

CHAPTER 3

Raman Spectroscopy

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3.1	Introduction	127
3.2	Theory	128
	A. Scattering of Light by Molecules	128
	B. Vibrational Raman Spectra	130
	C. Polarizability	130
	D. Raman Spectra of Some Simple Molecules	133
	E. Polarization Measurements	140
	F. Rules of Selection and Polarization	143
3.3	Experimental	144
	A. Light Sources	144
	B. Spectrometers	146
	C. Sampling Techniques	154
	D. Measurement of Depolarization Ratios	159
3.4	Applications	160
	Questions	163
	References	164

3.1 INTRODUCTION

The Raman effect was discovered in 1928 by Sir C. V. Raman¹⁻³ and complements the method of infrared spectroscopy in the study of the vibrational spectra of molecules. However, since it has a quite different physical basis, being a light-scattering effect rather than one involving the absorption of radiation, it often gives information additional to that obtained from infrared spectroscopy. For example, vibrational frequencies that are inactive in the infrared may often be observed in the Raman spectrum and vice versa.

When a beam of light of suitable frequency, chosen so that it is not absorbed, passes through a translucent medium, free from dust, most of the light is transmitted without change. However at the same time a small fraction is scattered by the molecules of the medium. The total intensity of scattered light is about 10^{-3} of the intensity of the incident light for liquids.

This classical or Rayleigh scattering effect has been known for many years,⁴ and its inverse proportionality to the fourth power of the wavelength is the basis for the explanation of the blue color of the sky.⁵ In Rayleigh scattering the frequency of the light remains unchanged, i.e., for a monochromatic incident beam the frequency of the scattered light is exactly equal to that of the incident beam.

Raman's discovery was that the scattered light also contains new frequencies (Raman frequencies) to both higher and lower frequencies of the frequency of the Rayleigh scattered light. These Raman lines are very weak (of the order of one-thousandth of the intensity of the Rayleigh scattering) and are therefore relatively difficult to detect. The differences of their frequencies from the frequency of the incident light are characteristic of the molecules of the scattering medium and are found to be equal to vibrational or rotational frequencies of the molecules. Vibrational shifts are readily resolved from the Rayleigh by means of a relatively simple prism spectrograph, while the pure rotational transitions lie so close to the Rayleigh line that their resolution is impracticable in most cases unless a grating spectrograph of very high resolution is used. Thus in normal practice only the vibrational Raman lines are commonly observed, and most of the work of practical importance in Raman spectroscopy is concerned with pure vibrational spectra.

Raman spectra can be observed when light is scattered by solids, liquids, or gases, and it is interesting to note that the method was more widely used in early investigations of the vibrational spectra of molecules than was infrared spectroscopy because it was at that time experimentally more accessible than infrared. In recent years, however, with the introduction of commercial infrared spectrometers, infrared spectroscopy has become widely practiced and Raman spectroscopy has come to be regarded by many as a rather specialized technique. Now, with the development of very high intensity light sources, including the laser, and the use of the photomultiplier tube for the detection of weak intensities, the way is open for rapid advances in technique, and Raman spectroscopy should soon be available as a routine tool.

3.2 THEORY

A. SCATTERING OF LIGHT BY MOLECULES

Only a simple presentation of the basic features of the theory of Raman spectroscopy is given here. More detailed and mathematical accounts are to be found elsewhere (see, for example, Refs. 6-9).

The simplest model that enables us to understand the scattering of light by molecules is to visualize the collision of a photon of incident light of frequency ν_0 (energy $h\nu_0$) with a molecule in the medium. Such a collision can occur *elastically* or *inelastically*. In an elastic collision the photon is scattered without change and is emitted with energy $h\nu_0$ (Rayleigh scattering), while in an inelastic collision (Raman scattering) the internal energy of the molecule changes by transfer of energy with the photon. Thus, the emitted photon has an energy $h\nu'$ different from that of the incident photon. In most instances the change in the internal energy results from a change in the vibrational energy of the molecule. If the transition is from the ground vibrational state ($v = 0$) to the first excited vibrational state ($v = 1$), the change in energy is $h\nu_1$, where ν_1 is a vibrational frequency. Thus,

$$h\nu' = h\nu_0 - h\nu_1$$

and the scattered light shows a frequency shift, relative to the Rayleigh scattering, toward the red end of the spectrum equal in magnitude to a vibrational frequency. If, however, a molecule that is already in its first vibrational state ($v = 1$) collides with a photon, it may transfer energy to the incident photon and fall back into the ground state ($v = 0$). In this event the emitted photon has energy $h\nu''$ where

$$h\nu'' = h\nu_0 + h\nu_1$$

and its frequency is shifted relative to that of the Rayleigh line toward the blue end of the spectrum with the same magnitude of frequency as before.

Thus, Raman frequencies are observed to both higher and lower frequencies, $\pm\nu_1$, of the incident frequency. The latter frequencies are called "Stokes lines" and the former, "anti-Stokes lines." Since at normal temperatures the number of molecules in the ground vibrational state far outnumber those in the first vibrational state, the intensity of Raman frequencies emitted with frequencies $\nu_0 - \nu_1$ is far greater than those with frequencies $\nu_0 + \nu_1$, and Stokes lines are relatively much more intense than anti-Stokes lines. In fact, the anti-Stokes lines are observed only in favorable cases. A molecular substance that gives a Raman spectrum where both Stokes and anti-Stokes lines are observed using a simple spectrometer is liquid carbon tetrachloride (Fig. 3.1).

For a polyatomic molecule several Raman lines may be observed, the shift of each from the exciting frequency being equal to the frequency of a fundamental mode of vibration or, more rarely, a combination of fundamental vibrational modes of the molecular species. For a polyatomic molecule containing n atoms, the maximum number of fundamental frequencies is $3n - 6$ ($3n - 5$ for a linear molecule). The number of vibrational frequencies observed in the Raman spectrum depends on the symmetry of the molecule.

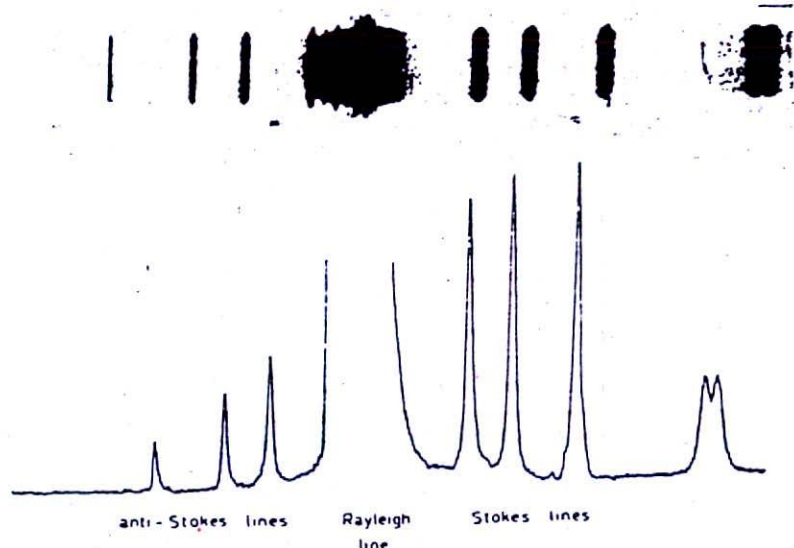


FIGURE 3.1: Photographically recorded spectrum of carbon tetrachloride showing Stokes and anti-Stokes lines.

B. VIBRATIONAL RAMAN SPECTRA

In infrared spectroscopy a vibrational frequency is active only if the molecular vibration involves a change in the permanent dipole moment of the molecule. Thus, for a homonuclear molecule such as N_2 which has a zero dipole moment its single vibrational mode, stretching of the $N \equiv N$ bond, is inactive in the infrared. However, the $N \equiv N$ stretching frequency is observed in the Raman spectrum at 2331 cm^{-1} . This comes about because a vibration is Raman active if it involves a *change in the polarizability* of the electrons in the molecule, i.e., a change in the induced dipole moment rather than a change in the permanent dipole moment.

C. POLARIZABILITY

A molecule may be regarded as a collection of positively charged nuclei embedded in a cloud of negative electrons. In the equilibrium configuration the electrical centers of the positive and negative charges may coincide, in which case the molecule has no dipole moment, or may *not* coincide, in which case the molecule possesses a permanent dipole moment. In both instances interaction with an electric field, for example with incident light, gives rise to an *induced dipole moment*, and if the field oscillates with a frequency that is large compared with nuclear vibrational frequencies, only the electron cloud (of relatively small inertia) will be distorted by the field and the nuclei will remain relatively unaffected.

The relation between the applied field strength E and the induced dipole moment M is given by

$$M = \alpha E$$

where α is the *polarizability* of the molecule. In this expression both E and M are vectors and α is a tensor. The nature of α may be visualized by resolving the induced dipole moment into three components M_x , M_y , and M_z in the x , y , and z directions of a coordinate system fixed in space and in the molecule, letting the corresponding components of the field be E_x , E_y , and E_z , i.e.,

$$M_x = \alpha_{xx}E_x + \alpha_{xy}E_y + \alpha_{xz}E_z$$

$$M_y = \alpha_{xy}E_x + \alpha_{yy}E_y + \alpha_{yz}E_z$$

$$M_z = \alpha_{xz}E_x + \alpha_{yz}E_y + \alpha_{zz}E_z$$

The tensor α is then defined by the set of six coefficients α_{xx} , α_{xy} , α_{xz} , α_{yy} , α_{yz} , and α_{zz} which may be used to represent α in a more pictorial way by forming the equation of an ellipsoid:

$$\alpha_{xx}x^2 + \alpha_{yy}y^2 + \alpha_{zz}z^2 + 2\alpha_{xy}xy + 2\alpha_{yz}yz + 2\alpha_{xz}xz = 1$$

This is the so-called *polarizability ellipsoid*, which can be visualized by drawing arrows from a common origin with lengths proportional to the polarizability in that particular direction. The heads of the arrows define the ellipsoid. If the ellipsoid is oriented for convenience with its principal axes along the x , y , and z axes of the coordinate system, the equation just presented reduces to the form:

$$\alpha_{xx}x^2 + \alpha_{yy}y^2 + \alpha_{zz}z^2 = 1$$

Figure 3.2 illustrates the polarizability ellipsoids of some simple molecules in their equilibrium configurations.¹⁰

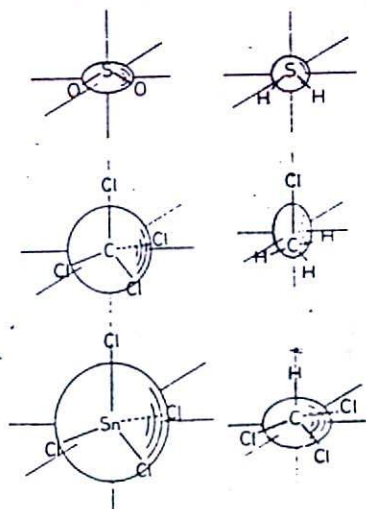


FIGURE 3.2: Polarizability ellipsoids of some simple molecules.

The molecular polarizability α_0 is a measure of the ease with which the electrons in the molecule (the cloud of electrons) are distorted. Thus a vibration that results in a distortion of the electron cloud, e.g., a symmetrical stretching frequency (Fig. 3.3), is Raman active, while, although it may be,

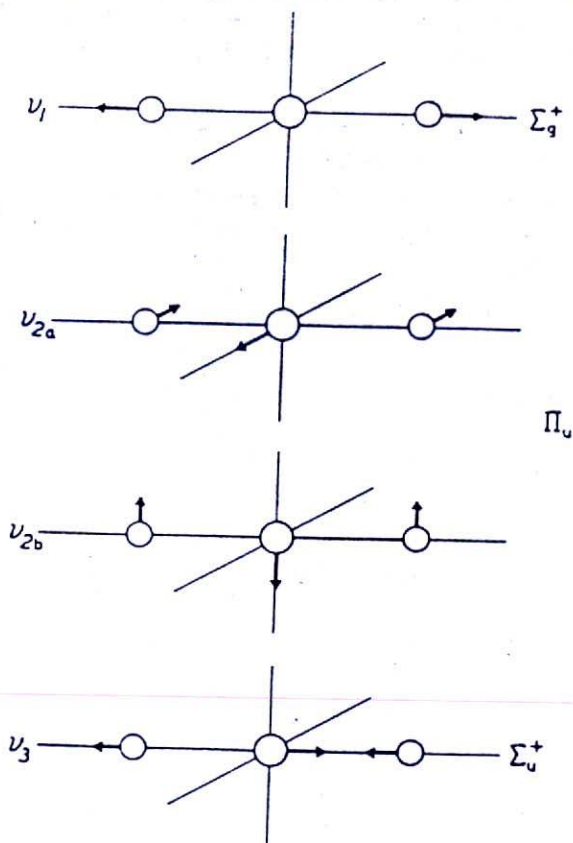


FIGURE 3.3: Normal modes of vibration for CO_2 .

it is not necessarily infrared active. Indeed it will not be active in the infrared unless the permanent dipole moment of the molecule changes during the molecular vibration.

By way of illustration we consider the fundamental vibrational modes of two simple triatomic molecules, carbon dioxide and sulfur dioxide, and those of a tetrahedral molecule, carbon tetrachloride.

D. RAMAN SPECTRA OF SOME SIMPLE MOLECULES

The linear CO_2 molecule has $3n - 5 = 4$ fundamental vibrations (Fig. 3.3), which are conveniently described as a symmetrical stretch ν_1 , an antisymmetrical (or antisymmetric) stretch ν_2 , and two symmetrical bends ν_3 . The two bends have identical frequencies and differ only in their dispositions in space, i.e., experimentally a single bending mode is observed which is doubly degenerate.* Figure 3.4 shows the way in which the polarizability ellipsoid changes during the normal modes of vibration of the CO_2 molecule.

During the symmetric stretching vibration ν_1 the polarizability changes and hence ν_1 is Raman active. However it is inactive in the infrared since the initially zero dipole moment remains zero during the vibration of the molecule. For the asymmetric stretch ν_2 the motion results in a loss of symmetry in the molecule, the dipole moment becomes nonzero, but the polarizability ellipsoid remains unchanged. Hence ν_2 is active in the infrared, but inactive in the Raman. Similarly, for the bending mode ν_3 the vibration is seen to be infrared active, but forbidden in the Raman. These results are perhaps not immediately obvious, but the following more detailed treatment should make the conditions under which the polarizability changes clearer.

In general for a small displacement of the nuclei in the molecule during vibration the distortion can be described by a *normal vibrational coordinate* q constructed so as to express all of the individual displacements of the nuclei involved. For small amplitudes of vibration the polarizability may be described by

$$\alpha = \alpha_0 + (\partial\alpha/\partial q)_0 q$$

where the zero subscript refers to values at the equilibrium configuration.

Thus for the electric moment induced by an applied field

$$M = \alpha E = \alpha_0 E + (\partial\alpha/\partial q)_0 q E$$

For a change in polarizability to occur during a particular mode of vibration the second term in this equation $(\partial\alpha/\partial q)_0 \times q$ must be nonzero, i.e., since q is finite $(\partial\alpha/\partial q)_0$ must be nonzero. Like α_0 , $(\partial\alpha/\partial q)_0$ is a tensor and is usually referred to as the "derived polarizability tensor" α'_0 of the normal vibration defined by q .

* When two or more molecular vibrations have the same frequency, they are said to be "degenerate." This may arise because of the symmetry of the molecule, in which case the degeneracy will be either twofold (doubly degenerate) or threefold (triply degenerate). Any molecule possessing a threefold, or higher, axis has some doubly degenerate vibrations, and a molecule with more than one threefold, or higher, axis will also have some triply degenerate vibrations.

Degeneracy may also occur accidentally if the frequencies of two or more different modes of vibration happen to coincide. In practice accidental degeneracies are quite rare. They often lead to Fermi resonance.

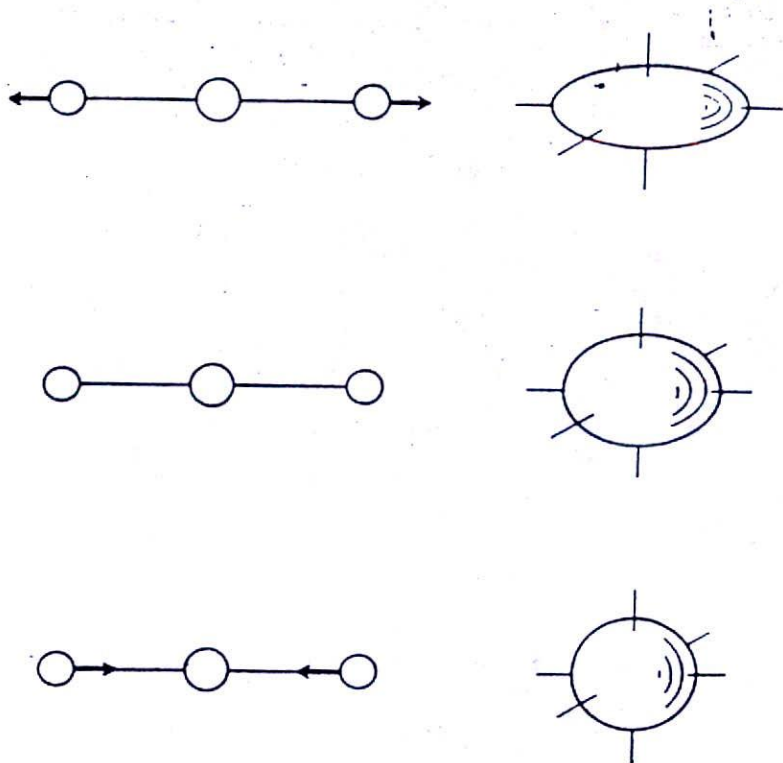


FIGURE 3.4: Change in the polarizability ellipsoid during the symmetrical stretching frequency (ν_1) of CO_2 : since the other modes ν_2 and ν_3 (Fig. 3.3) cause no change in polarizability they are not shown.

Deformation of a molecule during a normal vibration may affect the polarizability ellipsoid in several different ways. It may cause an alteration in the size and/or shape of the ellipsoid and/or it may lead to a change in the orientation of the polarizability ellipsoid in space; i.e., either distortion of the ellipsoid or a change in its orientation in space leads to a Raman active vibrational mode.

In the case of the asymmetric stretching mode ν_2 of carbon dioxide, and the bending mode ν_3 , the vibrations do not change the axes of the polarizability ellipsoid away from the fixed x , y , and z axes. Moreover since the polarizability will have, by symmetry, identical values x' at the two extremes of vibration

$$x' = x_0 + (\partial x / \partial q)_0(+q) = x_0 + (\partial x / \partial q)_0(-q)$$

and it follows that $(\partial x / \partial q)_0$ must be zero; hence $x' = x_0$, i.e., the polarizability is unchanged during the vibration.

Carbon dioxide is an example of a molecule with a center of symmetry.

The result that the infrared spectrum and the Raman spectrum are mutually exclusive, i.e., those frequencies that are active in the Raman are inactive in the infrared, and vice versa, is a general result that applies to all molecules possessing a *center of symmetry*. In particular the frequencies that are Raman active are totally symmetric with respect to the center of symmetry.

For sulfur dioxide, a bent triatomic molecule, the $3n - 6 = 3$ normal modes of vibration are shown in Fig. 3.5. They are conveniently described as a symmetric stretch ν_1 , a symmetric bend ν_2 , and an asymmetric stretch ν_3 . In the case of the symmetric stretch, the polarizability ellipsoid breathes with the

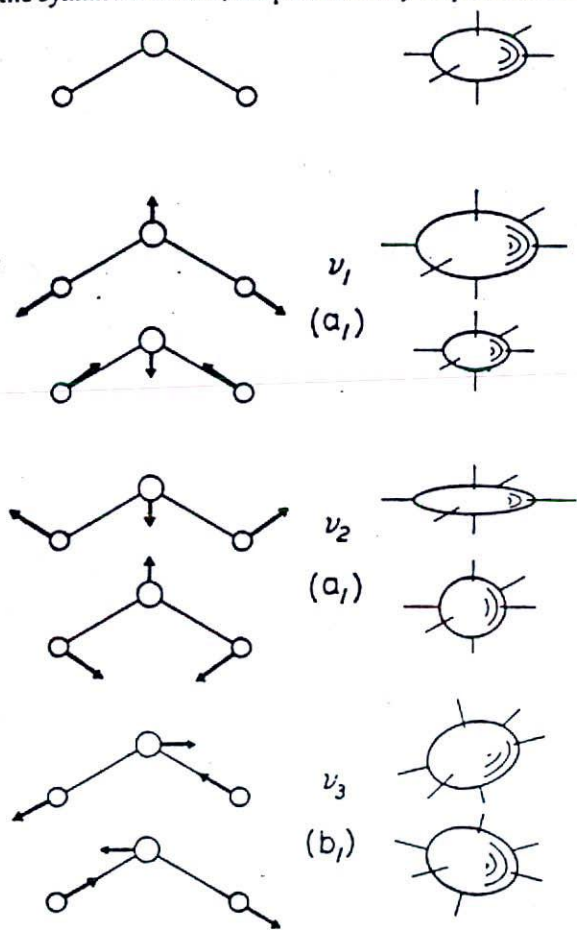


FIGURE 3.5: Normal modes of vibration and polarizability ellipsoids for SO_2 ; the two extreme displacements are shown for each vibration with the polarizability changes exaggerated.

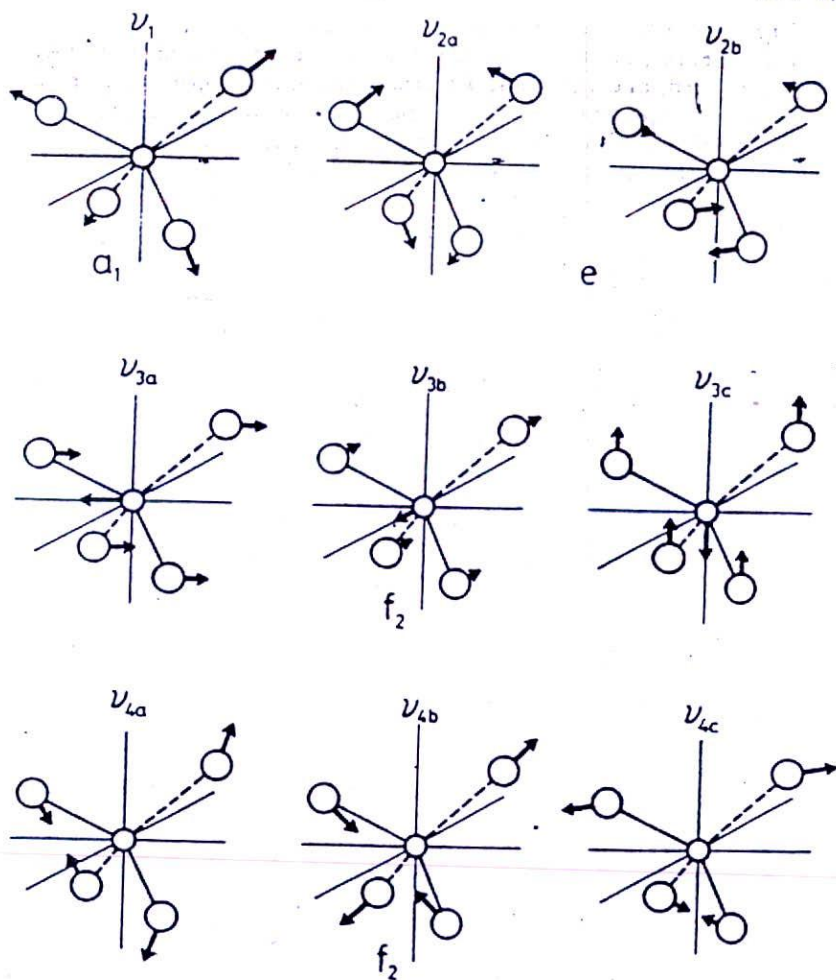


FIGURE 3.6: Normal modes of vibration for CCl_4 .

vibrational frequency as does the bend. Therefore both ν_1 and ν_2 are Raman active. For the asymmetric stretching mode ν_3 the size of the polarizability ellipsoid does not change with time, but its axes oscillate with respect to the fixed axes during the vibration. This fundamental vibration mode is therefore also active in the Raman by virtue of the oscillation of the axes of the polarizability ellipsoid relative to the fixed coordinate axes of the molecule. Thus all three normal vibrations are active in the Raman. They are also active in the infrared because in each instance the dipole moment of the molecule changes during the vibration.

A more complicated but common example is that of a tetrahedral molecule such as carbon tetrachloride. For this molecule the $3n - 6 = 9$ fundamental modes give rise to four Raman lines of which two are the only lines observed in the infrared spectrum. The normal vibrational modes are shown in Fig. 3.6.

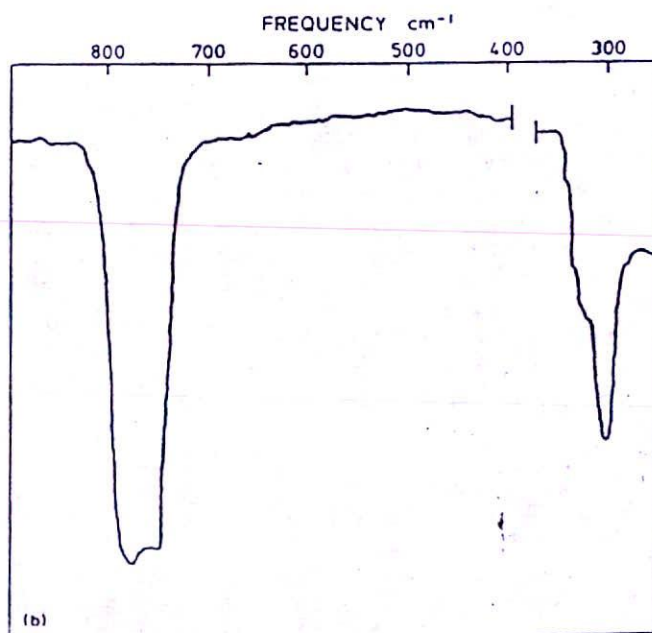
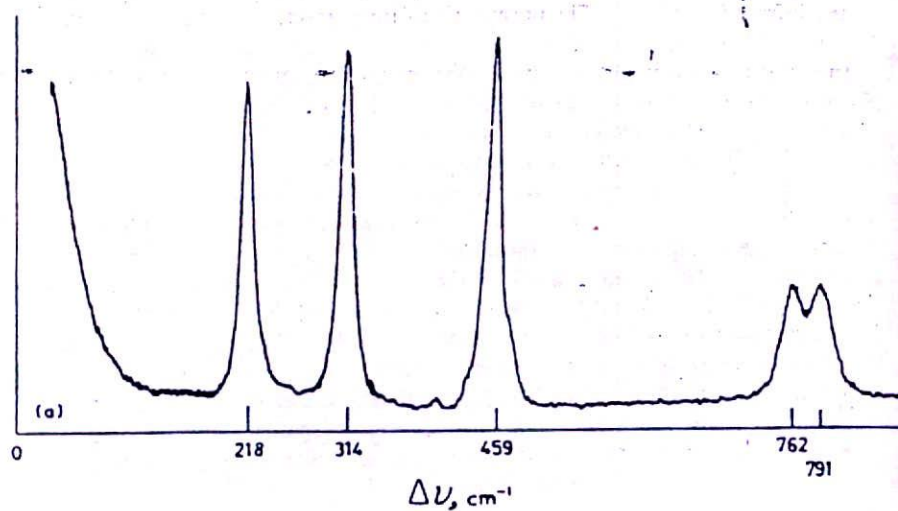
In carbon tetrachloride, because of the tetrahedral symmetry, one of the Raman-only active vibrations is doubly degenerate (E), and the two frequencies that are active in both the infrared and Raman are each triply degenerate (F_2). In the symmetric stretch ν_1 the polarizability ellipsoid, which is spherical in the equilibrium configuration of the molecule, breathes with the frequency of the vibration so that it remains spherical but changes in size. Hence ν_1 is Raman active, and since the initially zero dipole moment remains zero during the vibration, it is forbidden in the infrared. For the ν_2 bending vibration (doubly degenerate mode), the polarizability ellipsoid is distorted from spherical, but the dipole moment remains zero because the changes in the two halves of the molecule (above and below the xy plane) produce equal and opposite effects (this is most clearly seen in ν_{2a} , Fig. 3.6). Hence ν_2 is Raman active but infrared inactive. In the bending mode ν_4 (triply degenerate), for which there is a threefold axis of symmetry (conveniently chosen as either the x or the y or the z axis) the polarizability ellipsoid becomes distorted and the dipole moment becomes nonzero during the vibration. Thus the vibration is active in both the Raman and infrared. Similar considerations apply to ν_3 . The Raman and infrared spectra of CCl_4 are shown in Fig. 3.7.

Thus we have seen that in the vibrational spectrum of a molecule the fundamental vibrational frequencies may be Raman active and infrared inactive if a particular vibration involves a change in the polarizability but no change in the dipole moment; Raman active and infrared active if the vibrational mode causes no change in the polarizability but a change in the permanent dipole moment; active in both Raman and infrared if the vibration causes a change in both the polarizability and dipole moment, and forbidden in both Raman and infrared if neither the polarizability nor the dipole moment changes during the course of the vibration. The total number of observable vibrational frequencies and their activity in the Raman and infrared is determined by the symmetry properties of the particular molecule.

Thus observation of both the Raman and infrared spectra of a molecule provides important information regarding its geometric shape. Indeed in order to obtain a complete vibrational analysis of a molecule, both Raman and infrared spectra are important and usually necessary.

In the analysis of spectra it is convenient to classify the normal vibrations of a molecule into symmetry types by the methods of group theory (see e.g., Ref. 11).

The symmetry type or species of a vibration is indicated by a symbol; those proposed by Mulliken¹² are used almost universally for nonlinear molecules.

FIGURE 3.7: The Raman and infrared spectra of CCl_4 .

For linear molecules a convention established for electronic states is usually followed. Only Mulliken symbols will be discussed since the qualitative organic spectroscopist is rarely concerned with linear molecules. Furthermore no attempt will be made to discuss here the group theoretical arguments used to classify vibrations into species. These are fully covered in several textbooks (e.g., Ref. 11). We attempt only to give the reader a reasonable understanding of such a classification once it has been made.

A Mulliken symbol is one of the letters A , B , E , or F (T is used instead of F by some authors) to which subscripts or superscripts may be added. The symbols A and B are used exclusively for nondegenerate vibrations; E indicates a doubly degenerate vibration and F a triply degenerate vibration. Further distinctions for nondegenerate vibrations are easily understood by using a set of rules after one additional point has been discussed.

As we have discussed previously, molecules in their equilibrium positions may possess certain symmetry elements, but the configurations of the nuclei when displaced in a vibrational mode may not have the same symmetry as in the equilibrium configuration. If a given symmetry element of the equilibrium configuration is also present in the displaced configuration, the element is said to be "preserved," and the vibration is symmetric with respect to that symmetry element. If a symmetry element of the equilibrium configuration is not present in the displaced configuration, the element is not preserved, and the vibration is said to be "asymmetric" with respect to that element. As an example, consider the SO_2 molecule shown in Fig. 3.5. The molecule in its equilibrium configuration has C_{2v} symmetry, i.e., a twofold axis C_2 passing vertically through the sulfur atom, a vertical plane σ_v bisecting the OSO angle and perpendicular to the plane of the molecule and a second vertical plane σ_v' containing all three atoms. The displaced configuration for each vibration is obtained by moving each atom to the head of the arrow attached to it. (Since the atoms vibrate in phase, any other configuration occurring during the vibration will have the same symmetry.) The modes ν_1 and ν_2 are clearly symmetric with respect to all three symmetry elements. However the mode ν_3 is asymmetric with respect to C_2 and σ_v' , but symmetric with respect to σ_v , since all three atoms remain in this plane throughout the vibration.

The following rules explain the Mulliken symbols for *nondegenerate* vibrations:

1. A designates a vibration that is symmetric with respect to the principal axis (i.e., the axis of highest order). B designates a vibration that is asymmetric with respect to the principal axis.
2. Subscripts 1 and 2 designate vibrations that are, respectively, symmetric and asymmetric with respect to a twofold axis perpendicular to the principal axis, or, if these are absent, with respect to vertical planes.
3. Superscripts ' and " designate vibrations that are, respectively, symmetric and asymmetric with respect to a horizontal plane.

4. Subscripts g and u designate vibrations which are, respectively, symmetric and asymmetric with respect to a center of symmetry.

No more than two of the qualifying symbols in rules 2, 3, and 4 are needed in any one case, i.e., we find Mulliken symbols A , B_2 , A_2' , B_{1u} , for example, but not symbols of the type A_{1g} .

The symbols E and F may also carry subscripts and superscripts which follow definite rules. However in these cases the rules can only be stated mathematically. Most experimental spectroscopists do not concern themselves with the origin of the subscripts and superscripts that may accompany E and F , and we shall not do so here.

For linear molecules the symbols Σ^+ , Σ^- , and Π are equivalent to A' , A'' , and E , respectively. The subscripts g and u have the same meaning as in the case of nonlinear molecules.

One of the advantages of symmetry classification is that selection rules need not be worked out for each molecule separately. Once a molecule is classified into the appropriate symmetry class (point group), standard tables for the particular point group can be used.¹¹ In addition only totally symmetric vibrations (those of species A , A_1 , A_1' , A_g , A_{1g} , and A_g') will be polarized in the Raman spectrum (Section 3.2E).

Table 3.1 gives the selection rules for some common point groups. The reader should verify that use of this table leads to the same conclusions about Raman and infrared activity of the vibrations shown in Figs. 3.3, 3.5, and 3.6 for CO_2 , SO_2 , and CCl_4 as do considerations of change in dipole moment and polarizability. Note that a given molecule will not necessarily have vibrations belonging to all the species possible for that point group.

E. POLARIZATION MEASUREMENTS

An additional feature of Raman spectra is the ability to detect experimentally which of the observed fundamental modes are totally symmetric.

This kind of information is obtained experimentally most easily by irradiating the sample with plane-polarized light and examining the Raman scattering at right angles to the direction of incidence in two cases: where light incident in, say, the z direction is polarized, respectively, parallel to and perpendicular to the xy plane (Fig. 3.8). If the intensity of scattered light from light polarized parallel to the xy plane is I_{\parallel} and that from light polarized perpendicular to the xy plane is I_{\perp} , then the *depolarization factor* ρ is given by

$$\rho = I_{\perp}/I_{\parallel}$$

Born¹² has shown theoretically that for Rayleigh scattering ρ is given for a random arrangement of molecules in a fluid (liquid or gas) by

$$\rho = 6\gamma^2/(45\alpha^2 + 7\gamma^2)$$

where a , the mean value invariant, is given by

$$a = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

and γ , the anisotropy invariant, is given by

$$\gamma = \frac{1}{2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2]$$

Thus a is, roughly speaking, a measure of the size of the polarizability ellipsoid and γ a measure of the extent of distortion of the shape of the polarizability ellipsoid from spherical.

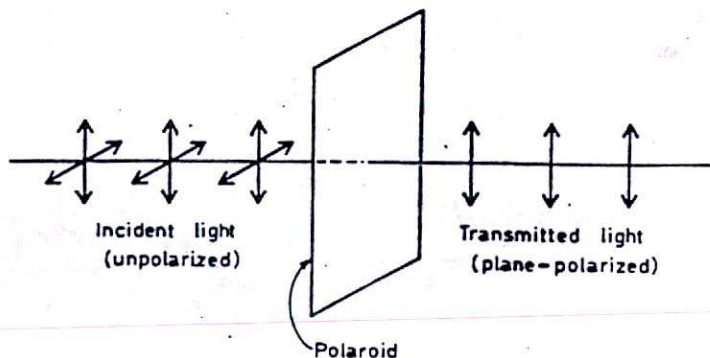


FIGURE 3.8: The production of polarized light.

In Raman scattering we are concerned with the derived tensor α'_0 rather than with the polarizability α_0 , and although it cannot be represented by an ellipsoid, nevertheless it possesses by analogy with α_0 a mean value invariant a' and an anisotropy invariant γ' , and the degree of polarization of the Raman line is given by

$$\rho = 6(\gamma')^2/[45(a')^2 + 7(\gamma')^2]$$

Thus the following possibilities are evident:

1. For $a' = \gamma' = 0$ the Raman line is said to be "forbidden."
2. For $a' \neq 0$, and $\gamma' = 0$, $\rho = 0$ and the Raman line is "completely polarized."
3. For $a' = 0$ and $\gamma' \neq 0$, $\rho = \frac{6}{7}$ and the Raman line is said to be "depolarized."
4. In all other cases $a' \neq 0$ and $\gamma' \neq 0$ and the value of ρ is between zero and $\frac{6}{7}$. The line is said to be "polarized."

Each coefficient of α'_0 is related to the corresponding coefficient of α_0 by an equation of the kind $\alpha'_{xx} = (\partial \alpha_{xx} / \partial q)_0$ (see Section 3.2D), i.e., $a' = (\partial a / \partial q)_0$, however $\gamma' \neq (\partial \gamma / \partial q)_0$.

TABLE 3.1

a. Selection rules for some common point groups			
Point group	Infrared active species	Raman active species*	Example
C_1	A, B	A, B	H_2O_2
C_2	A', A''	A', A''	$CHDCl_2$
C_{2v}	A_1, B_1, B_2	A_1, A_2, B_1, B_2	SO_2
C_{3v}	A_1, E	A_1, E	NH_3
D_{3d}	A_{1g}, E_g	A_{1g}, E_g	C_6H_{12}
D_{3h}	A_{1g}, E_{1g}	A_{1g}, E_{1g}, E_{2g}	C_6H_6
T_d	T_2	A_1, E, T_2	CH_4, CCl_4
$D_{\infty h}$	Σ_g^+, Π_g	$\Sigma_g^+, \Pi_g, \Delta_g$	CO_2

b. Raman and infrared spectra of some simple molecules

Vibrational mode	Frequency, cm^{-1}	
	Infrared	Raman
1. Carbon dioxide, CO_2 , $D_{\infty h}$ (gas)		
$\nu_2 (\Pi_g)$	667	Inactive
$2\nu_1 (\Sigma_g^+)$	Inactive	1286 pol.*
$\nu_1 (\Sigma_g^+)$	Inactive	1388 pol.
$\nu_3 (\Sigma_g^+)$	2349	Inactive
2. Sulfur dioxide, SO_2 , C_{2v} (gas)		
$\nu_2 (a_1)$	519	525 (l) pol.
$\nu_1 - \nu_2 (A_1)$	606	—
$\nu_1 (a_1)$	1151	1151 (g) pol.
$\nu_2 (b_2)$	1361	1336 (l) depol.*
$\nu_2 + \nu_3 (B_1)$	1871	—
$2\nu_1 (A_1)$	2305	—
$\nu_1 + \nu_3 (B_1)$	2499	—
3. Boron trifluoride, BF_3 , D_{3h} (gas)		
$\nu_2 (e')$	480*	480* depol.
	482	482
$\nu_1 (a_1')$	691*	Inactive
	720	Inactive
$\nu_1 (a_1')$	Inactive	888 pol.
$\nu_3 (e')$	1446*	—
	1497	—
4. Carbon tetrachloride, CCl_4 , T_d (liquid)		
$\nu_2 (e)$	Inactive	218 depol.
$\nu_1 (f_2)$	305	314 depol.
$\nu_1 (a_1)$	Inactive	458 pol.
$\nu_2 (f_2)$	768	762 depol.*
$\nu_1 + \nu_4 (F_2)$	797	791 depol.*

TABLE 3.1 (continued)

Vibrational mode	Frequency, cm^{-1}	
	Infrared	Raman
5. Chloroform, CHCl_3 , C_{3v} (liquid)		
$\nu_1 (e)$	260	262 depol.
$\nu_2 (a_1)$	364	366 pol.
$\nu_3 (a_1)$	667	668 pol.
$\nu_4 (e)$	760	761 depol.
$\nu_5 (e)$	1205	1216 depol.
$\nu_6 (a_1)$	3033	3019 pol.
6. Ethylene, C_2H_4 , D_{2h} (gas)		
$\nu_1 (a_g)$	Inactive	Inactive
$\nu_2 (b_{2g})$	Inactive	943 depol.
$\nu_3 (b_{1u})$	949	Inactive
$\nu_{10} (b_{2u})$	995	Inactive
$\nu_4 (b_{1u})$	Inactive	(1050) ^f
$\nu_5 (a_g)$	Inactive	1342 pol.
$\nu_{11} (b_{2u})$	1443	Inactive
$\nu_6 (a_g)$	Inactive	1623 pol.
$\nu_{11} (b_{2u})$	2990	Inactive
$\nu_7 (a_g)$	Inactive	3019 pol.
$\nu_8 (b_{2u})$	3106	Inactive
$\nu_9 (b_{1u})$	Inactive	3272 depol.

^a The species symbols follow a common convention that lower-case symbols are used for fundamentals and upper-case symbols for overtones and combination bands.

^b State of polarization of Raman lines: pol., polarized; depol., depolarized.

^c All bands except ν_1 , in which the boron atom does not move, show isotope splitting due to ^{10}B and ^{11}B .

^d Fermi resonance.

^e Estimated at 825 cm^{-1} from $2\nu_7 (A_g) = 1656$ observed in the Raman.

^f Should be Raman active, but is not observed. The frequency was estimated from $\nu_4 + \nu_{10} (B_{2u}) = 2047 \text{ cm}^{-1}$ and $\nu_{10} = 995 \text{ cm}^{-1}$.

F. RULES OF SELECTION AND POLARIZATION

We have seen previously that the vibrations of a molecule can affect the polarizability ellipsoid in three ways: by changing its size and/or shape and/or its orientation with respect to the fixed coordinates of the molecule.

1. Asymmetric Vibrations

We saw previously that for the asymmetric stretching vibration of the SO_2 molecule ν_3 the size of the polarizability ellipsoid remained unchanged during the vibration, i.e., $a' = 0$, but that its orientation with respect to the fixed

axes changed, i.e., $\gamma' \neq 0$. Thus the vibration obeys rule 3 and will have $\rho = \frac{2}{3}$.

This result is generally true for all asymmetric vibrations.

Rule: All asymmetric vibrations give depolarized Raman lines.

If in addition to the size of the polarizability ellipsoid remaining unchanged its orientation is also unaltered, because of some other symmetry property of the molecule, for example, as in the asymmetric stretching vibration of the linear CO_2 molecule, then γ' is also zero and the Raman line is forbidden, i.e., that frequency is inactive in the Raman (rule 1).

2. Degenerate Vibrations

In the degenerate ν_2 bending mode of CCl_4 , the size of the polarizability ellipsoid remains unchanged, but the shape changes. Thus $a' = 0$ and $\gamma' \neq 0$ and $\rho = \frac{1}{3}$, i.e., the Raman line is depolarized (rule 3). This is again a general result.

Rule: All degenerate vibrational modes give depolarized Raman lines.

3. Symmetric Vibrations

In symmetric vibrations the size of the polarizability ellipsoid changes during the vibration, $a' \neq 0$ and $\gamma' \neq 0$, and $\rho < \frac{1}{3}$, i.e., the Raman line is polarized (rule 4).

Rule: All totally symmetric vibrations are active in the Raman and polarized.

In the special case where the polarizability ellipsoid is spherical $a' \neq 0$, but $\gamma' = 0$, and the Raman line is completely polarized (rule 2). An example is the totally symmetric breathing frequency ν_1 of CCl_4 .

The state of polarization expected for the Raman frequencies of molecules in certain point groups are shown in Table 3.1.

3.3 EXPERIMENTAL

A. LIGHT SOURCES

Since Raman scattering is of relatively low intensity, the first requirement experimentally is for a very intense monochromatic light source of an appropriate wavelength that is not absorbed by the material under investigation. The most widely used source is the mercury emission lamp, which gives strong lines at 2537, 3650, 4057, 4358, 5461, 5770, and 5790 Å. The very intense blue 4358 Å line is usually used for obtaining spectra from colorless liquids and solutions, and the green line at 5461 Å for the spectra of colored

(yellow) substances. The 4358 Å line is particularly suitable since it is relatively far away from the line at 5461 Å. To provide a relatively monochromatic source wavelengths other than those required are eliminated by using appropriate filters such as those shown in Table 3.2.

In the early days of Raman spectroscopy simple high pressure lamps were employed which were capable of giving only relatively low intensities so that Raman spectra were obtained only with difficulty by using very sensitive photographic plates for detection, and even then very long exposure times were generally required. In addition this kind of lamp gives an undesirable

Table 3.2: Filters for Mercury Lamps

Exciting line, Å	Filter
2537	Mercury vapor
3650	Corning filter 7-51, or Eastman Kodak glass filter 18A
4047	Sodium nitrite solution, or Corning filter 5-58, or Eastman Kodak Wratten 2B filter, to remove 3650-Å line
4358	Solution of iodine in carbon tetrachloride, or 0.003 M potassium ferricyanide solution, to remove 4358-Å line
5461	Rhodamine 5GDN dye (DuPont), 0.009% solution slightly acidified with HCl, to remove higher wavelengths
	Basic sodium chromate (pH 8.7) for lines below 5461 Å; cupric nitrate solution; saturated neodymium chloride solution

continuous background. However in recent years H. L. Welsh and his co-workers at the University of Toronto¹⁴ have developed low pressure helical mercury lamps which give very high intensities free of continuous background. These enable spectra of, for example, liquid samples to be obtained within a few minutes exposure time.

The so-called Toronto arc requires high currents (of the order of 10 to 30 A), and thus the electrode pools have to be cooled and in some versions of the lamp a cooling coil passes through the center of the helix. The original lamp consisted of a four-turn spiral of Pyrex tubing; however, we have constructed similar lamps in our laboratory in recent years with as many as six turns (Fig. 3.9) and have obtained excellent results using currents up to 15 A without the necessity of cooling the helix. To start the lamp the mercury pools around the electrodes are preheated electrically for a few minutes and the emission then induced by means of a tesla coil held against a piece of aluminum foil that is wound around the helix. As soon as emission starts the cooling water through the electrodes is turned on.

Sources containing other metals and helium arcs have also been developed¹⁵⁻¹⁸ specifically for the study of colored compounds. In particular Ham and Walsh¹⁶ have described a microwave-powered source for use with many types of lamp.

Very recently an important advance in technique has been the introduction of the laser as a Raman source.¹⁹ The He-Ne laser is the most commonly used and gives a strong red monochromatic line a few hundredths of an Angstrom wide free from other emission lines or continuous background. This source has now been introduced in some of the commercial spectrometers such as the Cary model 81 and the Perkin-Elmer models LR-1 and LR-2. It seems quite possible that the introduction of the laser will make it possible to use Raman

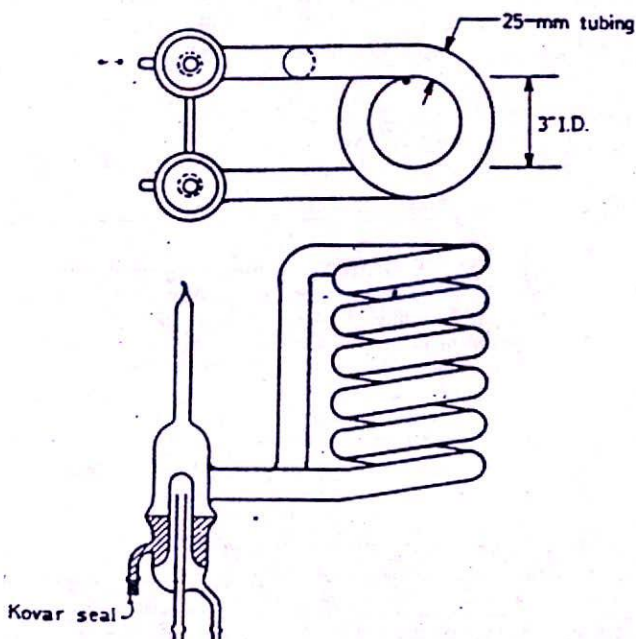


FIGURE 3.9: The Toronto arc.

spectroscopy as a routine tool for the examination of quite small quantities of both colorless and highly colored materials. The most suitable laser presently available appears to be the Spectral-Physics model 125 He-Ne 50- μ W source which emits at 6328 Å. However, developments in this field are so rapid that it is to be expected that other sources will be available in the near future.

B. SPECTROMETERS

In this section we shall describe only the most commonly used instruments; namely, the Hilger E612, the Cary model 81, and the Perkin-Elmer LR-1 (and LR-2) spectrometers.

The Hilger E612 instrument (Hilger and Watts, England), is a spectrograph employing two large glass prisms for dispersion and can be used either as a photographic or as a photoelectric recording instrument. The instrument with photographic detection is of moderate expense and therefore perhaps the most widely encountered. It is, however, confined, without adaptation, to the use of a mercury source. A simple schematic layout is shown in Fig. 3.10 and the instrument itself in Fig. 3.11. The Raman source in the commercial instrument is composed of four straight-tube low pressure mercury lamps which surround the sample cell, and relatively high intensity is obtained by enclosing the lamps in a magnesium oxide-coated reflector (Fig. 3.12).

The instrument consists of a solid cast-iron base to which is screwed the collimator and the box casting containing the prisms. Two cameras may be used for recording the spectra and in the purely photographic instrument are interchangeable in position, each being fixed onto an arm that can be rotated to bring either camera into action as desired. Plate holders for each camera are set in frames that can be raised or lowered to allow several spectra to be recorded on the same photographic plate. The spectrometer is calibrated by means of a standard iron or copper arc and functions best in a temperature-controlled room. The adjustable slit, with stainless-steel jaws, is mounted on the front of the collimator and is fitted with a shutter, reducing wedge, and Hartmann diaphragm. The collimator has a lens aperture of 86 mm and a focal length of approximately 60 cm. The camera that gives the greatest dispersion has a relative aperture of $f/5.7$ and gives a spectrum 86 mm in length, covering the range 3900 to 6300 Å. The inverse dispersion on the plate is 16 Å/mm at 4358 Å. Photographic plates, in size $3\frac{1}{2} \times 4\frac{1}{2}$ in., that are most suitable for use with the Hilger E612 are Eastman Kodak type 103a-O or 2a-O for Raman lines near to the 4358-Å mercury exciting line, or 103a-J or 103a-G for higher Raman frequencies in the region of 3000 cm^{-1} .

In the recording instrument the short focus camera is replaced by a photomultiplier scanning unit. The light is dispersed in the first passage through the prisms and reflected at a tilted mirror to obtain double dispersion. The mirror rotates automatically at one of four selected speeds and may be set to a calibrated scale. The dispersion at the photomultiplier is $6.8\text{ cm}^{-1}/\text{mm}$ at 4358 Å. The scattered light is monitored relative to the intensity of the source and automatically recorded. The basic photographic instrument may be purchased without the photoelectric recording unit, which can be readily added later.

In our laboratory we have replaced the Hilger-arc assembly by a Toronto arc to give a more flexible unit for some purposes. For example, polarization measurements are easily carried out (Section 3.3D), and a wide variety of Raman sample cells may be used (Section 3.3C).

The Cary model 81 Raman spectrophotometer (Applied Physics Corporation, USA), uses a 3-kw Toronto arc and/or a Spectral-Physics model 125

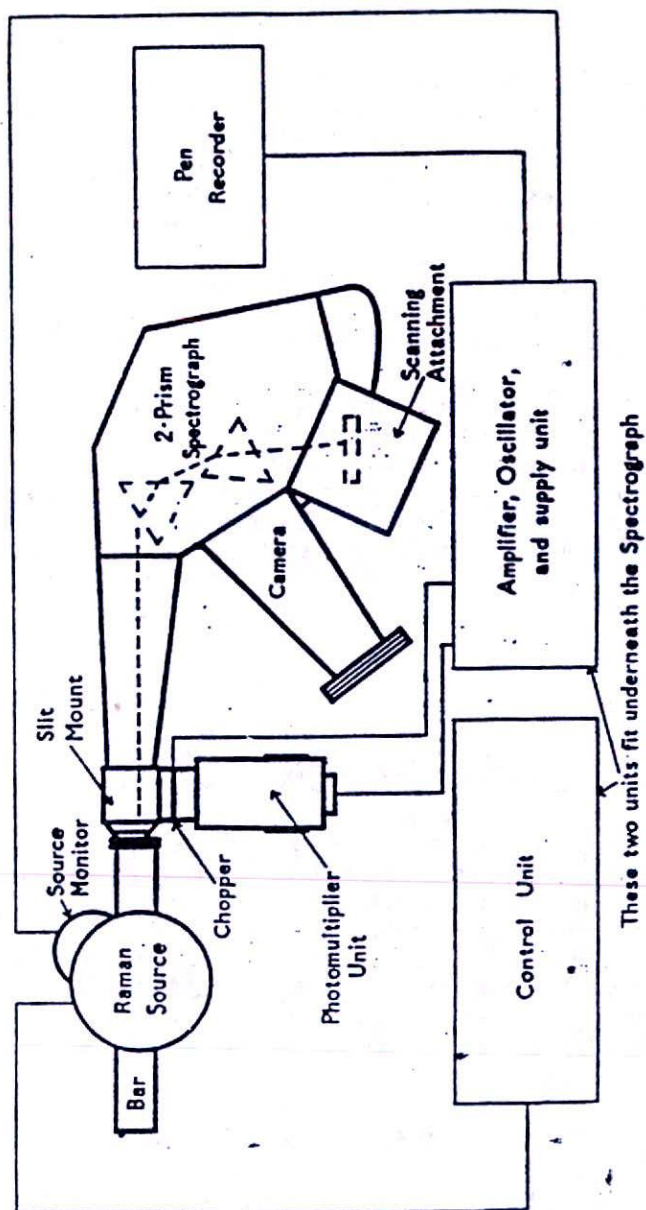


FIGURE 3.10: Schematic layout of the Hilger E612 spectrograph.

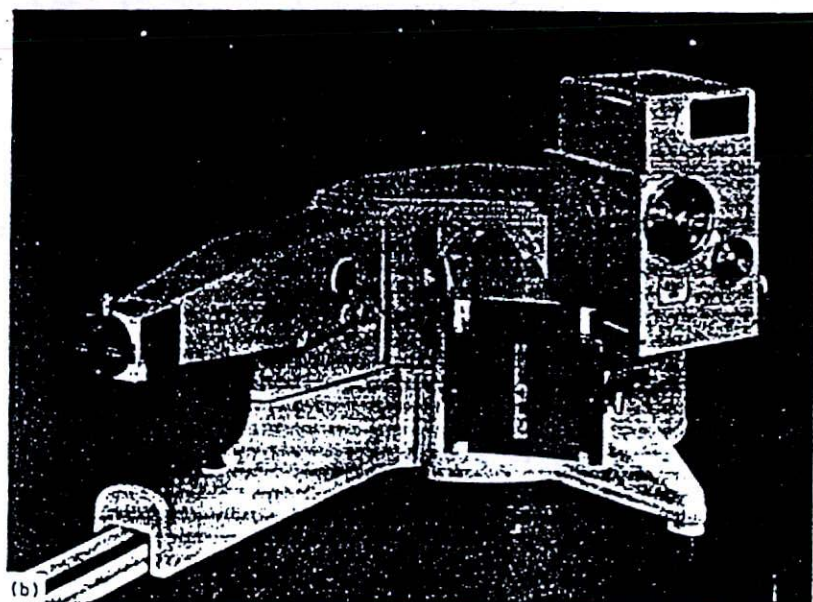
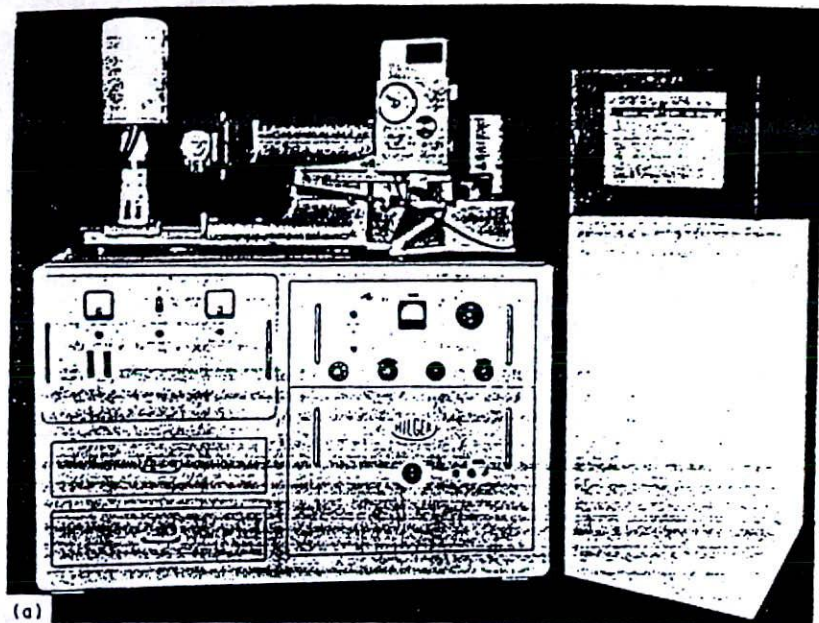


FIGURE 3.11: The Hilger E612 spectrograph.

He-Ne laser as source. Three versions are available; Toronto arc only (with provision for the later installation of the laser source), laser source only, and a version with both Toronto arc and laser.

The Toronto arc is of Corning 1720 glass tubing in the form of a helix that surrounds the sample cell. The helix is cooled with air from two blowers

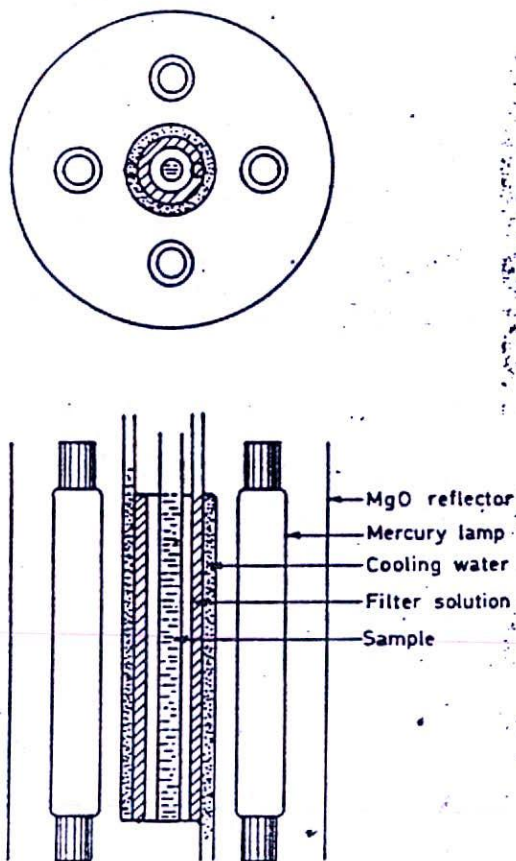


FIGURE 3.12: The Hilger source.

and the electrodes are cooled with thermostated circulating water that keeps the mercury vapor pressure low and thus reduces the lamp continuum. A cylindrical glass-filter jacket is located between the lamp and the sample, and a filter solution is circulated through the jacket. The filter solution is cooled and thermostated to keep the sample cool. Sample cells are mounted horizontally on the axis of the lamp and filter jacket. The optical system is shown schematically in Fig. 3.13 and the instrument in Fig. 3.14.

A unique feature of the Cary model 81 spectrophotometer is its use of image slicers (Fig. 3.15, items G and H) between the sample cell and entrance slit. These make it possible to use the rays from the entire end of the sample cell rather than just a narrow strip down the middle as in conventional spectrometers. The image from the end of the cell is divided into 20 strips which

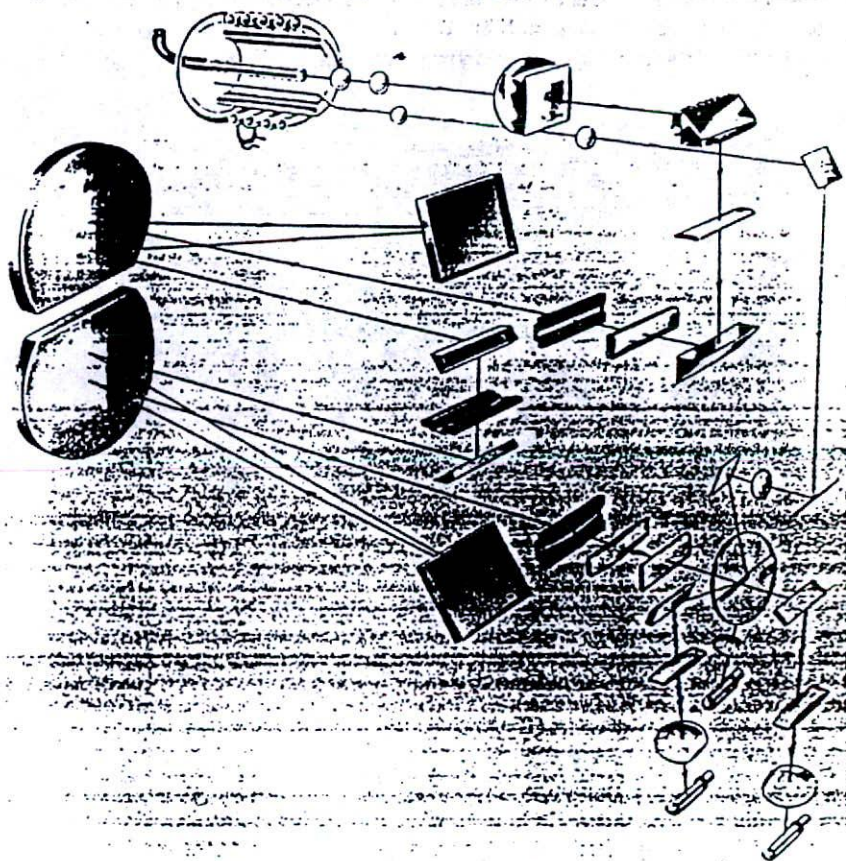


FIGURE 3.13: The Cary model 81 spectrophotometer—schematic layout of the optical system used in conjunction with the Toronto arc.

are superimposed in two sets of 10 strips each and then magnified to the exact size required to fill the double entrance slit. The monochromator is a dual grating, twin slit, double monochromator and has a focal length of 1000 mm. It is designed to give increased light-gathering power and is free from the effects of Tyndall and Rayleigh scattering in the sample. This greatly reduces the difficulty in sample preparation since the double monochromator rejects

scattered light, enabling the cell walls and other sources of scattered light to be viewed. Thus advantage may be taken of total reflection at the walls of the sample tubes to effectively increase the length of small diameter tubes many times. The gratings are ruled with 1200 lines/mm. High stability is achieved in the Cary model 81 by means of a chopped-radiation photometric system designed to retain the stability of such systems, but avoiding the 50% loss of light that normally results from chopping. A rotating semicircular

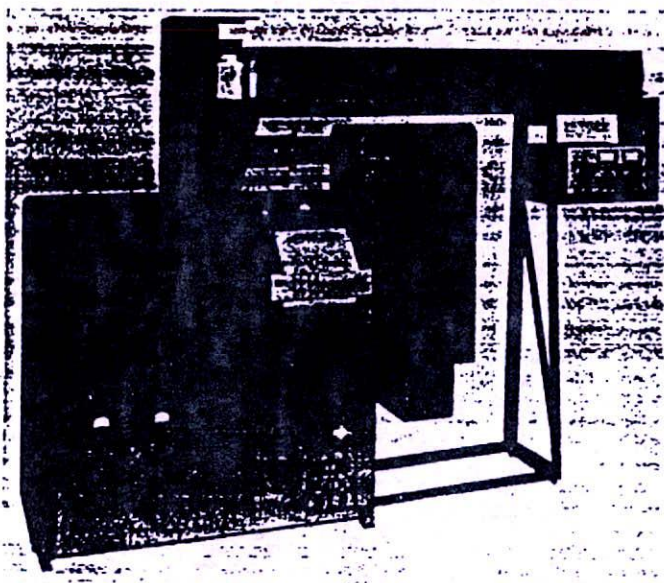


FIGURE 3.14: The Cary model 81 spectrophotometer.

mirror directs the radiation alternately to two phototubes each of which develops an independent Raman signal. The signals are later combined with a consequent improvement in the signal-to-noise ratio. At the same time non-dispersed light from the lamp is chopped by the same mirror and directed to a reference phototube.

The performance and areas of application of the Cary model 81 spectrophotometer have been increased by the introduction of the He-Ne laser source since the narrow intense line at 6328 Å that this emits can give Raman spectra from many fluorescing and most strongly colored compounds. A further advantage is the use of axial excitation in conjunction with a capillary liquid sample cell which permits an order of sample size comparable to that used in microinfrared work. The optical system of this spectrometer is shown in Fig. 3.15.

Two spectrophotometers with He-Ne laser sources have recently been developed by the Perkin-Elmer Corporation. The Model LR-1 is shown in Fig. 3.16 and diagrammatically in Fig. 3.17. It consists of a compact optical

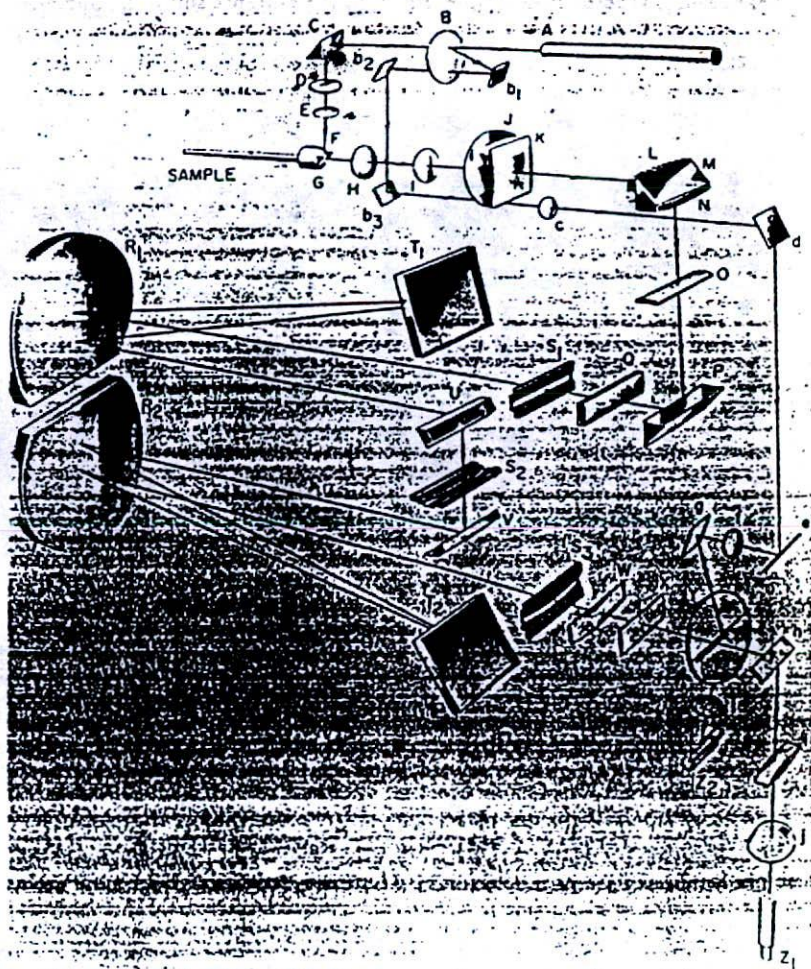


FIGURE 3.15: The Cary model 81 spectrophotometer—schematic layout of the optical system used in conjunction with the laser source.

unit and an associated electronics rack which contains the recorder and other electrical components, which are cable connected to the optical unit. A Perkin-Elmer model 5320 He-Ne gas laser mounted horizontally is used for excitation, and its beam falls on the sample cell, which is slightly wedge-shaped in order to permit multiple traversals of the incident light and hence

insure maximum excitation. Approximately 150 passes are thus made in a standard 5 ml cell. Scattered light is viewed at 90° with respect to the incoming beam and is focused by a simple lens onto the entrance slits of a double-pass monochromator equipped with a 1440 lines/mm replica diffraction grating blazed at 6200 \AA in the first order. An analyzer prism is mounted between the sample and the monochromator to measure the degree of polarization (Section 3.2E). It is removed when not in use. The monochromator may be

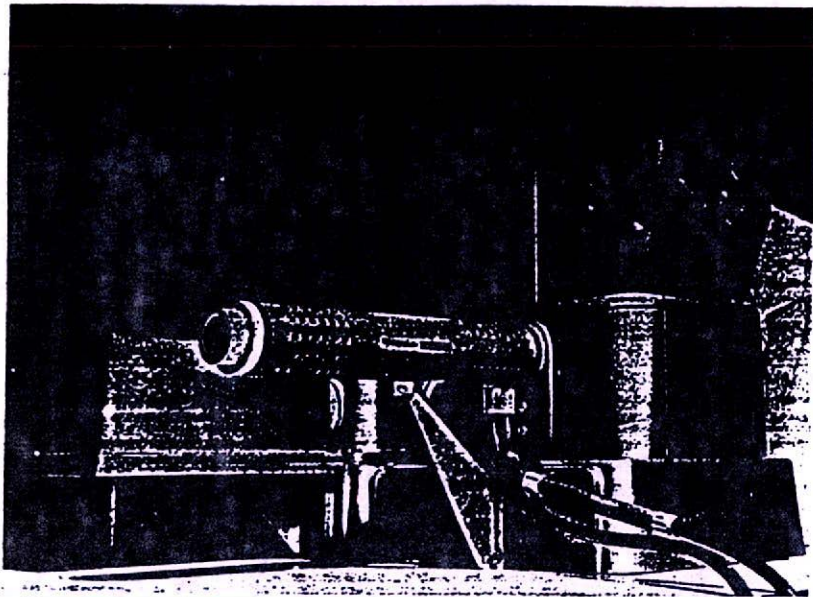


FIGURE 3.16: The Perkin-Elmer LR-1 spectrophotometer.

scanned either manually or by means of a multispeed automatic wavelength drive for Raman shifts from 0 to 3800 cm^{-1} . A 14 stage multiplier phototube is used as a detector. Its output is fed through an amplifier and displayed on a strip-chart recorder.

Recently the Spectro-Physics laser has been introduced as part of the LR-1 and an LR-2 is being developed. The latter features the Spectro-Physics laser and an improved monochromator.

C. SAMPLING TECHNIQUES

Gases, liquids, and solids can be studied by Raman spectroscopy, but different types of cell are normally required to obtain the spectra in each phase. Liquids and solutions present the least difficulties.

BLOCK DIAGRAM
LASER-RAMAN SPECTROMETER

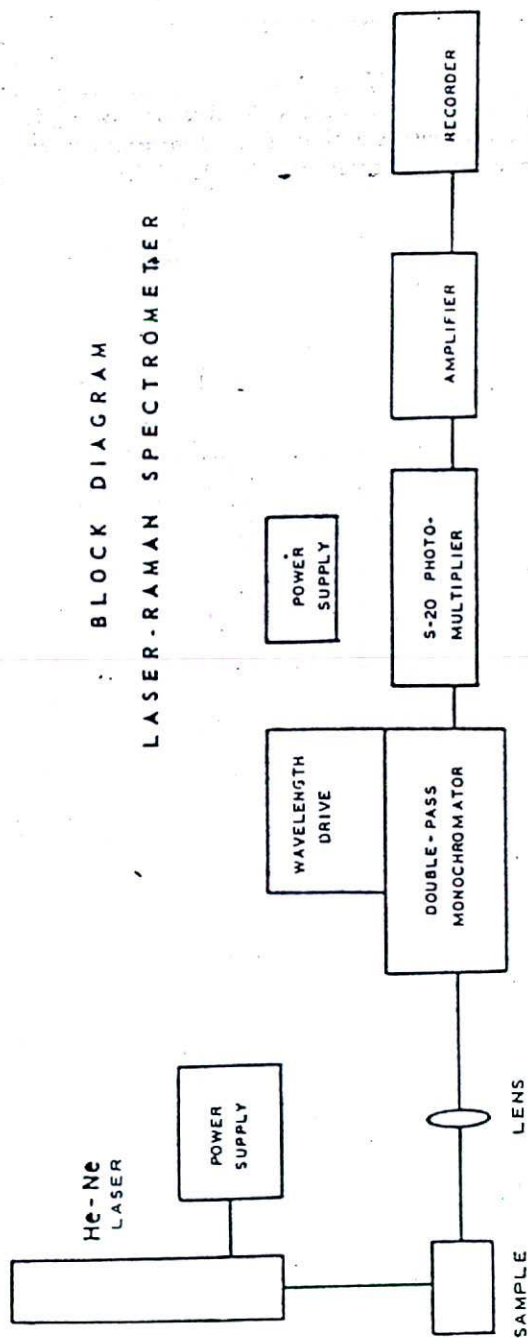


FIGURE 3.17: Schematic diagram of the Perkin-Elmer LR-1 spectrofluorometer.

The Hilger E612 spectrometer with the Hilger lamp assembly holds a simple glass cell for liquids of 7-ml capacity which fits inside a coaxial jacket. The jacket consists of three isolated concentric tubes and allows both cooling water and a filter solution to be placed between the lamp and sample. The

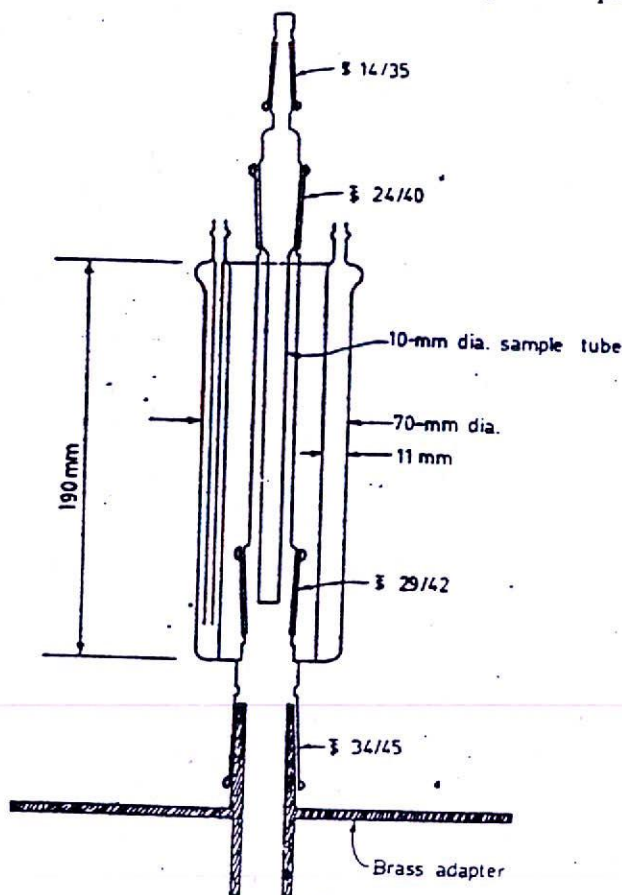


FIGURE 3.18: Raman cell used with a Hilger E612 spectrometer and Toronto-arc source.

Raman cells are straight cylindrical glass tubes with optically flat glass windows fixed to their lower ends.

In our laboratory replacement of the Hilger source by a large Toronto arc has given a more convenient arrangement for some purposes. It can be adapted for the study of liquids at high or low temperatures and for the study of solids. A variety of designs of Raman cells have been used with this

apparatus, which is shown schematically in Fig. 3.18. Provision of a standard tapered brass joint at the base of the filter jacket, and a standard glass joint inside it, allows for the rapid interchange of cells and easy access to the sample, and enables the cells to be surrounded by polaroid cylinders for polarization measurements (Section 3.3D).

In the Cary model 81 spectrophotometer with Toronto-arc source a wide range of cells is available. Some of these are shown in Fig. 3.19. The 7-mm

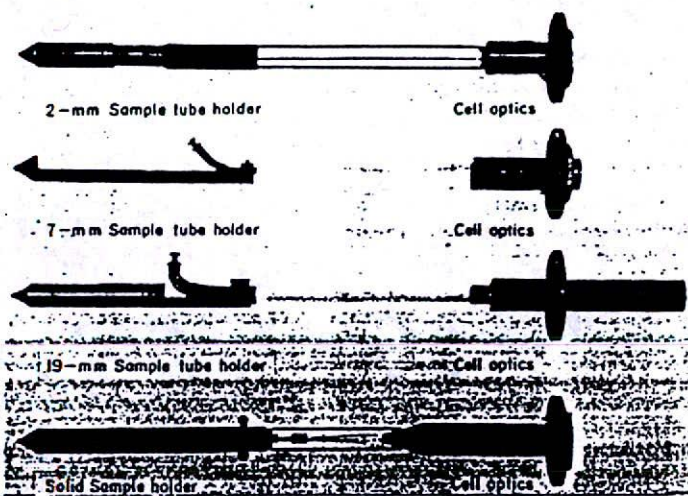


FIGURE 3.19: The Cary model 81 spectrophotometer—Raman cells.

outside-diameter cell for liquids has a capacity of 5 ml and the 19-mm outside-diameter cell has a capacity of 65 ml. Two 2-mm cells are available, one with a volume of 0.2 ml and the other with a volume of 0.6 ml. Selection of the most appropriate cell is important. In the 19-mm cell the monochromator does not see the cell walls, whereas the 7-mm and 2-mm cells depend on internal reflection from the wall surface. Therefore the monochromator does see the cell walls and any fluorescence that is developed in them. Thus cell selection becomes important when there is need to minimize cell fluorescence. Modification of the 5-ml cell system to permit more effective collection of the Raman radiation by a multiple reflection optical system has been described by Tunnicliff and Jones.²⁰ R. Norman Jones and co-workers have recently described capillary microcells of two sizes (Table 3.3) for use with the Cary model 81.²¹ One end of the capillary is sealed to obtain a symmetrical meniscus seal free from entrapped air, and the commercial cell holder was used to keep the closed end of the tube in contact with a wide-angled hemispherical collecting lens.

TABLE 3.3: Dimensions of Capillary Raman Tubes Used by Jones and Co-workers²¹

	Effective length, mm	Diameter, mm		Volume, ml	Solute required in different solvents, mg ^a		
		Inside	Outside		CS ₂	CHCl ₃	H ₂ O
Small	225	0.9 ± 0.1	2.0 ± 0.2	0.15	100	200	300
Large	225	1.7 ± 0.1	2.4 ± 0.2	0.50	200	300	300

^a Under favorable circumstances acceptable spectra were obtained with half these amounts.

In the spectrophotometer with laser source a microcell consisting of a capillary tube 5 cm long with a 0.5-mm inside diameter is used. This has a volume of 10 μ liters and can be used with samples as small as 1 μ liter.

For the Perkin-Elmer LR-1 spectrometer several cells are available commercially. The standard cell for liquids has a 2.5-ml capacity (Fig. 3.20). An 0.2-ml liquid cell and a special assembly for the sampling of solid powders is also available.

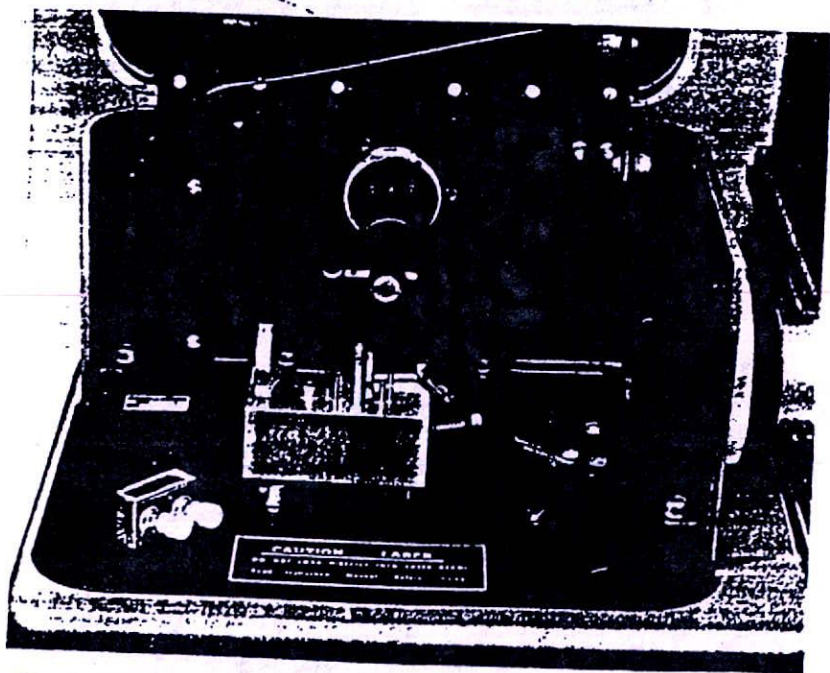


FIGURE 3.20: Cell and cell assembly for use with the Perkin-Elmer LR-1 spectrophotometer.

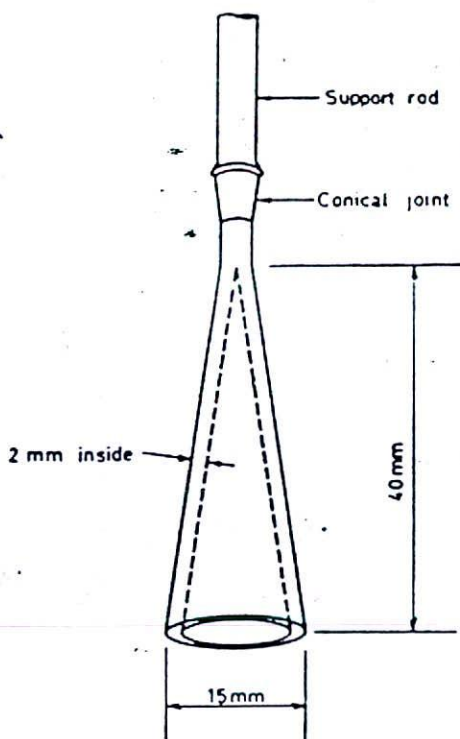


FIGURE 3.21: A Raman cell for solid powders.

The solid sample holder shown in Fig. 3.19 is used with the Cary model 81 spectrometer with Toronto-arc source, while for the instrument with laser source powders and fine crystals can be packed inside the capillary microcell, and large crystals can be mounted at the surface of the sample lens using a specially designed sample holder. Recently a novel cell for solids that can be used with the Hilger E612 spectrometer has been described.²² In this cell a solid powder is held between two concentric glass cones (Fig. 3.21).

The gas cell shown in Fig. 3.22 is used with the Cary model 81 equipped with a special source consisting of two Toronto arcs. It is of the multiple-reflection type and allows the light to pass as many as 44 times through the 20-in. path length of the cell. It has a capacity of 3½ liters and is designed to withstand pressures as high as 10 atm.

D. MEASUREMENT OF DEPOLARIZATION RATIOS

We have seen previously that the determination of the depolarization ratio ρ is important in assigning Raman lines to particular normal vibrations. The

absolute determination of depolarization ratios is difficult experimentally; however, it is sufficient in many studies to determine ρ only approximately.

With the Hilger E612 spectrometer the experimental method normally used is to compare the intensities of the Raman lines obtained in two separate experiments, one using light from the source polarized parallel to the axis of the Raman tube and the other using light polarized perpendicular to the axis of the Raman tube. To do this two polaroid cylinders constructed to fit around the Raman cell are used. One transmits the parallel, and the other the perpendicular, component. The intensities of the spectral lines in the two experiments may be compared using a suitable microdensitometer.

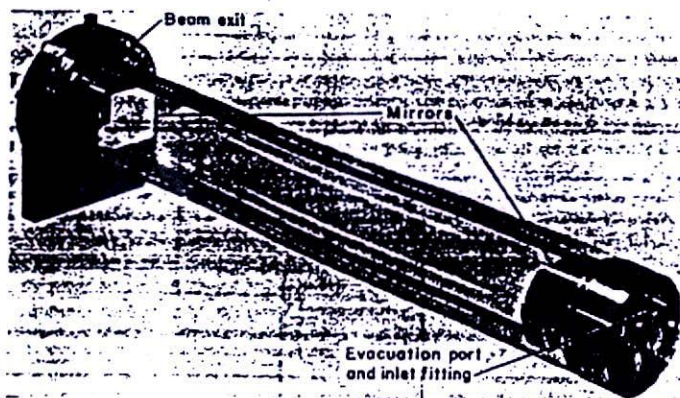


FIGURE 3.22: Gas cell for use with the Cary model 81 spectrophotometer.

The results of such experiments on a sample of carbon tetrachloride are shown in Fig. 3.23. The line at 459 cm^{-1} (ν_1) is polarized and therefore corresponds to a totally symmetric vibration, while the lines at 218, 314, 762, and 791 are depolarized and may be assigned to unsymmetrical vibrations.

Various authors have described other methods of measuring depolarization ratios which are more appropriate to a photoelectric instrument (e.g., Refs. 21, 23, and 24).

3.4 APPLICATIONS

Much of the work carried out to date in the field of Raman spectroscopy has been concerned with complete analyses of the vibrational spectra of simple molecules. Work of this kind requires measurement of both Raman and infrared spectra and is usually directed toward the determination of molecular geometry and the force constants of bonds in the molecules.

In contrast, infrared spectroscopy has been widely used in organic chemistry in recent years as a routine tool to give analytical information, largely from

group frequencies, concerning the presence of functional groups in molecules. That is not to say that Raman spectroscopy could not be equally useful for this purpose; however, while commercial infrared spectrometers are now required equipment in any organic laboratory, Raman spectrometers are found rather rarely. The situation has to do not only with the rather high cost of Raman spectrometers but also with the difficulty of the technique.

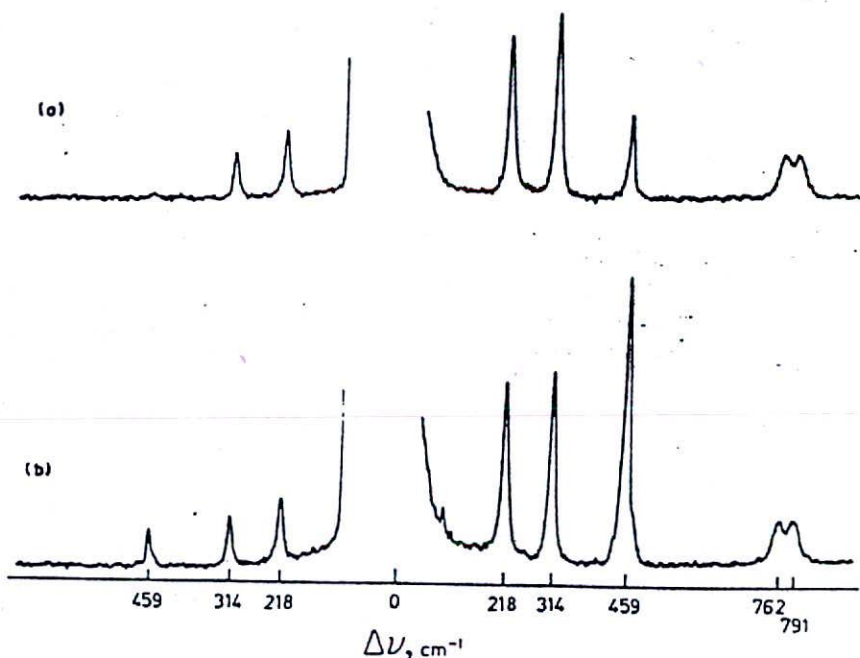


FIGURE 3.23: Polarization measurements on carbon tetrachloride.

While infrared measurements can be performed on very small samples, it has not been until very recently that the Raman spectra of microsamples could be obtained. However there is no doubt that since Raman and infrared spectroscopy provide complementary information about molecular vibrations, the routine accessibility of both kinds of spectra would greatly enhance the value of the group-frequency method of structural analysis.

Much of the work that has been reported on the Raman spectra of organic molecules has been reviewed by Jones and Sándorfy,²⁵ who give an excellent account of the use of both infrared and Raman spectroscopy in organic chemistry with emphasis not only on infrared but also on those cases where a knowledge of the Raman spectrum of a molecule proves particularly useful. They have discussed the whole scope of vibrational spectrum analysis as it applies to organic chemistry in a systematic way. The reader is referred to

their extensive discussion for a detailed account. Here, we shall restrict our comments to some points of general interest.

The literature of Raman spectroscopy is not as extensive as that of infrared, but the subject is well covered in various review articles and monographs. Those of note include the works of Hibben,²⁴ Kohlrusch,²⁷ Glockler,²⁸ Pajenkamp,²⁹ Braun and Fenske,³⁰ Stamm,³¹ and an up-to-date monograph by Brandmuller and Moser.³² Recent review articles include those by Rosenbaum,³³ Jones and Tunnicliff,³⁴ Jones,³⁵ and Jones and Jones.³⁶ A collection of spectra also appears in Landolt-Bornstein.³⁷ Two other articles that deal mainly with inorganic substances but are nevertheless of interest are those by Woodward⁶ and Tobias.³⁸

One of the important features of Raman spectroscopy that gives it an advantage over infrared spectroscopy is the ease with which low frequency vibrations (50 to 250 cm^{-1}) can be observed. In addition, because of its use of glass cells rather than infrared materials, aqueous solutions and solutions in other solvents such as strong acids can be studied.

In the case of low frequencies most conventional infrared spectrometers cover the region from 650 to 4000 cm^{-1} and more expensive grating instruments the region from 200 to 650 cm^{-1} . In the region below 200 cm^{-1} infrared detection is difficult because of the low energy of infrared radiation in this region. Two spectrometers which allow this region to be covered are the Perkin-Elmer 301 infrared spectrometer and the Beckman IRII spectrometer, however both spectrometers are very expensive and special cell materials are required. In contrast, even the simplest Raman spectrometer enables lines in the low frequency region to be observed easily.

Solvents such as water present difficulties in the infrared because of their very strong absorption so that the study of the infrared spectra of aqueous solutions presents great difficulties. In addition special cell materials such as polyethylene or silver chloride must be used because of the solubility in water of the more usual cell materials such as sodium chloride and potassium bromide. In the Raman water bands appear with rather weak intensities enabling the spectra of other species in solution to be readily observed.

As yet applications of Raman spectroscopy to organic chemistry have not been seriously exploited except in a few cases. However sufficient has been done to make it clear that some molecular groups are better characterized by their Raman spectra than by their infrared spectra. For example, the infrared spectra of the esters of compounds containing polymethylene chains, e.g., the methyl laurates,³⁹ are dominated by bands associated with the carbomethoxy group, whereas this group gives only weak bands in the Raman spectra, which are characteristic of the hydrocarbon skeleton. Similarly in the case of crystalline normal-paraffin hydrocarbons study of both the Raman and infrared spectra has shown a characteristic pattern of frequencies which enables a distinction to be made between molecules of odd and even chain length.⁴⁰

Infrared spectra unduly emphasize group frequencies of relatively polar

bonds involving hetero atoms and the C—C, C=C, C≡C, and C—H bonds of the structural skeleton which often give weak infrared bands usually give strong Raman lines. With the development of Raman techniques it is certain that useful new developments in structural analysis will result. The recent literature has been reviewed by Jones and Jones.^{3*}

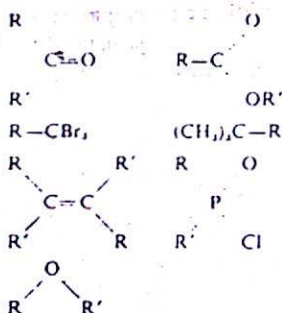
QUESTIONS

- Q3.1. Why is it not possible to use the blue (or indigo) mercury line at 4358 Å to obtain the Raman spectrum of yellow-colored solutions?
- Q3.2. What weight of a compound with a molecular weight of 100 would be required to make enough aqueous solution to fill a cylindrical cell 10 mm in diameter and 15 cm long if the solution must be 20% by weight? (Assume that the specific gravity of the solution is 1.) What volume of an ideal gas of the same molecular weight at 10 atm pressure and 25°C would be required in order that the same number of molecules would be irradiated?
- Q3.3. The inverse dispersion of a spectrograph is given by $\Delta\lambda/\Delta d$, where $\Delta\lambda$ is the difference in wavelength of two lines and Δd is the distance between the lines, i.e., when photographic detection is used, Δd is the actual distance between the images of the lines on the photographic plate. The Hilger E612 has an inverse dispersion of 16 Å/mm at 4358 Å, and approximately 41 Å/mm at 5461 Å. Tin tetrachloride has four fundamental vibrations which give rise to lines $\nu_1 = 424 \text{ cm}^{-1}$, $\nu_2 = 150 \text{ cm}^{-1}$, $\nu_3 = 608 \text{ cm}^{-1}$, $\nu_4 = 221 \text{ cm}^{-1}$. How far apart will the images of the ν_2 and ν_4 lines be in a spectrum excited by (a) the 4358-Å mercury line and (b) the 5461-Å mercury line? From which spectrum would you expect to get more accurate values for the Raman shifts?
- Q3.4. In the Raman spectrum of carbon tetrachloride the three lowest frequency vibrations (ν_1, ν_2, ν_4) usually give quite strong anti-Stokes lines (see Fig. 3.1). From the data in Table 3.1b calculate the wavelengths of the anti-Stokes lines in a carbon tetrachloride spectrum excited by the 4047-Å mercury line.
- Q3.5. The two possible isomers of 1,2-dichloroethylene have vibrational spectra which show the following fundamentals:

Isomer I		Isomer II	
Infrared, cm^{-1}	Raman, cm^{-1}	Infrared, cm^{-1}	Raman, cm^{-1}
570	173	620	349
694	406	820	758
857	563	1200	844
1303	711	3089	1270
1591	876		1576
3086	1179		1626
	1587		1692
	3077		3142
	3160		

Using simple selection rules, deduce the structures of the isomers.

Q3.6. Which of the following functional groups might you expect to be detected more easily in the Raman than in the infrared?



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