Part I

Fundamentals of Raman Spectroscopy

1

Basic Knowledge of Raman Spectroscopy

The term “Raman spectroscopy” is an abbreviation of “Raman scattering spectroscopy”. Basic knowledge of Raman spectroscopy can be gained by understanding the meaning of three words: “spectroscopy”, “scattering”, and “Raman”.

1.1 Spectrum and Spectroscopy

Spectroscopy can be considered in three parts: theory, experiment, and application. These will be described in more detail later. In this section, only spectrum are discussed.

1.1.1 Optical Spectrum

A band of colors is called a “spectrum”. The rainbow, as shown in Figure 1.1a (see color Plate 1 for the original Figure 1.1), is one example of a spectrum. A spectrum is usually one recorded by an artificial dispersive element called a spectrograph, as shown in Figure 1.1b.

1.1.2 Classification of Spectra

1.1.2.1 Classification Based on Optical Effects

When a medium is illuminated by light, the interaction between the light and the medium produces many kinds of optical effects and phenomena. Figure 1.2 shows some examples of major optical effects.

The spectrum is a record of all the optical effects. As such, the spectra can be divided into many types, based on the different optical effects such as reflection, transmission, absorption, emission (fluorescence, luminescence), and scattering spectra. All of these spectra help us to understand the kind of interactions and the inner structure and motion of the medium.

Raman Spectroscopy and its Application in Nanostructures, First Edition. Shu-Lin Zhang.

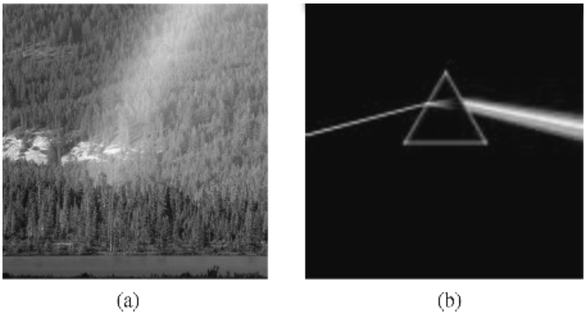

(a) (b)

Figure 1.1 *Examples of spectra: (a) a rainbow: (b) a scheme of spectra by a dispersive element prism*

For example, the measurement and understanding of atomic spectra led to the elucidation of the atom's inner structure and played a key role in the establishment and development of quantum theory.

This book concentrates on discussion of scattering spectra. Light scattering based on fundamental and broad ideas is introduced in detail in the next section.

1.1.2.2 Classification Based on Spectral Parameters

The spectrum, as a record of optical effects mentioned above, reflects the dependence of electromagnetic radiation intensity on its relevant parameters.

The radiation intensity, I, can be expressed as

$$\boldsymbol{I} = |\boldsymbol{E}|^2 \tag{1.1}$$

where $\boldsymbol{E}$ is the electric field given by

$$\boldsymbol{E}(\boldsymbol{r}, t) = \boldsymbol{E}_0(\boldsymbol{r}, t)e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)} \tag{1.2}$$

where ω, $\boldsymbol{k}$, $\boldsymbol{r}$, t, and $\boldsymbol{E}_0$ are the measured frequency (the reciprocal of wavelength λ), wave vector (representing the propagating direction), position vector, time, and the amplitude of the electric field, respectively. These are the only relevant parameters in the measurement of spectra.

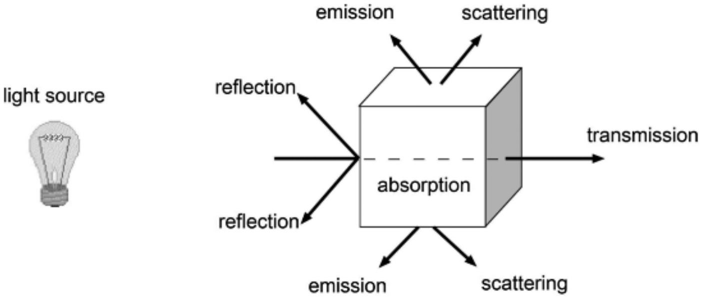


Figure 1.2 *Different optical effects caused by interaction between light and a medium. Reprinted from S.-L. Zhang, Raman Spectroscopy and Low-dimensional nanoscale Semiconductors, Science Press, (2008)*

Depending on the spectral parameter of interest, the measured spectra can be classified into different categories. With respect to different excited light wavelengths λ_0, spectra with spectral intensity $\boldsymbol{I}$ on the rest of the parameters ω, $\boldsymbol{k}$, $\boldsymbol{r}$, t, and $\boldsymbol{E}_0$ have been classified as:

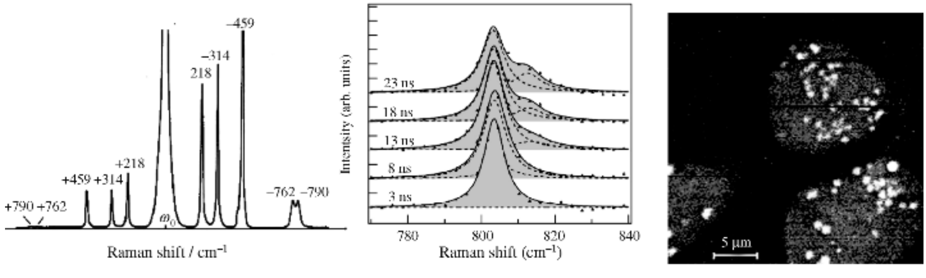
- *Visible and non-visible excited spectra*: these spectra are excited by visible and non-visible light, respectively. The non-visible excited spectra are further divided into ultraviolet (UV), infrared (IR), and Terahertz (THz, $\lambda = 0.1 \sim 1$ mm) excited spectra, and so on.
- *Visible and non-visible spectra*: the recorded spectral wavelength λ is localized in the visible and non-visible range. The non-visible spectra are further divided into the UV, IR, and THz spectra, and so on.
- *Spontaneous and stimulated spectra*: these spectra are due to spontaneous and stimulated radiation, respectively.
- *Linear and non-linear spectra*: the spectral intensity $\boldsymbol{I}$ depends on the first- and high-order of parameters $\boldsymbol{E}_{0,}$ respectively.
- *Single- and multi-order spectra*: these are the spectra at the single- and multiple-folded frequency ω of the Raman mode, respectively.
- *Angle distributed spectrum*: this is the dependence of spectral intensity $\boldsymbol{I}$ with respect to the direction of the parameter $\boldsymbol{r}$ of the measured position, that is, the propagating direction of spectral light, or the direction of parameter $\boldsymbol{k}$.
- *Polarized and non-polarized spectrum*: this spectrum is measured under excitation by polarized light and detection in a fixed polar direction, that is, in the direction that excited and recorded $\boldsymbol{E}$ are both fixed.
- *Steady state and transient (time resolved) spectra*: this is the spectral intensity $\boldsymbol{I}$ with respect to the parameter t at a long and very short duration, respectively (Figure 1.3a,b).
- *Far- and near-field spectra*: this is the measured spectral intensity $\boldsymbol{I}$ in the region of magnitude of the position parameter $\boldsymbol{r} \gg \lambda$ (light wavelength) and $\ll \lambda$, respectively.
- *Frequency and image spectra*: the former records the spectral intensity $\boldsymbol{I}$ variation with spectral parameters, ω, and the latter is the spectral intensity $\boldsymbol{I}$ distribution at a single wavelength at various sample positions, r_0 (Figure 1.3c).

Early traditional spectroscopy was measured with excitation by a mercury vapor lamp and the spectra were basically records of the spectral intensity with frequencies in the visible; they were spontaneous, linear, non-polarized, steady-state, and far-field spectra. In contrast, the spectra of non-visible, stimulated, non-linear, polarized, transient, near-field, and image at a spectral line are a more recent development. Since occurrence of the new-style Raman spectroscopy is mainly due to the introduction of the laser into the Raman spectrometer, it is now called laser Raman spectroscopy.

1.2 Scattering and Raman Scattering

1.2.1 General Scattering

Scattering is a common phenomenon in nature. When an incident particle hits the target along a certain direction (Figure 1.4), the direction and even the energy of the incident particle may be changed due to the interaction between the particle and the target, thus causing the scattering.



(a) (b) (c)

Figure 1.3 *Examples of various kinds of spectra: (a) Steady Raman spectrum of* CCl_4*. Reprinted from S.-L. Zhang, Raman Spectroscopy and Low-dimensional nanoscale Semiconductors, Science Press, (2008). (b) Transient spectra of ring-breathing mode of cyclohexane under shock compression. The solid and dashed lines show the fitted Lorentzian function and the separated peaks, respectively [2]. Reprinted from in A. Matsuda, G. Kazutaka and K. Kondo, Time-resolved Raman spectroscopy of benzene and cyclohexane under laser-driven shock compression, Phys Rev B, 65, 174116 (2002) with permission of the American Physical Society. (c) Image of spectral line of unstained and live HeLa cells [3]. Reprinted from A. Zumbusch, G. P. Holtom, and S. X. Xie, Three-Dimensional Vibrational Imaging by Coherent Anti-Stokes Raman Scattering, Phys Rev Lett, 82, 4142 (1999) with permission of the American Physical Society*

Scattering experiments have been an important method used to observe the interactions as well as the inner structure and motion of matter, on both macroscopic and microscopic scales. For example, E. Rutherford's experiment in 1911 verified that the atom has a nucleus with a small positive charge. A.H. Compton's experiment in 1920 proved that light possesses particle-like property. The scattering experiments in these classical examples used charged particles and alpha particles as the incident particles, respectively. Nowadays, most experiments of elementary particles still use scattering experiments of various incident particles and targets.

Based on the different kinds of incident particles, scattering can be categorized as neutron scattering, electron scattering, and photon (electromagnetic wave) scattering.

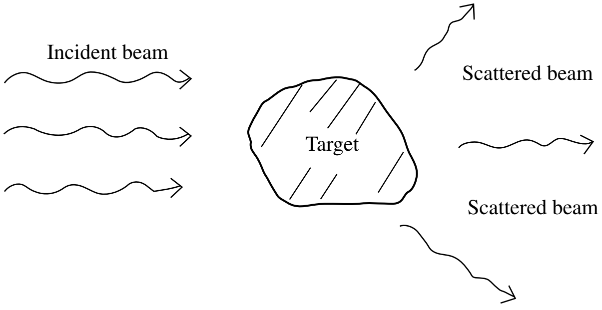


Figure 1.4 *Diagram of scattering phenomena. Reprinted from S.-L. Zhang, Raman Spectroscopy and Low-dimensional nanoscale Semiconductors, Science Press, (2008)*

Table 1.1 *Estimated values of energies and wavelengths of incident particles used in the scattering experiments of solid matter. Reprinted from S.-L. Zhang, Raman Spectroscopy and Low-dimensional nanoscale Semiconductors, Science Press, (2008)*

Category of Incident Particles		Energy		Wavelength	Uncertainty of Energy
		eV	Hz	nm	ΔE/E
Neutron		10^{-2}	10^{14}	10^{-1}	10^{-4}
Photon (Electromagnetic wave)	Visible laser	10^{0}	10^{16}	5×10^{2}	10^{-8}
	X-ray	10^{3}	10^{19}	10^{-1}	10^{-2}

Photon scattering can be sub-divided into gamma ray scattering, X-ray scattering, and (visible) light scattering, which uses light with different energies. Table 1.1 lists the common incident particles in the study of condensed matter, their energies, and their wavelengths.

Various kinds of scattering yield different information, which makes them particularly suitable for the study of various objects. For example, X-rays with a typical energy of 1 keV are suitable for detecting the location of atoms or ions in condensed matter, that is, its microstructure and geometric symmetry. Visible light, with energy of about 1 eV, is suitable for studying the molecular vibration and elementary excitation in condensed matter.

1.2.2 Visible Light Scattering

Visible light scattering is a phenomenon commonly observed in our daily life. When visible light travels through a uniform media such as purified glass or water, light cannot be observed in the media when viewed from the side. However, most media are not perfectly uniform and small particles (impurities) may exist (e.g., liquid with suspended particles or colloids). These impurities enable us to see the light ray in the media from the side. This is due to light scattering off the irregularities or particles in the media.

Based on different scattered objects, visible light scattering can be classified into many kinds, as described below.

1.2.2.1 Molecular Scattering

Molecular scattering is due to scattering caused by density fluctuations of molecules in pure gases or liquids from thermal motion, and for which the size of fluctuation is smaller than the wavelength of incident light. This can lead to critical opalescence, which is due to a huge amount of light scattering caused by large fluctuations at the critical point.

Lord Rayleigh, a British physicist, proposed his Law in 1897 when he was studying the intensity of molecular scattering [4]. Rayleigh's Law says that the intensity of scattered light is inversely proportional to the fourth power of the wavelength of the incident light.

1.2.2.2 Tyndall Scattering

In 1868, Tyndall found that when white light is scattered by suspended particles in liquids, the scattered light is blue with partial (linear) polarization [5]. Tyndall scattering is induced by particles in the media with a size comparable to or a little larger than the wavelength of the incident light, such as colloids, latex, smoggy air, and so on. When C. Mie studied Tyndall scattering in 1908, he found that, in contrast to molecular scattering, the fourth power relation was not followed [6]. In some literature, Tyndall scattering is also called Mie scattering.

1.2.2.3 Electron Light Scattering

Electron light scattering includes different modes of scattering by free electrons, such as Compton scattering and Thomson scattering. These types of scattering are discussed later in this book.

Electron light scattering also includes scattering by other charged particles, for example, light scattered by the electrons/holes, impurity charges and spins in condensed matter. The latter scattering is also called spin scattering. These types of scattering will also be discussed later in this book.

1.2.2.4 Atomic Light Scattering

Since the nucleus is too heavy to induce visible light scattering, atomic light scattering of visible light is actually scattered by orbital electrons.

1.2.2.5 Molecular Light Scattering

Molecular light scattering refers mainly to scattering by vibration and rotation of chemical bonds in chemical or biological molecules.

1.2.2.6 Solid Light Scattering

Solid light scattering is, in fact, due to scattering by "quasi-particles" in solids. "Quasi-particles" are also called "elementary excitations", and the important quasi-particles in light scattering are phonons (the quanta of lattice vibration waves), excitons, magnetons, and plasmons, and so on.

1.2.3 Inelastic and Raman Scattering

As mentioned in Section 1.2.1, the energy of the incident particle, for example, light, can be changed in the scattering process. In the twentieth century, people began to pay attention to the change of energy, that is, the change in wavelength, of the scattered light relative to that of the incident light. In light scattering experiments, the unit of the wavelength change is usually expressed as the reciprocal of wavelength (cm^{-1}). Table 1.2 lists light scattering classified into three categories, depending on the change in energy. Scattering with a change of light energy of less than $10^{-5}\,\text{cm}^{-1}$ is called Rayleigh scattering. Changes of about $0.1\,\text{cm}^{-1}$ were first observed by Brillouin in 1922 and are thus called Brillouin scattering [7]. Changes larger than $1\,\text{cm}^{-1}$ are called Raman scattering, as was first observed by C.V. Raman in 1928 [8]. When the wavelength (energy) of scattered light is the same as the incident light, it is known as elastic scattering. When the wavelength of the scattered light is

Table 1.2 *Energy change and corresponding classification of visible light scattering. Reprinted from S.-L. Zhang, Raman Spectroscopy and Low-dimensional nanoscale Semiconductors, Science Press, (2008)*

Change Range of Energy	Name of Category	Property of Scattering
$< 10^{-5}\,\text{cm}^{-1} \sim 0$	Rayleigh	Elastic
$10^{-5} \sim 1\,\text{cm}^{-1}$	Brillouin	Inelastic
$> 1\,\text{cm}^{-1}$	Raman	Inelastic

different, it is known as inelastic scattering. As the energy change in Rayleigh scattering is caused by the recoil of the target, it can still be regarded as elastic scattering. So Brillouin and Raman are inelastic scattering.

The above shows that Raman scattering is an inelastic light scattering, with energy change larger than 1 cm^{-1}.

1.3 Fundamental Features of Raman Scattering Spectra

Different spectra embody different properties and features, due to the difference in the mechanism generating the spectra. Raman scattering spectra is abbreviated as Raman spectra usually and have their own characteristics also, distinguishing them from other spectra.

Figure 1.5 shows the Raman spectra of $\mathrm{ClC_4}$, in which ω_0 is the frequency of the incident light. The energy is usually represented by wavenumber (cm^{-1}), while the wavenumber of the incident light, ω_0, is set as zero on the wavenumber axis. The frequency of scattered light, ω_S, relative to that of incident light, is called the Raman frequency or Raman shift. The basic features of Raman spectra will be discussed using the example in Figure 1.5.

1.3.1 Frequency

There are two basic features of Raman frequency.

- The frequency difference of Raman scattered light relative to that of incident light ω_0 can be negative and positive, of which the frequency of the former and the latter are known as the Stokes frequency ω_S and anti-Stokes frequency ω_{AS}, respectively. The absolute values of ω_S and ω_{AS} are equal; namely:

$$|\omega_S| = |\omega_{AS}| \tag{1.3}$$

Besides, the frequency of Raman scattering is independent of that of the incident light ω_0.

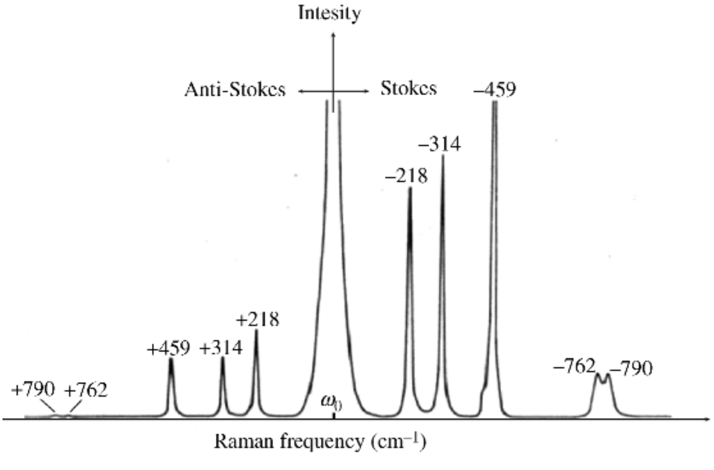


Figure 1.5 *Raman spectrum of $\mathrm{ClC_4}$. Reprinted from S.-L. Zhang, Raman Spectroscopy and Low-dimensional nanoscale Semiconductors, Science Press, (2008)*

- As mentioned above, the scattering originates from the interaction between the incident particles and scattered system. According to the energy conservation law, all scattering processes, including Raman scattering, must obey this relationship:

$$E_S - E_0 = E_K \tag{1.4a}$$

where E_0, E_S, and E_K represent the energy of incident light, the scattered light, and the scattered system, K, respectively.

As the energy, E, is given by $E = \hbar\omega$, where $\hbar$ is the reduced Planck constant, the Equation (1.4a) can be rewritten as:

$$\hbar(\omega_S - \omega_0) = \hbar\omega_k \tag{1.4b}$$

which can be reduced to

$$\omega_S - \omega_0 = \omega_k \tag{1.4c}$$

In most cases, E_k is an innate property of the system and is independent of the frequency of the incident light, ω_0. Thus, the Raman frequency ($\omega_S - \omega_0$) must also be independent of the frequency of the incident light according to Equation (1.4c). Furthermore, it becomes evident that the absolute value of the Stokes frequency ω_S equals that of the anti-Stokes frequency ω_{AS}.

The above mentioned two basic features of Raman frequency originate from energy conservation laws, so they are universal.

1.3.2 Intensity

The intensity of Raman scattering is very weak and usually amounts to just $10^{-6} \sim 10^{-12}$ of that of the incident light. It has been a major constraint to the application and development of Raman scattering in the past.

The intensity of a Stokes line, I_S, is much stronger than that of the anti-Stokes line, I_{AS}, and the ratio of their intensities can be expressed as

$$I_S / I_{AS} \sim \exp\left(\hbar\omega / k_B T\right) \gg 1 \tag{1.5}$$

where k_B and T stand for the Boltzmann's constant and the absolute temperature, respectively.

1.3.3 Polarization

When the orientation of molecules and crystals is fixed in space and the incident light is polarized, the polarization of scattered light is determined by the symmetry of molecular structure and crystals. This produces a selection rule in polarized Raman spectra, which is also known as the polarization selection rule and can be used to analyze the ascription of Raman peaks and the symmetry of crystals.

1.4 Discovery of the Raman Scattering Effects and Observation of the First Raman Spectrum

1.4.1 Discovery of Raman Scattering Effects [9]

In 1921, C.V. Raman was returning to India from England. When his ship was traveling in the Mediterranean Sea, he was deeply impressed by the beautiful blue color of the seawater.

A New Type of Secondary Radiation.

If we assume that the X-ray scattering of the 'unmodified' type observed by Prof. Compton corresponds to the normal or average state of the atoms and molecules, while the 'modified' scattering of altered wave-length corresponds to their fluctuations from that state, it would follow that we should expect also in the case of ordinary light two types of scattering, one determined by the normal optical properties of the atoms or molecules, and another representing the effect of their fluctuations from their normal state. It accordingly becomes necessary to test whether this is actually the case. The experiments we have made have confirmed this anticipation, and shown that in every case in which light is scattered by the molecules in dust-free liquids or gases, the diffuse radiation of the ordinary kind, having the same wave-length as the incident beam, is accompanied by a modified scattered radiation of degraded frequency.

The new type of light scattering discovered by us naturally requires very powerful illumination for its observation. In our experiments, a beam of sunlight was converged successively by a telescope objective of 18 cm. aperture and 230 cm. focal length, and by a second lens of 5 cm. focal length. At the focus of the second lens was placed the scattering material, which is either a liquid (carefully purified by repeated distillation *in vacuo*) or its dust-free vapour. To detect the presence of a modified scattered radiation, the method of complementary light-filters was used. A blue-violet filter, when coupled with a yellow-green filter and placed in the incident light, completely extinguished the track of the light through the liquid or vapour. The reappearance of the track when the yellow filter is transferred to a place between it and the observer's eye is proof of the existence of a modified scattered radiation. Spectroscopic confirmation is also available.

Some sixty different common liquids have been examined in this way, and every one of them showed the effect in greater or less degree. That the effect is a true scattering and not a fluorescence is indicated in the first place by its feebleness in comparison with the ordinary scattering, and secondly by its polarisation, which is in many cases quite strong and comparable with the polarisation of the ordinary scattering. The investigation is naturally much more difficult in the case of gases and vapours, owing to the excessive feebleness of the effect. Nevertheless, when the vapour is of sufficient density, for example with ether or amylene, the modified scattering is readily demonstrable.

C. V. RAMAN.
K. S. KRISHNAN.

210 Bowbazar Street,
Calcutta, India,
Feb. 16.

121, 501–502; 1928

Figure 1.6 *Photo of Raman and copy of his note published in Nature [8]. Courtesy of Avril Rhys.*

He thought of Rayleigh's proposal that the blue color of seawater was due to the reflection of light from the blue sky. But Raman did not accept this explanation and carried out a simple experiment while still on the ship. He set a Nicol prism at the Brewster angle in order to eliminate the reflected light from the seawater surface; nevertheless, the light from the deep seawater still exhibited the blue color. This led Raman to conclude that the blue color of seawater came from the scattering of seawater itself.

After Raman returned to India, he immediately started to research the scattering of water. In 1923, K.R. Ramanathan, a scholar in his research team, focused sunlight into water and other liquids held in slender-necked bottles and put light filters in the path of the incident and the scattering direction. Since the two filters chosen were complementary, allowing no light to pass through when both were placed together, the incident light ray should not have been seen from the other side. However, he observed light in the scattered direction. Ramanathan thought that the light originated from the weak fluorescence caused by impurities in the liquid; but even after repeated purification of the liquid, the weak "fluorescence" still remained.

Raman did not agree with his colleague's explanation of "the residual fluorescence". He thought that "the weak fluorescence" was similar to the newly found Compton effect of X-rays. In the winter of 1927, Raman deduced the Compton scattering formula using the classical approach, and apparently confirmed that the weak fluorescence was indeed similar to the Compton effect, that is, a certain kind of non-coherent scattering resulted in a wavelength change. Then Raman immediately instructed his students to improve the experiment, purifying and observing liquid time after time. In January 1928, they found that the scattered light from pure glycerin appeared green instead of the conventional blue color. This greatly encouraged them to do further research. On February 7th, 1928, K.S. Krishnan proved that "the weak fluorescence" observed by Ramanathan was pervasive in many kinds of organic liquids and their vapors. Eventually, after all the experimental results had been validated by Raman himself, he submitted a "note" titled *A New Type of Secondary Radiation* to the magazine *Nature* on February 16th, 1928. The note was rejected by the reviewer of the magazine. However, the publisher decided to publish anyway and it came out in *Nature* on March 31st [8]. Two years later, in 1930, the note of less than half a page led Raman to the Nobel Prize. Soon after, the research and application of Raman scattering became an active research field, which has continued to this day.

In the same year that Raman and Krishnan published their work, Russian scientists G. Landsberg and L. Mandelstam independently published their discovery of the same kind of scattering, but observed in crystalline quartz [10]. This scattering is also referred to as "combination scattering" in the Russian literature, although most scientists call it "Raman scattering". Later experiments showed that the scattering observed by Raman and Landsberg were the two satellite lines of the Rayleigh line predicted by A. Smekel in 1923 [11].

In *A New Type of Secondary Radiation* [8], Raman described their experimental equipment in detail (Figure 1.7). Sunlight was focused by two lenses: the first was an 18 cm diameter objective lens for a telescope with a focal length of 230 cm and the second was a lens with a 5 cm focal length. The scattering material was placed at the focal point of the second lens. The material was a liquid purified through distillation many times in a vacuum or its dustless vapor. The two optical filters in the setup were complementary blue–purple and yellow–green filters. The blue-purple filter was set in the path of the incident optics, so that no yellow-green light could pass through the liquid and vapor. When the yellow-green filter was placed between the sample and observer's eye, the re-appearance of yellow-green light served as evidence of Raman scattering.

The history mentioned above illustrates several interesting and meaningful developments of great experiments. First, the discovery by Raman originated from his observation of

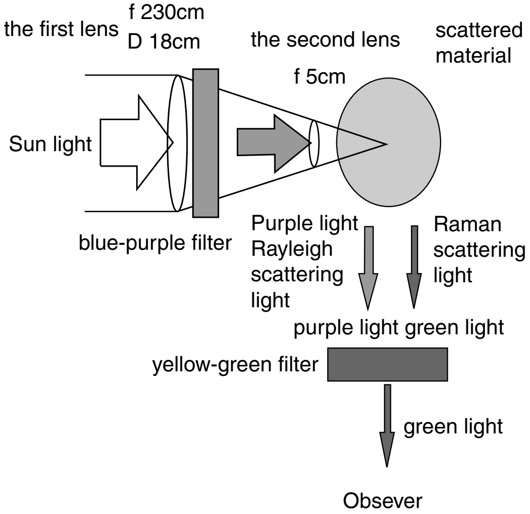


Figure 1.7 The experimental setup of Raman scattering as observed by Raman. Reprinted from S.-L. Zhang, Raman Spectroscopy and Low-dimensional nanoscale Semiconductors, Science Press, (2008)

the blue color of seawater, a common phenomenon that had apparently been explained by a great scientist. Second, the published note by Raman was a conclusion drawn from the accumulation of many meticulous and careful experiments carried out over seven years, and done with no awareness of a theoretical prediction for this effect. Only the theoretical understanding developed by Raman himself convinced him that the experimental results were not invalid and encouraged him to continue with more experiments. Finally, his experimental results were obtained by using very simple equipment. It was said that the entire setup cost only 500 rupees at the time.

1.4.2 The First Raman Spectrum

When Raman submitted his note to *Nature* in 1928, he was not content with the present experimental results. On 7th and 28th, using benzene, he observed sharp spectral lines in the blue-green region of the spectroscope with excitation by sunlight and the 435.9 nm spectral line of a mercury vapor lamp, respectively. Furthermore, based on the experimental setup of Raman, Krishnan took the first Raman scattering spectrum that included both Stokes lines and anti-Stokes lines using a Higer Baby's quartz spectrograph. Figure 1.8 shows the earliest published Raman scattering spectrum of CCl_4.

1.5 Historical Development of Raman Spectroscopy

1.5.1 The Rapid Growth and Early Development of Raman Spectroscopy

After the publication of the first two important papers by Raman [8], a huge surge of research and application of Raman spectra came out almost instantly around the world. In 1928, when

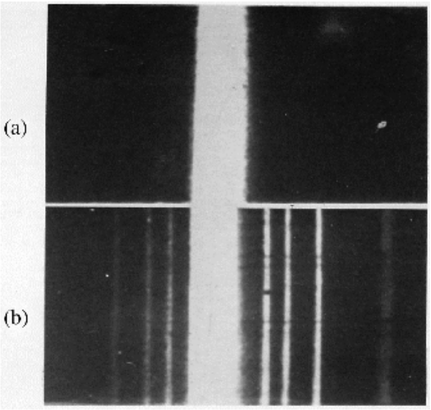
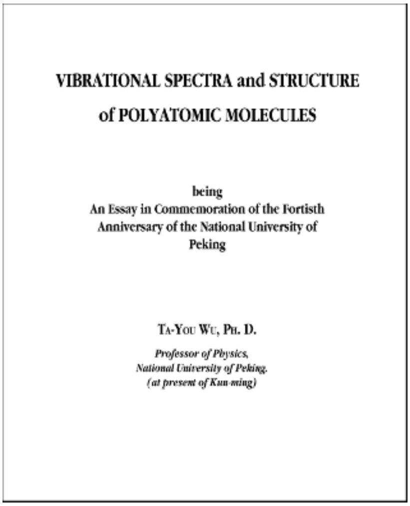


Figure 1.8 *The earliest published Raman scattering spectrum of CCl4 by Raman [1]. Reprinted from S.-L. Zhang, Raman Spectroscopy and Low-dimensional nanoscale Semiconductors, Science Press, (2008)*

Raman published his note in *Nature*, more than 60 papers pertinent to the Raman effect were published. And over 1757 papers on Raman spectroscopy had been published internationally by 1939 [12]. The decade after 1928 was the period when Raman spectroscopy grew rapidly and progressed prosperously. At the end of this period, in 1939, a review book on Raman spectroscopy *Vibrational Spectra & Structure of Polyatomic Molecules* [13] was published by Ta-You Wu, a professor at Peking University, during the difficult time when China was at a war (Figure 1.9). The book is the first overall review of Raman



VIBRATIONAL SPECTRA and STRUCTURE
of POLYATOMIC MOLECULES

being
An Essay in Commemoration of the Fortisth
Anniversary of the National University of
Peking

TA-YOU WU, PH. D.

Professor of Physics,
National University of Peking.
(at present of Kun-ming)

Figure 1.9 *The cover of* Vibrational Spectra & Structure of Polyatomic Molecules *by Wu [13]. Reprinted from S.-L. Zhang, Raman Spectroscopy and Low-dimensional nanoscale Semiconductors, Science Press, (2008)* spectroscopy experiments and became an instant reference book in this field. It is still cited worldwide today, after 60 years.

1.5.2 The Quiet Period of Raman Spectroscopy

As mentioned earlier, Raman scattering is very weak, while the intensity of Rayleigh scattering and other spurious light are always much stronger. With the use of spectral lines of a mercury vapor lamp as the excitation light source in the early Raman spectral experiments, Raman spectra could only be applied to studies on chemical molecular vibration. At the same time, due to the rapid development of IR devices and techniques during World War II, IR spectroscopy was making huge progress. Therefore, after the war, spectral research of chemical molecular vibrations was dominated almost entirely by IR spectroscopy, leaving Raman spectroscopy relatively quiet.

In this "silent period," theoretical research in understanding vibration spectra was not stagnant. The book, *Dynamical Theory of Crystal Lattices* [14], published in 1954, was an outstanding representative of work in this area (Figure 1.10). This book was written by the

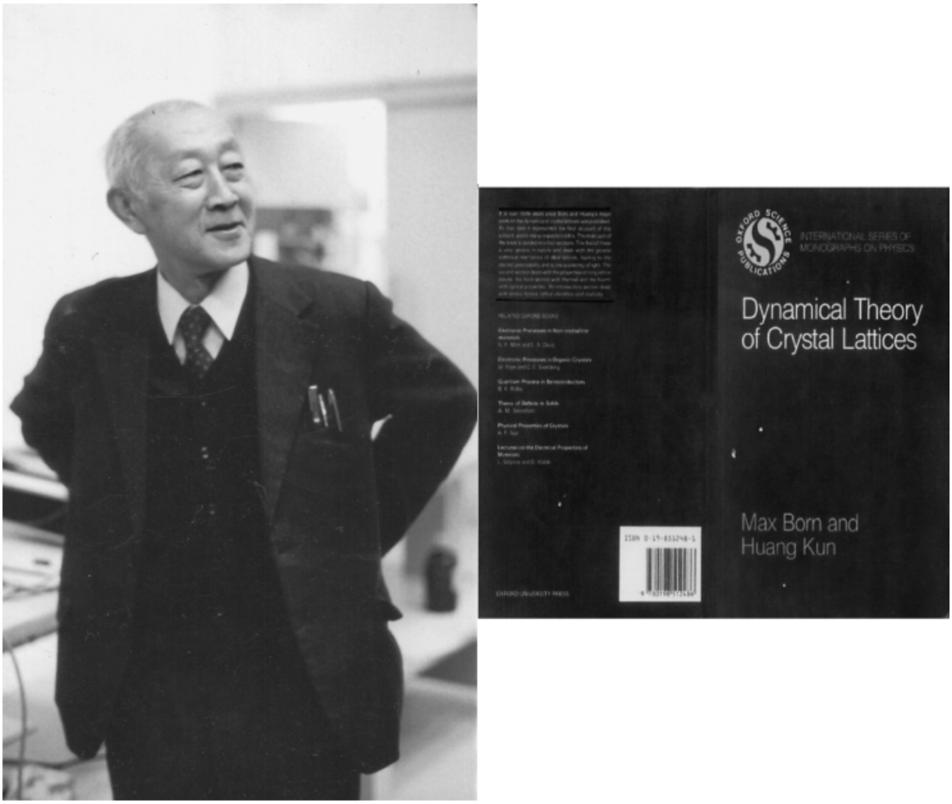


Figure 1.10 *The cover of* Dynamical theory of Crystal Lattices *by Max Born and Kun Huang [16]. Reprinted from S.-L. Zhang, Raman Spectroscopy and Low-dimensional nanoscale Semiconductors, Science Press, (2008)*

Nobel laureates Max Born and Kun Huang. The last chapter of the book "The Optical Effects" is practically dedicated to Raman scattering. In this last chapter, based on discussion of universal and profound problems in published literature in the past [15], the authors developed a theory of light scattering. The book has gone through three editions and been re-printed many times. In the third edition [16], published in 1985, the publisher offered an evaluation of the impact of the book: "It is over 30 years since Born and Huang's major works on the dynamics of crystal lattices was published. At that time it represented the final account of this subject and in many respects it still is." In fact, the book is held widely as the classic on solid state physics (especially on phonon physics) and lays the theoretical foundation for solid state Raman spectroscopy developed ten years later due to the invention of the laser.

1.5.3 The Renaissance and Flowering of Raman Spectroscopy

With the invention and availability of the laser in 1960 [17], the mercury vapor lamp as an excitation source of Raman spectrometer was soon replaced. In 1962, less than two years after the laser was invented, the first laser Raman spectra with excitation by a ruby pulse laser at 694.3 nm was published [18], marking the re-birth of Raman spectroscopy and the end of the traditional spectroscopy by excitation with the mercury vapor lamp.

In this new period of Raman spectroscopy, the studied objects are no longer restricted to chemical molecules. Nearly any object that is able to interact with light has been studied by Raman spectroscopy. The scientific and technological areas studied and applied by Raman spectroscopy have included single molecule, solid state matter (minerals, crystals, glasses, ceramics, disordered materials, nanostructure materials, ...), liquid, organism, medicines, and so on.

In addition, some Raman spectral phenomena, which could not to be studied by excitation light intesity in traditional Raman spectroscopy, are now possible because of the laser.

With further development of lasers (in terms of wavelength, with shorter and shorter duration) and significant improvement of other components of Raman spectrometers, the observable Raman spectra are different from the old ones spectroscopically. These developments will be discussed in greater depth in Chapters 3 and 4.

References

[1] Zhang, Shu-Lin (2008) *Raman Spetroscopy and Low-imensional Nano-semiconductors*, Science Press, Beijing

[2] Matsuda, A., Kazutaka, G., and Kondo, K. (2002) *Phys. Rev. B.*, **65**, 174116.

[3] Zumbusch, A., Holtom, G.P., and Xie, S.X. (1999) *Phys. Rev. Lett.*, **82**, 4142.

[4] Rayleigh, L. (1871) *Phil. Mag., XLI*, **274**, 447.

[5] Tyndall, J. (1868–1869) *Proc. Roy. Soc.*, **19**, 223.

[6] Mie, G. (1908) *Ann. Physik*, **25**, 377.

[7] Brillouin, L. (1922) *Ann. Phys. (Paris)*, **17**, 88.

[8] Raman, C.V. and Krishnan, K.S. (1928) *Nature*, **121**, 501.

[9] Jayaraman, A. (1989) C.V. Raman, the man and scientist, in *Raman Spectroscopy Sixty Years On* (eds H.D. Bist, J.R. Durig, and J.F. Sullivan), Elsevier Science Pub. Co. Inc., New York, p. xix.

[10] Landsberg, G. and Mandelstam, L. (1928) *Naturwiss*, **16**, 557, 772.

[11] Smekal, A. (1923) *Naturwiss*, **11**, 873.

[12] Hibbenm, J.H. (1939) *The Raman Effect and its Chemical Applications*, Reinhold Publishing Co., New York.

[13] Wu, T.Y. (1939) *Vibrational Spectra & Structure of Polyatomic Molecules*, The China Science Co., Shanghai.

[14] Born, M. and Huang, K. (1954) *Dynamical Theory of Crystal Lattices*, Oxford University Press, Oxford.

[15] Themer, O. (1952) *Proc. Phys. Soc.*, **65**, 38.

[16] Born, M. and Huang, K. (1985) *Dynamical Theory of Crystal Lattices*, Oxford University Press, Oxford.

[17] Maiman, T.H. (1960) *Nature*, **187**, 493.

[18] Porto, S.P.S. and Wood, D.L. (1962) *J. Opt. Soc.*, **52**, 251.