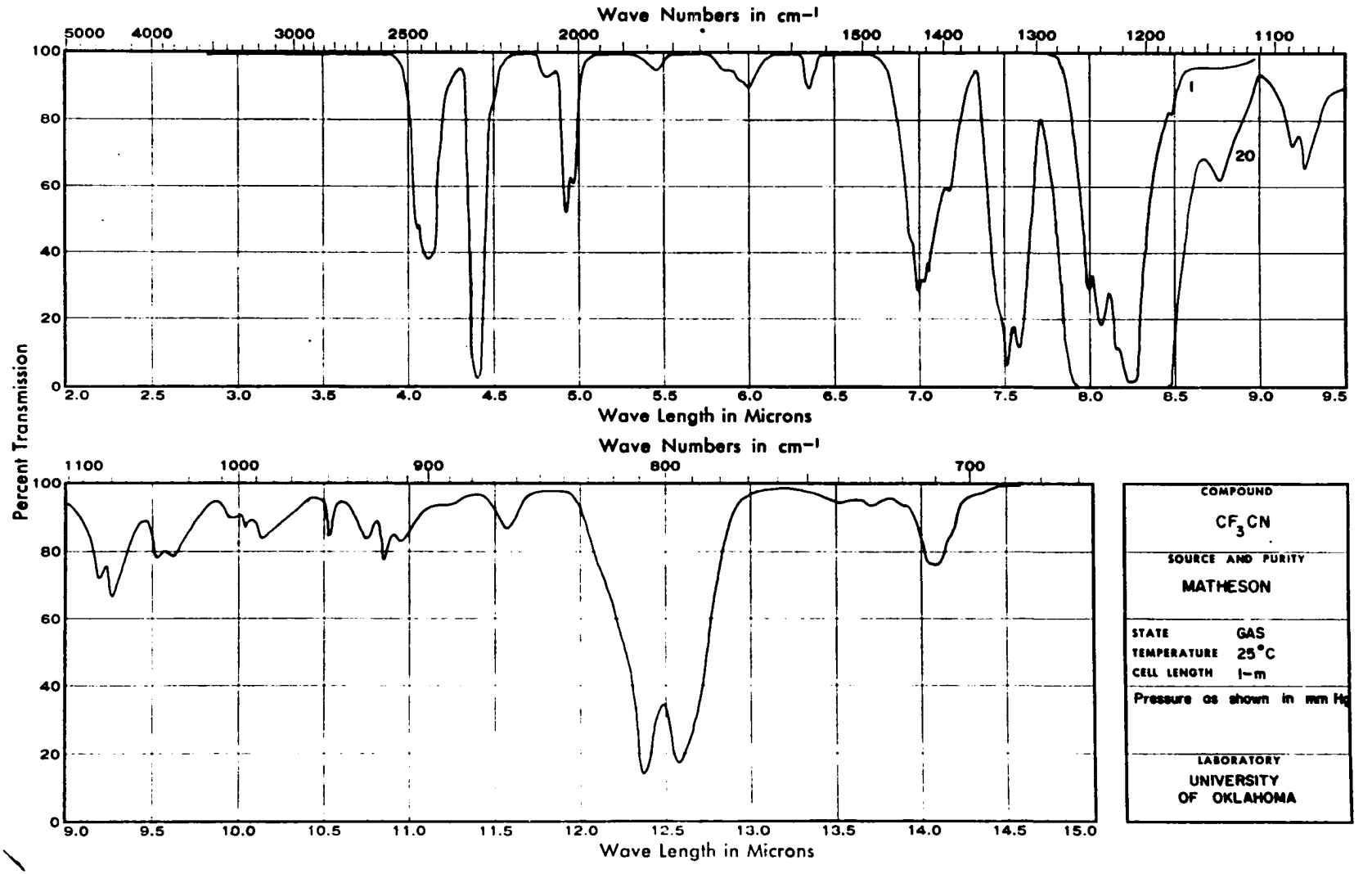

Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
Percent Transmission
100 80 60 40 20 0
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
1
20
Wave Numbers in cm⁻¹
1100 1000 900 800 700
100 80 60 40 20 0
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
COMPOUND
CF3CN
SOURCE AND PURITY
MATHESON
STATE GAS
TEMPERATURE 25°C
CELL LENGTH 1-m
Pressure as shown in mm Hg
LABORATORY
UNIVERSITY
OF OKLAHOMA

Figure 17

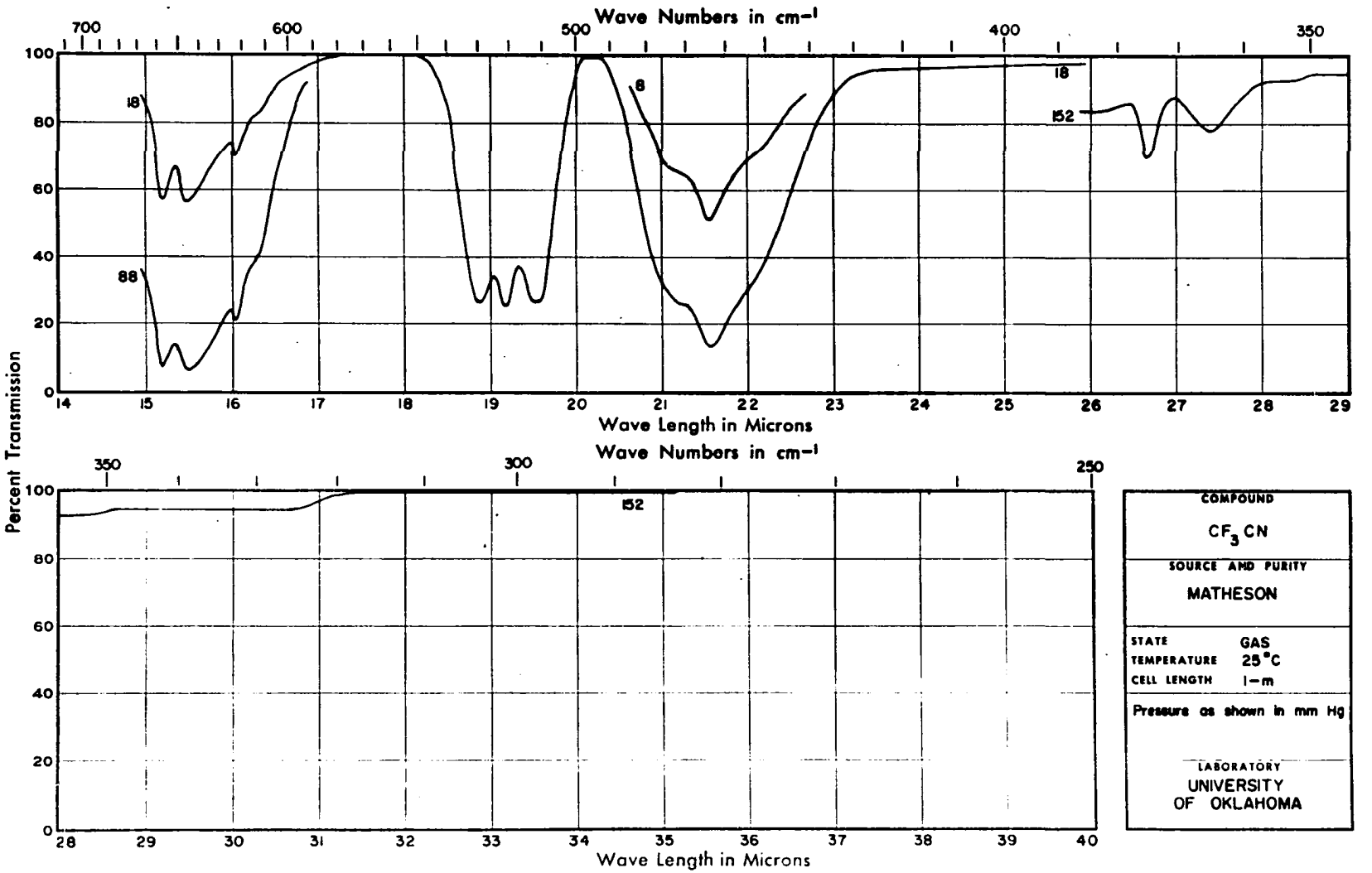

Wave Numbers in cm⁻¹
700
600
500
400
350
100
80
60
40
20
0
18
88
8
18
152
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
Wave Length in Microns
Percent Transmission
Wave Numbers in cm⁻¹
350
300
250
100
80
60
40
20
0
152
28
29
30
31
32
33
34
35
36
37
38
39
40
Wave Length in Microns
COMPOUND
CF3 CN
SOURCE AND PURITY
MATHESON
STATE GAS
TEMPERATURE 25°C
CELL LENGTH 1-m
Pressure as shown in mm Hg
LABORATORY
UNIVERSITY
OF OKLAHOMA

Figure 18

TABLE VIII

INFRARED SPECTRUM OF GASEOUS TRIFLUOROACETONITRILE

Wave Number	Description	Band Type	Interpretation
365	vw		impurity ?
375	vw		2 x 187 = 374 (A_1 + E)
~451	sd	⊥	e fundamental (464)
464	s		
~472	sd		
514	m	∥	a_1 fundamental (520)
522	m		
530	m		
624	vw		e fundamental
646	w		187 + 464 = 651 (A_1 + A_2 + E)
658	w		
694	vvw		1213 - 520 = 693 E
699	vvw		1225 - 520 = 705 A_1
710	w		187 + 520 = 707 E
730	vw		2 x 464 - 187 = 741 (A_1 + A_2 + 2E) ?
740	vw		
796	s		a_1 fundamental (~810) [a]
809	s		187 + 624 = 811 (A_1 + A_2 + E) [a]
~820	sd		
864	w		impurity ?

TABLE VIII - Continued

Wave Number	Description	Band Type	Interpretation
914	w		
922	m		2 x 464 = 928 (A_1 + E)
930	w		
950	w		impurity ?
987	vw		
996	vvw		187 + 810 = 997
1006	vvw		
1039	w		2 x 520 = 1040 A_1
1050	w		
1080	m		464 + 624 = 1088 (A_1 + A_2 + E)
1088	w		
1142	w		520 + 624 = 1144 E
1213	vvs		e fundamental (1213)
~1215	sd		
1225	vs		a_1 fundamental (1225)
1237	vs		
1248	s		2 x 624 = 1248 (A_1 + E)
1254	s		
1318	vs		
1330	vs		520 + 810 = 1330 A_1
~1337	sd		
1396	m		187 + 1213 = 1400 (A_1 + A_2 + E)

TABLE VIII - Continued

Wave Number	Description	Band Type	Interpretation
1417	s		187 + 1225 = 1412 E
1423	s		
1430	s		624 + 810 = 1434 E
1439	sd		
1574	w		2 x 187 + 1213 = 1587 (A_1 + E)
1669	w		464 + 1213 = 1677 (A_1 + A_2 + E)
1681	vw		464 + 1225 = 1689 E
~1700	sd		520 + 1213 = 1733 E
1832	vw		624 + 1213 = 1837 (A_1 + A_2 + E)
2014	m		810 + 1213 = 2023 E
2029	m		810 + 1225 = 2023 E
~2080	w		2273 - 187 = 2086 E
~2220	sd		
2270	s		a_1 fundamental (2273)
2427	m		2 x 1213 = 2426 (A_1 + E)
2463	m		187 + 2273 = 2460 E

[a]Fermi resonance.

Dimethyl Ether

The sample of dimethyl ether was supplied by the Matheson Company. Its purity was given as 99.5%.

The Raman spectrum of the gas was observed, at room temperature and a pressure of 3 atmospheres, with the aid of the multiple-reflection Raman irradiation apparatus. Since the Hg 4047 A radiation will cause the six C-H stretching fundamentals to lie near Raman bands of shifts about 1200 cm^{-1} from the Hg 4358 A line, it was decided to make exposures with and without a 1/4-saturated $NaNO_2$ filter. Three exposures of duration 2 1/2, 3 1/4 and 14 hours were made with a water filter, and three additional exposures, of duration 3 3/4, 15 and 53 hours, were made with a $NaNO_2$ filter. With this procedure, it was possible to determine, for each Raman band, the exciting Hg line and hence the correct Raman frequency. The enlargement of the films and measurements of the bands were made by Mr. A. T. Stair. The measured values of the Raman displacements, together with descriptions, are given in Table IX.

Sulphur Hexafluoride

The sample of sulphur hexafluoride was supplied by the Matheson Company. Its purity was given as 99%.

The Raman spectrum of the gas was obtained, at room temperature and a pressure of 4 atmospheres, with the aid of the multiple-reflection Raman irradiation apparatus. Water was placed in the filter jacket. Three exposures were made of duration 12, 36 and 34 1/2 hours. The films were given to Mr. A. T. Stair for evaluation and interpretation, and the

TABLE IX

RAMAN SPECTRUM OF GASEOUS DIMETHYL ETHER

Wave Number	Exciting Line	Description
392	e	vw,b
410	e	m,sh
448	e	vw
477	e	vw
928	e	vs,b[a]
1261 ?	e	vw
~1440	e	vw,b
~1457	e	vw,b
~1480	e	vw,b
2721	e	vvw
2762	e	vw
2819	e,k,i	vvs,sh
2870	e,k,i	vs,sh
2920	e,k,i	s,sh
2938	e,k	m,sh
2960	e,k,i	s,sh
2995	e,k,i	vs,sh

[a]Degraded toward low wave numbers.

results appear in his Ph.D. dissertation.[9] The values of the Raman displacements, together with their interpretations, appear in Table X.

1-Fluoro-1-chloroethylene

The sample was supplied by Peninsular Chemresearch, Incorporated. No information was given concerning the purity.

The Raman spectrum of the gas, at room temperature and a pressure of 3 atmospheres, was observed with the aid of the multiple-reflection Raman irradiation apparatus. Exposure times of 1/3, 5, 24 1/2 and 99 hours were used. A 1/4-saturated $NaNO_2$ filter was placed in the filter jacket. The films were given to Mr. J. C. Albright[10] for evaluation and interpretation. The results appear in his Ph.D. dissertation.[11] (See Table XI).

1,1-Difluoro-bromoethylene

The sample of 1,1-difluoro-bromoethylene was supplied by Professor J. D. Park, Department of Chemistry, The University of Colorado, Boulder, Colorado. It appeared to be of high purity.

The Raman spectrum of the gas was observed, at room temperature and a pressure of 1 1/3 atmospheres, with the aid of the multiple-reflection Raman irradiation apparatus. Exposure times were 3, 14 and 50 hours.

---

[9] A. T. Stair, "Vibrational Spectra of Compounds in Different States of Aggregation", (Unpublished Ph.D. dissertation, Department of Physics, The University of Oklahoma, 1956).

[10] Address: Continental Oil Company, Ponca City, Oklahoma.

[11] J. C. Albright, "Vibrational Spectra of Hexafluorobutadiene-1,3 and 1-Fluoro-1-chloroethylene", (Unpublished Ph.D. dissertation, Department of Physics, The University of Oklahoma, 1956).

TABLE X

RAMAN SPECTRUM OF GASEOUS SULPHUR HEXAFLUORIDE

Wave Number	Exciting Line	Description	Interpretation
515	e	w,d	f_{2g} fundamental
529	e	w,d	
628	e	w,d	e_g fundamental
639.5	e	w,sh	
652	e	w,d	
690	e	vvw,sh	2 x 344 = 688 (A_{1g} + E_g + F_{2g})
769.4	e,f,g,k,i	vs,sh	a_{1g} fundamental
~809 ?	e	vvw	-

TABLE XI

RAMAN SPECTRUM OF GASEOUS 1-FLUORO-1-CHLOROETHYLENE

Wave Number	Description	Interpretation
370	w,sh	a' fundamental
432	w,sh	a' fundamental
505 533	vvw,d	a" fundamental
698	m,b	a' fundamental
709	vvw	
823 844	vvw,d	a" fundamental
946	m,sh	a' fundamental
1338	w,sh	514 + 835 = 1349 A'
1375	w,sh	433 + 946 = 1379 A'
1380	w,sh	a' fundamental
1401	vvw	2 x 698 = 1396 A'
1422	vvw	610 + 835 = 1445 A'
1637	m,b	698 + 946 = 1644 A'
1654	s,sh	a' fundamental
1670	w,sh	370 + 610 + 698 = 1678 A' ?
1689	m,sh	2 x 835 = 1670 A'
3018	w,sh	a' fundamental
3062	m	1385 + 1654 = 3039 A' ?

TABLE XI - Continued

Wave Number	Description	Interpretation
3071	s,sh	a' fundamental
3102	vw	370 + 2 x 1385 = 3140 A' ?
~3160	w,d	433 + 2 x 1385 = 3203 A' 370 + 1185 + 1654 = 3209 A' ?

A 1/4-saturated $NaNO_2$ filter was employed. The films were given to Dr. Rose Theimer[12] for measurement and interpretation. The values of the Raman displacements, together with their interpretations, are given in Table XII.

[12]Address: The University of Oklahoma Research Institute, Norman, Oklahoma.

TABLE XII

RAMAN SPECTRUM OF GASEOUS 1,1-DIFLUORO-BROMOETHYLENE

Wave Number	Description	Interpretation
164	m,sh	a' fundamental
366	m,sh	a' fundamental
∿568	vvw	a' fundamental
768	m,sh	a' fundamental
957	w,sh	a' fundamental
1165	vvw	a' fundamental
1732	m	a' fundamental
1742	w,sh	
3135	s,sh	a' fundamental

CHAPTER V

INTERPRETATION AND DISCUSSION

Vinyl Chloride

The vibrational and rotational spectra of vinyl chloride have been studied by Thompson and Torkington,[1] Evans and Bernstein,[2] and others.[3,4,5] However, their assignments of the low frequency fundamentals[1,3] were based on the early work of Kohlrausch and Stockmair,[5] and others,[6] who observed the Raman spectrum of the liquid. The very recent work of Evans and Bernstein,[2] which was published after the present study of vinyl chloride was completed, also gives an assignment of fundamentals based in part on the Raman spectrum of the liquid.

Godnev and Filatova[7] calculated the free energy of vinyl

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[1]H. W. Thompson and P. Torkington, Proc. Roy. Soc. (London) A184, 3, 21 (1945).

[2]J. C. Evans and H. J. Bernstein, Can. J. Chem. 33, 1792 (1955).

[3]A. R. H. Cole and H. W. Thompson, Proc. Roy. Soc. (London) A200, 10 (1949).

[4]Ta-You Wu, Phys. Rev. 46, 465 (1934).

[5]K. W. F. Kohlrausch and W. Stockmair, Z. physik. Chem. B29, 292 (1935).

[6]M. de Hemptinne, Trans. Faraday Soc. 42, 5 (1946).

[7]I. N. Godnev and N. N. Filatova, Akad. Nauk SSSR (Moscow), Compt. Rend. (Doklady), Series 2, 52, 43 (1946).

chloride for a few temperatures, while Richards[8] calculated several thermodynamic functions over the temperature range 291-1500 °K. Kobe and Harrison[9] converted Richards' values into engineering units and developed an empirical equation for the heat capacity of vinyl chloride. A search of the literature failed to reveal either Raman spectra or calorimetric data for gaseous vinyl chloride.

The vinyl chloride molecule has the symmetry C_s. Its 12 normal vibrations divide into 9 of species a' (planar) and 3 of species a" (non-planar). All are active in both the Raman and infrared spectra. However, the a" vibrations in the Raman spectrum of the gas are usually diffuse, and consequently weak, since the Q branches are generally spread over a wide wave number range. Among the planar vibrations, there should be three C-H stretching vibrations, one C = C stretching vibration, one C-Cl stretching vibration and four deformation and rocking vibrations. The three non-planar vibrations involve twisting and wagging motions.

The principal moments of inertia of the vinyl chloride molecule have been calculated by various investigators.[10,11,12,8] The molecule

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[8]R. E. Richards, J. Chem. Soc. (London) 151, 1931 (1948).

[9]K. A. Kobe and R. H. Harrison, Petroleum Refiner 30, No. 11, 151 (1951).

[10]H. W. Thompson and P. Torkington, Proc. Roy. Soc. (London) A184, 3, 21 (1945).

[11]A. R. H. Cole and H. W. Thompson, Proc. Roy. Soc. (London) A200, 10 (1949).

[12]I. N. Godnev and N. N. Filatova, Akad. Nauk SSSR (Moscow), Compt. Rend. (Doklady), Series 2, 52, 43 (1946).

seems satisfactory and has been adopted in the present work.

The assignment of the fundamentals observed in the infrared spectrum (Table II) was easily accomplished, making use of previous assignments and what is known about the contours and P-R separations. All infrared bands not assigned as fundamentals have been satisfactorily interpreted. The interpretations agree in part with those of Thompson and Torkington,[16] who observed the infrared spectrum in the range 3-20 microns. In the present work many more bands were observed, although a few bands observed by Thompson and Torkington were not found.

The most recent previous assignment of fundamentals is that of Evans and Bernstein,[17] who based their assignment on observations of the Raman spectrum of liquid $CH_2 = CHCl$ at -100 °C, and the Raman and infrared (2-38 microns) spectra of liquid $CH_2 = CDCl$. Table XIII gives a comparison of their assignments and those of Thompson and Torkington with those of this work. The assignments agree very well, except that our wave numbers are somewhat higher because they apply to the gaseous state. However, it is interesting to note that the values for the three a" fundamentals assigned by Evans and Bernstein are all slightly higher than our values. The assigned values of the fundamentals are not identical with the measured values, since they are averages of the measured Raman and infrared wave numbers.

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[16]H. W. Thompson and P. Torkington, Proc. Roy. Soc. (London) A184, 3, 21 (1945).

[17]J. C. Evans and H. J. Bernstein, Can. J. Chem. 33, 1792 (1955).

is very nearly a symmetric top, having moments of inertia of approximately 15, 135 and 150 x 10^{-40}g cm^2. The non-planar vibrations are therefore expected to have essentially a perpendicular band contour in the infrared spectrum. The contours of the planar vibrations in the infrared should be a mixture of parallel and perpendicular type bands. Thompson and Torkington,[13] taking the principal moments of inertia to be I_A = 15 x 10^{-40}g cm^2 and $I_B = I_C$ = 143 x 10^{-40}g cm^2, have calculated the spacing of the infrared bands from the curves of Gerhard and Dennison.[14] The spacing of the P and R branches in a parallel band was found to be 17-18 cm^{-1}, while the spacing of resolved Q branches in a perpendicular band should be 3-4 cm^{-1}. Also, the Q branches in parallel bands should be weak.

The present work has essentially verified the previous assignments of Thompson and Torkington[13] and Evans and Bernstein.[15]

Eight of the a' fundamentals have been identified with bands observed in the Raman spectrum of gaseous vinyl chloride (see Table I). None of the a" fundamentals were found. The Raman bands not assigned as fundamentals have been interpreted satisfactorily, with the possible exception of the doublet at 3027 and 3033 cm^{-1}. This doublet has been interpreted by Evans and Bernstein[15] as an a' fundamental in Fermi resonance with a ternary combination of species A'. This interpretation

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[13]H. W. Thompson and P. Torkington, Proc. Roy. Soc. (London) A184, 3, 21 (1945).

[14]S. L. Gerhard and D. M. Dennison, Phys. Rev. 43, 197 (1933).

[15]J. C. Evans and H. J. Bernstein, Can. J. Chem. 33, 1792 (1955).

TABLE XIII

FUNDAMENTAL FREQUENCIES OF VINYL CHLORIDE

Thompson & Torkington[a]	Spectrum and State	Evans and Bernstein[b]	Spectrum and State	Present Work R,g	Present Work I,g	Assignment
395[c]	R,l	396	R,l	394	398	a'
622	I,g	623	R,l	-	620	a"
724	I,g	706	R,l	719	721	a'
895	I,g	901	R,l	-	896	a"
940	I,g	942	I,g(?)	-	941	a"
1030	I,g	1026	R,l	-	1030	a'
1280	I,g	1274	R,l	1279	1281	a'
1370	I,g	1363	R,l	1368	1370	a'
1610	I,g	1603	R,l	1607	~1611	a'
3030[c]	R,l	3027	R,l	3033	3029	a'
3078[c]	R,l	3079	R,l	3086	3086	a'
3134[c]	R,l	3112	R,l	3121	3121	a'

[a]H. W. Thompson and P. Torkington, Proc. Roy. Soc. (London) A184, 21 (1945).

[b]J. C. Evans and J. J. Bernstein, Can. J. Chem. 33, 1792 (1955).

[c]These values were taken by Thompson and Torkington from the Raman data of liquid vinyl chloride of Kohlrausch and Stockmair, Z. physik. Chem. B29, 292 (1935).

For the purpose of calculating the thermodynamic functions, the product of the principal moments of inertia was calculated by the method of Hirschfelder.[18] However, the thermodynamic functions are rather insensitive to even large changes in the value of this product. Richards,[19] who also calculated the thermodynamic functions, found, for example, that the maximum variation in entropy which would be caused by the maximum variation in the principal moments of inertia was 0.1 cal/mole deg. Our calculations agree fairly well with those of Richards, who used the values of the fundamentals given by Thompson and Torkington.[20] Differences of the order of 1.0 cal/mole deg are found in all of the functions. The temperature range of the calculations has an upper limit of 500 ^{o}K because it was felt that there would be appreciable dissociation of the vinyl chloride molecule at temperatures higher than this. This limit is somewhat arbitrary because no information on dissociation could be found in the literature.

Vinyl Bromide

The vibrational and rotational spectra of vinyl bromide have been studied by Thompson and Torkington,[20] de Hemptinne[21] and Torkington.[22]

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[18] J. O. Hirschfelder, J. Chem. Phys. 8, 431 (1940).

[19] R. E. Richards, J. Chem. Soc. (London) 151, 1931 (1948).

[20] H. W. Thompson and P. Torkington, Proc. Roy. Soc. (London) A184, 3, 21 (1945).

[21] M. de Hemptinne, Trans. Faraday Soc. 42, 5 (1946).

[22] P. Torkington, Proc. Roy. Soc. (London) A206, 17 (1951).

Thompson and Torkington based their assignment of fundamentals on incomplete infrared data and the Raman spectrum of liquid vinyl bromide which was studied by Kohlrausch and Stockmair[23] and others.[24] A normal coordinate analysis of substituted ethylenes, including vinyl bromide and vinyl chloride, was carried out by Torkington.[25] de Hemptinne[26] observed the Raman spectrum of liquid vinyl bromide.

The discussion of the molecular symmetry, the type and form of the normal vibrations and the contours of infrared bands given in the preceding section on vinyl chloride holds equally well for vinyl bromide. The principal moments of inertia were calculated by Thompson and Torkington[27] and others.[28,29] Thompson and Torkington found the moments of inertia to be approximately 17, 192 and 209 x 10^{-40} g cm^2. Taking the vinyl bromide molecule to be a symmetric top, they calculated the P-R separation of parallel bands to be about 16 cm^{-1} and the resolved Q branch separation

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[23]K. W. F. Kohlrausch and W. Stockmair, Z. physik. Chem. B29, 292 (1935).

[24]M. Borguel and L. Piaux, Bull. Soc. Chim. France (5) 2, 1958 (1935).

[25]P. Torkington, J. Chem. Phys. 17, 1279 (1949).

[26]M. de Hemptinne, Trans. Faraday Soc. 42, 5 (1946).

[27]H. W. Thompson and P. Torkington, Proc. Roy. Soc. (London) A184, 3, 21 (1945).

[28]I. N. Godnev and N. N. Filatova, Akad. Nauk SSSR (Moscow), Compt. Rend. (Doklady), Series 2, 52, 43 (1946).

[29]R. E. Richards, J. Chem. Soc. (London) 151, 1931 (1948).

in perpendicular bands to be about 3 cm^{-1}.

Richards[30] calculated thermodynamic functions for vinyl bromide over the temperature range 291-1500 °K. Kobe and Harrison[31] converted Richards' values into engineering units. A search of the literature failed to reveal either Raman spectra or calorimetric data for gaseous vinyl bromide.

Thirteen bands were observed in the Raman spectrum of gaseous vinyl bromide. Their wave numbers are listed in Table IV. Kohlrausch and Stockmair[32] had observed Raman bands of liquid vinyl bromide at 497 and 1166 cm^{-1}. The former frequency was taken to be an a" fundamental by Thompson and Torkington.[33] However, de Hemptinne[34] found neither of these bands in the Raman spectrum of the liquid (see Table XIV). Moreover, no bands were found at these frequencies in the present work. In agreement with the assignments of de Hemptinne, the bands observed at 344, 611, 1258, 1373, 1601, 3027, 3087 and 3112 cm^{-1} have been assigned as a' fundamentals. All of these bands were also observed in the infrared spectrum (see Table V). The strong infrared band at 1005 cm^{-1} is assigned as

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[30]R. E. Richards, J. Chem. Soc. (London) 151, 1931 (1948).

[31]K. A. Kobe and R. H. Harrison, Petroleum Refiner 30, No. 11, 151 (1951).

[32]K. W. F. Kohlrausch and W. Stockmair, Z. physik. Chem. B29, 292 (1935).

[33]H. W. Thompson and P. Torkington, Proc. Roy. Soc. (London) A184, 3, 21 (1945).

[34]M. de Hemptinne, Trans. Faraday Soc. 42, 5 (1946).

the one remaining a' fundamental. The infrared bands observed at 582, 901 and 941 cm^{-1} are assigned as the three a" fundamentals. The assigned fundamentals are listed in Table XIV together with those of Thompson and Torkington[35] and de Hemptinne.[36] Except for the lowest a" fundamental, there is good agreement between the previous assignments and those of the present work.

No explanation of the Raman band at 573 cm^{-1} seems possible except to assume that it is caused by an impurity in the sample. This assumption is supported by the fact that no previous worker has found a band at 573 cm^{-1} in the Raman spectrum of $CH_2 = CHBr$. The published spectra of various possible impurities were examined, but none could account definitely for this band. In this search, the possibility was considered that the Raman bands found at 2880, 2938, 2971 and 2990 cm^{-1} might also be caused by an impurity in the sample. The spectra examined included the possible reactants in the preparation of vinyl bromide; namely, acetylene and ethylene dibromide. Polyvinyl bromide may be an impurity but no Raman or infrared spectra of this compound could be found in the literature.

All but a few of the infrared bands not assigned as fundamentals have been satisfactorily explained as either overtones, sum bands or difference bands, or as probably due to the presence of water vapor. The

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[35]H. W. Thompson and P. Torkington, Proc. Roy. Soc. (London) A184, 3, 21 (1945).

[36]M. de Hemptinne, Trans. Faraday Soc. 42, 5 (1946).

TABLE XIV

FUNDAMENTAL FREQUENCIES OF VINYL BROMIDE (cm^{-1})

Thompson & Torkington[a] (I,gas)	de Hemptinne[b] (R,liq.)	Present Work (R,gas)	Present Work (I,gas)	Assignment
345[c]	348	344	345	a'
497[c]	-	-	582	a"
615	601	611	614	a'
902	906	-	901	a"
940	-	-	941	a"
1008	1004	-	1005	a'
1262	1253	1258	1258	a'
1377	1370	1373	1372	a'
1605	1596	1601	1603	a'
3014[c]	3014	3027	3026	a'
3075[c]	3075	3087	3089	a'
3103[c]	3103	3112	3111	a'

[a]H. W. Thompson and P. Torkington, Proc. Roy. Soc. (London) A184, 21 (1945).

[b]M. de Hemptinne, Trans. Faraday Soc. 42, 5 (1946).

[c]These values were taken by Thompson and Torkington from the Raman data of liquid vinyl bromide of Kohlrausch and Stockmair, Z. physik. Chem. B29, 292 (1935).

latter have been included in the percentage transmission curves because there remains some doubt about their interpretation.

The thermodynamic functions of vinyl bromide were calculated in the same fashion as for vinyl chloride. The results are presented in Table VI. The differences between the values of the thermodynamic functions calculated here and those of Richards[37] are in all cases less than 1.0 cal/mole deg.

Vinyl Chloride and Vinyl Bromide

It may be of interest to compare the assigned values of the fundamental frequencies of vinyl chloride with those of vinyl bromide. For this purpose the assigned values, together with rough characterizations of the motions, are listed in Table XV. As stated previously, the assigned values represent averages of the measured Raman and infrared frequencies. The two bending motions seem to be the least affected by substitution, while the "C-H wagging frequency" for vinyl bromide is 22 cm^{-1} less than the corresponding frequency in vinyl chloride.

It is interesting to make some further comparisons by means of Bernstein and Pullin's vibrational sum rule[38] and some recent calculations by Bernstein.[39] Bernstein calculated the sum of the in-plane and the out-of-plane frequencies for vinyl chloride and vinyl bromide. In addition, he has calculated the heat capacities, at 25 °C, of vinyl

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[37] R. E. Richards, J. Chem. Soc. (London) 151, 1931 (1948).

[38] H. J. Bernstein and A. D. E. Pullin, J. Chem. Phys. 21, 2188 (1953).

[39] H. J. Bernstein, J. Chem. Phys. 24, 910, 911 (1956).

TABLE XV

FUNDAMENTALS OF GASEOUS VINYL CHLORIDE AND VINYL BROMIDE

Vinyl Chloride	Vinyl Bromide	Species	Approximate Motion
396	344	a'	C = C-X rocking
620	582	a"	twisting
720	614	a'	C-X stretching
896	901	a"	wagging
941	941	a"	wagging
1030	1005	a'	CH_2 rocking
1280	1258	a'	CH rocking
1369	1374	a'	CH_2 deformation
1609	1602	a'	C = C stretching
3030	3027	a'	C-H stretching
3086	3087	a'	C-H stretching
3121	3112	a'	C-H stretching

chloride and vinyl bromide without making use of the fundamental frequencies. A comparison of the values calculated by Bernstein with those found in this work are made in the following table:

		$CH_2 = CHCl$	$CH_2 = CHBr$
$\sum \nu(a')$	calculated by Bernstein	15623	15365
	obs. in present work	15641	15423
$\sum \nu(a'')$	calculated by Bernstein	2453	2440
	obs. in present work	2457	2424
C_p^o (25°C)	calculated by Bernstein	12.82	13.29
	calculated in present work	12.83	13.26

The agreement between the values of the heat capacity of both compounds is remarkable, and the agreement of the sums is good for vinyl chloride, but not so close for vinyl bromide.

Trifluoroacetonitrile

The Raman spectrum of gaseous trifluoroacetonitrile (CF_3CN) has not previously been observed. The recently published work of Edgell and Potter[40] gives the Raman spectrum of liquid CF_3CN at -100 °C, and the infrared spectrum of the gas in the spectral range 2-38 microns. Edgell and Potter were able to make an assignment of fundamentals from their data and correlations for a number of substituted methanes of the type CF_3X.

It has been shown from the microwave spectrum[41] that CF_3CN is

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[40] W. F. Edgell and R. M. Potter, J. Chem. Phys. 24, 80 (1956).

[41] W. Gordy, Phys. Rev. 77, 292 (1954).

a symmetric top. The molecule thus has the symmetry C_{3v}, and has 4 totally symmetric (a_1) and 4 doubly degenerate (e) normal vibrations. All are both Raman and infrared active. Table XVI gives the resultant species of several possible combination and overtone bands.

TABLE XVI

SPECIES OF OVERTONE AND COMBINATION BANDS

Overtone or Combination	Resultant Species
$a_1 + a_1$	A_1
$a_1 + e$	E
$e + e$	$A_1 + A_2 + E$
$(a_1)^2$	A_1
$(e)^2$	$A_1 + E$
$(a_1)^3$	A_1
$(e)^3$	$A_1 + A_2 + E$

There arises the problem of whether the C-C ≡ N chain is linear or bent. If the chain is bent, the degeneracy would be removed from the vibrations of species e, and this would cause a splitting of those bands in the spectrum. Since no such splitting has been observed, it has been assumed that the chain is linear, in agreement with the microwave work.

Edgell and Potter[42] calculated the principal moments of inertia to be $I_A = 148 \times 10^{-40}$ g cm^2 and $I_B = I_C = 285 \times 10^{-40}$ g cm^2. In addition,

[42] W. F. Edgell and R. M. Potter, J. Chem. Phys. 24, 80 (1956).

from the formula of Gerhard and Dennison,[43] they calculated the P-R separation in parallel bands to be ~ 17 cm^{-1}.

From the above values for the principal moments of inertia and Figure 125 in Herzberg,[44] p. 421, the ratio of the intensity of the Q branch to the sum of the intensities of the P and R branches was found to be ~ 0.7. Thus, the Q branch in a parallel infrared band should be relatively weak as compared to the P and R branches. It is not possible to predict a priori the shapes of the perpendicular type infrared and Raman bands.

The Raman spectrum (Figure 16, Table VII) has been fully interpreted and seven of the bands have been assigned as fundamentals. The assignments are in essential agreement with those of Edgell and Potter (Table XVII). These authors observed one band at 192 cm^{-1}, whereas in the present work a band at 187 cm^{-1} with two rotational branches at separations of 10 cm^{-1} were observed. A Raman band arising from a degenerate vibration of a molecule of symmetry C_{3v} will, in general, consist of a superposition of two series of sharp Q branches corresponding to the two allowed values of ΔK (± 1, ± 2). The spacings of the Q branches are $2\left[A(1 - \zeta) - B\right]$ and $4\left[A(1 - \zeta/2) - B\right]$, for $\Delta K = \pm 1$ and $\Delta K = \pm 2$, respectively. ζ is the Coriolis constant. A and B are known for CF_3CN and by equating the above terms for the spacings of the Q branches equal to zero, two values of ζ are found (0.48, -0.96). The relatively strong central

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[43] S. L. Gerhard and D. M. Dennison, Phys. Rev. 43, 197 (1933).

[44] G. Herzberg, Infrared and Raman Spectra, Fifth Printing (New York: D. Van Nostrand, Inc., 1951).

branch of the 187 cm^{-1} band suggests that all of the Q branches of one series coincide, but the resolution is insufficient to determine which series is responsible and, therefore, the appropriate value of ζ. Also, Edgell and Potter found two bands at 803 and 818 cm^{-1}, while three bands, at 799, 809 and 818, were found in the present work. The interpretation of these three bands presented some difficulty, and their explanation as an a_1 fundamental in Fermi resonance with a binary combination may be regarded as somewhat uncertain.

All but one of the fundamentals found in the Raman spectrum have been observed in the infrared spectrum. The lowest e fundamental at 187 cm^{-1} fell outside of the available spectral range. Also, the one remaining fundamental was identified with the infrared band at 624 cm^{-1}. The values of fundamentals assigned by Edgell and Potter, together with those of this work, are listed in Table XVII. There is good agreement between their assignments and ours.

Satisfactory interpretations have been given for all infrared bands not assigned as fundamentals, with a few exceptions. The bands at 365 and 375 cm^{-1} may be impurity bands due to a trace of $CCl_2 = CCl - CF_3$, which was in the 1-m cell prior to CF_3CN. However, the 375 cm^{-1} band may be satisfactorily explained as an overtone of the lowest e fundamental ($2 \times 187 = 374$), leaving only the explanation of the band at 365 cm^{-1} as uncertain. Also, two bands at 864 and 950 cm^{-1} have not been satisfactorily explained. Edgell and Potter did not observe the latter two bands, so they may reasonably be considered as due to impurities. Apart from these questionable bands, there is good agreement between the interpreta-

TABLE XVII

FUNDAMENTAL FREQUENCIES OF TRIFLUOROACETONITRILE

Edgell and Potter[a]	Spectrum and State	Present Work	Spectrum and State		Assignment
192	R,l	187	R,g	e	C-C ≡ N bending
464	R,l;I,g	464	R,I,g	e	CF_3 bending
521	R,l;I,g	520	R,I,g	a_1	CF_3 deformation
625	R,l;I,g	624	I,g	e	CF_3 deformation
801	R,l;I,g	~810	R,I,g	a_1	C-C stretching
1215	R(?),l;I,g	1213	R,I,g	e	asym. CF_3 stretching
1228	R,l;I,g	1225	R,I,g	a_1	sym. CF_3 stretching
2271	R,l;I,g	2273	R,I,g	a_1	C ≡ N stretching

[a]W. F. Edgell and R. M. Potter, J. Chem. Phys. 24, 80 (1956).

tions given by Edgell and Potter and those of this work.

CHAPTER VI

SUMMARY

Since selection rules and band contours can usually be predicted only for non-interacting molecules, it is desirable to obtain the vibrational spectra of compounds in the gaseous state. However, the low densities of gases make it very difficult to obtain their Raman spectra by ordinary experimental methods. The purpose of the present work has been to develop an efficient Raman irradiation apparatus for gases and to obtain the Raman and infrared spectra of selected compounds in the gaseous state.

Following an optical design given by Welsh, et al.,[1] a multiple-reflection Raman tube for gases has been designed and constructed. The illuminated section is 100 cm in length and has a diameter of 6 cm. Two 1500 watt Hg lamps are used as sources of excitation. It is estimated that the multiple reflections increase the intensity of the Raman scattered light entering the spectrograph by a factor of about 20.

With the aid of this apparatus and a three-prism spectrograph of reciprocal linear dispersion 15 A/mm, the Raman spectra of the following compounds in the gaseous state at room temperature were obtained: vinyl chloride, vinyl bromide, trifluoroacetonitrile, dimethyl ether,

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[1]Welsh, Cumming and Stansbury, J. Opt. Soc. Am. 41, 712 (1951).

sulphur hexafluoride, 1-fluoro-1-chloroethylene, 1,1-difluoro-bromoethylene and ethylene oxide. In addition, the infrared absorption spectra were obtained for the gases vinyl chloride, vinyl bromide and trifluoroacetonitrile, with the aid of a Perkin-Elmer Model 112 double-pass spectrometer equipped with prisms of LiF, NaCl and CsBr.

The Raman and infrared spectra of vinyl chloride and vinyl bromide have been interpreted, and the following assignments of fundamentals (in cm^{-1}) have been made: $CH_2 = CHCl$, species a': 396, 720, 1030, 1280, 1369, 1609, 3030, 3086 and 3121; species a": 620, 896 and 941; $CH_2 = CHBr$, species a': 344, 614, 1005, 1258, 1373, 1602, 3027, 3087 and 3112; species a": 582, 901 and 941. These assignments agree with those of previous workers,[2,3,4] except for the lowest a" fundamental of $CH_2 = CHBr$, which has previously been taken to be 497 cm^{-1}, and except for small changes in the wave numbers.

The entropy, the heat content function, the free energy function and the heat capacity have been calculated for vinyl chloride and vinyl bromide in the ideal gas state at one atmosphere pressure and over the temperature range 273.16-500 °K.

The eight fundamental vibrational frequencies of CF_3CN have been assigned as follows: species a_1: 520, approx. 810, 1225 and 2273; species e: 187, 464, 624 and 1213 cm^{-1}. The exact value of the a_1

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[2]H. W. Thompson and P. Torkington, Proc. Roy. Soc. (London) A184, 21 (1945).

[3]J. C. Evans and H. J. Bernstein, Can. J. Chem. 33, 1792 (1955).

[4]M. de Hemptinne, Trans. Faraday Soc. 42, 5 (1946).

fundamental near 810 cm^{-1} is somewhat uncertain, since three Raman bands are found here, at 799, 809 and 818 cm^{-1}. They are interpreted as resulting from approximate coincidence of the combination 187 + 624 = 811 ($A_1 + A_2 + E$) with the a_1 fundamental, and Fermi resonance between the latter and the A_1 component of the combination. Also, in the Raman spectrum of CF_3CN, the e fundamental at 187 cm^{-1} consists of a strong and fairly sharp zero branch surrounded by rotational wings. This is interpreted to mean that all of the Q branches of one set coincide. After completion of the present work, Edgell and Potter[5] reported Raman data for liquid CF_3CN at -100 °C and infrared data for gaseous CF_3CN. They assign the fundamentals in agreement with the present work.

[5]W. F. Edgell and R. M. Potter, J. Chem. Phys. 24, 80 (1956).

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APPENDIX I

IMPROVEMENTS IN THE MULTIPLE-REFLECTION RAMAN APPARATUS FOR GASES

Some recent improvements in the Raman apparatus for gases and some observations concerning its performance have recently been made. They are briefly as follows:

1. A modified condensing lens mount has been designed and constructed. An achromatic lens, of focal length 25.0 cm has been substituted for the lens (f = 25.4 cm) employed in the present work. A simle calculation shows that the lens must be placed 31.9 cm from the slit for proper focusing of the Raman tube. The lens aperture should be readjusted accordingly.

2. The legs of the table on which the optical bench rests have been reinforced to insure greater rigidity.

3. The sample gas inlet system has been modified to include two stainless steel fritted filters and a drying agent[1] (activated alumina). The sample gas is thus made to pass through the first filter, which has an average pore size of 5 microns, then though the drying agent and finally through the second filter, which has an average pore

[1]Trade Name: Ansul "T-flo" drier cartridge. Manufactured by the Ansul Chemical Company, Marinett, Illinois.

size of 10 microns. The behavior of the drying agent is such that there is a very high heat of adsorption. This was first noticed, but not understood, when ethylene oxide was passed through the drier. Mr. P. J. Ehman,[2] through private communication, has advised us of the high heat of adsorption and has given the opinion that the activated alumina would have no effects on the chemical composition of the gases which have been studied. His communication and other information pertaining to the care and cleaning of the stainless steel filters are now on file here in the laboratory.

4. It should be noted that the rear window of the Raman tube must be completely blocked-off with black material at all times. Otherwise, room light will pass into the spectrograph.

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[2]Address: P. J. Ehman, Manager Chemical Research Department, Ansul Chemical Company, Marinett, Illinois.

APPENDIX II

RAMAN SPECTRUM OF GASEOUS ETHYLENE OXIDE

Experimental. The sample of ethylene oxide was supplied by the Matheson Company and had a stated purity of 99.8%.

The Raman spectrum was observed with the aid of the multiple-reflection irradiation apparatus. Two series of exposures were made, both resulting in a somewhat incomplete spectrum. The first of these, three exposures of duration 2, 6 and 23 hours, at 2 atmospheres pressure, yielded more information than the second attempt, four exposures of lengths 4, 24, 71 and 73 hours at one atmosphere pressure. The lower pressure was the result of the limited amount of sample remaining. Also, during the second series of exposures a considerable amount of difficulty was experienced with the optical alignment of the condensing lens. In both series of exposures a 1/4-saturated $NaNO_2$ filter was used.

The films were enlarged in the usual manner and measurements were made of the Raman displacements. The results are listed in Table XVIII. The band at 1268 cm^{-1} may be taken as correct to ± 1 cm^{-1}, while the others are probably correct to ± 2 cm^{-1}.

Conclusions. Before an effort can be made to interpret the Raman spectrum of ethylene oxide, a more complete spectrum is necessary. It is suggested that a series of exposures be made with freshly re-coated

TABLE XVIII

RAMAN SPECTRUM OF GASEOUS ETHYLENE OXIDE

Wave Number	Exciting Line	Description
~481	e	vvvw,sh
587	e	vvvw,sh
~1100	e	vvw
1123	e	vw,sh
1205	e (2973,k)	vvw
1268	e	vs,sh
~1415	e	vvw
~1438	e	vvw
2925	e	vs,sh
2968	e	vs,sh
3018	e	vs,sh

mirrors, and with the pressure of the sample as high as possible. Also, the optical alignment should be as nearly perfect as possible. It is necessary to make the efficiency a maximum because of the poor scattering properties of ethylene oxide. However, under conditions of maximum efficiency, it is believed that a satisfactory spectrum can be obtained.