Reactive Molecular Dynamics Simulations for Vibrationally Induced Sulfuric Acid (H$_2$SO$_4$) Dissociation

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Introduction

Anomalous concentrations of small condensation nuclei (CN) have been observed at the top of aerosol layer in polar spring and in midlatitude air of polar origin. While nucleation of previously evaporated sulfuric acid and water might be expected as temperatures decrease in polar winter, the CN layer is only observed upon the return of sunlight in spring. Such delayed timing suggested a photochemical trigger.

Two mechanism are possible: i) UV photolysis and ii) photolysis by visible and near IR light [1]. On the other hand, there is not experimental confirmation that H$_2$SO$_4$ has any significant absorption in UV. Here we use Adiabatic Reactive Molecular Dynamics (ARMD) [2] to simulate photolysis of H$_2$SO$_4$ by visible and near IR light in gas phase.

Methods:

- **Force Field Parametrization:**
  - Geometry
  - Dihedral Angles
  - Reaction path

Calculated Potential Energy Surface for hydrolysis of H$_2$SO$_4$ in the space defined by distances O6-H7 and S1-O4 at the MP2/6-311G**(2d,2p) level. Color lines represent different reactive trajectories for v$_9$ = 5; i) white 10 trajectories with $\tau$ approx 5 ps; green 10 trajectories with $\tau$ approx 250 ps and red 10 trajectories with $\tau$ approx 600 ps.

Results

- Normalized distribution of dissociation times p(\tau) from ARMD simulations with excitation of v$_9$ = 4 (panel A), v$_9$ = 5 (panel B) and v$_9$ = 6 (panel C). Distributions in all excitation, fits in a gamma-distribution form (green). Note the different $\tau$-axes in the three panels.

Average dissociation times are 753, 201 and 40 ps for v$_9$ = 4, v$_9$ = 5 and v$_9$ = 6 respectively.

Conclusion:

Extensive ARMD simulations with tailored force fields lead to argue that in gas phase vibrational excitation of v$_9$ > 4 leads to photodissociation H$_2$SO$_4$ into SO$_3$ + H$_2$O. Typical reaction times for v$_9$ = 4 to v$_9$ = 6 are on the picosecond time scale or faster. Mechanistically anything between impulsive H-transfer to almost complete IVR with subsequent dissociation are found.

References:


Founding:

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