Rate enhancement in collisions of sulfuric acid molecules due to long-range intermolecular forces

Roope Halonen\textsuperscript{1}, Evgeni Zapadinsky\textsuperscript{1}, Theo Kurtén\textsuperscript{2}, Hanna Vehkamäki\textsuperscript{1}, and Bernhard Reischl\textsuperscript{1}

\textsuperscript{1}Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, P.O. Box 64, 00014, Helsinki, Finland
\textsuperscript{2}Institute for Atmospheric and Earth System Research/Chemistry, Faculty of Science, University of Helsinki, P.O. Box 55, 00014, Helsinki, Finland

Collisions of molecules and clusters play a key role in determining the rate of atmospheric new particle formation and growth. Traditionally the statistics of these collisions are taken from kinetic gas theory assuming spherical noninteracting particles, which may significantly underestimate the collision coefficients for most atmospherically relevant molecules. Such systematic errors in predicted new particle formation rates will also affect large-scale climate models. We studied the statistics of collisions of sulfuric acid molecules in a vacuum using atomistic molecular dynamics simulations. We found that the effective collision cross section of the H$_2$SO$_4$ molecule, as described by an optimized potentials for liquid simulation (OPLS) all-atom force field, is significantly larger than the hard-sphere diameter assigned to the molecule based on the liquid density of sulfuric acid. As a consequence, the actual collision coefficient is enhanced by a factor of 2.2 at 300 K compared with kinetic gas theory. This enhancement factor obtained from atomistic simulation is consistent with the discrepancy observed between experimental formation rates of clusters containing sulfuric acid and calculated formation rates using hard-sphere kinetics. We find reasonable agreement with an enhancement factor calculated from the Langevin model of capture, based on the attractive part of the atomistic intermolecular potential of mean force.