WHAT IS RAMAN SPECTROSCOPY?

Raman spectroscopy studies the inelastic scattering of light. The Raman effect was predicted as early as 1923 by Adolf Smekal. In practice it was observed in 1928 by the Indian scientist Sir Chandrasekhara Venkata Raman (physics Nobel price in 1930) in liquids and independently by Grigory Landsberg and Leonid Mandelstam in crystals. In contrast to IR spectroscopy a change of the polarization potential, i.e., deformation of the electron cloud, is necessary for a molecule to exhibit a Raman effect. The intensity of the scattered light is dependent on the amount of the polarization potential change. As opposed to **Brillouin spectroscopy**, which studies elastic properties of materials, photons are scattered by the interaction with vibrational and rotational transitions in molecules. Raman spectroscopy is used to study a material's chemical composition. Further applications are:

- mineral identification and structural characterization
- analyses of gemstones and archaeometric objects
- mineral inclusions
- speciation & concentration
- characterization of e.g., thermal maturity, metamictization, OH content,
 impurities

Advantages of Raman spectroscopy are its non-destructive nature, small sample amounts can be studied and no sample preparation is necessary.

Theory

At temperatures higher than absolute zero all matter vibrates. A molecule can be transferred to an excited state (vibration) through the absorption of a photon. The energy has to be equal to the energy difference between the two vibrational states (see IR spectroscopy - frequency principle). However, in Raman spectroscopy UV, VIS or NIR light is used as radiation source, which has a much higher energy than those energy differences and absorption of photons is impossible. Instead the incident light will excite the system to a high-energy state. When it recovers from this state (immediately), scattering reactions occur. The elastically scattered light has the same energy as the incident light - **Rayleigh scattering**. If the system gains energy during this process, the scattered light loses this amount of energy and the system reaches a higher energy state (higher energy level) than it had before -Stokes scattering. Of an already vibrating system is excited, it loses energy during this process and the system reaches a lower energy level than it had before - **Anti-Stokes scattering.** The latter process is much more rare, since at room temperature most molecules are in the ground state as opposed to a higher energy level.

The **polarizability** is a measure for the electron cloud's ability to deform in contrast to the atomic nuclei. When placed into an electric (or oscillating) field the electrons are pulled towards the positive charge and the atomic nuclei towards the negative charge, which induces a dipole moment and results in scattering reactions. The change of the polarizability depends on the molecule geometry. For example, during the symmetric stretching vibration of the linear CO2 molecule the polarizability gets smaller during the stretching as opposed to the compression. It changes, and the vibration is Raman-active (but IR-inactive). During the asymmetric stretching vibration on the other hand the polarizability does not change, and the vibration is Raman-inactive (but IR-active).

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 $https://serc.carleton.edu/NAGTWorkshops/mineralogy/mineral_physics/raman_ir.$