## Infrared (IR) and Raman Spectroscopy

IR and Raman spectroscopy measure the energy difference of vibrational energy levels in molecules, they are energy sensitive methods. They are based on interactions of electromagnetic radiation and material but the main differences between these two spectroscopic techniques are the physical effects. For infrared spectroscopy the absorption process of polychromatic IR radiation due to the molecule cause a change in the dipole moment of the molecule and the molecule will be translated from a ground state to a vibrational excited state. Whereas the monochromatic radiation, for Raman spectroscopy, is inelastic scattered at the electron shell of the molecule which changes the molecular polarizability and the radiation will be shifted in frequency (light source: UV, VIS or NIR lasers). The "Raman effect" was discovered by the Indian physicist, C. V. Raman inn 1928.

Selection rules: Whether or not a vibrational mode is active or inactive for one of these complementary (inversely related) techniques depends on the symmetry of the molecules. For example, homonuclear diatomic molecules are not IR active, because they have no dipole moment, but they are Raman active. Because of the stretching and contraction of the bond changes the interactions between the electrons and nuclei, this causes a change of polarizability. For highly symmetric polyatomic molecules possessing a center of inversion, the bands are IR active (Raman inactive) for asymmetric vibrations to i and for symmetric vibrations to i the bands are Raman active (IR inactive). A mode can be IR active, Raman inactive and vice-versa however not at the same time. This fact is named as mutual exclusion rule. For molecules with little or no symmetry the modes are likely to be active in both IR and Raman.

The oscillating nonlinear or linear molecules with N atoms have 3N-6 or 3N-5 possible vibrations. In a nonlinear molecule, 3 of these degrees are rotational and 3 are translational and the remaining corresponds to fundamental vibrations. In a linear molecule, 2 degrees are rotational and 3 are translational.

**Vibrations**: The position of a given stretch vibration can be related to two factors, the masses of the atoms involved (light atoms vibrate at higher frequencies than heavier ones) and the strength of the bond (sp/sp<sup>2</sup>/sp<sup>3</sup>). Furthermore the position of a vibrational mode is also dependent on the environment of a molecule (molecular substituents, molecular geometry and hydrogen bonding).

## **Special aspects for Raman:**

Raman scattering is a consequence of quantized vibrations of molecules irradiated with monochromatic light. Some light is scattered at the same frequency (Rayleigh) and some light is scattered at different frequencies (Raman). The difference in frequency corresponds to the energy of vibrational transition. The Raman scattering can be divided into to parts, the Stokes line and the antistokes line. For the Stokes line the energy of the scattered radiation is less than the incident radiation, so there is a loss of energy and a longer wavelength results. For the anti-stokes line the energy of the scattered radiation is more than the incident radiation, so there is a gain of energy and a shorter wavelength results. The increase or decrease of energy from the excitation is related to the vibrational energy spacing in the ground electronic state of the molecule. The anti-stokes line is less intense, because only molecules that are vibrational excited prior irradiation can give rise to this line. In this case only the more intense Stokes line is normally measured.

Application: These spectroscopic techniques are useful to study intermolecular interactions and can give information about geometry of crystalline compounds. Both methods are sensitive to changes in bond length and symmetry of molecules. In crystals, localized vibrations can occur near defects, also additional lines can appear in the spectrum (satellites resulting from coupling).

## **References:**

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