Introduction

Reactive uptake of atmospheric trace gases such as HCl and HNO₃ 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 performed a laboratory study to model heterogeneous reactions on ice surfaces which generated gaseous Cl₂ 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 using standard QM/MM simulations. They found that HCl initiation in water cluster is a barrierless process.

Adaptive QM/MM

• Fixed distance based adQM/MM method
• QM: PM3-MAIS semiempirical Hamiltonian
• MM: sPC/Fc/ice/F model

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

Absorption and Dissociation of HCl on Ice Surface

<table>
<thead>
<tr>
<th>Simulation condition</th>
<th>190 K, m=0, J=5, 45° incident angle</th>
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</thead>
<tbody>
<tr>
<td>Total # of trajectories</td>
<td>188</td>
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<tr>
<td>Fraction of trajectories HCl absorbed on ice surface</td>
<td>0.82</td>
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<tr>
<td>Average residual time on surface (scattered trajectories)</td>
<td>2.96 ps</td>
</tr>
<tr>
<td>Fraction of trajectories HCl dissociated on ice surface (n=15 Å)</td>
<td>0.46</td>
</tr>
<tr>
<td>Average lifetime of molecular HCl on ice surface (dissociative trajectories)</td>
<td>4.61 ps</td>
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<tr>
<td>Average lifetime of Cl⁻ H₃O⁺ contact ion pair (for the trajectories that showed contact on pair dissociation)</td>
<td>4.24 ps</td>
</tr>
<tr>
<td>Fraction of trajectories for H exchange reaction (for both absorbed &amp; scattered trajectories)</td>
<td>0.44</td>
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</tbody>
</table>

Simulation Conditions

AdQM/MM

HCI reactive scattering: representative examples

References


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