

2.164 Heterogeneous Photochemistry on Tropospheric Aerosols as an Alternative Pathway for HONO and NO_x formation.

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Abstract:

Nitric acid (HNO₃) and particulate nitrates have long been considered a sink for atmospheric NO_x. However, recent studies have shown that tropospheric aerosols provide a reactive surface for the uptake of atmospheric HNO₃, resulting in the renoxification of the atmosphere. Yet, little is known about the role of solar radiation in these atmospheric heterogeneous processes. Sunlight can excite photoactive components of atmospheric particulate matter, initiating indirect photochemical processes on nitrated particles. First, adsorbed nitric acid can undergo symmetry breaking, resulting in changes in its photochemical reactivity. Second, semiconductor components of atmospheric aerosols can induce photocatalytic decomposition of adsorbed HNO₃. Finally, chromophores within tropospheric aerosols can photosensitize nitrate particles and enhance its photodecomposition. In this work, we present the role of these three indirect heterogeneous photochemical pathways in the formation of HONO, N₂O and NO_x from chemisorbed nitric acid and nitrate particles. We present a combination of vibrational spectroscopy and quantum calculations for the study of nitrated tropospheric aerosols and gaseous products generated from its photodecomposition. First, insulator components of tropospheric aerosols, such as γ-Al₂O₃, are compared to semiconductor components (TiO₂, α-Fe₂O₃, ZnO) to contrast the heterogeneous photochemistry via symmetry breaking to that of a photocatalytic process. Photocatalysis of HNO₃ on TiO₂ was found to have the highest photochemical rate constant at $(7.6 \pm 0.6) \times 10^{-5} \text{ s}^{-1}$, almost doubling the second fastest rate constant observed, the photodecomposition of HNO₃ on γ-Al₂O₃. All heterogeneous photoreactions produced HONO, N₂O and NO_x. The effect on relative humidity on the HNO₃ photocatalysis was examined spectroscopically and computationally, with water participating in the photocatalytic reaction of HNO₃. Finally, we also present nitrate photodegradation by humic acids (HA), a proxy for humic substance in sea spray aerosol (SSA). We find that humic substances within SSA photosensitize nitrate particles and NO₂, opening an additional pathway for daytime HONO formation.