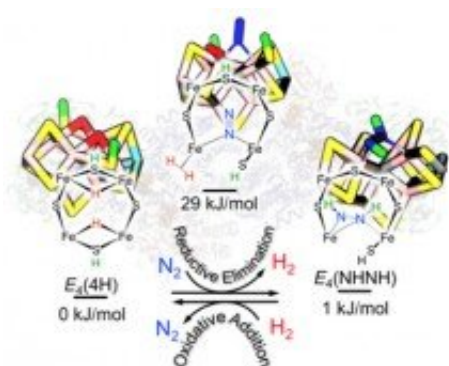


# Illuminating how nitrogenase makes ammonia

January 7 2019



Water molecules bound closest to the mineral have a rigid, ice-like structure and cannot move into arrangements that enable chemical reactions. Water molecules farther from the mineral surface have a less constrained, liquid-like structure and can organize to promote reactivity. Credit: Environmental Molecular Sciences Laboratory

A team of researchers led by PNNL computational scientist Simone Raugei have revealed new insights about how this complex enzyme does its job, finding that the seemingly wasteful formation of hydrogen has an essential purpose. Their paper, "Critical computational analysis illuminates the reductive-elimination mechanism that activates nitrogenase for  $N_2$  reduction," was published in the *Proceedings of the National Academy of Sciences* in November 2018. Raugei's co-authors are Lance Seefeldt, who holds a joint appointment at PNNL and Utah State University, and Brian Hoffman of Northwestern University.

Nitrogenase can convert nitrogen to [ammonia](#) at room temperature and atmospheric pressure. Industry, on the other hand, relies on the Haber-Bosch process, a century-old technique using high temperature and pressure. Fossil fuels typically provide the energy for this process, which is why industrial [ammonia production](#) alone accounts for more than 1% of the world's total energy-related carbon emissions. Understanding what lends nitrogenase its bond-breaking muscle can lead to new, stimulating ideas for the design of synthetic catalysts to make ammonia.

For every molecule of nitrogen transformed to ammonia, nitrogenase makes at least one molecule of hydrogen ( $H_2$ ), which is "one of the most puzzling mysteries of nitrogenase," Raugei said. "Instead of just producing ammonia, you also produce this byproduct. Why is that necessary?"

The researchers found that this phenomenon actually helps nitrogenase tackle nitrogen's strong bonds. "Nature found a solution by coupling the production of hydrogen, which releases energy, with cleaving nitrogen, which requires energy," Raugei said. "It's total balance."

To arrive at the results, the team used a blend of theoretical and experimental methods. Raugei conducted quantum chemical calculations on models of the core of the enzyme, relying on guidance from Seefeldt and Hoffman, who are experts on the biochemistry of nitrogenase. Their [experimental data](#) helped inform the computations, and vice versa.

The researchers focused on the nitrogenase catalytic core, composed of iron, molybdenum and sulfur (FeMo-co). During the catalytic event, when FeMo-co has acquired a critical number of electrons and protons ( $H^+$ ) in the form of two bridging hydrides (Fe-H-Fe) in its peripheral belt, generation of an  $H_2$  bound to FeMo-co and its displacement by  $N_2$  provides the give and take of energy to spark nitrogen reduction, the researchers found.

"We were very well positioned to make to this breakthrough because we combined experimental information on nitrogenase with the computational information," Raugei said. "That was key."

The researchers seek to extend the research by examining the fine details of electron- and proton-accumulation at the active site of [nitrogenase](#) and exactly how the N<sub>2</sub> bond is broken to form ammonia.

**More information:** Simone Raugei et al. Critical computational analysis illuminates the reductive-elimination mechanism that activates nitrogenase for N<sub>2</sub>reduction, *Proceedings of the National Academy of Sciences* (2018). [DOI: 10.1073/pnas.1810211115](https://doi.org/10.1073/pnas.1810211115)

Provided by Environmental Molecular Sciences Laboratory

Citation: Illuminating how nitrogenase makes ammonia (2019, January 7) retrieved 25 April 2024 from <https://phys.org/news/2019-01-illuminating-nitrogenase-ammonia.html>

<p>This document is subject to copyright. Apart from any fair dealing for the purpose of private study or research, no part may be reproduced without the written permission. The content is provided for information purposes only.</p>
--