

A NEW HIGH INTENSITY EXCITATION UNIT
FOR THE STUDY OF THE RAMAN SCATTERING
OF COLORED COMPOUNDS

by

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INTRODUCTION

The Raman effect has become an increasingly useful tool for determining the molecular structure of chemical compounds. The effect is observed when the light, which can be considered to be electromagnetic radiation in the wavelength range 2000 to 8000A, scattered by a substance is observed after passage through a spectrograph. It was found by Sir C. V. Raman that associated with the primary molecular scattering of the Rayleigh-Einstein type, there was another type which differed from the primary scattering in that it was from a hundred to a thousand times less intense, did not have the same wavelength and was characteristic of the compound being studied. It was further observed that the frequency shifts of the "Raman lines" from the excitation frequency often coincided with frequencies observed in a compound's infra-red spectrum (8).

These new lines are directly attributable to interactions between the intramolecular movements of molecular species and the incident electromagnetic radiation. The Raman shifts are thus direct measures of the vibrational frequencies of molecules.

It is possible to treat a molecule as a geometrical entity whose number of parts are determined chemically and whose exact geometrical configuration is evinced by a consideration of the number of possible active vibrations which could be displayed by a given model. Since it is possible by using the theory of groups to predict the number and expected coincidence of infrared

and Raman active frequencies which a configuration would be expected to give, the structure can be determined by comparing the frequencies observed with the number predicted (Herzberg, 6). Such complete schemes are of necessity limited to molecules which possess a high degree of symmetry. However, since functional groups exhibit characteristic frequencies it is possible to determine something about the molecular structure of complex molecules. Raman spectroscopy in this respect supplements infrared but offers several advantages, among these the use of aqueous solutions and the possibility of determining low frequencies, i.e. 50 cm^{-1} to 200 cm^{-1} .

RAMAN EFFECT IN COLORED COMPOUNDS

Until recently the Raman effect had not been observed in colored compounds, these being substances which absorbed radiation in the region $4000 \rightarrow 8000$ angstroms. Theory naturally predicted that such compounds would display Raman scattering but in no case had this scattering been observed. The reason was that the colored sample attenuated the incident radiation by absorbing it, thus reducing the amount of radiation available for scattering. In addition the intensity of the radiation which does appear as Raman scattering is itself reduced by the self-absorption of the sample. These two results for colored compounds being investigated reduce the intensity of the scattered radiation to an undetectable level.

There are two possible methods of attacking this problem. The first involves determining an optimum concentration for the colored substance in a solvent transparent to both the exciting and scattered radiation. This effect has been observed by Lippincott and Fisher (4) and appears to be a general phenomenon. This optimum concentration results when a compromise is reached between the reduction in intensity of the scattered radiation due to a decrease in concentration of the scattering compound, and an increase in intensity resulting from a decrease in the extent of absorption of the incident radiation and the resulting Raman scattering.

The second possibility, which is the subject of this thesis, involves the use of incident radiation which would not be absorbed by the sample, that is, the frequency of the scattering radiation should be such that it does not coincide with those frequencies absorbed by the molecules being studied. Though this solution seems fairly obvious, a consideration of the characteristics of an efficient source for Raman spectroscopy will illustrate the difficulties of such a solution.

EXCITATION SOURCES FOR RAMAN SPECTROSCOPY

Mercury Excitation

The development of Raman spectroscopy was dependent on light sources whose radiation was concentrated in a few intense

lines which were easily isolated from the rest of the spectral lines. In addition, the source must be virtually free of continuous background radiation and possess a high degree of operational stability. The source which possessed these characteristics was the mercury vapor lamp. A low pressure, enclosed arc in which mercury vapor was electrically excited, had reached a high degree of perfection when light scattering studies were being done by Raman and his co-workers. This source is particularly useful because of the number and separation of the intense emission lines. The lines used for Raman spectroscopy are the 2537 Å and 3650 Å lines in the ultraviolet, the 4047 Å and 4358 Å blue lines and the 5461 Å green line. These lines when suitably filtered (2,5) from the weaker lines and the low level continuous background provide intense monochromatic radiation. Although the 5461 Å green line has been used for compounds whose absorption spectra extend into the blue, when more highly colored compounds are investigated the sample absorbs the scattering radiation too strongly. The optimum concentration does enable one to obtain spectra in some cases but this extension is quite limited.

Other Light Sources

Few elements have emission spectra which could be used to study the Raman effect. Among these are the alkali metals, gallium and thalium and perhaps cadmium. Although lamps

utilizing these metals have been constructed (Alterthum and Reger, 1), only in the case of sodium is there available a well engineered, high intensity light source.

Sodium Lamps

The most pronounced feature of the emission spectrum of sodium is the yellow doublet with lines at 5890 and 5895.5 angstroms. In response to the demand for an efficient lamp for outdoor lighting the General Electric Company developed a high intensity arc lamp using sodium vapor as the source of light. The light from this type of lamp is very intense and the lamp, itself, is of a rugged, trouble free construction. For these reasons this lamp was selected as a source of radiation for a Raman excitation unit for use with colored compounds.

SODIUM EXCITATION UNIT

Design and Construction

The new source is modeled after the Hilger mercury excitation unit and is mounted on the optical bench in the same manner, being supported by three cylindrical legs which are fastened to the adjustable base as is the Hilger source.

The sodium source consists of a cylindrical housing with suitable openings at the top and bottom to permit the positioning of the lamps. (Plate I, Appendix). The illumination is provided by four GE sodium vapor lamps (Type NA-9) aligned parallel to the filter cell and spaced symmetrically about it.

The type of lamp used (Plate II, Appendix) is a tubular bulb with two cathodes connected by leads to a pin type base. It is filled with neon at low pressure (for starting) and pure sodium. The manufacturer recommends operation of the lamps in an unsilvered Dewar flask, however this would have made the source too large. It was found feasible to insulate the container with glass wool and sheet asbestos and to rely on the four lamps to provide sufficient heat to vaporize the sodium. The bottom of the unit was both stiffened and insulated by affixing a circular piece of Masonite. The glass wool and asbestos were applied in thin layers, the outermost layer was asbestos. The edges were sealed with an aqueous suspension of sodium silicate which upon drying forms a hard heat resistant coating (Strong, 10).

The inside of the metal housing was coated with magnesium oxide to insure maximum reflection from its periphery. This coating was applied by burning pieces of strip magnesium inside the housing. This provides a coating of very high reflectivity which adheres to the metal quite well, does not yellow upon exposure to intense radiation and can be easily renewed.

The lamps which project into the housing through four equally spaced holes in the top of the source are held in place at their lower end by an asbestos covered cup and at their upper end by a circular wooden disc through which their bases project and are held by means of clamps.

Each lamp has its own power supply. Each unit is connected to its lamp by a four strand cord and a four prong plug. The four power supplies are housed together in a box and are run off a 110 volt transformer. The lamps are put into operation by connecting the transformer to the 220 volt line. When the arc strikes the neon gives off a reddish glow, as the heat is stored the color gradually changes to yellow, the characteristic color of sodium. Full light output is reached after about 15 minutes. The light flux emitted by each lamp is approximately 10,000 lumens. It is evident that this type of lamp provides a very intense source of radiation, particularly, since the radiation is concentrated in the 5890 Å doublet.

Because neon is present as a starter gas the emission of the source is not monochromatic. Although the yellow doublet is much more intense than any of the neon lines, a photographic plate when exposed over a considerable period of time will record the neon lines superimposed on the Raman spectrum. Because this complicates the reading of a plate it was found necessary to provide suitable filters to render the light, entering the Raman tube, monochromatic.

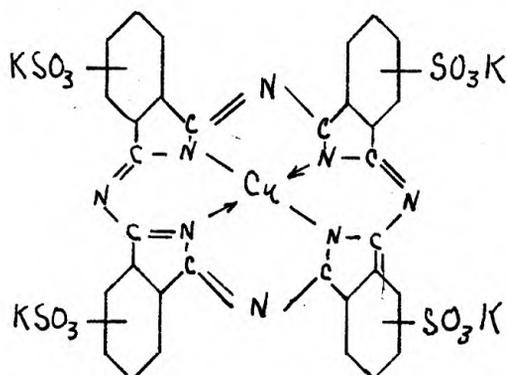
Filters

An ideal filter would completely absorb all extraneous radiation without diminishing the intensity of the light of the desired wavelength. In practice this ideal is never reached, any filter has a finite band pass. In addition the filter should be easily used, in Raman scattering work liquids are usually desirable, and stable to light so that the absorption characteristics of the filter do not change with time.

Numerous substances have been used with the mercury source (2,5), but no filters were available for isolating the 5890 Å sodium doublet.

After a considerable search a filter was obtained which had maximum absorption in the region 6000 to 7000 angstroms but absorbed little of the 5890 Å doublet, was stable to light and whose absorption spectra did not change with concentration. Several dyes were considered but it was found that although their spectra in dilute solution appeared promising they displayed metachromic shifts when used in concentrated solutions. It was necessary to use concentrated solutions because of the thinness of the compartments in the filter cell (Plate III, Appendix).

The compound which was found most effective was the potassium salt of the tetrasulfonic acid of copper phthalocyanine. Although this pigment is a brilliant blue when dry or in aqueous solution its spectra changes to a deep



green in sulfuric acid-water mixtures, (Plate IV, Appendix). In a solution of 90 per cent sulfuric acid the compound is stable for long periods of time (at least 6 months).

Advantages and Disadvantages

Since the doublet is 429 Å (1343 cm⁻¹) to longer wavelength than the very useful mercury green line (5461 Å) it can be used to obtain Raman spectra of compounds which have absorption bands occurring between 5000 and 6000 angstroms. Because the exciting "line" is a doublet each Raman line will also be a doublet. This is advantageous in that it makes possible a double check on the frequency shift of the Raman line from the source line. However, in the case of broad diffuse lines, this could be less advantageous and would necessitate measuring from the center of the double to the center of the line. For this reason Plate VIII, (Appendix) contains a tabulation of cm⁻¹ from the lines of the doublet and the center of the doublet.

It must be noted that although the intensity of the scattered light increases inversely as the 4th power of the wavelength of the exciting radiation according to the Rayleigh Scattering Law (11).

N = Avogadros number

ν_0 = Natural frequency of the scattering species

$$\frac{F_s}{I} = \frac{8\pi N e^4}{3m^2 c^4 \left(\frac{\nu_0^2 - 1}{\nu^2} \right)^2}$$

ν = Frequency of the incident radiation

$\frac{F_s}{I}$ = Fraction of incident radiation scattered

e = Charge on electron

The intensity is also a function of the spacing of the electronic levels of the molecule. This dependency results in an increase in intensity of scattering if the frequency of the exciting line is near the frequency of an electronic transition in the molecule being studied.

It is well'known that certain compounds decompose when exposed to light. In order that this may occur it is necessary that the compound absorb the incident radiation. Because colored compounds absorb more light than colorless compounds, that is, their electronic absorption spectra extend into the visible region, they are generally more easily decomposed by light. It becomes important then in Raman spectroscopy to use an excitation frequency which is not absorbed. The sodium source then is a more likely choice of excitation for photo-active compounds than is the mercury arc. It is also a fact

that in order to fluoresce a substance must absorb light, therefore, since fluorescence is a serious problem in Raman spectroscopy again the use of yellow excitation is decidedly advantageous.

It was pointed out in the section on construction of the sodium excitation unit that the spectrum of the unfiltered lamp is rich in neon lines. The majority of these appear in the region 6000 to 7000 angstroms and are spread quite uniformly through this region. Since it is necessary to determine the wave number difference of each Raman line from the exciting line, each plate must have its own wavelength calibration. The usual procedure is to expose the plate to an iron arc using a Hartman diaphragm to place the calibration spectra above and below the Raman spectra. The sodium lamps provide their own standard, that is the neon spectrum. It is only necessary to raise the filter cell slightly so that unfiltered light from the source falls on the slit. A photographic print of a nitro benzene spectrum along with the neon lines used to determine the wave number shifts is shown in Plate V in the Appendix. By measuring the distance of a Raman line from either one of the sodium lines or the center of the doublet with a traveling microscope, the spacing in wave numbers can be determined by referring to Plates VI and VII in the Appendix.

The use of sodium excitation with a fast spectrograph such as the Hilger ($f=1.5$), has one definite drawback in that the dispersion of prism instrument decreases as the wavelength

increases. This definitely limits the accuracy with which a wave number shift can be specified. However the possibility of obtaining the Raman spectra of compounds which were previously untouchable more than compensates for the loss in dispersion.

EXPERIMENTAL RESULTS

Nitrobenzene

The first compound run with the new unit was nitrobenzene. This compound did not constitute a rigorous test of the usefulness of the sodium source since it is only slightly colored and not photo-sensitive. It did show that the use of sodium excitation is practical. Table 1 shows a comparison of the wave number shifts obtained with the published results (7).

Iron Pentacarbonyl

The second compound studied was iron pentacarbonyl. Until the present this compound had resisted previous attempts to obtain its Raman spectrum (Duncan and Murray, 3).

This compound is a reddish orange liquid (melting point -20.3°C boiling point 103°C) and reacts in light according to the equation

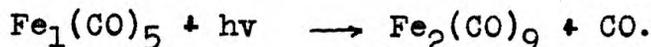


Table 1. Raman frequencies of nitrobenzene

Observed cm ⁻¹	I	:	Literature
185	(w)*		183
			408
605	(m)		604
			792
851	(m)		853
1006	(s)		1000
1112	(m)		1112
1159	(w)		---
1342	(v.s)		1341
1520	(w)		1526
1590	(s)		1587

*Intensity key v.s=very strong; s=strong; m=medium
 w=weak; v.w=very weak

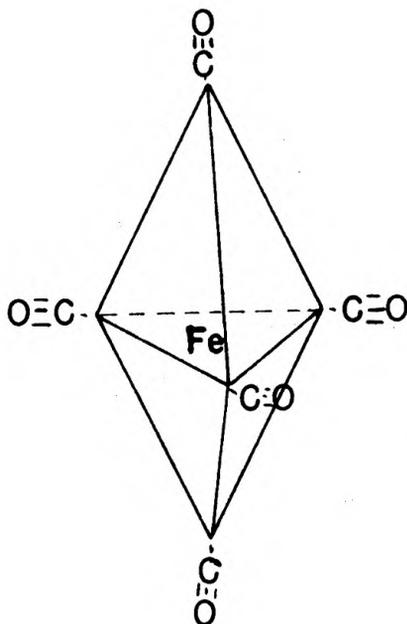
The original purpose of this research was to construct a light source which would make it possible to obtain the Raman spectra of such compounds as iron pentacarbonyl.

Clearly, even if the optimum concentration principle were operative, irradiation with either blue or green excitation would cause the sample to decompose. The new source proved its usefulness since several Raman lines have been observed. The compound is so sensitive that even yellow excitation causes the sample

to decompose slightly, however the rate was slow enough to permit the stronger lines to be photographed.

That the work on this compound is not complete is evident from a consideration of group theory as applied to molecules.

X-Ray, electron diffraction and infra-red spectra work indicate that the $\text{Fe}(\text{CO})_5$ molecule is a trigonal bipyramid.



The symmetry classification of this configuration is D_{3h} . Such a structure containing 11 atoms should give rise to 27 normal vibrations, of which 13 should be Raman active and 10 infra-red active. Shelton and Pitzer (9) have obtained the infra-red spectra of iron pentacarbonyl and made tentative assignments of the 10 frequencies found but have pointed out

the need for a successful Raman spectra. In the work to date, 3 lines have been found corresponding to 7 frequencies. These are listed in Table 2.

Table 2. Raman frequencies and assignments of iron pentacarbonyl

cm ⁻¹	:	Assignment
110 (s)*	ν ₁₄ , ν ₁₅	Fe-CO bending
410 (w)	ν ₃ , ν ₄	Fe-CO stretching
1995 (s)	ν ₁ , ν ₂ , ν ₁₅	C≡O stretching

*Intensity key s= strong; w=weak

Additional work will be needed to detect the weaker Raman lines. This will involve using a suitable filter to eliminate the 5682-5688 sodium green doublet. (Plate VII, Appendix) is a plot of the absorption spectra of Ponceau 3R, a dye which shows promise, and when this is done, longer exposures with less decomposition of the sample will be possible. A further study of the optimum concentration affect will be of assistance in detecting these weaker Raman lines.

EXPERIMENTAL PROCEDURES

Nitrobenzene

The nitrobenzene was student preparation. It was washed

with sulfuric acid and twice distilled in air. A 13 ml. sample from a middle cut of the second distillation was distilled under vacuum in an all glass apparatus into the Raman tube. Exposures of 15, 30, and 60 minutes were taken using a 103a-E BKD Plate (Eastman Kodak Co.) and a slit width of 0.15 mm. The plate was developed in D-19 for 3 minutes at 65°F.

Iron Pentacarbonyl

Iron pentacarbonyl (General Aniline and Film Corporation) was distilled under vacuum in an all glass apparatus into the Raman tube. Concentrations of 100, 44.5, 28.6, 13.8, 16.7 mole per cent were used. When cyclohexane (Eastman Kodak Spectrograde) was used as a solvent both substances were introduced into the apparatus at the same time. In each case the total volume of the sample was 12 to 13 cc. All work with iron pentacarbonyl was done in a darkened room to minimize decomposition. Cold water was kept flowing through the outer jacket of the filter cell when the lamps were operating. The two inner jackets contained a saturated solution of potassium dichromate and the phthalocyanine pigment, respectively. The plates and processing were the same as those used for the nitrobenzene. The absorption spectra of the phthalocyanine pigment and the Ponceau 3R dye were obtained with a Beckman DU using minimum slitwidths and 1 cm. cells.

SUMMARY

A high intensity Raman source has been designed and constructed which makes it possible to obtain Raman spectra of colored and photoactive compounds.

The source uses four General Electric sodium vapor lamps of 10,000 lumens output each, arranged in an insulated unit patterned after the mercury excitation source designed for the Hilger Raman spectrograph.

Filters have been found which render the output virtually monochromatic.

The spectra of nitrobenzene has been obtained and compared to published work.

Several Raman frequencies of the vibration spectra of iron pentacarbonyl have been observed.

SUGGESTIONS FOR FUTURE WORK

Although the new source has proven its usefulness it should be possible to improve its performance by obtaining better filters and determining an optimum concentration for such filters. Such a procedure would permit spectra to be taken with shorter exposure periods.

More colored compounds can be investigated. These may include diazocyclopentadiene, chromyl chloride, both red liquids, and iodoform, a yellow compound which is extremely photo-active in solution.

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. Ellis R. Lippincott for his help and guidance throughout this research.

Aid in the form of a graduate assistantship furnished by the Department of Chemistry is gratefully acknowledged.

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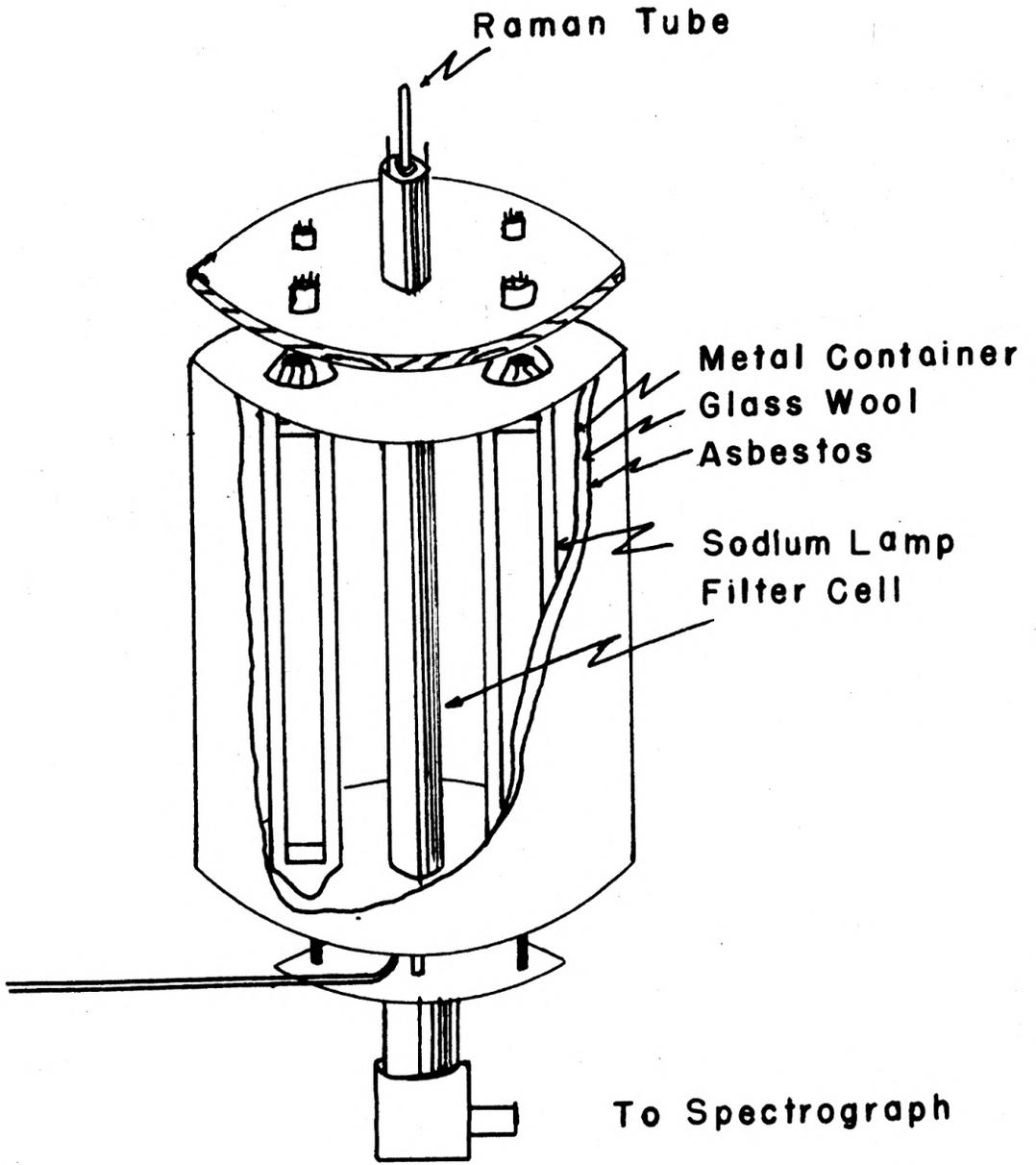
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A P P E N D I X

EXPLANATION OF PLATE I

Sodium excitation unit

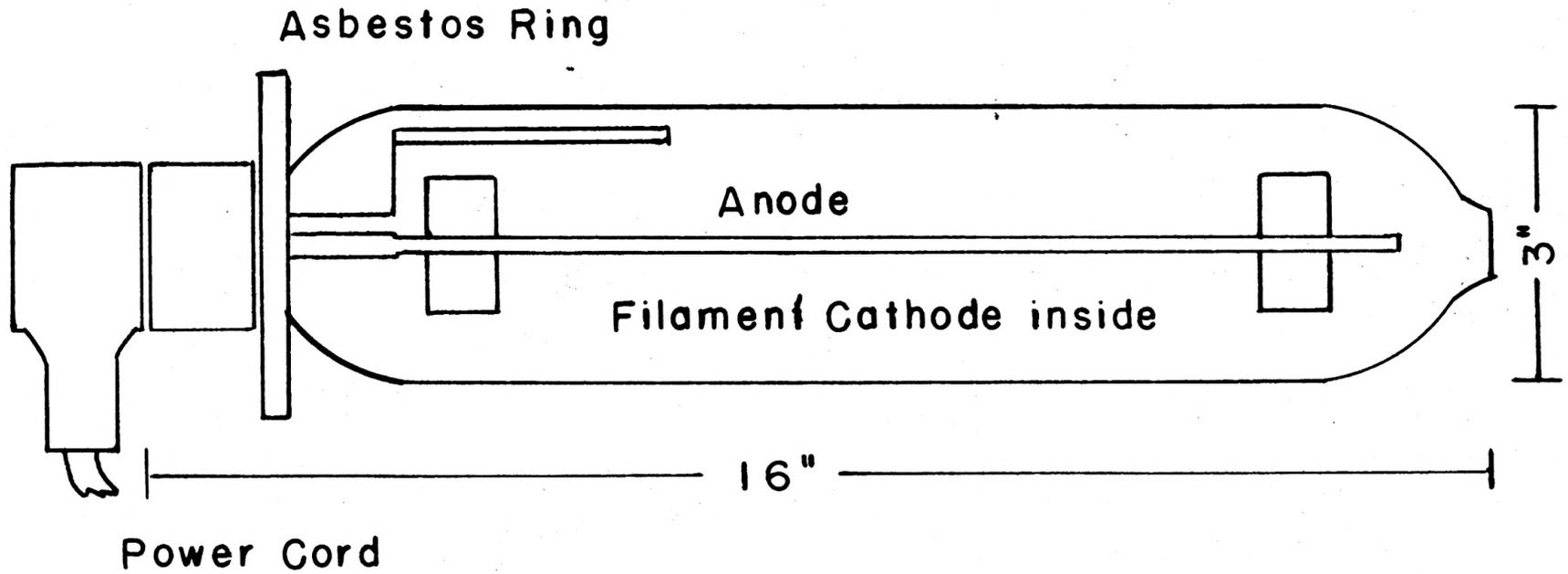
PLATE I



EXPLANATION OF PLATE II

G. E. sodium vapor lamp

PLATE II

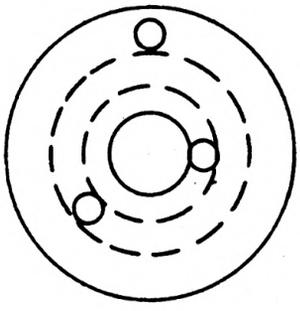


EXPLANATION OF PLATE III

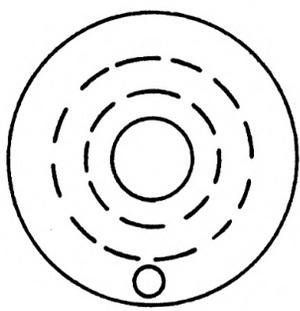
Three jacket Raman filter cell

PLATE III

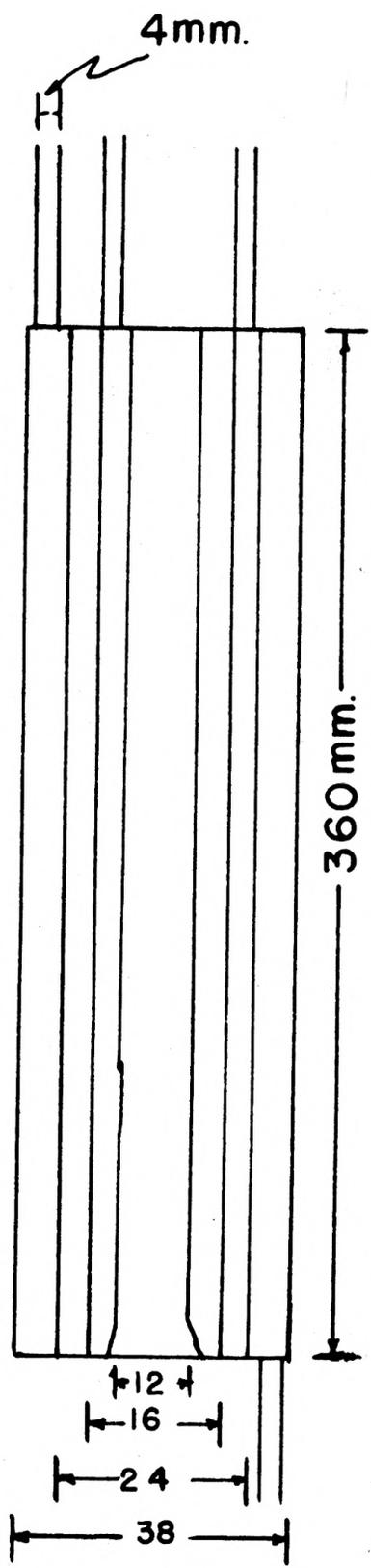
Top View



Bottom View



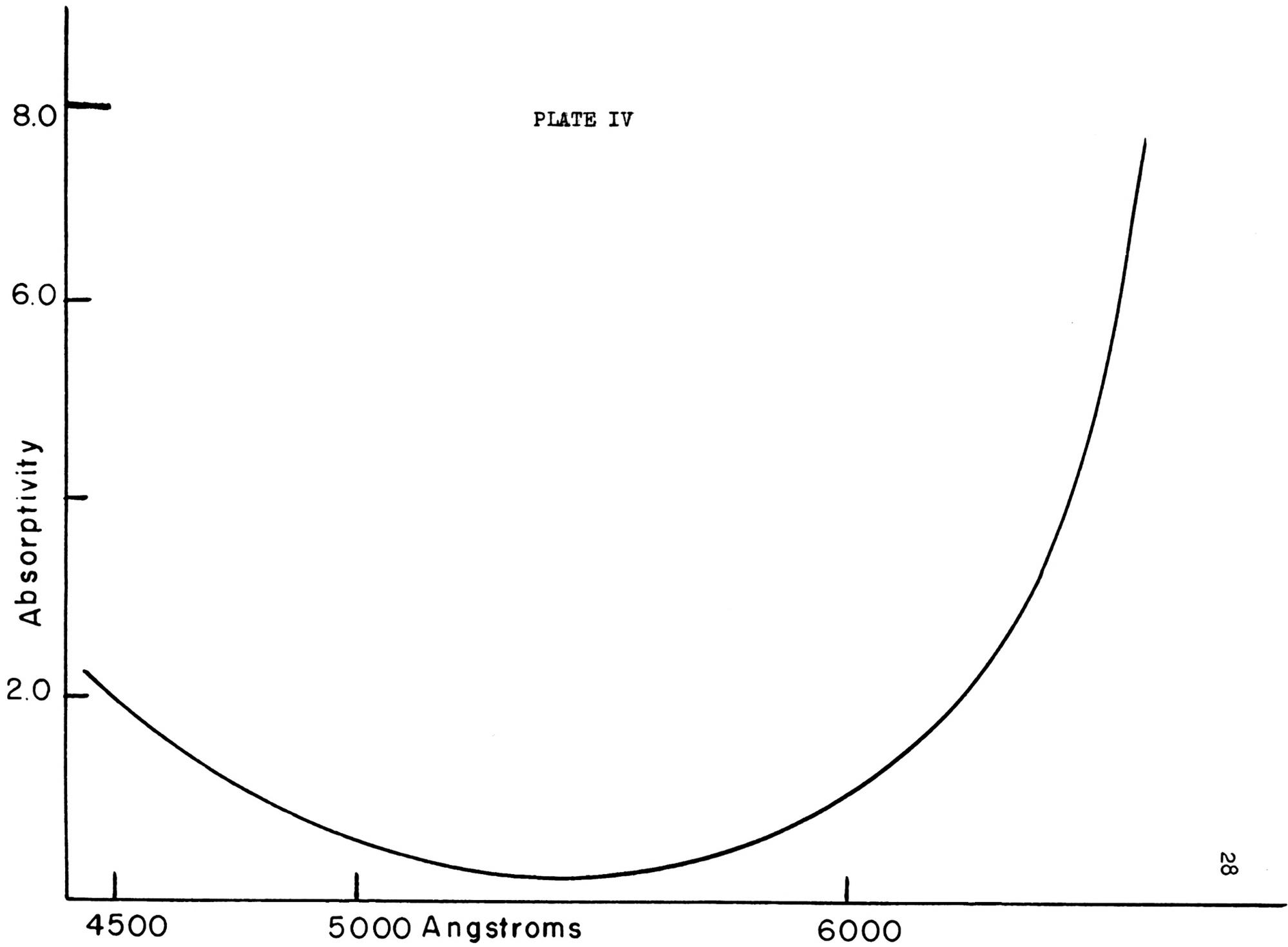
Dimensions in mm.



EXPLANATION OF PLATE IV

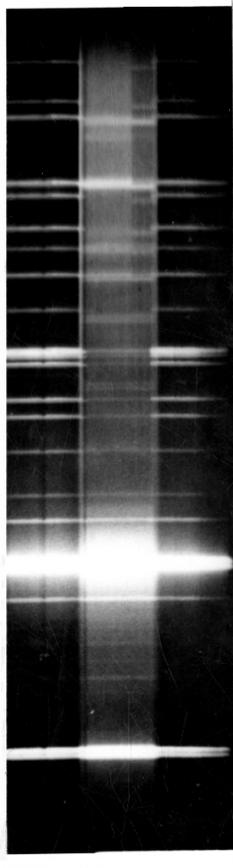
Absorption spectrum of the potassium salt of copper phthalocyanine tetrasulfonic acid in 90 percent sulfuric acid.

PLATE IV



EXPLANATION OF PLATE V

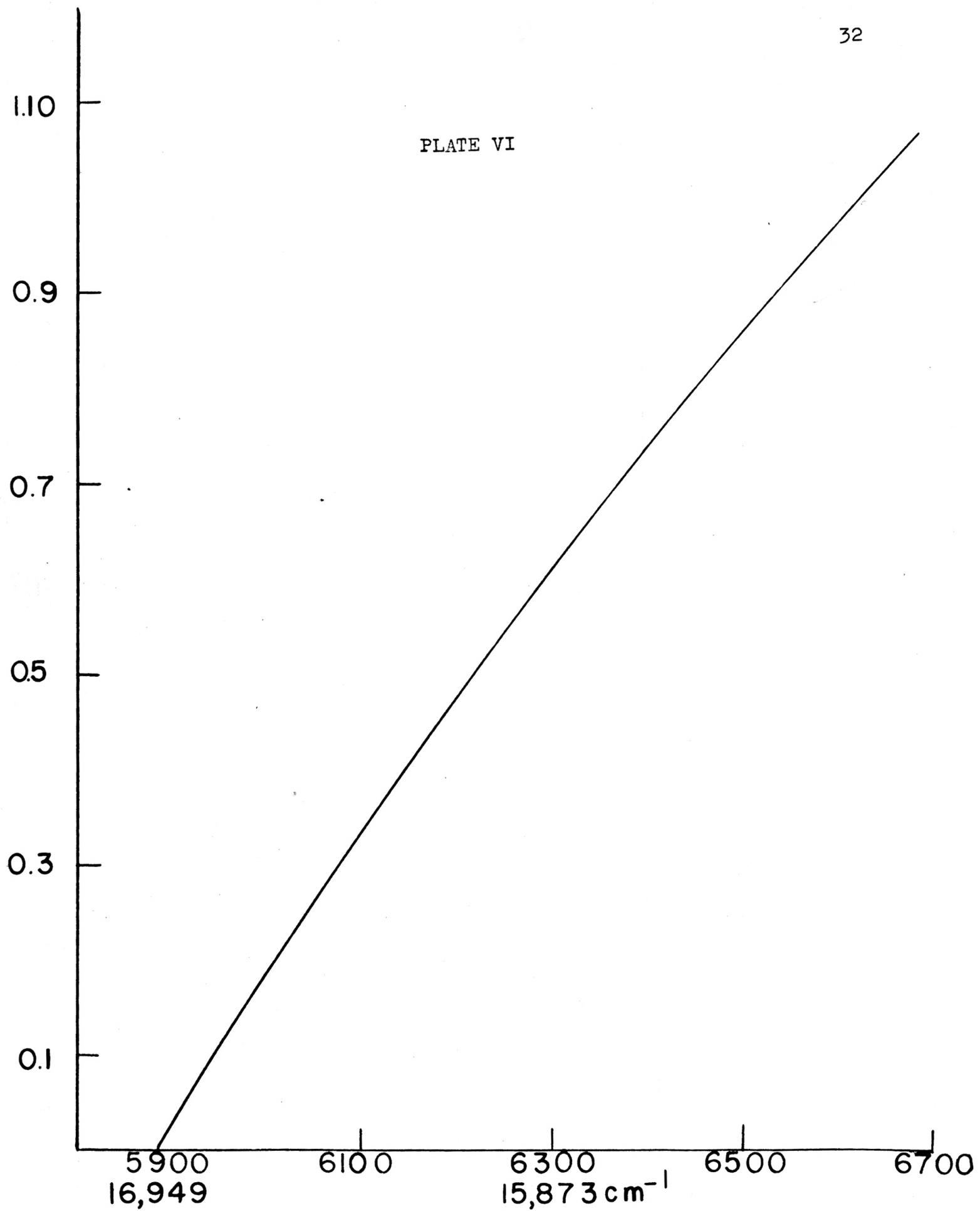
Raman spectrum of nitrobenzene. Exposure was 60 minutes, slit width was 0.15 mm. Sodium excitation.



EXPLANATION OF PLATE VI

Distance in mm. from the 5890 angstrom sodium line vs
wavelength in angstroms.

PLATE VI



EXPLANATION OF PLATE VII

Neon spectrum from sodium source. The wavelength and wave number shifts of each neon line from the lines of the doublet and the center of the doublet are given.

PLATE VII

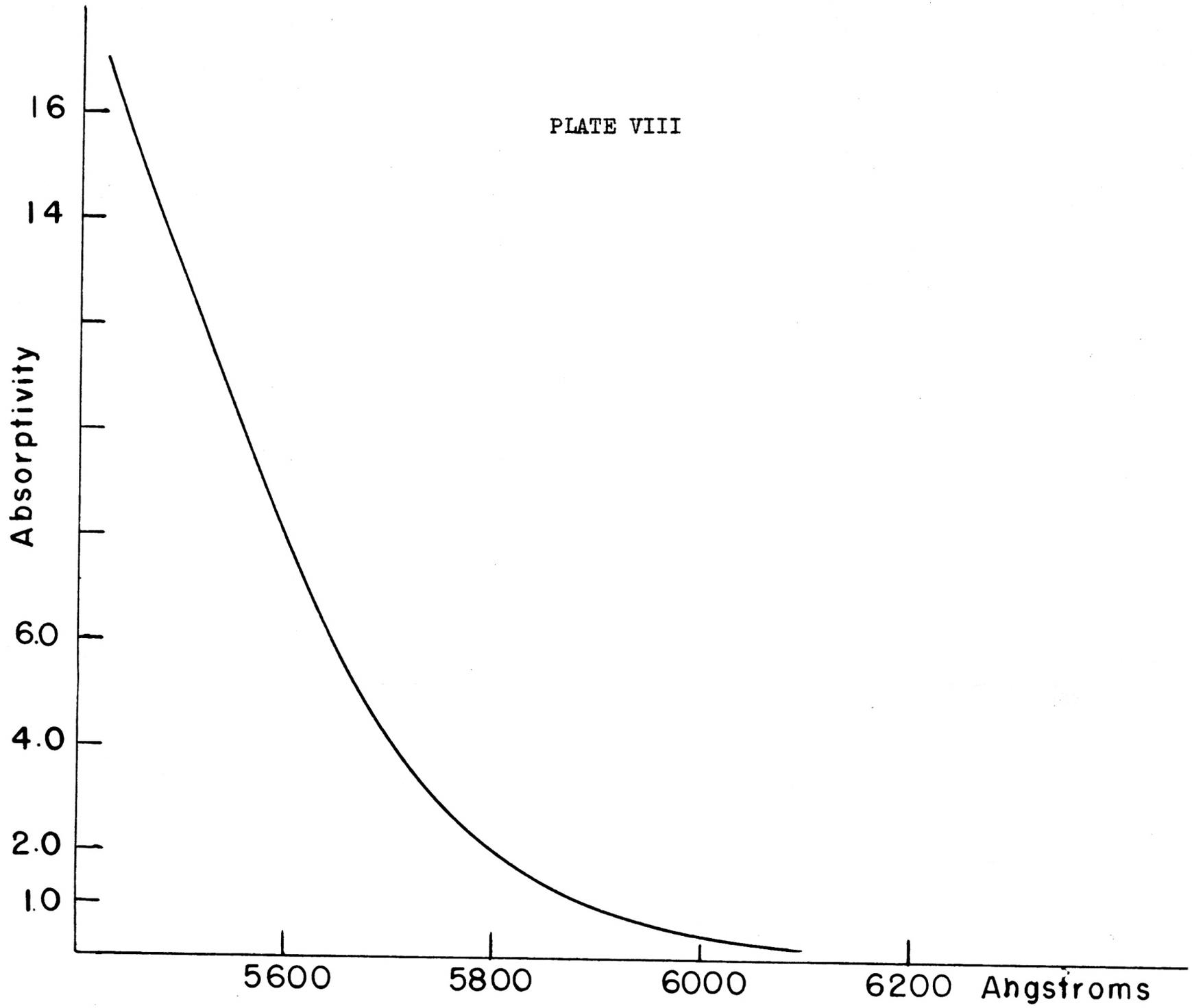
Wave number differences from: :
 5890.0 : 5895.9 : average=16,969.4 : Angstroms

2004.0	1987.0	1995.5		6678.3
1824.0	1807.0	1815.5		6598.9
1670.7	1653.7	1662.2		6532.8
1608.7	1591.7	1600.2		6506.5
1358.3	1341.3	1349.8		6402.2
1311.3	1294.3	1302.8		6382.9
1191.1	1174.1	1182.6		6334.4
1139.3	1122.3	1130.8		6313.7
1020.0	1003.0	1011.5		6266.5
893.7	876.7	885.2		6217.3
753.6	736.6	745.1		6163.6
728.6	711.6	720.1		6154.1
699.5	682.5	691.0		6143.1
574.1	557.1	565.6		6096.1
515.2	498.2	506.7		6074.3
394.1	377.1	385.6		6030
240.4	223.4	231.9		5974.6
156.5	139.5	148.0		5944.8
				5895.9
				5890.0

EXPLANATION OF PLATE VIII

Absorption spectra of FD and C red #1 (Ponceau 3R)

PLATE VIII



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The Raman effect has become an increasingly useful method for determining the molecular structure of chemical compounds, however as a general rule, colored compounds have resisted all efforts to obtain their Raman spectra. The difficulties have been experimental rather than fundamental.

Two methods can be used to circumvent the difficulties involved; the first utilizes the optimum concentration effect, the second the use of excitation radiation which is not absorbed by the sample being investigated.

This thesis describes a new, high intensity excitation source which has been designed for use with a Hilger Raman spectrograph. The source uses four General Electric sodium vapor lamps, housed in an insulated container, each with an output of 10,000 lumens. The yellow doublet at 5890-5895 A is the excitation "line". The source will be particularly useful for obtaining the Raman spectra of compounds which are photosensitive.

The Raman spectra of nitrobenzene has been obtained and compared with published data. Iron pentacarbonyl, a colored and photosensitive compound has been run, a total of seven of the expected thirteen normal frequencies has been obtained and tentatively assigned. It is expected that additional work using the optimum concentration effect will uncover the weaker Raman lines. When this is done it will be possible to confirm the tentative assignment of the frequencies in the infrared and Raman spectra, and thus show conclusively that iron pentacarbonyl has the bipyrimidal structure.