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

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Abstract:

Nitric acid (HNO$_3$) 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 HNO$_3$, 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 HNO$_3$. Finally, chromophores within tropospheric aerosols can photosensitize nitrated particles and enhance its photodecomposition. In this work, we present the role of these three indirect heterogeneous photochemical pathways in the formation of HONO, N$_2$O 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-Al$_2$O$_3$, are compared to semiconductor components (TiO$_2$, α-Fe$_2$O$_3$, ZnO) to contrast the heterogeneous photochemistry via symmetry breaking to that of a photocatalytic process. Photocatalysis of HNO$_3$ on TiO$_2$ was found to have the highest photochemical rate constant at $(7.6\pm0.6)\times10^{-5}$ s$^{-1}$, almost doubling the second fastest rate constant observed, the photodecomposition of HNO$_3$ on γ-Al$_2$O$_3$. All heterogeneous photoreactions produced HONO, N$_2$O and NO$_x$. The effect on relative humidity on the HNO$_3$ photocatalysis was examined spectroscopically and computationally, with water participating in the photocatalytic reaction of HNO$_3$. 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 NO$_2$, opening an additional pathway for daytime HONO formation.