

Photochemistry of single particles using acoustic levitation coupled with Raman microspectrometry

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The photoreactivity of single particles with atmospheric interest was studied by using an acoustic levitation system coupled to Raman microspectrometry. Both, inorganic and organic single particle phototransformation has been investigated without any surface contact. The Raman microspectrometry has suitably provided the identification, the chemical heterogeneity as well as the formation rates of products. Complex surface limited processes are demonstrated for photolysis of both nitrate-rich and sulfur-rich droplets. Copyright © 2017 John Wiley & Sons, Ltd.

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Introduction

Manipulating micro-sized particles and determining their physicochemical properties in controlled environment have many interest in various areas of science and technology. So far, levitation-based setups, i.e. optical levitation,^[1,2] electrodynamic balance^[3,4] and ultrasonic trapping,^[5–8] have been shown to be suitable and powerful techniques for wall-less investigations. When coupled with micro-Raman scattering, the composition, size and phase partitioning of different chemical components within a liquid or solid droplet can be investigated, and then, many fundamental physical and chemical processes at the single particle scale with *in situ* conditions have been unravelled.^[9,10] Although photochemical processes are of prime importance in physical chemistry, the single particle studies were mainly dedicated to the photopolymerization of single optically levitated particles.^[11] Authors demonstrated the reaction in a single micrometer-sized monomer droplet initiated by UV radiation. To the best of our knowledge, there is no study dedicated to the photoreactivity of acoustically levitated particles with atmospheric relevance. This work demonstrates the feasibility of performing photochemical studies by using Raman spectroscopy on single ultrasonically levitated particles through *on line* and *in situ* characterization of the products and their distribution within the droplet.

Materials and methods

The experimental device consists in coupling an acoustic (ultrasonic) levitator equipped with an environmental cell to a Raman microspectrometer (RMS). The theory of acoustic levitation has been described in details.^[12,13] We have modified an ultrasonic levitator (APOS BA 10, Tec5, Germany) to be installed within an environmental levitation cell consisting of 4 quartz windows

allowing the exposure to UV–Vis light and the particle analysis. Two inlet/outlet valves are used for gas supplies to modify the environment inside the cell including the relative humidity (RH). A sensor (Sensirion, SHT75) was placed into the cell to control the RH and temperature values. The control of humidity and temperature allows for a limitation of droplet evaporation and for long-term monitoring of the particles. The levitation cell was designed and horizontally adapted to the Raman microscope as shown in Fig. S1 (Supporting Information). Raman microspectrometer measurements were performed with a LabRAM confocal spectrometer (Horiba Scientific, S.A). The instrument was equipped with a $\times 50$, 0.45 numerical aperture Olympus objective (WD = 13.8 mm) and a He–Ne laser ($\lambda = 632.8$ nm – 6 mW) given a theoretical lateral resolution ~ 2 μ m and a depth of the laser focus corresponding to 16 μ m with a Δz limit $\geq \pm 3$ μ m (see details in Supporting Information). The cell is mounted on a XYZ stage under the objective allowing adjustment of the droplet in the optimal position for measurement. Additionally, the droplet may be probed in various XYZ points for assessing the distribution of species. A high-speed high-resolution video camera CMOS monochrome (Basler Ace NIR, 2048 \times 2048 pixels) was also adapted to the Raman

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microscope allowing the visualization of morphological changes of the particle with a resolution time of millisecond.

Results and discussion

A first experiment was conducted on levitated sodium nitrate (NaNO_3) containing particles. The photolysis of aqueous nitrate ions has been the subject of detailed investigations and constitutes a source of nitrite (NO_2^-) ions and radicals in the environment.^[14–17]

Microdroplets of a solution of NaNO_3 salt (3 mol l^{-1}), with sizes ranging between 40 and 100 μm and $\text{pH} = 6$, were trapped into the acoustic cavity (20°C , 80%RH). After trapping and Raman analysis of the single levitated particle, the droplet was exposed to UV light from a Hg-Xe arc lamp (Hamamatsu, LC8 Lightningcure, 200 W) limited by a dichroic filter ($\lambda = 250 \pm 6 \text{ nm}$). The diameter of the UV spot from the lamp is larger than the droplet size resulting in the entire irradiation of the droplet. Irradiation of NO_3^- droplet produced NO_2^- and ONOO^- ions which were observed in the Raman spectrum at 815, 1278 and 1330 cm^{-1} for aqueous NO_2^- ^[17] and 980 cm^{-1} for ONOO^- ^[18] as shown in Fig. 1(a). The fundamental Raman bands of NO_3^- were observed at 719, 1051 and 1413 cm^{-1} which are in agreement with the reported values.^[19] It is well known that in bulk solution the photon absorption by NO_3^- at $\lambda < 280 \text{ nm}$ triggers two reactions leading to NO_2^- and ONOO^- ion formation, i.e. $\text{NO}_3^- + h\nu \rightarrow \text{NO}_2^- + \text{O}^-$ ^[20,21] and

$\text{NO}_3^- + h\nu \rightarrow \text{ONOO}^-$. At the particle scale, the NO_3^- photolysis likely proceeds to similar photoprocesses because ONOO^- and NO_2^- were observed as the stable final products.

The nitrite and peroxyxynitrite photoproducts exhibited different behaviour in time (Fig. 1(b)), i.e. NO_2^- remained stable after 75 min of irradiation when the production of ONOO^- markedly increased after 20 min of irradiation. The mechanism of peroxyxynitrite decomposition and its reactions with reactive nitrogen and oxygen species are complex and produce NO_2^- and/or NO_3^- as stable products depending mainly on the pH as detailed elsewhere.^[22] The variation of pH likely occurs in the droplet together with the chemical composition during the irradiation time and explains the complex curve observed for ONOO^- rate (Fig. 1(b)). To explain the detailed mechanisms of ONOO^- photoconversion in a single droplet, further experiments including flash photolysis experiments are required.

At fixed %RH, the particle diameter was reduced by 10% (i.e. <30% in volume), and the particle colour changes (see Fig. S2 of the Supporting Information). These observations confirm the chemical composition modification within the droplet together with a mass loss of the droplet which can be explained by the formation of gaseous product during the photoreaction.^[16,21] Interestingly, by varying the laser beam focus from the droplet surface into the core, the composition of the droplet seems to evolve. Indeed, a plot of Raman intensity versus depth (with a $\Delta z \sim 100 \mu\text{m}$) presented in Fig. S3 (of the Supporting Information) indicates more NO_2^- and ONOO^- on the particle surface than on the core compared to NO_3^- which could be explained by the formation of photoproduct on the particle surface. However, according to the axial resolution, the surface concentration cannot be clearly demonstrated here. Moreover, although the radial oscillation is reduced in our system, the particle agitation may result in particle stirring and homogenization of photoproducts on the aqueous particle. After 2 h of irradiation, no further evolution either in chemical composition or in the optical aspect of the particle has been observed. The process is likely a self-inhibited surface process which would also explain the limited ion formation observed on kinetic curve (Fig. 1(b)).^[22] These results occurring at single particle scale are complementary to the photolysis results obtained from experiments achieved on bulk aqueous nitrate ions solutions.

A second experiment was performed using pure methyl thioglycolate (MTG) as photosensitive organic compound. Microdroplets ranging from 40 to 80 μm and composed of $\text{MTG-CH}_3\text{OC(O)CH}_2\text{SH}$ (Alfa Aesar) were trapped into the cavity (20°C , 40–50%RH). Raman spectra of the levitated droplets, collected immediately after injection, displayed mainly the Raman bands characteristic of liquid MTG.^[23] After 16 h of levitation in ambient air, a complete oxidation of MTG to their disulphide derivative [$\text{CH}_3\text{OC(O)CH}_2\text{S}_2$], dimethyl dithiodiglycolate (DTG), was evidenced before irradiation by the appearance of a band around 510 cm^{-1} , assigned to the S–S stretching mode of the disulphide compounds, accompanied by the disappearance of the band near to 2568 cm^{-1} , belonging to the S–H stretching mode of MTG. The full Raman spectra of MTG and DTG are shown in Fig. S4, and the main Raman bands are listed in Table S1 of the Supporting Information. The drop was subsequently exposed to a monochromatic radiation of 325 nm from a CW He–Cd laser (Kimmon – Koha). The power measured at the sample was 0.1 mW. The particle composition was probed perpendicularly to the UV-irradiation beam by RMS. The transformation of the Raman spectra was observed upon irradiation (Fig. 2(a)), with appearance of new bands attributed to sulphate (SO_4^{2-}) centred at 618 and 976 cm^{-1} ,^[24] in complement

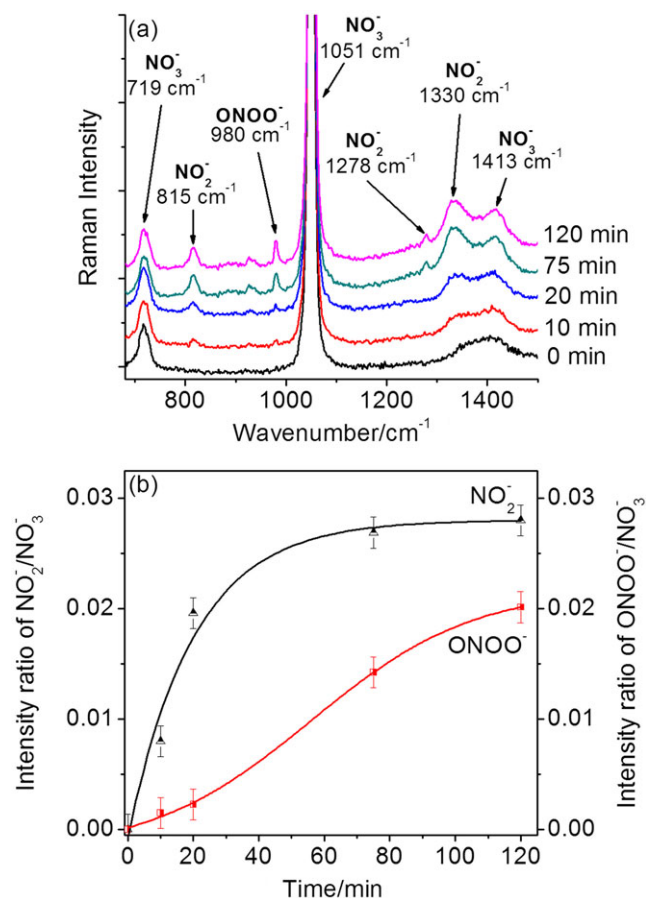


Figure 1. (a) Raman spectra of NaNO_3 for various irradiation times with UV-Vis light ($244 \leq \lambda \leq 256 \text{ nm}$) (spectra recorded on the particle surface). (b) Intensity ratio of $\text{NO}_2^-/\text{NO}_3^-$ and $\text{ONOO}^-/\text{NO}_3^-$ as a function of the irradiation time. [Colour figure can be viewed at wileyonlinelibrary.com]

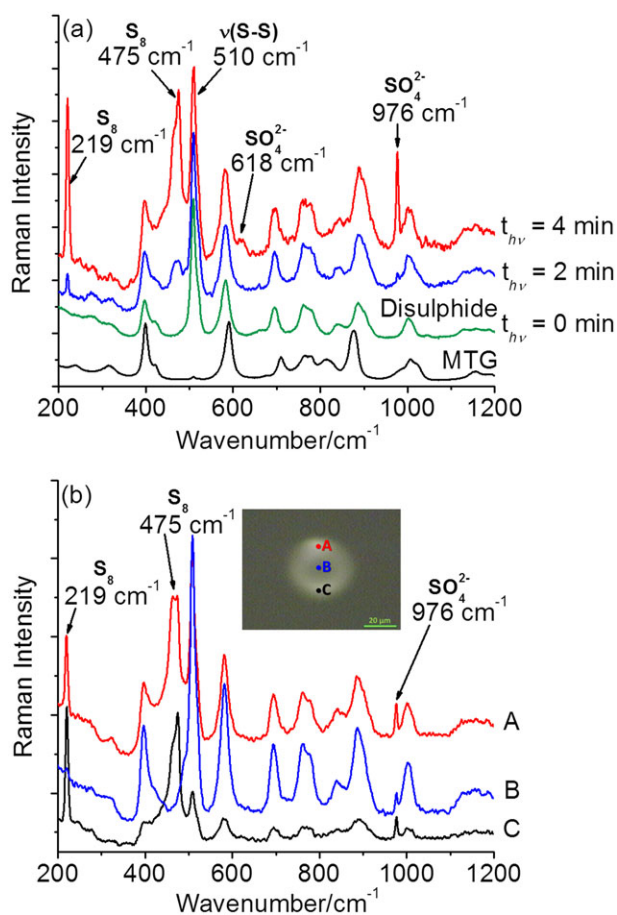


Figure 2. Raman spectra of a droplet initially containing pure MTG (a) immediately after injection, after 16 h of levitation in contact with air, and after 2 and 4 min of irradiation with 325-nm monochromatic light. (b) Heterogeneous distribution of the products onto the irradiated droplet. [Colour figure can be viewed at wileyonlinelibrary.com]

to the bands attributed to elemental sulphur (α -S₈) at 219, 463 and 475 cm⁻¹.^[25] The UV-Vis absorption spectra of both MTG and DTG show intense bands for $\lambda < 260$ nm and $\lambda < 300$ nm, respectively (see Fig. S5 of the Supporting Information) confirming the photosensitivity of both species. The mechanisms of the photochemical degradation of MTG and DTG are not known yet and will be detailed elsewhere. Sulphate and sulphur were observed for the first time as final photoproducts of MTG and DTG degradation and displayed some heterogeneous distribution on the particle surface as depicted in Fig. 2(b). Because of using objective instead of lens as it is commonly used for system using acoustic levitator coupled with Raman,^[11] our experimental device allows for probing the single particle in various XYZ points. Indeed, the photoproducts are observed along the laser beam way (point A and C), whereas initial species, i.e. DTG, still remains on the particle area which is moderately affected by the UV-laser irradiation (point B). Obviously, the UV beam promotes the sulphate and sulphur formation within the droplet. The different viscosity and miscibility of MTG, DTG and final photoproducts may explain the heterogeneous distribution of species within the particle. The product formation depends on the irradiation power which is observed through the variation of the Raman spectra intensity of the photoproducts between A and C Raman spectra. Then, a surface phototransformation is expected by using a UV lamp; the α -S₈ can be observed at the particle surface by varying the z focus.

Conclusions

We have shown that photoreactivity of single particles, without the influence of a contacting surface, can be studied by using an acoustic levitation system coupled to Raman microspectrometry for application in atmospheric chemistry. The developed experimental device allowed monitoring the laser beam in XYZ positions; thus, surface *versus* bulk as well as distribution of the products can be assessed. Photochemistry of several systems (organic, inorganic and mixed samples) in condensed phase can be levitated and monitored by Raman microspectrometry providing a reliable configuration to study the photoevolution in systems with micrometric accuracy that are complementary to bulk experiments.

Acknowledgments

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Supporting information

Additional Supporting Information may be found online in the supporting information tab for this article.