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Introductory Chapter: The Multiple Applications of Raman Spectroscopy

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1. Introduction

The vibrational spectroscopies have been largely employed in the determination of the molecular structure and played a central role in many areas, from fundamental chemistry to materials engineering. Among these techniques, the Raman spectroscopy is essential today in the study of nanostructured materials and biological systems in *in situ* and *in vivo* conditions. In addition, by intensification process, very small quantities can be analyzed (for certain cases in the limit of single molecule regime). Detailed information about the molecular structure can be obtained, because each vibration of atoms shows a characteristic position and intensity. Both position and intensity are influenced by the chemical environment, or in other words by chemical bonds, inter- and intramolecular forces.

2. Raman scattering

The Raman spectra have a different origin compared to infrared absorption (IR); an inelastic scattering process is responsible for the appearance of the vibrational bands. In IR spectroscopy, the radiation is absorbed by available vibrational states ($E_1, E_2, E_3, \dots, E_N$), it means that photon energy must be coincident with the energy difference between two available states. Thus, $E_N - E_1 = h\nu$, being h the Planck's constant. In Raman spectroscopy, a molecule can scatter a monochromatic (ν_0) radiation. Typically, lasers with photon energies ranging from UV to near-IR region are used in the Raman experiments. The elastic scattering is called Rayleigh scattering, and it is much more intense than the inelastic Raman scattering (approximately 10^{-8} lower than the intensity of the incident radiation). The Raman spectrum appears in a wavelength (λ_0) slightly higher or lower than the incident radiation [1–5].

Hence, this scattering process can be visualized as a perturbation of the molecule by incident photon, which *eigenstate* can be described as the linear combination of the *stationary-state* (or *time-independent*) wave functions of the molecule. The pertubated states of the molecule are called “*virtual*” because they are not states from the stationary condition (*eigenstates*). The photon released when the molecule returns to electronic ground state has, more often, the same incident photon energy, characterizing then the Rayleigh scattering. The Raman scattering, that contents the vibrational information, can be exemplified in the energy diagram represented in **Figure 1**. The photon energy ($\nu_o - \nu_m$) appears in the region of the spectrum called Stokes region; in addition, the photons with energy ($\nu_o + \nu_m$) appear in the anti-Stokes region. The bands observed in anti-Stokes region are less intense than those in the Stokes region due to the differences in population according to the *Maxwell-Boltzmann* distribution, making the bands from Stokes region more intense than the anti-Stokes Raman region [6–8].

A vibration (vibration coordinate q) is Raman active when the polarizability (α) (or induced dipolar momentum) of the molecule is changed; being described as: $\left(\frac{\partial \alpha}{\partial q}\right) \neq \emptyset$. Hence, as the nature of the Raman effect is physically different from the infrared, the selection rules are also different, which lead to different spectra. In fact, these two techniques are complementary, being used in many cases combined for structural elucidation.

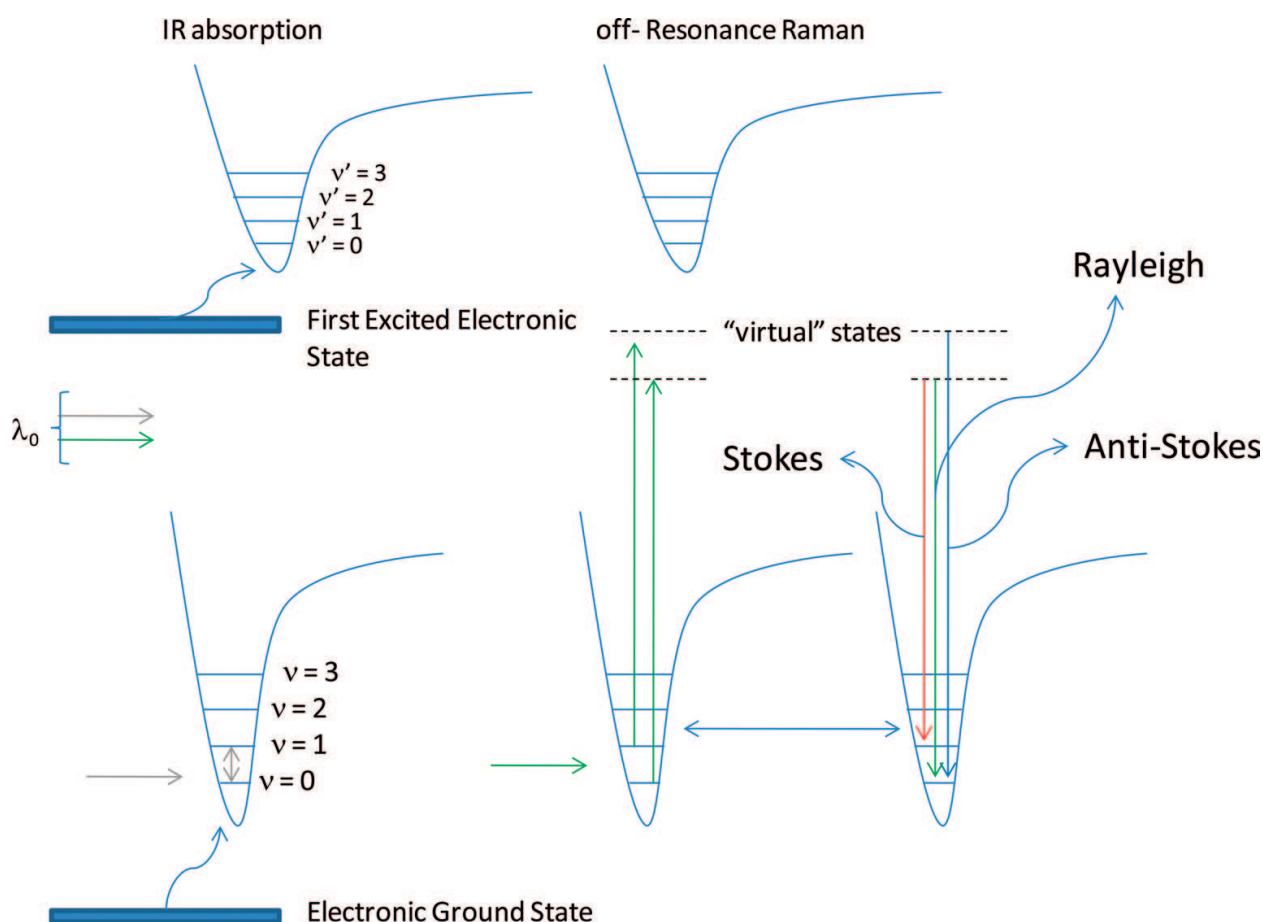


Figure 1. Schematic representation of the energy diagrams for a diatomic molecule. The figure represents the IR absorption and the Raman scattering in off-resonance or normal condition, by using a laser line with energy is far enough to excite the molecule to other electronic states.

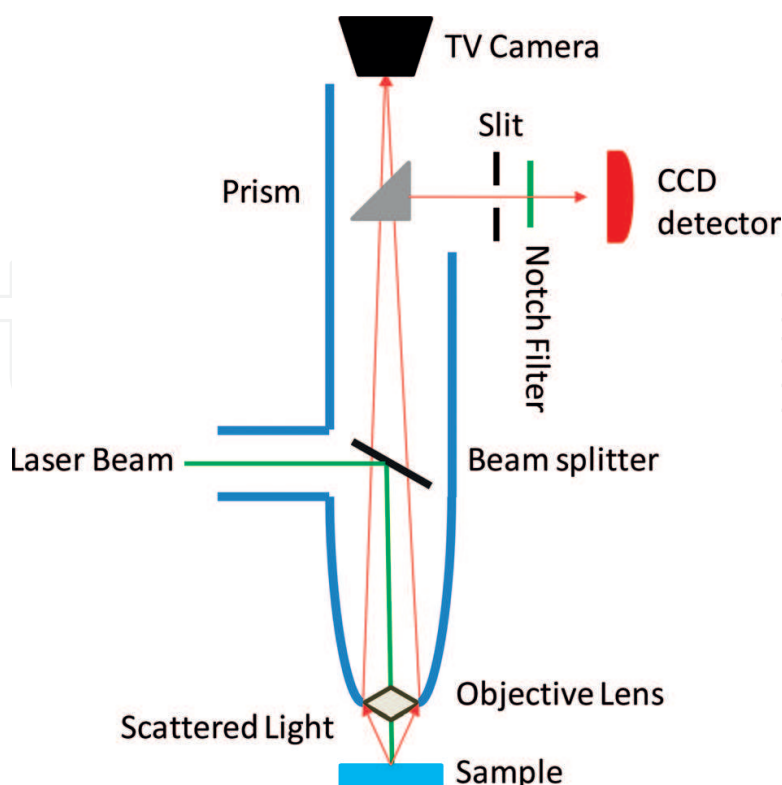


Figure 2. Conventional Raman microscope.

Nowadays, the Raman spectra can be collected in instruments having microscope (see **Figure 2**). The laser line is introduced to the sample on the microscope stage. In fact, more sophisticated microscopes can be attached in the Raman spectrograph, as STM or AFM microscopes and also electron microscopes [9, 10]. The scattered light is collected at 180° , and a high efficiency notch filter must be used to cutoff the incident radiation and also the elastic scattering because the Raman signal is very small (typically a cross section factor of 10^{-6} to 10^{-12} of the incident radiation). Raman microscopy is a nondestructive technique and usually has no requirement for sample preparation, and the measurements can be done in aqueous solution (not possible in conventional IR spectroscopy). The main advantage here is the ability to focus the laser on a very small part of the sample ($1\ \mu\text{m}$ approximately or smaller). The high lateral resolution and depth of field (the order of a few micrometers) are very useful, for instance, in the study of nanostructured materials and *in situ* measurements [11–15].

3. Resonance Raman

In the off-resonance or normal Raman spectroscopy, the intensities are linearly proportional to the intensity of the incident light (I_0 , see **Figure 3**), proportional to the fourth power of the wavelength of the scattered light (λ_s^4 or ν_s in wavenumber units), and proportional to the square of the polarizability tensor ($[\alpha]^2$) [6–8, 16]. However, when the laser line has similar energy to a permitted electronic transition, the Raman signal is amplified for about 10^5 magnitude orders; this is what characterizes the resonance Raman effect. The theoretical

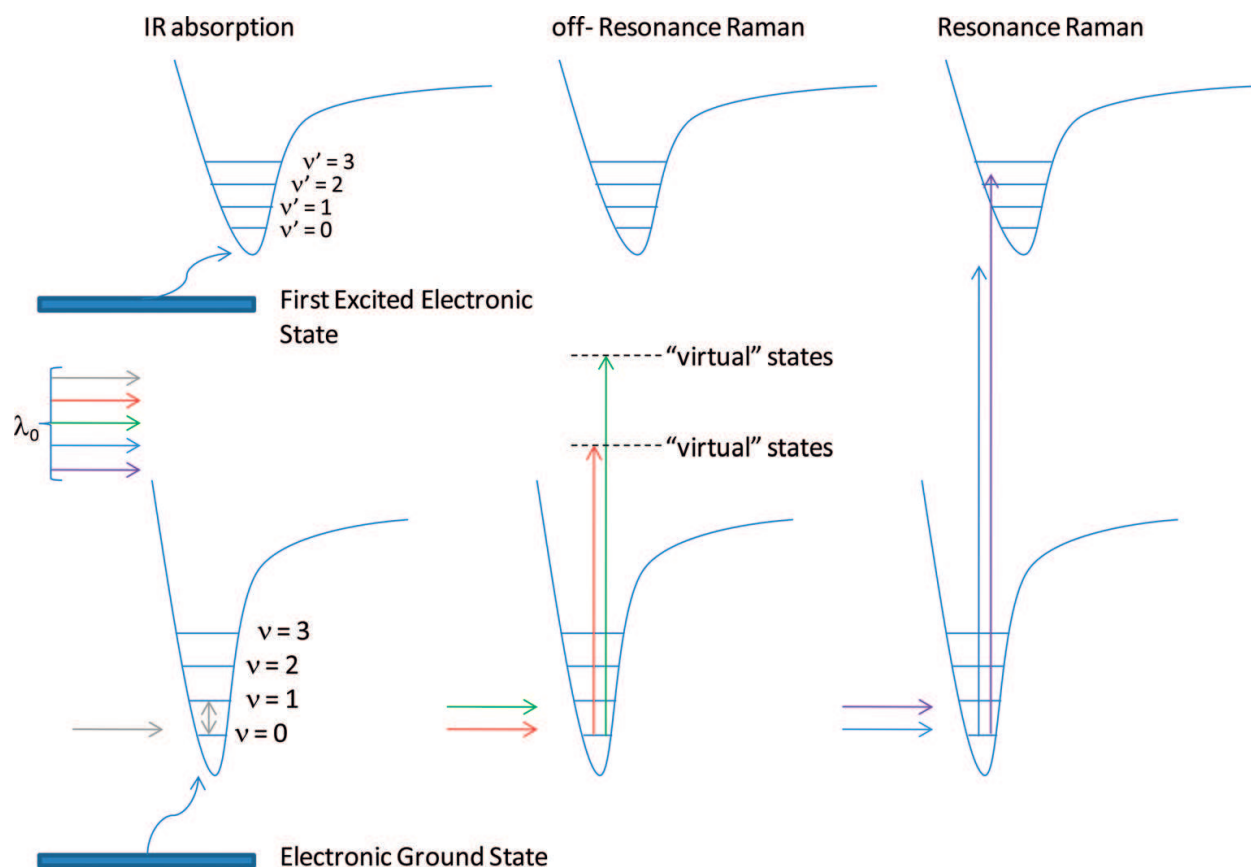


Figure 3. Schematic representation of two electronic states (ground and excited) and their respective vibrational levels. The arrows indicated the possible transitions. In figure ν_0 and ν_s (the scattered frequency is composed of: $\nu_{ev,gm}$ and $\nu_{ev,gn'}$ the Stokes and anti-Stokes components, respectively) are the laser line and the scattered frequencies. The equation that describes the resonance Raman scattering is formed in the numerator part by transition dipole moment integrals between the electronic ground state (g, for the vibrational m or n states) and an excited electronic state (e, for any vibrational v states). The sum is done over all possible (e,v) states. The denominator part is the difference or sum of the scattered and incident light, added by the dumping factor ($i\Gamma_{ev}$) that contains information about the lifetime of the transition states.

formalism developed by Albrecht et al. is commonly employed in the interpretation of the resonance Raman [6–8, 16].

Generally, the tensor of polarizability is described as shown in **Figure 3**. The equation is formed in the numerator part by transition dipole moment integrals between the electronic ground state (g, for the vibrational m or n states) and an excited electronic state (e, for any vibrational v states). The sum is done over all possible (e,v) states. In the denominator part is the difference or sum of the scattered and incident light, added by the dumping factor ($i\Gamma_{ev}$) that contains information about the lifetime of the transition states. This enormous intensification makes, in principle, the Raman spectrum easy to be acquired. But, in a state of resonance, a lot of radiation is absorbed, leading to a local heating and frequently can be observed a decomposition of the sample. Despite this problem, the RR spectroscopy has been largely used in the study of the different chromophore units present in many compounds varying from conducting polymers, nanocomposites, carbon allotropes to DNA [17–21].

4. Surface-enhanced Raman spectroscopy

The Raman signal can also be amplified by the adsorption of molecules in certain metallic surfaces. This behavior was discovered in 1974 by Fleischmann, Hendra and McQuillan [22]. Initially, the phenomena was associated to the increase of metallic surface area during oxidation–reduction cycles, but soon, it was evident that the strong increase of the Raman signal cannot be explained only considering the changes in metallic surface [23–25]. Finally, this new intensification process is known as surface enhanced Raman spectroscopy (SERS), evidently this process can be combined to RR effect and the acronym for this behavior is SERRS.

There are two main mechanisms to explain the SERS effect: (1) the electromagnetic model and (2) the charge transfer or chemical model. In the electromagnetic model, the interactions among the incident electromagnetic radiations (laser lines) with the surfaces are the main concerns. In this model, the form, size, alignment and type of metallic substrate are the main characteristics to shape the absorption of the surface plasmon resonance. The enhancement of the local electromagnetic field promoted by surface plasmon resonances is more efficient in metallic regions named hot-spots (nanoscale gaps or nanoholes), and as a consequence, the SERS signal from molecules adsorbed in hot-spots dominates the overall detected intensity [26, 27].

In the charge-transfer or chemical model, the interactions between the adsorbed molecules (mainly molecular orientation) with the metallic atoms involved in adsorption (atoms organization) are considered. The adsorption increases the polarizability of the molecule, which can be further increased by charge transfer between the adsorbed molecule and the metallic surface induced by the incident radiation [28, 29]. The applied electrical potential can also be considered in cases where the molecules are adsorbed in an electrode. The SERS technique permits the study of surface interactions, adsorption process, electrode reactions, biological systems, single molecule detection, and so on [30–33].

5. Outlook

Hence, this introduction tries to summarize the principles of main mechanisms of intensification of the Raman signal. These two effects (Resonance Raman and SERS) can be used separately or combined in the structural studies. In addition, the attachment of powerful microscopes with atomic/molecular resolution can also amplify the Raman signal, and this is the case of Tip-enhanced Raman spectroscopy (TERS). As a consequence, this combination opens the opportunity to study the Raman signal at unparalleled spatial resolution. In the present book, some examples of the state-of-the-art applications of Raman spectroscopy in characterization of materials and biomaterials, mainly through resonance Raman (RR) and surface-enhanced Raman spectroscopy (SERS) are deeply discussed.

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