CHAPTER 13

Visualizing Chemical Reactions in Solution with Femtosecond X-ray Scattering

SHIN-ICHI ADACHI*\textsuperscript{a,b} AND HYOTCHERL IHEE*\textsuperscript{c,d}

\textsuperscript{a}Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan; \textsuperscript{b}Department of Materials Structure Science, School of High Energy Accelerator Science, The Graduate University for Advanced Studies, 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan; \textsuperscript{c}Center for Nanomaterials and Chemical Reactions, Institute for Basic Science (IBS), Daejeon 305-701, Republic of Korea; \textsuperscript{d}Department of Chemistry, KAIST, Daejeon 305-701, Republic of Korea

*E-mail: shinichi.adachi@kek.jp, hyotcherl.ihee@kaist.ac.kr

13.1 Introduction

Long-lived electronic excited states of photoactive molecules govern the functional efficiencies involved in their functional transitions. In fact, the fate of the excited molecules is often determined by the early stages of their photoinduced reactions, involving bond breaking and bond making, and therefore understanding the mechanism of the initial reaction steps leading to the functional transitions is of supreme importance. For several decades, ultrafast bond-breaking processes of various molecular systems have been studied intensively using a variety of time-resolved techniques.\textsuperscript{1-5} Contrary to the case of the bond-breaking process, which is essentially a unimolecular
process and therefore can be initiated by laser photolysis in a synchronized manner, bond making is a bimolecular process that requires two reactant parties to meet each other in order to form a chemical bond. In such a case, its reaction rate is limited by slow diffusion of the reactants through the solvent, and thus the moment of the encounter of two parties cannot be synchronized with laser excitation. Therefore, it is difficult to initiate and follow the process with ultrafast time resolution.

In this respect, a gold oligomer complex, \([\text{Au(CN)}_2^-]_n\), can serve as a good model system.\(^5\)-\(^11\) Au(1) atoms in gold oligomer complexes have a closed-shell d\(^{10}\) electronic configuration with a low coordination number, thereby exhibiting a non-covalent interatomic interaction caused by the relativistic effect, which is termed aurophilicity.\(^9\)-\(^11\) Aurophilicity makes Au(1) atoms weakly bind to each other by van der Waals interactions, forming an aggregate complex, \([\text{Au(CN)}_2^-]_n\), without any covalent bond. In the viewpoint of the bimolecular reaction, the two reactant parties, i.e., the \([\text{Au(CN)}_2^-]\) monomer, that are involved in the bimolecular reaction are already “prepared” in close proximity. Upon photoexcitation of the complex, an electron is excited from an antibonding \(d_{z^2}\sigma^*\) orbital to a bonding \(p\sigma\) orbital, leading to the formation of covalent bonds among Au atoms.\(^7\) Since Au atoms belong to the same solvent cage in the ground state of the \([\text{Au(CN)}_2^-]_n\) complex, the formation of Au–Au covalent bonds occurs without being limited by slow diffusion through the solvent. Therefore, the ultrafast time resolution can be achieved for probing this bond-making process as in typical unimolecular reactions synchronized with laser photolysis, but the ensuing reaction is a bimolecular reaction between \([\text{Au(CN)}_2^-]\) monomers.

Recently, ultrafast Au–Au bond formation in gold dimer and trimer complexes, \([\text{Au(CN)}_2^-]_2\) and \([\text{Au(CN)}_2^-]_3\), was investigated using transient absorption (TA) spectroscopy.\(^12\),\(^13\) In the case of the gold trimer complex, the transient changes of absorption were observed with time constants of 500 fs, 2 ps and 2 ns. The first kinetic component (500 fs) was ascribed to the intersystem crossing to a triplet state, which is presumably preceded by rapid contraction of Au–Au bonds within 500 fs.\(^12\) The second kinetic component (2 ps) was assigned to a conformational change from the bent to linear structure. It is worth noting that the second kinetic component (2 ps) is missing in the case of the dimer complex, suggesting that the 2 ps process is related to the intrinsic nature of the trimer complex.\(^13\) Since the TA signal is not directly related to the molecular structure, those structural assignments were solely based on the theoretical electronic absorption spectra of model structures. Those structural assignments were disputed by a study using \textit{ab initio} molecular dynamics simulation.\(^14\) According to this study, the bent-to-linear transition occurs on a 500 fs time scale, although it was assigned to the 2 ps kinetic component in the TA study. Such a discrepancy between experiment and theory, mainly due to limited structural information obtained from experiments, is a rather common problem in chemistry in general. In order to resolve the discrepancy, we used time-resolved X-ray liquidography (TRXL), also known as time-resolved X-ray solution scattering (TRXSS), to elucidate
the ultrafast structural dynamics of Au–Au bond formation in $[\text{Au(CN)}_2]_3$ at the atomic level.$^{15,16}$

TRXL, one of the time-resolved X-ray diffraction techniques,$^{17–49}$ is an effective method for probing photoinduced structural changes of molecules in solution and has been used for studying the dynamics and mechanisms of many molecular reaction systems, ranging from small molecules$^{25–39}$ to biological macromolecules.$^{40–49}$ Thus far, the temporal resolution of TRXL has been limited to only 100 ps, preventing the observation of ultrafast processes on the time scales of femtoseconds to picoseconds. This limit can be overcome with the recent development of X-ray free electron lasers (XFELs), which generate ultrashort ($\sim 100$ fs long) X-ray pulses with $\sim 10^{12}$ photons per pulse.$^{50–58}$ As a result, it has become possible to explore chemical processes occurring on the sub-picosecond time scale using TRXL. In this section, we describe the study of ultrafast structural dynamics of bond formation in $[\text{Au(CN)}_2]_3$ in solution with sub-picosecond time resolution and sub-angstrom spatial resolution by performing the TRXL experiment at both an XFEL facility and a synchrotron.

### 13.2 Experimental

The TRXL experiment is schematically shown in Figure 13.1. Scattering patterns, $S(q,t)$, from $[\text{Au(CN)}_2]_3$ solution were measured at various time delays up to 1 µs, including a reference time delay ($-5$ ps). By taking the difference between the scattering patterns measured at a positive time delay and the reference time delay, we obtained time-dependent difference scattering patterns, $\Delta S(q,t)$, which contain information on the structural change of reacting $[\text{Au(CN)}_2]_3$ molecules with all other contributions from non-reacting molecules removed. The contribution of solvent heating was determined by a separate experiment on a laser dye and subtracted from the experimental scattering curves with proper scaling.

#### 13.2.1 Data Collection

TRXL data were collected at the BL3 beamline of SACLA and the NW14A beamline of KEK. X-Ray pulses with sub-100 fs duration generated from SACLA and 100 ps duration generated from KEK were used for measuring the data at early time delays (from $-800$ fs to 100 ps) and late time delays (from 100 ps to 1 µs), respectively. The reproducibility of the X-ray scattering signal at the two beamlines were checked by comparing time-resolved difference scattering curves, $q\Delta S(q,t)$, as shown in Figure 13.2.

The two difference scattering curves at a common time delay (100 ps) are identical to each other within the experimental error, indicating that our measurement is highly reproducible and independent of the facility. Difference scattering curves in the entire time range (from $-800$ fs to 1 µs) are shown in Figure 13.3.
Visualizing Chemical Reactions in Solution with Femtosecond X-ray Scattering

Figure 13.1 Schematic of femtosecond TRXL (top) and the data analysis (bottom). The photochemical reaction of solutes supplied by the liquid-flowing system is triggered by a femtosecond optical laser pulse. Subsequently, a time-delayed X-ray pulse synchronized with the laser pulse probes the structural dynamics of the reaction. The scattered signal is detected by a fast two-dimensional (2D) CCD detector. Solvent contributions were subtracted by taking the Fourier transform and compensating the depletion of the initial solute contribution due to the photochemical reaction. We obtained radial distribution functions (RDFs) in real space, which display the interatomic distances of transient species and products. As a result, the Au–Au bond lengths of the [Au(CN)$_2$]$^-$ complex were identified with sub-angstrom accuracy, providing the time-dependent structural changes of the metal complex in real time. Reprinted by permission from Macmillan Publishers Ltd: Nature (ref. 15), copyright (2015).
13.2.1.1 Data Collection at SACLA

TRXL measurement at early time delays (−800 fs–100 ps) was performed at the BL3 beamline of SACLA. Femtosecond laser pulses at 800 nm were generated from the Ti:sapphire regenerative amplifier and converted to the pulses at 267 nm or 310 nm wavelength. The laser beam was focused by a lens, where the laser beam was overlapped with the X-ray beam with the crossing angle of 10°. The 267 nm laser pulses were focused to a spot of 300 µm diameter, yielding a fluence of 2.1 mJ mm⁻², and the 310 nm laser pulses were focused onto a spot of 0.095 × 0.12 mm² size, giving the fluence of ∼2 mJ mm⁻². The femtosecond X-ray pulses were generated from the XFEL at SACLA by self-amplified spontaneous emission (SASE). The X-ray pulses have narrow energy bandwidth (ΔE/E = 0.6%), a pulse duration of <100 fs, a center energy of 15 keV and a photon flux of ∼10¹¹ photons per pulse. We used an aqueous solution of the oligomer of the gold complex, [Au(CN)₂⁻]ₙ. The aggregation number of the gold oligomer and the position of an absorption peak in the ultraviolet (UV) region change depending on the concentration of the sample solution. In this work, we focus on the trimer, [Au(CN)₂⁻]₃, which is formed in a solution of 300 mM concentration and can be excited by the laser pulses of 267 nm or 310 nm. Upon photoexcitation, the trimer undergoes structural changes, including variation of its geometric structure and the formation of Au–Au covalent bonds. The solution sample was circulated through a sapphire nozzle with 100 µm-thick aperture to supply fresh sample for every laser shot. The structural change was monitored by the scattering pattern generated by X-ray pulses and measured with an area detector (Rayonix LX255-HS). The time resolution of the TRXL experiment was ∼500 fs, which was limited by the timing jitter between the laser and X-ray pulses.

Figure 13.2 Comparison of the difference scattering curves at a common time delay, 100 ps, measured at SACLA (blue) and KEK (red). The two curves are nearly identical to each other within the experimental error, indicating that the difference scattering curves are highly reproducible and independent of the facility. Reprinted by permission from Macmillan Publishers Ltd: Nature (ref. 15), copyright (2015).
Visualizing Chemical Reactions in Solution with Femtosecond X-ray Scattering

The laser-off images were acquired with the laser pulse arriving 5 ps later than the X-ray pulse (that is, −5 ps time delay) in order to probe the (unexcited) molecules in the ground state while assuring the same average temperature of the sample solution. These laser-off images were used as a reference for calculating the time-resolved difference X-ray scattering patterns. To achieve a high enough signal-to-noise ratio for data analysis, about 50 images were acquired at each time delay. The scattering curves were measured at the following time delays: −5 ps, −800 fs, −300 fs, 200 fs, 700 fs, 1.2 ps, 1.7 ps, 3.2 ps, 5.2 ps, 10 ps, 20 ps, 30 ps, 50 ps and 100 ps. Time zero was determined by fitting the time trace of the difference scattering data for the sample solution with a convolution of a Gaussian function representing an instrument

Figure 13.3 TRXL data of [Au(CN)$_2$]$_3$. (A) Experimental difference scattering curves, $q\Delta S(q)$, measured at various time delays from −800 fs to 300 ns. Data at only selected time delays are shown for clarity. (B) Radial distribution functions, $r^2 S(r)$, obtained by sine-Fourier transformation of $q\Delta S(q)$ after subtracting solvent contributions. The RDF of the $S_0$ state was added to the RDFs at all time delays to emphasize only the contributions of the transient solute species associated with the bond formation. Reprinted by permission from Macmillan Publishers Ltd: *Nature* (ref. 15), copyright (2015).
response function (IRF) and the sum of exponential functions representing the transition dynamics among intermediate states. The scattering signals arising from solvent (water) heating were also measured using a 40 mM FeCl$_3$ solution with the same experimental conditions.

### 13.2.1.2 Data Collection at KEK

The TRXL measurement at late time delays (100 ps–1 µs) was performed at the NW14A beamline of KEK. The laser pulses with a center wavelength of 267 nm or 310 nm were focused onto a spot, where the laser beam overlapped with the X-ray beam with a crossing angle of 10°. The 267 nm laser pulses were focused to a spot of 300 µm diameter, yielding a fluence of 3.67 mJ mm$^{-2}$, and the 310 nm laser pulses were focused onto a spot of 0.343 × 0.492 mm$^2$ size, giving the fluence of ∼0.2 mJ mm$^{-2}$. The laser pulses were synchronized with X-ray pulses from the synchrotron by an active feedback control loop that adjusts the laser oscillator cavity length, and the relative time delay between the laser and X-ray pulses was controlled electronically. The time-delayed X-ray pulses were selected by using a synchronized mechanical chopper. A multilayer optic coated with depth-graded Ru/C layers ($d = 40$ Å; NTT Advanced Technology, Japan) produced a Gaussian-type X-ray spectrum with a center wavelength of 0.83 Å and ∼5% energy bandwidth. The scattering patterns generated by X-ray pulses of 100 ps (full width at half maximum, FWHM) duration were measured with an area detector (MarCCD165, Mar USA) with a sample-to-detector distance of 40 mm. The sample solution with the same concentration as used at SACLA was circulated through the sapphire nozzle with a 300 µm-thick aperture. The laser-off images were acquired with the X-ray pulse arriving 3 ns earlier than the laser pulse (that is, −3 ns time delay) in order to eliminate the contribution of the (unexcited) ground-state reactants. These laser-off images were used as a reference for calculating the time-resolved difference X-ray scattering patterns. To achieve a high enough signal-to-noise ratio for data analysis, more than 50 images were acquired and averaged at each time delay. The scattering curves were measured at the following time delays: −3 ns, −150 ps, 100 ps, 150 ps, 300 ps, 1 ns, 3 ns, 10 ns, 30 ns, 100 ns, 300 ns and 1 µs. The scattering signals arising from solvent (water) heating were also measured using a 40 mM FeCl$_3$ solution with the same experimental conditions.

### 13.2.2 Data Processing

#### 13.2.2.1 Removal of the Solvent Contribution

In order to study only the dynamics of the Au–Au bond formation, the scattering arising from heating of pure solvent induced by laser excitation was subtracted from the experimental scattering data. The water heating signal was obtained by a separate solvent heating experiment on an FeCl$_3$ solution.
Visualizing Chemical Reactions in Solution with Femtosecond X-ray Scattering

at the same time delays used for the \([\text{Au(CN)}_2^-]_3\) solution. Singular value decomposition (SVD) of the data identified only one component, implying that only a single difference scattering curve accounts for the contribution of solvent heating in the time range up to 100 ps. In addition, the difference scattering curve of the \([\text{Au(CN)}_2^-]_3\) solution at 1 µs time delay is identical to the one for solvent heating, confirming that the difference scattering curves of \([\text{Au(CN)}_2^-]_3\) at late time delays are dominated by the solvent heating contribution due to reversibility of the reaction. The amount of heat dissipated in the sample solution can be determined from the scaling between these two curves. The obtained solvent heating contribution was subtracted from the experimental difference scattering curves at all time delays. The resultant difference scattering curve obtained by subtracting the solvent heating contribution can be regarded as the solute-only term because the contribution of the cage term (solute–solvent cross term) is negligibly small.

13.2.2.2 Sine-fourier Transformation of \(q\Delta S(q)\)

The difference radial distribution function, \(r^2\Delta S(r,t)\), is a measure of the radial electron density change as a function of interatomic distance \(r\) in real space and was obtained by sine-Fourier transformation of the \(q\Delta S(q,t)\) curves:

\[
r^2\Delta S(r,t) = \frac{r}{2\pi^2} \int_0^\infty q\Delta S(q,t)\sin(qr)e^{-q^2\alpha}dq, \tag{13.1}
\]

where the constant \(\alpha (\alpha = 0.03 \text{ Å}^2)\) is a damping term that accounts for the finite \(q\) range in the experiment. Difference RDFs represent the change of Au–Au interatomic distance in the molecules participating in the reaction, and thus provide an intuitive picture of change in the molecular structure.

13.2.3 Data Analysis

13.2.3.1 SVD

As the step for determining the kinetic model of the photoinduced reaction of \([\text{Au(CN)}_2^-]_3\) and obtaining the species-associated RDFs for each transient state, we applied the SVD analysis to our experimental RDFs. From the TRXL data, we can build an \(n_r \times n_t\) data matrix, \(A\), where \(n_r\) and \(n_t\) are the number of \(r\) points in the RDFs and the number of time-delay points, respectively. Matrix \(A\) is decomposed into three matrices satisfying the relationship of \(A = USV^T\), where \(U\) is an \(n_r \times n_t\) matrix whose columns are time-independent \(r\)-spectra, also called left singular vectors (lSVs), \(V\) is an \(n_t \times n_t\) matrix whose columns are amplitude changes of \(U\) as time evolves, also called right singular vectors (rSVs), and \(S\) is a diagonal \(n_t \times n_t\) matrix whose diagonal elements are called singular values and can possess only non-negative values. The matrices \(U\) and \(V\) follow the relationships of \(U^TU = I_{n_r}\) and \(V^TV = I_{n_t}\), respectively, where \(I_{n_i}\) is the identity matrix. The diagonal elements of \(S\) (i.e., singular values)
represent the weight of lSVs in $U$. Since the singular values are ordered so that $s_1 \geq s_2 \geq \ldots \geq s_n \geq 0$, both lSVs and rSVs on the more left or right are supposed to have larger contributions to $A$. The lSVs, when linearly combined together, give information on the RDFs associated with distinct transient species, while the rSVs contain information on the population dynamics of the transient species. Thus, the SVD analysis provides a model-independent estimation of the number of structurally distinguishable transient species and the dynamics of each species.

By performing the SVD analysis on our experimental difference RDFs, $r^2S(r,t)$, we identified four singular components with significant singular values, indicating the existence of four structurally distinguishable transient states. The rSVs of these four significant singular components were fitted by a convolution of a Gaussian function representing IRF and a sum of three exponential functions representing transitions among the transient intermediate states. As a result, we obtained the exponentials with the time constants of $1.6 \ (\pm 0.1) \ \text{ps}$, $3 \ (\pm 0.5) \ \text{ns}$ and $100 \ (\pm 20) \ \text{ns}$, and an IRF with $480 \ \text{fs} \ (\pm 10) \ \text{fs}$ width (FWHM). Thus, we identified four transient states and three kinetic components connecting the four species.

13.2.3.2 Kinetic Analysis

In order to obtain the species-associated RDFs of the four transient states identified in the SVD analysis, we performed kinetic analysis on the $U$ and $V$ matrices using an appropriate kinetic model. First, following the result of the SVD analysis, we defined new matrices, $U'$, $V'$ and $S'$, that contain only the first four elements of $U$, $V$ and $S$. In other words, $U'$ is an $n_r \times 4$ matrix containing only the first four left singular vectors of $U$; $S'$ is a $4 \times 4$ diagonal matrix containing only the first four singular values of $S$; and $V'$ is an $n_t \times 4$ matrix containing the first four right singular vectors of $V$. Among various kinetic models, the only kinetic model that can account for the four transient states and the three kinetic components is the sequential model. Therefore, by solving rate equations based on the sequential model, the concentrations of the four transient states can be calculated using the three kinetic components determined from the SVD analysis. We defined a matrix $C$ that represents the time-dependent concentrations of the four transient states and related it to $V'$ using a parameter matrix $P$ that satisfies the relationship of $V' = CP$. In other words, the linear combination (by $P$) of the concentrations of the four transient states ($C$) gives the four rSVs constituting $V'$. In our analysis, $C$ is an $n_t \times 4$ matrix containing the time-dependent concentrations of the four transient states denoted as $S_0$, $S_1$, $T_1$ and tetramer states, and $P$ is a $4 \times 4$ matrix containing coefficients for the time-dependent concentrations of the transient states. Once we determine $C$ by solving the rate equations and convoluting with the IRF, the theoretical RDFs at various time delays, $A'$, can be generated as follows.

$$A' = U'S'V'^\top = U'S'(CP)^\top = U'S'(P^\top C)^\top = (U'S'P)^\top C^\top$$  \hspace{1cm} (13.2)
The matrix $P$ can be optimized by minimizing the discrepancy $\chi^2$ between the theoretical and experimental difference scattering curves using the Minuit library:

$$\chi^2 = \sum_{i=1}^{n_r} \sum_{j=1}^{n_t} \left( \frac{r^2 \Delta S_{\text{exp}} (r_i, t_j) - r^2 \Delta S_{\text{theory}} (r_i, t_j)}{\sigma_{ij}} \right)^2,$$  \hspace{1cm} (13.3)

where $r^2 \Delta S_{\text{exp}}(r_i, t_j)$ and $r^2 \Delta S_{\text{theory}}(r_i, t_j)$ are the experimental and theoretical RDFs at given $r$ and $t$ values, respectively, and $\sigma_{ij}$ is the experimental standard deviation at given $r$ and $t$ values. From eqn (13.2), we can define a matrix $B$ as $B = U' S' P^T$, that is, a linear combination (by $P$) of the four lSVs constituting $U'$ that are weighted by their singular values in $S'$. As a result, matrix $B$, an $n_r \times 4$ matrix, contains the RDFs directly associated with the transient states. Thus, by optimizing matrix $P$, we obtain the time-independent, species-associated RDFs of the intermediate species (optimized $B$).

### 13.2.3.3 Calculation of Theoretical Radial Distribution Functions

For individual transient states, theoretical RDFs were expressed as a sum of multiple RDFs, $S_{R_i}$, each of which corresponds to an Au–Au pair,

$$r^2 S_{\text{theory}}(r) = r^2 \sum_{i=1}^{n} S_{R_i}(r),$$  \hspace{1cm} (13.4)

where $R_i$ is the Au–Au distance for an $i$th pair of Au atoms. For the trimer states ($S_0$, $S_1$ and $T_1$) and the tetramer, $n$ was set to be three and six, respectively. Each $S_{R_i}(r)$ curve was calculated by sine-Fourier transformation of the theoretical scattering curve, $S_{R_i}(q)$, as follows:

$$r^2 S_{R_i}(r) = \frac{r}{2\pi} \int_0^\infty q S_{R_i}(q) \sin(qr) e^{-qr^\alpha} dq.$$  \hspace{1cm} (13.5)

The damping constant ($\alpha$) used for obtaining the experimental RDFs was also used to obtain the theoretical RDFs. The theoretical scattering curves $S_{R_i}(q)$ from Au–Au pairs were obtained by the simple Debye formula,

$$S_{R_i}(q) = F_{\text{Au}}^2(q) \frac{\sin(qR_i)}{qR_i},$$  \hspace{1cm} (13.6)

where $F_{\text{Au}}$ is the atomic form factor of the gold atom. By substituting eqn (13.5) and (13.6) into eqn (13.4), we obtained:

$$r^2 S_{\text{theory}}(r) = \sum_{i=1}^{n} \frac{r}{2\pi} \int_0^\infty q F_{\text{Au}}^2(q) \frac{\sin(qR_i)}{qR_i} \sin(qr) e^{-qr^\alpha} dq.$$  \hspace{1cm} (13.7)

The theoretical RDFs for the transient states were calculated by eqn (13.7). We note that the only variables in eqn (13.7) are the Au–Au distances.
13.2.3.4 Structural Fitting Analysis

To reconstruct the structures of the four states (S₀, S₁, T₁ and the tetramer) and extract the Au–Au distances for each state, we performed structural fitting analysis of the species-associated RDFs of the four states. As fitting parameters of the analysis, we considered three Au–Au distances for the S₀, S₁ and T₁ states, six Au–Au distances for the tetramer, and a scaling factor between the number of excited molecules and the signal intensity. It should be noted that we did not use any structural constraint that might impose a certain structure or symmetry. The maximum likelihood estimation (MLE) with the χ² estimator was employed with four (for S₀, S₁ and T₁ states) or seven (for tetramer) variable parameters. The chi-square (χ²) is given by eqn (13.8):

\[ \chi^2(R_1, R_2, R_3, A) = \frac{1}{N - p - 1} \sum_i \left( \frac{S_{\text{theory}}(r_i) - S_{\exp}(r_i)}{\sigma_i^2} \right)^2, \quad (13.8) \]

where \( N \) is the total number of \( r \) points (\( = 500 \)), \( p \) is the number of fitting parameters (\( = 4 \) or \( 7 \)) and \( \sigma_i \) is the standard deviation. The likelihood \( (L) \) is related to \( \chi^2 \) by eqn (13.9):

\[ L(R_1, R_2, R_3, A) \propto \exp(-\chi^2/2). \quad (13.9) \]

The errors of the multiple fitting parameters can be determined from this relationship by calculating the boundary values at 68.3% of the likelihood distribution. The calculation was performed by using the MINUIT software library and the error values were provided by the MINOS algorithm in MINUIT. Since we used the standard deviation of the measurement when calculating \( \chi^2 \), the quality of the fit becomes better as the \( \chi^2 \) approaches one.

13.2.3.5 Determination of RDF of the S₀ State

Time-independent species-associated difference RDFs of the transient states were obtained by the SVD and kinetic analyses of the experimental (time-dependent) difference RDFs. These difference RDFs correspond to \( r^2(S_{S_0}(r) - S_{S_0}(r)), r^2(S_{S_1}(r) - S_{S_0}(r)), r^2(S_{T_1}(r) - S_{S_0}(r)) \) and \( r^2(S_{\text{tetramer}}(r) - S_{S_0}(r)) \). From the structural fitting analysis described in Section 13.2.3.4, we were able to determine not only the RDFs of the transient states (S₁, T₁ and the tetramer) but also the RDF of the S₀ state. We used a common S₀ structure when fitting the four species-associated difference RDFs. By optimizing the fit between the experimental and the theoretical difference RDFs for each transient species, we were able to obtain the theoretical RDF of the S₀ state in addition to the RDFs of the other states. In order to emphasize only the contributions of transient solute species associated with the bond formation, we added the RDF of the S₀ state to the experimental difference RDFs at all time delays and obtained RDFs, \( r^2S(r,t) \).
13.3 Results and Discussion

A comparison of the data obtained with excitation at two different wavelengths (267 and 310 nm) shows that the results are independent of excitation wavelength. Thus, hereafter we show the TRXL data at 267 nm excitation, which has better data statistics.\(^{15,16}\) Experimental difference scattering curves, \(q\Delta S(q,t)\), measured at various time delays from \(-800\) fs to 300 ns are shown in Figure 13.3A. The difference scattering curves show distinct oscillatory features along the \(q\) axis, indicative of a large structural change of [Au(CN)\(_2\)]\(^-\), during the formation of Au–Au covalent bonds. Considering that the oscillatory features appear distinct even at the earliest time delay (200 fs) of our measurement, the first step of the bond formation in [Au(CN)\(_2\)]\(^-\) must occur impulsively within the time resolution of our experiment (\(\sim 500\) fs). The oscillatory features change further over time and almost disappear after 300 ns with only the contribution from solvent heating remaining thereafter.

A more intuitive picture of the structural change of [Au(CN)\(_2\)]\(^-\) can be obtained by converting \(q\Delta S(q,t)\) into difference RDFs, \(r^2\Delta S(r,t)\), in \(r\)-space by sine-Fourier transformation. In order to emphasize the contributions of transient solute species associated with the bond formation alone, the RDF of the ground (S\(_0\)) state was added to the difference RDFs at all time delays, yielding \(r^2S(r,t)\), as shown in Figure 13.3B. Since the solvent contributions were eliminated and the contributions from carbon and nitrogen atoms in [Au(CN)\(_2\)]\(^-\) are almost negligible compared with the strong scattering from Au atoms, RDFs shown in Figure 13.3B actually represent the interatomic distances among the gold atoms of [Au(CN)\(_2\)]\(^-\) in real space.

Two peaks denoted as \(p_1\) and \(p_2\) are distinct in the RDFs in Figure 13.3B. Considering that [Au(CN)\(_2\)]\(^-\) is a trimer and the intensity of \(p_1\) is about twice as large as \(p_2\), we can assign \(p_1\) to the Au–Au (R\(_{12}\)) and Au–Au (R\(_{23}\)) pairs, and \(p_2\) to the Au–Au pair (R\(_{13}\)). In the S\(_0\) state (i.e., RDF at \(-800\) fs time delay), R\(_{12}\) and R\(_{23}\) (\(\sim 3.6\) Å as indicated by the position of \(p_1\)) are relatively large compared with the typical length of an Au–Au covalent bond (\(\sim 2.7\) Å), and R\(_{13}\) (\(\sim 5.6\) Å as indicated by the position of \(p_2\)) is smaller than the sum of R\(_{12}\) and R\(_{23}\), indicating weakly bound Au atoms and a bent structure, respectively. As expected in the \(q\)-space data, the RDF at 200 fs time delay is significantly different from the one at \(-800\) fs, suggesting that the first step of the bond formation in [Au(CN)\(_2\)]\(^-\) occurs within the time resolution of our experiment. Compared to the S\(_0\) state, R\(_{12}\) and R\(_{23}\) decrease significantly, indicating the formation of Au–Au covalent bonds at this step. Simultaneously, R\(_{13}\) (\(\sim 5.6\) Å) becomes similar to the sum of R\(_{12}\) and R\(_{23}\) (\(\sim 2.8\) Å each), which is evidence of a conformational transition from bent to linear geometry. We note that the time scale of the bent-to-linear transition determined from our TRXL experiment is in good agreement with the time scale predicted from the previous theoretical study.\(^{14}\) From 200 fs to 10 ps, \(p_1\) and \(p_2\) shift to smaller distances, indicating further decrease of Au–Au distances due to the formation of stronger Au–Au covalent bonds. In this time range, the ratio between (R\(_{12}\) + R\(_{23}\)) and R\(_{13}\) remains at 1 : 1, indicating that the linear structure is preserved.
After 100 ps, \( p_3 \) appears at \( \sim 8.5 \) Å and grows up until 10 ns. Since the position of \( p_3 \) is too large for the Au–Au distance in the trimer complex, \( p_3 \) must be a signature of the formation of a tetramer complex. Also, increased intensities of \( p_1 \) and \( p_2 \) account for a larger number of Au–Au pairs present in the tetramer. After 10 ns, the RDF returns gradually back to the RDF of the \( S_0 \) state.

By SVD and principal component analysis (PCA), we obtained species-associated RDFs for four states assigned as \( S_0 \), \( S_1 \), a triplet (\( T_1 \)) and tetramer, and their kinetics. We fitted the experimental RDFs at various time delays by linear combinations of the species-associated RDFs, and determined the time-dependent concentration of each state (Figure 13.4A). As a result, we obtained three kinetic components with time constants of 1.6 (±0.1) ps, 3 (±0.5) ns and 100 (±20) ns, which correspond to the transition from \( S_1 \) to \( T_1 \), the transition from \( T_1 \) to the tetramer, and the transition from the tetramer to \( S_0 \), respectively. The obtained values are summarized in Table 13.1.

The time scales of the three kinetic components match well with the ones identified in the previous TA study,\(^1\) except that our TRXL data lack the ~500 fs component, which was assigned to intersystem crossing to a triplet state in the TA study. Here, we note that the 500 fs component was assigned to the \( S_1 \)-to-\( T_1 \) intersystem crossing in the TA study but was not observed by TRXL. This discrepancy suggests that the intersystem crossing, if the assignment in the TA study is correct, does not involve any significant structural change detectable by TRXL, and thus we termed the initially formed \( T_1 \) state as \( T_1' \), which is structurally indistinguishable from \( S_1 \).

The reconstructed structures of the four states from structural fit analysis presented in Figure 13.4B and Table 13.2 are in good agreement with the structural changes inferred from Figure 13.3B. In the \( S_0 \) state, \( R_{12} \) and \( R_{23} \) are relatively large and \( R_{13} \) is smaller than the sum of \( R_{12} \) and \( R_{23} \), indicating weakly bound Au atoms and the bent structure of the \( S_0 \) state. \( R_{12} \) and \( R_{23} \) are different from each other, which can be attributed to the asymmetric structure of the \( S_0 \) state or broadening of the RDF induced by the relatively free movements of weakly bound Au atoms if the \( S_0 \) state were symmetric. In the \( S_1 \) state, the Au–Au distances become considerably shorter, indicating that Au–Au bonds become stronger with covalent character. \( R_{13} \) in the \( S_1 \) state becomes longer than the one in the \( S_0 \) state and is identical to the sum of \( R_{12} \) and \( R_{23} \), revealing that the conformational transition from bent to linear structure occurs in the \( S_1 \) state. In addition, \( R_{12} \) and \( R_{23} \) are identical to each other within experimental error despite the lack of any constraint on the two variables, indicating that the structure of the \( S_1 \) state is symmetric. As the \( S_1 \) state transforms to the \( T_1 \) state, the Au–Au distance further decreases with the linear and symmetric structure maintained, implying the formation of strong Au–Au covalent bonds. Since this process (further contraction of Au–Au bond in 2 ps) is missing in the case of the dimer complex,\(^2\) the structural change is originated from the intrinsic nature of the trimer complex, which will be the subject of future study. Later, the trimer reacts with a free \( \text{Au(CN)}_2^- \) monomer to form a tetramer, \( [\text{Au(CN)}_2^-]_4 \), before ultimately returning to the \( S_0 \) state. The changes in the Au–Au distances and the conformations of the
**Figure 13.4** Time-dependent structural changes of [Au(CN)₃]⁻. (A) Time-dependent concentrations of the four states and their transition kinetics. The name of each species is indicated above each trace. (B) Species-associated RDFs of the four structures obtained from the SVD and PCA analyses (black), and their fits using model structures containing multiple Au–Au pairs (red). As fitting parameters, we considered three Au–Au pairs for the S₀, S₁, and T₁ state, and six Au–Au pairs for the tetramer. Reprinted by permission from Macmillan Publishers Ltd: *Nature* (ref. 15), copyright (2015).

**Table 13.1** Kinetic parameters determined from the data analysis.

<table>
<thead>
<tr>
<th></th>
<th>S₁ to T₁</th>
<th>T₁ to tetramer</th>
<th>Tetramer to S₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time constant</td>
<td>1.6 ± 0.1 ps</td>
<td>3 ± 0.5 ns</td>
<td>100 ± 20 ns</td>
</tr>
</tbody>
</table>
S₀, S₁, T₁ and tetramer states in Figure 13.4B are in good agreement with the results of the previous theoretical calculation.\(^{14}\)

The previous TA study identified the changes of transient absorption on 500 fs, 2 ps and 2 ns time scales.\(^{12}\) Based on the measured time constants and the theoretical electronic absorption spectra, the following mechanism was suggested for the Au–Au bond formation in [Au(CN)₂]₃. The S₁ state is rapidly populated within a few hundred femtoseconds accompanying contraction of the Au–Au bonds, but without any bent-to-linear transition. Subsequently, the T₁ state of a linear staggered structure is formed in 2 ps via the bent-to-linear transition, and then the trimer associates with a free monomer to form a tetramer in 2 ns. The time scales of the transitions found in the TA study match well with the results of this work, but the detailed structural changes were assigned differently. In particular, from our TRXL measurement and analysis, the bent-to-linear transition was found to occur within a few hundred femtoseconds rather than on the time scale of 2 ps.

To account for this discrepancy, we determined the structure of the S₁ state more carefully by fitting the experimental difference scattering curve at 200 fs time delay using two different model structures as shown in Figure 13.5. One is a linear structure where R₁₂ is equal to the sum of R₁₃ and R₂₃, and the other is a bent structure where the Au–Au–Au bond angle of the S₀ state is preserved for the S₁ state. In Figure 13.5A, it is clearly seen that the theoretical scattering curve calculated from the linear structure (χ² = 1.70) fits the experimental scattering curve at the 200 fs time delay much better than the one calculated from the bent structure (χ² = 4.81). The difference between the linear and bent structures can be seen more distinctly in the RDFs in r-space shown in Figure 13.5B. In the bent structure, R₁₃ is too small to fit the experimental RDF at 200 fs. Therefore, the bent-to-linear transition must be completed at 200 fs time delay.

Based on the reconstructed structures of the four different states and the transition dynamics among them, we summarized the mechanism for photoinduced formation of Au–Au covalent bonds in [Au(CN)₂]₃ in Figure 13.6 with the assignments of kinetics from the TA and TRXSS studies. The S₀ state with weakly bound Au atoms in a bent geometry transforms within a few hundred femtoseconds to the S₁ state with tightly bound Au atoms (2.8 Å Au–Au distances) in a linear and symmetric geometry. The S₁ state transforms to the T₁ state with 1.6 ps time constant accompanying further contraction of Au–Au bonds by 0.1 Å. Then, the T₁ state converts to a tetramer in 3 ns via
formation of another Au–Au bond and, ultimately, the $S_0$ state is recovered in $\sim 100$ ns. Considering that TRXL is only sensitive to the processes accompanying structural change, the intersystem crossing processes on $\sim 500$ fs and 13 ns time scales, which were not observed in the TRXL measurement, are likely to involve no structural change.

### 13.4 Conclusion

Here, we demonstrated the capability of femtosecond TRXL provided by an XFEL facility by elucidating the overall mechanism for the formation of Au–Au covalent bonds in the $[\text{Au(CN)}_2]_3$ complex with rich structural information.
Femtosecond TRXL offers the opportunity to visualize the entire process of photoinduced reactions in real time and real space, and can be used as a fundamental tool for studying the reaction dynamics of chemical and biological systems.

**Acknowledgements**

We thank Prof. Munetaka Iwamura, Prof. Koichi Nozaki, Dr Satoshi Takeuchi and Dr Tahei Tahara for helpful discussions. This work was supported by IBS-R004-G2, the X-ray Free Electron Laser Priority Strategic Program of MEXT, the Innovative Areas "Artificial Photosynthesis (AnApple)" (no. 25107527) grant from the Japan Society for the Promotion of Science (JSPS), and Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (NRF-2014R1A1A1002511). The experiments were performed at the BL3 of SACLA with the approval of the Japan Synchrotron Radiation Institute.

References

