



Raman Spectroscopy: an elegant and effective method, from single crystals to the planet Mars

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Illuminated by a monochromatic light wave (e.g. a laser), matter interacts with this wave in several ways: most of the energy is re-emitted without change in wavelength in all directions (elastic Rayleigh scattering); a much weaker part is emitted after having received or given up energy to the material by coupling between the magnetic and electric vectors of the wave with the variations of the electronic distributions (in other words the chemical bonds). This inelastic scattering is called the Raman Effect, named after the scientist who first published his evidence 95 years ago and for this won the Nobel Prize in 1930.

The year 2023 marks the 95th anniversary of the discovery of the Raman effect. After the discovery of the Raman Effect in 1928, the researchers all over the world became interested in this new technique which is based on the inelastic scattering of light, and today it has established itself as an indispensable technique of investigating the molecular species in all phases of matter and as a tool for research in interdisciplinary fields encompassing almost all branches of science [1]

Ceramist by first training, I first practiced the synthesis of single crystals and therefore crystallography, a method which required patience to mount and orient the crystals, to make the recordings of the hundreds of Bragg spots in Weissenberg or precession chamber for different orientations in order to determine the class of symmetry then to collect on a diffraction instrument with 3 or 4 circles, as many spots as possible in order to solve the structure after many trials: at the time (1975) this required the perforation of hundreds of cards and the printing of many views in Fourier cross-sections using the biggest computer of the time to see if the electronic residues did not reveal partially occupied sites. Days of exposure were required for each film and months of work to solve a structure.

It was also the time of the first Ar⁺ or Kr⁺ ion plasma lasers giving high power (1 W) making it possible to obtain good spectra on a spectrometer with triple monochromator stage, at high resolution (0.5 cm⁻¹), over a large spectral window, from ~3 cm⁻¹ to more than 4000 cm⁻¹ (Fig 1a). The optical adjustment was an art: for a crystal positioned in a cryostat, the alignment could take several hours; a good spectrum might take several hours, the photomultiplier detectors were not very sensitive and had to be protected from the laser exposure: we spent all day to adjust and at night to record a 'good' spectrum. A measurement campaign depending on the temperature required several days. The new possibility offered by triple-monochromators to access to very low wavenumbers made it possible to study the soft modes of certain phase transitions of ferroelectric materials, the damped modes of ionic superconductors, the tinny signature of polaritons, etc. competing with neutron spectroscopy and, to a certain extent also with NMR, which alone could then provide this information, on the condition of having access to the few centers in the world with high-performance instruments and crystals of the necessary composition and (very big) size; those other techniques required crystals about ten times larger than those required by Raman analysis.

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The strength of Raman analysis was in collecting the entire polarizability tensor components (90° setting) by changing the orientation of the electric vector of the laser beam and scattered light according to the procedure and notation of S P S Porto [2] to access an understanding of the structure as good as in crystallography, and even better concerning the static and dynamic disorder. The analysis in group theory of the structure supposedly well explained in the work of Poulet & Mathieu [3] made it possible by comparing with the measurements to validate or not the hypothesis. Indeed a structure based on the collection of Bragg spots symmetrizes too much the real structure and simplifies reality, because the imperfect and local orders lead to diffuse diffractions not measured by diffraction and whose study requires very specific techniques such as the method of Laue under polychromatic X-rays, very greedy in counting time, or TEM diffraction, requiring very specialized expertise. On the contrary, despite the long counting times of the 1980s, Raman scattering was the - in my view - most elegant method of understanding solids. The study of the forms of peaks, of the dependencies in temperature, in pressure, as well as the comparison between the symmetry seen by the lattice modes and that seen by the vibrational units (group of the site of Baghavantam) confronted with the conclusions of the crystallography gives a more reliable view of 'real' matter.

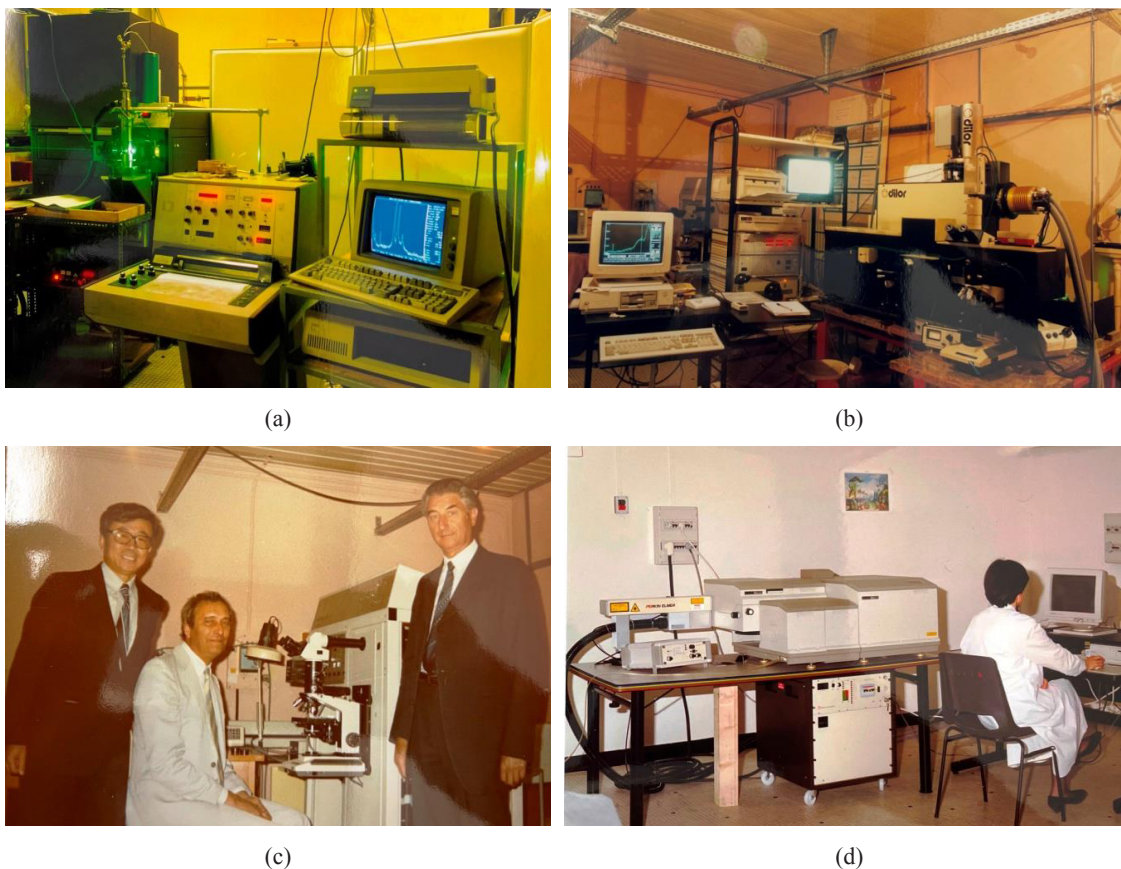


Fig 1. Evolution of Raman spectrometers between the 1970s and 1990s: (a) Triple monochromator with photomultiplier detector (measurement at 90° in He cryostat); (b) Double multi-channel monochromator with CCD detection cooled by liquid Nitrogen; (c) MOLE spectrometer with CCD detection (on the right, Professor Michel Delhaye); (d) Spectrometer excited by an IR laser (1064 nm) where the gratings have been replaced by an interferometer due to the weakness of the signal (this type of instrument opened up the field of studying polymers and many biological or organic compounds which under 'classic' laser excitation, from UV to red, gave strong fluorescence signal masking the Raman spectrum (Photo: P Colombar).

My first ICORS Raman Congress in 1978 allowed me to see and hear the pioneers and discover the potential of the newly discovered SERS (Surface Enhanced Raman Scattering: In 'contact' with a metallic surface, i.e. 'electron donor' the spectrum of matter is multiplied by several orders of magnitude). France occupied an important place in the production of Raman spectrometers with Coderg (T800), with Dilor (RTI, OMARS, LABRAM, RTI, XY) (Fig 1b), with Jobin-Yvon (RAMANOR, MOLE), (Fig 1c) [4]. Indeed, a revolution started with the replacement of the photomultiplier first with a linear diode array (OMARS-89 Dilor Instrument; Optical Multichannel Analyzer Raman Spectrophotometer), rapidly substituted by Charge Coupled Devices (CCD) matrices [4]. The gain obtained with these advanced detectors offers the possibility to decrease the power of illumination and thus to study coloured matter and the technique then started to be used in Material Science analyses. Michel Delhaye (The head of my Laboratory, the LASIR located in two towns Thiais a suburban close to Paris and Lille, north of France) and Paul Dhamelincourt (LASIR) were the first to build a Raman microprobe, the MOLE (Molecular Optic Laser Examiner) in 1974 [5]. The MOLE microprobe started to be commercialized in 1976 by ISA Jobin-Yvon (now HORIBA Scientific). The combination of optical microscopy in a back scattering setting with different laser sources covering from violet to red excitation with a double holographic gratings spectrometer equipped with an intensified advanced photomultiplier offered the possibility to analyse a large variety of organic and inorganic materials, even coloured, including thin films; the counting time required to achieve a “convenient” spectrum for a mineral, ceramic, glass, polymer, etc. decreased to about 1 hour. Very rapidly the MOLE found application in many fields. The first application to Cultural Heritage [5] was presented by M L Dele, P Dhamelincourt and H J Schubnel in 1978 at a meeting for the identification of gems. At the same time C Truchet, M. Delhaye and P Dhamelincourt started coupling the Raman spectrometer with an electron microscope. It took more than 50 years to have commercially available instruments.

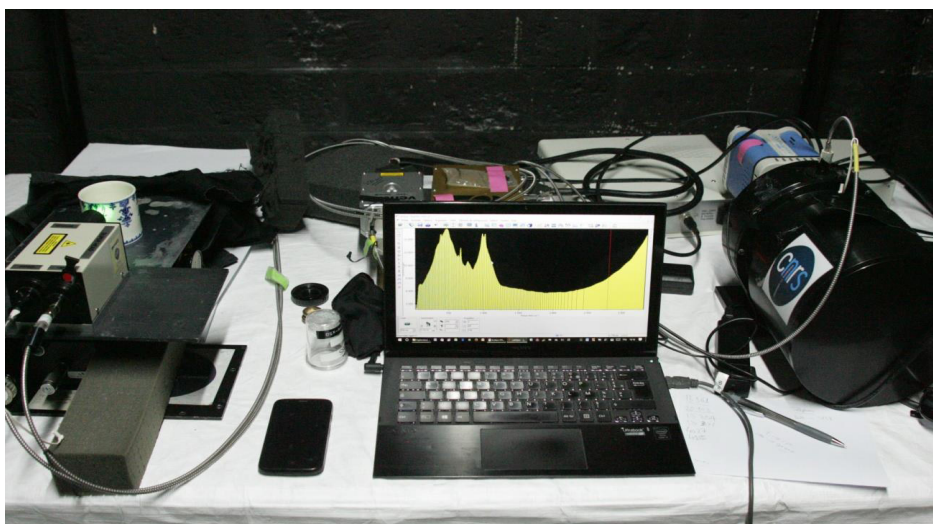


Fig 2. Mobile Raman set-up for onsite Raman analysis: on the left, the remote measuring head connected by optical fibers to the compact YAG laser source (behind the lap top) and to the spectrometer (on the right, with the CCD detector in blue); a spectrum of the glaze of the soft-paste porcelain cup is visible on the screen.

A second revolution started in 2000 with the availability of air-cooled lasers and Peltier-cooled CCD detectors, the only contingency was to have an electric plug for the electricity supply for the Raman spectrometer. We conducted the first studies with mobile Raman set-up in 2002 [7,8].

All these instrumental developments find their origin in those of the pioneers studying the light-matter interaction, in first C V Raman and K S Krishnan, but also Léon Brillouin, A Smekal, G Landsberg

and L Mandelstam, P A Fleury and many others. The instruments are now compact enough to equip rovers exploring Mars [9] or to detect traces of drugs or pesticides [10].

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Photo 1. Prof Vinod Rastogi (left) honouring Prof Philippe Colomban (middle) by a Shawl. Er Manoj Kumar is also seen (extreme right).



Photo 2. Vinod Rastogi (left), Philippe Colomban (middle) and Basant G Sathe (extreme right) during ICOPVS22, at Indore, India.