

Institutsseminar

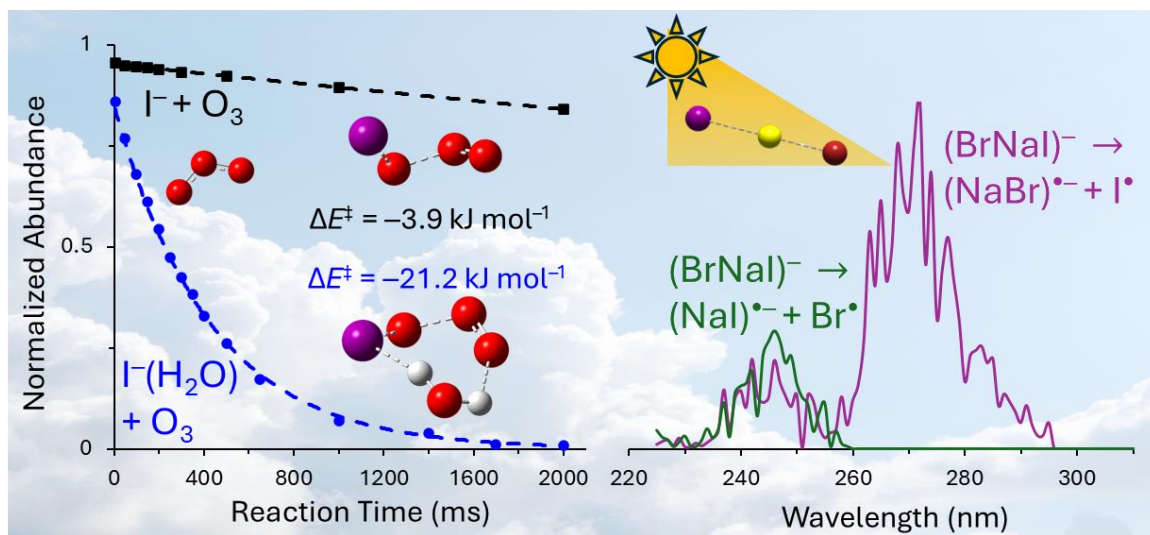
Reactions of Iodide in Atmospheric Clusters with Ozone and Ultraviolet Radiation

Samuel C. Brydon

Queensland University of Technology – Australia

Iodine emissions have tripled since the mid-20th century with a significant influence on the oxidizing capacity of the atmosphere and human health, yet the underpinning atmospheric chemistry has been relatively unexplored compared to chlorine and bromine. Recent detection of iodide and higher oxides as both ambient ions at high altitudes and as a significant fraction of total iodine in both tropospheric and stratospheric particles has prompted more detailed modelling with indications iodine may contribute around 70% of halogen-induced destruction of ozone. Whilst studies have focused on this chemistry in bulk solution or microscale droplets, there have been limited investigations into reactions of iodide-containing clusters with ozone to understand microscopic effects of hydration or salinity. Similarly, little is known about the photostability of these clusters and potential production of free radicals, particularly in the UV region of the solar spectrum relevant to the polar regions and stratosphere. Here, the fate of iodide coordinated to water or alkali halide salts upon exposure to ozone or UV light is examined using mass spectrometry to investigate potential roles of these species in ozone destruction.

Monohydrated iodide was generated by electrospray ionization (ESI) of *m*-iodobenzoic acid to give the corresponding benzoate, which upon collision-induced dissociation yielded $I(H_2O)^-$ (m/z 145) by reaction with background water in a modified linear ion-trap mass spectrometer. Isolation of this ion in the presence of ozone showed a 27-fold acceleration in the initial oxidation to hypoiodite (IO^- , m/z 143) relative to the bare iodide anion, supported by a lower transition state barrier from *ab initio* calculations and kinetic modelling. For the salt clusters, solutions containing either sodium or potassium iodide in combination with other halide salts were infused by ESI to generate the iodide-containing clusters. The presence of a sodium halide salt also accelerated the rate of reaction of $I(NaX)^-$ clusters with ozone to a similar extent as a water ligand, whilst potassium salts reacted slightly faster. Photodissociation of these alkali halide salt clusters over 225-300 nm showed relatively facile loss of iodine radicals around 275 nm with a red shift for potassium compared to sodium clusters, representing important photochemical pathways for halogen radical generation. Together these data highlight the need to explore the reactivity of these clusters with atmospheric gases and various wavelengths of light as nanoscale particles may have an outsized role in the oxidizing capacity of the troposphere and destruction of the ozone layer in the stratosphere.



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