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New technique overturns assumption on light-generated nitric oxide molecules

BUFFALO, N.Y. -- A new technique developed by University at Buffalo chemists that combines X-ray diffraction with laser excitation has fundamentally altered a widely held assumption dating back 25 years about what happens to certain types of molecules that play a basic role in body chemistry when they are pumped with laser light.

The technique is allowing the UB researchers to determine the structures of normally unstable chemical species and providing new information on how certain nitrous-oxide compounds, which have a wide range of biological functions, bind to proteins.

Called photocrystallography, the technique consists of using a laser to pump, or excite, a molecular crystal while the X-ray diffractometer probes its structure.

"Chemistry often is called the science of molecular change," said Philip Coppens, Ph.D., SUNY Distinguished Professor in the Department of Chemistry in the UB College of Arts and Sciences and principal investigator. "This technique allows us to probe deeply into that science at the atomic level."

The researchers are extending the technique to molecules that exist for just millionths or even billionths of a second -- while one molecule is binding to another -- using very intense light sources at the National Synchrotron Light Source at Brookhaven National Laboratory and the Advanced Photon Source at Argonne National Laboratory.

The technique has overturned the assumption, widely held for the past quarter-century, that the new chemical states of nitrosyl compounds (compounds where nitric oxide is bound to a metal atom) generated by illumination with laser light were electronically excited states; that is, they involved one or more of the electrons in the atoms gaining energy while the molecule remained essentially the same.

The UB work has found that the light-generated molecules are not electronically excited states, but linkage isomers -- meaning they have different atomic arrangements. "In short, for a very brief time, they become different molecules," said Coppens. Using photocrystallography, Coppens and his graduate students have found that very small, common molecules bind to transition metal atoms, such as iron and nickel, in previously unknown ways when the compounds are irradiated with laser light.

"That is significant, as such simple molecules play a crucial role in body chemistry, in vasodilation, inhibition of platelet aggregation and in nerve transmission," he said. In the blood, for example, nitric oxide binds to iron atoms, which are the transition metal atoms in hemoglobin, Coppens explained.

"It is nitric oxide in the blood that regulates blood pressure by activating an enzyme that, in

turn, catalyzes a reaction, causing blood vessels to constrict or relax," he said.

Coppens is collaborating with George B. **Richter-Addo**, a professor in the Department of Chemistry and Biochemistry at the University of Oklahoma, and Kimberly Bagley, professor of chemistry at Buffalo State College, on using photocrystallography to investigate light-induced processes in nitrous-oxide model compounds for proteins, such as NO hemoglobin.

He noted that the technique also is relevant to studying light-induced processes in nitrophorins, a family of proteins that occurs in the salivary glands of Cimex lectularius and Rhodnius prolixus, blood-sucking bugs found in Latin America. Bites from these bugs, which are painful, but not fatal, cause these proteins to transport NO to the blood of victims, resulting in vasodilation and reduced blood coagulation.

The work is relevant for a detailed understanding -- at the atomic level -- of a wide range of processes, including photosynthesis, which occurs in bacteria and plants. These light-induced changes may have potential for the design of very-high-energy storage devices since the change induced by laser light in a crystal can be highly localized and may be reversed by illumination with a different type of light, Coppens said.

Coppens will discuss the technique at several upcoming conferences, including the British Crystallographic Association on April 8, a Gordon Research Conference in Mt. Holyoke, Mass., on July 8 and the International Conference on the Organic Solid State in Mainz, Germany, in early August.

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