Chapter 3

Raman and Brillouin Scattering
3.1 Physics of Inelastic Light Scattering

Raman scattering, a nondestructive spectroscopic technique whereby light is inelastically scattered by atomic vibrations, has been the main tool to study acoustic/optical vibrations over the years. Recently, it has started to reveal its full potential with experiments on very high quality samples. This is due to the development of instrumentation and the sensitivity of vibrations to the exact microscopic structures. As the detection of light inelastically scattered by a single nanoparticle is not yet possible for very small nanoparticles, more monodisperse systems are needed. Having systems for which the shape and size of the nanoparticles are controlled as well as their crystallinity and environment enables the observation of experimental features that would otherwise be hidden by inhomogeneous broadening.

In order to investigate acoustic vibrations of nanoparticles, it is natural to turn to vibrational spectroscopies such as Raman, Brillouin, pump probe, infrared and inelastic neutron scattering. Indeed, the first experimental technique used to observe the acoustic vibrations of nanoparticles was inelastic light scattering (Raman scattering) [1,2]. Since then, experimental evidences have been obtained using a variety of different techniques. Other usual vibrational spectroscopies such as infrared absorption [3, 4] or inelastic neutron scattering [5] have had limited success. In the literature, “Raman scattering” is often used as a generic term for both Raman and Brillouin scattering. Several famous physicists had theoretically predicted the possibility of Raman scattering before its experimental discovery. The first one was Adolph Smekal in 1923. Independently of A. Smekal, Sir Chandrasekhara Venkata Raman found accidentally some peculiarities in the polarization of light scattered by distilled water in 1921 but at that time he did not conceive what kind of effect he had observed.
3.1.1 Short Historical Recall

a) Order 0

b) Order 1

Fermi

Figure 3.1: Optical processes: a) Order 0: Propagation of light in a medium, i, with energy $E_i$, and momentum $\sim k_i$; b) Order 1: Absorption or emission of light creating or annihilating an electron e-hole $h$ pair. Enrico Fermi (1901-1954); c) Order 2: Elastic light scattering producing photons with scattered energy $E_s$ equal to $E_i$, but momentum $\sim k_s$ different to $\sim k_i$. Sir Joseph John Thomson (1856-1940) and Lord John William Strutt Rayleigh (1842-1919); d) Order 3: Inelastic light scattering by the vibrations where energy $E_s$ of the scattered photon is reduced by the energy of the vibration $E_{vib}$. Sir Chandrashekhara Venkata Raman (1888-1970) and Léon Brillouin (1889-1969).
Within two years he showed that this fact had a strong connection with the presence in the medium of some other radiation with wavelength appreciably different from the one of incident light. It is important to note that Raman scattering is not the absorption of the photon, followed by the emission of a photon of less energy that instead describes fluorescence. Firstly, luminescence was the main hypothesis for the origin of this additional radiation but this interpretation did not agree with the fact that purification of the water would not remove the effect. This latter observation led Raman to the idea that this phenomenon was of a new type and in 1923 Raman started a purposeful investigation of this “new light”. In 1928 Raman assumed that the effect he observed was an analog of the Compton Effect (the scattering of photons from electrons) through which photon energy can be absorbed partially. Raman carried out the experimental inspection of this hypothesis and finally discovered the discrete spectrum of the scattered radiation. In 1930 Raman was awarded the Nobel Prize “for his work on the scattering of light and for the discovery of the effect bore his name”.

Light-matter interaction can be described by quantum mechanics in the framework of the perturbation theory. Order 0 event corresponds to the propagation of an electromagnetic radiation (i.e. photon) without interaction (Figure 3.1a). Fermi’s golden rule gives the transition rates between eigen states, and is the first order of the perturbation theory. These transitions correspond to one-step absorption or emission of a photon by creation or annihilation of an electron-hole pair (Figure 3.1b). If the photo excited electron-hole pair scatters elastically, for instance by impurities or defects before recombining, then the light scattering process is energy conserving and is called Rayleigh scattering (Thomson scattering in the case of free charged particles) (Figure 3.1c). The scattered photon wave vector satisfies both $\vec{K}_s \neq \vec{K}_i$ and $|\vec{K}_s| = |\vec{K}_i|$. This
optical process is the order 2 of the perturbation theory. Light is inelastically scattered (order 3) when there is some energy and wave vector transfers from the electron bath to the phonon bath (e.g. creation or annihilation of vibrations): \( E_s \neq E_i \). In such case, the inelastic scattering process is called Raman-Brillouin scattering (Figure 3.1d).

Raman scattering is a widely used method to identify molecules by means of their vibrational fingerprint. However, spontaneous Raman is incredibly feeble with a cross-section of \( \sim 10^{-30} \text{ cm}^2 \) and therefore various techniques have been applied to increase its sensitivity.

3.1.2 Nature of the Phenomena

Figure 3.2: Light scattering by an induced dipole moment due to an incident EM wave.

The scattering of light may be thought of as the redirection of light that takes place when an electromagnetic (EM) wave (i.e. an incident light ray) encounters an obstacle or no homogeneity, in the case of the scattering material (like solid, liquid or gas). As the EM wave interacts with the matter, the electron orbits within the constituent molecules are perturbed periodically with the same frequency \( (\nu_o) \) as the electric field...
of the incident wave. The oscillation or perturbation of the electron cloud results in a periodic separation of charge within the molecules, which is called an induced dipole moment. The oscillations induced dipole moment is manifest as a source of EM radiation, thereby resulting in scattered light. The majority of light scattered is emitted at the identical frequency \( (\nu_o) \) of the incident light, a process referred to as elastic scattering. However, as explained below, additional light is scattered at different frequencies, a process referred to as inelastic scattering. Raman scattering is one such example of inelastic scattering. In summary, the above comments describe the process of light scattering as a complex interaction between the incident EM wave and the material’s molecular/atomic structure.

An incident electromagnetic wave induces a dipole moment during the light material interaction. The strength of the induced dipole moment, \( P \), is given by

\[
P = \alpha \ E
\]  

(3. 1)

Where \( \alpha \) is the polarizability and \( \vec{E} \) is the strength of electric field of the incident EM wave. The polarizability is a material property that depends on the molecular structure and nature of the bonds. For the incident EM wave, the electric field may be expressed as

\[
\vec{E} = E_o \cos \left( 2\pi \nu_o t \right)
\]  

(3.2)

where \( \nu_o \) is the frequency (Hz) of the incident EM \( (\nu_o = \frac{c}{\lambda}) \). Substituting Eqn. (3.2) into (3.1) yields the time-dependent induced dipole moment,

\[
P = \alpha E_o \cos \left( 2\pi \nu_o t \right)
\]  

(3. 3)

Because the ability to perturb the local electron cloud of a molecular structure depends on the relative location of the individual atoms, it follows that the polarizability is a
function of the instantaneous position of constituent atoms. For any molecular bond, the individual atoms are confined to specific vibrational modes, in which the vibrational energy levels are quantized in a manner similar to electronic energies. The vibrational energy of a particular mode is given by

$$E_{\text{vib}} = \left(j + \frac{1}{2}\right) h V_{\text{vib}}$$  \hspace{1cm} (3.4)

where \(j\) is the vibrational quantum number \((j = 0,1,2\ldots)\), \(V_{\text{vib}}\) is the frequency of the vibrational mode, and \(h\) is the Planck constant. The physical displacement \(dQ\) of the atoms about their equilibrium position due to the particular vibrational mode may be expressed as

$$dQ = Q_o \cos(2\pi V_{\text{vib}} t)$$ \hspace{1cm} (3.5)

where \(Q_o\) is the maximum displacement about the equilibrium position. For a typical diatomic molecule (e.g. \(N_2\)), the maximum displacement is about 10% of the bond length. For such small displacements, the polarizability may be approximated by a Taylor series expansion, namely,

$$\alpha = \alpha_o + \frac{\partial \alpha}{\partial Q} dQ$$ \hspace{1cm} (3.6)

Where \(\alpha_o\) is the polarizability of the molecular mode at equilibrium position. Based on the vibrational displacement of Eqn. (3.5), the polarizability may be given as

$$\alpha = \alpha_o + \frac{\partial \alpha}{\partial Q} Q_o \cos(2\pi V_{\text{vib}} t)$$ \hspace{1cm} (3.7)

Finally, Eqn. (3.7) may be substituted into Eqn. (3.3), which yields

$$P = \alpha E_o \cos(2\pi V_{\text{vib}} t) + \frac{\partial \alpha}{\partial Q} Q_o E_o \cos(2\pi V_{\text{vib}} t)\cos(2\pi V_{\text{vib}} t)$$ \hspace{1cm} (3.8)
Using a trigonometric identity, the above relation may be recast as

\[ P = \alpha E_o \cos(2\pi \nu_o t) + \frac{\partial \alpha}{\partial Q} Q_o \left\{ \cos[2\pi (V_o - V_{\text{vib}})] + \cos[2\pi (V_o + V_{\text{vib}})] \right\} \]

(3.9)

Examination of the above equation (3.9) reveals that the induced dipole moments are created at three distinct frequencies, namely \( \nu_o, (\nu_o - \nu_{\text{vib}}), \) and \( (\nu_o + \nu_{\text{vib}}) \), which results in scattered radiation at these same three frequencies. The first scattered frequency corresponds to the incident frequency, hence is elastic scattering (e.g. Mie or Rayleigh), while the latter two frequencies are shifted to lower or higher frequencies and are therefore inelastic processes. The scattered light in these latter two cases is referred to as Raman scattering, with the down-shifted frequency (longer wavelength) referred to as Stokes scattering, and the up-shifted frequency (shorter wavelength) referred to as anti-Stokes scattering. Note, however, that the necessary condition for Raman scattering is that the term \( \frac{\partial \alpha}{\partial Q} \) must be non-zero. This condition may be physically interpreted to mean that the vibrational displacement of atoms corresponding to a particular vibrational mode results in a change in the polarizability.

For example, consider a diatomic molecule A-B, with maximum vibrational displacement \( Q_o \), as shown below.

**Figure 3.3:** Vibrational displacement of A-B about the equilibrium position.
In consideration of the above figure, it is apparent that the ability to perturb the electron cloud by an incident electric field will depend on the relative position of the atoms. For example, when A-B is at maximum compression, the electrons from a given atom feel the effects of the other atom’s nucleus and are therefore not perturbed as much. Hence the polarizability is reduced for the minimum bond length. In contrast, when A-B is at maximum expansion, the electrons are more readily displaced by an electric field due to the greater separation (i.e. less influence) from the other atom. Therefore, the polarizability is increased at the maximum bond length. One might make a plot of the polarizability as a function of displacement about equilibrium, which would look something like the following for the diatomic molecule A-B.

As we can see the Raman scattering arises from the electric dipoles oscillating at the shifted frequencies which appear due to a modulation of the frequency of the electromagnetic field by vibration of the molecule. To understand the qualitative analysis discussed about, we have briefly described the phenomena of inelastic light scattering. Let us consider the field of incident light \( \tilde{E}(\tilde{r},t) = E_0 e^{i(k\tilde{r} - \omega t)} \) scattered by a small volume of the medium and we estimate the scattered field far from the point of scattering (doing this we avoid the influence of the scattering from the other points).

This field is described by Maxwell’s equations and from them one can show that [6]:

\[
\tilde{E}'(\tilde{R}) \propto \rho(\tilde{r},t) e^{i\tilde{k}' \cdot \tilde{R}} dV
\]

(3.10)

where \( \tilde{R} \) is a vector joining a point inside the illuminated volume to the point of observation of the field. The wave vector \( k' \) expresses the change of the wave vector in the medium, so \( \tilde{k}' = \frac{n \omega \tilde{l}_k}{c} \) with \( \tilde{l}_k \) a unit vector and \( n \) is the refractive index of the
medium. Time \( t' \) is the retarded time \( t - \left( \frac{R - \bar{r}}{c_m} \right) \) because a value of the speed of light inside the medium \((c_m)\) differs from that outside \((c)\). This integral does not depend on the point of observation. Remembering that the origin of scattering is an oscillation of the polarizability \((\text{Eq.}(3.6))\) and assuming these oscillations very weak function of time

\[
\alpha(\bar{r},t) = \alpha_o + \delta\alpha(\bar{r},t)
\]  

(3.11)

\[
\frac{\partial^2 \tilde{p}(\bar{r},t)}{\partial t^2} = -\omega^2 \tilde{p}(\bar{r},t)
\]  

(3.12)

If we plug expressions (3.6) and (3.11) into equation (3.10) assuming that \( R \gg \bar{r} \) we obtain \([7]\]

\[
\tilde{E}'(\bar{r},t) = -\left( \frac{\omega}{c} \right) \frac{e^{i(k \cdot \bar{r} - \omega t)}}{R} \bar{l}_k \times \bar{l}_k \times \int_V (\alpha_o + \delta\alpha(\bar{r},t)) \tilde{E}_o e^{i(k \cdot \bar{r})} d^3 r
\]  

(3.13)

This equation shows a superposition of all waves with different phases scattered by all scattering points of the medium. If the fluctuations of polarizability induced by the vibrations \( \delta\alpha \) are zero, the integral in equation (3.13) is zero too except the case of integration in the forward direction (when \((k = \bar{k})\) when the contribution of is not \(\alpha_o\) is not zero. Indeed: as far as the integral applies for a volume and due to the symmetry and anisotropy of the volume the integration over other directions leads to the cancellation of the scattered waves (the mathematical proof can be found in ref \([7]\).

Hence, we again come to the conclusion that the source of the scattering is a fluctuation of polarizability of the medium. From this expression it is also possible to single out two types of scattering: Rayleigh (if \( \delta\alpha(\bar{r},t') = \delta\alpha(\bar{r}) \)) and inelastic (if polarizability is a function of both time and space).
Vibrations that cause inelastic scattering are divided into two groups: propagating mode (Brillouin scattering) and non-propagating modes (Raman scattering). We now briefly describe these two phenomena.

3.1.3 Brillouin and Raman Scattering

3.1.3.1 Brillouin Scattering

Brillouin scattering is an effect caused by the $\chi^{(3)}$ nonlinearity of a medium, specifically by that part of the nonlinearity which is related to acoustic phonon. An incident photon can be converted into a scattered photon of slightly lower energy, usually propagating in the backward direction, and a phonon i.e. Brillouin scattering originates from plane acoustic waves that induces polarizability fluctuation. These waves arise from the collection coherent vibrational motions of the atoms and are characterized by a wave vector $q$ which in the Debye approximation is proportional to frequency $\omega(q)$ \cite{8}. The frequency of the reflected beam is slightly lower than that of the incident beam, the frequency difference $V_B$ corresponds to the frequency of emitted phonons. This is so-called Brillouin frequency shift is set by a phase-matching requirement. For pure backward Brillouin scattering the Brillouin shift can be
calculated from the refractive index $n$, the acoustic velocity $V_a$ and the vacuum wavelength $\lambda$;

$$
\nu_B = \frac{2nV_a}{\lambda}
$$

(3.14)

In homogeneous media this value implies that one can consider the continuous elasticity approximation. It is also worth to note that the frequency shift of this type of scattering depends on $\overline{q}$ through the angle $\theta$ hence on the geometry of the experiment. This difference helps us to distinguish the Brillouin signal from the Raman one, which does not depend on $\overline{q}$ on the experimental spectrum.

**Figure-3.4:** (a) The $\omega$-$q$ dependence for the optical branch of lattice vibrations. (b) Conservation of energy for Raman scattering (Stokes shift).

### 3.1.3.2 Raman Scattering

This type of scattering is produced by non-dispersive optical modes for which the frequency hardly depends on $\overline{q}$ i.e $\omega(\overline{q}) = \omega_o$ (see fig 3.5) unlike acoustic modes.

The frequency of optical phonon with wave vectors such as those transferred from visible light is almost a constant.
To analyze the microscopic aspect of Raman spectroscopy a quantum mechanics approach becomes necessary. The electromagnetic (em) radiation having high frequency cannot interact directly with phonons because of the large difference in frequency. Therefore, the electromagnetic radiation will interact only with the electrostatic causing a virtual transition. The excited electronic state will decay back in its ground state exchanging energy with phonons. Raman scattering may also be interpreted as a shift in vibrational energy state due to the interaction of an incident photon. The incident em wave induces an oscillating dipole moment, as discussed above, thereby putting the molecular system into a virtual energy state. The energy level of the virtual state is generally much greater than the vibrational quantum but is not necessarily equal to any particular electronic quantum energy. Therefore, the molecule stays in its ground electronic state. The linear behavior depicts the Debye approximation state. However, during the interaction with the incident photon, some quantum of energy equal to the vibrational mode may be imparted to the molecule. As a result, the remaining quantity of photon energy leaves the molecules as Raman scattered radiation.

As the molecular system is much more likely to be originally found in the ground vibrational state, the stokes scattering as depicted above is the most common Raman scattering process. For the case of anti-stokes scattering, the molecule is originally found in an excited vibrational state. During the interaction of the incident photon with the molecule, the vibrational energy state is relaxed back to a lower level,
and the vibrational quantum of energy associated with the change in vibrational state is then added to the incident photon, resulting in a scattered photon of energy $h (\nu_o + \nu_{vib})$. For a large system of molecules, it is expected that both stokes and anti-stokes Raman scattering will occur simultaneously, with the stokes scattering intensity generally greatly exceeding the anti-stokes intensity. The scattering process can be described by the absorption of a photon of frequency $w_I$ which brings the initial electronic state $|i\rangle$ to an excited state $|n\rangle$. This is then scattered to a secondary state $|n'\rangle$ by the emission or absorption of a phonon with frequency $q$. The $|n'\rangle$ state will decay to the former initial state emitting a photon having an energy $w_S$ which can be $>$ or $<$ than the incident radiation $w_I$. The first case where $w_I > w_S$ is known as stokes scattering and a phonon is created in the material, while the second where $w_I < w_S$ is known as anti-stokes scattering where a phonon is annihilated in the crystal. The two processes are schematized in the Fig. 3.6. The Raman scattering is defined as weak in intensity (scattered power), therefore it is necessary to calculate the scattering probability using a third order perturbation theory. According to the refs. [9, 10], the scattering probability of a system going from initial state $|i\rangle$ to the final state $|f\rangle$ can be calculated using Fermi’s golden rule. For one phonon scattering six time ordered processes are possible, they are described by as many Feynman’s diagrams and quantum mechanical terms appearing in the scattering probability equation. Approximating the process only with the first Feynman’s term there will be three equations describing the vertexes in the diagram.

The first vertex will express the excitation by the incident radiation of the electronic state from $|i\rangle$ to $|f\rangle$. 

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where \( w_1 \) is the exciting photon frequency and \( H_{eR}(w_1) \) is the Hamiltonian which describes the interaction between \( e.m. \) radiation and the ground electronic state. The second vertex describes the creation or annihilation of a phonon and the decay of the electronic excited state to the intermediate state \( |n'\rangle \) as result of the interaction with the phonon.

\[
\sum_{n,i} \frac{\langle n | H_{eR}(w_L) | i \rangle}{\hbar w_L - (E_n - E_i)}
\]  

(3.15)

Figure 3.6: The transverse phonons \( \|k\| = \frac{2\pi}{\lambda} \) in a 1D-solid with unit cell parameter \( l \) Ref 7(b).

\[
\sum_{n,i} \frac{\langle n' | H_{e-ion}(w_0) | n \rangle \langle n | H_{eR}(w_i) | i \rangle}{\hbar w_i - (E_n - E_i)(\hbar w_i - \hbar w_0 - (E_n - E_i))}
\]  

(3.16)

where \( H_{e-ion} \) is the Hamiltonian which describes the interaction between the electron and the phonon. Finally, considering energy conservation in Raman scattering process and applying, Fermi’s Golden rule, we obtain the following equation for the scattering power

\[
P(w_s) = \left( \frac{2\Pi}{\hbar} \right) \sum_{n,i} \langle i | H_{eR}(w_s) | n' \rangle \langle n' | H_{e-ion}(w_q) | n \rangle \langle n | H_{eR}(w_L) | i \rangle^2 \delta\left(\hbar w_L - \hbar w_q - \hbar w_s\right)
\]  

(3.17)
Here the final energy denominator is converted to a Dirac-delta function to express the conservation of energy and to have the final state $|f\rangle$ the same as initial $|i\rangle$.

### 3.2 Raman Scattering from Modes of Spherical Nanoparticles: Acoustic Phonon Quantization

The sole use of frequency as identification criterion for the interpretation of nanoparticles vibration modes might be error-prone since several vibrations can exist in a given narrow frequency range. The knowledge of the symmetry of the modes is therefore required in order to derive the selection rules that restrict the number of modes observable by a given technique. For example, to interpret Raman spectra, point group theory can be used to classify the vibrations of objects much smaller than the wavelength of light into Raman active and inactive ones. The symmetry of the particle results in a number of irreducible representations, which characterize the eigen modes of vibrations. Only some of these representations correspond to Raman active modes. The procedure to follow is well known and commonly applied to molecules. However, its application to spherical isotropic nanoparticles is a bit special since such particles are invariant under every rotation whose axis goes through the center of the particle and no molecule having such a high symmetry can exist as shown in figure 3.7

The symmetry group and the associated irreducible representations and selection rules have been derived by Eugène Duval [11] for nanoparticles whose diameter is small compared to the wavelength of the incident photons. This condition typically applies to Raman scattering, as it is conventionally conceived, i.e., as a molecular spectroscopy. The point group associated to an isotropic spherical nanoparticle is the group of the proper and improper rotations (O(3)). The irreducible representations are noted as $D^{(l)}_g$ and $D^{(l)}_u$. The irreducible representation corresponding to a spheroidal vibration is
\[ D_s^{(i)} \] for even \( \ell \) and \( D_u^{(i)} \) for odd \( \ell \). The irreducible representation corresponding to a torsional vibration is \( D_s^{(i)} \) for odd \( \ell \) and \( D_u^{(i)} \) for even \( \ell \). For a nanoparticle whose diameter is small compared to the wavelength of light, the Raman active vibrations have the \( D_s^{(0)} \) or \( D_s^{(2)} \) irreducible representation due to the symmetry of the polarizability tensor.

**Figure-3.7:** (a) Description of one nanoparticle in the Elastic Sphere Model (ESM). (b) Oscillation of a free sphere in a single spheroidal mode. (c) Oscillation of a free sphere in a single torsional mode Ref 7(b).

Therefore, Raman active modes are spheroidal modes with either \( \ell = 0 \) or \( \ell = 2 \). Polarization rules enable to distinguish between these two families as only the scattering by \( \ell = 0 \) modes is polarized (i.e., not observable when the polarization of the incident photons and that of the detector are perpendicular). Because these \( \ell = 0 \) modes have a longitudinal character (radial motions only), this polarization rule is equivalent to the polarized scattering from longitudinal acoustic modes in classical Brillouin scattering.
In Raman scattering the transition operator is the polarizability tensor \( \alpha_{ij} \), which is symmetric \( \alpha_{ij} = \alpha_{ji} \), consequently the polarizability tensor components transform according to the irreducible representations resulting from the symmetrical product [12]

\[
\left[ D_u^{(1)} \times D_u^{(1)} \right]_{\text{sym}} = D_g^{(0)} + D_g^{(2)}
\]  

(3.18)

Therefore, the only observable Raman transitions are the transitions creating (stokes) and annihilating (anti- stokes) one phonon of the spherical mode \( D_s^{(0)} \) or one phonon of the quadrupolar modes \( D_s^{(2)} \). The torsional modes are not observed by Raman scattering. These selection rules have been extended to nanoparticles with much larger dimensions (Montagna 2008) which case is more relevant of Brillouin scattering; in the following we will essentially consider selection rules that pertain to small nanoparticles, i.e., to Raman scattering.

However, recently derived Raman selection rules of Kanehisa preclude the observation of spheroidal modes and state that only the torsional mode with \( l = 2 \) is Raman-active [13]. It is shown that the assignment of parity in previous works by Duval et al [11] neglected the vector nature of the elastic field and thus the resultant selection rules are erroneous. For example, Duval et al. [2] observed two peaks while Mariotto et al [14] observed only \( l=2 \) and explicitly stated that the spherical mode \( l=0 \) could not be found experimentally. Champagnon et al [15] again observed one peak in the HH configuration and two peaks in the HV configuration, exactly as predicted by Duval [11]. But this result was refuted by Rajalakshmi et al [16] who observed a single peak in the HH configuration only. Sometimes deviation from completely spherical form of nanoparticles is invoked to explain the “breaking” of selection rules. But this
would also imply existence and possibly splitting of main modes [17,18] which is not observed. Further, in the case of embedded spheres, it is necessary to assign observed peaks to the torsional modes, which would normally be forbidden according to Duval [11]. The experimental situation is thus confusing. If, however, one usually observes only one peak in Raman scattering, not two, the observed peak is depolarized; thus it cannot be the totally symmetric mode with \( l=0 \), which would give a fully polarized peak and favors selection rule proposed by Kanehisa et al [12].

To explain the non-observation of overtones, Duval et al [2] suggested that the low-frequency modes are surface modes similar to the one suggested by Tamura et al, [19] which may be preferentially excited by incident photon. This explanation off course is not satisfactory, because bulk vibrational modes are also observed at the same time. The correct answer, in our opinion, requires radial selection rule. Probably a selection rule of the form \( n=\pm 1 \) holds, like in molecular oscillations observed by infrared and Raman spectroscopy.

Further, the comment, by Goupalov et al [20], which refuted his model and his subsequent rebuttal [21] have exacerbated the controversy. However, it is important to realize that, unlike the parity of a scalar function, the parity of a polar vector function, such as the displacement field, does not coincide with the parity of the orbital angular momenta associated with the function. This is in agreement with the paper of Montagna and Dusi [22]. Failing to notice this difference, Kanehisa [13] wrongly concluded that “the assignment of parity in previous works neglected the vector nature of the elastic field.” Doing the parity assignment the right way, the spheroidal and torsional modes characterized by an even are, respectively, even and odd, as clearly shown before. This confirms that the breathing mode \( l=0 \) and the spheroidal mode with \( l=2 \) are even. As a result, a phonon can participate in a first-order Raman process if and
only if its irreducible representation is the same as one of the irreducible representations which occur in the reduction of the representation of the polarizability tensor [11, 23]. Macroscopically, the same selection rules follow from the analysis of the number of independent components of the third-rank tensor of susceptibility or polarizability derivatives [24-26]. Thus, it remains to determine the type of representation responsible for the rotation-inversion group transforms. Furthermore, the corresponding irreducible representation is characterized by the angular momentum and parity is still undetermined. Interestingly, Tanaka et al. [27] claimed that both spheroidal modes of even \( l \), and torsional modes of odd \( l \) are Raman-active.

### 3.2.1 Pump Probe Technique

![Figure-3.8: Pump-probe spectroscopy principle sketch.](image)

Femtosecond pump-probe spectroscopy is a good dynamic analysis technique in femtosecond scale. Femtosecond pump-probe spectroscopy enables to follow in real time vibrational motions coupled to electronic transitions. Indeed, if the system is excited by a pulse shorter than the vibrational period, vibrational coherence is induced both in the ground and excited electronic states, providing information also on the excited state nuclear dynamics. In addition, time-domain vibrational spectroscopy circumvents the experimental difficulty of Raman spectroscopy in discriminating the low-frequency modes against the laser line. In a pump-probe experiment, the output pulse train from an ultrafast laser, is divided into two beams: the sample is excited by one pulse train (pump) and the changes it induces in the sample are probed by the second pulse train (probe), which is suitably delayed with respect to the pump. Some properties related to the probe
(reflectivity, absorption, luminescence, Raman scattering) is then monitored to investigate the changes produced by the pump in the sample. There is a time delay between the pump pulse train and the probe pulse train. With the change of the delay between the two pulsed trains, we can get a spectrum of reflectivity, absorption, luminescence, or Raman scattering of the probe after the sample. In this way, the change caused by the pump is studied. From Boyd's book [28], the response time of the nonlinear refractive index from electronic polarization is in femtosecond scale, and that from molecular orientation is in picosecond scale. This kind of physical process can be reached by femtosecond pump-probe spectroscopy. We have, however not used Brillouin and pump-probe techniques in the present study.

3.3 Experimental Raman Techniques

The instrumentation required for Raman spectroscopy measurements, in particular the monochromator unit is far more complicated and sophisticated then the ones used absorbance and fluorescence. The main reason is that in comparison with techniques, the Raman spectroscopy requires a high spectral resolution. The spatial resolution is also very important especially in the study of nanostructured materials. A high spatial resolution allows selecting a very small area of the sample from where the signal is collected, therefore, to get the information only from the area of interest or at least reduced as much as it is possible. In this way, the signal contribution from other not interesting areas of the sample will be drastically reduced. Unfortunately, the spatial resolution is limited by the well known diffraction limit which does not allow pushing it below ~500 nm. By this Raman setup it is possible to work with three different spatial resolutions corresponding to three different instrumental configurations. The macro- Raman configuration is used to collect the scattered
radiation from homogenous samples with large area where not a particularity high spatial resolution is required, e.g. samples in UHV chamber or liquids and solution in glass cuvette. With this configuration, the spatial resolution can be in the best cases of some microns.

With the micro-Raman configuration, the spatial resolution in this configuration, a nanometer resolution is available, however, it is not yet fully operative and it was not used for the measurements on CdS quantum dots and it will not be described here.

In this study, only micro-Raman configuration was used thus will be described more in detail in respect with the other two can pushed down ~500 nm in the X and Y directions. This high resolution is used essentially for spectroscopy of solid bulk and nanostructured semiconductors. This optical setup is also equipped with nano- Raman facility.
However, it is worthwhile to remark that the three optical configurations differ between them only in the light focusing and light collection optics. The optical setup consists of a visible and UV light laser sources, a coherent Innova 200 Ar\textsuperscript{+} laser which
can provide a wide spectral range from the visible to the near UV (from 514nm to 350nm). Light powers of > 2 W in the visible and of ~1 W in the UV are available.

Along the light path, from laser output to the entrance slit of the monochromator, the laser beam can be opportunely polarized with a Fresnel prism, and reduced in power when necessary, by set reflective or absorptive filters. Moreover, the Ar plasma lines produced in the laser tube can be filtered by interferometric filters specific for each wavelength. However, the plasma lines (required for the spectra calibration) filter can be easily removed. The laser light is focused on the sample by a microscope objective which at the same time collects the scattered light. The scattered light is focused on the monochromator entrance slit by a set of parabolic mirror. In order to have a high confocality of the optics, in between of the first two parabolic mirrors, just in their foci is placed a 10μm pinhole attached by a three stage micrometric positioned. The elevate confocality allows to select the signal only from small portion of the three dimensional focus on the sample to jettison the unwanted radiation, e.g. signals from the lens coating. With a pinhole of 10μm it is possible to reach a spatial resolution of ~250 nm along the x-y axis and ~500 nm along the z axis.

For the sample positioning, the setup is equipped with x, y, z micrometric screws positioned.

However, the upgraded version has been equipped with two closed-loop piezoelectric stages (x, y) and an open-loop piezo mounting (z focus positioning) capable of 2 nm and 0.1μm translational resolution respectively. Both piezo positioners are driven by RHK SPM electronics.

Thanks to this last upgrade it is possible to perform confocal spectroscopy i.e. to acquire point by point the signal from the surface obtaining a mapping of the intensity.
To get the intensity mapping, different kind of light signal can be acquired, *e.g.*, scattered laser light, a chosen Raman line or the PL signal. The signal is detected by a photomultiplier or a photodiode and then acquired by the SPM electronic which merges it with the sample position information. The spatial resolution may variate from case to case. The core of the setup is represented by the Dilor triple grating monochromator which can operate in additive or subtractive mode. This monochromator has a spectral resolution determined experimentally of 2 cm\(^{-1}\) in the subtractive mode and 1 cm\(^{-1}\) in additive mode. For the light detection, the monochromator is equipped with a liquid nitrogen cooled CCD Horiba Jobin Yvon CD3000v placed after the spectrometer output slit and of a Peltier-effect cooled Hamamatsu photomultiplier placed after the two monochromator grating slits.

The entire optical system is placed on a vibrational-damped optical table. The damping is performed in the low frequency range by the laminar flow pneumatic legs, while, in the high frequency range (ν>100Hz) by an auto-tune active damping technology. This damping is based on the interference between the vibrations of table surface and the oscillations produced of two piezoelectric crystals. This damping system is of fundamental importance during confocal spectroscopy measurement, where the eventual vibrations, when undamped, have amplitudes up to 100 μm. Consequently, they will strongly disturb the positioning performed by the x, y piezo-table which has maximum scanning area of 16 μm, a value more than 5 times smaller than the amplitude of vibrations. However, the vibration does not come only from the environment but they can be produced also by the instrumentations present on optical table. It was found that a very important sources of vibrations was the Laser equipment, in particular its water cooling system. Due to the pulsed flow produced by the water pump a very strong vibrational noise with a frequency of ~50 Hz was
transmitted on the table, and it could not be erased by the active damping. However, a series of investment has allowed to drastically reducing this noise. They consisted in introducing four further pneumatic dampers below the aluminum board bearing the laser tube and rearranging entirely the hydraulic system of the laser cooling in order to quite the water flow and damp the pressure of the pulses produced by the water pump. The Raman scattering measurement are carried out using a Spex 14018 double monochromator equipped with a Ar+ laser and photomultiplier tube (Hamamatsu R943-02).
References


[23] P. M. Morse, and H. Feshbach, Methods of Theoretical Physics, in 2 parts Mc Hill, New York (1953).


