

## Does H<sub>4</sub>SO<sub>5</sub> exist?

Murillo F.

Vargas-Caamal A.

Pan S.

Cabellos J.L.

Mora-Fonz M.J.

Muñoz-Castro A.

Restrepo A.

Merino G.

The possible existence of H<sub>4</sub>SO<sub>5</sub> in aqueous sulfuric acid is analyzed in detail. For bare H<sub>4</sub>SO<sub>5</sub>, the computed free energy barrier for the exergonic transformation of H<sub>4</sub>SO<sub>5</sub> into the H<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O complex is only 3.8 kcal mol<sup>-1</sup>. The presence of water or sulfuric acid catalyzes the dehydration to such an extent that it becomes almost a barrierless process. In the gas phase, dehydration of H<sub>4</sub>SO<sub>5</sub> is an autocatalytic reaction as the water molecule produced by the decomposition of one H<sub>4</sub>SO<sub>5</sub> molecule induces further dissociation. Thus, in solution, the surrounding water molecules make the para-sulfuric acid a very vulnerable species to exist. The simulated Raman spectra also corroborate the absence of H<sub>4</sub>SO<sub>5</sub> in solution. © 2017 the Owner Societies.