University of Toronto
ADVANCED PHYSICS LABORATORY

RAM

Raman Effect

Revisions:

2021 September:	Robin Marjoribanks (Minor changes, safety) v1.4
2020 August:	Robin Marjoribanks (Major revision, laser version)
2019 August:	David Bailey (Minor changes)
2014 October:	Henry van Driel
1991 September:	John Pitre

Please send any corrections, comments, or suggestions to the professor currently supervising this experiment, the author of the most recent revision above, or the Advanced Physics Lab Coordinator.

Overview

The purpose of this experiment is to introduce Raman scattering, a powerful tool that allows one to determine vibrational and rotational properties of molecules. It is used here to measure the frequencies of some vibrational modes of sulphur in the solid state, and carbon tetrachloride and benzene in the liquid state.

Introduction

Light scattering can be classified in many different ways. In general, <u>elastic</u> light scattering produces light with no change in frequency from the incident beam. An example is Rayleigh scattering, which occurs from particles much smaller than an optical wavelength such as atoms or molecules; it is responsible for, *e.g.*, the blue sky. In <u>inelastic</u> light scattering the scattered light has a different frequency from the incident beam. <u>Stokes scattering</u> occurs if the wavelength shift is to a lower frequency while <u>anti-Stokes scattering</u> involves a shift to higher frequency. Inelastic light scattering is a sensitive probe of *time-dependent* material phenomena, including material excitations such as molecular rotations or vibrations. Common forms of inelastic light scattering are Brillouin and Raman scattering. <u>Brillouin scattering</u> is inelastic light scattering from *collective* excitations of a condensed matter system (solid or liquid) such as acoustic phonons (sound waves) that produce time-dependent density changes. <u>Raman scattering</u> occurs from *individual* molecules in which there is a change in the electronic or nuclear configuration (*e.g.* through a vibrational or rotational mode). If the molecule gains energy in the scattering process, one has Stokes scattering. If the molecule is initially in an excited sate and loses energy in the scattering process, one has anti-Stokes scattering. Adolph Smekal predicted the existence of Raman scattering in 1923 but the effect is named after C.V. Raman, an Indian scientist, who first observed it experimentally together with K.S. Krishnan in 1928. Raman received the Nobel Prize in physics for discovering the effect, although in some of the German literature the effect is often referred to at the Smekal-Raman effect. Because molecules have distinct vibrational and rotational frequencies Raman scattering has become an essential fingerprinting technique in modern diagnostic methods allowing one to determine the composition of materials.

Classical Explanation of Rayleigh and Raman Scattering

To understand the basic idea behind Rayleigh and Raman scattering, we initially offer a classical approach. Consider a light beam with angular frequency ω_0 whose electric field at a given point is given by

$$\vec{E}(t) = \vec{E}_0 cos(\omega_0 t). \qquad (1)$$

If this beam is propagating inside an isotropic material it induces an electric polarization density whose strength is governed by an electric susceptibility. For a crystal the susceptibility is typically a matrix but for a fluid, as considered here, one can employ a scalar χ, so that

$$\vec{P} = \varepsilon_0 \chi \vec{E}(t). \qquad (2)$$

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This oscillating polarization density is the source for all re-radiated light including reflected, transmitted and scattered light. The susceptibility χ consists of a time-independent piece that leads to the reflected and transmitted light along particular directions and Rayleigh scattered light that propagates in all directions. However, since the susceptibility depends on the atomic or molecular coordinates, which, in turn, depend on the time-dependent vibrational and rotational modes of the molecules, the susceptibility has a time dependent part. To avoid becoming bogged down in notation we ignore rotational modes of the molecule and only consider one vibrational mode (as would be the case for, *e.g.,* molecular hydrogen, oxygen, etc.) considered as a single harmonic oscillator. The amplitude of vibration can be written as $Q=Q_0 cos(\omega_0 t)$ and the susceptibility can be expanded in a Taylor series as

$$\chi = \chi_0 + \frac{\partial \chi}{\partial Q}Q + ... \ = \chi_0 + \frac{\partial \chi}{\partial Q}Q_0 \, cos(\Omega t) + ... \tag{3}$$

where the first term on the right-hand side is time independent and Ω and Q are the (angular) frequency and generalized co-ordinate (bond vibration amplitude in the case of molecular hydrogen) of the mode. Hence the polarization density can be written:

$$\vec{P} = \left[\varepsilon_0 \chi_0 cos(\omega_0 t) + \varepsilon_0 \frac{\partial \chi}{\partial Q}Q_0 cos(\omega_0 t)cos(\Omega t) \right] \vec{E}_0$$

$$= \left\{ \varepsilon_0 \chi_0 cos\,(\omega_0 t) + \frac{1}{2}\varepsilon_0 \frac{\partial \chi}{\partial Q}Q_0 \left[cos\left([\omega_0 - \Omega]t \right) + cos\left(\ [\omega_0 + \Omega]t \right) \right] \right\} \vec{E}_0 \tag{4}$$

The first term on the right-hand side, and which has the same temporal frequency as the incident light beam, corresponds to an oscillating electric polarization density responsible for all the elastically scattered light (reflected, transmitted, and Rayleigh) at the same frequency as the incident light. The last two terms are responsible for Stokes and anti-Stokes inelastically scattered light at frequencies different from that of the incident light. In essence, the time-dependence or modulation of the electric susceptibility produces "side-bands" at higher and lower frequency than the incident light.

We now consider more complex molecules with *N* atoms. In general *3N* coordinates are needed to specify the locations of all the atoms; the molecule is said to have *3N* degrees of freedom. However, if we confine ourselves to motion about the centre of mass (rotational or vibration) we can take away the 3 degrees of freedom associated with centre of mass motion. For a linear molecule there are 2 degrees of rotational freedom (about two orthogonal axes passing through the centre of mass) while for non-linear molecules there are 3 degrees of rotational freedom. Hence for a linear molecule there are 3*N*-5 vibrational degrees of freedom or distinguishable vibrational modes, while for a non-linear molecule there are 3*N*-6 degrees of vibrational freedom. For example, In the case of carbon tetrachloride (CCl_4) studied here there are 9 distinct or normal vibrational modes, while for Benzene there are 30. However, some of these vibrational modes are degenerate, meaning that they have the same frequency. A detailed analysis of the vibrational dynamics shows that for CCl_4 there is one non-degenerate mode, one doubly degenerate mode and two three-fold degenerate vibrational modes, hence only four distinct vibrational frequencies. For these more complicated molecules the first two terms of the Taylor expansion of Eq. 4 has possible contributions from all these modes and becomes

$$\vec{P} = \left\{ \varepsilon_0 \chi_0 cos\left(\omega_0 t\right) + \frac{1}{2}\varepsilon_0 \sum_\iota \frac{\partial \chi}{\partial Q_\iota} Q_{0\iota} \Big[cos\big([\omega_0 - \Omega_\iota]t\big) + cos\big([\omega_0 + \Omega_\iota]t\big) \Big] \right\} \vec{E}_0 \qquad (5)$$

where the summation is taken over all the different vibrational and rotational modes of the molecule with generalized co-ordinate Q_i and normal mode frequency Ω_i. The strength of the Raman scattered light for a particular mode depends on the value of $\partial \chi / \partial Q_\iota$. If the value is non-zero the mode is said to be <u>Raman-active</u>. Note as well, that if for a complex molecule we extend the Taylor series expansion of Eq. 3 to second order terms we introduce terms such as

$$\frac{\partial^2 \chi}{\partial Q_\iota \, \partial Q_j} Q_\iota Q_j \qquad (6)$$

It is straightforward to show that such higher order terms will add oscillating terms at frequencies $\omega_0 \pm (\Omega_\iota \pm \Omega_\varphi)$ to Eq. 5. Light emitted at these additional frequencies are referred to as <u>overtones</u>. In general this scattered light is much weaker than the Stokes or anti-Stokes radiation, but you may actually observe one or more overtones in the CCl_4 Raman spectrum.

The rotational Raman shifts are generally much smaller than the vibrational Raman shifts and our experimental arrangements are not able to resolve them. We therefore ignore them in our subsequent discussion and focus on the Raman spectra of the vibrational modes. In the case of CCl_4, for example, we can expect 4 Stokes and 4 anti-Stokes lines of varying strength.

## Quantum Basis of Rayleigh and Raman Scattering

The classical explanation cannot account for all details of Raman scattering such as why certain modes are Raman active and the actual relative intensities of Stokes and anti-Stokes light. These depend on a fully quantum treatment of the electronic, vibrational and rotational motion as well as incident photon absorption and scattered photon emission processes. However, a full treatment of this is beyond a typical undergraduate course in quantum mechanics, invoking concepts such as time-dependent perturbation theory and group theory. We therefore only provide some insight into the key quantum concepts needed beyond the classical model.

We consider a molecule whose complete quantum state at any time is specified by electronic, vibrational and rotational quantum numbers of all the modes. For simplicity, as with the classical case we suppress all reference to electronic and rotational parameters and focus only on one vibrational mode (v) whose energy is $E_v = \hbar \Omega_v (n_v + 1/2)$, where n_v is the mode quantum number. When a photon interacts with a molecule, the quantum state of the molecule may or may not be altered. In the case of Rayleigh scattering, an incident photon of energy $\hbar \omega_0$ is absorbed and the molecule makes a transition to an excited state as shown in Figure 1 below. The molecule then makes a transition back to the initial (usually the ground) state and a photon of the same energy is emitted.

In the case of Stokes scattering, following absorption of the incident photon, the molecule makes a transition to an excited state with vibrational quantum number $n_v + 1$ and a photon of energy

$\hbar\omega_0 - \hbar\Omega_v = \hbar(\omega_0 - \Omega_v)$ is emitted as shown in Figure 1. In the case of anti-Stokes scattering the incident photon is absorbed from a molecule in an excited vibrational state with quantum number $n_v + 1$ and the molecule makes a transition to a less excited state of vibrational quantum number n_v with emission of a photon of energy $\hbar\omega_0 + \hbar\Omega_v = \hbar(\omega_0 + \Omega_v)$. Hence in Stokes scattering, energy is imparted to a molecule while in anti-Stokes scattering it is taken away.
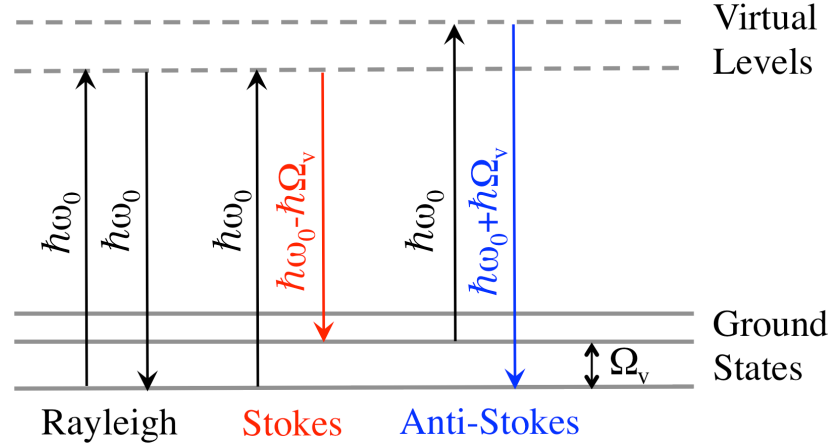
Figure 1: Scattering energy level transitions

Assuming that the scattering medium is in temperature equilibrium at absolute temperature T, there is a Boltzmann distribution of molecules over the energy states and the ratio of the number of molecules $N(n_v + 1)$ in a state of energy $\hbar\Omega_v(n_v + 3/2)$ to the number of molecules $N(n_v)$ in a state of energy $\hbar\Omega_v(n_v + 1/2)$ is given by**

$$\frac{N(n_v + 1)}{N(n_v)} = e^{-\hbar\Omega_v/kT} \tag{7}$$

Since quantum mechanics also shows that the total amount of scattered light is proportional to the fourth power of the frequency then the relative total number of anti-Stokes to Stokes photons is given by

$$\frac{number\ of\ anti\text{-}Stokes\ photons}{number\ of\ Stokes\ photons} = \left(\frac{\omega_0 + \Omega_v}{\omega_0 - \Omega_v}\right)^4 e^{-\hbar\Omega_v/kT} \tag{8}$$

where k is Boltzmann's constant. Note that in general the number of anti-Stokes photons is less than the number of Stokes photons. Because the emission process is governed by molecular lifetime effects the emitted light has a small spread in frequencies giving rise to a linewidth for the emission process. The total number of photons is therefore that emitted over the entire linewidth and not just the peak value recorded in a spectrum. The above analysis applies to all the modes observed in Raman scattering.

As noted above we have not considered the Raman process in connection with rotational or even electronic degrees of freedom. In the case of rotation the Raman shifts are too small to be resolved with the spectrometer available to you.

Since Raman shifts are equal to molecular vibration or rotation frequencies, they are equal to frequencies that might appear in the infrared spectrum. This does not mean that the Raman spectrum is merely the infrared spectrum transferred to a higher frequency region. Different selection rules govern Raman transitions from those that govern radiative transitions. This means that some transitions may be Raman active but may not appear in the absorption spectrum. The two are often complementary.

SAFETY REMINDERS

- Prolonged exposure to carbon tetrachloride, benzene, chloroform, or fumes from other samples used in this lab may be harmful to your health, so you should read the MSDS (Material Safety Data Sheets) for CCl_4 (https://bit.ly/2zaHHAa), C_6H_6 (https://bit.ly/1vrRT0N), or other samples you use.[1] These sheets are also available nearby the apparatus and from the lab technologists. Risk is minimal since the Raman samples are just a few mL, and are sealed, but if there is an accidental spill of any chemical the room should be calmly evacuated and lab staff consulted immediately.
- The 40mW 532nm laser output is Class 3B and can damage eyesight, if directly exposed, or if an accidental unanticipated reflection is created. It does not produce a hazard for skin exposure, and will create no sparks or ablation. Alignment: It is possible to view the laser beams safely to align, provided that the current to the diode is <u>first reduced below 140 mA</u>. This reduces the laser power below 5 mW. Even so, care should be taken not to allow any direct or accidental beam to enter the eye.
- The 60mm rail system with all optical components has an enclosure with an interlock: if the case is removed, the laser is switched automatically to 5mW maximum power. It is not necessary to operate the laser at full power with the enclosure open, and the interlock must not be interfered with. Speak with a Supervising Professor before attempting any open-enclosure operation. https://ehs.utoronto.ca/our-services/laser-safety/
- The sample heater is capable of being hot enough to be a concern, and it may take a long time to cool down. Attention and caution should be used. The heater controller in this experiment has a set temperature limit of 50 °C.

NOTE: This is not a complete list of all possible hazards; we cannot specifically warn against all possible creative failures of judgement. Experimenters must use common sense to assess and avoid risks, e.g. never open plugged-in electrical equipment, watch for sharp edges, don't precariously balance heavy objects, etc. If you are unsure whether something is safe, ask the supervising professor, the lab technologist, or the lab coordinator. If an accident or incident happens, you must let us know. More safety information is available at http://www.ehs.utoronto.ca/resources.htm.

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[1] Contact the Supervising Professor or Lab Coordinator if these internet links are broken.

Experimental

Raman spectra of sulphur, carbon tetrachloride (CCl_4) and benzene are studied in this experiment. Advanced versions may include chloroform and deuterium-substituted chloroform (to change vibration frequencies). Discuss with the Supervising Professor, if you want to try something else.

The Raman-source laser – The source of light used is a DJ532-40 diode-pumped solid state infrared laser which is frequency-doubled to 532nm. It consists of a combination of $Nd:YVO_4$ and KTP crystals within a mirror cavity, together with a 808 nm laser diode. Its maximum power output is 40 mW of green light, controlled by the current supplied to the 808 nm laser diode which pumps the $Nd:YVO_4$ laser medium. A current of 325mA is suitable for collecting spectra; a current below 140mA provides low-power output safe for viewing by eye. The system must not be operated above 140mA except that the whole system is completely enclosed (or else everyone in the room is wearing specific, appropriate, laser goggles). Currently, the whole laser and sample system is contained within an enclosure that contains the laser beam.

The enclosure has an interlock installed: with the case fully in place, the laser automatically runs at maximum power; with the case removed, the laser automatically runs at a power which is less than 5mW, similar to a strong legal laser-pointer. No-one must interfere with safety interlocks. If you suspect anything may be irregular, turn off the laser power and report the issue immediately to a Supervising Professor.

The power and spectrum of the laser are only stable if its temperature is, also. The unit contains a thermoelectric cooler operated by a separate controller unit.

Note: this is not a laser pointer, its maximum power is an order of magnitude greater than an eye-safe consumer pointer used in presentations. This is a Class 3B laser, for more information on laser Classes and laser safety see https://ehs.utoronto.ca/our-services/laser-safety/.

Turning on the pump laser –

1) TED200C – Turn on the thermoelectric cooler controller for the diode-pumped laser: first the main power, and then the TEC ON button. Cooling is necessary to protect the laser and to stabilize its output wavelength, it should stabilize in 10 minutes at ~22.5°C. Do not adjust the PID (proportional-integral-derivative) control settings, they're optimized and take an hour to set properly.
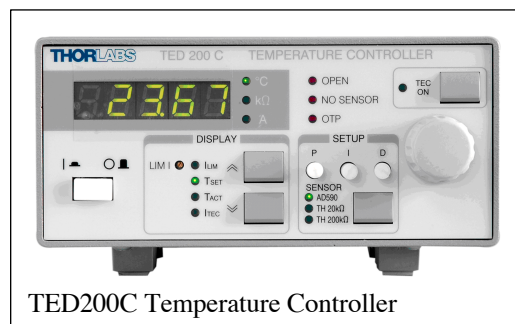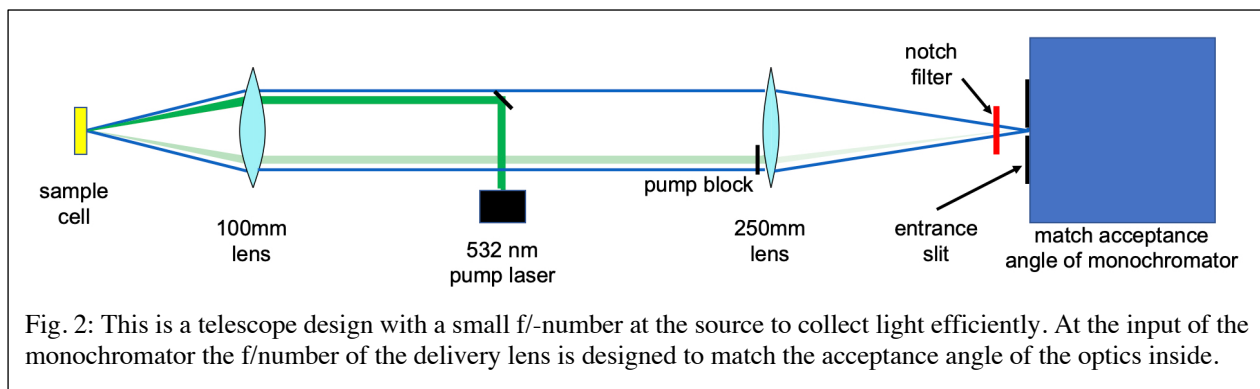

TED200C Temperature Controller

LCD200-Series Laser Diode Controller

2) LDC205C Turn on the laser diode controller: first the main power and then the LASER ON button. Currently, the interlock system on the case controls the laser power to be at one of two levels: FULL, with the case in place, and 5mW with the case removed. There are currently no student-adjustable settings, and the controller must operate in constant-current mode (CONST: I). You may wish to record the current ILD, which you can display, but this model of laser-diode (DJ532-40) is not equipped with

a photodiode to read out actual laser power, thus that function of the unit is not available here. You must not adjust LIM or CAL. Both TED200C and LDC205C controllers must be on, for temperature to stabilize correctly.

Collection of light from sample – CCl_4 is a classic sample for study because of its symmetry, which makes it easy to picture all the normal-mode oscillations, and makes it simple for group-theory representation analysis. Only a small fraction (often less than a part in 10^6) of the incident light is scattered by the liquid and of this, most is found in the Rayleigh line. To observe the Raman lines, it is necessary to illuminate the sample very strongly and to ensure that only scattered light can enter the spectrometer. In the apparatus provided, the laser is introduced from the side and a small mirror puts the pump beam aligned with the optic axis of a beam telescope. The 100 mm lens serves two purposes: to focus the pump laser onto the sample; and to efficiently collect scattered light from the sample and relay it along to the 250mm lens which puts the light onto the entrance slit of the scanning spectrometer. The scanning spectrometer is lined up with the axis of the telescope design so that it accepts only light introduced to it along the axis.
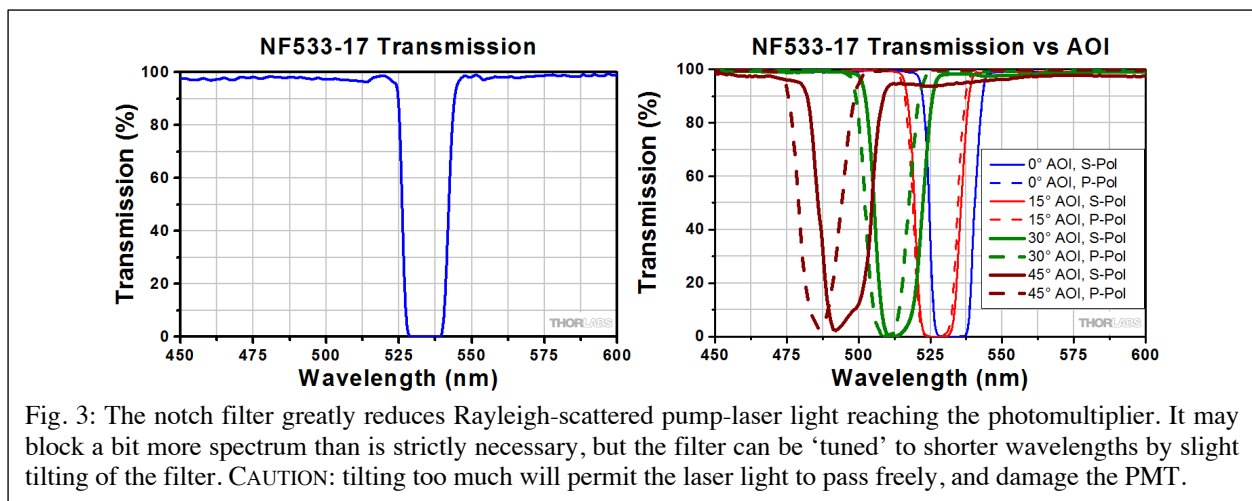
The arrangement of image-relaying from sample cell to spectrometer input slit is shown in Fig. 2.

Fig. 2: This is a telescope design with a small f/-number at the source to collect light efficiently. At the input of the monochromator the f/number of the delivery lens is designed to match the acceptance angle of the optics inside.

Pump block: The specular reflection of the pump laser, from the sample holder, occupies just a small part of the solid angle collected by the 100mm lens, and this gives an opportunity to block the reflected 532nm light before it is sent to the spectrometer and photomultiplier tube, which can be destroyed if exposed to bright light. This is currently done near the surface of the 250mm lens, before all the collected diffuse light from the sample is gathered up to a focus at the entrance slit.

Notch filter: Another opportunity to cut down the super-bright pump light is a *notch filter* – an interference filter which creates a narrowband spectral *mirror* 17nm wide at around 533 nm (see Fig. 3). Since this is a mirror, when the case is open, be careful about where the strong reflection of intense laser light goes – eye injuries often come from uncontrolled stray beams. At its peak, the notch filter attenuates by a factor of about 10^6.

This filter is sensitive to angle-of-incidence, as all interference coatings shift their action to shorter wavelengths when tilted. Slight tilting will permit you to look at Raman lines *close* to the pump wavelength which are blocked by the notch filter when it is used at normal incidence. To permit wavelengths *near* to the pump frequency to pass, but still to block the 532nm laser pump, the filter should not be tilted to more than about 15° angle of incidence.

Fig. 3: The notch filter greatly reduces Rayleigh-scattered pump-laser light reaching the photomultiplier. It may block a bit more spectrum than is strictly necessary, but the filter can be 'tuned' to shorter wavelengths by slight tilting of the filter. CAUTION: tilting too much will permit the laser light to pass freely, and damage the PMT.

<u>Photomultiplier</u> (see Appendices for specifications) — The photomultiplier voltage should be ~800 V, and the shutter should remain closed except when recording to protect the photomultiplier. Data on the scanning monochromator and photomultiplier unit are given in Appendix II. One should understand what is going on inside the scanning monochromator and not treat it just as a "black box". The cover of the scanning monochromator can and should be removed (or see figures attached here after Bibliography) so that the optical configuration of the unit can be examined. Never touch any of the optical surfaces — some types of mirror can be cleaned, but unprotected front-surface mirrors and diffraction gratings require special heated-vapour cleaning, if they can be cleaned at all.

<u>Alignment</u>: Rarely, the system may need realignment. This is done principally by tiny horizontal adjustments to the tiny mirror for the pump laser, in the middle of the 60mm cage system, at low power with the enclosure removed and room lights out, while monitoring photodiode signal (preferably with the monochromator set to the wavelength of one of the lines in sulphur). A Thorlabs 5/64" ball-end driver is provided for this adjustment.

A full level-zero alignment procedure is documented by video and available to TAs and professors on the password-protected webpages for the experiment (RSM).

Sample Heater Controller (in development)

1) TC200 – This unit can heat the entire sample holder, and read out the temperature. Currently it provides a maximum of only 34C (it should heat more, if fully working). Consult with the APL Supervisor if you wish to go beyond what this unit currently provides.

TC200 Sample Heater Controller
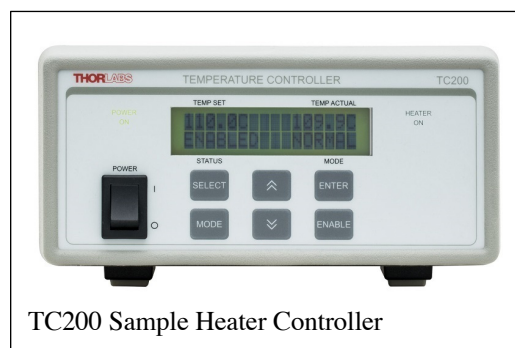
SUGGESTED EXERCISES

1. Begin with the cuvette of powdered sulphur, it makes strong signals and a well-known spectrum. Find good ways to record your wavelengths, given that your chart-recorder software records only time on the abscissa. Spectroscopy often uses convenient units of *wavenumber* (cm^{-1}), proportional to frequency and to energy. Remember that a spectrum is a *distribution*, and the integral in each photon range should be preserved, regardless of units — therefore the distribution values must also be changed, whenever changing units (the Jacobian).

   Convert your recorded data to plots which use this unit, with the zero set to the 532nm pump wavelength, so you identify shifts in energy for each line. Sulphur is a good sample to tinker with, for small changes in the angle of the notch filter, changes in scan speed, slit width, and other adjustments you may wish to optimize.

2. Record the Raman spectrum of CCl_4 at two or more temperatures, and that of C_6H_6 at one temperature. Use the heater controller provided, driving the heater-block into which the cuvettes are inserted. Consider how long it may take to reach equilibrium in your sample, when changing temperature.

3. Measure the frequency shifts of the Stokes Raman lines excited by the 532 nm pump.

4. Determine the ratio of the intensities $\frac{I_{anti-Stokes}}{I_{Stokes}}$ for each pair of anti-Stokes and Stokes lines for CCl_4. Compare your results to equation (17).

5. Other liquids and materials are possible, including regular chloroform and deuterated chloroform, for which atomic mass changes shift the frequency of some vibrations. Consult with your supervising professor about other materials you may be interested in, such as paint pigments, tooth enamel, ceramics, mixed alcoholic drinks, soft drinks, Jello, Kool-Aid, etc. The laboratory has a few other cuvettes, depending on type of material it must contain.

QUESTIONS

1. CCl_4 molecule basic ideas.
   a. What is the shape of the CCl_4 molecule?
   b. Are the distances between the chlorine atoms all equal?
   c. Are the carbon to chlorine bonds all of the same length?
   d. Are the Cl-C-Cl bond angles all the same?
   e. Where is the center of mass situated? (Herzberg p. 165)

2. How many fundamental frequencies does CCl_4 have?

3. Vibrations and degeneracy.
   a. Which fundamental mode is associated with each Raman Stokes line that you observed.
   b. For CCl_4 why does the v_2 vibration have the least energy associated with it?
      Hint: Think in terms of changing bond lengths during the vibration and the associated bond strengths.
   c. Which vibrations are degenerate and what is the degree of their degeneracy?

d. Be able to describe the normal modes of vibration of the CCl_4 molecule using drawings or a physical model. (Herzberg pp. 99-101).

4. How many of the fundamental frequencies did you see in your Raman spectrum? (Herzberg pp. 310-312)

5. Symmetry.

   a. What is a centre of symmetry?

   b. Does the CCl_4 molecule have a centre of symmetry? (Wheatley p. 16)

6. What is the condition for a molecule to be Raman active?

7. Dipole moments.

   a. Does CCl_4 have a permanent dipole moment?

   b. Does H_2 have a permanent dipole moment?

   c. Does HCl have a permanent dipole moment?

8. In the Raman effect the induced dipole moment $\vec{P}$ changes with the electric field. Do $\vec{P}$ and $\vec{E}$ have the same direction in general? Explain. (Herzberg p. 243).

9. Comment on the truth or falsehood of the following statement. "In CCl_4 the direction of the induced dipole moment $\vec{P}$ does not coincide with the direction of the field $\vec{E}$ producing it". (Herzberg p. 244).

10. Comment on the statement: "Any set of mutually orthogonal axes for the CCl_4 molecule are principal axes of the polarizability ellipsoid and so $\alpha_{xx} = \alpha_{yy} = \alpha_{zz}$ and all the other components of the polarizability tensor e.g., α_{xy}, α_{yz}, etc. are zero". (Herzberg p. 244).

11. The following statement is true. "In order to observe vibrational Raman spectra, the amplitude of the dipole moment induced by the incident radiation must change during the vibration considered". Show that this is consistent with the statement that the normal vibration v_I will appear in the Raman spectrum if and only if at least one of the six components of the tensor which is the change of polarizability, $\left(\dfrac{\partial \alpha_{xx}}{\partial \xi_i}\right)_0, \left(\dfrac{\partial \alpha_{xy}}{\partial \xi_i}\right)_0$ … etc. is different from zero. (Herzberg pp. 242-245).

12. Knowing the structure of the CCl_4 molecule, comment on the following statement. "In each of the lines of the Raman spectrum of CCl_4 as observed in the undergraduate laboratory at the U. of T. there is a superposition of rotational and vibrational Raman spectra but the resolution of the equipment is not great enough to allow one to see the rotational structure which is present in each of the lines". (Herzberg p. 458).

OPTIONAL QUESTIONS

These questions draw on materials available to all students, in the references. Students who've taken group and representation theory, or atomic and molecular physics, will especially benefit from engaging with these questions.

1. Spherical and symmetric top molecules.

a. What is meant when it is said that CCl_4 is a spherical top molecule?

b. What is the difference between a spherical top and a symmetric top? (Herzberg p. 22 and p. 37)

2. CCl_4 belongs to the point group T_d (or $\bar{4}3m$). What are the symmetry elements of this group? Be able to explain what these elements mean in terms of a model or diagram. (Colthrup, Daly and Wiberley p. 107; Wheatley p. 16; Herzberg p. 9)

3. Explain the difference between the terms Infrared Rotation Spectrum (Pure Rotation) and Rotational Raman Spectrum. (Herzberg pp. 19-24; Colthrup Daly and Wiberley p. 34; Wheatley p. 49)

4. Rotation spectra (assume no vibration is taking place).

a. Does CCl_4 have a pure rotation spectrum?

b. Does H_2 have a pure rotation spectrum?

c. Does HCl have a pure rotation spectrum?

5. Rotational Raman spectra (assume that no vibration is taking place).

a. Does CCl_4 show a rotational Raman spectrum?

b. Does H_2 show a rotational Raman spectrum?

c. Does HCl show a rotational Raman Spectrum?

6. Is the following statement true or false? "In order to observe a rotational Raman spectrum the polarizability of the molecule perpendicular to an axis of rotation must be anisotropic". Explain (Wheatley p. 34)

7. Is the following statement true or false? "In order to show a rotational Raman spectrum, a molecule must possess a permanent dipole moment". Explain. (Wheatley p. 49)

8. Cubic point group.

a. What is a point group? (Herzberg p. 9)

b. Is the following statement true or false? "Any molecule that belongs to a cubic point group does not have a pure rotation spectrum.". Explain (Herzberg p. 41)

9. All the fundamental frequencies of the CCl_4 molecule are Raman active. Give an example of a simple molecule for which one of the vibrations is Raman inactive. Be able to explain the reason for this inactivity. (Herzberg pp. 242, 66).

10. Given a CO_2 molecule in the vibrational mode v_2 (see Herzberg p. 66 for a diagram), explain why the polarizability is the same at the opposite phases of the vibrational motion. (Herzberg p. 242).

11. The CO_2 molecule in the displaced position of the v_2 vibration is a planar XY_2 molecule. State what point group it belongs to and hence show that in the displaced position, the polarizability ellipsoid has the same axes as it has in the equilibrium position.

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SPECIFICATIONS

MONOCHROMATOR UNIT

The Monochromator Unit contains the optical system, mechanical drive, and electric motors that operate on signals from the Control Unit.

Type Of Mount. . . . .   Single-pass Czerny-Turner mounting with folding mirrors to provide entrance and exit beams on a common optic axis.

Aperture Ratio.   f/6.8 at 2000 angstroms.

Focal Length. . . . .   350 millimeters.

Resolving Power.   Better than 1 angstrom; Line-profile half-width less than 0.5 angstrom, with 3 mm slit height.

Stray Light.   0.1% or less within ±1-1/2 bandwidths of a given line.

Wavelength Range (mechanical). . . . .   Zero order to 10,000 angstroms, first order.

Wavelength Accuracy. . . . .   ±1 angstrom throughout usable wavelength range.

Wavelength Resetability. . . . .   ±0.1 angstrom on the basis of resetting on the maximum of a narrow emission line, with photo-detected recorder output as indicator.

Reciprocal Dispersion. . . . .   Approximately 20 angstroms per mm at exit slit with 1180 lines per mm grating, depending on wavelength.

Grating. . . . .   Precision plane grating replica: 48 mm x 48 mm ruled area. Standard grating of 1180 lines per mm, blaze wavelength 2500 angstroms. (Gratings of other line spacing and blaze will be made available in the future.)

Mirrors. . . . .   Aluminized first-surface mirrors with MgF_2 overcoating. Optical surfaces corrected to 1/4-wave mercury green line.

Collimating and focusing mirrors: 50 mm diameter, parabolic, 350 mm focal length.

Folding mirrors: 25 mm x 35 mm plane.

Slits. . . . .   Ground and polished straight knife edges, bilaterally adjustable; entrance and exit slit width ganged to single control.

Slit Width. . . . .   Continuously variable between 5 and 2000 microns; a 4-digit counter reads directly in microns.

Slit Height. . . . .   12 mm maximum; provision for intermediate heights of 0.5, 1, 3, and 5 mm.

M2   M3

entrance   exit
slit   slit

                    grating
M1   M4

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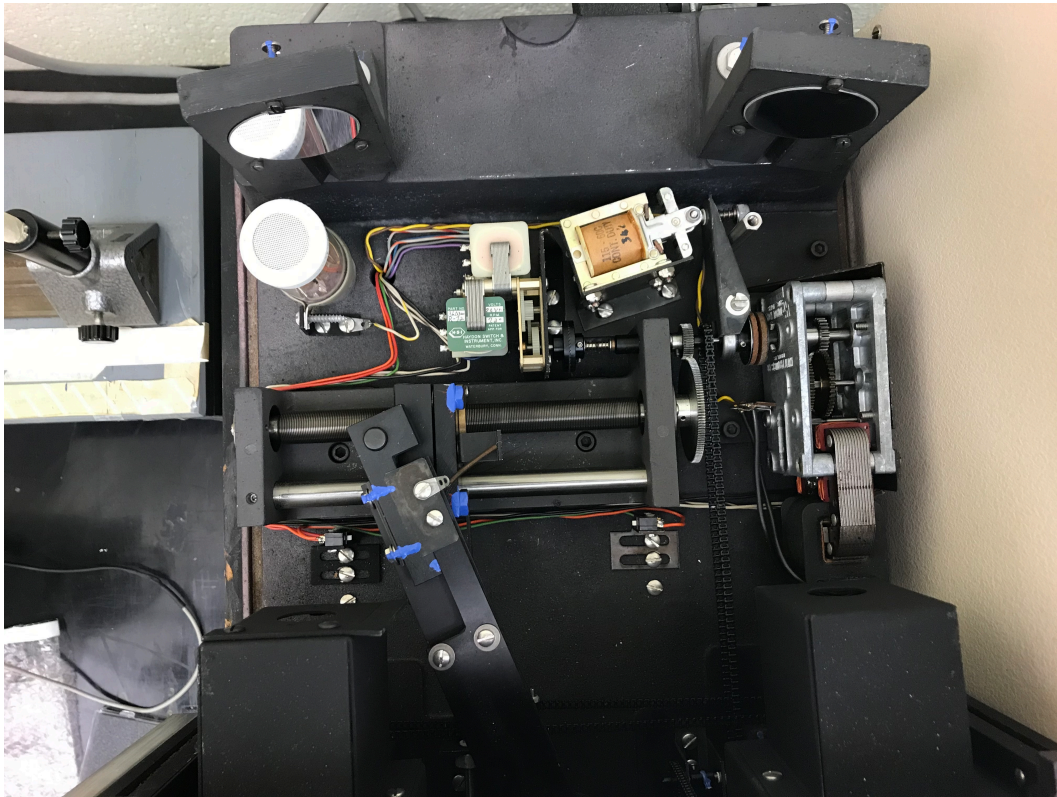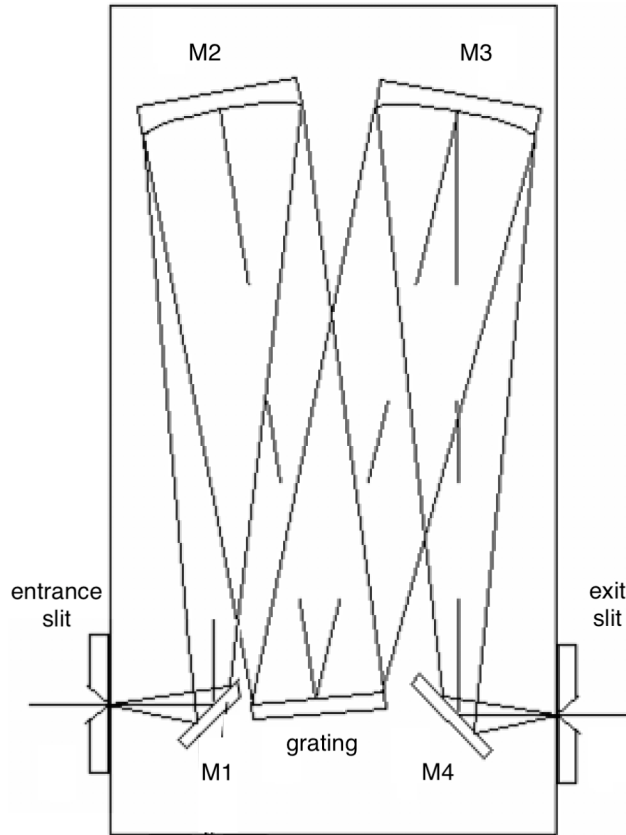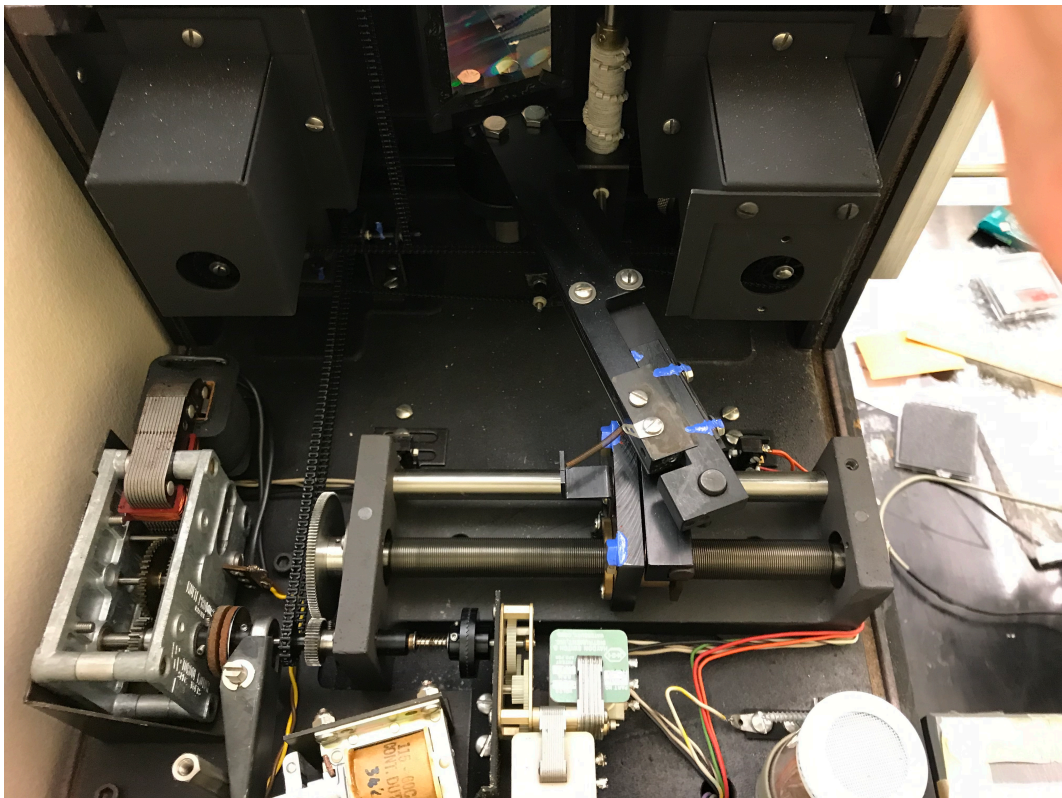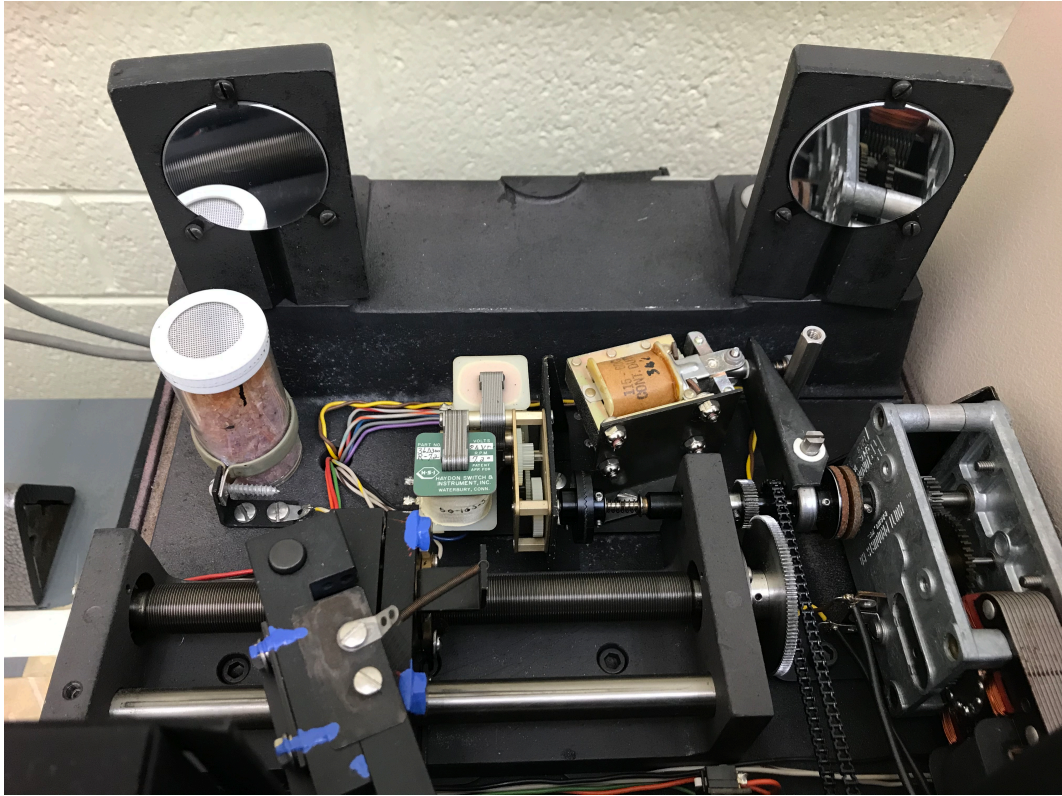
MONOCHROMATOR UNIT-
CONTROLS AND CONNECTORS

NOTE: Monochromator Unit controls and con-
nectors are shown in Figure 4-1 and 4-2.

SLIT WIDTH CONTROL

The only control located on the Monochromator
Unit is the Slit Width control, as shown in Figure
4-1. The entrance and exit slits are ganged
together and are operated by the single knob.

Slit width is indicated on a 4-digit counter that
reads directly in microns. For example, the
counter shown in Figure 4-1 indicates a slit
width of 120 microns for both the entrance and
the exit slits.

One complete turn of the knob changes the slit
width by 50 microns. Limit stops on the knob
shaft prevent the slits from being over-closed,
or opened too far. As with other measuring
devices, maximum accuracy and precision is
obtained when the slit width setting is made
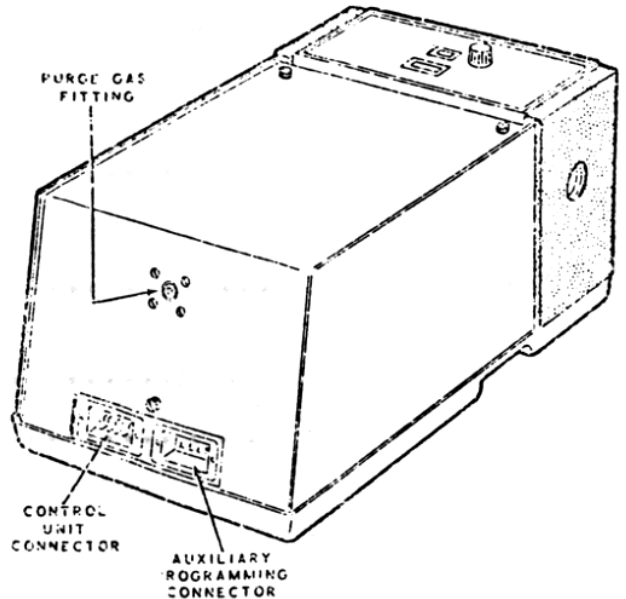in a positive direction.

WAVELENGTH INDICATOR

Wavelength is read on a 5-digit counter as
illustrated in Figure 4-1. The wavelength indi-
cated in the figure is 2345.1 angstroms.

CONTROL UNIT CONNECTOR

Located near the bottom of the rear panel is a
15-pin male connector for electrically connect-
ing the Monochromator Unit to the Control Unit.
See Figure 4-2.

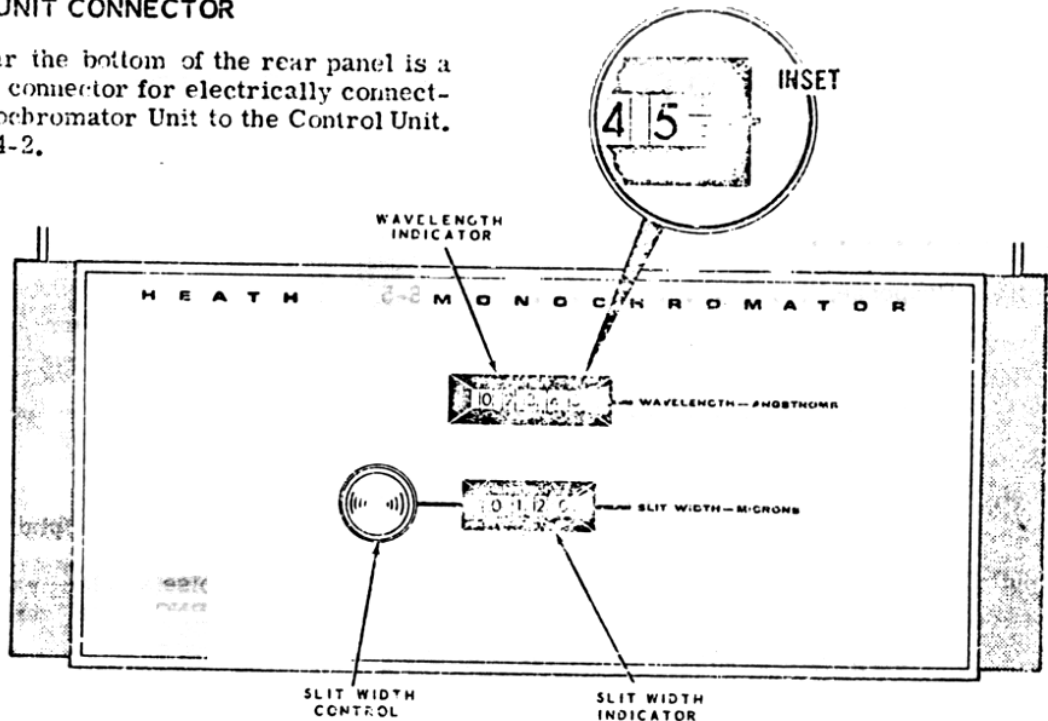
Figure 4-2   Monochromator rear panel

Figure 4-1   Monochromator control panel

CONTROL UNIT

An electronic digital system in the wavelength Control Unit supplies pulses to a stepping motor which drives the precision leadscrew and permits exact synchronization of wavelength scan with a strip-chart recorder at constant or variable scan rates.

Scanning Rates. . . . . Nine digitally controlled scanning speeds: 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10, and 20 angstroms per second in the direction of increasing wavelength.

Slew Rates. . . . . Rapid traverse in either direction at approximately 5400 angstroms per minute.

Internal Oscillator Frequency. . . . . 600 Hz, locked to 50 or 60 Hz line frequency.

External Input. . . . . Any waveform with pulse width greater than 50 nanoseconds and amplitude between 2 and 10 volts with zero reference. Frequency limited only by divided frequency maximum of 100 Hz at motor driver input, point CPX.

Output Pulse Amplitude To Chart Recorder. . +3.6 volts with no load.

Output Resistance. . . . . 700 ohms.

Pulse Rise And Fall Time. . . . . Less than 1 μs.

PHOTOMULTIPLIER SECTION

PHOTOMULTIPLIER TUBE

1P28A.

Spectral Response. S-5
(See RCA IP28 Data Sheet for Luminous Sensitivity, Dark Current and other specifications.)

Leakage. . . . . Normal room lighting will cause less than a 1% change in the dark current value.

Output. . . . . Directly from photomultiplier tube anode to BNC connector on reference plate.

Output Cable. Four foot, low-noise shielded cable terminated at both ends with BNC cable connectors.

CONTROL UNIT-
CONTROLS AND CONNECTORS

NOTE: Control Unit controls and connectors are shown in Figure 4-3 and 4-4.

SCAN RATE SELECTOR SWITCH

One of nine calibrated wavelength scan rates (20, 10, 5, 2, 1, .5, .2, .1, or .05 angstroms per second) can be selected by the SCAN RATE selector switch that is located on the front panel of the wavelength Control Unit. See Figure 4-3. The OFF position of the SCAN RATE switch turns off all of the electronic circuits that control the scan motor and chart recorder drive motor.

UNCAL LIGHT

The UNCAL (uncalibrated) lamp lights when the INT-EXT switch on the rear of the Control Unit is in the EXT position. With the switch in the INT position (UNCAL lamp not lit) the scan rates are based on the internal 600 Hz oscillator and the calibrated positions of the SCAN RATE switch. When the INT - EXT switch is in the EXT position, an external frequency source, connected to the EXT INPUT terminals, can be used to set the scan rates. The use of an external frequency source will be discussed later.

SCAN SWITCH

The scan motor that drives the wavelength scanning mechanism is started or stopped by the 3-position lever-type SCAN switch. Wavelength scan can be momentarily operated by holding the SCAN switch lever down to the MOMENTARY position. When the switch is released, spring action returns it to the center OFF position.

When the SCAN switch lever is raised to the CONTINUOUS position, wavelength scan continues until the lever is manually returned to the center OFF position, or the scan is stopped by an automatic limit switch at approximately 10,000 angstroms.
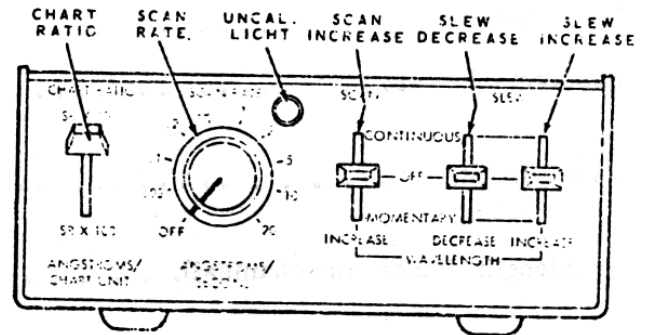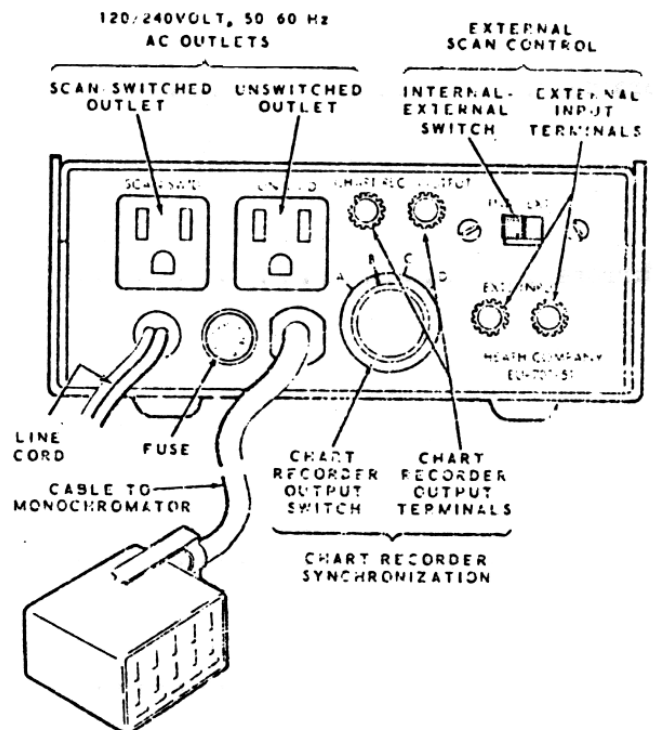

Figure 4-3   Control Unit front panel

Figure 4-4   Control Unit rear panel

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SLEW SWITCH

A specific wavelength region can be rapidly approached by means of a high-speed slewing drive controlled by the two lever-action switches marked SLEW on the front of the Control Unit (Figure 4-3). The switch labeled DECREASE, or the switch labeled INCREASE changes the wavelength at a rate of more than 5000 angstroms per minute. By momentarily depressing the proper SLEW switch to the MOMENTARY position, the wavelength setting can be decreased or increased in small increments. By raising the proper switch lever to the CONTINUOUS position, wavelength will be increased or decreased until manually returned to the center OFF position. If left in the CONTINUOUS position, the wavelength will change at the slewing rate until stopped by an automatic limit switch near either end of the leadscrew at approximately 0 or 10,000 angstroms. Because of a double-clutch drive system, it is acceptable to leave the SCAN switch in the CONTINUOUS position while operating the SLEW switches.

CHART RECORDER OUTPUT TERMINALS

This pair of terminals, located on the rear panel of the wavelength Control Unit, are used for chart recorder synchronization.

For example, if the external oscillator frequency is 6 Hz, and the SCAN RATE switch is set at 1 Å/sec, then

$$\text{scan rate} = \frac{6 \times 1}{600} = 0.01 \text{ Å/second}$$

A great number of other scan rates may be obtained by using an external oscillator and other positions of the SCAN RATE switch. However, the external oscillator frequency must not be greater than required to produce a scan rate of 20 angstroms per second.

SCAN SWITCHED OUTLET

On the rear panel of the Control Unit is an AC line voltage outlet marked SCAN SW'D. See Figure 4-4. Power is present at this outlet only when the SCAN RATE switch is in any position except off, and the SCAN switch is in either the MOMENTARY or CONTINUOUS position. This outlet can be used for synchronization of other devices with Monochromator scanning operations. CAUTION: Maximum power output from this outlet must be limited to 60 watts (0.5 ampere, 120 volts, 60 Hz, or, 0.25 ampere, 240 volts, 50/60 Hz).

UNSWITCHED OUTLET

Also on the rear panel is an AC line voltage convenience outlet, marked UNSW'D, for use with accessory instruments. Line voltage is present at this outlet whenever the wavelength Control Unit is connected to an AC line. Maximum power from this outlet should be limited to 600 watts (5 amperes, 120 volts, 60 Hz, or, 2.5 amperes, 240 volts, 50/60 Hz).

INT-EXT SWITCH

This switch selects the internal or an external frequency source for wavelength scan. The switch should be in the INT position when the calibrated switch-selected Scan Rate values are desired. The switch should be in the EXT position when an external frequency source is used to provide other scan rates, or for programming of the scan rate. The UNCAL light on the front panel glows to indicate when the INT-EXT switch is in the EXT position.

EXTERNAL INPUT

The output of a fixed or variable-frequency oscillator can be connected at the EXT INPUT terminals to provide scan rates different from those indicated by the front-panel SCAN RATE selector switch, and also to provide programmed variable-rate scanning.

The following formula is used to determine the scan rate when using an external oscillator signal:

$$\text{scan rate (Å/sec)} = \frac{F \text{ (ext)} \times SR}{F \text{ (int)}}$$

where: F (ext) = external oscillator frequency (Hz)

F (int) = 600 Hz = fixed internal oscillator frequency

SR = SCAN RATE switch position

CHART RECORDER OUTPUT SWITCH

This 4-position rotary switch selects the proper ratio of pulses for synchronizing the stepping motor in the Monochromator Unit to specific types of servo chart recorder stepping motor drive systems.

CHART RATIO SELECTOR SWITCH

This switch, located at the left side on the front panel is used to establish the desired ratio of servo chart recorder speed with respect to the Monochromator scanning rate.

BASIC OPERATING PROCEDURE

The following procedure is intended as a guide and checklist for the basic operation of the Heath EU-700/E Monochromator as a fixed-wavelength monochromator and as a scanning spectrometer. This operational sequence is suggested for systematic operation of the Monochromator, but can be modified at will without risk of damage to the instrument. To utilize the unusual versatility of the scanning system, with respect to servo chart recorder synchronization.

Basic operation of the Monochromator should include the following check points:

1. Check the Monochromator Unit for proper placement on a firm base, and attach the source and detector devices.

2. Connect the wavelength Control Unit to the Monochromator Unit and plug the power cord into the proper AC service outlet.

3. Set the SLIT WIDTH to the desired reading on the digital counter.

4. Insert the appropriate aperture disc behind the light seal coupling. See Section 7 for information on selecting the aperture disc.

5. Check the following controls and switches on the Control Unit for the proper initial setting:

SCAN RATE. . . . set to appropriate value, as discussed under Controls and Connectors.

SCAN. . . . . OFF.

SLEW. . . . . OFF.

INT-EXT. . . . . . INT or EXT, depending on scan-rate requirements.

6. For operation of the Monochromator at a specified wavelength value, set the digital WAVELENGTH counter to the desired value by combined use of the SLEW and SCAN switches. The following procedure is suggested:

a. Using the SLEW controls, set the WAVELENGTH counter to approximately 5 angstroms less than the desired value.

b. With the SCAN RATE set at 0.5 or 1 angstrom per second, hold the SCAN switch in the MOMENTARY position and step up to the desired wavelength reading. For precise wavelength setting within 0.1 angstrom of the peak of a narrow emission line, such as from a hollow-cathode discharge, set the SCAN RATE switch at 0.1 angstrom per second and use photo-detector readout to indicate the line peak.

7. For operation as a scanning spectrometer:

a. Set the WAVELENGTH counter to the starting value of the scan in the same manner as in Step 6.

b. Set the SCAN RATE to an appropriate value with regard to the spectral character of the input radiation, and to the pen response of the servo chart recorder, if used. Atomic or molecular emission spectra require a SCAN RATE of 0.5 angstrom per second or less with typical chart recorders having a pen period of 1 second. Spectral continua or broad-band absorption spectra permit a SCAN RATE setting as high as 20 angstroms per second.

c. Set the SCAN switch to CONTINUOUS, then return the switch to the OFF position after the desired wavelength range has been scanned.