

Reactivity of organic sulfur compounds deposited on the surface of sea salts: Influence of humidity and UV-Vis light

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In the atmosphere, gaseous sulfur compounds are highly reactive and play a key role in the formation of acid rain and the production of secondary atmospheric aerosols (Andreae 1986, Brandt & van Eldik 1995). They can have an industrial origin (ie biogas, wastewater treatment, etc) linked to the natural or biological activities (acid production amino sulfolipides, some vitamins and sulfate esters by phytoplankton, zooplankton etc.). Oxy acids such as sulfuric, sulfurous, sulfonic, dithionic, hydroxyl-sulfonic, thiosulfuric, polythionic and pyrosulfurous and their salts, as well as sulfides (MetalS, H₂S, R-SH, R-S-R) and polysulfides (CS₂) are the most recognized sulfur compounds that exist or are expected to exist in aerosol particles under atmospheric conditions. Detailed studies on the sulfur species other than sulfates are not common. Recent studies have demonstrated that sulfates are not the only form of aerosol sulfur species and that significant contribution of additional sulfur needs further investigation (Shakya & Peltier, 2013). Photo-reactivity of sulfur compounds in the atmosphere is complex and has been widely studied in the gaseous phase (Sze & Ko, 1980, Qiao *et al.* 2011). However little is known about their photo-reactivity when they interact with sea salts particles.

In this study, laboratory experiments were conducted to simulate heterogeneous reaction at the surface of sea salt particle (NaCl) coated with Methyl thioglycolate (MTG) and exposed to humidity and UV-Vis light. We have used MTG (CH₃OC(O)CH₂SH) as a model of low volatile sulfur compound of industrial or biological origin. Observation of processes occurring on NaCl surfaces was performed by μ -Raman spectroscopy, μ -FT-IR, Atomic Force Microscopy (AFM), and time-of-flight secondary ion mass spectrometry (ToF-SIMS). The combined use of these techniques is a powerful tool to determine the morphology and the distribution of molecular species, as well as the first layers (few nm) at the surface of particles (Scolaro *et al.* 2009, Gaspar *et al.* 2004).

MTG deposited on the NaCl (100) surface by evaporation formed micrometric size droplets (Fig.1) composed of the disulfide derivative of MTG, identified by both μ -Raman and μ -FTIR.

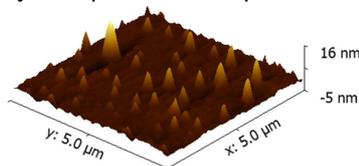


Figure 1. AFM image of NaCl(100) after coating with MTG.

After irradiation with UV-Vis light, formation of sulfate on the surface of NaCl was evidenced at the surface scale (Fig.2). Complementary, the formation of SO₄²⁻ was confirmed by ToF-SIMS measurement.

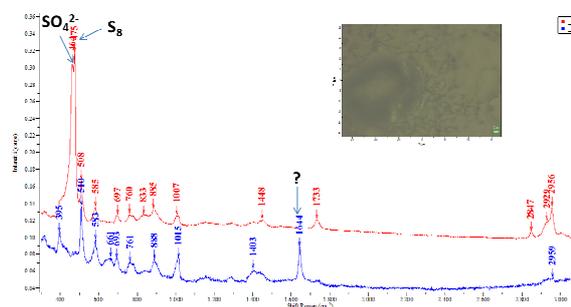


Figure 2. Typical Raman spectra obtained after irradiation of the disulfide derivative deposited on NaCl surface at RH ~50%.

The photochemical behavior of sulfur compounds on sea salt surface was investigated by complementary approaches. Experiments showed original and non-expected results with atmospheric interest. The formation of SO₄²⁻ through the photo-degradation of an organosulfur compound on NaCl surface is for the first time demonstrated. The combination of μ -Raman spectroscopy, μ -FT-IR, AFM and ToF-SIMS imaging has shown to be a powerful tool for studying the heterogeneous chemistry of the particle surfaces.

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