

Raman Polarization Accessory for the RamanStation 400



Raman spectroscopy is an ideal tool for qualitative and quantitative material characterization where it measures the unique Raman 'fingerprint' displayed by every molecular species. The characteristic spectrum of each chemical can be readily identified by spectral comparison or automated library searching. Relative concentrations of species in a mixture can be determined from the Raman spectrum by measuring band ratios or using chemometrics.

In Raman spectra, band positions can be assigned to molecular vibrations, giving valuable information about the structure of the molecule. For example, peaks at 1000 cm^{-1} can usually be attributed to an aromatic ring stretching, peaks at $1900\text{--}1600\text{ cm}^{-1}$ relate to C=O (carbonyl bonds), whereas bands at 2200 cm^{-1} and 2500 cm^{-1} are good indicators of C≡N (cyano) and S-H (thiol) bonds respectively.

Key Features

- ▶ Adjustable laser and Raman polarizers
- ▶ Removable polarizers for standard Raman spectral acquisition
- ▶ Depolarizer on Raman optical pathway
- ▶ Integral video camera and white light sample illumination
- ▶ XYZ motorized stage
- ▶ Rotatable optical head for versatile sample analysis

Raman polarization studies

There is additional information hidden within a Raman spectrum that is seldom exploited due to the complex instrumentation historically required for these studies. In undergraduate degree courses, Raman polarization theory is often studied since it gives insight into the links between group theory, symmetry, Raman active vibrations and the corresponding Raman spectrum. When it comes to everyday Raman analysis, however, this technique is generally overlooked because of the need for specialist or modified instrumentation.

Polarized Raman measurements should not be confused with the use of polarized light in visible image analysis. Polarized Raman uses polarized laser excitation and a polarization analyzer that can be used to acquire spectra, either parallel or perpendicular to the excitation laser. The resulting spectral information gives an insight into molecular orientation and vibrational symmetry. In essence, it allows the user to obtain valuable information relating to molecular shape, for example in synthetic chemistry or polymorph analysis, and is most often used to understand the orientation of molecules in organized environments such as crystal lattices, liquid crystals and polymer samples.

The ratio of the peak intensity of the parallel and perpendicular component is known as the depolarization ratio and can be obtained as shown in equation 1.

$$\rho = I_{\perp} / I_{\parallel} \text{ OR } I_{\text{depolarized}} / I_{\text{polarized}}$$

Equation 1. Raman depolarization ratio. Where '⊥' signifies the peak intensity with excitation and Raman analysis polarizers orientated perpendicular to one another, and '∥' signifies parallel orientation.

If ρ for a particular peak is less than 0.75, then that peak has arisen from a totally symmetric vibrational mode. This peak/vibration is called a *polarized band*. Non-symmetric modes have a depolarization ratio of 0.75 and these are called *depolarized bands*.

Figures 1 and 2 demonstrate the parallel and perpendicular spectra obtained for cyclohexane. It is apparent that certain peaks are highly polarized and there are significant differences in peak intensity depending on the polarizer orientations. The PerkinElmer® Raman Polarization Accessory is designed for use with the RamanStation™ 400 and offers easy access to this rich source of molecular and macromolecular information.

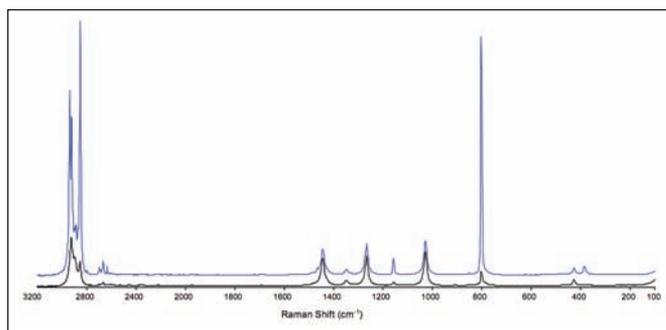


Figure 1. Raman spectra of cyclohexane from analysis Parallel (Blue) and Perpendicular (Black) to the excitation laser polarization. Spectra are offset for clarity.

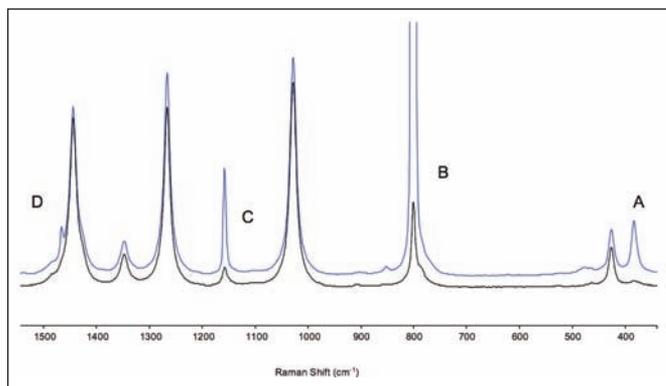


Figure 2. Expansion of fingerprint region of cyclohexane. The large changes in peaks A-D signify that they arise from totally symmetric vibrations.

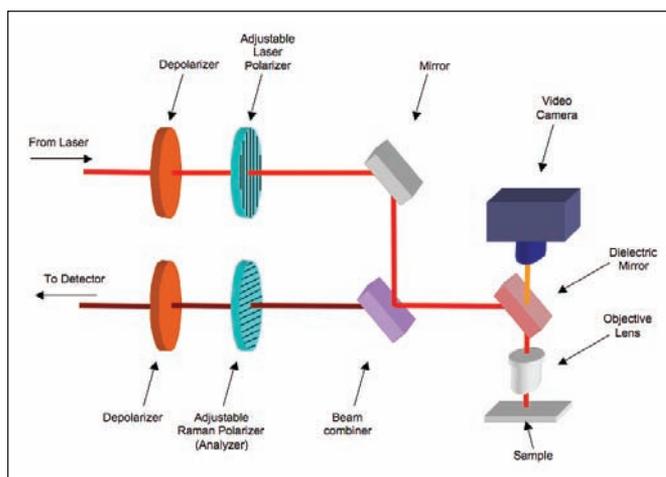


Figure 3. Schematic of the optical configuration of the Raman Polarization Accessory, showing adjustable polarizers.

Figure 3 shows the optical path for the Raman Polarization Accessory. Since most lasers have some degree of inherent polarization, a depolarizer is used to scramble the laser radiation. The scattered radiation from the sample passes through a second adjustable polarizer (analyzer) and a depolarizer before reaching the detector. This scrambling of the scattered radiation is required to remove polarization bias from the optical components in the system.

Adjustable polarization for excitation and analysis

The laser polarization orientation can easily be adjusted to be either parallel or perpendicular to the orientation of the instrument (or sample) and the polarization analyzer can also be adjusted to be parallel or perpendicular to the orientation of the excitation laser. Table 1 contains details on the various polarizer options.

Table 1. Polarizers can be positioned in several orientations and can even be removed for acquisition of non-polarized Raman spectra.

	Laser Pathway	Raman Detection
Parallel	↔	↔
Perpendicular	↔	↕
Parallel	↕	↕
Perpendicular	↕	↔
Non-polarized Raman (polarizers removed)	✱	✱

Polarized Raman studies do not require that molecules are aligned to the polarization of the excitation laser. As is demonstrated in Figures 1 and 2, polarized Raman spectra can be obtained from randomly oriented samples such as liquids (cyclohexane), slurries, gels or micro-crystalline powders.

The ability to change the laser polarization is extremely useful when studying samples that contain oriented molecules, for example the oriented polymer chains of single crystals, polymers or fiber samples. In fact, polarized Raman is a powerful tool to understand the chain orientation and degree of orientation in most polymeric samples.

Stage motorization and sample visualization

The Raman Polarization Accessory is equipped with a high quality video camera, with a built-in sample illumination source. This camera is essential for accurate sample positioning and alignment. The visible image survey functionality is used to obtain a significantly greater field of view image than the field of view of the camera.

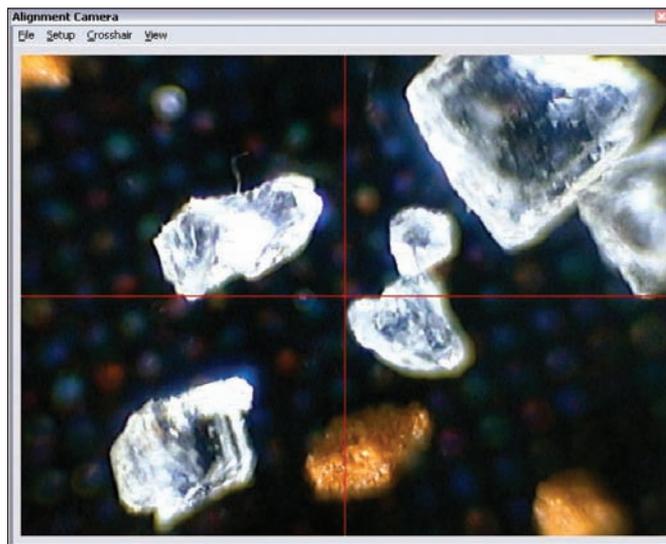


Figure 4. Visible image from the polarization accessory video camera.

The stage's optical head (camera and objective lens) can easily be rotated to allow the head to be oriented downwards (as in Figure 5). This is ideal for working with samples on microscope slides and with pieces of fabric or plastic. The head can also be clicked in to the horizontal analysis position (as in Figure 6) for analysis of samples in cuvettes, capillary tubes and vials.

The Raman Polarization Accessory is based on a high-precision motorized XYZ stage (Figure 5), for ease of sample positioning, automated multi-sample analysis, line scanning and chemical imaging. The XYZ stage can accommodate standard multiwell plates or the versatile sample holder, provided with the accessory. The versatile sample holder can accommodate cuvettes, capillary tubes, vials and samples on microscope slides.



Figure 5. Accessory optical head pointing downwards



Figure 6. Accessory optical head pointing horizontal.

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