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# Cavity enhanced spectroscopy as a diagnostic for micro-particles levitated in a plasma

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## Introduction

Cavity enhanced spectroscopy has been successfully used as a diagnostic for aerosol droplets [1]. In the present investigation the feasibility of applying this technique to solid micron sized particles levitated in an rf-plasma has been studied. A pulsed laser is used to excite whispering gallery modes (cavity resonances) in individual micro spheres leading to enhanced Raman scattering at corresponding wavelengths. This non-invasive method gives direct access to the size and also the chemical composition of the micro spheres, and is thus a very interesting tool for the characterisation of growing layers deposited on micro particles i.e. in molecular plasmas.

If a droplet or a micro particle is struck by a laser beam, under the right conditions and at particular resonant wavelengths the light can undergo total internal reflection and become trapped inside the droplet for long periods. Long here means on the order of nanoseconds with the result that the light travels a few metres inside the particle. The trapped laser light leads to stimulated Raman scattering at particular resonant wavelengths within the Raman spectrum and an enhanced Raman scattering signal can be detected. The resonant behaviour can be accurately described by MIE scattering theory. Figure 1a shows a spectrum of a water droplet illuminated with a laser at a wavelength of 590 nm. Sharp equally spaced peaks appear at a Raman of ca. 3400 $cm^{-1}$ corresponding to the O-H stretching band of water .

Cavity resonances can be thought of as the light forming standing waves inside the particle. They are particular solutions of the MIE scattering problem and can be assigned a mode number, which corresponds to the number of wavelengths in the standing wave, and a mode order, which corresponds to the number of radial intensity maxima. Resonances of the same mode order and polarisation are approximately equally spaced. From the line spacing we readily arrive at the particle size. The following formula gives an approximation for the particle radius $r$ [1]:

$$r \approx \frac{\tan^{-1}\sqrt{m^2-1}}{\sqrt{m^2-1}} \cdot \frac{1}{2\pi\,\Delta k} \qquad (1)$$

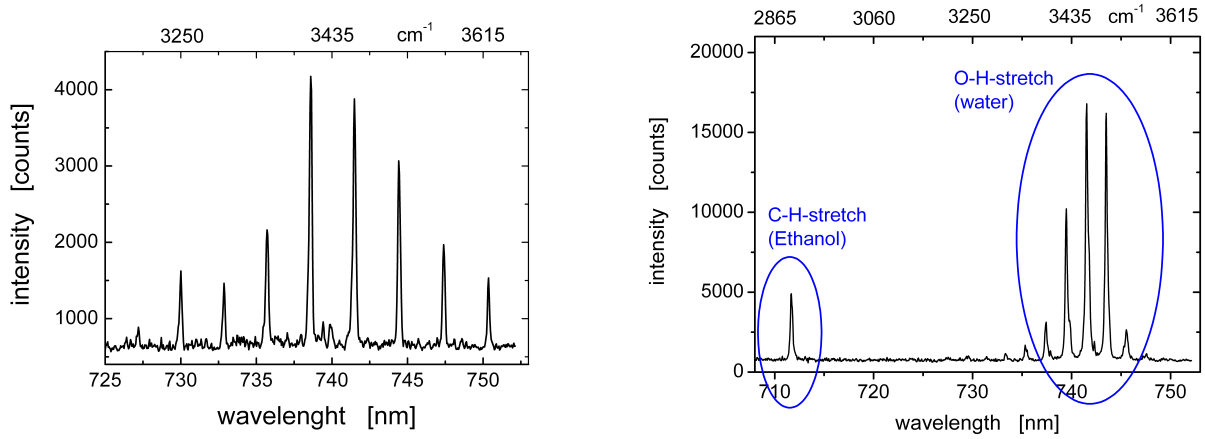


Figure 1: Cavity enhanced Raman spectrum from: a) a water droplet ($r = 24.5\mu$m), b) a water/ethanol droplet ($r = 35\mu$m).

Here $m$ is the refractive index of the material and $\Delta k$ the line spacing between resonances of consecutive mode numbers. By this formula particle sizes can be calculated with an accuracy of a few hundred nanometres.

If the droplet composition is not pure water but e.g. a water / ethanol - solution, in addition to the Raman scattering from water another peak appears at a wavenumber shift of ca. 2900 cm$^{-1}$, which corresponds to the C-H stretching band of ethanol (Fig. 1b). From averaging over many spectra it is possible to determine the concentration of the ethanol component in the droplet. In fact the Raman signal increases exponentially with the ethanol concentration [2].

**Experiment**

Micro particles that are injected into an rf-plasma acquire a negative surface charge due to electron and ion fluxes in the plasma. A multitude of forces act on the charged particles, which have been discussed extensively in the literature [3]. The particles will attain an equilibrium position, where the sum of all acting forces vanishes. The particles are confined in the plasma sheath where the electrostatic force caused by the strong fields in the sheath balances the other forces. In our case, the system is dominated by gravitational and electrostatic forces, while thermophoresis, neutral and ion drag are of minor importance.

For the experiments a capacitively coupled rf-discharge (13,56 MHz) in Argon ($P_{rf} \approx 10$ W, $p \approx 10$ Pa) was used (see fig. 2a). The cylindrical reactor vessel with 40 cm in diameter and 50 cm in height contains two horizontal electrodes (diameter 13 cm) with a distance of 10 cm. The upper electrode is rf-driven, the lower electrode is a so called adaptive electrode (AE), consisting of 101 identical square segments ($7\times7$ mm$^2$) surrounded by 4 larger segments and an outer ring electrode. Each segment can be biased independently with dc and/or ac voltage

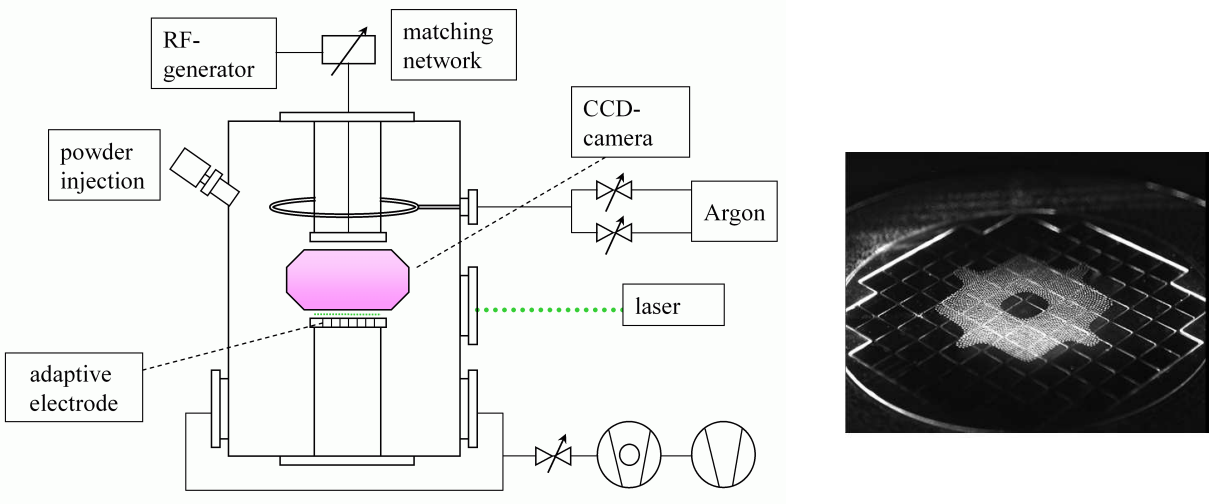


Figure 2: a) Experimental setup (PULVA-INP). b) Micro particles (Melamine formaldehyde, ∅ 10 $\mu$m) levitated in an Argon-rf-plasma above the adaptive electrode. Negative bias voltage is applied to the central segment and to the segments surrounding the particles.

of up to $\pm$100 V and frequencies of maximum 50 Hz. This arrangement allows distinct local manipulations of the plasma sheath and therefore of the position of levitated particles (see fig. 2b). The particles that are suspended above the adaptive electrode are illuminated by a spatially broad laser beam at a wavelength of 532nm and viewed orthogonally with a CCD camera.

To excite cavity enhanced scattering a pulsed tunable dye laser centered at 590 nm with pulse energies of ca. 1.5 mJ/pulse was used. It was pumped by an Nd:YAG-laser (532 nm), which was also used directly for some experiments. The spectra were resolved and captured by a spectrograph and an ICCD-camera. The signal was sent to the entry optics of the spectrograph via an optical fibre which could be positioned at a variable angle with respect to the laser beam.

**Results**

Before investigating solid micro particles in the plasma, experiments were performed on micro particles in air. We investigated spheres of different sizes and chemical composition. Cavity enhanced Raman scattering could be successfully detected from polymer spheres. Figure 3a shows a spectrum measured at a PMMA(polymethylmethacrylate)-particle with a diameter of 50 $\mu$m. Clear peaks appear at a Raman shift of 2900 cm$^{-1}$ in the C-H stretching region. Calculating the particle size from the spectrum gives a value of 51 $\mu$m, which is in good agreement with the value specified by the sphere manufacturer.

Next, particles that were coated with a fluorescent dye (Rhodamine B) were investigated. Analogous to cavity enhanced Raman scattering the fluorescence signal is enhanced at wavelengths corresponding to cavity resonances. The resulting spectra show peaks superimposed

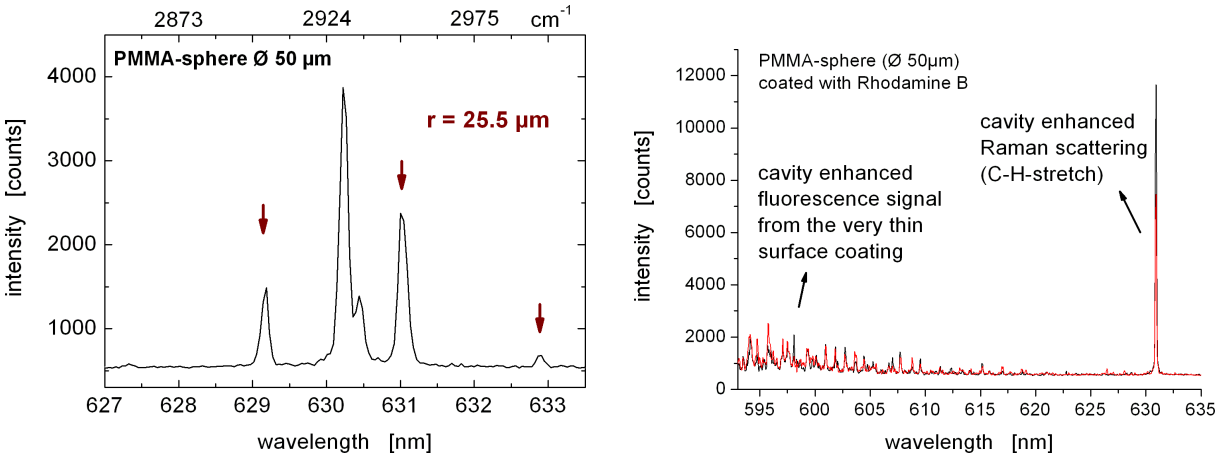


Figure 3: a) Cavity enhanced Raman spectrum from a PMMA-sphere. b) Spectrum from a polymer sphere ($\varnothing$ 50 $\mu$m) coated with Rhodamine B. The spectrum shows cavity enhanced Raman scattering in the C-H-stretching region at a shift of ca. 2900 $cm^{-1}$ and also enhanced fluorescence from the dye covering the surface.

on the broad fluorescent band, where the signal is enhanced through coupling into cavity resonances. Figure 3b shows a spectrum from a Rhodamine-B-coated PMMA-sphere where both the cavity enhanced Raman signal and the fluorescence signal originating from the particle surface can be seen. These results prove that cavity enhanced spectroscopy is a surface-sensitive technique.

## Conclusion

We have shown that it is possible to detect cavity resonances from the surface of a single particle, making it a suitable technique for the characterisation of growing layers in plasmas. After the encouraging results obtained from micro particles in air the investigations will be continued for particles levitated in an rf-plasma.

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