VIBRATIONAL SPECTROSCOPIC TOOLS AND TECHNIQUES AND THEIR APPLICATIONS IN THE STUDY OF NONLINEAR OPTICS

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Abstract

The search of a novel non linear optical material is usually done by intelligent assumption and synthesis feasibility. Vibrational spectroscopy is based on vibrational transitions due to absorption and emission of electromagnetic radiations. Vibrational spectroscopic analysis provides a dynamic view of the molecule. Computational chemistry along with vibrational spectroscopy can provide experimentalists with precise information regarding the properties and behavior of materials. These techniques can help resolve issues that cannot be practically achieved due to instrumentation limits. The analysis of the Infrared (IR) and Raman spectra is now helpful not only for the structural characterization of molecular compounds, but also to derive detailed information on the electronic response from spectroscopic observables.

Keywords: Spectroscopy, Raman, IR, FT-IR, Nonlinear optics, NLO, NLO materials, SHG, frequency doubling, polarizability

Vibrational Spectroscopy

Vibrational spectroscopy provides precious information about the structural properties of molecules such as inter and intramolecular forces, hydrogen bonding, isomerism etc. Vibrational spectroscopy is based on vibrational transitions due to absorption and emission of electromagnetic radiations. These transitions are caused due to the vibrations of atoms constituting the molecule and appear in the waveumber range from 10^2 to 10^4 cm^{-1}. The vibrational energies of the molecule can be explored by infrared (IR) and Raman spectroscopy. The information provided by IR and Raman spectroscopic methods is often complementary. Thus to obtain complete vibrational analysis, both methods are necessarily be implemented [1-3]. By introducing the laser as a source for Raman and FT-IR spectrometers, vibrational spectroscopy has become a very powerful tool for the elucidation of molecular structure [4-5]. Vibrational spectroscopic analysis provides a dynamic view of the molecule. It has considerably contributed to the development of different areas such as polymer chemistry, fast reaction dynamics, catalysis and charge-transfer complexes [6]. The implementation of spectroscopy for exploring the structure of simple and complex molecules has been of great value in the field of structural study of organic, inorganic and organo-metallic compounds, biological molecules, polymers and minerals [7-12]. A brief description of these two experimental techniques is given below:

Infrared Spectroscopy (IR)

Infrared (IR) spectroscopy [13] is based on the atomic vibrations of the molecule and one of the most common spectroscopic techniques applied by organic and inorganic chemists. The vibrations of every bond in a molecule make changes in its dipole moment and provide a mechanism for the absorption of radiation. In principle, the IR spectrum is the measurement of the absorption of different IR frequencies by placing a sample in the path of an IR beam. The absorbed energy corresponding to the frequency of a vibration of a part of a sample molecule appears as a peak in an absorption spectrum. The main purpose of IR spectroscopic analysis is to identify the chemical functional groups in the sample. The IR technique when coupled with intensity measurements may be applied for qualitative and quantitative analysis. IR spectroscopy deals with the measurement of the wavenumber and intensity of the absorption in mid infrared region. Mid-infrared region of spectrum (4000- 200 cm^{-1}) is enough energetic to excite molecular vibrations to the higher energy levels. Each atom has three degrees of freedom along the three Cartesian coordinate axes. Thus, a polyatomic molecule containing n atoms has $3n$ total degrees of freedom. Since the three degrees of freedom are required to describe translational motion and additional 3 degrees of freedom correspond to rotational motion of the molecule through the entire space. Thus, the remaining $3n - 6$ degrees of freedom are true for nonlinear molecules. So a non-linear molecule has $3n$-6 modes of vibrations. Linear molecule acquires $3n$–5 fundamental vibrational modes because it requires only 2 degrees of freedom to describe rotational motions. All the 3n – 6 or 3n – 5 fundamental vibrations are also known as normal modes of vibration. Those vibrations which cause a net change in the dipole moment may result in an IR activity and those that produce polarizability changes may give Raman activity. However, some vibrations can be both IR and Raman-active. Generally, the total number of observed absorption bands in IR spectra is different from the total number of fundamental vibrations. It is different in number because some modes are not IR active, while other additional bands are originated by the appearance of overtones or combination bands (Fermi resonance), differences of fundamental frequencies, coupling interactions of two fundamental absorption frequencies and coupling interactions between fundamental vibrations. The intensities of the fundamental bands are greater than the intensities of overtone, combination and difference bands [14]. The combination of all the factors affecting the absorbance is responsible to create a unique IR spectrum corresponding to each compound. The major types of vibrations are stretching and bending modes of vibration. Infrared radiation is absorbed and provides the energy to activate the vibrations such as bond stretching, bending, torsion, wagging, rocking etc. The absorption causes the discrete and quantized energy levels. But, the individual vibrational motion is generally appeared with other rotational motions. These grouping lead to the absorption bands commonly observed in the mid IR region, not as the discrete lines. The alternating electrical field of the radiation interacts with the changes in the dipole moment of the molecule. The radiation is absorbed by the molecule if the frequency of the radiation matches with the vibrational frequency of the molecule and causes a change in the amplitude of molecular vibration.

Fourier Transform Infrared (FT-IR) spectrometry

In order to overcome the limitations of conventional IR spectroscopy, Fourier Transform Infrared (FT-IR) spectrometry was developed. The main complexity of conventional IR spectroscopy was the slow and individually scanning process. A technique was needed for measuring all the infrared frequencies simultaneously rather than individually. As a solution of this difficulty, the development of FT-IR spectroscopy came in to account. It generates a signal containing all the infrared frequencies, programmed in to it. The signal can be considered very quickly as of the order of one second or so. Thus, the time element per sample is reduced to few seconds rather than the several minutes. FT-IR works on the idea of the interference of radiation between two beams. The output is produced as an interferrogram which records a signal produced as a function of the change of path length between the two beams. Then with the help of Fourier transformation, the two domains of frequency and distance are made inter-changeable [15].

In FT-IR, the radiation produced by the source is passed through an interferometer to the sample then reach to a detector. High-frequency contributions are removed by a filter on being amplification of the signal. Then the data is transformed to digital form by an analog-to-digital converter and send to the computer for Fourier-transformation.

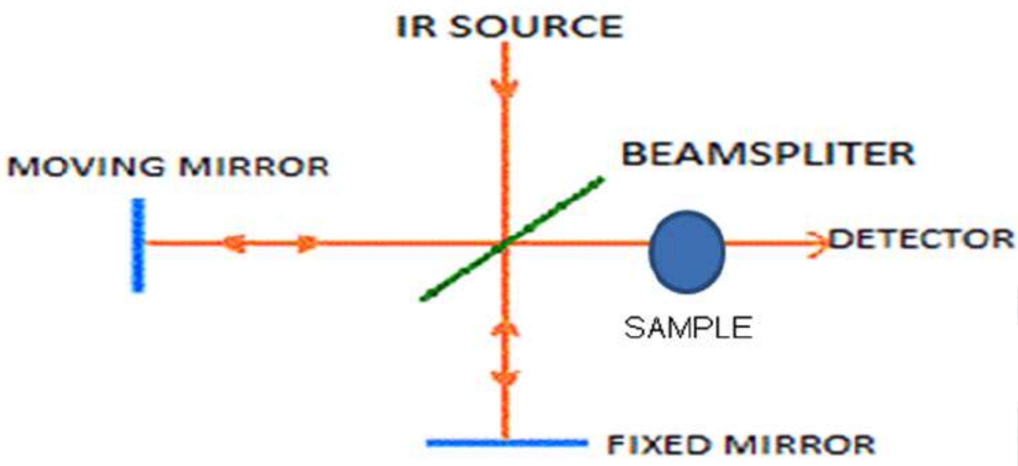

Figure 1: Schematic diagram of IR spectrometer

Raman spectroscopy

Raman spectroscopy is an emerging tool for the analysis of structure of molecules and it is considered as a complementary technique for IR. Sir C. V. Raman in 1928 was awarded Nobel Prize for discovering Raman Scattering or the Raman Effect. When a monochromatic light falls on the substance, it is scattered and results in the spectrum consisting of a strong line (the exciting line) of the same frequency as the incident illumination together with weaker lines on either sides. These lines are shifted from the exciting line by wavenumbers ranging from a few to about 3500 cm^{-1}. The lines, which appear at lower frequency side than the exciting lines, are known as Stokes lines while the lines which appear on higher frequency side than the exciting line, are known as anti-Stokes lines. A schematic energy level diagram is shown in Figure 2.

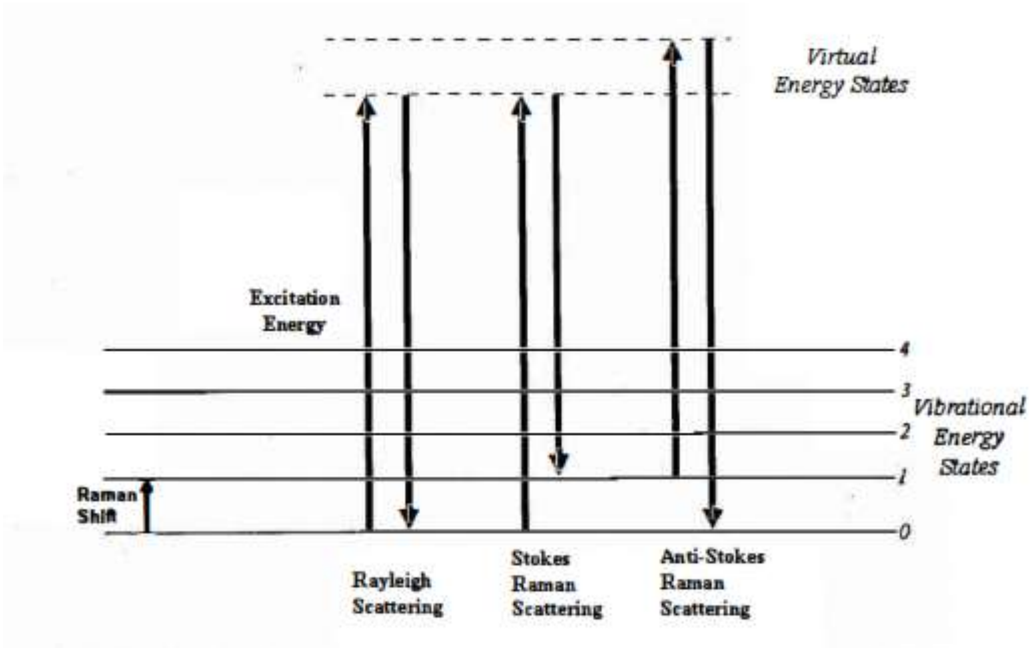

Figure 2

These Stokes and anti-Stokes lines occur due to inelastic scattering of light. The frequency of photons in monochromatic light alters upon interaction with a sample due to inelastic scattering. Photons of the monochromatic light are absorbed by the sample and then reemitted. The frequency of the reemitted photons is either increased or decreased in comparison with original monochromatic frequency. This effect is called the Raman effect. The difference in frequency or energy of photon takes place due to the change in the rotational and vibrational energy of the molecule and provides the information about its energy levels. The Raman Effect is determined by molecular polarizabilities α and is based on molecular deformations in presence of electric field (E). Raman spectroscopy can be applied for the study of solid, liquid and gaseous samples. [16-17].

Raman Vs IR spectra

The combination of Raman and IR spectra provides a lot of information about symmetric and asymmetric bond nature of the molecule. Raman spectroscopy plays a very important role as a practical tool in the quick identification of molecules and minerals. The Raman scattering mechanism is different from the mechanism of infrared absorption; on a comparative study both Raman and IR spectra provide complementary information about the molecule. Raman spectroscopy is a spectroscopic technique originated from the inelastic scattering of monochromatic light, generally from a laser source. This technique is typically applicable to structure determination, multi-component qualitative analysis, and quantitative analysis. Raman spectroscopy also provides structural insights into small molecule due to its involvement in interplay between atomic positions, electron distribution and intermolecular forces. The study of materials that was previously impossible because of fluorescence has been made possible by the use of FT-Raman spectroscopy. [18].

IR and Raman -Merits and limitations

Infrared spectroscopy and Raman spectroscopy are complementary techniques, because the selection rules are different. For example, homonuclear diatomic molecules do not have an infrared absorption spectrum, because they have no dipole moment, but do have a Raman spectrum, because stretching and contraction of the bond changes the interactions between electrons and nuclei, thereby changing the molecular polarizability. For highly symmetric polyatomic molecules possessing a center of inversion (such as benzene) it is observed that bands that are active in the IR spectrum are not active in the Raman spectrum (and vice-versa). In molecules with little or no symmetry, modes are likely to be active in both infrared and Raman spectroscopy.

Conclusion

Infrared spectroscopy and Raman spectroscopy are complementary techniques, because the
Vibrational spectroscopic analysis provides a dynamic view of the molecule. It is used for the determination of the molecular energies. The two branches of the the vibrational spectroscopy are infrared (IR) and Raman spectroscopy. As the selection rules in the two spectroscopy are different, the information provided by IR and Raman spectroscopic methods is often complementary. For the complete information of the molecule both IR and Raman should be done. Molecules shows extraordinary first and second order hyper polarizability are considered to be good nonlinear optical materials. In order to investigate vibrational dynamics of nonlinear optical materials spectroscopic tools and techniques play vital role.

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