

IR- and Raman Spectroscopy

Molecular vibrations can be excited by IR-radiation, which is divided into (1) near IR (0.8-10 μ m), (2) mid region IR (10-40 μ m) and (3) far IR (40-1000 μ m).

In emission spectroscopy (Raman-spectroscopy), a molecule undergoes a transition from a state of high energy E1 to a state of lower energy E2 and emits the excess as a photon. In absorption spectroscopy (IR-spectroscopy), the absorption of nearly monochromatic (single frequency) incident radiation is monitored as the radiation is swept over a range of frequencies. In vibration spectroscopy the reciprocal wavelength called wavenumber (in reciprocal centimeters) is used.

The vibration frequency is given by $\nu_{osc} = 1/2\pi\sqrt{k/\mu}$ and the vibration energy by

is given by $E_v = 1/2\pi\sqrt{k/\mu} * (n + 1/2)$. The parameter k is called the force constant and is a value for the strength of an atomic bond. μ is the reduced mass and n is the vibration quantum number. The energy levels are discrete and quantized. *Important relationship:* high bonding forces will lead to high wave numbers, high molar masses will lead to low wave numbers!

For IR-spectroscopy a polychromatic radiation source is used. From this radiation certain wavelength will be absorbed to activate a transition from the ground state to a higher vibration energy level when the beam passes the sample.

Raman-spectroscopy uses a monochromatic light source (laser), which has not enough energy to activate an electronic transition. This type of radiation shows different interactions with a molecule. On the one hand there will be elastic scattering of the light with the same energy and on the other hand the light is scattered inelastic. For the last case the radiation will excite the molecule to a higher state but it will not relax back to the ground state and stay in a state in between. Therefore the scattered light, which is detected afterwards, has a lower energy (lowered by the respective vibration energy).

For the determination of IR- or Raman- activity an exclusion rule is valid. The dipole moment of a molecule changes during a vibration, it has IR-activity, if the polarizability changes during a vibration, it is Raman active.

The vibration that is symmetric with respect to the center of symmetry is Raman-active but not IR-active, whereas those that are antisymmetric with respect to the center of symmetry are IR-active but not Raman-active. This condition is called the *mutual exclusion principle* and holds for any molecule having a center of symmetry.

The application of the discussed spectroscopic methods is the determination of functional groups of molecules, mainly in the organic chemistry, or the identification of symmetry elements.

Questions

- 1) What the difference between the radiation source of IR and Raman?
- 2) For a high bonding force, a higher or lower frequency and energy will be reached?