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Oxidation of NaBr aerosol by ozone and solvation of alkyl bromides at the air/water interface: Modeling heterogeneous atmospheric processes by molecular dynamics simulations

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The release of Br atoms from photolyzable bromine species is responsible for the almost complete destruction of ground-level ozone observed in the Arctic after polar sunrise. A concerted approach combining aerosol chamber experiments, computer kinetics modeling, and molecular dynamics simulations was used to investigate the mechanism of the reactions of O3 with NaBr aerosol. Experimental results are not reproduced well by the known gas phase and aqueous phase bromine chemistry alone. With the inclusion of a reaction at the air-water interface between gaseous ozone and aqueous bromide ion to produce Br_2, the model satisfactorily reproduces experimental results. Molecular dynamics simulations provide further support for the proposed surface reaction mechanism. They show that ozone strongly prefers to reside at the interface rather than in the bulk solution, and that O3 comes frequently into contact with bromide ion on the surface.

Alkyl bromides play an important role in atmospheric chemistry as a source of bromine. To obtain molecular level insight into the aqueous solvation of alkyl bromides at the air/water interface, we studied a series of alkyl bromides (C_nH_(2n+1)Br, n = 1 – 4) in a liquid water slab using classical molecular dynamics simulations. While methyl bromide (CH_3Br) is atmospherically the most relevant species to study, its higher homologues, because of their lower volatility, are likely to be better candidates for experimental investigation using techniques sensitive to interfaces. Our molecular dynamics simulations contribute to interpretation of such

experiments.