Micro-Raman monitoring of photoevolution and hygroscopicity of single particles by using an environmental acoustic levitation cell

Y.A. Tobon, M. Moreau, S. Sobanska and J. Barbillat

Laboratoire de Spectrochimie Infrarouge et Raman, UMR CNRS 8516, Université de Lille 1 Sciences et Technologies, Bât. C5, 59655 Villeneuve d'Ascq Cedex, France
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Presenting author email: yeny.tobon-correa@univ-lille1.fr

In atmospheric chemistry, aerosols play an essential role mainly concerning the heterogeneous chemistry in the atmosphere (Andreae and Crutzen 1997). However, studying the aerosol properties remains a challenge and it's indispensable to try to understand the chemical processes which occur at the particle or at the surface scale. Laboratory experiments are the most common way to go towards to real processes under controlled conditions, and it's necessary to look for techniques or combination of techniques which permit to simulate the conditions occurring in the atmosphere.

Raman spectroscopy is a non-destructive technique that provides detailed molecular and structural information with a spatial resolution of about $1 \mu m^3$, and it is a valuable tool to follow real-time evolutions of volume or surface structures under controlled conditions. Micro-Raman spectroscopy, coupled to an environmental levitation cell, is especially useful for studying, at micrometric scale, the *in-situ* modifications of aerosol when exposed to reactive environments or humidity without the influence of a contacting surface (Krieger, et al. 2012). Moreover, photochemical transformation can be followed by irradiation of the particles.

In this presentation, we used an environmental acoustic levitation cell coupled to the micro-Raman spectroscopy to monitor the physical and chemical processes occurring in particles of atmospheric interest when exposed both, to humidity and UV-Vis light. Physical and chemical changes can be followed at the interface or deeper depending on the optical properties of the particle. Particles, as small as 20 µm, can be levitated and studied by micro-Raman spectroscopy. Hygroscopic property evolution of nitrate containing aerosols (NH_4NO_3) when irradiated with UV-Vis light was investigated by using this experimental set up.

Environmental levitation cell coupled to micro-Raman spectroscopy

An ultrasonic levitator (APOS BA 10, Tec5, Germany) was modified to be installed within a small dimension environmental levitation cell and was horizontally coupled to the Raman microscope as shown in figure 1. The cell consists of 4 optics accesses, and transparent quartz windows allowing the exposure to UV radiation. Two inlet/outlet valves are used for gas supplies to modify the environment inside the cell. The relative humidity and the temperature are measured within the cell by using an adapted sensor.

The spectrometer used for the coupling is a Horiba Scientific LabRam HR visible, equipped with a CW 633 nm laser and a Liquid Nitrogen-cooled CCD camera. We used the micro arrangement in backscattering mode.

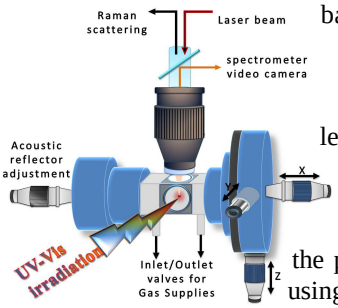

Figure 1. Schematic diagram of environmental levitation cell coupled to the Raman microscope

The size evolution of the particles was measured by using the spectrometer video camera and the growth factor was calculated by comparing geometric diameter evolution for various RH. The chemical evolution, i.e liquid versus solid and NO_3 to NO_2, was followed through Raman spectra acquired with time steps ranging between 2 and 10 s.

Hygroscopicity and photochemical transformation

Deliquescence and efflorescence processes of NH_4NO_3 were evidenced by the transformation of the Raman spectra. The shift on the NO_3 symmetric stretching vibration near to 1040 cm^{-1} is the most common change reported on the literature as an evidence of the transitions. However, our experiments showed that other structural changes occur before shifting of the 1040 cm^{-1}-band is produced. By using spectral data treatments the transformation rate was drawn.

The levitated aerosol particles were exposed to broad-band UV-visible radiation ($250 \leq \lambda \leq 800$ nm). The Raman spectrum was recorded for different times of irradiation to closely scrutinize any decay of the nitrate bands due to the photo-degradation of the aerosol and the growth of bands due to the nitrite photoproduct. The experiment was reproduced for various RH and compared. The influence of humidity on the nitrate photo-degradation was demonstrated for individual particles.

These experiments have permitted to validate the ensemble and the smooth running of the device, giving us access to study the reactivity and the physical chemistry processes occurring on the interfaces of single aerosol particles.

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