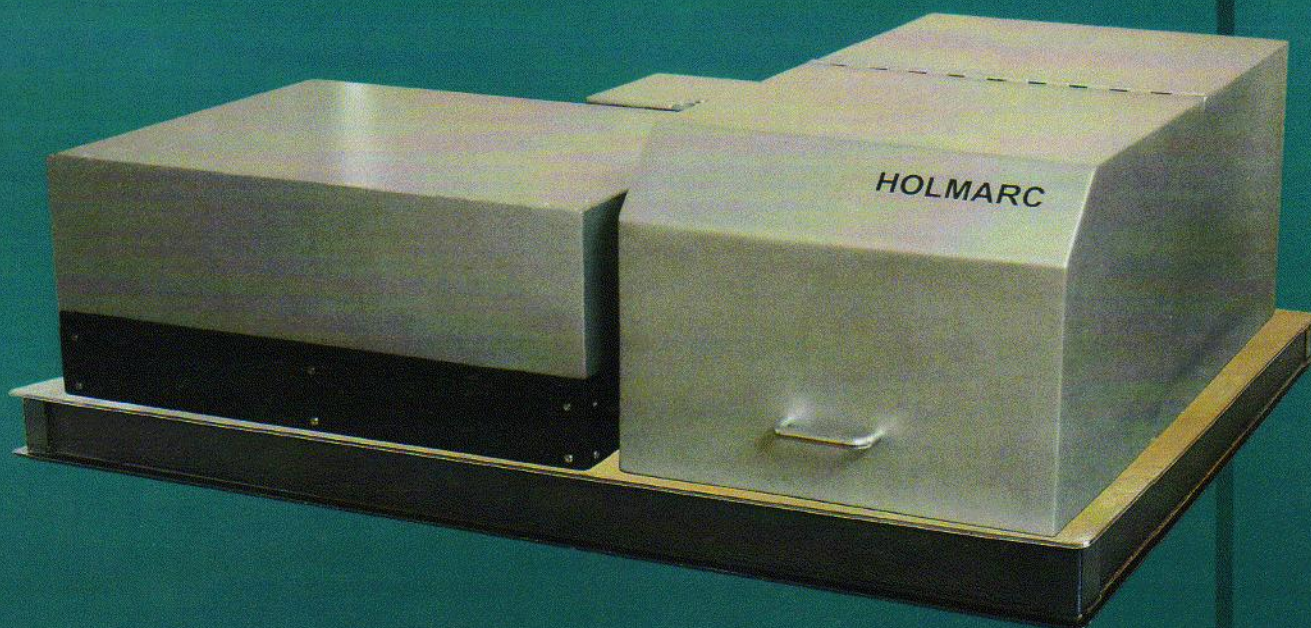




HOLMARC
OPTO-MECHATRONICS PVT. LTD

Laser Raman Spectrometer



CONTENTS

1. Introduction
2. Principle of Raman Scattering
 - i Dipole radiation
 - ii Mechanism of Raman scattering
 - iii Symmetrical properties and vibrational Raman spectrum of CCl_4 molecule
3. Introduction to experimental technology of Raman spectrum
 - i Light source
 - ii External optical path
 - iii Monochromator
 - iv Receiving system
 - v Information processing and display system
4. Experiment examples
 - i Basic experiment: recording the vibrational Raman spectrum of CCl_4 molecule
 - ii Record the polarized Raman Stokes spectrum of CCl_4 molecule
 - iii Identify chemical samples through Raman spectrum

Introduction

When light is incident on a sample, expect for the light that is absorbed, reflected and transmitted by the media, there always exist scattering light. According to the frequency of scattering light, there are three kinds of light. First, the frequency of incident light and that of scattering light are approximately the same, the frequency shift is less than 3×10^5 Hz (namely the wave number difference is less than 10^{-5} cm^{-1}). It is usually called Rayleigh scattering. Second, the frequency difference of scattering light and that of incident light is very large, larger than 3×10^{10} Hz (or wave number shift is larger than 1 cm^{-1}). This is Raman scattering. The frequency difference between scattering light and incident light of Brillouin scattering is larger than Rayleigh scattering, but smaller than Raman scattering. The intensity of Rayleigh light is 10^{-3} times the intensity of incident light, is much larger than that of Raman light which is 10^{-6} times the intensity of incident light.

Raman effect was first discovered by an Indian scientist C.V. Raman, and a Soviet Union scientist, Mandelstam, independently in 1928. Because of the weak intensity of Raman scattering, Raman spectrum study was limited to linear Raman spectrum originally, and was mostly used in structure chemistry. After the emerging of laser and improvement of detecting technology since 1960s Raman spectrum study broke the limitation and developed rapidly. In experiment, resonant Raman scattering, hyper-Raman, inverse Raman scattering, stimulated Raman scattering and coherent Raman, non-linear Raman scattering, time resolution Raman scattering and space resolution Raman scattering have emerged. With the development of Raman spectrum technology, Raman scattering of electron wave, spin wave and other elementary excitation in condensed matter are continuously detected. Now Raman spectrum is widely used in chemistry, physics, geosciences, and life science.

This experiment note discusses only the linear vibrational Raman spectrum. The basic principle of Raman scattering and the basic experimental technology will be explained through the experiment of Raman spectrum study of typical molecules.

Principle of Raman scattering

We will discuss the light scattering based on the classical theory of electromagnetic radiation. Through discussion, we can roughly understand the mechanism of light scattering. Next, we will discuss the light scattering based on the classical radiation theory of a dipole.

Dipole radiation

An oscillating dipole of circular frequency ω which is either the intrinsic of matter or produced by external field will radiate an electromagnetic wave of frequency ω . As shown in figure 2.1, a dipole p is situated at origin, when r is larger than the light wavelength, the E that is produced by a dipole p is

$$\frac{W_2 \rho_0 \sin \theta}{c^2} \frac{1}{r} \cos (wt - kr) e_E \quad (1)$$

Where ρ_0 is the amplitude of the dipole, c is the speed of light in vacuum, k is the wave vector with $k = \frac{\omega}{c}$, e_E is the unit vector of E that is normal to r , and coplanar with p and θ is the angle between r and p . the

$$\frac{W_4 \rho_0^2 \sin^2 \theta}{4 \pi^2 c^3 r^2} \cos^2 (wt - kr) e_r$$

Where e_r is the unit vector of r . Average flux density of energy $\langle s \rangle$ is :

$$\langle s \rangle = \frac{W_4 \rho_0^2}{8 \pi^2 c^3 r^2} \sin^2 \theta e_r \quad \theta e_r = \frac{2 \pi^3 c v^4 \rho_0^2}{r^2} \sin^2 \theta e_r$$

Where $v = \omega / 2 \pi c$ is the wave length of radiating light.

Dipole can be induced when the light of frequency ω_0 casts on a molecule. According to the first order approximation, the relation between induced dipole p and electric field E can be expressed as:

$$P = A.E$$

P and E are usually not in the same direction. So, a , which is usually called susceptibility tensor, should be a second – order tensor. According to the previous discussion, if the incident light of frequency ω_0 , the dipole here can only radiate the light of the frequency ω_0 which is the same as the incident light. If the internal motion of a molecule is considered, we will find that the radiating frequency of the induced dipole is different from ω_0 . Next, we will discuss in detail the radiation of the induced dipole when the internal motion of a molecule is considered.

Mechanism of Raman scattering

Molecule susceptibility is a function of the internal motion of a molecule. The atoms in the molecule vibrate around the equilibrium position caused by thermal motion. So the susceptibility of a molecule is

different from that of the molecule whose internal state is in equilibrium. Molecule susceptibility A can be expanded respect to normal coordinate σ . a_{ij} is a component of Taylor's expansion of A .

$$a_{ij} = (a_{ij})_0 + \sum_m \left(\frac{(\sigma a_{ij})}{\sigma Q_k} \right)_0 Q_k + \frac{1}{2} \sum_{kl} \left(\frac{\sigma^2 a_{ij}}{\sigma Q_k \sigma Q_l} \right) Q_k Q_l \quad (4)$$

The symbol $()_0$ in the equation denotes the values in equilibrium. Q_k and Q_l are vibrational normal coordinates of frequency ω_k and ω_l , and sum over all the normal coordinates. In the following discussion, only the first order terms are kept. Take classic normal coordinate Q_k as example, equation (4) reduced to

$$(a_{ij})_k = (a_{ij})_0 + (a_{ij})_k Q_k \quad (5)$$

$$\text{Where, } (a_{ij})_k = \sigma a_{ij} \frac{(\sigma a_{ij})}{\sigma Q_k}$$

The tensor associated with component expression (5) is;

$$A_k = A_0 + A'_k Q_k \quad (6)$$

The vibration can be considered as harmonic, when the amplitude of the internal vibration of a molecule is not very large. Vibrational coordinate can be expressed as:

$$Q_k = Q_{k0} \cos(\omega_k t + \phi_k)$$

Where Q_{k0} denotes the vibrational amplitude, ω_k is the vibrating frequency, ϕ_k is the initial phase, t denotes the time. Substitute the above expression into equation (5) and (6) respectively, we can obtain:

$$(a_{ij})_k = (a_{ij})_0 + (a'_{ij})_k Q_{k0} \cos(\omega_k t + \phi_k)$$

$$A_k = A_0 + A'_k Q_{k0} \cos(\omega_k t + \phi_k)$$

The electric field E of the light of frequency ω_0 can be expressed as:

$$E = E_0 \cos \omega_0 t \quad (7)$$

Where E_0 is the vector amplitude of the electric field E . From the discussion before, the molecule will generate an induced dipole when it is by the ligh of the electric field E . We will only discuss the typical vibration Q_k . Substitute equation (6) and (7) into equation (8), dipole P_k ,

$$P_k = A_k \cdot E$$

$$= A_0 \cdot E_0 \cos \omega_0 t + A'_k Q_{k0} \cdot E_0 [\cos \omega_0 t \cdot \cos(\omega_k t + \phi_k)]$$

$$= A_0 \cdot E_0 \cos \omega_0 t + \frac{1}{2} A'_k Q_{k0} \cdot E_0 \cos[(\omega_0 - \omega_k) t + \phi_k] + \frac{1}{2} Q_{k0} A'_k \cdot E_0 \cos[(\omega_0 + \omega_k) t + \phi_k] \quad (8)$$

If we use the following symbols:

$$P_0 = A_0 \cdot E_0 \quad P_{k0} = \frac{1}{2} Q_{k0} A'_k \cdot E_0 \quad (9)$$

$$P_0(\omega_0) = P_0 \cos \omega_0 t \quad (10)$$

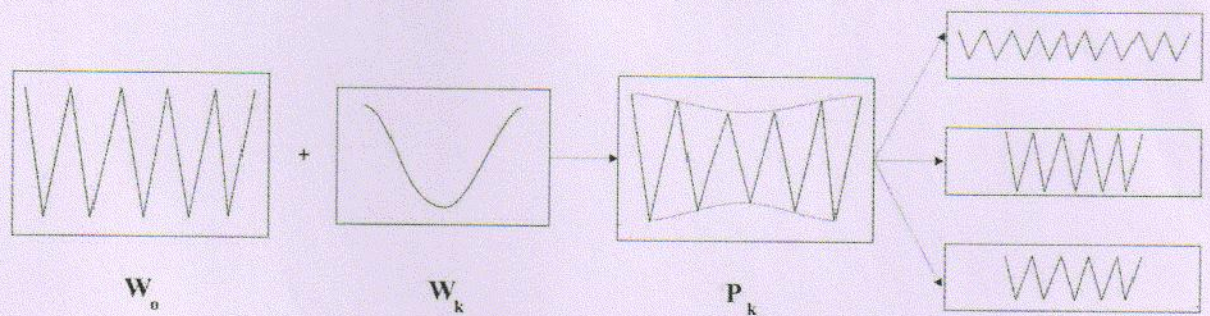
$$P_0(\omega_0 \pm \omega_k) = P_{k0} \cos [(\omega_0 \pm \omega_k) t + \phi_k] \quad (11)$$

Equation (8) can be reduced:

$$\begin{aligned} P_k &= P_0 \cos \omega_0 t + P_{k0} \cos [(\omega_0 - \omega_k) t + \phi_k] + P_{k0} \cos [(\omega_0 + \omega_k) t + \phi_k] \\ &= P_0(\omega_0) + P_k(\omega_0 - \omega_k) + P_k(\omega_0 + \omega_k) \end{aligned} \quad (12)$$

From the discussion above, it is clearly that:

- (1) According to the classical radiation theory, there are kinds of induced oscillating dipoles in equation (12): $P_0(\omega_0)$ and $P_0(\omega_0 \pm \omega_k)$ which radiate electromagnetic waves of frequency ω_0 , $(\omega_0 - \omega_k)$ and $(\omega_0 + \omega_k)$ respectively. They associate with Rayleigh scattering, Stokes and anti-stokes Raman scattering.
- (2) From the derivation of equation (8), Raman scattering can be considered as a process of wave modulating. Incident light of frequency ω_0 is modulated by the vibrational molecule of frequency ω_k . In addition to radiating the wave of frequency ω_0 , it also radiates difference frequency light $(\omega_0 - \omega_k)$ and sum frequency light $(\omega_0 + \omega_k)$. The former is Rayleigh scattering, the Raman scattering. Visual representation of this process is shown in figure.



- (3) Note that : radiation intensity I can be expressed as: $I = \langle S \rangle / r^2$, substitute equation (9) into equation (2), obtain the Raman scattering intensity

$$I_k = \left[\frac{\langle Q_{k0} \rangle (\omega_0 \pm \omega_k)^4}{32 \pi^2 c^3} \sin^2 \Theta \right] |A_k \cdot E_0|^2$$

This indicates that the Raman scattering intensity is proportional to the intensity of incident light and is approximately proportional to the frequency of incident light quadric.

- (4) It is easy to deduce from equation (9) and (1) that, if the spatial orientation of a molecule is fixed, the spatial orientation of induced dipole is also fixed; if the incident light polarized, the scattering light is also polarized. Note that, if spatial orientation of a molecule is not fixed or is random, the deduction above usually is not right.
- (5) Due to the existence of the initial phase, Raman scattering of different molecules is incoherent. The total Raman scattering intensity is the algebraic sum of Raman scattering intensity of different molecules. However, Rayleigh scattering of different molecule is coherent. So the total Rayleigh scattering intensity is not the simple sum of the intensity of different molecules.
- (6) If vibration Q_k can activate Raman scattering, Q_k is said Raman active condition can be deduced from equation (9): more than one component of $(a'_{ij})_k$ of differential susceptibility tensor A'_k is not zero. This is the classical selection rule of Raman scattering. The concrete deduction of this selection rule is very complicated, it will not be discussed further.

Raman scattering associated with the higher orders in equation (4) are called second- order, third- order..... Raman scattering respectively. Above discussion is based on first- order (or linear) Raman scattering. Classical theory of Raman scattering enables us to basically understand the mechanism of light scattering. In the following section, the mechanism of light scattering based on quantum theory will make up the disadvantages of classical theory.

In quantum mechanisms, quantum state is described by wave function; the energy state of the system is usually discrete. Transmission of system state from one state to another usually radiates out energy, scattered light is generated along with the transmission of the system from one energy state to another when the system is cast by light. Transmission probability is proportional to transmission matrix, namely:

$$\left| \sum \frac{\langle \varphi_f | e_0 \cdot p | \varphi_n \rangle \langle \varphi_n | e_r \cdot p | \varphi_i \rangle}{W_{ni} + \omega_r} + \frac{\langle \varphi_f | e_r \cdot p | \varphi_n \rangle \langle \varphi_n | e_0 \cdot p | \varphi_i \rangle}{W_{ni} - \omega_r} \right|$$

Where φ_f , φ_n and φ_i are final, intermediate and initial states; e_0 and e_r are polarized unit vectors of the incident and scattered light respectively; ω_0 and ω_r are circular frequencies of incident light and scattered light respectively. Sum up all the intermediate states.

The quantum interpretation of light scattering is different from the classical interpretation of light scattering fundamentally. Figure 2.3 represents the semi-classical quantum interpretation of light scattering. According to Figure 2.3 and Equation 13, the physical process of light scattering: incident light of frequency ω_0 leads to the transition from initial state i to final state f , at the same time, the light of frequency $\omega = \omega_0 + \omega_f$ is radiated. If the energy level of the initial state is higher than that of the final state, this process is called Anti-Stokes Raman scattering; on the contrary, the process is called Stokes Raman scattering. If the initial state and the final state are in the same level, this process is called Rayleigh scattering. Furthermore, the light scattering and self-radiating are different in that the transition process caused by scattering must undergo an intermediate state and the self-radiating process does not experience by an intermediate state.

Secondly, there are several discrete energy levels in system. For the N -molecule system, the molecule number at k_{th} vibrational level in equilibrium obeys Boltzmann distribution. So the intensity of Stokes Raman scattering I_{ks} is different from that of anti-Stokes Raman scattering I_{kas} , they can be expressed as

$$I_{ks} \propto N/[1 - \exp(-h\omega_k/kT)]$$

$$I_{kas} \propto N/[\exp(+h\omega_k/kT) - 1]$$

The ratio of their intensities is:

$$I_{ks}/I_{kas} \propto \exp(h\omega_k/kT)$$

In general, $\exp(h\omega/kT)$ is much greater than unit. Therefore, quantum theory can interpret that Stokes intensity is stronger than that of Anti-Stokes, but classical theory cannot explain it.

Thirdly, the Raman activity of the vibrational mode in the classical theory is same as that the k_{th} vibrating matrix is not zero in semi-classical quantum theory, i.e., the selection rule of quantum transition. In quantum mechanics, Raman activity of a certain vibrational mode can be decided from the characteristic of the symmetry of system wave function. It does not need complicated calculation.

Symmetrical properties and vibrational Raman spectrum of CCl₄ molecule

In this experiment, we take CCl₄ (carbon tetrachloride), as sample first. According to the principle, we will introduce the connection between molecular structure, symmetrical properties and vibrational Raman scattering. It can provide a base for spectrum analysis.

1 Molecular structure and symmetrical properties of CCl₄ molecule.

CCl₄ is composed of a carbon atom and 4 chlorine atoms. Figure 1 shows its structure. 4 chlorine atoms are positioned at 4 vertices of regular tetrahedron; a carbon atom is positioned at the center of tetrahedron. The symmetry operation of a molecule, e.g., rotation about an axis, inversion ($r \rightarrow -r$) or rotation plus inversion carries the molecule into itself. Symmetry operation is equivalent to symmetrical transformation

that is discussed before. Figure 2 shows the symmetrical axes of a CCl_4 molecule. As can be seen from the figure, there are 24 symmetry operations (excluding identity operation E). These symmetry properties. The five symmetry elements of CCl_4 are:

$E, 3C_2, 8C_3^{j+/-}, 6iC_2^p, 6iC_2^{m+/-}$

The concrete meanings of the above symbols are:

C_n axis of rotation, subscript represents the rotating angle is $2\pi/n$;

i inversion

m rotating axes are x, y, z axis

j rotating axis is body diagonal that through origin o, $j = 1, 2, 3, 4$;

p rotating axes pass through origin O and direction of the connecting line of the midpoint of opposite axis, $p = a, b, c, d, e, f$; + or - stands for rotating clockwise or anticlockwise.

The numbers in front of the symbols are symmetry in these symmetry elements.

2. Vibrational mode and vibrational Raman spectrum of CCl_4 molecule.

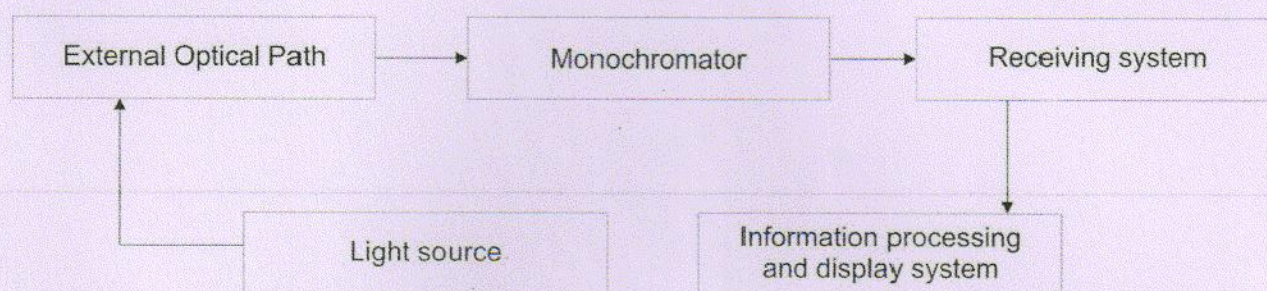
A molecule, composed of N atoms ($N \geq 3$), has $(3N - 6)$ internal vibrational freedoms. So CCl_4 molecule has nine normal vibrational modes. They can be divided into four classes. According to the reflecting properties, these four classes are divided into symmetrical vibration and anti-symmetrical vibration. The first class is symmetrical vibration and the other 3 classes anti-symmetrical vibrations. Although the vibration modes in the same class are different, vibrational energy of different modes are equal. In general, if there are L classes of vibration, the vibrational Raman spectrum lines are no more than L . If the perturbation, induced by the vibration coupling, is considered, some spectrum line may split into two. The weakest double line is induced by the perturbation coupling of the strongest spectrum lines. The number of vibrational modes is equal to degeneracy in quantum mechanics. If there are g vibrational modes in a certain class, this class of vibration is g -degeneracy.

According to the principle of Raman spectrum discussed above, on the one hand, the outline of Raman spectrum of a molecule: e.g. number of spectrum lines, approximate position, polarized properties and their relative intensity can be deduced from the structure and symmetrical properties of a molecule. On the other hand, number of spectrum lines, intensity and vibrational mode (some times with the help of IR) can be obtained through experiment. Combining and comparing the above two aspects, Raman spectrum can provide the information of the structure and symmetry properties of a molecule.

In the discussion of principle of Raman, in addition to the molecular structure and vibrational mode, other properties of a molecule have not been discussed. It can be deduced That: the outline of the Raman spectrum of the same space structure but different composing atoms are similar. In practice, the unknown molecular structure and symmetrical properties are from the comparison of a Raman spectrum of unknown molecular structure and that of known molecular structure. Atoms, atomic distance and atomic interaction of different molecules with the same molecular structure can be very different. So, the Raman spectra of different molecules are different in details and every molecule has its intrinsic Raman spectra.

Raman spectrum provides means to identify and analyze the chemical element and structure properties. Molecular structure and motion can be affected by external conditions. The effect of concentration, temperature and pressure can be studied through Raman spectrum.

Introduction to experimental technology of Raman spectrum



Basic structure of Raman spectrometer

In the discussion of the mechanism of Raman scattering, the intensity of Raman scattering is proportional to the intensity of incident light. The intensity of the Rayleigh scattering, along with Raman scattering, is 1000 times stronger than that of Raman scattering. So, in the process of designing a Raman spectrometer and carrying out the Raman scattering experiment, you must consider to enhance the intensity of incident light and to collect the scattered light as possibly as you can, to control and eliminate background stray light that mainly comes from Rayleigh scattering, and to improve the ratio of signal to noise.

Raman spectrometer is composed of five parts, as shown in figure we will discuss the functions of different components.

Light source:

Wave length / nm	Wave number in vaccum / Cm^{-1}	He - Ne	Ar	Kr	Ar - Kr
487.99	20487	70	1000	200	200
514.53	19430		1500	500	200
530.87	18832				200
632.82	15793				
647.09	15450				

Its function is to provide good monochromatic, large power and multi-wavelength incident light. At present, the mercury lamp that was used as the source in Raman study is completely substituted by laser. For the conventional Raman spectrum experiment, the common gas lasers can basically meet the needs of experiment. The above table lists some common gas lasers. High resolution Raman spectrum needs a laser much narrower line width. This can be achieved through the compression of line width, e.g. after the compression of an Ar laser, line width at the wavelength of 514.5nm is compressed from 0.15cm^{-1} to 0.001cm^{-1} . Resonant Raman spectrum needs dye laser whose wave length can be tuned continuously. Nonlinear Raman spectrum usually needs high power pulse laser. Some Raman spectrum experiments need very stable intensity of incident light; in this case, the out put power of laser must be very stable.

External optical path

External optical path includes focusing lens, condensing lens, sample holder, filter and polarizer etc...

Light focusing : The function of converging lens is to enhance the radiating power that cast on a sample. The laser is focused by a suitable lenses, which makes the sample at the waist of a focusing beam. 80% energy of focusing laser beam is distributed in the cylinder (diameter d , length l) shown in figure there are below approximate relations among d , l and diameter of incident parallel light D and lens focal length f .

$$d \approx \frac{4\lambda}{\pi} \frac{f}{D}, \quad L \approx \frac{16\lambda}{\pi} \left(\frac{f}{D}\right)^2$$

For example, give laser wavelength $\lambda = 500\text{nm}$, $D = 50\text{mm}$, then $d \approx 0.01\text{mm}$, $L \approx 0.7\text{mm}$ and $\frac{D}{d} \approx 3 \times 10^3$. From this example, the radiating power is 3×10^5 times that of unfocused light. However, actual effect will be certainly much lower after the consideration of aberration and other factors.

Light condensing : The function of a condenser is to collect scattering light effectively. It is usually composed of a large aperture lens and / or a concave mirror. Except requiring the optimal solid angle between the condenser and scattering light, the distance l between the condenser and the incident slit of the spectrometer needs also to satisfy

$$\Phi = l \times f$$

Where Φ is the condenser diameter, F is relative aperture of the spectrometer.

In addition, a concave mirror can be positioned at the opposite of the condenser and along the propagating direction of illuminative light in order to collect more scattering light.

Sample holder : the design of sample holder ensures the largest efficiency and least stray light, especially avoiding the incident laser to get into the slit of the spectrometer. Take transparent samples as an example, the best placement of a sample is that the light collecting direction is perpendicular to the propagating direction of incident light.

Light filter : The function of a filter is to control stray light and improve the signal-to-noise ratio of Raman scattering. Placing a filter in front of the sample holder is to eliminate the stray light of incident laser that is induced by plasma radiation. The placement of small aperture is a simple method. Interference filter and prepositive monochromator can completely eliminate the plasma lines to purify the incident light. Placing a filter at back of sample holder is to eliminate Rayleigh scattering light from the scattered light. The filtering function can be achieved through an absorption box of interference filter and a holographic filter.

Polarization Components: Polarization components must be included in the external optical path when polarization measurement is required. They are composed of a polarization rotator, a polarizer and an analyzer. In order to eliminate the polarizing disturbance, a polarization intruder is often placed in front of the incident slit, which makes the light coming into the instrument become completely depolarized.

Monochromator: a monochromator makes Raman scattering light separate in space according to their wave length. Because the intensity of Raman scattering is very weak, so the instrument must be good at stray light level. Stray light level of the instrument is measured by the value of the stray light power $\eta\Delta\nu$. Assume the wave number of incident light is ν_0 , the intensity collected by the spectrometer is I_{ν_0} , the intensity detected by the spectrometer at $\nu_0 + \Delta\nu$ is $I(\nu_0 + \Delta\nu)$, the definition of stray light power is $\eta\Delta\nu = \frac{I(\nu_0 + \Delta\nu)}{I_{\nu_0}}$, in general ($\Delta\nu = 20\text{cm}^{-1}$). Stray light power of the best spectrometers is less than 10^{-14} , the spectrometer can be used to analyze the Raman spectrum of gas or liquid samples. The spectrometer whose $\eta\Delta\nu$ is less than 10^{-3} is usually useless in the analysis of Raman spectrometer.

Receiving system: The receiving system of Raman signal is divided into two types; single channel receiver and multi-channel receiver. PMT is the common single channel receiver; photo plate was the traditional multi channel receiver. Silicon image intensifier of diode array and CCD (charge coupling device) are now multi-channel receivers which overcome the disadvantage of long scanning time of PMT. However, high quality multi-channel receivers are more expensive than PMT.

Information processing and display system: Its function is to amplify Raman signal, control stray light signal and the real Raman signal. DC amplification, amplification of frequency selection, photon counting, data processing are the common methods. Nowadays, most of Raman spectrometers are equipped with a microcomputer which controls the operation of instrument, acquirers and process the data. This significantly improves the efficiency and the performance of Raman spectrometer

Experiment examples:

Basic experiment: Recording the vibrational Raman spectrum of CCl_4 molecule

Objective:

Record Rayleigh Stokes, anti-stokes lines, learn the basic experiment technology of Raman scattering and understand the relation between the molecule structure and the key characters of its Raman scattering spectrum.

Steps:

The external optical path of a Raman spectrometer has been adjusted to make the incident beam to pass through the center where the sample is placed. Experiment is carried out according to following steps:

1. Put the sample on the holder and make sure the sample is in the best illumination. Rotate the polarization rotator PR, adjust the position of sample holder and make sure the laser beam is at the center of sample observed from every direction.
2. Adjust condensing lens L_1 forward and backward so that the illuminated sample image is observed on the slit and clear. Adjust the polarization direction of incident laser beam so that the maximal brightness of sample image on slit is achieved.
3. Choose the suitable gain of PMT.
4. Record the peaks by using soft ware and plot the Graph.

Requirements of experiment report

- (1) Record all the experiment parameters, especially the geometrical width of slit and scanning range of wave length (the maximum Raman shift of CCL_4 is $|\Delta\nu| \approx 800\text{Cm}^{-1}$).
- (2) (i) Convert wave length scale to wave number difference. (ii) Note wave number difference of every peak. (iii) The sequence order of the intensity of vibrational Stokes Raman lines from high to low are class I, IV, II and III. Compare the relative intensity of every spectrum line.
- (3) Observe the difference of same illumination with the change of polarization direction of incident light, try to explain it.

Record the polarized Raman Stokes spectrum of CCL_4 molecule

Record the polarized Raman Stokes spectrum of CCL_4 molecule, analyze the symmetrical characteristics through depolarization.

Steps

- (1) When carrying out step (4) of previous basic experiment, polarization analyzer PA is positioned vertically with respect to the scattering plane.
- (2) Record Raman spectra at scattering intensities of $\perp I_{\perp} (\Pi/2)$ and $\parallel I_{\parallel} (\Pi/2)$ (slit width is within $5-10^{-1}$). The illumination is in optimal position and other parameter are kept identical in two recordings.

Requirements of experiment report

- (1) Record the experiment parameters, especially the geometrical width of slit and scanning range of wave length (the maximum Raman shift of CCL_4 is $|\Delta\nu| \approx 800\text{Cm}^{-1}$).
- (2) (i) Convert wave length scale to wave number difference. (ii) Note wave number difference of every peak. (iii) The sequence order of the intensity of vibrational Stokes Raman lines from high to low are class I, IV, II and III. Compare the relative intensity of every spectrum line.

- (3) According to the definition of depolarization equation (16), evaluate the depolarization of spectrum lines and give their symmetry.
- (4) Decide whether the depolarization of this experiment should be corrected by efficiency curves of spectrometer and explain the reason.

Identify chemical sample through Raman spectrum.

Objective

Record the Raman spectra of the two chemical samples. According to standard spectra, identify them.

Steps

Operation steps are the same as those in basic experiment; select the slit width and other parameters according to real condition.

Requirements of experiment report

- (1) Record the experiment parameters, especially the geometrical width of slit and scanning range of wave length (the maximum Raman shift of CCL_4 is $|\Delta\nu| \approx 800\text{cm}^{-1}$).
- (2) (i) Convert wave length scale to wave number difference. (ii) Note wave number difference of every peak.
- (3) According to standard spectra, label the names and quantities of ingredients included in sample on the spectrum graph.

