Trapping intermediates of the NO_2 hydrolysis reaction on ice

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The hydrolysis of NO_2 at the air/ice interface plays an important role in regulating the oxidative capacity of the atmosphere[1]. Indeed, the reaction yields nitric acid and nitrous acid, compounds that acidify precipitations, but also create photochemical sources of NO_x and OH radicals. In the gas phase, NO_2 is at equilibrium with its dimers, N_2O_4, which can exist in the form of constitutional isomers and stereoisomers, but whose abundance and reactivity towards hydrolysis continue to be debated[2]. Computational chemistry results reported in the literature state that the isomer *trans*-$ONONO_2$ is a key intermediate species in the hydrolysis reaction mechanism, but experimental evidence to confirm this hypothesis is still lacking. These uncertainties regarding the reaction mechanism hamper heterogeneous NO_2 hydrolysis to be accurately accounted for in atmospheric chemistry models[3].

Using Electric Field Standing Waves (EFSW) to enhance the sensitivity and selectivity of Reflection-Absorption IR Spectroscopy (RAIRS)[4], along with molecular beam deposition techniques, it is shown that the relative abundance of the nitrogen oxides in the gas phase can be controlled experimentally, enabling the control over the distribution of *cis*-$ONONO_2$ and *trans*-$ONONO_2$ metastable isomers of N_2O_4 in NO_2 vapors[5]. The study of the reactivity of each species towards heterogeneous hydrolysis on ice can thus be done independently allowing invaluable molecular-level insight into the reaction mechanism using vibrational spectroscopy.

A detailed account of the molecular-level interactions of nitrogen oxides with water molecules was elaborated using computational chemistry investigations of mixed $(NO_2)_n•(H_2O)_m$ clusters ($n = 1,2$; $m = 0\text{-}8$), allowing the experimental identification of the reaction intermediates at the ice surface. In addition to understanding how the structural changes and shifts in the vibrational frequencies inform and reflect on the relative reactivity of the different reaction intermediates, the molecular modeling results obtained indicate that the isomers *trans*-$ONONO_2$ and *cis*-$ONONO_2$ tend to self-ionize towards $ON^+ONO_2^-$, a trend that is confirmed experimentally. These insights in the molecular-level understanding of the hydrolysis reaction mechanism will hopefully improve its inclusion thereby improving future atmospheric chemistry models.

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