

IR- and Raman Spectroscopy

It is possible to excite molecular vibration by using radiation in the IR-range, which covers the wavelength from

0,8 - 10 μm near IR
10 - 40 μm middle IR
40 - 1000 μm far IR

The measurement is done by an absorption spectrum (IR-spectroscopy) or by an emission spectrum (Raman-spectrum). Within the spectrum the absorbed or emitted wavelength can be seen as a line or a band. In general the reciprocal value of the wavelength is shown, which is

called wave number $\bar{\nu} = \frac{1}{\lambda} [\text{cm}^{-1}]$ and is connected to the frequency ν and the energy.

$$\nu \cdot \lambda = c \Rightarrow \nu = \frac{c}{\lambda} \Rightarrow \nu = c \cdot \bar{\nu} \quad E = h \cdot \nu \Rightarrow E = h \cdot c \cdot \bar{\nu}$$

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

$$E_{vib} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \left(n + \frac{1}{2} \right). \text{ The parameter } k \text{ is called the force constant and is a value for the}$$

strength of an atomic bond. μ is the reduced mass and n the vibration quantum number. The energy levels are discrete and quantized. For a high bonding force ν_{osc} will increase and therefore a high wave number is reached, and for a high molecular mass ν_{osc} will decrease, which results in a low wave number.

For the 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. In that the detected spectrum the absorbed wavelength is damped. 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 fall 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).

It is not possible to see every vibration of a molecule in each of the spectroscopic methods. For the determination of IR- or Raman- activity an exclusion rule is valid

- IR-activity \rightarrow the dipole moment changes during a vibration
- Raman-activity \rightarrow the polarizability changes during a vibration

For a molecule with a centre of inversion all vibrations symmetric to its centre are Raman-active and all vibrations asymmetric to this centre are IR-active.

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

References:

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