In nitrogenase - enzyme critical for life, X-ray emission cracks mystery atom

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Like a shadowy character just hidden from view, a mystery atom in the middle of a complex enzyme called nitrogenase had long hindered scientists' ability to study the enzyme fully.

But now an international team of scientists led by Serena DeBeer, Cornell assistant professor of chemistry and chemical biology, has pulled back the curtain using powerful synchrotron spectroscopy and computational modeling to reveal carbon as the once-elusive atom.

The research was published online Nov. 17 in the journal *Science*.

"For chemists, one of the first steps you want to be able to take is to actually model the site," said DeBeer. "It turns out that the chemistry of how this cluster behaves will be different depending on what atom is in the middle. This is the first step toward trying to unravel its mechanism."

Why nitrogenase? In nature, all life requires the element nitrogen from the atmosphere to form amino acids and build proteins. Bacteria need to convert nitrogen to ammonia as a precursor to more complex biosynthetic processes. The enzyme that catalyzes all this is nitrogenase, and it does it by breaking one of the strongest bonds in chemistry – the nitrogen triple bond.

The chemical industry has figured out how to convert nitrogen to ammonia in high-temperature and high-pressure industrial environments. There's a fascination with understanding how the enzyme makes this

same process work in nature, DeBeer said.

DeBeer and colleagues honed in on a subset of atoms in the relatively large enzyme, called the iron-molybdenum cofactor, which was thought to be the site where dinitrogen (N_2) gets converted to ammonia, and where the mystery atom is situated inside.

The team used a method called X-ray emission spectroscopy (XES) at the Stanford Synchrotron Radiation Light Source to excite the electrons in the cofactor's iron cluster and to watch how electrons refilled the spots, called "holes," they left behind. The holes were sometimes filled by an electron belonging to a neighboring atom – emitting X-ray signatures with distinct ionization potentials that would distinguish between different kinds of atoms.

This was how it was revealed that the cofactor contained a carbon atom, rather than a nitrogen or an oxygen atom, that was bound to the iron atoms in the cluster.

More information: X-ray Emission Spectroscopy Evidences a Central Carbon in the Nitrogenase Iron-Molybdenum Cofactor, Science 18 November 2011: Vol. 334 no. 6058 pp. 974-977 DOI: 10.1126/science.1206445 www.sciencemag.org/content/334/6058/974

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