HCl Scattering on Ice Surfaces: Modeling Heterogeneous Chemistry in the Stratosphere

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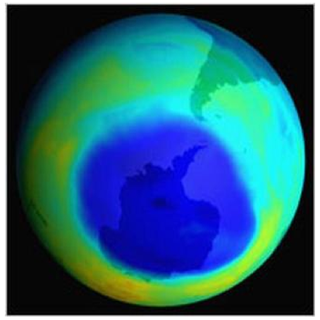
Introduction

Reactive uptake of atmospheric trace gases such as HCl and HNO_3 are directly related to ozone depletion in the stratosphere. Absorption and dissociation of gaseous molecules change the chemical composition and morphology of ice surfaces, which leads to changes in catalytic activity. Understanding the mechanisms of acid uptake on ice surfaces is important due to its relevance as elementary steps of active Chlorine generation in the stratosphere.

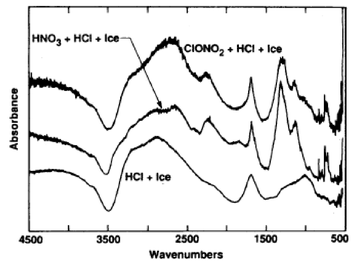


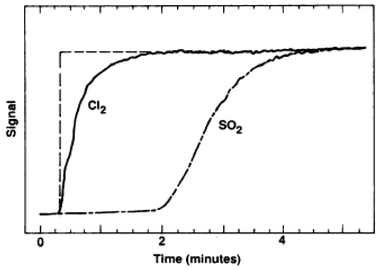
Computer simulations to model reactive collisions of HCl on ice surfaces were performed using adaptive QM/MM method implemented in AMBER molecular dynamics package. The results were used to understand mechanisms of HCl dissociation on the ice surface and the thermodynamics of the ice surface induced by the acid uptake.

Previous Studies

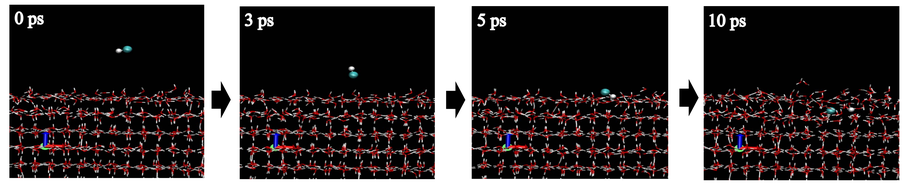
Many studies have been conducted on the reactive uptake of HCl on ice surfaces. Molina and co-workers[1]. performed a laboratory study to model heterogeneous reactions on ice surfaces which generated gaseous Cl_2 molecules. Their experimental results showed that HCl absorption on the surface is an important elementary step in active Chlorine formation. HCl absorption and diffusion on ice surfaces were rapid and thermodynamically favored in a temperature range relevant to stratospheric conditions.

A theoretical study on HCl dissociation in water clusters was conducted by Bolton and Pettersson[2] using standard QM/MM simulations. They found that HCl ionization in water cluster is barrierless process.

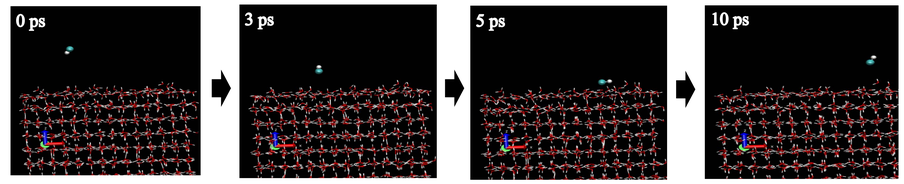




Reactive Trajectory



Non Reactive Trajectory



Molecular Dynamics Simulations

A + BC → Random sampling of initial conditions

$$\mathbf{q}^0_{A,B,C};\mathbf{p}^0_{A,B,C}$$

Numerical integration of

$$-\frac{\partial V}{\partial q_i} = m_i \frac{d^2 q_i}{dt^2}$$

or

$$\frac{\partial H_n}{\partial p_i} = \frac{dq_i}{dt};\quad -\frac{\partial H_n}{\partial q_i} = \frac{dp_i}{dt}$$

$V(\mathbf{q})$ and $\partial V/\partial q_i$ are obtained from QM, MM, or QM/MM methods at each numerical integration step

$$\mathbf{q}_{A,B,C};\mathbf{p}_{A,B,C}$$

→ Energy, structures, etc

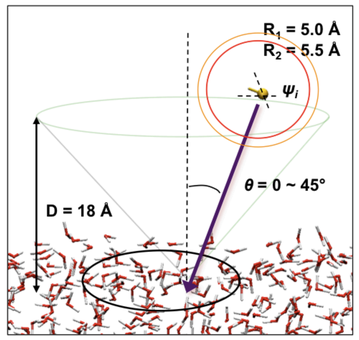
Simulation Conditions

AdQM/MM

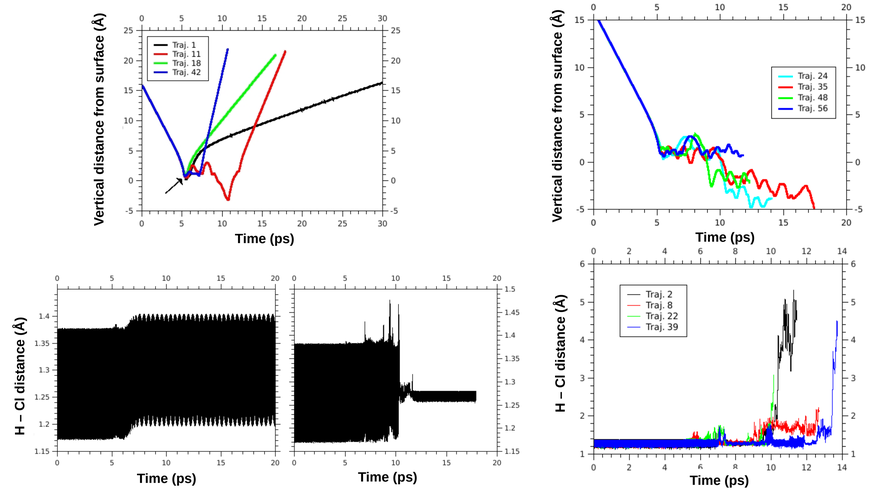
- Fixed distance based adQM/MM method[4]
- QM: PM3-MAIS[5] semiempirical Hamiltonian
- MM: aSPC/Fw/iced[6] model

Trajectory initial condition

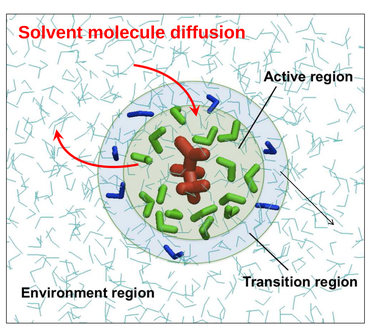
- Initial distance from the surface : 18 Å
- Projectile incident angle : 0°, 45°
- Vibration & rotation quantum number (*n*,*J*):
  (0,0), (0,3), (0,5)
- Surface temperature : 100, 190 and 250 K
- Impact site on the surface and orientation (ψ_i) of molecules were sampled randomly



HCl reactive scattering : representative examples



Adaptive QM/MM[3,4]



Contrary to standard QM/MM approaches, the adaptive QM/MM method enables an accurate description of reactive processes in systems where molecular diffusion is important. This is achieved by allowing the solvent molecules to diffuse in and out of the QM region through the definition of multiple QM/MM partitions.

Absorption and Dissociation of HCl on Ice Surface

Simulation condition	190 K, n=0, J=5, 45° incident angle
Total # of trajectories	188
Fraction of trajectories HCl absorbed on ice surface	0.82
Average residual time on surface (scattered trajectories)	2.96 ps
Fraction of traj. In which HCl dissociated on ice surface (in ~15 ps)	0.46
Average lifetime of molecular HCl on ice surface (dissociative trajectories)	4.81 ps
Average lifetime of Cl^- H_3O^+ contact ion pair (for the trajectories that showed contact ion pair dissociation)	4.24 ps
Fraction of trajectories for H exchange reaction (for both absorbed & scattered trajectories)	0.45

References

1. M. Molina, T. Tso, L. Molina, F. Wang, "Antarctic Stratospheric Chemistry of Chlorine Nitrate, Hydrogen Chloride, and Ice: Release of Active Chlorine", *Science* **238**, 1253 (1987).
2. K. Bolton, J. Pettersson, "Ice-Catalyzed Ionization of Hydrochloric Acid", *J. Am. Chem. Soc*. **123**, 7360 (2001).
3. K.Park, A. Gotz, R. Walker, F. Paesani, "Applicaton of Adaptive QM/MM Methods to Molecular Dynamics Simulations of Aqueous Systems", *JCTC*, in press.
4. R.E. Bulo, B. Ensing, J. Sikkema, L. Visscher, "Toward a Practical Method for Adaptive QM/MM Simulations", *J. Chem. Theory Comput*. **5**, 2212 (2009).
5. O.I. Arillo-Flores, M.F. Ruiz-Lopez, M.I. Bernal-Uruchurtu, "Can Semi-Empirical models describe HCl dissociation in water?", *Thoer. Chem. Acc.*,**118**, 425 (2007)
6. K. Park, W. Lin, F. Paesani, in preparation.

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