THE DESIGN AND TESTING OF A LOW-TEMPERATURE
RAMAN EXCITATION UNIT

by

ROBERT VINCENT FITZSIMMONS

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A THESIS

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INTRODUCTION

Since the discovery of the Raman Effect by Sir C. V. Raman in 1928 (9), it has proven itself to be a very useful tool in the elucidation of molecular structures.

If a substance is irradiated with an intense monochromatic radiation, some of the light is scattered perpendicularly to the direction of the incident light. The spectrographic examination of this scattered light shows that it is no longer monochromatic but consists of several frequencies. The most intense of these has the same frequency as the incident light (Rayleigh Line) but a series of weaker lines (Raman Lines) do not. The difference in frequency between the Raman lines and the Rayleigh line is called the Raman frequency shift and is characteristic of the scattering substance.

Raman scattering may be regarded as the result of the interaction of a light quantum with a molecule with a change in energy of the scattered quantum of light. The molecule may either gain or lose energy in this interaction. If the molecule absorbs some of the energy from the light quantum, the emitted light appears as a line of lower frequency (Stokes Raman line). If the molecule is in an excited state, it may lose some of its energy to the light quantum which now appears as a line of higher frequency (Anti-Stokes line). In either case only certain exact values of energy will be exchanged, and these quantities are characteristic of the vibrational and rotational energies of the molecule.

The Raman frequency shifts correspond to the infra-red absorption frequencies. However, not all of the absorption frequencies appearing in the infra-red are present in the Raman spectra and vice versa. From a consideration of the geometric symmetry of the molecule, it is possible to predict the number of frequencies appearing in either the Raman or the infra-red spectra and those appearing in both. In practice, molecular models are assumed and the predicted frequencies are compared with those actually observed.

The principal advantages of Raman spectroscopy are that it allows the investigation of the important low frequency region below 300 cm^{-1} which cannot be observed with most infra-red spectrometers, and also it permits the use of water solutions.

LIGHT SCATTERING IN VARIOUS MEDIA

The intensity of the light scattered by gases is very weak but converges to a larger value as the critical point; i.e., the temperature and pressure at which the gas begins to condense, is approached (Bhagavantam, 1). Because of the extremely weak intensity of the light scattered by gases, Raman spectra are usually taken in the liquid phase. At ordinary temperatures, however, many substances are gases, and it is desirable to condense them to liquids in order to obtain their Raman spectra in reasonably short exposure times. Also the phenomenon of Raman line polarization is observed more readily in the liquid phase. The higher boiling gases, with boiling points in the neighborhood of $0°$ C., may be condensed directly into the sample tube, and when sealed off they

remain liquid at higher temperatures under their own vapor pressure. For the lower boiling substances, however, the condensed phase must be continually cooled to prevent it from vaporizing.

NATURE OF THE PROBLEM

In order to reach the low temperatures necessary to condense low boiling gas samples such as nitric oxide (b.p. = -152° C.) and dinitrogen trioxide (m.p. = -102° C.), an instrument was required which was capable of cooling the Raman sample over extended periods of time while it was being irradiated with intense light. It was apparent that the present excitation unit of our Hilger Raman Spectrograph, Model E-612, could not be modified for low temperature work. A completely new unit, therefore, had to be designed and constructed. The requirements of this new unit were as follows:

1. It must be compact and interchangeable with the original unit.

2. It must use the same source of exciting radiation and the same power supply as the original source.

3. It must be designed so that the sample tube can be placed into position and easily aligned with the optical system of the spectrograph.

4. It must be a permanent unit which is capable of continuous operation for long periods of time.

PREVIOUS LOW-TEMPERATURE WORK

In general, there have been two approaches to the problem of observing Raman spectra at low temperatures. One called for the immersion of the sample in a liquid refrigerant and the other used a flow of cold gas to cool the sample.

Liquid Refrigerant Method

A vertical Dewar flask, in which the Raman tube was immersed in cooled ethyl alcohol, was essentially the apparatus used by Sutherland (10). The Dewar flask was only partially silvered to allow the passage of the exciting light from a single mercury vapor lamp to the sample. With this system he was able to reach temperatures down to the freezing point of ethyl alcohol. For lower temperatures, liquid air was used as the refrigerant. The light scattered perpendicularly to the incident light passed through the flat glass bottom of the Dewar flask and into the spectrograph. With this system very good cooling of the sample was possible but the liquid refrigerant absorbed much of the exciting light, and long exposures were necessary.

Some of the first low temperature Raman work was done by McLennan and McLeod in 1929 (8). They sought to obtain the Raman spectra of O_2, N_2, H_2 and other low boiling gases in their condensed phases. Their apparatus was, of necessity, elaborate for the maintenance of very low temperatures. The sample tube was a slender Dewar flask immersed in a second Dewar flask containing liquid air. The gas sample was continually condensed directly into

the sample tube while the Raman spectrum was recorded. The sample was irradiated by four mercury vapor lamps placed around it, and the scattered light was reflected upward along the axis of the tube by a plain mirror placed at the bottom. Such an elaborate apparatus is not necessary for most work, and here again much of the exciting radiation was absorbed by the liquid refrigerant requiring longer exposures.

Cold Gas Method

Among the first work using a flow of cold gas to cool the Raman sample was that done by Kahovec and Wagner in 1941 (4). They constructed a Dewar flask which was only partially silvered to allow the exciting light to pass through to the sample tube, and which had a glass tube sealed into the base. The sample tube, standing vertically in this flask, was cooled by a flow of cold air (boiled from liquid air) which flowed in at the bottom of the Dewar flask and spilled over the top. They were able to reach temperatures as low as -120° C. with this system but there was always a large temperature gradient along the irradiated length of the Raman tube.

A somewhat different approach was used by several investigators (Long, et al., 6; Lord and Nielson, 7). Instead of cooling the sample tube in a closed bottom Dewar flask, a vacuum jacketed sleeve was placed around the sample tube and extended along the length of the latter. Cold gas entered this sleeve, cooled the sample, and escaped through loosely-fitted plugs. In some cases

it was even possible to introduce the vacuum sleeve around the Raman tube with only minor modifications in the design of the existing apparatus. These sleeves were usually of bulky construction, were not very efficient, and sometimes caused frosting of the optical parts of the system.

DESIGN AND CONSTRUCTION OF A LOW-TEMPERATURE UNIT

The low temperature unit was modeled after the Hilger Excitation unit (Hilger Raman Source, Model FL 1), and was mounted on the base plate on the optical bench of the Hilger spectrograph in the same manner. The unit was designed to be interchangeable with the Hilger unit. It could easily be attached to and removed from the base plate. The mercury lamps providing the exciting radiation could be placed through the top of the assembled unit, and provision had been made for the centering and vertical alignment of the Raman tube (Plates VI and VII, Appendix).
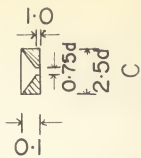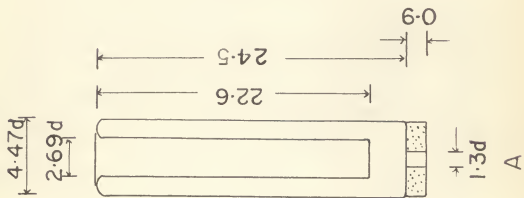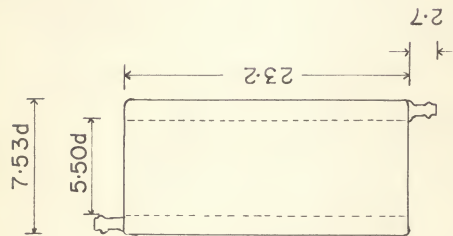
Dewar Flask (A, Plate I)

The Raman sample tube was cooled in a cylindrical, unsilvered, Pyrex glass Dewar flask. The tube was centered in this by a small metal ring (C, Plate I) at the base and a bored cork at the top of the Dewar flask. The light scattered vertically along the Raman tube, passed through the double-walled glass base of the Dewar flask and into the spectrograph. The glass surfaces at the bottom of the flask were flat and parallel to allow maximum transmission of the scattered light. The entire unit was built around this specially constructed Dewar flask. The latter rested on a flat cork

EXPLANATION OF PLATE I

A. Dewar flask.

B. Cooling jacket.

C. Metal ring for centering Raman tube in Dewar.

(Units in cm.)

PLATE I

which was cemented to the base of the flask, and had a central hole for the passage of the scattered light.

Cooling Jacket (B, Plate I)

Surrounding the Dewar flask and allowing space for plastic sheet filters was the cylindrical Pyrex glass cooling jacket. This was 23.2 cm. in length and had an inner diameter of 5.5 cm., an outer diameter of 7.5 cm., and short lengths of glass tubing sealed to each end. The purpose of the cooling jacket was to protect the Raman sample from the intense heat of the mercury lamps, but it could also function as a filter cell by circulating cooled filter solutions through it. The cooling jacket was about 1 cm. shorter than the Dewar flask to allow for the easy removal of the latter from the assembled unit. The cooling jacket rested on a flat cork ring (B, Plate V) in a metal cup at the base of the apparatus.

Mercury Lamps

Four low pressure mercury vapor lamps from the Hilger source unit were placed symmetrically around the cooling jacket. The lamps were separated by a distance of 5.5 cm. and were 0.9 cm. from the cooling jacket. These Mazda 400 watt (MAL/V) lamps were 3.5 cm. in diameter with a glass length of 14.5 cm. and 4.5 cm. metal ends. When the unit was in operation the lamps generated a considerable amount of heat, and the entire unit had to be adequately cooled to maintain the correct operating temperature of the lamps. At their maximum output the lamps gave an intense

radiation which could be rendered virtually monochromatic by using filters.

Construction of the Housing

The housing for the Dewar flask, cooling jacket and mercury lamps was constructed entirely of metal. It was designed to concentrate the radiation on the sample tube in the center of the unit and to prevent any stray radiation from reaching the spectrograph. The housing was cylindrical with a diameter of 20 cm. and a height of 16.6 cm. It was supported on three brass legs which were secured to the base plate in the same manner as the original Hilger unit (Plate VII, Appendix).

The ends of the housing were round brass plates, 3 mm. thick. Each plate was 20.0 cm. in diameter and had a central hole 8.4 cm. in diameter to accommodate the cooling jacket and Dewar flask.

The top plate had four symmetrically placed holes of 3.8 cm. diameter for the mercury lamps (A, Plate II). The center of each of these holes was 6.5 cm. from the center of the plate. A number of small holes (0.4 cm. diameter) was drilled into the top plate to allow hot air to escape from the unit.

The bottom plate also had four holes for the mercury lamps, but these were 3.2 cm. in diameter so that the mercury lamps could pass only part way through and rest on the plate on their first flange (B, Plate II). The bottom plate had three small holes lying on a circle of 7.7 cm. radius from the center of the plate. These holes were large enough for 7/32 inch bolts to secure the housing to the three inner threaded brass legs (B, Plate II).

EXPLANATION OF PLATE II

A. Top plate.

B. Bottom plate.

(Units in cm.)

PLATE II

A

B
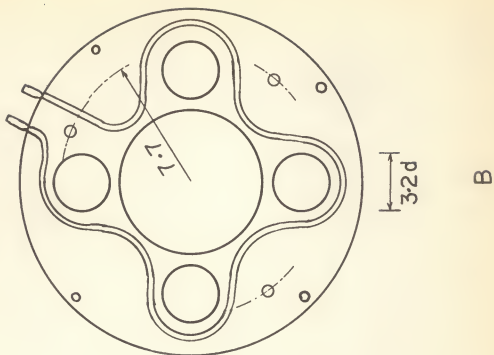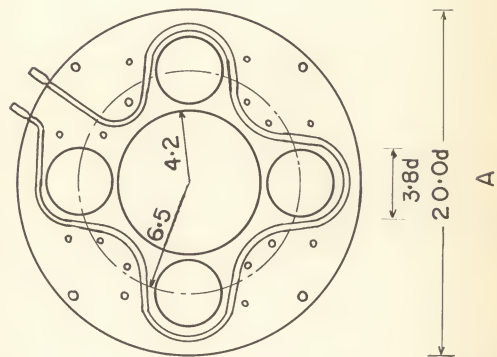
In order to obtain better dissipation of the heat from the mercury lamps, good contact between the metal ends of the lamps and the cooled plates was desired. For this purpose brass rings of 3.8 cm. outer diameter and 1.5 cm. in height were soldered to the inner surface of the bottom plate around the mercury lamp holes. Similarly, brass rings of 3.2 cm. inner diameter and 1.3 cm. in height were soldered to the outer surface of the bottom plate just around the rims of the mercury lamp holes (B, Plate III). The inner surfaces of these sockets were sanded until the metal ends of the lamps fitted snugly into them.

Sockets were made from brass to fit the top metal ends of the lamps also, as shown in Plate III, A. The inside surfaces of these sockets were machined and sanded so that they fitted tightly on the metal ends of the lamps. These sockets were made to fit tightly into the 3.8 cm. lamp holes of the top plate by flowing soft solder on the sides, and filing until a good fit was obtained.

For the construction of the wall of the unit, a 16 x 66 cm. sheet of copper metal of 1 mm. thickness was used. One-centimeter lengths on both ends were doubled, bent to a 90° angle and three holes were drilled into each end (A, Plate IV). This sheet was bent into a cylindrical shape and wrapped around the unit.

To provide for cooling of the metal housing, water was circulated through a 14 foot length of 1/8 inch diameter copper tubing soldered to the outer surface of the wall (A, Plate IV). Furthermore, air was blown up through the inside of the housing. A very good soldered contact between the copper tubing and the metal housing was required for efficient cooling.

EXPLANATION OF PLATE III

A. Top mercury lamp socket.
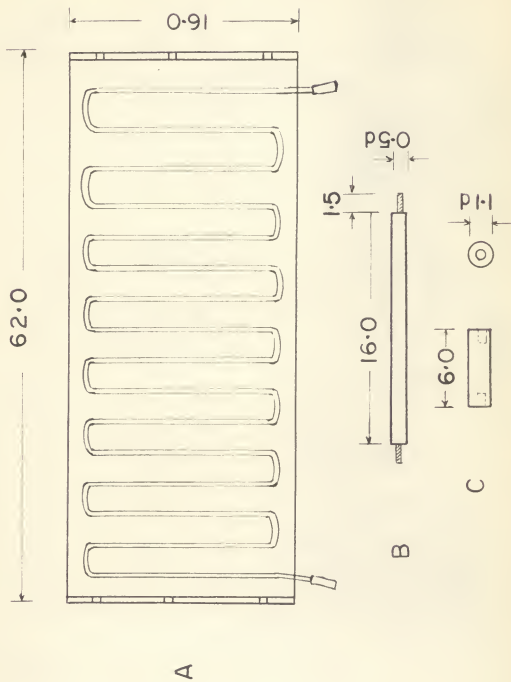
B. Lower lamp socket.

   (Units in cm.)

PLATE III
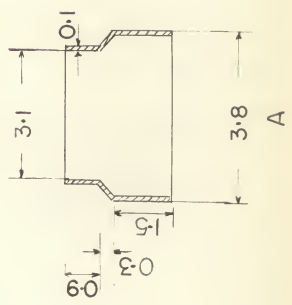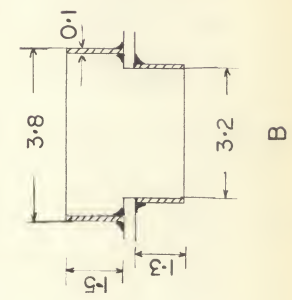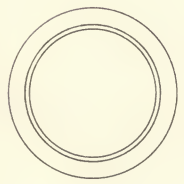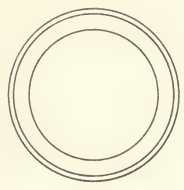
EXPLANATION OF PLATE IV

A. Wall of unit.

B. Connecting rod.

C. Support rod.

(Units in cm.)

PLATE IV

To the outer surfaces of each of the end plates, a 32 inch length of 3/16 inch diameter copper tubing was soldered around the mercury lamp terminals (A and B, Plate II).

At the ends of the 1/8 inch and 3/16 inch diameter copper tubings, short lengths of 1/4 inch diameter copper tubing were soldered and flared out at the end to insure a tight fit with the rubber tubing.

The maximum rates of water flow through the wall and plate copper tubings; i.e., the rates of flow which did not cause too much pressure on the rubber tubing leading to the tap, were found to be about 0.5 liter per minute in the 1/8 inch tubing and about 3 liters per minute in the 3/16 inch tubing. These flow rates were found to be sufficient to cool the entire housing during the operation of the unit.

To provide for additional cooling of the housing by air, a 26 inch length of 3/8 inch diameter copper tubing was sealed at one end, bent into a ring, and clamped to the inner surface of the bottom plate. Holes were drilled along one side of this ring so that the air flow could be directed upward.

The top and bottom plates were connected by four brass rods of 0.5 cm. diameter. These rods were 19 cm. long, and 1.5 cm. lengths on each end were threaded for 1/8 inch nuts so that the spacing between the plates was exactly 16.0 cm. (B, Plate IV). The three brass legs connecting the unit to the Hilger base were 6 cm. long, 1.1 cm. in diameter, with each end inner threaded for a 7/32 inch bolt (C, Plate IV).

A metal cup was designed to be placed through the central hole in the lower plate and extend toward the base plate. The cup was constructed of sheet metal brass of 1 mm. thickness. It was 3.1 cm. in height and had an outer diameter of 8.3 cm. Suitable holes were made in the bottom for the central brass tube from the Hilger base plate and the water inlet tubing of the cooling jacket (A, Plate V). A circular strip of brass, 3 mm. wide, was soldered to the brim of the cup so that it could be placed through the central hole, and rested on the inner surface of the bottom plate. The cup was lined with aluminum foil and sheet asbestos. A cork ring which supported the cooling jacket was fitted to the cup with ample room cut from the center for the Dewar flask (B, Plate V).

The inner metal surfaces of the housing were first coated with MgO to give a reflecting surface. Although this provided a highly reflective coating, it was rubbed off easily and blown away by the cooling air. TiO_2 was found to give a much more suitable coating. Aqueous alcoholic suspensions of TiO_2 were applied to the cleaned inner surfaces of the housing with a soft bristle brush, and this coating was allowed to dry at about 150° C. for 20 minutes. A durable, highly reflective coating which did not yellow and could withstand high temperatures was obtained in this manner.
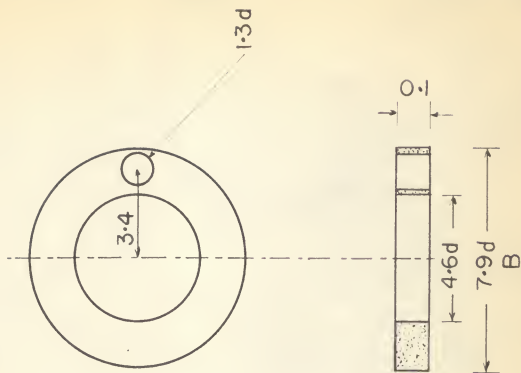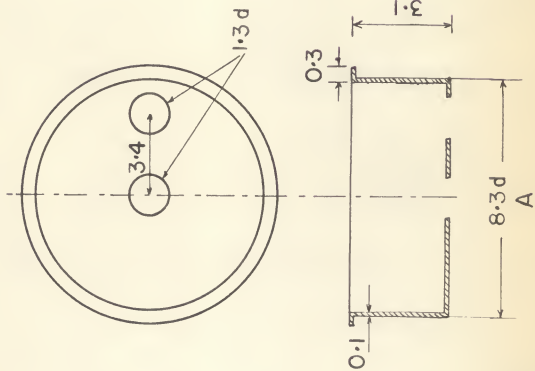
Assembly of the Unit

The end plates were connected by the four brass connecting rods. The threaded ends of the latter were placed through the

EXPLANATION OF PLATE V

A. Lower cup extension.

B. Cork ring for cooling jacket.

(Units in cm.)

PLATE V

1·3 d

3·4

0·1

4·6d

7·9 d

B

1·3 d

3·4

0·3

3·1

8·3 d

A

0·1

holes at the rim of each plate and secured with 1/8 inch nuts.
The plates were held rigidly in this manner at a distance of
16 cm. apart. The brass legs were secured to the bottom plate
with 7/32 inch bolts. The connected plates were fixed in position
on the optical bench by bolting the three brass legs to the base
plate of the Hilger unit.

The metal cup for the lower extension of the Dewar flask and
the cooling jacket was set in position through the hole in the
bottom plate. The brass tube, which leads to the right angle
prism reflecting the scattered light into the spectrograph slit,
extended 0.8 cm. up into the metal cup.

A short length of rubber tubing was fitted to the glass tubing
at one end of the cooling jacket before the latter was lowered in-
to position through the hole in the top plate. The rubber tubing
was directed through the side hole in the metal cup, and the cool-
ing jacket was set in position on the cork ring. The top portion
of the cooling jacket was painted black inside, and the outer sur-
face was wrapped with glass wool covered with aluminum foil. The
cooling jacket was held in rigid vertical alignment by an aluminum
ring.

The top of the Dewar flask was painted black and wrapped with
black plastic tape down to a distance of about 8 cm. A 5 cm.
length at the bottom was also wrapped with black tape to prevent
any direct radiation from reaching the spectrograph. The Dewar
flask was placed inside the cooling jacket and rested in the lower
cup just above the protruding end of the brass tube from the base

plate. The Dewar flask was held in vertical alignment by insert-
ing a rubber ring (made by wrapping a loop of copper wire with
thick rubber tape) between the inner top surface of the cooling
jacket and the Dewar (Plate VIII, Appendix).

The mercury lamps were placed through the top plate and
fitted into their lower sockets on the bottom plate. The top lamp
sockets were placed over the metal ends of the lamps and fitted
tightly into the holes of the top plate (Plate IX, Appendix).

The sheet copper wall was wrapped around the apparatus be-
tween the plates and held together by three bolts placed through
the ends.

Three water cooling circuits were made to the copper tubing
on the metal housing and to the cooling jacket as follows: one to
the 1/8 inch tubing on the walls, another to the 3/16 inch tubing
on the end plates, which were connected in series, and a third to
the inner cooling jacket (Plate VII, Appendix).

Tygon tubing was used for the connections from the laboratory
water outlets and to the drain. Each connection was made secure
by binding the ends with brass wire so that the water pressure
would not cause the tubing to slip off. A rubber tubing connected
the air cooling tube on the bottom plate to the laboratory air
outlet.

Electrical Connections

The four mercury lamps were connected in series. The top
lamp lead wires were connected with two short lengths of drilled
out aluminum cylinders. The wires were placed in the ends of these

and secured with set screws. The lower lamp lead wires were con-
nected to the original Hilger terminal blocks on the base plate of
the spectrograph. The lamp lead wires were shielded with ceramic
beads. The total current to the mercury lamps was supplied by one
main lead from the power supply unit which plugs into one of the
terminal blocks. The present unit was not equipped with a thermal
safety switch as was the Hilger unit. The Hilger control unit,
Model FL 2, was used to operate the lamps. The normal operating
voltage and amperage were found to be about 130 volts and 13
amperes.

TESTING OF THE UNIT

The operating characteristics of the low temperature unit
were found to be identical to those of the original Hilger unit.
With the air and water cooling, the housing was found to be just
warm to the touch even after about 12 hours of continuous opera-
tion. The operating voltage and current could be kept constant
by adjusting the flow of cooling air.

LOW-TEMPERATURE WORK

Method of Temperature Measurement

The temperature in the Dewar flask was measured with a double
junction, copper-constantan thermocouple. The reference junction
was placed in an ice-distilled water mixture and the other was
placed in the Dewar flask near the bottom of the Raman tube.
Junction voltages were read from a direct reading potentiometer.

The temperatures were determined from a previously calibrated Temperature vs. Potential plot.

Sample Tube Cooling

The sample was cooled by a flow of cold gas. A slender glass tubing (0.6 cm. diameter) was placed parallel to the Raman tube inside the Dewar flask. The tubing was sealed at one end and several holes were cut along its length for the cold gas outlets. This gas delivery tube was connected to a 52 cm. length of vacuum jacketed, silvered glass tubing by means of a 12/5 glass ball joint. This system was used for delivery of cold gas to the sample tube.

Methods of Cooling

For moderately low temperatures it was sufficient to pass dry air (house air passed through an 8 foot column of activated alumina) through an 8 foot length of 3/8 inch diameter copper tubing heat exchange coil immersed in a dry ice-acetone bath (Plate X, Appendix). With this system it was possible to cool the sample to about -50° C. for many hours. Dry ice was consumed at the rate of about 1 pound per hour at -30° C.

For lower temperatures, cold nitrogen gas, obtained by boiling liquid nitrogen, was used to cool the sample. A nichrome wire electric heater was immersed in a 25 liter, metal Dewar flask of liquid nitrogen. The nichrome heater was controlled by a variac. As the liquid nitrogen boiled, the cold gases passed through the vacuum jacketed tubing into the Dewar flask (Plate XI, Appendix).

With this system, temperatures of about -80° C. were easily attained. The consumption of liquid nitrogen at -30° C. was found to be about 1 liter per hour.

The temperature inside the Dewar flask can be held constant to within ± 2° C. by regulating the flow of cold air or nitrogen. The temperature gradient along the irradiated length of the sample tube was found to be about 5° C. at -30° C.

SUMMARY

An excitation unit for taking Raman spectra at low temperatures has been designed and constructed. This unit is interchangeable with the Hilger Excitation Unit, Model FL 1, and attaches to the Hilger Raman spectrograph, Model E-612, in the same manner.

The sample was cooled in a cylindrical Dewar flask and was irradiated by four low pressure mercury vapor lamps.

Two methods of cooling the sample tube with a flow of cold gas have been used. For moderately low temperatures, dried air was cooled by passage through a dry ice-acetone bath and conveyed to the sample tube. For lower temperatures, cold nitrogen gas, boiled from liquid nitrogen, was passed directly into the Dewar flask. With both methods a good control of the temperature has been achieved by regulating the flow of cold gas.

SUGGESTIONS FOR FUTURE WORK

The low temperature unit has been successfully used to obtain the Raman spectrum of liquid N_2O_4 at temperatures very near its freezing point.

The Raman spectra of a large number of low boiling substances should be investigated in their condensed phases with this apparatus. In particular, an attempt should be made to study the other low boiling oxides of nitrogen; i.e., nitric oxide and dinitrogen trioxide, in the liquid phase.

ACKNOWLEDGMENT

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APPENDIX

EXPLANATION OF PLATE VI

Low Temperature Excitation Unit
(cross section)

A. Raman sample tube.

B. Dewar flask.

C. Rubber alignment ring.

D. Cooling jacket.

E. Glass wool shield.

F. Aluminum ring.

G. Upper lamp socket.

H. Hilger Raman lamp.

I. Lower lamp socket.

J. Hilger Raman Unit, Model FL 1,
    base plate.

K. Metal cup.
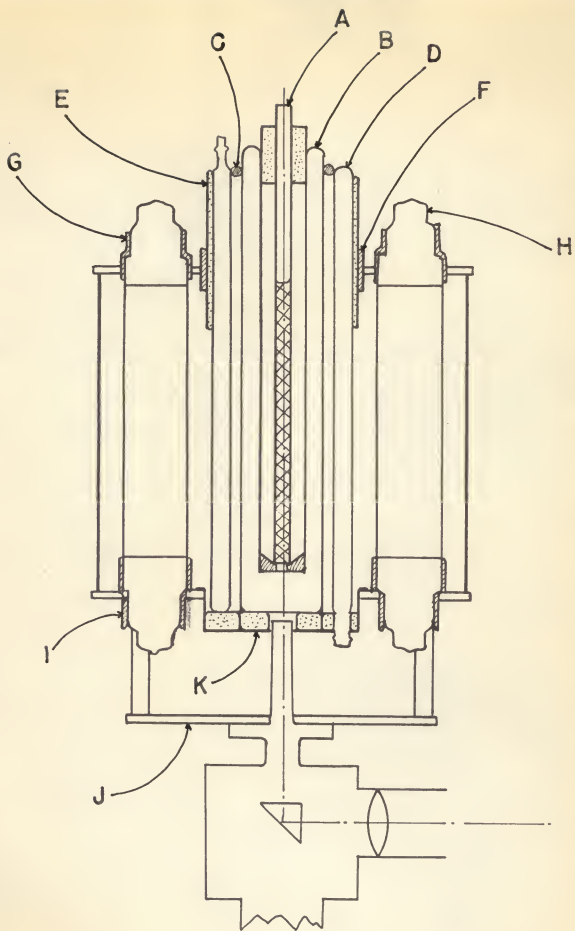
EXPLANATION OF PLATE VII

Assembled Low Temperature Excitation Unit
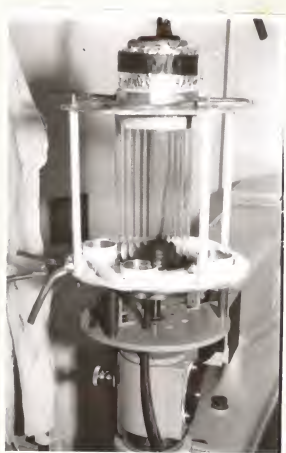(Without inner Dewar vessel)

PLATE VII

EXPLANATION OF PLATE VIII

Assembled Plates with Dewar Vessel
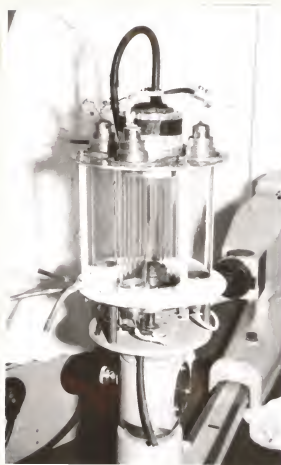and Cooling Jacket in Position

PLATE VIII

EXPLANATION OF PLATE IX

Assembled Plates with Dewar Flask, Cooling
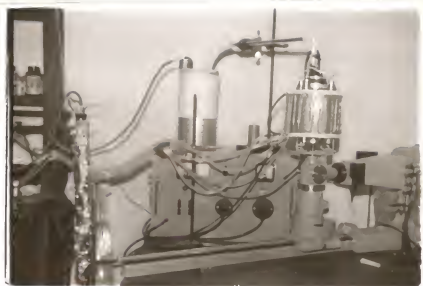Jacket, and Mercury Lamps in Position

PLATE IX

EXPLANATION OF PLATE X

Low Temperature Excitation Unit

with Dry Ice-Acetone Cooling System

PLATE X

EXPLANATION OF PLATE XI

Low Temperature Excitation Unit
with Liquid Nitrogen Cooling System

PLATE XI

THE DESIGN AND TESTING OF A LOW-TEMPERATURE
RAMAN EXCITATION UNIT

by

ROBERT VINCENT FITZSIMMONS

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AN ABSTRACT OF A THESIS

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The Raman effect has proven itself to be a very useful tool in the determination of molecular structures. Because the intensity of Raman scattered radiation depends upon the number of molecules scattering the incident light, it is much stronger in liquids than in gases, and for this reason Raman spectra are usually observed in the liquid phase. Many substances with low boiling points, however, must be continually cooled in their liquid phase and this presents the problem of maintaining the Raman sample at low temperatures.

It is the purpose of this thesis to explain the design and construction of a low temperature Raman excitation unit which could be used with the Hilger spectrograph, Model E-612, and which could be operated continuously for long periods of time.

The low temperature unit was designed to be interchangeable with the Hilger Raman source, Model FL 1. The Raman sample tube was cooled in a central glass Dewar flask which was protected from the heat of the lamps by a water cooling jacket placed around it. Four mercury lamps placed symmetrically around this central glassware provided the exciting radiation. The entire unit was enclosed in a cylindrical metal housing which was cooled by the circulation of water through copper tubing soldered to its walls.

Two methods have been used to cool the sample with a flow of cold gas. Dry air, cooled in a dry ice-acetone bath, has been found effective in cooling the sample down to about -50° C. For lower temperatures, cold nitrogen gas has been boiled from liquid nitrogen and passed into the Dewar flask. With the latter system,

temperatures of about -80° C. were easily attained, and much lower temperatures are possible.