LECTURE - DRAFT

# Fundamental Theory and Techniques of Raman Spectroscopy

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In 1928 Professor Chandrasekhara Raman in India announced a new spectroscopic effect now known universally as The Raman effect. This effect had been predicted in 1923 by Smekal and is sometimes referred to in the early German literature as the Smekal-Raman effect. Shortly after, the effect was observed by Landsberg and Mandelstam in Russia. In Russian literature the effect is usually referred to as "Combinational Scattering". Raman observed that if monochromatic light (light of a single wavelength) is passed into a transparent substance and if the scattered light is examined spectroscopically, new weak lines of different frequencies appear in the spectrum in addition to the exciting frequency. These weak lines are characteristic of the scattering substance.

Before going deeper into the Raman effect I would like to review a few fundamentals necessary to understanding the phenomenon. Experimental observations and the quantum theory have shown us that the internal energy of a molecule does not have a continuous range of values but is restricted to a series of discrete levels or stationary states. The emission or absorption of energy or radiation by a molecule takes place by a transition of the molecule from one of these stationary states to another. The study of the spectra of a molecule thus provides a powerful tool to find out about the internal energy levels of a molecule. These are in turn related strongly to the structure and properties of the molecule. The internal energy of a molecule comes partly from the motions of the electrons, partly from rotation of the whole molecule, and partly from vibrations of the atoms of the molecule. To a first approximation the interaction between these motions may be neglected and the observed spectra can be divided into rotational, vibrational, and electronic spectra. The vibrational energy levels are characteristic of the bonds between atoms and thus are of special interest to the chemist who deals with chemical compounds made up of

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various atoms bound together in different ways and who studies the intractions between various atoms and molecules.

Two widely used spectral methods are in use today to study these molecular energy levels. The study of infrared spectra and the study of Raman spectra. These two methods are complimentary and I want to say a few words about infrared spectra before turning to the details of Raman spectral observations.

The electromagnetic spectrum extends from gamma rays with short wavelengths and with long wavelength and low energy. Electronic energy states are of the order of a few electron volts above the ground state and the energies are comparible to that of ultraviolet and visible radiation. The vibrational energy levels lie only a few tenths of an electron volt above the ground state, and the rotational levels a few hundreths of an electron volt above the ground level. The rotational and vibrational spectra (or energy levels) lie in the infrared region of the electromagnetic spectrum.

Let us talk for a minute about units of frequency, wavelength, or energy measurement. For all electromagnetic waves, including light, the formula $\lambda \times \nu = c$ holds; wavelength x frequency = speed of light (cm) x (cycles/sec) = $3 \times 10^{10}$ cm/sec

The energy of the radiation can be calculated from the formula; $E = h\nu$ where h is Planks constant = $6.624 \times 10^{-27}$ eng·sec. Thus the energy of the light is seen to be proportional to the frequency $\nu$. Now $\nu = c/\lambda$, so the energy is also proportional to $1/\lambda$ which is defined as $\tilde{\nu}$, $cm^{-1}$, or wave numbers. This unit wave numbers is widely used in both infrared and Raman spectroscopy. The vibrational energy states of molecules lie roughly between 100 $cm^{-1}$ and 5000 $cm^{-1}$.

The vibrational spectra of a molecule can be explained in terms of stretching and bending motions (normal modes of vibration) involving various bonds of the molecule. In general there are 3N-6 (3N-5 for a linear molecule) normal vibrational modes for a molecule. N is the number of atoms in the molecule.

For example diatomic molecules have one fundamental vibrational frequency

| | |
|---|---|
| H-H | 3118 cm$^{-1}$ |
| H-Cl | 2990 cm$^{-1}$ |
| N-N | 2360 cm$^{-1}$ |
| I-I | 215 cm$^{-1}$ |

Heavier atoms give slower (less energetic) vibrations while stronger bonds give higher frequency (more energetic) vibrations. $CO_2$ has 3x3-5 = 4 normal vibrations

$\leftarrow$ O-C - O $\rightarrow$ sym. stretch 1388 cm$^{-1}$

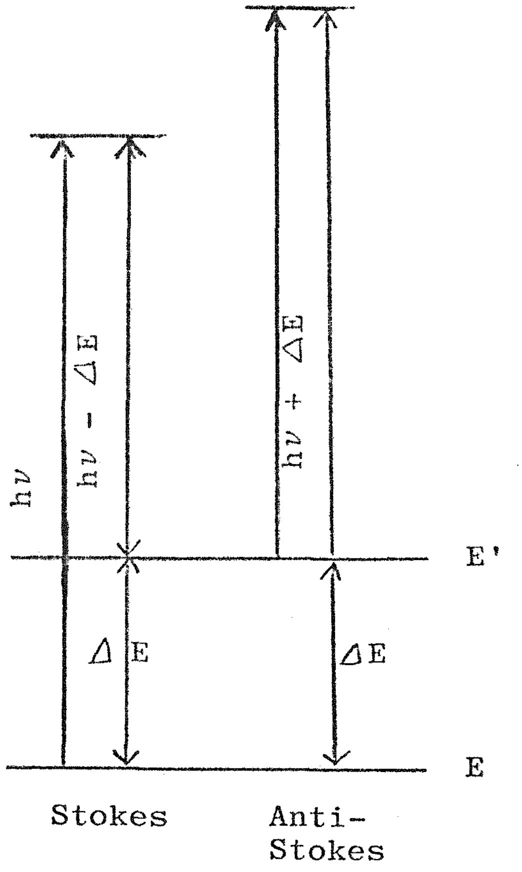
$\leftarrow$ O-C $\rightarrow\leftarrow$ O asym. stretch 2349 cm$^{-1}$

(-)O-C(+)-O(-) Two bends 667 cm$^{-1}$

When broad band infrared light of all frequencies is passed through these molecules, the light will interact with the molecules provided the vibration involved is accompanied by a change in dipole moment. The molecules will absorb definite discrete amounts of energy from the light equal to the energies necessary to excite the vibrational energy levels of the molecule and various combinations of those levels. If we plot light energy vs light ~~energy~~ frequency in cm$^{-1}$, we will find various absorption bands in our broad infrared centinium which are characteristic of the molecular vibrations (or energy levels) of the substance examined. One must use the correct frequency of light to match the energy levels of the molecules and this is difficult because infrared light will not pass thru glass and very special materials such as salt (NaCl), cesium bromide (CsBr), or silver chloride (AgCl) must be used for cells or optical elements.

Now let us return to the Raman effect. When monochromatic light (of any wavelength) is passed into a transparent substance (gas, liquid, or solid) some light is scattered in all directions. If the scattered light is examined with a spectroscope we find a very strong line with the same frequency as the illuminating light and then several new very weak frequencies. For example, if a substance is illuminated with light of frequency $\nu$ and the scattered light examined, several new frequencies will be found $\nu - \nu_1$, $\nu - \nu_2$, $\nu - \nu_3$, etc., of lower energy called Stokes lines, and $\nu + \nu_1$, $\nu + \nu_2$, $\nu + \nu_3$, etc., of higher energy called anti-Stokes lines. These lines are symmetrically disposed around the exciting frequency and the values of $\nu_1$, $\nu_2$, etc. are often found to coincide with observed infrared frequencies. The Stokes lines are found to be much more intense than the anti-Stokes lines and if the exciting frequency $\nu$ is changed the values of $\nu - \nu_1$ change but the frequency shifts ($\nu_1$, $\nu_2$, etc.) remain the same. The intensity of the Raman line is proportional to the fourth power of the frequency of the exciting light so that blue light gives much more intense Raman lines than red light.

The quantum theory of the Raman effect is as follows. An incident light quantum, $h\nu$, collides with a molecule. It can be scattered elastically in which case its energy and frequency remain unchanged (Rayleigh scattering); or it can be scattered inelastically (that is, give up or receive energy from the molecule). The light quantum can give to or take up energy from the system only in amounts equal to the energy difference between the stationary states of the system. If the system (molecule) is initially in the lower energy state E, it may be brought up to the upper state E' by the scattering of a light quantum; the energy $\Delta E = E' - E$ being taken from the light quantum. Thus the scattered light energy is $h\nu - \Delta E$. If, however, the molecule was initially in the upper state E' and is transferred to the lower state E by the light quantum, the light quantum will possess the energy $h\nu + \Delta E$ after the scattering. This latter case (the anti-Stokes case) is less probable since fewer molecules are in excited states than in the ground state. If the frequencies are measured in $cm^{-1}$, the Raman shifts give directly the energy differences of the system in $cm^{-1}$.


hν
hν - ΔE
hν + ΔE
ΔE
ΔE
E'
E
Stokes
Anti-
Stokes

It is found theoretically and experimentally that the vibrational spectra observed by the Raman effect is similar to that observed in the infrared but that some vibrations are found in one and not the other. Infrared transitions are observed where there is a difference in dipole moment between the states, while in the Raman effect lines are observed when a difference in the polarizability of the states exists. Thus the information from infrared and Raman spectra are complimentary. If a molecule has a center of symmetry, as $CO_2$ or $N_2O_4$, the rule of mutual exclusion holds and all Raman frequencies will be inactive in the infrared and all infrared frequencies inactive in the Raman.

Now let us turn to the slides. Slide (1) shows the electromagnetic spectra we have already discussed. A micron is $10^{-4}$ centimeters so the point at start of the infrared region is $10^{-4}$ cm or $10^4$ (10,000) $cm^{-1}$. One of the advantages of Raman spectral work is that the frequency of the exciting light may be varied and thus visible or even ultra violet radiation may be used. Since the intensity of the scattered line is inversely proportional to the fourth power of the wavelength, there is considerable advantage in using short wave-length lines. Slide (2) illustrates the formation of Stokes and anti-Stokes lines by the Raman effect. Stokes lines are those with less energy or lower frequency than the exciting radiation. Slide (3) is a sketch of the type apparatus used by Raman to observe the effect. "A" is a bright source of light which gives off a definite line spectra; such as a mercury lamp, a sodium lamp, or a helium lamp. This light passed through a lens is focused on a sample volume, "B", and then is observed at right angles through a spectrometer, "S", either visually or recorded on a photographic plate. Raman lines are very weak, something like $10^4$-$10^8$ times weaker than the exciting line and it is necessary to use bright sources and collect as much light as possible. A more advanced Raman appparatus is shown on the next slide (4). Here, a long tube of sample is used, illuminated by a tube-like mercury arc lamp and surrounded by a reflector. A filter has been inserted between the light and the sample. This filter ideally should remove all of the mercury lines except the one strong and sharp line being used for the observations. This is necessary since each spectral line that enters the scattering substance will be scattered with a number of energy losses producing a complex mixture of overlapping Raman spectra if the number of exciting lines is more than one. The light scattered at right angles is passed through a spectrograph and the spectrum registered on a photographic plate. Photographic exposures varied from a few minutes to several days. The next slide (5) shows an enlarged example of a photographic Raman spectrum. Here the wavelength scale runs vertically with the longer wavelength or lower energy being at the bottom. The strong 4358 Å (or 22,938 $cm^{-1}$) line of mercury is the exciting line on the right. $CCl_4$ is the substance being studies and the five characteristic Stokes lines of $CCl_4$ can be seen below the exciting line. The weaker anti-Stokes lines are above and only three of these can be seen. Now the spectrometer is not linear in wave numbers, but if the change in frequency from the center line is calculated in wave-numbers the value $\Delta\nu$ is exactly the same for the Stokes and anti-Stokes lines and these frequencies are found to be 218, 314, 458, 762, and 791 $cm^{-1}$. Now if we continue on toward the violet end of the spectrum, there is another strong mercury line that can be used as a Raman source and this is at 4046 Å (24,706 $cm^{-1}$). There are several other interferring mercury spectrum lines at 4077 Å and 4108 Å but five lines due to the Raman scattering of the 4046 Å mercury line by $CCl_4$ can be seen. Since the scale is not linear, the spacing is different; but if the frequencies of these lines are measured, converted to wave numbers, and that of the exciting line subtracted, one finds the $\Delta\nu$'s are again 218, 314, 458, 762, and 791 $cm^{-1}$. This illustrates the extreme versatility of the Raman effect that I mentioned--one can get fundamental information concerning the energy levels of the molecule using any number of different frequencies of exciting light. Slide (6) shows an actual spectral plate made with a simple demonstration spectrometer at the University of Tennessee. The spectra of Neon has also been recorded for reference. This plate is of $CCl_4$, also, and one can see the same lines upon close examination as shown on the previous slide.

Slide (7) shows a schematic diagram of the Cary Model-81 Raman spectrophotometer which we used previously at Oak Ridge National Laboratory. This instrument used a Toronto mercury arc which surrounded the sample tube with a coil of mercury discharge light. The sample beam passed through an optical system consisting of lenses, image slicers, and slits to a monochromator consisting of a double mirror and grating system. The monochromatic light then passed to a photomultiplier tube and amplifier system and was recorded on a strip chart.

Slide (8) shows a photo of the mercury arc. A large sample was placed inside this arc and light poured onto the sample from 360°. The Raman light was then observed at right angles by means of a lens system. Slide (9) shows the large sample cells which it was necessary to use to obtain Raman spectra with this instrument. Slide (10) shows the Raman spectrum of $CCl_4$ taken with this photoelectric instrument. Here we see in much easier to read form the 4 spectral lines of $CCl_4$ observed on the previous photographic plate. Slide (11) shows the Raman spectrum of liquid water. One of the tremendous advantages of using Raman spectra is the fact that the Raman spectrum of water is fairly weak and is free of bands in the lower wavelength regions. Here we see really two main bands one weak band at 1650 $cm^{-1}$ and one strong band made up of various stretching vibrations and overtones.

In 1960 the laser became available as a source of intense monochromatic light and in the 1960's Raman spectroscopy was advanced tremendously by the use of laser light sources. Slide (12) shows the modification made to our Cary-81 spectrometer for laser light source use . Now we illuminate a very small sample with a very bright sharply focused beam of monochromatic laser light. We use photon counting electronics to actually count the photons of Raman light and thus increase our detection capability. Slides (13) and (14) show the laser light from either a helium near laser (red), or an argon ion laser (blue or green) being used for Raman excitation. Slide (15) is a schematic of our new Raman spectrometer, the Ramanor. This instrument uses the same system of two monochrometers in series to reject the scattered Raleigh light. It is unique in using a curved holographic gratings for dispersion which eliminates the 4 extra curved mirrors found in the older machine. A photomultiplier detector tube and photon counting electronics is also used to record the spectra. A signal averager system stores the data and allows it to be put on magnetic tape or recorded in various formats on graph paper. Slide (16) shows this new instrument. Slide (17) shows the tuneable dye laser we use to generate yellow or red light. The blue and green light from the argon-ion laser is focused into a jet stream of flowing dye and the laser cavity tuned to yield yellow, orange or red light. Various colors of light are used to obtain Raman spectra of colored compounds or solutions.

Now let us look at some Raman spectra;

Slide (18) shows an aqueous solution of $NaClO_4$. In addition to the water bands we see the 4 characteristic bands of the $ClO_4^-$ ion. The band at 938 is especially strong and is due to the symmetrical stretching frequency of the $ClO_4^-$ ion. This pattern also tells us that the $ClO_4^-$ ion has a tetrahedral structure and its vibrational force constants. Slide (19) Benzene shows a more complicated pattern. The band near 1000 $cm^{-1}$ is due to the C-C ring vibrations and the lines near 3000 $cm^{-1}$ are ascribed to C-H vibrations. The groups present in organic molecules can be picked out in this manner and identification can be made. Slide (20) shows an interesting effect where a portion of the spectrum of $Cu_2Cl_2 \cdot 8NH_4Cl \cdot CO$ is shown. This vibrational mode is the CO stretching mode and the sample was enriched in $^{13}C$ to about 13%. The spectrum clearly shows the lower frequency peak due to the $^{13}C$-O vibration. By using Raman spectra in this way we are able to analyze few isotopic content or to calculate isotopic equilibrium constants. Slide (21) shows a recent study we have made of equilibrium in a solution containing uranyl ($UO_2^{++}$) ion. Here as we vary the pH of the solution the spectrum shifts as the proportion of monomer, dimer, and trimer in the solution varies. The Raman spectra are especially valuable in studying species in solutions or melts and their equilibria. The structure of new compounds may also be determined by the Raman and infrared spectrum.

Slide (22) is an illustruation of this point. This shows the Raman spectra of two new compounds $ClF_5$ and $XeOF_4$. Their structure was immediately established by the close resemblence of their spectra to those of $IF_5$ and $BrF_5$.

I hope that this gives you a brief idea of the theory and uses of the Raman effect. I think that you will be hearing about it a lot in the future.

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* Operated by Union Carbide Corporation, Nuclear Division, under contract W-7405-eng 26 with the Department of Energy.

# ELECTROMAGNETIC SPECTRUM

$\lambda$ (WAVELENGTH) TIMES $\nu$ (CYCLES PER SECOND) = C (VELOCITY OF LIGHT)

WAVELENGTH UNITS

A = ANGSTROM UNIT = $10^{-4}\mu = 10^{-8}$ CM

$\mu$ = MICRON = $10^{4}$A = $10^{-4}$ CM

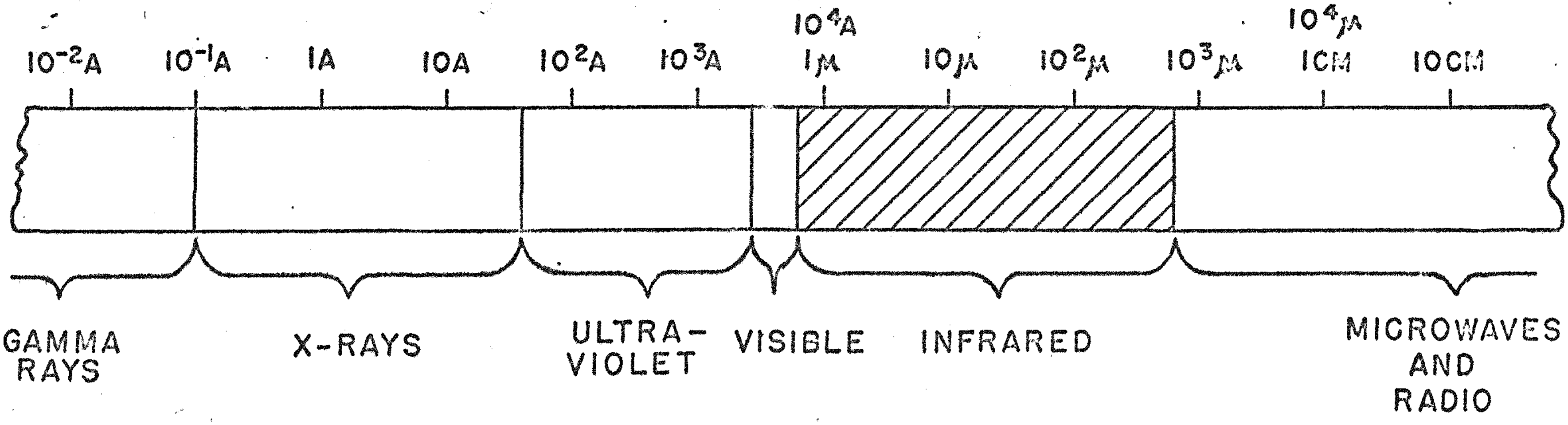
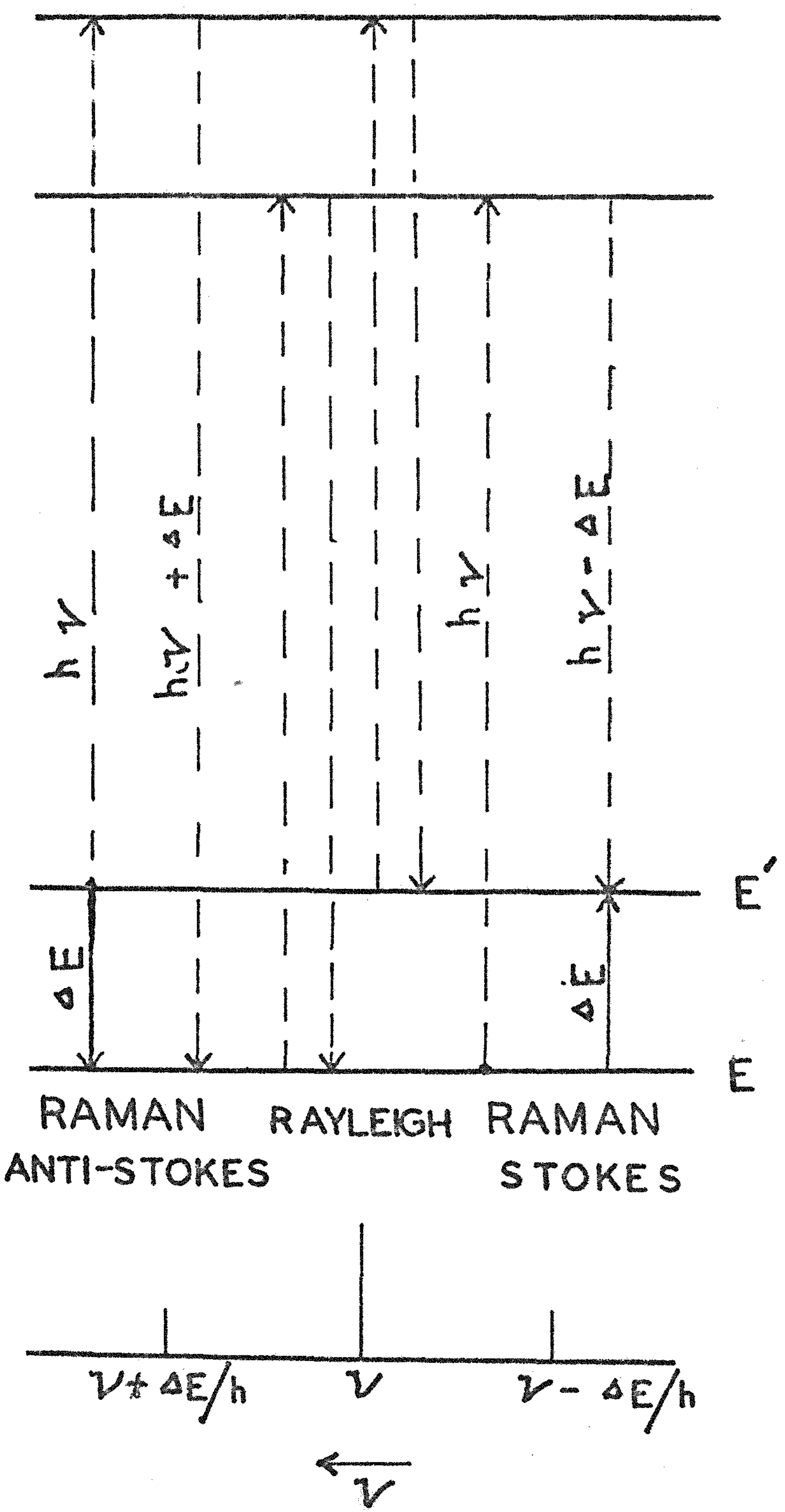
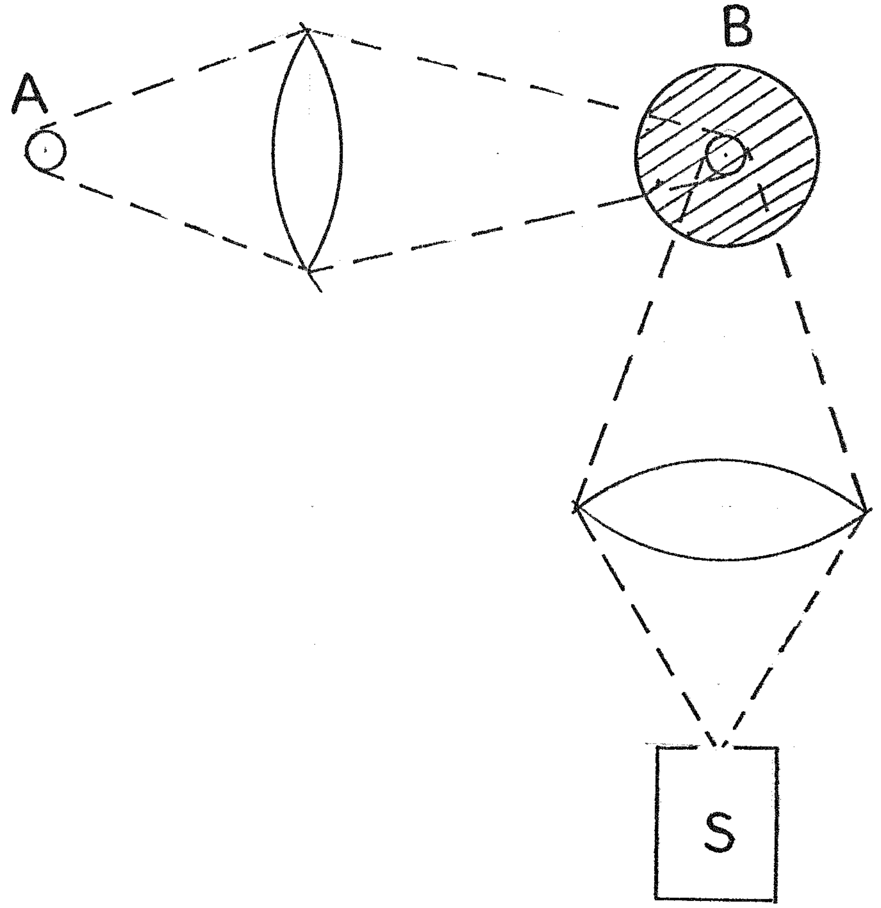


FIGURE 1

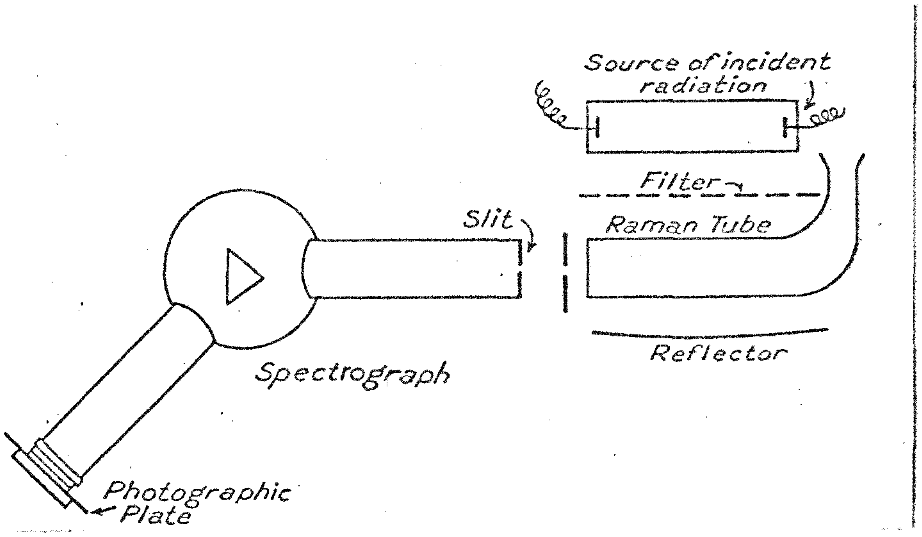
②


h ν
h ν + ΔE
h ν
h ν - ΔE
ΔE
ΔE
E'
E
RAMAN
ANTI-STOKES
RAYLEIGH
RAMAN
STOKES
ν + ΔE/h
ν
ν - ΔE/h
ν

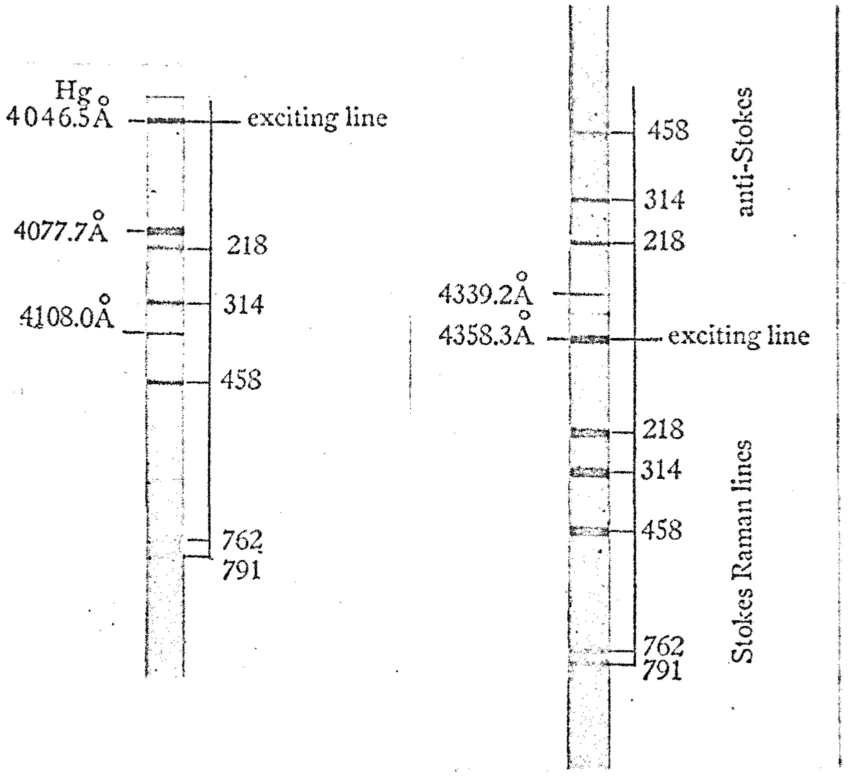


EARLY RAMAN SPECTROMETER

④



PHOTOGRAPHIC RAMAN SPECTROMETER

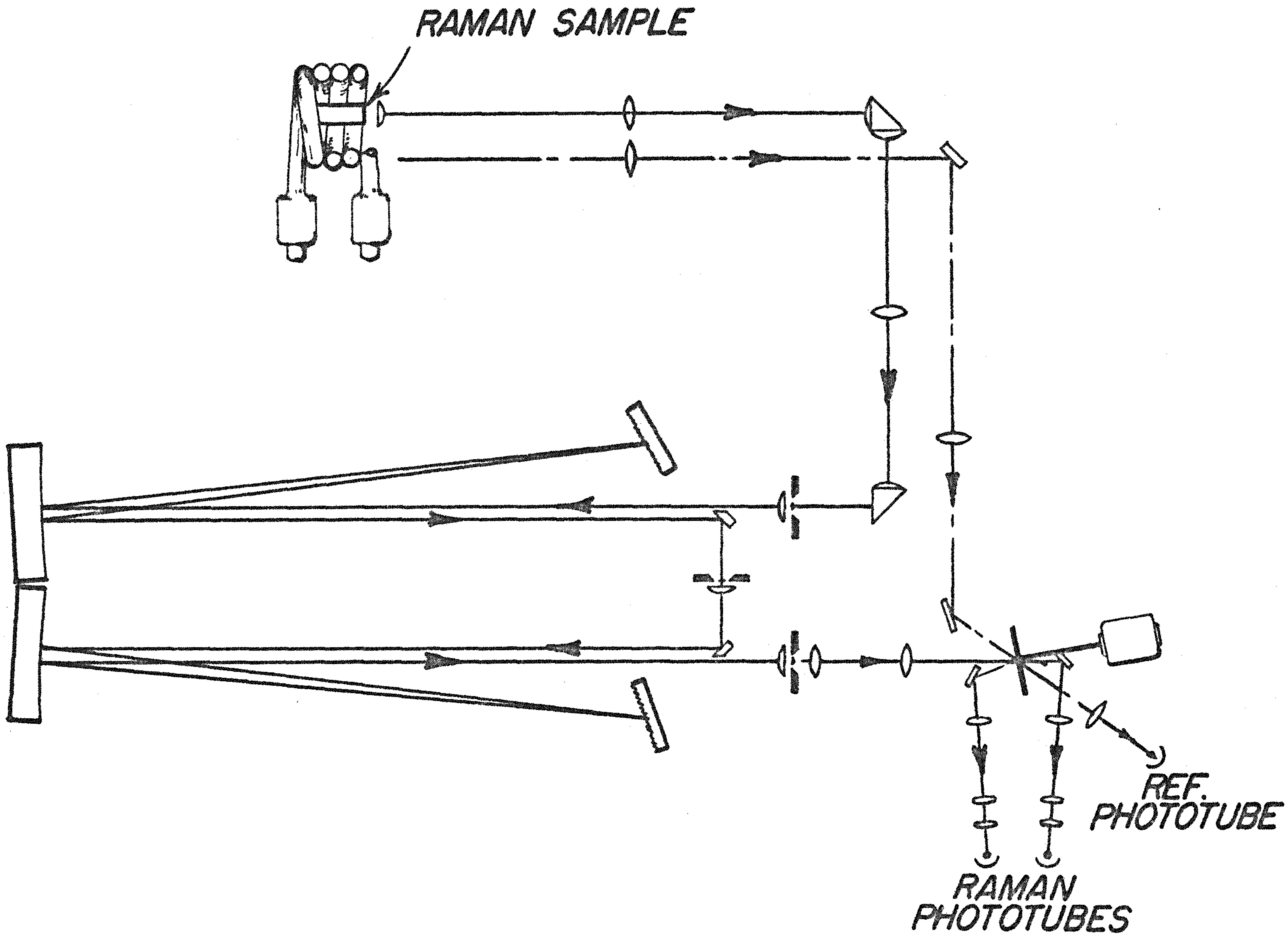


RAMAN SPECTRA- C $Cl_4$

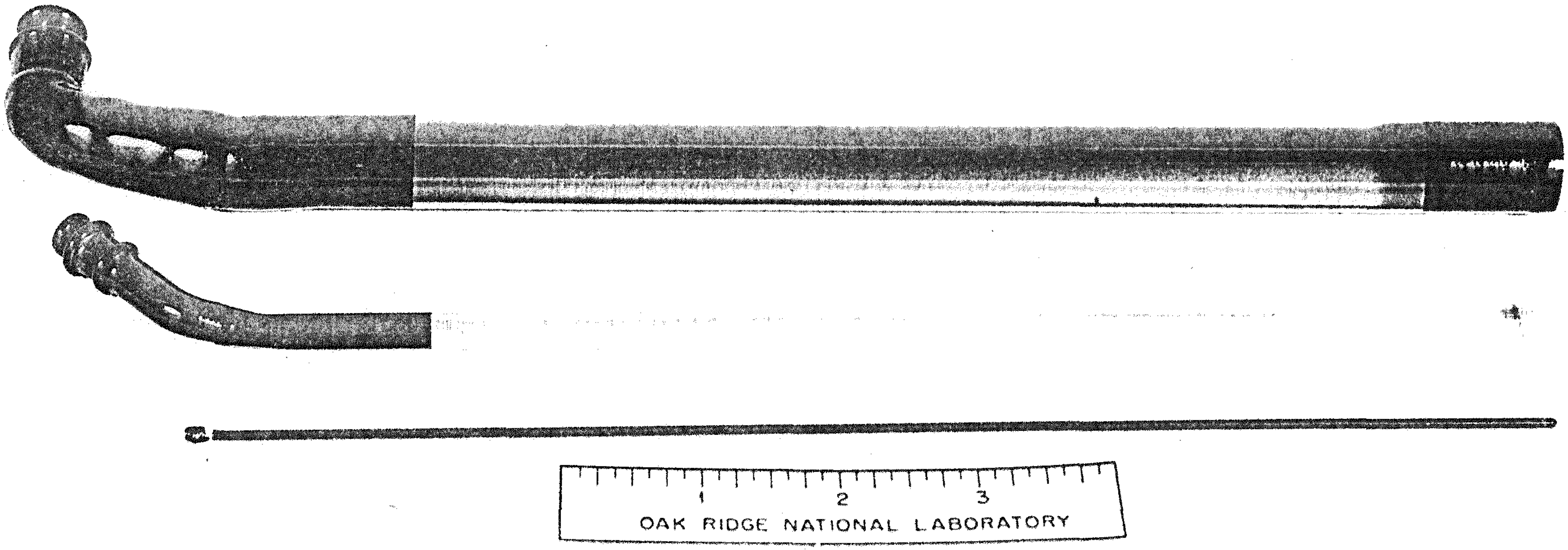
Slide 6

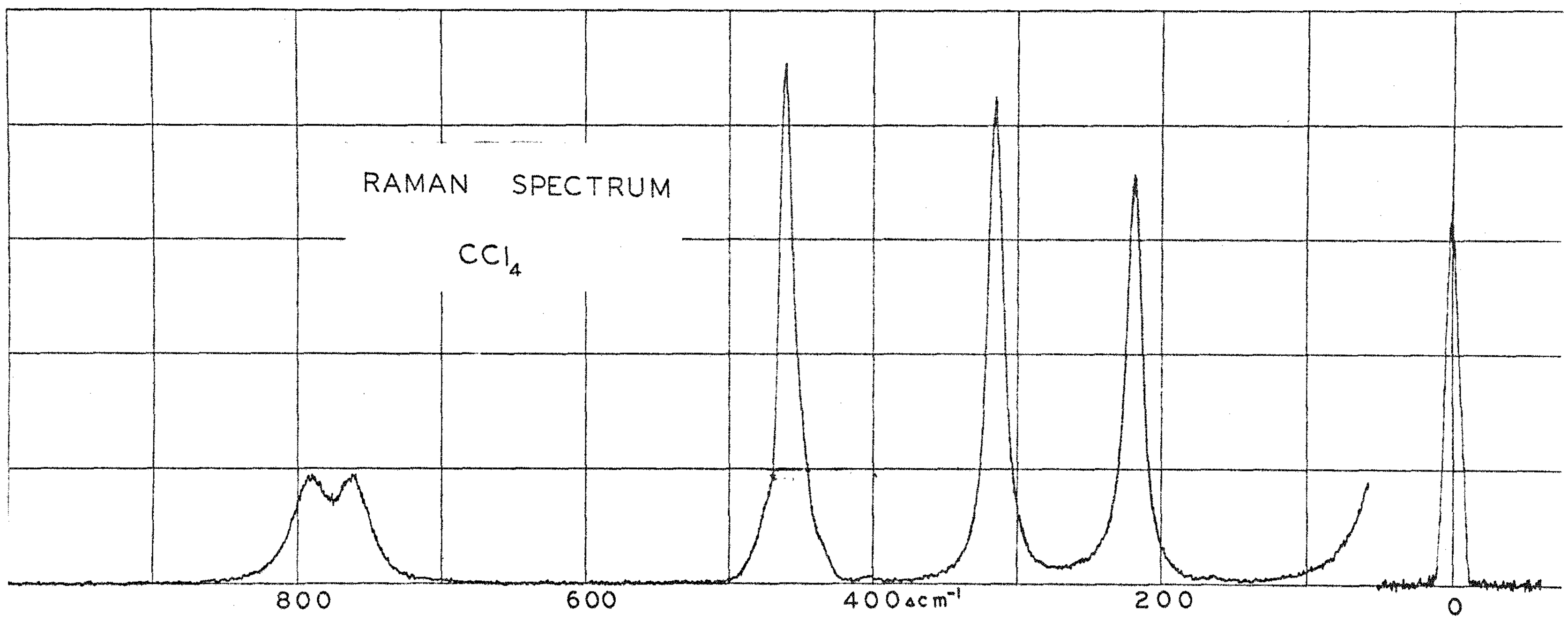
Photographic Plate

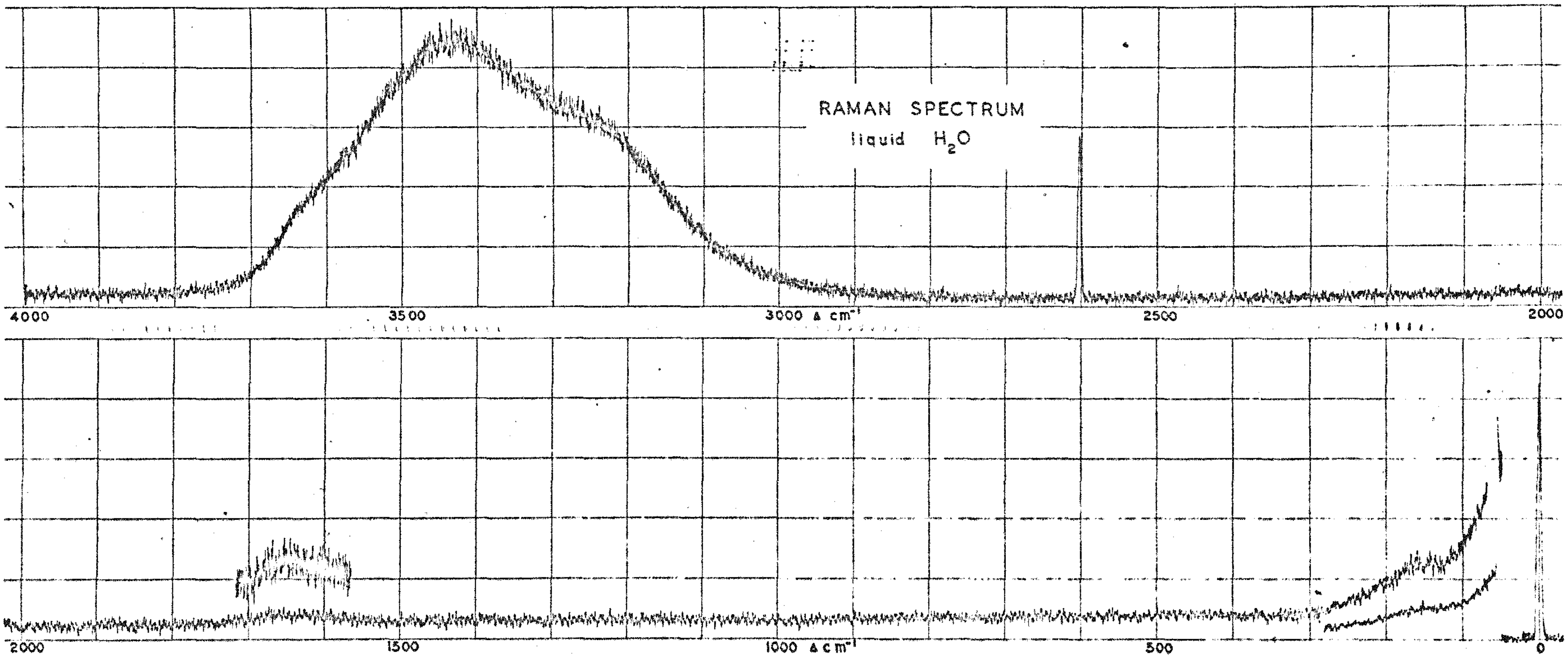
⑦



Slide 8 photo of
mercury Arc

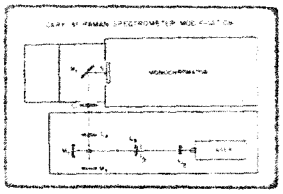

1
2
3
OAK RIDGE NATIONAL LABORATORY


RAMAN SPECTRUM
CCl4
800
600
400 Δcm⁻¹
200
0


RAMAN SPECTRUM
liquid $H_2O$
4000
3500
3000 Δ cm⁻¹
2500
2000
2000
1500
1000 Δ cm⁻¹
500
0

11

12



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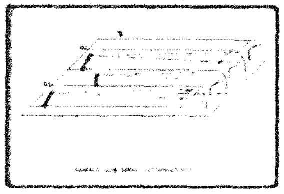
⑬ ⑭

Slide 13 photo of Laser Beam

Slide 14 photo of ~~Dye Laser~~
Sample cell in Laser Beam

⑮



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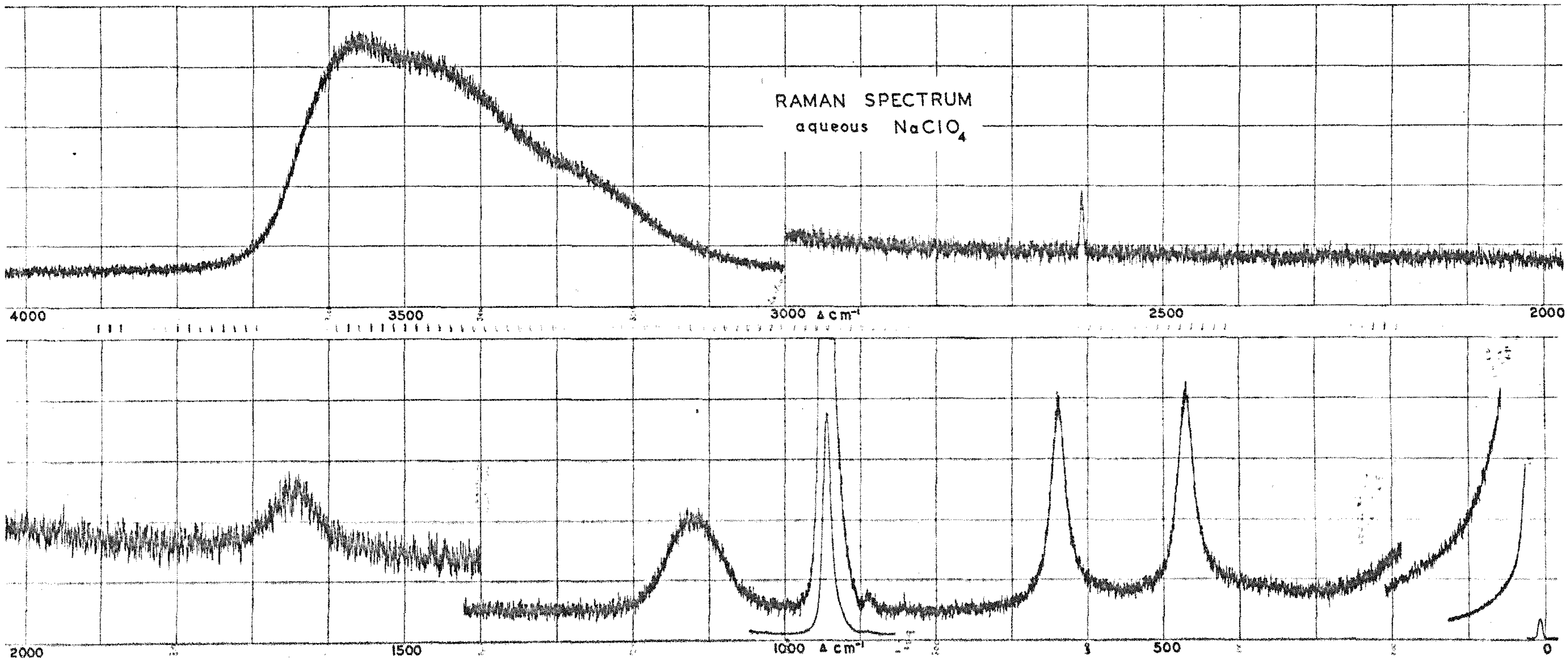
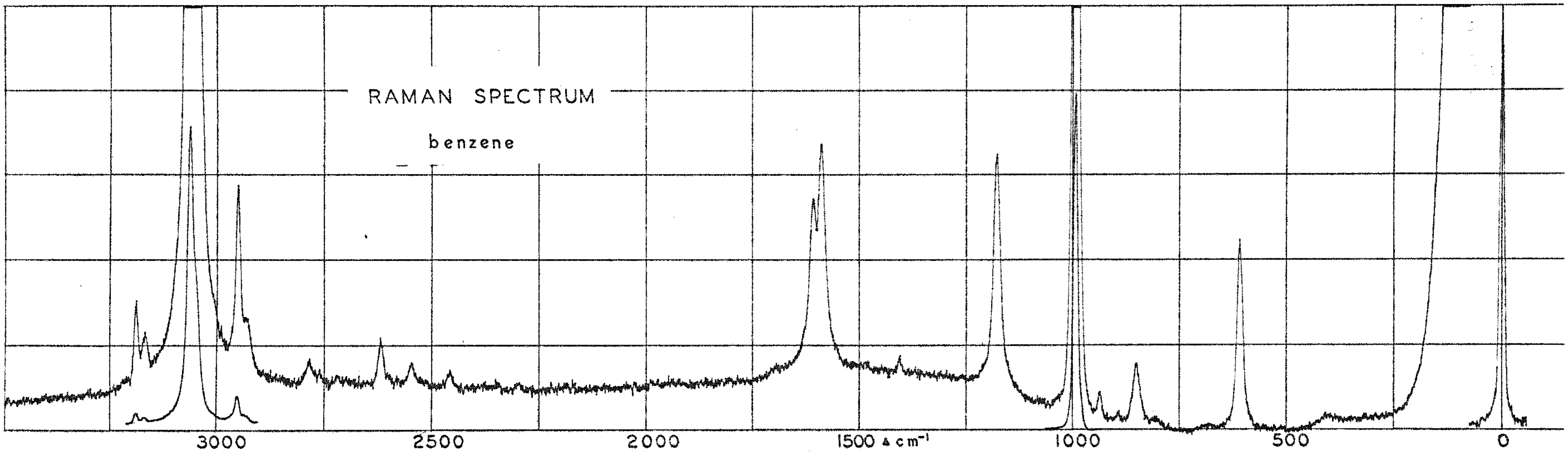
Raman Spectrometer Program

⑯ ⑰

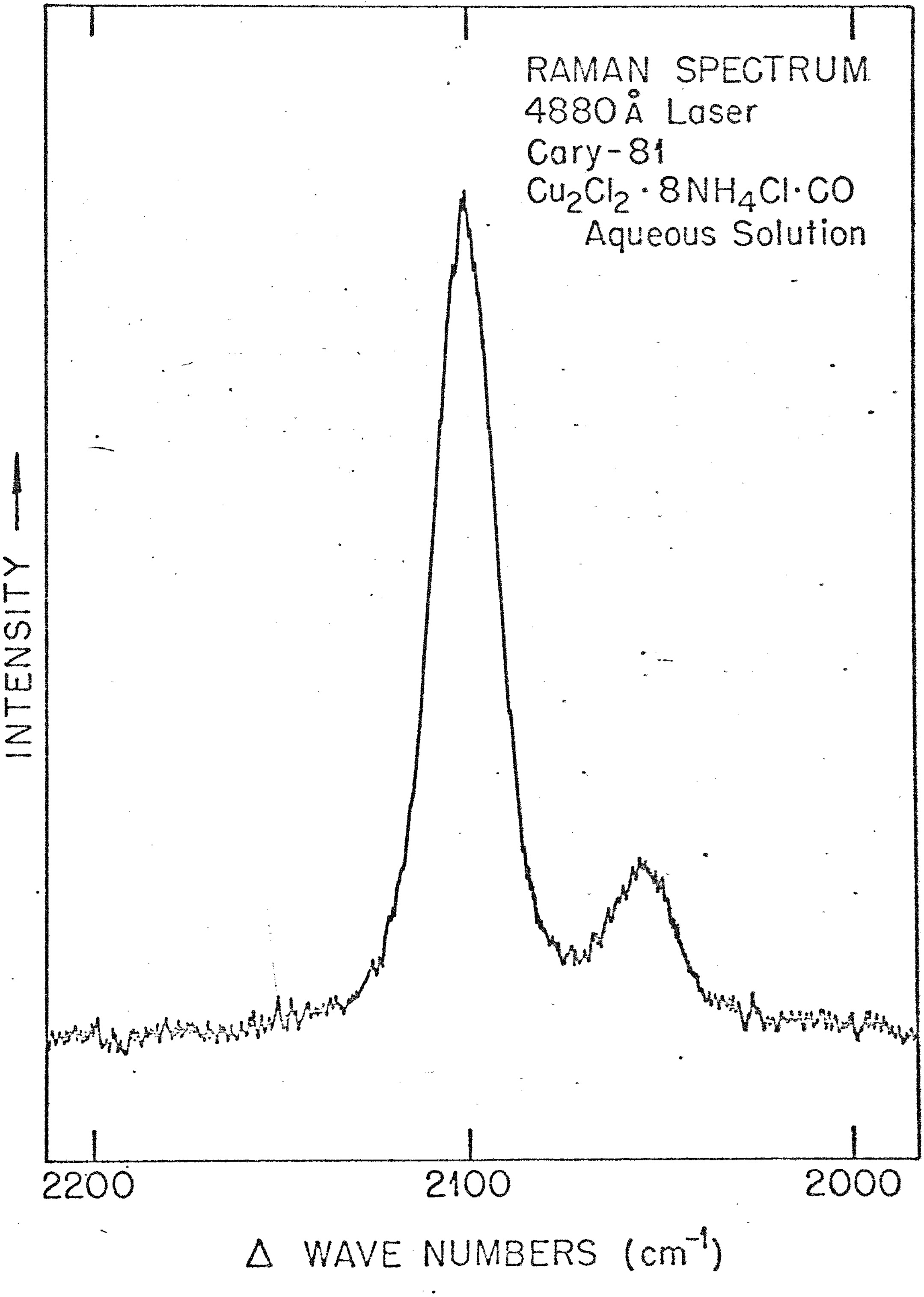
16 Photo of Spectrometer

17 Photo of Tuneable Dye Laser

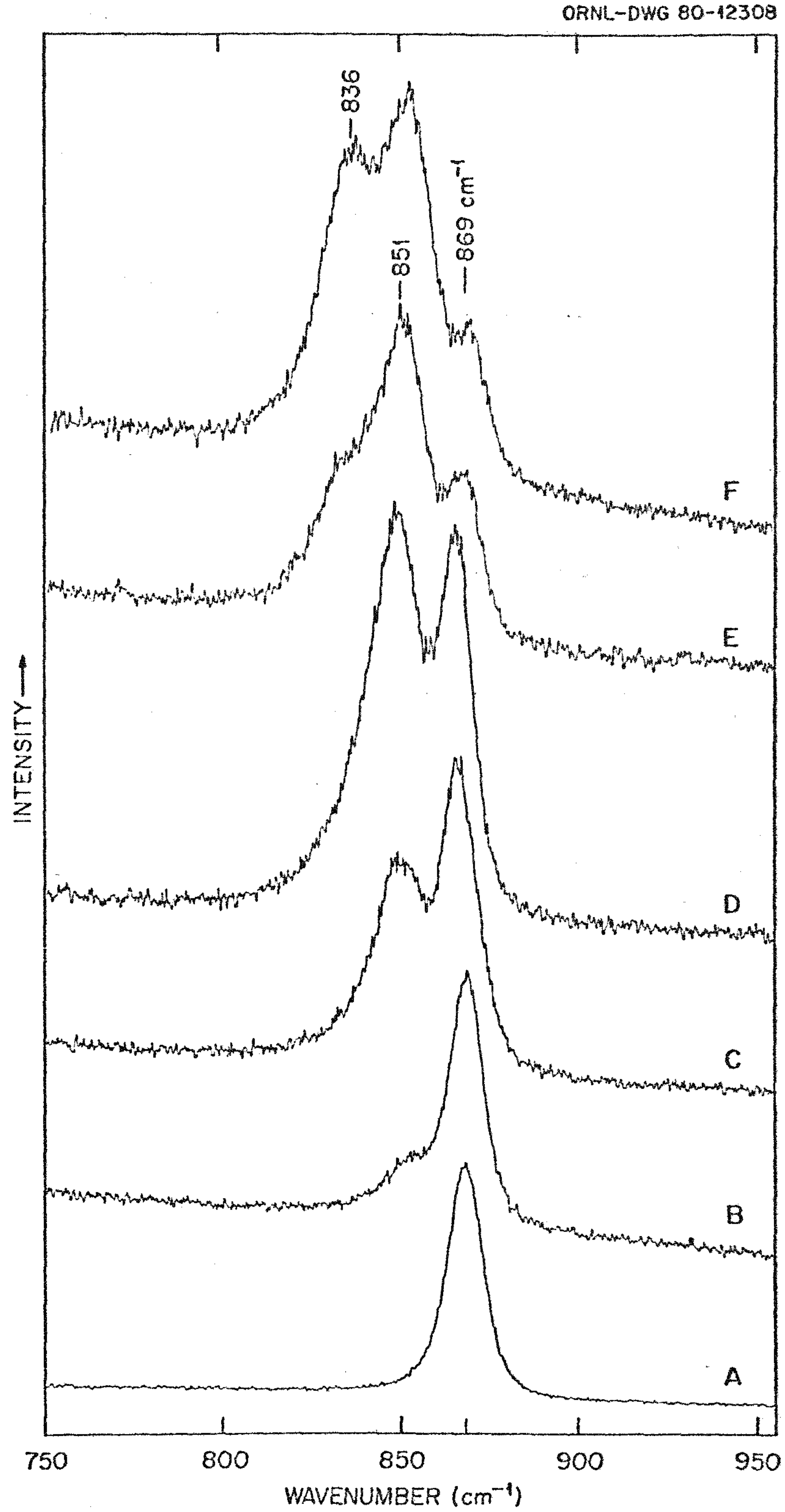

RAMAN SPECTRUM
aqueous $NaClO_4$
4000
3500
3000 Δ cm⁻¹
2500
2000
2000
1500
1000 Δ cm⁻¹
500
0


RAMAN SPECTRUM
benzene
3000
2500
2000
1500 Δ cm⁻¹
1000
500
0

ORNL-DWG. 70-6582



Mass Spec 12.8 % $C^{13}$
Raman-Optical 13.4 %


ORNL-DWG 80-12308
836
851
869 cm$^{-1}$
F
E
D
C
B
A
INTENSITY ⟶
750
800
850
900
950
WAVENUMBER (cm$^{-1}$)

UNCLASSIFIED
ORNL-DWG 63-7945