RAMAN UPDATE

by: The Raman Division
JOBIN YVON HORIBA

Issue: Autumn 2004

The LabRAM INV

For Biological and Life Science Applications

µm Scale Spectroscopic Analysis

For biological and life science applications in particular, the conventional upright optical microscope has many limitations : Non optimal sampling conditions, Lack of specific chemical information.

Living cellular samples are often routinely studied with a more adaptable inverted microscope geometry due to the sample structure and properties. It is also often the case that several types of measurement technique are advantageous - for example, optical and fluorescence images and specific spectroscopic data.

The next dimension in analysis comes from the capability of the LabRam INV to combine inverted optical microscopy with laser induced Raman and fluorescence spectroscopic information.

With highly specific spectral information, a precise characterisation of the sample is possible. Details not usually accessible with normal optical imaging modes become apparent such as specific molecular identification, phase determination, and other subtle molecular bonding and interaction information.

Contact your nearest Jobin Yvon representative

Forthcoming Exhibitions

8-13th August 2004, ICORS Queensland, Australia

1-3rd September 2004, JAIMA, Tokyo, Japan

5-10th September 2004, EUCMOS 2004, Krakow, Poland

6-9th September 2004, Photon, Glasgow, UK

3-7th October 2004, FACSS, Portland, Orlando, USA

6-7th October 2004, Photonex Europe, Coventry, UK

9-13th October 2004, National Geofluid & Fluid Inclusions Symposium, Beijing, China

19-21st October 2004, MesurExpo Paris, France

20-21st October 2004, EMN04 Noisy Le Grand, France

30th Nov - 2 Dec 2004, MRS Fall, Boston, MA, USA

25-27th January 2005, Photonics West, San José,CA, USA

Don't forget to check out our website:
www.jobinyvon.com
where you can find details on all our systems, accessories, along with complementary information including our application notes.

For further information on any of the articles within this newsletter, or should any of your colleagues wish to be part of our mailing list, or should you have any queries or comments, please contact any of the following addresses :

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JOBIN YVON HORIBA

Welcome to the Raman Update, produced by Jobin Yvon's Raman Team, to provide our customers, colleagues & friends with up-to-date information in the field of Raman Instrumentation and Application

Don't forget to see us at:

ICORS 2004 - Australia,

JAIMA - Japan

Contents

The New Member of the LabRAM Product Family

NEW

LabRAM *ARAMIS* New Advances

Advanced Raman Instrumentation with Innovative Automation

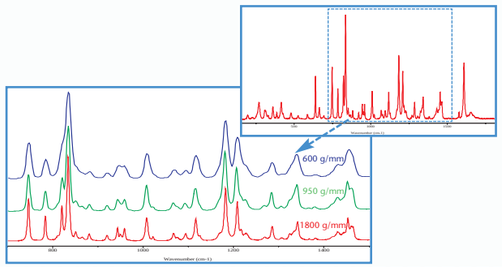
Jobin Yvon Raman Division introduces a new Raman Instrument: The LabRAM ARAMIS. Innovative Automation provides easy PC controlled operation for quality dependent applications for analytical and research applications without sacrificing on needed flexibility.

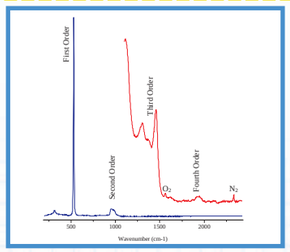
Features of the LabRAM ARAMIS:

- Full spectral coverage from the UV to NIR
- Up to 3 integrated Lasers
- Additional Laser entrance for additional lasers
- Up to four optimized gratings on a motorized turret
- Class 1 Microscope security compartment
- Macro chamber with 90° or 180° Laser excitation
- True confocal arrangement
- Patented Notch filter selector
- Fibre entrance for remote Raman
- Line mode for fast Raman mapping
- Choice of dedicated microscopes
- SameSpot™ Technology

Quad Grating turret

The new 4 position grating turret not only selects the most efficient grating for spectral ranges from UV to NIR, it also gives you the choice to define the spectral resolution to achieve the best band separation.





Sensitivity and confocality at it's best

The LabRAM ARAMIS provides exceptional detectivity as shown on the 4th order of Silicon.
On our spectrum, the intensities of the O_2 and the N_2 bands are weak compared with the third and fourth order bands of silicon. This proves the advantages of a confocal microscope, as it permits to discriminate signals coming from different layers.

Application

The New Wave of Carbon NanoTube Characterisation

Which should you use: Microscopic or spectroscopic method?

Written by Dr. Y NAKATA, Application Centre, Horiba Ltd. Japan, supported by Prof. Shinichi Kitamura, Osaka Prefecture University and Dr. Shigeo Maruyama, University of Tokyo

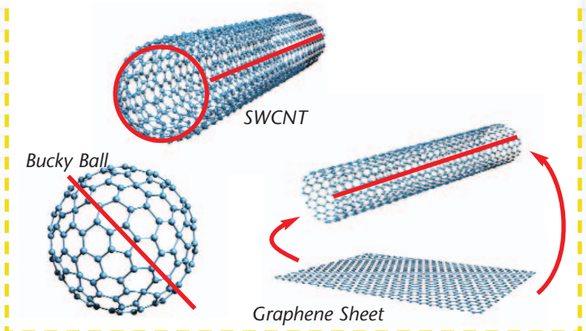
Since the discovery of carbon nanotubes (CNTs) in 1991, their technological development has been making rapid progress. The development of CNTs has entered into a new phase, in which the fruit of years of basic study has been applied to real products using the latest nano-technologies.

Single-walled carbon nanotubes (SWCNTs) are especially important nanomaterials because of their unique physical properties. A number of test productions using SWCNTs as molecular wires, logic gates, displays, and nanometer-scale mechanical parts have been reported. Various methods have been proposed for the large-scale production of SWCNTs.

The physical properties of SWCNTs:
- Superstrong
- Low weight
- Stable
- Flexible
- High heat conductivity
- Large surface area
- Variety of electronic properties
- Can be conjugated to organic materials for pharmaceuticals, composites, etc.

The geometric structure of a SWCNT is a rolled-up hexagonal-mesh graphene sheet capped by half-bucky-balls at both ends of the tube. To control the physical properties, it is important to identify "chirality", that is, how the graphene sheet rolls up:
- If the hexagons are aligned along the axis, the tubes are metallic.
- If the hexagons twist around the axis, the tubes are semiconducting.

Microscopic methods with high resolution, such as the High-Resolution Transmission Electron Microscope (HR TEM) or the Scanning Tunneling Microscope (STM) have been used to determine the chirality of SWCNTs, however, they need advanced techniques in high vacuum.



Raman spectroscopy, often used to analyze materials containing elemental carbon, is also an important and powerful technique applied widely to CNTs, because of its high information content, non-contact microprobe, and performance under atmospheric pressure and even in solution. The wavenumbers of SWCNTs' Raman bands in radial-breathing (RB) mode are correlated linearly with the reciprocal of tube diameter. These bands also show electric properties of SWCNTs depending on their chirality. The excitation wavelength is varied in order to probe the resonance behavior, and selectively enhances a selected species.

A Raman spectrum of SWCNTs in the low-frequency region, measured by a LabRAM HR800, is shown in Figure 1. The spectrum was recorded using 488 nm and 514.5 nm laser lines. Note that the Raman bands of the RB mode vary with resonance by excitation wavelength. These bands are useful in searching SWCNTs using the Raman imaging method. Figure 2 shows the Raman image of SWCNTs with a peak between 263 cm^{-1} and 271 cm^{-1}, the corresponding tube diameter is about 0.9nm.

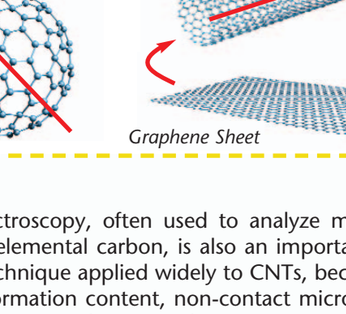


Figure 1: Raman Spectra of SWCNTs (blue recorded using 488nm; green recorded using 514nm)

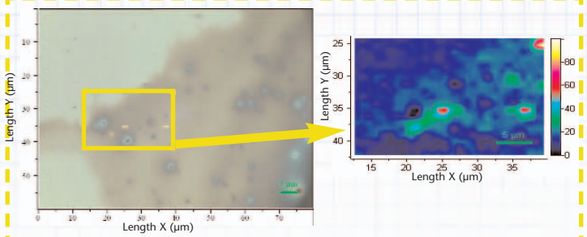


Figure 2: Raman Image of SWCNTs dispersed in polymer. Excitation wavelength was 514.5nm. (Data Courtesy: Prof. Shinichi Kitamura, Osaka Prefecture Univ)

Recently, bright photoluminescence (PL) of SWCNTs grown by the CCVD method was successfully observed in the near-IR at room temperature. The authors of this study expect optoelectronic applications of SWCNTs. PL measurements will become important for the characterization of SWCNTs.

In the forefront of nanotechnology, a combination of several high-precision analyses is needed for characterization of nano-materials. Jobin Yvon-Horiba offers a unique Raman PL bench-top system based on the LabRam HR800. The prime advantage of combining these two techniques in the same instrument is the possibility of making both analyses at exactly the same point.

Fluorescence spectroscopy is also a new, useful method to determine the identity of various species of SWCNTs. A matrix plot of fluorescence data is shown in Figure 3. The values for absorption and emission vary with SWCNT chirality. The Fluorolog®-3 spectrofluorometer has the sensitivity and flexibility to perform fluorescence measurements in the near-IR.

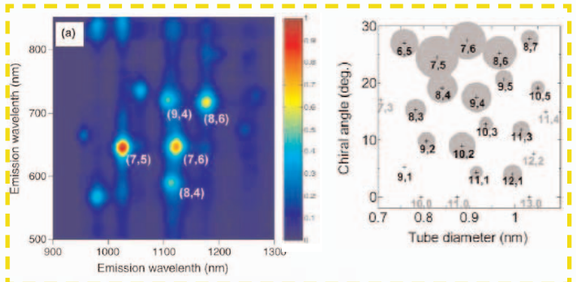


Figure 3: Matrix plot of Fluorenscence data and chirality distribution of alcohol CCVD SWCNTs (Data Courtesy of Dr. Shigeo Maruyama, The University of Tokyo)

Conclusion:

Which should you use: microscopic or spectroscopic method?

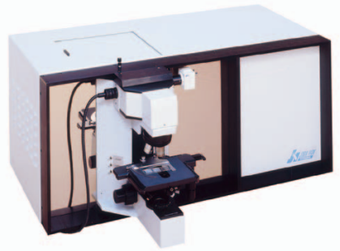
Microscopic methods are important tools for the study of CNTs. However, spectroscopic methods will become more important as already mentioned . These methods are compared with microscopic methods in Table 1. An advantage of spectroscopic methods over microscopic methods is convenience: structural information of CNTs can be monitored under ambient conditions. Only Jobin Yvon/Horiba can supply the total solution for spectroscopic characterization of CNTs.

Microscopic	Information	Sample Environment
STM	Molecular structure, Chirality	High vacuum
HR TEM	Molecular shape, Tube diameter	
HR SEM	Molecular shape, Tube diameter	
AFM		Atmosphere
Spectroscopic	**Information**	**Sample Environment**
Raman	Purity, Tube diameter, Chirality	Atmosphere
PL	Tube diameter	Solution
Near IR Fluorescence	Chirality	Solution

Table 1: Comparison of Methods

The System

LabRAM HR800



The LabRAM HR800 is a High Resolution Raman system which provides an uniquely high spectral resolution typically three times that achieved by other systems available. Ideally suited to stress measurements in semiconductors, phase and crystal structure characterization and for subtle band analysis.
The dual CCD/IR array detection option allows for Raman and PL measurements beyond 1.6µm wavelength range. The multiple gratings capability offers the highest performance and flexibility in terms of spectral resolution and coverage.