

Direct Observation of Gold-Gold Bond Formation in Solution

Bond making and bond breaking are essential processes in chemistry, but visualizing the track of atomic rearrangement is challenging and often requires a technique with high temporal and spatial resolutions. Visualizing the bond formation in the solution phase is especially elusive, because the synchronization of the meet-up of two reactants with ultrafast time resolution is mandatory. Here, we investigate the photo-induced formation of gold-gold (Au-Au) covalent bonds among weakly bound Au atoms in a gold trimer complex. Based on time-resolved X-ray scattering data, we visualize subtle structural changes of the metal complex in real time in the form of Au-Au interatomic distances in real space.

For several decades, ultrafast bond-breaking processes of many molecular systems have been studied intensively using various time-resolved techniques. In contrast, the dynamics of bond making, particularly in solution, have been rarely studied because bond making is a bimolecular process limited by slow diffusion through the solvent, making it difficult to initiate and follow the process with ultrafast time resolution.

In order to overcome the difficulty in capturing bond formation, a gold complex, $[\text{Au}(\text{CN})_2]_n$, plays as an ideal model system [1]. Au atoms in $[\text{Au}(\text{CN})_2]_n$ exhibit an interatomic interaction caused by the relativistic effect, which is often called as aurophilicity or aurophilic interactions [1]. Due to this unique interactions, Au atoms are weakly bound to each other, forming an aggregated complex $[\text{Au}(\text{CN})_2]_n$ even in the ground state. Upon photoexcitation of the complex, an electron is excited from antibonding to bonding orbital, resulting in formation of strong Au-Au covalent bonds. Since Au atoms belong to the same solvent cage in the ground state of

the $[\text{Au}(\text{CN})_2]_n$ complex, the formation of Au-Au covalent bonds occurs without being limited by slow diffusion through the solvent.

Recently, ultrafast Au-Au bond formation in a gold trimer complex, $[\text{Au}(\text{CN})_2]_3$, was investigated using transient absorption (TA) spectroscopy [2], and the transient changes of absorption were observed on the time scales of 500 fs, 2 ps and 2 ns. The first two time constants, 500 fs and 2 ps, were ascribed to the changes of molecular structure leading to the formation of Au-Au covalent bonds, that is, (i) contraction of Au-Au bonds and (ii) conformational change from bent to linear structure, respectively. However, because the TA signal is not directly related to the molecular structure, those structural assignments were solely based on the assumption of theoretical TA spectra of model structures. In this work, we applied time-resolved X-ray solution scattering (TRXSS) (Fig.1) to directly elucidate the ultrafast structural dynamics of Au-Au bond formation in $[\text{Au}(\text{CN})_2]_3$ [3].

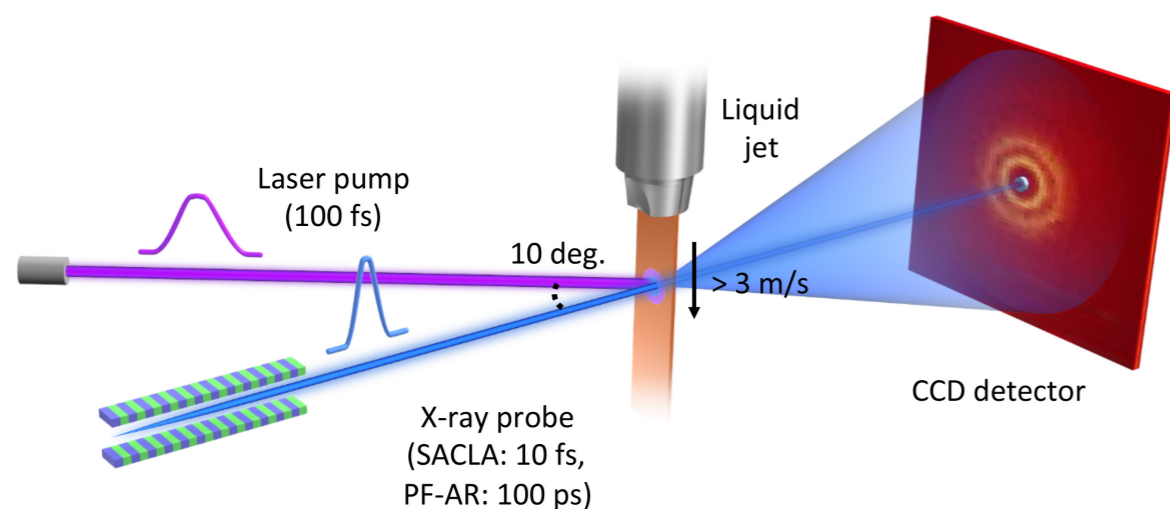


Figure 1: Schematic view of the experimental setup of time-resolved X-ray solution scattering (TRXSS). The sample solution is circulated and injected into the sample position by the liquid jet system to avoid sample damage caused by intense X-ray and optical laser pulses.

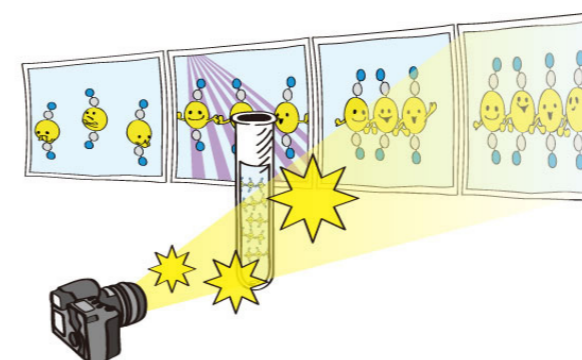


Figure 2: Schematic view of capturing the "molecular movie" of photochemical reaction dynamics by TRXSS

TRXSS is a powerful method for probing photoinduced structural changes of molecules in solution and has been used for revealing the dynamics and mechanism of many molecular reaction systems ranging from small molecules to biological macromolecules. The recent development of X-ray free electron lasers (XFELs), which generate ultrashort (~ 10 fs duration) X-ray pulses with $\sim 10^{12}$ photons per pulse made it possible to explore chemical processes occurring down to sub-ps time scale using TRXSS. By performing the TRXSS experiment at PF-AR (KEK) and SACLA (RIKEN) facilities complementarily, structural dynamics of bond formation of $[\text{Au}(\text{CN})_2]_3$ in solution was elucidated from femtosecond to nanosecond time domain (Fig.2) [3].

The initial photo-induced formation of Au-Au covalent bonds among weakly bound Au atoms in a gold trimer complex, $[\text{Au}(\text{CN})_2]_3$ was investigated by using femtosecond TRXSS at SACLA. Based on the TRXSS data, subtle structural changes of the metal complex were visualized in real time and real space. Upon photoexcitation, the trimer with an asymmetric bent structure and weakly bound Au atoms (3.3 Å and 3.9 Å Au-Au distances) in the ground (S_0) state rapidly converted into a symmetric and linear structure in the electronic excited (S_1) state where stronger Au-Au bonds (2.8 Å Au-Au distances) are formed (Fig. 3). Subsequently, the S_1 state transforms to the T_1 state with 1.6 ps time constant while accompanying further contraction of Au-Au bonds by 0.1 Å. Later, the T_1 state of the trimer converts to a tetramer on nanosecond time scale. Finally, the bond lengths and bond angles of the reactant (S_0 of the trimer), the transient species (S_1 and T_1 of the trimer) and the final product (the tetramer) was successfully determined with sub-angstrom spatial resolution.

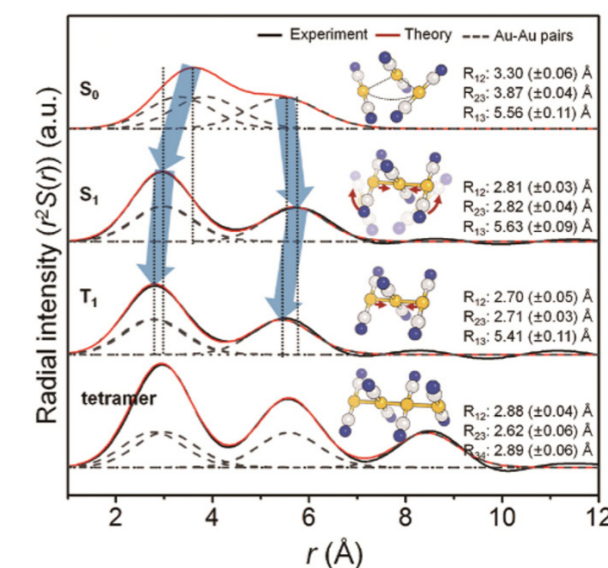


Figure 3: Time-dependent modulation of the radial distribution functions directly reflecting time-dependent change of molecular structure of gold complex. Yellow, white, and blue atoms represent gold, carbon, and nitrogen atoms, respectively.

The TRXSS method offers a means of visualizing the whole processes of photo-induced reactions in real time and real space, and will be used as a fundamental tool to study the reaction dynamics of chemical and biological systems, such as artificial and natural photosynthetic reactions.

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