

Introduction to light spectroscopy: Raman spectroscopy

(1) Basics

Raman spectroscopy is based on the Raman effect, an inelastic scattering process that was discovered by the Indian physicist C.V. Raman in 1928. The basic principle of this technique is that a monochromatic beam of light is focused onto the sample, and the energy-shifted fraction of the scattered light is detected. The Raman Effect is commonly explained using an electro-dynamical and a quantum-mechanical model, which are summarized below.

Electro-dynamical model: The majority of the scattered light is of the same frequency and wavelength as the incident beam of light, because it has not undergone any interaction with molecular vibrations of the sample. It is called the (elastically scattered) Rayleigh light. However, a tiny fraction of the incident light may also interact with atomic vibrations in an inelastic scattering process, called Raman scattering. In this case, the high frequency vibration of the electric field vector of the incident light induces a time-dependent dipole momentum. The resulting interaction of the time-dependent dipole momentum and the electromagnetic wave itself is controlled by the polarizability of the molecule. Only vibrations leading to (time-dependent) changes in polarizability are Raman-active. The geometry-dependent ability of a molecule to be detected by Raman spectroscopy is described by selection rules.

Quantum-mechanical model: The vibrational states of a molecule are characterised by a limited number of allowed, discrete energies. Upon irradiation with light, a molecule can be transferred to an excited vibrational state. However, light photons can only be absorbed upon excitation of a vibration when their energy is equivalent to the energy difference between two allowed vibrational levels. Such direct absorption, where the absorption of a light quantum (photon) generates a vibrational quantum (phonon) of the same energy, is possible for light in the middle to far infrared range [Fig. 1, (1)]. Visible light, in contrast, cannot be absorbed to excite vibrations because its energy is much higher than the energy differences between vibrational states. Hence in most cases no interaction occurs (i.e., the molecule does not change its vibrational state) and the scattered light has the same photon energy as the incident laser [Rayleigh scattering; Fig. 1, (2)]. Only in rare cases, Raman scattering occurs and a higher or lower vibrational state than before the interaction is reached. The photon energy of such Raman scattered light differs from that of the incident light [Fig. 1, (3a) and (3b)]. Note that energy differences of between Raman-scattered photons and incident photons correspond to phonon energies of vibrations in the samples.

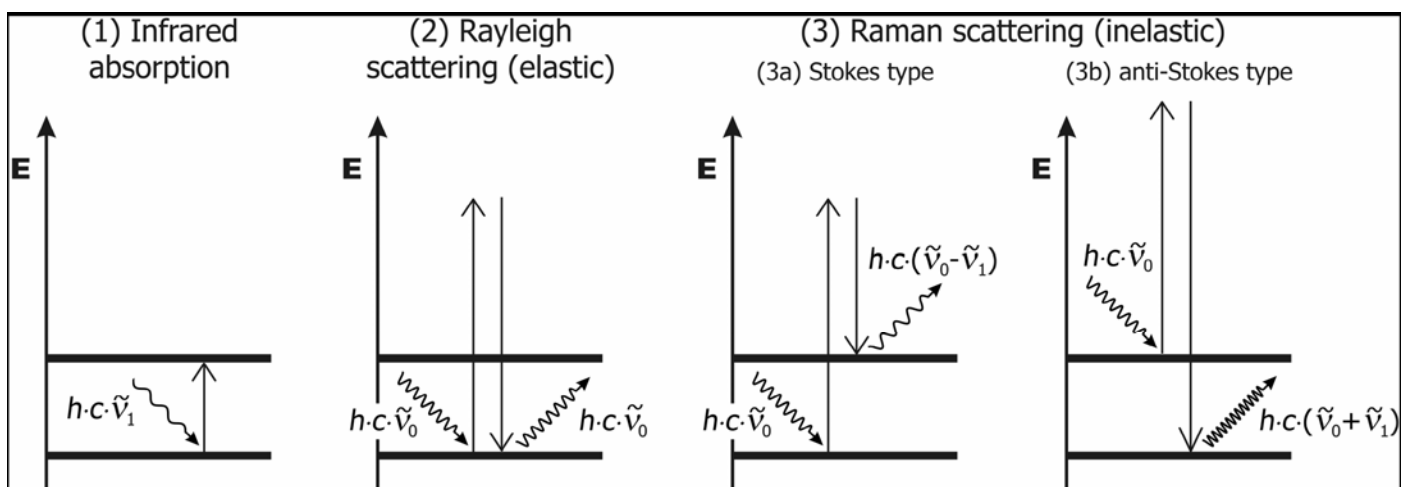


Figure 1: Simplified energy level diagram showing the different interactions of light and molecule. See text for explanations. From Nasdala et al. (2004a).

(2) Interpretation of spectra; applications

A Raman spectrum is a plot of light intensity (usually given in counts, counts per second or arbitrary units) *versus* photon energy (usually relative wavenumbers). The Rayleigh line is observed at zero Raman shift. Anti-Stokes Raman bands have negative and Stokes Raman bands have positive relative wavenumbers. For most applications only the (more intense) Stokes Raman bands are recorded.

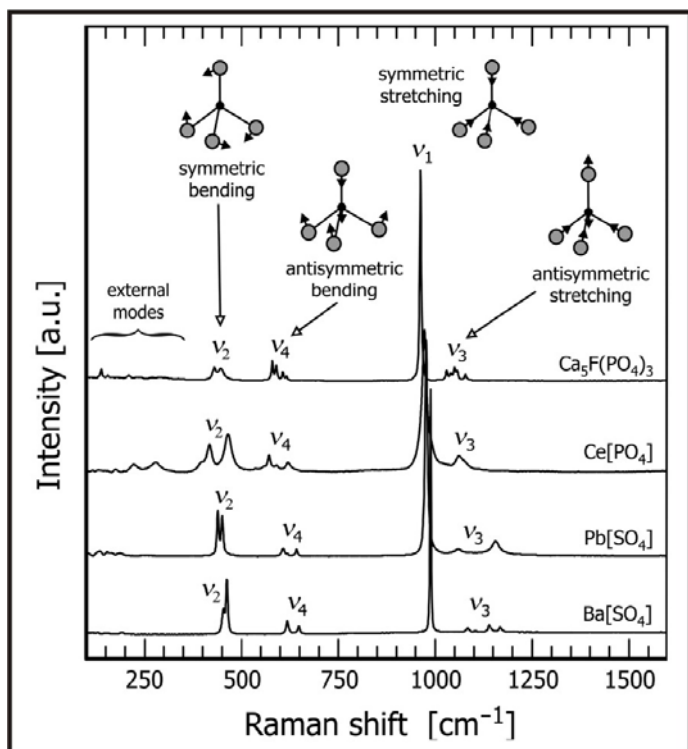


Figure 2: Spectra of apatite, monazite, anglesite, and barite, and general assignment of internal XO_4 modes. Differences among the spectra are due to (1) different central ions of the tetrahedrons, (2) different degrees of distortion of the XO_4 groups, and (3) different types and arrangements of nearest neighbouring ions of tetrahedrons. Figure from Nasdala et al. (2004a).

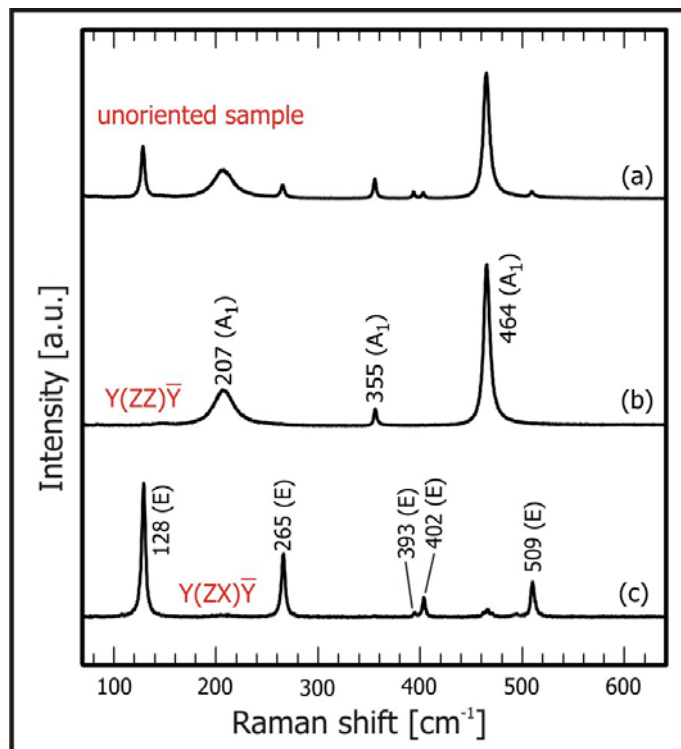


Figure 3: Three α -quartz spectra obtained in quasi-backscattering geometry, showing the directional dependence of Raman band intensities: (a), powdered sample analyzed without polarizers; (b) and (c), single-crystal analyzed with polarizers. Scattering geometries are described using the Porto notation (for details see Damen et al., 1966). Figure modified after Nasdala et al. (2004b).

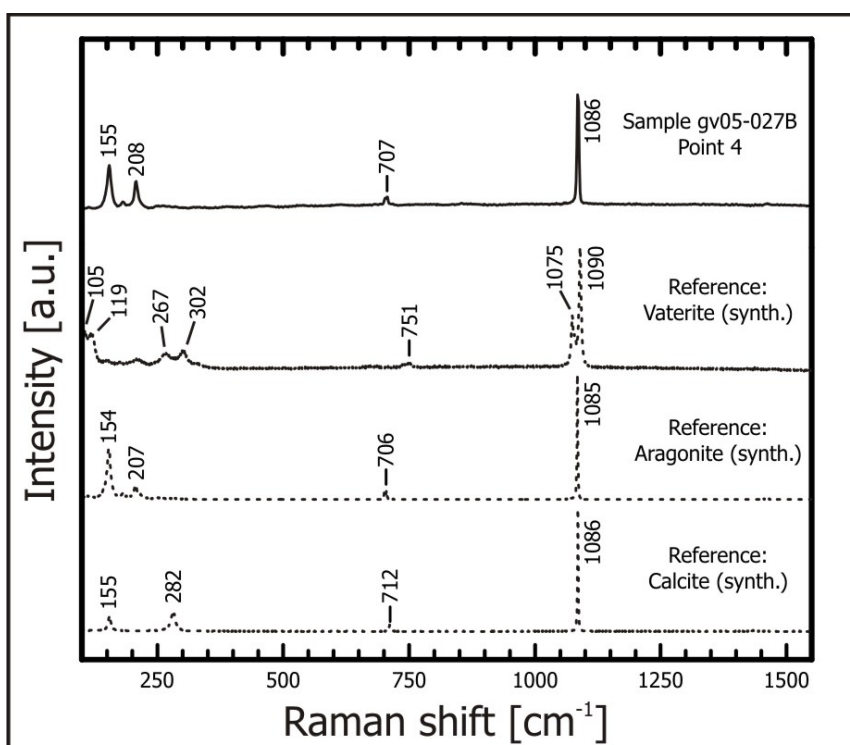


Figure 4: Aragonite Raman spectrum obtained from a rainbow trout (*Oncorhynchus mykiss*) otolith, compared with spectra of synthetic reference materials of the three $CaCO_3$ polymorphs. Figure modified from Veinott et al., submitted. These authors found strong correlations between trace Sr and Mg content and calcium carbonate polymorph.

Each band in a Raman spectrum represents the interaction of the incident light with a certain vibration of the nuclei. The vibrations are controlled by the sizes, valences and masses of the atomic species, the bond forces between these atoms and the symmetry of their arrangement in a crystal structure. Interpreting Raman spectra, not only Raman shifts, but also the number of observed Raman bands, their relative intensities, their widths and their polarisations give useful information about the sample.

A common problem in using Raman spectroscopy is the emission of photoluminescence that is simultaneously excited by the laser beam; the latter may easily obscure the Raman scattered light. Problems can be avoided by using an excitation wavelength with which the Raman spectrum lies in a spectral range that is not affected by the luminescence signal. Other possible artefacts, especially in Raman microprobe analysis, are due to local temperature increase (strong light absorption because of high power density) that may result in alteration or decomposition of the sample, and lack of confocality (i.e., insufficient depth resolution).

Figure 5: Spectrum of a natural, radiation-damaged monazite (lower spectrum) and its annealed analogue (upper spectrum). Note the shifted and broadened bands as well as the lowered intensities of the untreated sample due to its reduced short range order. Modified after Ruschel et al. (2008).

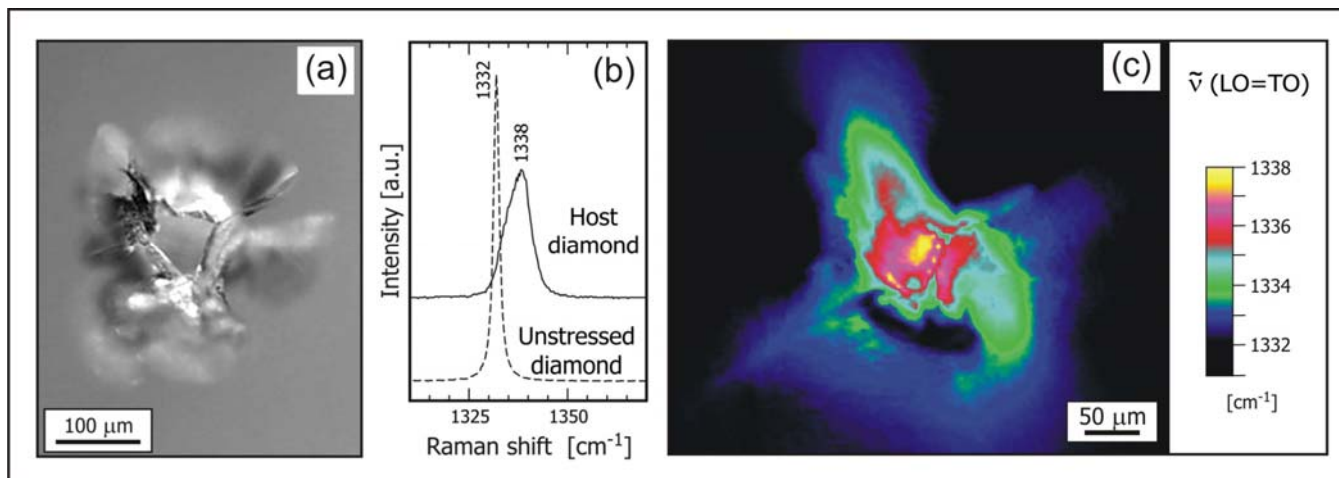
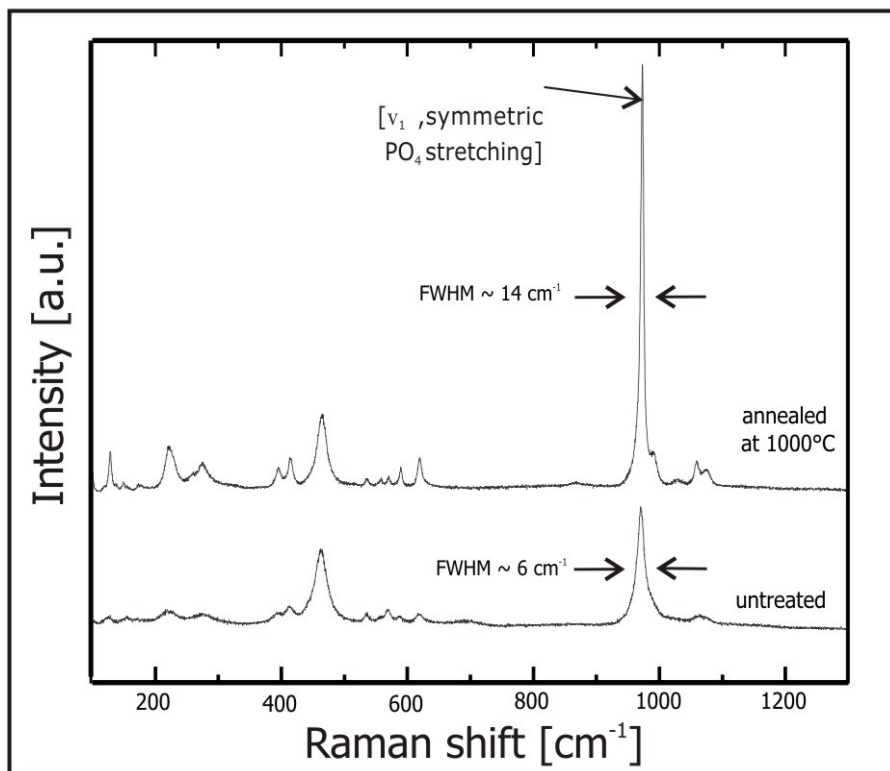


Figure 6: Raman mapping applied to study strain effects in diamond. (a) Microphotograph of a lamite inclusion in a diamond from the Kankan district, Guinea. (b) Raman spectra of the (strain-affected) host diamond near the inclusion, and unstressed diamond. (c) Raman map of the host diamond, showing a halo of compressive strain around the inclusion. The latter was generated from a hyper-spectral data set consisting of about 70.000 single Raman spectra (one full spectrum was obtained for each pixel of the color-coded image). For more details see Nasdala et al. (2003).

Raman spectroscopy is used in many disciplines including pharmaceuticals, forensic science, polymer research, semiconductor physics, and many more. Applications cover virtually all sub-disciplines of the in the Earth sciences. Raman spectra are highly specific for a certain type of sample and hence they are used for the identification and structural characterisation of unknowns. Due to the high volume resolution small amounts of sample material can be analyzed. Raman spectroscopy is applied to study solids as well as liquids and gases, having the additional advantage that no special sample preparation is needed. Being a non-destructive method, Raman spectroscopy is predestined to analyse gemstones or archaeometric objects. Measurements can even be done without any contact of the sample, which is for instance used to analyze mineral inclusions or inside pressure cells.

Literature:

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