

Computational Calculations of the Effects of Surface Water on the Photocatalysis of HNO₃ on TiO₂

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Atmospheric aerosols are known to provide an active surface for the adsorption of tropospheric gases, upon which the molecules undergo symmetry-breaking that change their electronic and vibrational transitions. These changes have significant implications in the optical and chemical properties of atmospheric aerosols and the formation of products during photocatalysis. In this study we show how nitrate symmetry changes as a consequence of its adsorption onto TiO₂, impacting the photocatalytic degradation of surface nitrate. The addition of co-adsorbed water in this reaction, a simulation of atmospheric relative humidity (RH), further affects the coordination symmetry and reactivity of the nitrates adsorbed onto a surface. Several coordination structures of nitrate ions adsorbed onto TiO₂ were modeled in the presence of co-adsorbed water. The structures were minimized on a binuclear cluster using Becke's three-parameter hybrid method with the LYP correlation functional (B3LYP) and a basis set of 6-31+G(d). Our optimizations of chemisorbed nitrates under dry conditions yielded five distinctive structures in which nitrate shifts from D_{3h} symmetry in favor of C_{2v} symmetry. With the addition of co-adsorbed water, the symmetry-breaking effect is reduced as the nitrates become solvated and undergo the caging effect of water, resembling aqueous phase nitrate. Vibrational frequency calculations were correlated to experimental data by fitting the minimized nitrate geometries to deconvoluted experimental vibrational spectra of nitric acid chemisorbed onto TiO₂ under dry and humidified conditions. We have found that simulations with 3 to 5 coadsorbed water molecules per surface nitrate yield good correlation with nitrated surfaces humidified up to 20% RH. In addition, our calculations confirm that water competes for TiO₂ active sites, limiting the nitrate coordination modes to only one structure when coadsorbed with 5 water molecules. Consequently, the photocatalytic rate constant decreases from $(4.6 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$ on a dry surface to $(7.8 \pm 0.2) \times 10^{-4} \text{ s}^{-1}$ when nitrate is coadsorbed with 20% RH. This sixth-fold decrease in the kinetic constant is mostly due to water competition for active TiO₂ sites, although it is inferred that the photocatalytic rate also drops as a consequence of the symmetric shift of adsorbed nitrate towards a more aqueous phase.