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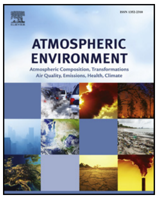

Deliquescence behavior of photo-irradiated single $NaNO_3$ droplets

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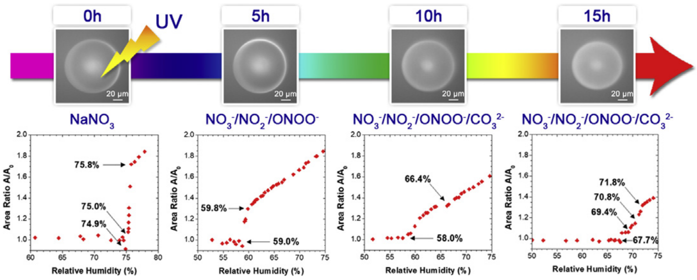
GRAPHICAL ABSTRACT



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ABSTRACT

Nitrate-containing particles are ubiquitous in the troposphere because of their secondary production due to anthropogenic emissions of NO_x from the combustion of fossil fuels. Nitrate ions are recognized as photoactive species that may contribute to the formation of oxidants in the atmosphere through heterogeneous photochemical reactions. The chemical transformation of aerosol particles in the atmosphere often leads to modification of the particles' hygroscopic properties. Although the photo-transformation of nitrate ions into nitrite within aerosol particles has been investigated, the influence of the photoproducts formation on the hygroscopic behavior of particles has not been reported. In this study, we examined the hygroscopic properties of single, ultraviolet-irradiated $NaNO_3$ droplets using Raman microspectrometry. We are the first demonstrated that irradiating $NaNO_3$ particles affects their hygroscopic behavior. For short-term exposures, regarding hygroscopic behavior, the irradiated particles exhibited two-stage transitions that were clearly reproduced in the experimental $NaNO_3$-$NaNO_2$ phase diagram. The production of NO_2^- decreased the deliquescence relative humidity values. For long irradiation times (> 5 h), these values are even more affected by the additional production of peroxynitrite and carbonate ions in individual droplets. The $NaNO_3$-$NaNO_2$ deliquescence phase diagram cannot explain the hygroscopic behavior of long-term irradiated particles. Finally, we demonstrated the influence that CO_2 has on the photo-transformation process in $NaNO_3$ droplets.

1. Introduction

In the atmosphere, the interaction between water vapor and aerosol particles has a crucial influence on many relevant atmospheric processes, such as (i) particle aerodynamic properties and then their wet and dry depositions, (ii) cloud-droplet nucleation efficiency; (iii) optical properties of aerosols, which contribute to the direct and indirect radiative forcing in climate change; (iv) chemical reactivity of

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particles and (v) oxidative capability of the atmosphere (Seinfeld and Pandis, 2006; Andreae and Rosenfeld, 2008; Boucher et al., 2013; Ramanathan et al., 2001; Kaufman et al., 2001). The water uptake by aerosol particles mainly depends on their chemical composition, which is generally a complex mixture of numerous inorganic salts and organic materials. The hygroscopic properties of aerosols have been extensively studied (Shaw and Rood, 1990; Tang and Munkelwitz, 1993; Wise et al., 2009). In addition, theoretical models with thermodynamic considerations have been used to predict the hygroscopic behavior of single- and multiple-component aerosol particles. It is well-established that the hygroscopic properties are drastically different for each type of particle because they depend on the particles' composition (Gupta et al., 2015; Li et al., 2014; Potukuchi and Wexler, 1995a, 1995b; Wexler and Seinfeld, 1991). The chemical composition of aerosols is source-dependent, but aging processes in the atmosphere can significantly modify this chemical composition. The aging of aerosols in the atmosphere involves complex and heterogeneous physical and chemical processes that are induced by interactions between particles and/or gaseous phase, as well as by solar radiation. Some chemical compounds present within atmospheric aerosols absorb light, which may lead to direct photolysis and transformation of the particles properties. Nitrate ions (NO_3^-) are recognized as photoactive species in the aqueous phase, and these ions contribute to the formation of free OH radicals in the atmosphere. The photochemistry of nitrate ions has been extensively investigated because NO_3^- is one of the most common groundwater pollutants; there are concerns about photolytic nitrite (NO_2^-) production (Mark et al., 1996). The absorption spectrum of NO_3^- is dominated by a weak $n \rightarrow \pi^*$ band around 302 nm ($\varepsilon = 7.2\,M^{-1}\,cm^{-1}$) and a much stronger $\pi \rightarrow \pi^*$ band at 200 nm ($\varepsilon = 9900\,M^{-1}\,cm^{-1}$) (Goldstein and Rabani, 2007; Mack and Bolton, 1999). It is well-known that the overall stable products of the photolysis of aqueous NO_3^- at $\lambda > 280$ nm are nitrite (NO_2^-) and peroxynitrite ($ONOO^-$) ions; these are produced through complex photo-processes (Mack and Bolton, 1999). Nitrate ions are also ubiquitous in atmospheric particles, especially in urban areas, as nitrate-rich particles are derived from anthropogenic NO_x emissions (Vaida, 2005; George et al., 2014, 2015). Consequently, comprehensive photochemistry of nitrate ions in solution can be extended to aerosols' atmospheric photochemistry (George et al., 2015). Actually, the photo-transformation of nitrate ions into nitrite within aerosol particles has been recently reported (Gankanda and Grassian, 2014; Benedict et al., 2017). The formation of photoproducts and/or intermediates in aerosol particles could induce microphysical changes in particles' properties, including their hygroscopic properties. Studying the processes of single aerosols leads to a better understanding of the physicochemical mechanisms that intervene in the atmosphere (Ault et al., 2013; Laskin et al., 2016; Steimer et al., 2015). The results obtained from levitated-particle and deposited-single-particle experiments strongly support the need for single-particle investigations, especially to measure particles' hygroscopic properties (Cotterell et al., 2014; Krieger et al., 2012). The particles' size changes, chemical heterogeneity and microphysical states can be unambiguously identified with a high degree of spatial resolution (both lateral and axial), which is a crucial requirement for aerosol research.

In this work, changes in the hygroscopic behavior of single nitrate-containing droplets upon UV-irradiation have been investigated both in air and on hydrophobic substrate. In both cases, the chemical compositions of particles were probed using Raman microspectrometry (RMS). To fully understand the deliquescence behavior of UV-irradiated particles, we have complementary described the hygroscopic behavior of $NaNO_3$-$NaNO_2$ binary aerosol particles; this behavior cannot be predicted using the currently available thermodynamic simulation software (e.g. E-AIM). We also discuss photochemistry's potential impact on atmospheric particles' hygroscopic properties.

2. Experimental

2.1. – *Single-particle reactors coupled with Raman microspectroscopy*

Two experimental setups were used for investigating the hygroscopic behavior of single particles consisting of small reactor chambers for single-particle investigation coupled with a Raman microspectrometer. First, we employed an acoustic levitator to study coarse particles in contactless conditions. Second, we deposited the particles on a hydrophobic substrate for use in the experiments.

This levitation experimental setup was previously described in Tobon et al. (2017) and is shown in Fig. S1 in the supporting information. It consists of a modified ultrasonic levitator (APOS BA 10, Tec5, Germany) within a small, homemade environmental cell that had been adapted for use on the microscope of a Raman microspectrometer. The environmental acoustic levitation cell was equipped with two valves for the input or output of dry or humid N_2 to vary and stabilize the cell's relative humidity (RH) between 10 and 90%, with an accuracy of ± 0.9%. The RH and temperature were measured with a sensor (Sensirion, SHT75) placed close to the levitated particle. The levitation cell contained three quartz windows to allow for in situ irradiation of the levitated particle. Aerosol droplets were introduced into the chamber using a nebulizer (OMRON MicroAIR U22) that generated droplets of ~5 μm in size. Larger microdroplets formed through coalescence in the levitation cell. The experimental device allowed for the microdroplets to be trapped and stabilized within the acoustic levitation cell using 2D-projected diameters ranging from 30 to 120 μm; the microdroplets remained there for a few days without any changes in size or composition.

Because the environmental cell dimensions were adapted to the Raman microspectrometer, the chemical compositions of the levitated particles were probed using RMS with in situ conditions. Measurements were performed with a LabRam visible spectrometer (Horiba Scientific) equipped with a CW 633 nm laser, a 1800 $gr{\cdot}mm^{-1}$ grating and a Synapse 1024 × 256 charge-coupled device (CCD) detector, coupled with an Olympus BX40 microscope using a Nikon 50 × (N.A. = 0.45; WD = 13.8 mm) objective. A high-resolution video camera (Basler Ace NIR, 2048 × 2048 pixels) adapted to the optical microscope measured the changes in the trapped particles' physical appearance (size and shape) with a millisecond time resolution.

The hygroscopic behavior of photo-irradiated $NaNO_3$ particles with size ranging from 10 to 30 μm was investigated on a hydrophobic substrate. The particles were generated by an ultrasonic nebulizer (Omron, NE-U07) and deposited on a glass slide treated with dichlorodimethylsilane to obtain hydrophobic surface. A focused laser beam from a DPSS laser (671 nm, Shanghai Dream Lasers, SDL-671-300T) through an objective lens (× 100, N.A. = 1.30) was used as excitation light source for Raman spectroscopy. The same objective lens collected the Raman scattering light from the single droplets. After passing through a long-pass edge filter (Semrock, LP02-671RU-25) to remove the Rayleigh scattering, Raman scattering light was focused onto the entrance slit of a polychromator (SOLAR TII, MS3504i, 1200 $gr.mm^{-1}$) and analyzed by a cooled electron-multiplying CCD (EMCCD) detector (ANDOR, Newton DU970N-BV). The RH in the chamber was controlled with a flow system described in a previous work (Ishizaka et al., 2014) and measured using a humidity probe (A1-SDI-9130.52, Lufft). Bright-field images under the microscope were observed by using a CCD camera (TOSHIBA TELI, CS9301-03).

2.2. *Preparation of mixed $NaNO_3$-$NaNO_2$ particles and UV irradiation of pure $NaNO_3$ droplets*

First, the binary $NaNO_3$-$NaNO_2$ diagram was established by measuring the deliquescence properties of single particles composed of a mixture of both pure species. Commercial sodium nitrate ($NaNO_3$) and sodium nitrite ($NaNO_2$) powders (Alfa Aesar, 99.999% purity) and

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