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This report results from a contract tasking University of Cambridge as follows: Understanding the role of nano and micro sized particles in industrial processes and in the atmosphere using plasmas has become very important. The grantee proposes to develop a novel, sensitive and non-invasive diagnostic technique for probing the chemical composition of solid particle surfaces in dusty plasmas. Specifically, pulsed tuneable lasers will be used to excite whispering gallery modes (WGMs) in individual silica microspheres trapped in a plasma crystal. This novel chemical probe will link the particle composition to the chemical composition of the plasma.

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Abstract:

Understanding the role of nano and micron sized particles in the atmosphere and in industrial processes is becoming increasingly important. The goal of this project was to develop a novel non-invasive diagnostic technique for probing the surface layers of micron sized solid particles in dusty plasmas. A pulsed tuneable visible laser is used to excite whispering gallery modes (wgm), also called cavity resonances, in individual spherical particles called microspheres which are levitated in a molecular rf-plasma. The microspheres act as an optical cavity leading to high scattering intensities for frequencies corresponding to resonant modes of the cavity. The size of the microsphere and the chemical composition of the particle surface will be determined from the associated wgm Raman spectrum. The method has considerable technological potential for fast, sensitive, and non-invasive identification of toxic or corrosive coatings on small particles in the atmosphere, combustion systems and in plasmas.

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References
1. Project Overview

1.1. Objectives / Project Plan

Cavity Enhanced Raman Spectroscopy (CERS) has been very successfully used as a diagnostic for aerosol droplets [1, 2].
We want to investigate the feasibility of using Cavity Enhanced Raman Spectroscopy as a novel diagnostic technique for particles levitated in a plasma.
The objectives of this study are threefold: To study the surfaces of micron sized particles as a function of their size (diameter) and material composition; Levitate the particles in a molecular plasma and identify the chemical nature of the adsorbed surface layers; Understand the kinetics and dynamics of the particle – plasma interactions. To achieve these objectives we envisaged the project proceeding in three distinct steps. Firstly measuring wgm Raman spectra of micron sized aerosol droplets in air to familiarise ourselves with the techniques required. Step two of the project is the investigation of solid microspheres in air, where they can be handled in an easier way. We have several types of microspheres with different sizes and from different material at our disposal. Step three is the investigation of microspheres in the plasma itself, first in Argon, later in molecular gases to study the deposition of layers on the particles.

1.2. Status

As can be seen from the results cited below some aspects of the project have gone very well and in some it took a lot of time to achieve the first success. The results very much encourage a continuation of the research.
The experiments have led to some improvements in the experimental arrangement, in particular the incorporation of a slightly tuneable excitation laser which should considerably enhance matching the laser modes to the wgm modes of the particle.
A droplet generator was constructed, which proved to work very well, generating droplets of stable size. From those droplets very satisfactory spectra could be obtained under a range of conditions. It was more difficult to obtain spectra from solid microspheres. Just recently we succeeded. Investigations of relatively large particles (Ø 150 µm), glued to the tip of thin wires, were not successful. Although the cavity resonances are energetically closer spaced and thus it is easier to match the laser frequency to them, their intensity drops too much to be detected by our system. We then investigated smaller spheres, which were set on top of a thin glass plate and illuminated with the laser from below. From those we could measure cavity enhanced Raman scattering. Some microspheres were also coated with a fluorescent dye. Analogous to the enhanced Raman scattering the fluorescence gets enhanced at wavelengths corresponding to cavity resonances. Good wgm-fluorescence spectra could be obtained demonstrating the surface sensitivity of this technique.
Since it was more difficult to obtain spectra from solid microspheres than we had expected, we were not yet able to investigate the spectra of microspheres levitated in the plasma. Nevertheless we are able to trap the microspheres in the rf-plasma, control their position and hit them with the laser beam.
2. Theoretical Background

2.1. Cavity Enhanced Raman Scattering (CERS)

If a droplet (or for that matter 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 times. Long here means on the order of nanoseconds with the result that the light travels a few metres inside the droplet. The trapped laser light leads to stimulated Raman scattering at particular resonant wavelengths within the Raman spectrum. This “double resonance” leads to an enhanced scattering signal at certain wavelengths depending on the particle geometry. Fig. 1 shows two spectra measured from water droplets. The observed signal depends very much on the illumination geometry. In the left hand figure the laser beam struck the droplet in the center, in the right hand figure it was struck tangentially with the result that most of the intensity is coupled into one resonant mode only.

![CERS spectra from water droplets](image)

Cavity resonances which are also referred to as whispering gallery modes (wgms; after the whispering gallery in St. Pauls Cathedral in London) 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. Figure. 2 shows two more measurements of water droplets. In the first one only resonances of one mode order are excited. The equally spaced peaks belong to resonances of consecutive mode numbers. In the second diagram are resonances of three different mode orders, peaks of the same color belong to one mode order, respectively.

![Cavity resonances](image)
2.2. Determination of size and composition

From the spacing between lines belonging to different mode numbers we readily get access to the droplet size. The following formula gives an approximation for the droplet radius [1]:

\[ r \approx \tan^{-1} \frac{\frac{1}{\sqrt{m^2 - 1}}}{\frac{1}{2\pi \Delta k}} \]

\[ r \ldots \text{radius} \]
\[ m \ldots \text{refractive index of medium} \]
\[ \Delta k \ldots \text{line spacing in wavenumbers} \]

(1)

With this formula droplet sizes can be calculated with an accuracy of a few hundred nanometres. For higher accuracies i.e. down to a few nanometres, it is necessary to exactly determine which mode each peak belongs to.

If the droplet composition is not pure water but e.g. a water / ethanol – mixture, in addition to the Raman scattering from water (O-H-stretching band) another peak appears at a wavenumber shift of ca. 2900 cm\(^{-1}\), which corresponds to the C-H stretching band of ethanol (Fig.3). 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 [3].
2.3. Trapping of micro particles in an RF-plasma

Particles injected into an rf-plasma become negatively charged due to the higher mobility of the electrons compared to the ions. They acquire a floating potential as do all isolated bodies present in a plasma. Depending on their size they can carry several thousand elementary charges.

Several forces act on these charged particles. For bigger particles (> a few µm) the gravitational force and the electrostatic force are the most dominant. The particles get confined in the plasma sheath where the electrostatic force caused by the strong fields in the sheath balances the other forces.

A more detailed description of the forces acting on particles in a plasma and on the growing number of applications of dusty plasmas can be found in the literature [4, 5].

3. Experimental Setup

The principal components of the apparatus assembled for the project were as follows.

**Laser system:**
We used a pulsed tuneable dye laser centred at 590 nm with pulse energies of ca. 1.5 mJ/pulse. To allow a better coupling into an input resonance of the microspheres the laser linewidth was increased to $0.4 \text{nm} \cong 11.5 \text{ cm}^{-1}$ by using a prism and a mirror instead of two gratings in the resonator. The dye laser is pumped by a Nd:YAG-laser (532 nm). It is also possible to use the Nd:YAG-laser directly for the experiments.

**Detection system:**
A spectrograph "Spectra Pro 2500i" (Acton Research) and ICCD camera (Andor iStar) were used to resolve and capture wgm-Raman spectra. The signal is sent to the entry optics of the spectrograph via an optical fibre which is positioned at a variable angle with respect to the laser beam. The laser and the ICCD-camera are synchronised using a function generator. Fig. 4 shows the setup.

![Fig. 4: Schematic of the experimental setup](image)
3.1. Experiments on liquid droplets and microspheres in air

Optical Setup:
The laser is focussed onto the droplets using 2 lenses (+50mm) and an iris is inserted between them at the focus of the first lens. Another lens (+50mm) is positioned after the droplets interact with the laser to form a 1:1 image on the entrance of the optical fibre (Fig. 5).

![Optical setup for the measurements on droplets](image)

Droplet generator:
A droplet generator (VOAG; vibrating orifice aerosol generator) was constructed in house and is shown in Fig. 6.

![Cut through the droplet generator (VOAG)](image)

The necessary water pressure feeding the VOAG was generated by means of a commercially available pressure cooker (pressure ca. 2 bar). A ss-standard-flow-orifice (Lenox Laser) with diameters of 15 or 20 µm was used to form the droplets. The piezoelectric ceramic was driven with a square wave modulation of amplitude 20V at frequencies up to 100 kHz. The droplet generator is installed on two linear transition stages for exact x-y-positioning with respect to the laser beam with a precision of 100 nm.

To synchronise an individual laser pulse with a single droplet the square wave signal driving the VOAG is sent to a delay generator. This triggers a 10 ms long pulse which in turn triggers the laser flash lamps as well as the gate of the ICCD-camera. The gate pulse is further delayed by the Q-switch delay of the laser (170 µs).
3.2. Experiments on microspheres in the RF-plasma

For this project we used a custom made plasma reactor, called PULVA-INP [6], which is shown in figure 7. The cylindrical vacuum vessel with a diameter of 40 cm contains two electrodes (Ø 13 cm) separated by 10 cm. The upper electrode is driven at a frequency of 13.56 MHz. The RF power is supplied by a Dressler RF generator in combination with an automatic matching network. Generally work was conducted at pressures of ca. 10 Pa and RF-powers of 5-10 W. The particles are injected into the discharge and become suspended above the lower electrode. They are illuminated by a spatially broad laser beam at a wavelength of 532nm and viewed orthogonally with a CCD camera. An example is shown in figure 9.

![Fig. 7: The experimental plasma reactor PULVA-INP.](image1)

The special feature of this reactor is the lower electrode, a so called adaptive electrode (see Fig. 8), which is divided into 101 identical square segments (7x7 mm²) surrounded by 4 larger segments and an outer ring electrode. Each segment can be individually biased with a DC-voltage (-100V ... +100V), three of the segments can also generate RF-voltages. This allows precise local manipulations of the plasma sheath and therefore specific manipulation of individual particles (moving and positioning of particles for treatment and diagnostic).

![Fig. 8: The adaptive electrode.](image2)

![Fig. 9: Micro particles (here: Melamine formaldehyde (MF) – particles with Ø 10 µm) 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.](image3)
Fig. 10: Optical setup for CERS-measurements on particles levitated in the RF-plasma.
4. Results

4.1. Aerosol Droplets

Measurements on aerosol droplets were done using water and water/ethanol mixtures. Some diagrams showing typical measurements on droplets have already been shown in section 2.

To characterize the droplet generator (VOAG) the droplet radius was measured with changing frequency of the VOAG using a water/ethanol mixture (15% ethanol). With increasing frequency the droplet size decreases as expected (Fig. 11). The fitted curve was calculated using the averaged flow rate estimated with the following formula: $Q \approx \frac{1}{3} \pi r^3 \cdot f_{\text{VOAG}}$, where $r$ is the droplet radius and $f_{\text{VOAG}}$ is the frequency of the VOAG.

The droplet size is much more stable (has a smaller size dispersion) for higher frequencies.

From formula (1) (section 2.2) we see that the mode spacing increases with decreasing radius:

$$r \propto \frac{1}{\Delta k}$$

Fig. 12 shows a comparison of three spectra from pure water in different sized droplets. The smaller the droplet the further apart the resonances are, and the greater the difficulty to couple the laser light into an input cavity resonance and to fulfil the resonance conditions for stimulated Raman scattering. Hence this technique is most applicable to spheres with diameters in the range of a few µm up to ca. 100 µm.
4.2. Microspheres in air

The experiments on aerosol droplets were very successful and cavity enhanced Raman spectra could be easily obtained. In contrast it proved much more difficult to get successful measurements from solid particles.

We had solid particles of different sizes and from different materials at our disposal:

- glued to the tip of thin wires:
  - glass Ø ca. 200 µm
  - polystyrene Ø 150 µm
  - PMMA (polymethylmethacrylate) Ø 150 µm

- for use in the plasma:
  - PMMA Ø 50 µm
  - MF (melamine formaldehyde) Ø 1 … 10 µm
  - hollow glass spheres Ø ca. 50 µm

The polymer spheres have an excellent size distribution and a very smooth surface.

We started with relatively large spheres (Ø150…200µm), because these could be handled most easily, and glued them to the tip of thin wires. For these sized spheres we were not able to detect a cavity enhanced signal. The larger the particles are the closer is the mode spacing and thus the probability to couple into a resonance, but also the signal intensity decreases much.

We then investigated smaller spheres (Ø 50 µm) that were put onto a glass plate and illuminated with the laser from below. That proved successful.

Two types of experiments were done:
Firstly cavity enhanced Raman scattering from the microspheres was investigated.
Secondly the fluorescence spectrum from spheres coated with a fluorescent dye was investigated. In an analogous way to cavity enhanced Raman scattering the fluorescence signal is enhanced at wavelengths corresponding to cavity resonances.
Cavity enhanced Raman scattering

For these investigations we used PMMA-spheres with a diameter of 50 µm. For PMMA we expect Raman scattering at a shift of ca. 2900 cm\(^{-1}\) [7]. Using the Nd:YAG laser with a wavelength of 532 nm, this corresponds to a wavelength of 630 nm. Using the dye laser with a wavelength of 590 nm, the Raman scattering would occur at 712 nm.

The diagrams in fig. 14 show clear cavity enhanced Raman signals in the C-H stretching region at the expected wavelengths. When the particle is illuminated at the particle edge only one mode order is excited, when it is hit more in the center peaks of several mode orders appear.

![Graph showing cavity enhanced Raman signals from a 50µm-PMMA-sphere illuminated at the particle edge and center.](image)

**Fig. 14:** CERS-signal from a 50µm-PMMA-sphere:
- a) illuminated with the Nd:YAG laser (532 nm)
- b) illuminated with the dye laser (590 nm)
Cavity enhanced fluorescence from coated microspheres

To coat the microspheres a drop of Rhodamine-B-solution of very low concentration was put on them and they were left to dry. The resulting very thin coating smoothly covered the whole particle surface.

The diagram in Fig. 15 shows the fluorescence spectrum of a coated 50µm-PMMA-sphere. Peaks appear superimposed on the broad fluorescence band, where the signal is enhanced through coupling into cavity resonances.

![Diagram showing fluorescence spectrum](image)

**Fig. 15:** cavity enhanced fluorescence from a 50µm-PMMA-sphere coated with Rhodamine B

Fig. 16 shows a spectrum where only peaks belonging to one mode order appear. Calculating the droplet size from these results yields a value for the diameter of the microsphere of 50.8 µm, which is in good agreement with the value given by the microsphere manufacturer.

![Diagram showing fluorescence spectrum](image)

**Fig. 16:** cavity enhanced fluorescence from a 50µm-PMMA-sphere coated with Rhodamine B
Fig. 17 shows an interesting measurement where both cavity enhanced Raman scattering and cavity enhanced fluorescence can be seen. The fluorescence signal arises only from the particle surface, while the Raman signal originates from deeper inside the sphere.

![Graph showing Raman and fluorescence signals](image)

The measurement on spheres coated with fluorescent dye show that it is possible to detect a cavity enhanced signal only from the surface of the microsphere. This finding is an important requirement for the investigation of particle surfaces in molecular plasmas.

### 4.3. Microspheres in the RF-plasma

Microspheres have been trapped above the central segment of the adaptive electrode. To achieve this the segments of the electrode surrounding the central segment were set to a negative bias voltage of ca. -90V, thus forming a potential well which confined the particles. These can be seen as the small group of seven bright dots in the middle of the photograph in figure 18.

![Photograph showing trapped microspheres](image)

It proved relatively straight forward to handle the particles in the plasma potential well and to control their position and strike them with the laser beam. We have not so far been successful
in detecting a cavity enhanced Raman signal from particles in the plasma. However, these experiments are at an early stage and are continuing.

5. Conclusions / Outlook

The results obtained so far are very encouraging. We have achieved excellent data for liquid droplets which matches that reported in the literature and from these results have built up expertise in understanding the conditions under which wgms can be observed. Furthermore it is clear that resonances from different molecular species can be separated from each other (resolved). Experiments on solid microspheres are more challenging but we have made significant steps forward. We have shown that it is possible to detect wgms from the surface of the particle only. With liquid droplets there was some ambiguity as to how far inside the droplet the signal originated. By showing that for solid microspheres the technique is surface sensitive further experiments aimed at detecting wgm spectra from particles levitated in plasmas would be well worthwhile.
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I certify that there were no subject inventions to declare during the performance of this grant.