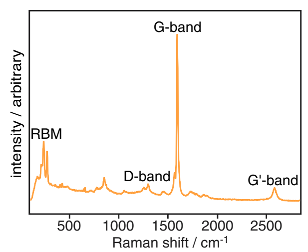
Probing carbon nanotubes with Renishaw Raman microscopy

Since their first observation by Sumio Iijima in 1991,[1] carbon nanotubes have attracted intense scientific interest due to their extraordinary electronic, thermal, and mechanical properties. The structure can be visualized as a graphite layer rolled up into a seamless cylinder, with each end either open or capped with half a fullerene molecule. The points at which the rolled up graphite sheet is connected define the tube's diameter and chirality, which, in turn, governs its properties.

Most current research is focused on single-wall nanotubes (SWNTs) as they have superior electrical, thermal, and mechanical properties to their earlier discovered multi-wall counterparts (made up of concentric tubes). Ten times stronger than steel, and six times lighter, SWNT composite materials are expected to reduce spacecraft weight by at least 50%. Depending on their diameter and chirality, SWNTs can show metallic or semiconducting electrical behaviour, leading to nanoscale wires and electrical components, whilst their high thermal conductivity (as high as diamond), makes them ideal for thermal materials and sensors.



785 nm excitation Raman spectrum of SWNTs

Data courtesy of Prof. RJ Young, Materials Science Centre, UMIST/Uni. of Manchester, UK.

Raman spectroscopy is ideal for studying SWNTs as it is non-invasive, requires little or no sample preparation, and can be performed under a range of conditions, including ambient conditions. The main features in the Raman spectrum of a carbon nanotube are the radial breathing mode (RBM) of A symmetry, the disorder-induced D-band of A symmetry and its corresponding second-order G'-band, and the tangential G-band, which is made up of A, E_1 and E_2 modes.

Carbon nanotubes normally form as an entangled mass of ropes or bundles, and, since the frequency of the RBM (usually in the region 150 cm^{-1} to 300 cm^{-1}) depends directly on tube diameter, resonance Raman spectra of this mode are used to provide an easy and quick determination of the tube diameter distribution in a sample.[2] Features in the tangential G-band have differing dependencies on diameter and chirality, and the most intense diameter-dependent feature (around 1590 cm^{-1}) in conjunction with the RBMs can be used to help identify individual metallic and semiconducting SWNTs.[2] The G-band has also been used to measure strain in SWNTs embedded in a matrix, and hence evaluate their load transfer effectiveness,[3] crucial for the design of super-strength composite materials. The frequency of the disorder-induced D-band depends on nanotube diameter *and* chirality, making it strongly dependent on the electronic structure. Unlike the D-band, the intensity of its G'-band overtone is not reduced in highly ordered crystals so is more often used to provide electronic structural information on isolated SWNTs.[4]

Many carbon nanotube researchers are already using Renishaw's Raman microscopes to characterize their samples.[2-4] One such researcher, Prof. Mildred Dresselhaus of MIT, USA, speaking at the European materials research society meeting in June 2002, outlined how the ability to analyse one single nanotube and identify its chirality and diameter solely by Raman spectroscopy represents 'a fundamental advance in the field'.

If carbon nanotubes are to attain their promised potential, and their properties exploited to the full, synthetic methods capable of controlling the diameter, chirality, and hence electrical, thermal and mechanical characteristics are required. For commercial viability, these will need to produce high yields at low cost. Renishaw is certain that its RM series and inVia Raman microscopes will play a key role in achieving these goals.

For more information, please contact your local Renishaw representative.

1 Iijima, S. *Nature,* **1991**, *354,* 56.
2 Jorio, A; Souza Filho, *AG;* Dresselhaus, G; Dresselhaus, MS; Swan, AK; Ünlü, MS; Goldberg, BB; Pimenta, MA; Hafner, JH; Lieber, CM. *Phys. Rev. B,* **2002**, *65 (15),* 155412.
3 Cooper, CA; Young, RJ; Halsall, M. *Composites A: Applied Science and Manufacturing,* **2001**, *32 (3-4),* 401.
4 Souza Filho, AG; Jorio, A; Swan, AK; Ünlü, MS; Goldberg, BB; Saito, R; Hafner, JH; Lieber, CM; Pimenta, MA; Dresselhaus, G; Dresselhaus, MS. *Phys. Rev. B,* **2002**, *65 (8),* 085417.

If you or any of your colleagues would like to be added to our mailing list, or if you would like further information about our spectroscopy products or applications, please contact us.

Renishaw plc

Spectroscopy Products Division,
Old Town, Wotton-under-Edge,
Gloucestershire GL12 7DW UK

T +44 1453 844302
F +44 1453 844236
E raman@renishaw.com

www.renishaw.com

Printed in England 0802 Part No. L-8012-1397

Issue 7
Newsletter from the Spectroscopy Products Division

RENISHAW
apply innovation

Spectroscopy Innovations

Announcing...inVia Raman microscopes

The introduction of the RM Raman microscope by Renishaw in 1992 heralded a new age in Raman spectroscopy. Renishaw's Raman microscopes have become the instruments of choice for users requiring the highest levels of flexibility, sensitivity, and reliability.

More than ten years later, Renishaw's RM Series Raman microscopes still offer more flexibility and sensitivity than any other Raman instrument on the market.

So why change them?

At Renishaw, apply innovation is not just a slogan, it's our practice. By applying innovation to every aspect of our design and engineering, we have introduced even more flexibility and more automation for greater ease-of-use; we present inVia Raman microscopes.

Unparalleled flexibility and sensitivity

You choose the functionality and level of automation that you need and add to it as your requirements change.

Whichever inVia Raman microscope configuration you choose, you will have one of the most flexible and sensitive Raman systems on the market.

Ease-of-use without compromise

Renishaw's inVia Raman microscopes add simplicity of operation to the high performance and unparalleled flexibility for which Renishaw Raman systems are renowned.

Apply innovation. See www.renishaw.tv and click on promotions to find out more.

RENISHAW
apply innovation

Renishaw - built on innovation and engineering excellence

The first Renishaw product was invented in 1972 by Sir David McMurtry, now Chairman and Chief Executive of Renishaw plc, whilst Assistant Chief of Engine Design at the Rolls-Royce Filton works, Bristol, UK. He invented the touch-trigger probe (TTP) for use on Co-ordinate Measuring Machines (CMMs) to address difficulties in the measurement of complex narrow pipework fitted to the Olympus engines used on Concorde. David built the first probe at home over a week-end and Rolls-Royce took out a patent on the design, which was filed on 21st September 1972, with David acknowledged as the inventor.

Original 3D touch-trigger probe and patent

David discussed the matter with John Deer, now Deputy Chairman of Renishaw plc, who was also working at Rolls-Royce at the time. John had a background in machine shop engineering and was interested in having his own business.

Thus, the first Renishaw company, Renishaw Electrical Ltd, was registered on 4th April 1973, and acquired its first commercial premises in 1976 in Wotton-under-Edge, Gloucestershire, UK. At the time its nine employees made the TTPs, already being used by almost all major CMM manufacturers in the world. By 1981, with annual sales approaching £3 million, Renishaw (Ireland) Ltd was established in Dublin. 1981 also saw the acquisition of the New Mills site just outside Wotton-under-Edge and the establishment of the first overseas subsidiary company near Chicago, Illinois, USA. Renishaw now has over 20 sites worldwide and over 1500 employees, with around 1100 in the UK and 400 overseas.

To date, a wide range of automated probing systems have been developed to meet the needs of post-process inspection for quality control. Comprehensive machine calibration can be undertaken using Renishaw's innovative laser calibration systems. Laser scale systems have been developed for applications which vary from determining track positional information on computer disk drives, to use as a positioning system on large machines which manufacture parts for the aerospace industry. Renishaw has also developed linear scale and encoder systems for fitting to a variety of machines, to provide axis displacement measurement.

In the 1990s Renishaw applied its innovative approach to Raman spectroscopy and combined the application of a number of technologies, including its own encoder systems, to the development of smaller instruments. Another key development was the efficient coupling of the Raman spectrometer to a standard optical microscope, the first commercially available RM series Raman microscope being manufactured by Renishaw in 1992.

Renishaw's encoder technology has been employed for accurate positioning of spectrometer motorized components and accessories, such as the motorized grating stage and the motorized sample positioning stage.

The company has been honoured with nine Queen's Awards, recognizing Technological Achievement, Export Achievement, and Enterprise. Numerous other awards for manufacturing, design, innovation, market development, and export have also been conferred. Many of Renishaw's products have been recognized with awards, including Renishaw's Raman microscope which received the Prince of Wales Award for Innovation in 1993 and the 1995 Award by the Worshipful Company of Instrument Makers.

David McMurtry has received a number of personal awards for his contributions to technology and industry, both in the UK and overseas. In the New Year's Honours List for 2001, he was appointed a Knight Bachelor "for services to Design and Innovation" and was formally invested as Sir David McMurtry in March 2001.

Renishaw's own state-of-the-art Machine Hall at New Mills, where Renishaw employs its own products throughout production to ensure that exacting manufacturing specifications are met efficiently.

Renishaw is committed to providing innovative solutions for manufacturers and scientists in industry and research.

To deliver innovations, we have assembled a team of staff dedicated to the application of cutting-edge science and engineering. Working in the fields of mechanical and electronics design, software, optics, lasers, control and systems design, and material research, we are constantly seeking ways to apply the latest technologies to meet the needs of our customers.

For more details please contact your local Renishaw representative.

Chemical mapping with Renishaw Raman

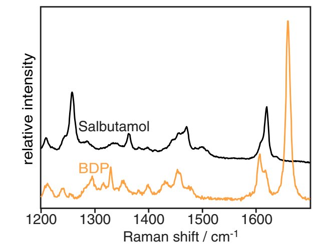
Asthma affects over 150 million people worldwide, and current research indicates that it's on the increase. There is no known cure, but there are treatments available to relieve the symptoms and help prevent the onset of an attack.

Preventer medicines are designed to reduce the likelihood of an attack occurring and usually consist of a corticosteroid, which is a steroid used to relieve inflammation of the airways. Inhalation is an effective way of delivering the steroid straight to the lungs and the total dose needed is very small. Reliever medicines are sometimes called bronchodilators and are used to relieve the symptoms of an attack by relaxing the tightened airways, enabling the sufferer to breathe more easily. These medicines can be taken in the form of tablets or syrup, but work much more quickly when inhaled.

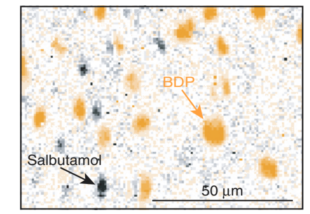
Combination treatments are now available where a reliever and preventer are delivered from one pressurized metered dose inhaler. New research by D F Steele *et al.* at the University of Bath, UK, in collaboration with Renishaw, shows how Raman mapping can be used to investigate the drug distribution deposited from such a delivery system, detect drug-drug interactions within the mixture, and indicate the particle sizes of the deposited components.

The formulation investigated was a combination asthma therapy containing salbutamol bronchodilator (delivered dose 100 µg) and beclomethasone dipropionate (BDP) corticosteroid (delivered dose 50 µg). The mixture was deposited from the inhaler *in vitro* and Raman spectra were recorded using a Renishaw RM series Raman microscope and a Renishaw high power 785 nm diode laser as excitation source. The spectra were acquired at 1 µm steps for 20 seconds each over a single deposit using the automated xyz microscope stage to control sample movement. Raman spectra of the pure drugs were used to identify the components in the deposit and generate a chemical map.

The Raman map illustrates the distribution of both BDP and salbutamol in the sample and confirms the particle size ranges expected by the researchers for each component. The Raman data also allow drug-drug interactions to be detected: any chemical changes lead to Raman band wavelength shifts and/or the emergence of new peaks in the spectra; since no such effects were observed in this case, drug-drug interactions can be ruled out.



Raman spectra of pure samples of BDP and salbutamol



Raman map of BDP and salbutamol distribution

Data courtesy of D F Steele, University of Bath, UK.

The researchers conclude that the technique is a 'useful additional procedure in the *in vitro* investigation of pharmaceutical aerosols'.[1] Chemical mapping is just one example of how Renishaw Raman spectroscopy is attracting interest from the pharmaceutical field: writing in the *European Pharmaceutical Review* recently, another Renishaw user, Dr. Rolf Hilfiker of Solvias AG, described Raman spectroscopy as 'the tool of choice' for polymorph differentiation.[2]

The unparalleled flexibility and sensitivity, and uncompromised ease-of-use of Renishaw's inVia Raman microscopes makes them ideally suited for pharmaceutical applications whether they be routine QA analyses or cutting edge research projects.

For more information, please contact your local Renishaw representative.

[1] Steele, DF; Young, PM; Smith, T; Price, R; Lewis, D. *Submitted to Int. J. Pharm.*
[2] Hilfiker, R; Berghausen, J; Marcolli, C; Szelagiewicz, M; Hofmeier, U. *European Pharmaceutical Review*, **2002**, *7 (2)*, 37.

Would you like a chance of winning a handheld computer and see your work featured in the next issue?

If your answer is 'yes' and you've got some exciting new results using Renishaw's spectroscopy products, we'd like to hear from you.

For your chance to see your work featured in the next issue of *Spectroscopy Innovations* and enter the prize draw for a Palm™ m500 Handheld computer, simply email, fax, or mail your Renishaw spectroscopy article to your local Renishaw representative.

Please clearly mark all entries 'Spectroscopy Innovations' and include brief details of the Renishaw products used, and how we can contact you.

Each article featuring work using Renishaw spectroscopy products submitted by email, fax or mail to your local Renishaw representative will be entered into a free prize draw for a Palm™ m500 Handheld computer or equivalent. Entry is not dependent upon the article actually being featured in Spectroscopy Innovations nor is the winner's article guaranteed to be featured. The closing date for receipt of entries is 28th February 2003 and the draw will be held on 28th March 2003. The winner will be the person submitting the article that is drawn on the draw date. No cash alternative is available. The winner will be notified using the contact information supplied within 2 weeks of the draw date. By submitting your articles to us, you agree that the article may be edited by us and published in full or part by us in Spectroscopy Innovations and other literature produced by the Renishaw Group. For further information, please contact your local Renishaw representative at the address on the back cover.