

Quantum Mechanical Calculations of Nitric Acid Chemisorbed on the Crystalline Structure of TiO₂.

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The surface of atmospheric aerosols is known to adsorb tropospheric gases, leading to various coordination modes between surface and substrate. Among the components of these tropospheric aerosols, semiconductor metal oxides, such as titanium dioxide, are commonly found. These semiconductor components can trigger photo-induced heterogeneous reactions on surface bound species with important environmental implications. For example, the optical properties of chemisorbed nitrates change with coordination symmetry, impacting the ion's photochemical fate and climate effects. Yet, experimental vibrational spectroscopy studies of nitric acid adsorbed onto TiO₂ are difficult to interpret because of the convoluted spectrum resulting from multiple adsorption coordinations of nitrates on titanium oxide.

In this work, several coordination structures of nitrate on TiO₂ were modeled. Vibrational frequency calculations correlated the minimized nitrate geometries with a deconvoluted experimental infrared spectrum of nitric acid chemisorbed onto TiO₂. The electronic structure minimizations and vibrational frequencies were performed 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 yield four distinct structures in which nitrate lose its D_{3h} symmetry. By adding co-adsorbed water to simulate the deliquescent layer of an aerosol particle, the frequencies of chemisorbed nitrate suggest that the substrate consist on partially solvated nitrate ions.