Understanding the use of Raman spectroscopy in the AOT-100

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The Biral AOT-100 is a unique instrument which allows individual aerosol droplets to be isolated in an optical trap and studied for extended periods of time. A key strength of the instrument is the novel use of Raman spectroscopy for retrieving the droplet radius and refractive index at a precision far beyond the capability of traditional aerosol analysis techniques. This technical note will describe how Raman spectroscopy is used for this purpose alongside the more conventional employment of identifying chemical components.

Spontaneous Raman spectroscopy

When a sample is exposed to an external light source the molecular vibrations of individual chemical bonds can be excited to a higher (virtual) energy level. The majority of these excited vibrations subsequently relax back to their original energy level and reradiate light at the same frequency as the external source (known as Raleigh scattering). However, a small proportion relaxes to a different energy level and radiates at a different frequency to the external source (Stokes or anti-Stokes scattering). This change in frequency, referred to as a spontaneous Raman shift, is indicative of the specific chemical bond and Raman scattered light can be observed to probe the chemical composition of the sample.

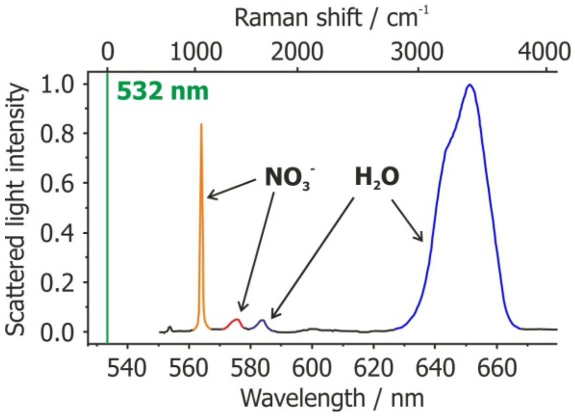

Figure 1: Example of a typical Raman spectrum observed from a bulk sample

Figure 1 is an example of a typical Raman spectrum acquired from a bulk sample. It consists of a series of broad spontaneous Raman bands each identifying a chemical component, in this case NO3- and H2O. The broad bands occur because each type of bond emits Raman scattered light over a range of frequencies depending on the individual energies of each bond of that type. Sometimes the same chemical group can give rise to multiple Raman shifts depending on the different vibrations being stimulated. Note the intense signal at 532nm which identifies the external light source.

Cavity enhanced Raman spectroscopy

In the AOT-100 the sample being observed is a droplet with a spherical structure, rather than a bulk solution. This fact can be exploited to extract more information using Raman spectroscopy than would normally be available. The spherical droplet acts as an optical cavity that resonates the spontaneous Raman scattered light at certain discrete frequencies which couple to the resonant modes of the cavity. In physical terms a resonance occurs when the frequency of light is such that it forms a standing wave, composed of an integer number of wavelengths, around the circumference of the droplet. Resonating light stimulates more emission at the same frequency, as is illustrated in Figure 2, and can

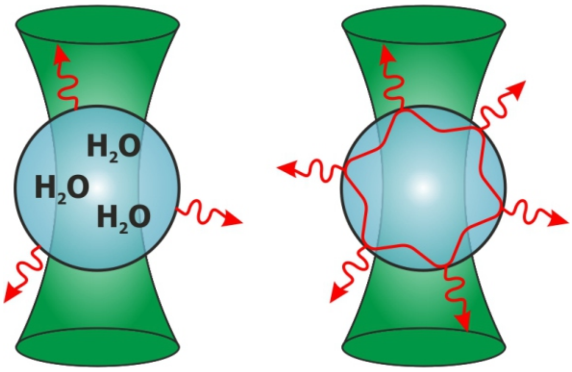

Figure2: An illustration of Raman scattering in the AOT-100.
Left: traditional spontaneous Raman scattering.
Right: stimulated Cavity enhanced Raman scattering.

be observed as peaks in the Raman spectrum.

A typical Raman spectrum acquired from the AOT-100 is shown in Figure 3. The resonant peaks of stimulated Raman intensity are superimposed on a broad underlying spontaneous band centred at around 650nm which is indicative of the OH stretching vibrations of the water contained within the droplet. The peaks are referred to as whispering gallery modes (WGMs), named in reference to the famous whispering galleries found at such places as St Pauls Cathedral. A single spontaneous Raman band can give rise to several WGMs with each WGM uniquely identified by the number of wavelengths forming the standing wave, the number of radial maxima within the particle and the particular polarisation state.

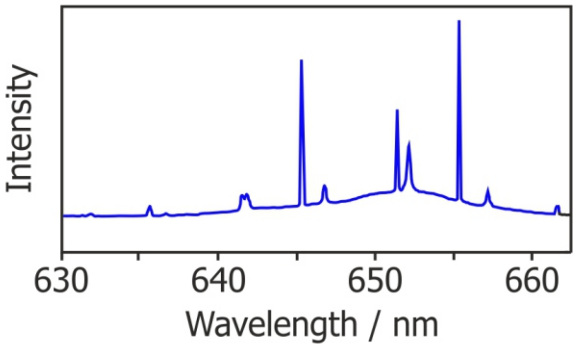

Figure 3: Example of a typical Raman spectrum acquired from a droplet sample using the AOT-100.

As the wavelengths of the WGMs are highly dependent on the physical properties of the droplet they can provide a fingerprint of the radius and refractive index. For example, a decrease in radius causes the WGMs to track to shorter wavelengths. The AOT-100 uses an algorithm to compare the wavelengths of the WGMs observed using Raman spectroscopy with predictions from Mie theory to calculate the radius and refractive index simultaneously and with extremely high precision. Spectra are acquired at a rate of 1s or quicker, allowing the continuous measurement of dynamic properties for droplets undergoing chemical or physical change.

References

T.C. Preston and J.P. Reid, 'Accurate and Efficient Determination of the Radius, Refractive Index and Dispersion of a Weakly Absorbing Spherical Particle using Whispering Gallery Modes', J. Opt. Soc. Am. B 20 (2013) 2113-2122.

R. Symes, R.M. Sayer, and J.P. Reid, 'Cavity enhanced droplet spectroscopy: Principles, perspectives and prospects', Phys. Chem. Chem. Phys. 6 (2004), 474-487.

Please see www.biral.com for more technical information.

About the Author

Dr Walker is a Project Scientist for Biral, UK. He has a PhD in Physical Chemistry and several years' experience in research and development of optical techniques for measuring individual aerosol particles. He has written over 10 scientific papers in atmospheric aerosol and optical trapping techniques, which have been published in international peer-reviewed journals.

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