Press Release

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- Paper Title: Mapping the emergence of molecular vibrations mediating bond formation

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Every moment of ultrafast chemical bonding now captured on film

The emerging moment of bond formation, two separate bonding steps, and subsequent vibrational motions were visualized.

Targeted cancer drugs work by striking a tight bond between cancer cell and specific molecular targets that are involved in the growth and spread of cancer. Detailed images of such chemical bonding sites or pathways can provide key information necessary for maximizing the efficacy of oncogene treatments. However, atomic movements in a molecule

have never been captured in the middle of the action, not even for an extremely simple molecule such as a triatomic molecule, made of only three atoms.

A research team led by IHEE Hyotcherl of the Institute for Basic Science (IBS, South Korea) (Professor, Department of Chemistry, KAIST), in collaboration with scientists at the Institute of Materials Structure Science of KEK (KEK IMSS, Japan), RIKEN (Japan) and Pohang Accelerator Laboratory (PAL, South Korea), reported the direct observation of the birthing moment of chemical bonds by tracking real-time atomic positions in the molecule. “We finally succeeded in capturing the ongoing reaction process of the chemical bond formation in the gold trimer. The femtosecond-resolution images revealed that such molecular events took place in two separate stages, not simultaneously as previously assumed,” says Associate Director IHEE Hyotcherl, the corresponding author of the study. “The atoms in the gold trimer complex atoms remain in motion even after the chemical bonding is complete. The distance between the atoms increased and decreased periodically, exhibiting the molecular vibration. These visualized molecular vibrations allowed us to name the characteristic motion of each observed vibrational mode.” adds Ihee.

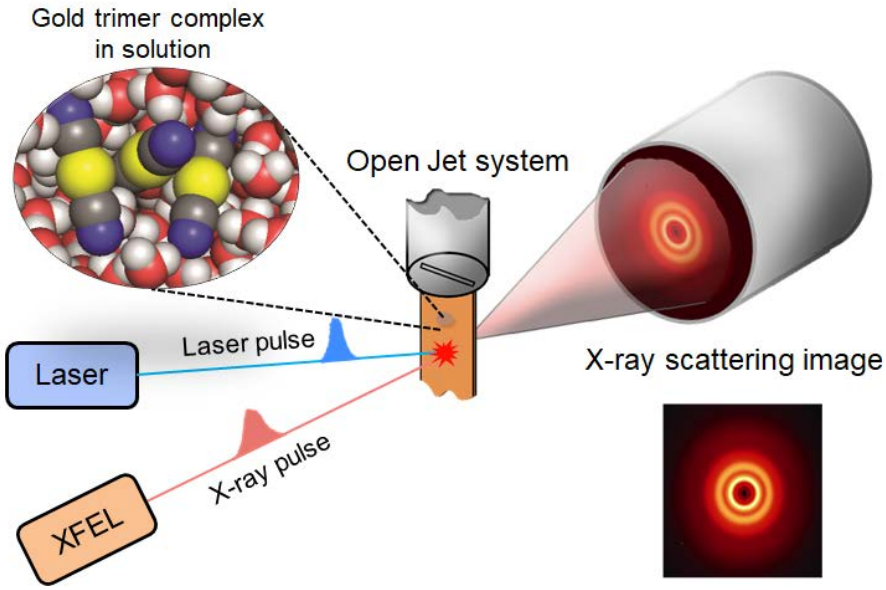


Figure 1. A schematic of the femtosecond x-ray scattering technique. The bond formation reaction in a gold trimer complex is initiated by a laser pulse, and a three-dimensional structure after a certain time delay is detected by an x-ray scattering image. (Credit: IBS)

Atoms move extremely fast at a scale of femtosecond (fs) — quadrillionths (or millionths of a billionth) of a second. Its movement is minute in the level of angstrom equal to one ten-billionth of a meter. They are especially elusive during the transition state where reaction intermediates are transitioning from reactants to products in a flash. The research team made this experimentally challenging task possible by using femtosecond x-ray liquidography (solution scattering). This experimental technique combines laser photolysis and x-ray

scattering techniques. When a laser pulse strikes the sample, X-rays scatter and initiate the chemical bond formation reaction in the gold trimer complex. Femtosecond x-ray pulses obtained from a special light source called an x-ray free-electron laser (XFEL) were used to interrogate the bond-forming process. (Figure 1) The experiments were performed at two XFEL facilities (4th generation linear accelerator), PAL-XFEL in South Korea and SACLA in Japan, and this study was conducted in collaboration with researchers from KEK IMSS, Pohang Accelerator Laboratory (PAL), RIKEN, and the Japan Synchrotron Radiation Research Institute (JASRI).

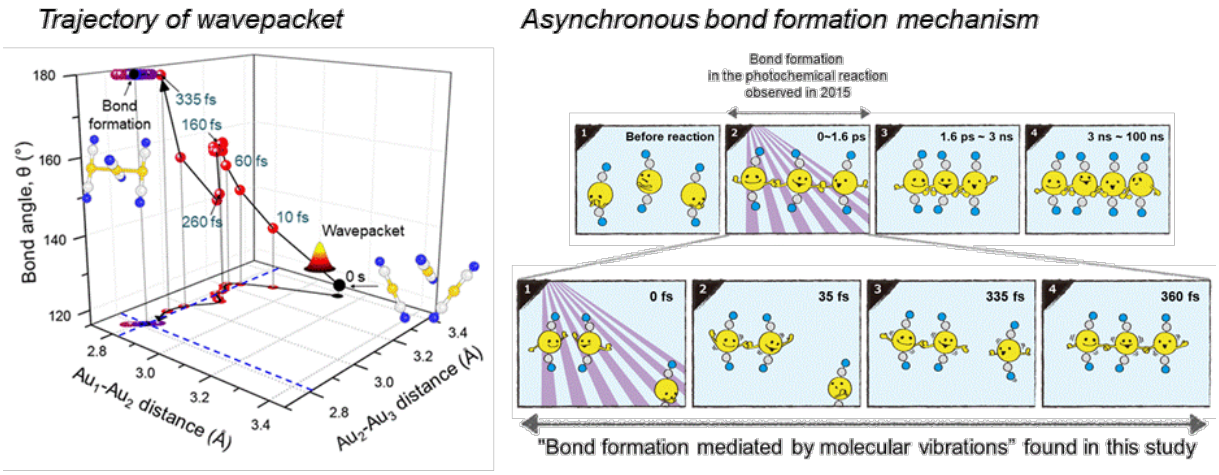
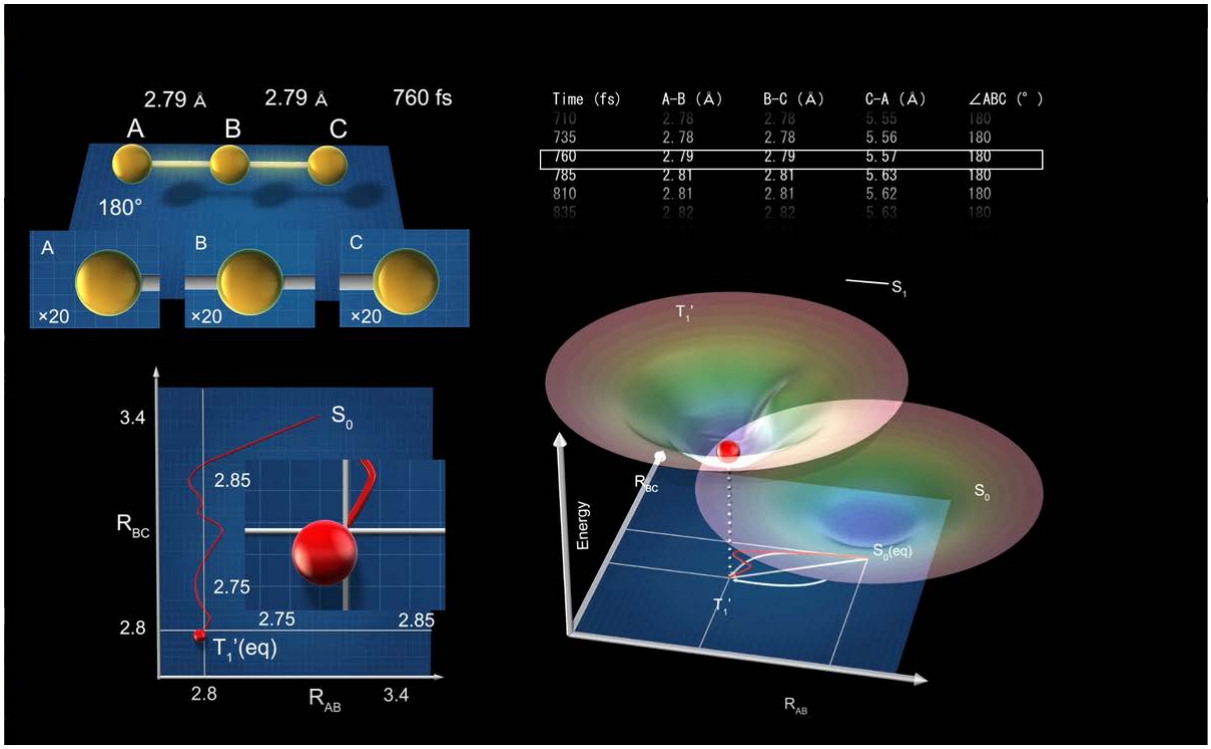


Figure 2. (left) Time-dependent positions of the wave packet in the multidimensional nuclear coordinates were obtained from the femtosecond x-ray scattering experiment on a gold trimer complex. (Credit: Nature & IBS)
(right) By inspecting the motion of the wave packet, it was revealed that the bond formation reaction in the gold trimer complex occurs through an asynchronous bond formation mechanism. (Yellow: gold atoms, gray: carbon atom, blue: nitrogen atom, 1000 times 1 fs is 1 picosecond (ps), 1000 times 1 ps is 1 nanosecond (ns)) (Credit: KEK IMSS)



Movie: Emergence of molecular vibrations and the evolution to covalent bonds observed in this research. (Credit: KEK IMSS)
（URL: https://youtu.be/e8-vdKTD8cY）

The movement of three gold atoms measured in this study is shown on the upper left. At 0 fs, the sample was excited by UV light. The table on the upper right shows the measured values of the molecular structure during the photochemical reaction. The horizontal and vertical axes of the 2D graph on the lower left are the distances between gold atoms A-B and B-C, respectively. In the 2D graph, the points represented by S0 and T1' correspond to the molecular structures before the photochemical reaction and after linear transformation during the reaction process, respectively. The molecular structure changed from S0 to T1' along the red line known as a "reaction path". The 3D graph shown in the lower right was made by adding an energy axis to the 2D graph. The curved surface drawn in the 3D graph is known as a "potential energy surface (PES)". The photochemical reaction is described by the movement of the corresponding position in the 3D graph, and the reaction path can be expected to connect the valleys of the PES. Before UV light excitation, the corresponding position is at the bottom of the PES of S0. When a molecule is excited by UV light, the energy of the molecule is increased, but the molecular structure is still maintained. Therefore, the corresponding position moves vertically in the 3D graph. Then, the molecule structure begins to change with a decrease of its energy, and the corresponding position slides down the PES of T1' along the valley. Finally, the molecular structure becomes linear, and the corresponding position reaches the bottom of the PES of T1'. Until now, to calculate the reaction path, the structural change during a chemical reaction has been discussed. However, in this research, we are able to determine the reaction path without relying on a calculation.

Scattered waves from each atom interfere with each other and thus their x-ray scattering images are characterized by specific travel directions. The IBS research team traced real-time positions of the three gold atoms over time by analyzing x-ray scattering images, which are

determined by a three-dimensional structure of a molecule. Structural changes in the molecule complex resulted in multiple characteristic scattering images over time. When a molecule is excited by a laser pulse, multiple vibrational quantum states are simultaneously excited. The superposition of several excited vibrational quantum states is called a wave packet. The researchers tracked the wave packet in three-dimensional nuclear coordinates and found that the first half round of chemical bonding was formed within 35 fs after photoexcitation. The second half of the reaction followed within 360 fs to complete the entire reaction dynamics. (Figure 2)

They also accurately illustrated molecular vibration motions in both temporal- and spatial-wise. This is quite a remarkable feat considering that such an ultrafast speed and a minute length of motion are quite challenging conditions for acquiring precise experimental data.

In this study, the IBS research team improved upon their 2015 study published by *Nature*. In the previous study in 2015, the speed of the x-ray camera (time resolution) was limited to 500 fs, and the molecular structure had already changed to be linear with two chemical bonds within 500 fs. (Figure 2, upper right) In this study, the progress of the bond formation and bent-to-linear structural transformation could be observed in real time, thanks to the improvement time resolution down to 100 fs. Thereby, the asynchronous bond formation mechanism in which two chemical bonds are formed in 35 fs and 360 fs, respectively, and the bent-to-linear transformation completed in 335 fs were visualized. (Figure 2, lower right) In short, in addition to observing the beginning and end of chemical reactions, they reported every moment of the intermediate, ongoing rearrangement of nuclear configurations with dramatically improved experimental and analytical methods.

They will push this method of 'real-time tracking of atomic positions in a molecule and molecular vibration using femtosecond x-ray scattering' to reveal the mechanisms of organic and inorganic catalytic reactions and reactions involving proteins in the human body. "By directly tracking the molecular vibrations and real-time positions of all atoms in a molecule in the middle of reaction, we will be able to uncover mechanisms of various unknown organic and inorganic catalytic reactions and biochemical reactions," notes Dr. KIM Jong Goo, the first author of the study.

Notes for editors

- References

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Choi, Joonghan Kim, Taiha Joo, Jeongho Kim, Shin-ichi Adachi, and Hyotcherl Ihee*. *Nature*. DOI: 10.1038/s41586-020-2417-3

- About the Institute for Basic Science (IBS)

IBS was founded in 2011 by the government of the Republic of Korea with the sole purpose of driving forward the development of basic science in South Korea. IBS has 30 research centers as of January 2020. There are ten physics, two mathematics, six chemistry, six life science, one Earth science, and five interdisciplinary research centers.
https://www.ibs.re.kr/eng.do

- About Korea Advanced Institute of Science and Technology (KAIST)

KAIST is the first and top science and technology university in Korea. KAIST was founded by the Korean government in 1971 as the nation's first research-oriented science and engineering institution.
https://www.kaist.ac.kr/en/

- About High Energy Accelerator Research Organization (KEK)

KEK was established to promote various types of researches as a center of excellence for overall development of Japan's accelerator science (particle and nuclear research using high energy accelerators, research on the structure/function of matter including living organisms, research on improving the accelerator performance, and related basic technologies). As the Inter-University Research Institute Corporation, KEK provides researchers across the country and abroad with opportunities for research. With the Tsukuba and Tokai campuses as centers for excellence, KEK joins international collaboration experiments and developments.
In addition, KEK is in charge of the School of High Energy Accelerator Science of the Graduate University for Advanced Studies (SOKENDAI).
https://www.kek.jp/en/

- About Pohang Accelerator Laboratory (PAL)

PAL is an affiliated research institute of Pohang university of science and technology, founded in 1988. PAL operates Pohang Light Source (PLS), a synchrotron radiation facility, and PAL-XFEL, an x-ray free-electron laser.
http://pal.postech.ac.kr/paleng/

- About RIKEN

RIKEN is Japan's largest comprehensive research institution renowned for high-quality research in a diverse range of scientific disciplines. Founded in 1917 as a private research foundation in Tokyo, RIKEN has grown rapidly in size and scope, today encompassing a network of world-class research centers and institutes across Japan.
https://www.riken.jp/en/

- About Japan Synchrotron Radiation Research Institute (JASRI)

JASRI is a public interest incorporated foundation in charge of the operation, maintenance, management, and provision of support for users of the SPring-8 synchrotron radiation

facility, as well as the provision of support for users of the X-ray free electron laser SACLA. JASRI is a highly professional, advanced, interdisciplinary, and international institute. (SPring-8/SACLA http://www.spring8.or.jp/en/, JASRI http://www.jasri.jp/en/index.html)