Mapping the emergence of molecular vibrations mediating bond formation

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Fundamental studies of chemical reactions often consider the molecular dynamics along a reaction coordinate using a calculated or suggested potential energy surface¹⁻⁵. But fully mapping such dynamics experimentally, by following all nuclear motions in a time-resolved manner-that is, the motions of wavepackets-is challenging and has not yet been realized even for the simple stereotypical bimolecular reaction⁶⁻⁸: $A-B+C \rightarrow A+B-C$. Here we track the trajectories of these vibrational wavepackets during photoinduced bond formation of the gold trimer complex $[Au(CN)_2]_3$ in an aqueous monomer solution, using femtosecond X-ray liquidography⁹⁻¹² with X-ray free-electron lasers^{13,14}. In the complex, which forms when three monomers A, B and C cluster together through non-covalent interactions^{15,16}, the distance between A and B is shorter than that between B and C. Tracking the wavepacket in three-dimensional nuclear coordinates reveals that within the first 60 femtoseconds after photoexcitation, a covalent bond forms between A and B to give A-B+C. The second covalent bond, between B and C, subsequently forms within 360 femtoseconds to give a linear and covalently bonded trimer complex A-B-C. The trimer exhibits harmonic vibrations that we map and unambiguously assign to specific normal modes using only the experimental data. In principle, more intense X-rays could visualize the motion not only of highly scattering atoms such as gold but also of lighter atoms such as carbon and nitrogen, which will open the door to the direct tracking of the atomic motions involved in many chemical reactions.

The $[Au(CN)_2^-]_3$ complex serves as a valuable model system for studying photoinitiated processes in solution. Irradiation with ultraviolet light excites $[Au(CN)_2^-]_3$ from its ground state (S_0) to the singlet state (S_1) , which within 20 fs undergoes intersystem crossing to reach a triplet excited state $(T_1)^{17}$. A further transition from T_1' to another triplet excited state (T_1) then occurs with a time constant of about 1–2 ps, completing the formation of covalent bonds and transformation of the complex from a bent to a linear structure ^{9,17,18} (see Supplementary Information for details of the notations of electronic states).

Formation of the bonds could involve any of the three possible candidate trajectories sketched in Fig. 1b. The equilibrium structure in the ground state determines the position of the Franck–Condon (FC) region in the excited state; the excited-state wavepacket created in the FC region can be considered as the reactants (A + B + C) of the reaction. This wavepacket moves towards the equilibrium structure of T'₁, which is the product (A–B–C) with two equivalent covalent Au–Au bonds. Using three-dimensional nuclear coordinates R_{AB} , R_{BC} and R_{AC} , if the FC region is located at the point at which R_{AB} is shorter than R_{BC} , the shortest pathway connecting the FC region and the equilibrium structure of T'₁ is path 2, corresponding to the concerted bond formation. Alternatively, two covalent bonds can form sequentially in time (that is, asynchronously), as in path 1 and path 3, which differ only by the order in which covalent bonds are formed: path 1 represents a pathway in which the covalent bond between A and B is formed first, and path 3 represents the case in which the bond between B and C is formed first (Fig. 1c). To determine the position of the FC region and whether the reaction trajectory involves concerted or asynchronous bond formation, the initial motions of the wavepacket starting from the FC region

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Fig. 1 | Schematics of the mechanisms for reactions involving three atoms and two bonds. a, A representative reaction trajectory for $A-B+C \rightarrow A+B-C$. b, Representative reaction trajectories for $A+B+C \rightarrow A-B-C$. c, Candidate pathways of the reaction in b. Path 2 represents a pathway whereby the two covalent Au–Au bonds are formed simultaneously, corresponding to a concerted bond formation mechanism. Path 1 and path 3 represent pathways whereby the two bonds are formed sequentially in time, corresponding to an asynchronous bond-formation mechanism. Path 1 and path 3 are distinct, depending on which bond is formed first, as described in the text. To determine the reaction pathway, the initial motion of the wavepacket must be tracked.

on a multidimensional potential energy surface (PES) need to be observed directly–something not achieved in previous studies (see Extended Data Fig. 1 for details).

Femtosecond electron and X-ray scattering^{10,11,19-26} and X-ray absorption spectroscopy^{19,27,28} have both the structural sensitivity and the temporal resolution needed for probing ultrafast changes of molecular structure in real space and real time. They have been used to observe vibrational motions^{10,11,19-24,27,28}, but mostly to observe diatomic molecules that have only a single nuclear coordinate or polyatomic molecules that were approximated as pseudo-diatomic species. This reflects the challenging nature of tracking wavepacket motions in the multidimensional nuclear coordinates of polyatomic molecules.

We accomplished this task using time-resolved X-ray liquidography (TRXL)⁹⁻¹², also known as time-resolved X-ray solution scattering. Time-resolved difference scattering curves, $q\Delta S(q, t)$, for the momentum-transfer vector $q = (4\pi/\lambda)\sin(2\theta/2)$, where λ is the X-ray wavelength and 2θ is the scattering angle, and a measurement time t, are shown in Extended Data Fig. 2a. Details of experimental procedures and data analysis are described in Methods and Supplementary Information. The temporal changes of $q\Delta S(q, t)$ can be determined from the first two right singular vectors (RSVs) obtained from a singular value decomposition (SVD) of $q\Delta S(q, t)$. The two RSVs are well fitted by an exponential function with a time constant of 1.1 ± 0.1 ps (mean \pm s.e.m.), which is related to the T'_1 -to- T_1 transition⁹, convoluted with the instrument response function, IRF(t) (Extended Data Fig. 2c). Apart from these population kinetics, oscillations are observed in the first to fourth RSVs (Extended Data Fig. 2d). To analyse the oscillations in more detail, we extracted the oscillating components from the experimental $q\Delta S(q, t)$ by subtracting the contributions of the T'₁-to-T₁ transition and the solvent heating, yielding residual difference scattering curves $q\Delta S_{\text{residual}}(q, t)$. The two-dimensional $q\Delta S_{\text{residual}}(q, t)$ curve in the q domain and the t domain provides direct information on the time-dependent

molecular structure and eventually enables us to track the motions of the wavepacket in multidimensional nuclear coordinates.

Figure 2a shows $q\Delta S_{residual}(q, t)$ measured at time delays from -1,040 fs to 2,235 fs. The TRXL signal is sensitive to wavepacket motions in any of the structurally distinct states (that is, the S_0 , T'_1 and T_1 states) and we therefore first examined which state is associated with the observed features of the residual difference scattering curve. As detailed in Methods and Supplementary Information, the best fits shown in Fig. 2a were obtained by considering the ground state S₀ and excited state T'₁, indicating that the residual difference scattering curves arise from wavepacket motions on the PESs of both S_0 and T'_1 . In Fig. 2b-e, we show the time-dependent changes of the structural parameters, R_{AB} , R_{BC} , R_{AC} and the Au–Au–Au angle, θ , obtained from the structural analysis. From the time evolution of these structural parameters, the trajectories of the excited-state (Fig. 3a) and ground-state (Fig. 3c) wavepackets can be reconstructed in multidimensional nuclear coordinates, R_{AB} versus $R_{\rm BC}$ versus θ , which describe the relative positions of all three Au atoms in the gold trimer complex. We note that these trajectories are obtained purely on the basis of the experimental data, without recourse to theoretical calculation, thanks to the structural sensitivity of TRXL.

The trajectories of the wavepackets occur in two distinct time regimes: (1) the initial motion on the PES of T₁ starting from the FC region of S₁ at earlier times (t < 360 fs), and (2) subsequent harmonic oscillations around the equilibrium structures of T'_1 at later times (t > 360 fs). At earlier times, the excited-state and ground-state wavepackets each move on their own PES to approach their own equilibrium structure. To examine the reaction mechanism of the bond formation, we first inspected the initial motion of the excited-state wavepacket with respect to the progress of the covalent-bond formation and the bent-to-linear transformation. Specifically, as shown in Fig. 3a, the excited-state wavepacket is generated in the FC region $(R_{AB} = 3.13 \text{ Å}, R_{BC} = 3.38 \text{ Å}, \theta = 119^{\circ})$ by an interaction with the pump pulse and then moves on the PES of T'_1 towards the equilibrium structure of $T'_1(R_{AB} = 2.82 \text{ Å}, R_{BC} = 2.82 \text{ Å}, \theta = 180^\circ)$. Along the coordinates of θ , the excited-state wavepacket in T₁' starts from the FC region (θ = 119°) and reaches the equilibrium of $T'_1(\theta = 180^\circ)$ within 335 fs, giving the timescale of the bent-to-linear transformation. The progress of the covalent-bond formation can be visualized more clearly by projecting the trajectory of the excited-state wavepacket onto the $R_{AB} - R_{BC}$ plane as shown in Fig. 3a and Supplementary Fig. 5a. The trajectory of the excited-state wavepacket reveals that the formation of two covalent bonds does not occur in a concerted, synchronous manner (as exemplified by path 2 in Fig. 1). Instead, R_{AB} decreases rapidly down to the covalent Au-Au bond length of the equilibrium of $T'_1(2.82 \text{ Å})$ at a 35-fs time delay, and at 60 fs it becomes even shorter, reaching the minimum length along the entire trajectory, whereas $R_{\rm BC}$ remains much longer than the covalent bond length (2.82 Å) at those time delays (Fig. 3a and Supplementary Fig. 5a). This trajectory at earlier times indicates that the shape of the PES around the FC region is steeper along the R_{AB} axis than along the $R_{\rm BC}$ axis. Subsequently, $R_{\rm BC}$ continues decreasing and R_{AB} oscillates around the equilibrium bond length with a frequency of 97 cm⁻¹ until $R_{\rm BC}$ eventually reaches the equilibrium bond length at 360 fs. These observations indicate asynchronous bond formation as in path 1, with the covalent bond formed earlier in the Au-Au pair with a shorter distance in the ground state.

We note that the temporal changes in R_{BC} are correlated with the temporal oscillations of R_{AB} . In the time range from 0 fs to 60 fs, both R_{AB} and R_{BC} rapidly decrease by 0.35 Å and 0.16 Å, respectively. In the subsequent time range, from 60 fs to 260 fs, R_{AB} increases by 0.09 Å, whereas R_{BC} continues to decrease, but only by 0.12 Å and with a much lower rate than in the range t < 60 fs. Then, in the time range from 260 fs to 360 fs, both R_{AB} and R_{BC} decrease, by 0.03 Å and 0.25 Å, respectively, such that the rate of decrease of R_{BC} recovers to its initial rate. This correlation between the changes in R_{AB} and R_{BC} indicates that the symmetric stretching mode of the gold trimer complex mediates the bond



Fig. 2 | **Structural analysis using residual difference scattering curves. a**, Experimental residual difference scattering curves, $q\Delta S_{\text{residual}}(q, t)$ (left) and their theoretical fits (right) obtained from the structural analysis performed by considering wavepacket motions in the states S_0 and T'_1 . **b**, **d**, Top, time-dependent Au–Au distances $R_{AB}(t)$ (black), $R_{BC}(t)$ (red) and $R_{AC}(t)$ (blue); and bottom, Au–Au–Au angle, (θ, teal) of T'_1 (**b**) and S_0 (**d**), determined from the

formation. Detailed structural changes of the gold trimer complex associated with the initial wavepacket motion on the PES of T'_1 are summarized in Fig. 3b.

The trajectory of the ground-state wavepacket in S₀ is represented in Fig. 3c and its projection onto the $R_{AB}-R_{BC}$ plane is shown in Fig. 3c and Supplementary Fig. 5b. The ground-state wavepacket is generated by two interactions with the pump pulse, that is, via resonant, impulsive stimulated Raman scattering²⁹, and then within 100 fs is seen to move in the direction of decreasing R_{AB} and increasing θ . This initial motion should reflect the initial structural changes occurring in the excited state—that is, the ultrafast bond formation and the bent-to-linear transformation (see Supplementary Information for details). Detailed structural changes associated with the initial wavepacket motion on the PES of S₀ are shown in Fig. 3d.

structural analysis. **c**, **e** Magnified views of the structure at t > 360 fs for $T'_1(c)$ and $S_0(e)$. The measured $R_{AB}(t)$, $R_{BC}(t)$ and $R_{AC}(t)$ (black open circles) are fitted by a sum of two damping cosine functions (red lines), the frequencies of which are given at the top left. As described in the text, specific normal modes of T'_1 and S_0 were assigned to these oscillations of the Au–Au distances.

After the initial motions of the wavepackets in the ground and excited states as described above, at later times (t > 360 fs) the wavepackets oscillate around their equilibrium structures. Molecular vibrations play an important part in the progress of chemical reactions by providing atomic motions along the reaction coordinates and are often discussed as key parameters in the interpretation of reaction dynamics measured with various time-resolved spectroscopies^{1–5,19,2728}. The temporal changes of the structural parameters of T_1' and S_0 after 360 fs are shown in Fig. 2c, e, respectively. It can be seen that all the structural parameters simply oscillate around their own equilibrium values, without any major changes observed in the wavepacket motion at earlier times. To characterize these oscillations at later times, we fitted $R_{AB}(t)$, $R_{BC}(t)$ and $R_{AC}(t)$ of T_1' and S_0 obtained from the structural analysis with various combinations of the vibrational normal modes, that is, the



Fig. 3 | **Trajectories of the excited-state and ground-state wavepackets determined from TRXL data. a**, **c** Motions of the excited-state wavepacket in $T'_1(\mathbf{a})$ and the ground-state wavepacket in $S_0(\mathbf{c})$ represented in the multidimensional nuclear coordinates R_{AB} versus R_{BC} versus θ . The projection of the wavepacket motion onto the R_{AB} - R_{BC} plane is shown at the bottom. The equilibrium distances of R_{AB} and R_{BC} in T'_1 and S_0 are indicated by the red dashed lines. The positions of the wavepacket at measured time points are indicated by dots, the colours of which represent time delays given by the colour scale. Several representative time delays, given in femtoseconds, are shown next to

symmetric stretching, asymmetric stretching and bending modes. For $T'_{L'}$ a sum of two symmetric stretching modes with frequencies of 79 cm⁻¹ and 125 cm⁻¹ gives a satisfactory fit to the temporal changes in Au–Au distances, as shown in Fig. 2c. Accordingly, those two oscillations at 79 cm⁻¹ and 125 cm⁻¹ are assigned to two symmetric stretching modes of T'_{1} : T_{1} _#6 (theoretical frequency, 63 cm⁻¹) and T_{1} _#12 (theoretical frequency, 92 cm⁻¹) (see Extended Data Fig. 6), respectively, identified by density functional theory (DFT) calculations (see Methods and Extended Data Fig. 6 for details). Similarly, from the fitting of the temporal changes of the structural parameters of S_0 , a symmetric stretching mode with frequency 44 cm⁻¹ were identified, as shown in Fig. 2e, and assigned to S_0 _#6 (theoretical frequency, 58 cm⁻¹) and S_0 _#5 (theoretical



the corresponding wavepacket position. The black curves connect the dots, ordered by time; they correspond to the trajectory of the wavepacket over time. **b**, **d** Transient structures of $T'_1(\mathbf{b})$ and $S_0(\mathbf{d})$ at representative time delays. The Au atoms at each time delay are represented by yellow dots, and the Au atoms in the FC region are represented by grey dots. In **b**, the covalent bonds formed in the excited state are indicated by the black solid lines. The change in interatomic distance and angle are indicated by red and blue arrows, respectively. The ligands are omitted for simplicity. Structural changes are exaggerated for clarity.

frequency, 43 cm^{-1}) of S₀, respectively (see Methods and Supplementary Information for details).

The trajectories of the wavepackets in T'_1 and S_0 at later times (>360 fs) are shown in the nuclear coordinates R_{AB} versus R_{BC} in Fig. 4a, b, respectively. The displacements of the wavepackets from the equilibrium structures are represented by the sum of structural changes along the two normal coordinates of the activated vibrational modes (T_{\perp} #6 and T_{\perp} #12 for T'_1 ; S_{0} _#6 and S_{0} _#5 for S_0). As shown in Fig. 4a, b, both wavepackets oscillate with respect to the normal coordinates of the activated vibrational modes of the activated vibrational structures with vibrational dephasing. Therefore, we conclude that in the late time range, both excited-state and ground-state wavepackets exhibit harmonic oscillations around the equilibrium structures.



Fig. 4 | **Harmonic oscillations of the ground-state and excited-state wavepackets at** t > 360 fs. **a**, **b** Later-time (>360 fs) trajectories of the excited-state wavepacket in T'_1 (**a**) and the ground-state wavepacket in S_0 (**b**), represented in the multidimensional nuclear coordinates R_{AB} versus R_{BC} versus time (t). The wavepacket trajectories are indicated by black curves. The wavepacket positions at several representative time delays (given in femtoseconds) are indicated by red dots. The equilibrium distances of R_{AB} and R_{BC} in T'_1 and S_0 are indicated by the red dotted lines in **a** and **b**, respectively. The normal coordinates Q of the two symmetric stretching modes for T'_1 , $Q(T_L#6)$ and $Q(T_L#12)$ (**a**), and the symmetric and asymmetric stretching modes for S_0 , $Q(S_0_{a}#6)$ and $Q(S_0_{a}#5)$ (**b**) are indicated by blue arrows. At the end of each arrow, the representative structure, with Au atoms as yellow spheres, is shown to indicate the displacements of three Au atoms according to the corresponding normal coordinate, and the positions of the Au atoms in the equilibrium structures are represented by grey spheres. The red arrows in the representative structures indicate the displacement vectors of the Au atoms for each mode; they are exaggerated for clarity. In **a**, the normal coordinates– exactly on the diagonal direction of the $R_{AB}-R_{BC}$ plane–are each slightly displaced for clarity. The projections of the trajectories onto the $R_{AB}-R_{BC}$ plane are shown in Supplementary Fig. 5c, d, respectively. **c**, Averaged Fourier power spectrum of $q\Delta S_{residual}(q, t)$ at later times (>360 fs). The peak positions were determined to occur at 32 cm⁻¹, 79 cm⁻¹ and 125 cm⁻¹, by fitting the power spectrum with the sum of three Gaussian functions, represented by the red curves. The vertical bars below the Fourier spectrum indicate the DFT-calculated frequencies of the normal modes of S₀ (blue) and T₁ (green) in the frequency range 20–170 cm⁻¹.

Importantly, these harmonic oscillations, manifested by the motions of wavepackets, can be unambiguously assigned to specific normal modes, because the TRXL signal contains information on the vibrational frequency as well as on the atomic-level movement pattern of a vibrational mode (Extended Data Fig. 4).

These assignments can be compared with those made on the basis of only the frequencies of normal modes. The oscillation frequencies can be easily extracted from the Fourier power spectrum of $q\Delta S_{residual}(q, t)$ at later times. The Fourier transform spectrum shown in Fig. 4c shows a major peak at 32 cm⁻¹ and minor peaks at 79 cm⁻¹ and 125 cm⁻¹. As detailed in Supplementary Information, if one follows the normal practice of choosing the normal mode with the most similar frequency as the 32 cm⁻¹ oscillation from among the 11 modes identified by DFT calculations for S_0 and T_1 , a bending mode of T_1 with a frequency of 33 cm⁻¹ would be incorrectly chosen. Also, the additional mode (an asymmetric stretching mode with a frequency of 44 cm⁻¹) discovered by TRXL data analysis would not be identified in the Fourier transform spectrum. Therefore, the results of this work showcase that the assignment of the observed oscillations to specific vibrational modes on the basis of a simple numerical comparison of vibrational frequencies is susceptible to misinterpretation for polyatomic molecules, which have many normal modes.

These observations illustrate that femtosecond TRXL can map the real-time trajectories of nuclear wavepackets and thereby identify how vibrational motion drives asynchronous bond formation. Although in this study we have tracked only the motions of highly scattering gold atoms, it is in principle also possible to visualize the motions of lighter atoms such as carbon and nitrogen–especially once next-generation X-ray sources such as LCLS-II HE³⁰ become available (see the simulation for O₃ presented in Supplementary Information).

Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41586-020-2417-3.

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Methods

TRXL experiments at PAL-XFEL

TRXL experiments were performed at the XSS beamline of PAL-XFEL (the Pohang Accelerator Laboratory X-ray free-electron laser). In the TRXL experiment, the sample solution of $[Au(CN)_2]_3$ was excited by an optical laser pulse to initiate a photoinduced reaction of the sample molecules and a time-delayed X-ray pulse was used to probe the progress of the reaction. Femtosecond laser pulses at the centre wavelength of 800 nm were generated from a Ti:sapphire regenerative amplifier and converted to 100-fs pulses at a wavelength of 267 nm by third-harmonic generation. The laser beam was focused by a lens to a spot of 200-µm diameter at the sample position, yielding a laser fluence of 1.5 ml mm⁻². Femtosecond X-ray pulses were generated from an X-ray free-electron laser (XFEL) by self-amplified spontaneous emission. The X-ray pulses have a centre energy of 12.7 keV with a narrow energy bandwidth ($\Delta E/E = 0.3\%$). The X-ray beam was focused to a spot 40 µm in diameter at the sample position. The laser and X-ray beams were overlapped at the sample position with a crossing angle of 10°. The X-ray scattering patterns from the photoexcited $[Au(CN)_2]_3$ solution generated by the X-ray pulses were measured with an area detector (MX225-HS, Rayonix) over a q range of 1.37 Å⁻¹ to 6.5 Å⁻¹ with a sample-to-detector distance of 46 mm.

The TRXL data were measured at various time delays in the range -1,040 fs to 2,235 fs with a time step of 25 fs, yielding a total of 132 time delays. The laser-off images were acquired with the X-ray pulse arriving 20 ps earlier than the laser pulse (that is, with a -20 ps time delay) to probe the (unexcited) molecules in the ground state while ensuring the same average temperature of the sample solution. These laser-off images were repeatedly measured before every laser-on image and were subtracted from the laser-on images to yield time-resolved difference scattering patterns of the [Au(CN)₂⁻]₃ solution. Each scattering image was obtained with a single X-ray pulse and, to achieve a signal-to-noise ratio sufficient for data analysis, around 2,800 images were acquired at each time delay. The resultant time-resolved difference scattering curves are shown in Extended Data Fig. 2a.

For the sample, we used an aqueous solution of a gold oligomer complex, $[Au(CN)_2^{-}]_n$. In the solution of $Au(CN)_2^{-}$ at the 300 mM concentration used in this work, the $[Au(CN)_2^{-}]_3$ trimers are dominantly present compared with dimers or monomers of $Au(CN)_2^{-}$. The sample solution was excited by the laser pulses of 267-nm wavelength. The sample solution was circulated through a nozzle with a 100-µm-thick aperture. To supply a fresh sample for every laser and X-ray shot, the flow velocity of the sample was set to be over 3 m s⁻¹. To prevent the scattering signal from contamination by radiation-damaged sample molecules, the sample in the reservoir was replaced with a fresh one whenever the transient signal measured at 100 ps was no longer reproduced. Even if the transient signal at 100 ps did not change, the sample in the reservoir was regularly replaced (every 2–3 h of measurement) to ensure the supply of fresh samples.

TRXL experiments at SACLA

The TRXL experiments were also performed at the BL3 beamline of SACLA (the SPring-8 ångstrom compact free-electron laser). In the TRXL experiment, the photoinduced reaction of the gold complex was initiated by an optical laser pulse and its progress was probed by a time-delayed X-ray pulse. Femtosecond laser pulses at a centre wavelength of 800 nm were generated from a Ti:sapphire regenerative amplifier and converted to 200-fs pulses at a wavelength of 267 nm by third-harmonic generation. The laser beam was focused by a lens to a spot of 300-µm diameter at the sample position, yielding a laser fluence of about 2 mJ mm⁻². Femtosecond X-ray pulses were generated from an XFEL by self-amplified spontaneous emission. The X-ray pulses have a centre energy of 15 keV with a narrow energy bandwidth ($\Delta E/E = 0.6\%$). The X-ray beam was focused to a spot of diameter 200 µm

at the sample position. The laser and X-ray beams were overlapped at the sample position with a crossing angle of 10°. The X-ray scattering patterns from the photoexcited [Au(CN)₂⁻]₃ solution generated by the X-ray pulses were measured with an area detector (LX255-HS, Rayonix) over a *q* range of 1.37 Å⁻¹ to 6.5 Å⁻¹ with a sample-to-detector distance of 30 mm. To improve the time resolution of the TRXL measurements, a timing monitor installed at SACLA was used. The TRXL data were measured at various time delays from -740 fs to 2,260 fs with a time step of 25 fs, yielding a total of 121 time delays. At each time delay, about 2,000 images were accumulated. The same data-acquisition scheme as that used at PAL-XFEL was used for the TRXL experiment at SACLA. The resultant time-resolved difference scattering curves are shown in Extended Data Fig. 2b.

As can be seen in Extended Data Fig. 2a, b, the two TRXL datasets measured at PAL-XFEL and SACLA are nearly identical, except for the time resolution (170 fs at PAL-XFEL and 320 fs at SACLA), indicating that the difference scattering signals are highly reproducible at either facility. In this work, we primarily used the TRXL dataset measured at PAL-XFEL, which has better time resolution and signal-to-noise ratio.

To eliminate the contribution of solvent heating, the difference scattering signal of 40 mM FeCl₃ solution was measured from a separate TRXL experiment, as shown in Extended Data Fig. 8, with the same experimental conditions used in the TRXL experiment on the gold trimer complex at SACLA (See Supplementary Information for details).

Singular value decomposition

To extract the kinetics from the measured TRXL data of $[Au(CN)_2]_3$, we applied an SVD analysis. To do so, we built an $n_a \times n_t$ data matrix, A, the column vectors of which are experimental time-resolved difference scattering curves, where n_a is the number of q points in the difference scattering curves and n_i is the number of time-delay points. By SVD, the matrix A is decomposed into three matrices satisfying the relationship $A = USV^{T}$ (where V^{T} is the transpose of matrix V). U is an $n_{a} \times n_{t}$ matrix the column vectors of which are called the left singular vectors (LSVs) of A, V is an $n_t \times n_t$ matrix the column vectors of which are the RSVs of A, and S is a diagonal $n_t \times n_t$ matrix the diagonal elements of which are called the singular values of A. The matrices U and V follow the relationships $U^{T}U = I_{n}$ and $V^{T}V = I_{n}$, respectively, where I_{n} is an $n_{t} \times n_{t}$ identity matrix. The LSVs represent time-independent q spectra, the RSVs represent the time-dependent amplitude changes of the corresponding LSVs, and the singular values represent the weights of the corresponding LSVs and RSVs. The singular values are ordered such that $s_1 \ge 1$ $s_2 \ge ... \ge s_n \ge 0$, and so (both left and right) singular vectors in the left-hand columns have larger contributions to the experimental data matrix A. The first and second RSVs shown in Extended Data Fig. 2c were well fitted with the convolution of a Gaussian function with a full width at half-maximum (FWHM) of 170 ± 50 fs and an exponential function with a time constant of 1.1 ± 0.1 ps. The errors are the standard errors of the mean determined from around 2,800 independent measurements.

Residual difference scattering curves, $q\Delta S_{residual}(q, t)$

To more effectively visualize the scattering intensities arising from wavepacket motions, we extracted residual difference scattering curves, $q\Delta S_{\text{residual}}(q, t)$, from raw experimental difference scattering curves, $q\Delta S(q, t)$, of photoexcited $[\text{Au}(\text{CN})_2^-]_3$. $\Delta S(q, t)$ can be represented as follows:

$$\Delta S(q, t) = c_{T_{1}'}(t) [S_{T_{1}'(t)}(q) - S_{S_{0}^{eq}}(q)] + c_{T_{1}}(t) [S_{T_{1}(t)}(q) - S_{S_{0}^{eq}}(q)] + [c_{T_{1}'}(t) + c_{T_{1}}(t)] [S_{S_{0}(t)}(q) - S_{S_{0}^{eq}}(q)] + \Delta S_{heat}(q, t),$$
(1)

where $S_{S_0(t)}(q)$, $S_{T_1(t)}(q)$ and $S_{T_1(t)}(q)$ are the scattering patterns of the instantaneous structures of the S₀, T'₁ and T₁ states, respectively, that evolve following vibrational wavepacket motions. $S_{S_1^{ee}}(q)$ is the

scattering pattern of the equilibrium S_0 structure, and $c_{T'_1}(t)$ and $c_{T_1}(t)$ are the time-dependent relative populations of the T'_1 and T_1 states, respectively. $\Delta S_{heat}(q, t)$ represents the change in scattering intensity induced by solvent heating.

Alternatively, $\Delta S(q, t)$ can be represented as the sum of scattering contributions of: (1) the dynamics of the T₁'-to-T₁ transition, $\Delta S_{\text{transit}}(q, t)$; (2) the temporal oscillations of scattering intensities owing to vibrational wavepacket motions in the S₀, T₁' and T₁ states—that is, the residual difference scattering curves, $\Delta S_{\text{residual}}(q, t)$; and (3) the solvent heating, $\Delta S_{\text{heat}}(q, t)$, as

$$\Delta S(q, t) = \Delta S_{\text{transit}}(q, t) + \Delta S_{\text{residual}}(q, t) + \Delta S_{\text{heat}}(q, t), \quad (2)$$

where

$$\Delta S_{\text{transit}}(q,t) = c_{T_1'}(t) [S_{T_1'^{\text{eq}}}(q) - S_{S_0^{\text{eq}}}(q)] + c_{T_1}(t) [S_{T_1^{\text{eq}}}(q) - S_{S_0^{\text{eq}}}(q)], \quad (3)$$

$$\Delta S_{\text{residual}}(q, t) = [c_{T_{1}'}(t) + c_{T_{1}}(t)][S_{S_{0}(t)}(q) - S_{S_{0}^{\text{eq}}}(q)] + c_{T_{1}'}(t)[S_{T_{1}'(t)}(q) - S_{T_{1}^{\text{req}}}(q)] + c_{T_{1}}(t)[S_{T_{1}(t)}(q) - S_{T_{1}^{\text{eq}}}(q)]$$
(4)

and $S_{T_1^{req}}(t)$ and $S_{T_1^{eq}}(q)$ are the scattering intensities arising from the equilibrium structure of the T_1' and T_1 states, respectively. To extract the residual difference scattering curves, $q\Delta S_{residual}(q, t)$, we subtracted the contributions of: (1) the T_1' -to- T_1 transition dynamics; and (2) the solvent heating from $\Delta S(q, t)$, as described in the following.

We note that $\Delta S_{\text{transit}}(q, t)$ shows the dynamics described by an exponential with a time constant of 1.1 ps, whereas $\Delta S_{residual}(q, t)$ exhibits temporal oscillation owing to wavepacket motions. To extract $\Delta S_{\text{residual}}(q, t)$ from $\Delta S(q, t)$, we examined the RSVs obtained from the SVD analysis described in the previous section. As can be seen in Extended Data Fig. 2d, the first two RSVs exhibit exponential dynamics with superimposed temporal oscillations, whereas other RSVs oscillate only around zero. By removing the exponential components from the first two RSVs, we can remove the scattering contribution of the T'_1 -to- T_1 dynamics, $\Delta S_{\text{transit}}(q, t)$, and the contribution of the solvent heating, $\Delta S_{\text{heat}}(q, t)$. In fact, as can be seen in Extended Data Fig. 7, the TRXL data from our previous TRXL study⁹ on [Au(CN)₂⁻]₃, which involves only the contributions from $\Delta S_{\text{transit}}(q, t)$ and $\Delta S_{\text{heat}}(q, t)$, can be well explained by the first two RSVs. Therefore, the removal of the exponential components from the first two RSVs of $\Delta S(q, t)$ removes $\Delta S_{\text{transit}}(q, t)$ and $\Delta S_{\text{heat}}(q, t)$, leaving only $\Delta S_{\text{residual}}(q, t)$.

To eliminate the exponential components from the first two singular vectors, we defined new matrices, U', V' and S', which contain only the first two column vectors of U, V and S, respectively. In other words, U' is an $n_q \times 2$ matrix containing only the first two LSVs of U, S' is a 2×2 diagonal matrix containing only the first two singular values of S, and V' is an $n_t \times 2$ matrix containing only the first two RSVs of V. We then defined a matrix C that represents the exponential temporal profiles of the two RSVs. Elements of the matrix C were calculated as follows:

$$\mathbf{c}_1(t) = \text{IRF}(t) \otimes [\exp(-t/1.1\text{ps})\theta(t)]$$
 and

$$\mathbf{c}_{2}(t) = \mathsf{IRF}(t) \otimes [(1 - \exp(-t/1.1\mathsf{ps}))\theta(t)], \tag{5}$$

where $\mathbf{c}_1(t)$ and $\mathbf{c}_2(t)$ are the first and second column vectors of *C*, IRF(*t*) is the instrument response function determined from the fitting of the first and second RSVs shown in Extended Data Fig. 2c, $\theta(t)$ is the Heaviside step function and \otimes is the convolution operator. Then, a 2 × 2 parameter matrix *P* is defined to relate *C* to *V'*. Elements of *P* were adjusted to minimize the discrepancy between *V'* and *CP*. As a result, the exponential components contained in the first two RSVs (*V'*) can be represented by an optimized *CP*. Then, time-dependent scattering intensities, which are governed by the exponential dynamics of the

first two RSVs, were calculated by the following relationship, $A' = U'S'(CP)^{T}$, where the scattering intensities are column vectors of the A' matrix. Finally, A' was subtracted from A, giving $\Delta S_{residual}(q, t)$ as column vectors of the matrix A - A'.

Structural analysis using residual difference scattering curves As shown in Fig. 2, we fitted $\Delta S_{residual}(q, t)$ by the theoretical difference scattering curves, $\Delta S_{theory}(q, t)$, to extract the temporal changes of the individual interatomic Au–Au distances– $R_{AB}(t)$, $R_{BC}(t)$ and $R_{AC}(t)$ –from the experimental residual difference scattering curves, $\Delta S_{residual}(q, t)$. To do so, we constructed theoretical difference scattering curves, $\Delta S_{theory}(q, t)$, as follows:

$$\Delta S_{\text{theory}}(q,t) = [c_{T_1'}(t) + c_{T_1}(t)] \Delta S_{S_0}(q,t) + c_{T_1'}(t) \Delta S_{T_1'}(q,t) + c_{T_1}(t) \Delta S_{T_1}(q,t).$$
(6)

In equation (6), $\Delta S_X(q, t)$ is the difference in scattering intensity arising from a transient structure of state $X(S_X(q, t); X = \{S_0, T'_{1'}, T_1\})$, and that arising from the equilibrium structure of state $X, S_{\chi^{eq}}(q)$, calculated by the following equation:

$$\Delta S_{\chi}(q,t) = S_{\chi}(q,t) - S_{\chi^{eq}}(q).$$
⁽⁷⁾

Scattering intensities arising from the molecular structures of S_0 , T'_1 and T_1 were calculated using the Debye equation as follows:

$$S(q) = 3F_{Au}^2(q) + 2F_{Au}^2(q) \left(\frac{\sin(qR_{AB})}{qR_{AB}} + \frac{\sin(qR_{BC})}{qR_{BC}} + \frac{\sin(qR_{AC})}{qR_{AC}}\right), \quad (8)$$

where $F_{Au}(q)$ is the atomic form factor of an Au atom. Debye–Waller factors (DWFs) were introduced to consider distributions of interatomic distances: for S₀, arising from the weak Au–Au bonding in S₀, and for T'₁, arising from the spatial broadening of the initially created wavepacket, (which is induced by a finite pulse duration of the pump pulse), on the PES of T'₁. DWFs for T₁ were not used, as their use did not improve the fit quality. When including the DWF, here equation (8) is modified to become equation (5) of the Supplementary Information. The DWFs for S₀ and T'₁ used in the fitting analysis are shown in Supplementary Table 1.

For the fitting, the discrepancy between $\Delta S_{\text{residual}}(q, t)$, and $\Delta S_{\text{theory}}(q, t)$ was minimized by independently adjusting the structural parameters (R_{AB} , R_{BC} and θ) of the S₀, T'₁ or T₁ states at each time delay, and time-dependent molecular structures were obtained from the fit over the entire time range. At each time delay, the molecular structure was optimized using a maximum likelihood estimation with the χ^2 estimator, which is given by the following equation:

$$\chi^{2} = \frac{1}{n_{q} - p - 1} \sum_{i}^{n_{q}} \frac{(c_{s} \Delta S_{\text{theory}}(q_{i}, t) - \Delta S_{\text{residual}}(q_{i}, t))^{2}}{\sigma(q_{i}, t)^{2}}.$$
 (9)

Here, n_q is the number of fitted q points, p is the number of fitting parameters, σ is the standard deviation of the data and c_s is the scaling factor between the theoretical and experimental difference curves. The fitting was performed with the MINUIT software package and the error values were obtained with the *MINOS* algorithm in MINUIT.

The TRXL signal can be sensitive to wavepacket motions on any of the structurally distinct S_0 , T'_1 and T_1 states, and so we examined which state is associated with the residual difference scattering curves. The first, second and third terms in equation (6) correspond to wavepacket motions in S_0 , T'_1 and T_1 , respectively. Depending on the number of participating states, those terms were selectively used. For example, when we considered the wavepacket motion in a single electronic state, we considered only the term corresponding to that electronic state among the three terms in equation (6); the other two terms were neglected. When we considered wavepacket motions in two electronic states, we considered the corresponding two terms in equation (6) and neglected the remaining term. We first tried structural analysis considering only one of S₀, T'₁ and T₁. As shown in Extended Data Fig. 3, the structural analysis performed using only S₀ yielded the best fit to the experimental data among the three cases, but there still remained a discrepancy between the experimental data and the theoretical fits. We therefore considered additional contributions: the best fit to $\Delta S_{\text{residual}}(q, t)$ —shown in Fig. 2a and Extended Data Fig. 3—was obtained when T'₁ was considered together with S₀, indicating that the residual difference scattering curves arise from wavepacket motions on the PESs of both S₀ and T'₁.

We note that the structural analysis described above was conducted for time delays later than the experimental IRF (>170 fs). The structural analysis for time delays earlier than 170 fs is described in the section 'Structural analysis for transient structures around t = 0'. Although we used all of the structural parameters (R_{AB} , R_{BC} and θ) of S₀ and T'₁ as fitting parameters in the structural analysis, we observed relatively small structural changes at later times (t > 360 fs), compared with structural changes at earlier times; in particular, the changes in R_{AB} and R_{BC} of T'_1 showed a strong correlation. Accordingly, we checked whether the experimental data could be satisfactorily fitted even when fewer structural parameters of T'_1 were used for fitting in the later time range. To do so, we classified vibrations of T'_1 at later times into three types of vibrational motions (symmetric stretching, asymmetric stretching and bending), and the fitting parameters of T₁ were collectively adjusted to simulate each type of motion. For simulating symmetric stretching, the transient structures of T'_1 at later times were set to be $R_{AB} = R_{BC} = R$ and $\theta = 180^\circ$, leaving R as the only fitting parameter at each time delay. For simulating asymmetric stretching, the parameters of T₁ were adjusted as $R_{AB} = 2.82 \text{ Å} + R$, $R_{BC} = 2.82 \text{ Å} - R$ and $\theta = 180^\circ$, also leaving R as the only fitting parameter at each time delay. Finally, for simulating bending, R_{AB} and R_{BC} of T₁ were fixed to 2.82 Å and θ was used as the only fitting parameter at each time delay. As a result, only one fitting parameter of T₁ was used for all the three types of vibrational motions in the late time range (t > 360 fs). By contrast, for S₀ we used all three structural parameters, R_{AB} , R_{BC} and θ .

Following this approach, we performed the structural analysis for each of the three types of vibrational motions. As can be seen in Extended Data Fig. 9a–c, the structural analysis considering the symmetric stretching yielded the best fits to the experimental data among the three cases. Also, the fits using symmetric stretching are equally good as the fits obtained by using all the three structural parameters of T₁, as shown in Extended Data Fig. 9d. This result indicates that only symmetric stretching is observed for T₁ in the current TRXL data. We also note that, after 1,500 fs, the transient structures of T₁ ($R_{AB} = 2.82$ Å, $R_{BC} = 2.82$ Å, $\theta = 180^{\circ}$) for simplicity, as shown in Fig. 2b, c, because the quality of the fit to $q\Delta S_{residual}(q, t)$ did not deteriorate even when the structure values of T₁ were set to the equilibrium structure values for all time delays after 1,500 fs.

From the structural analysis described above, we obtained transient structures of S_0 and T'_1 in the time range from 170 fs to 2,235 fs, as shown in Fig. 2b–e. To identify the reaction mechanism of ultrafast bond formation in the gold trimer complex, we tracked the wavepacket motion in the excited state by inspecting the structural changes of T'_1 at earlier times. For example, we checked the transient structure of T'_1 at 185 fs ($R_{AB} = 2.81$ Å, $R_{BC} = 3.13$ Å, $\theta = 158^{\circ}$) and 210 fs ($R_{AB} = 2.83$ Å, $R_{BC} = 3.11$ Å, $\theta = 157^{\circ}$) and found that for these time delays, the values of R_{AB} for T'_1 are similar to the equilibrium value, that is, 2.82 Å. By contrast, the values of R_{BC} for T'_1 at 185 fs and 210 fs are longer than R_{BC} at equilibrium (2.82 Å). This observation indicates that the covalent bond in the shorter Au–Au pair (of the ground state) is formed sooner, during the earlier time range, whereas the other covalent bond, in the longer Au–Au pair, forms later, supporting path 1 of Fig. 1.

In the structural analysis presented in this work, we used an asymmetric equilibrium structure for S_0 . In our previous TRXL study⁹ on $[Au(CN)_2^-]_3$ —performed with lower time resolution than in this work—the TRXL data were equally well fitted by a symmetric S_0 structure when an appropriate Debye–Waller factor was used. Therefore, in the present work, we also considered the possibility that S_0 has a symmetric structure where R_{AB} is equal to R_{BC} . As shown in Extended Data Fig. 10, the structural analysis using the symmetric equilibrium S_0 structure does not give satisfactory agreement with the experimental data. Thus, by performing the TRXL measurement with higher time resolution and resolving the signatures of molecular vibrations, we confirm that the equilibrium structure of S_0 is asymmetric.

Structural analysis for transient structures around t = 0

To extract the wavepacket trajectory and obtain the transient structures of S₀ and T₁ on timescales shorter than the temporal width of the experimental IRF (<170 fs), and to visualize the progress of the bond formation process more clearly and obtain accurate timescales of the earlier bond formation, we performed a structural analysis for transient structures around t = 0 considering the convolution of the molecular response with the IRF, instead of conducting the structural analysis directly on the residual difference scattering curves described in the previous section. To do so, we modelled the interatomic Au–Au distances of S₀ and T₁', $R_{AB}(t)$, $R_{BC}(t)$ and $R_{AC}(t)$, from 0–170 fs using the polynomial functions

$$R(t) = \sum_{i=0}^{N} a_{N-i} t^{N-i}, \qquad (10)$$

where *N* represents the *N*th order polynomial function and a_{N-i} is the coefficient of the polynomial function. Also, constraints were applied to the Au–Au distances calculated by the polynomial functions to smoothly connect the structure at 0 fs (S_0^{eq} = the FC region) and the structure at 185 fs obtained from the structural analysis.

Using the Au–Au distances calculated by the polynomial functions at various time delays, we calculated the theoretical difference scattering intensities, $\Delta S_{\text{theory}}(q, t)$, following equations (6)–(8), then convoluted them with the IRF determined in Extended Data Fig. 2c, IRF(t), using equation (11):

$$\Delta S_{\text{conv}}(q,t) = \Delta S_{\text{theory}}(q,t) \otimes \text{IRF}(t).$$
(11)

The resultant convoluted curves, $\Delta S_{conv}(q, t)$, were compared with the experimental residual difference scattering curves, $\Delta S_{residual}(q, t)$, in a time range from –140 fs to 160 fs, to optimize the coefficients of the polynomial functions using the χ^2 estimator, given by

$$\chi^{2} = \frac{1}{n_{q}n_{t} - p - 1} \sum_{i}^{n_{q}} \sum_{j}^{n_{t}} \frac{(c_{s}\Delta S_{conv}(q_{i}, t_{j}) - \Delta S_{residual}(q_{i}, t_{j}))^{2}}{\sigma_{ij}^{2}}, \quad (12)$$

where n_q is the number of fitted q points, n_t is the number of fitted time delays (-140 fs $\leq t \leq 160$ fs), p is the number of fitting parameters, σ_{ij} is the standard deviation, and c_s is the scaling factor between the theoretical and experimental difference curves.

The structures around t = 0 shown in Fig. 2b, d were obtained using fourth-order polynomial functions because the third-order and fifth-order polynomial functions yielded fitting qualities poorer than and similar to the fourth-order polynomial functions, respectively.

Normal-mode calculation

Geometry optimization and normal-mode calculations were performed using DFT for the S_0 and T_1 states of $[Au(CN)_2^-]_3$, and using time-dependent DFT for the S_1 state of $[Au(CN)_2^-]_3$. For the S_0 state, the PBE0 exchange-correlation functional with empirical dispersion

(Grimme's D3 method) was used to reasonably describe the weak interaction between Au atoms. The ωB97XD functional was used for the S₁ and T₁ states. The aug-cc-pVTZ-PP relativistic effective core potentials were used for Au atoms and the aug-cc-pVDZ basis set was used for C and N atoms. The solvent (water) effect was modelled using the integral equation formalism version of the polarizable continuum model. Normal modes of the T₁ state were calculated for the equilibrium structure that was optimized by the DFT calculation, and the optimized structure was in agreement with the equilibrium structure of T₁ determined from the experimental data. By contrast, from the DFT calculation the optimized structure of S_0 was determined to be symmetric, and therefore, instead, the normal modes of the S_o state were calculated by a single-point calculation using the asymmetric equilibrium structure refined with the experimental data. Several normal modes for S₀ and T₁ are shown in Extended Data Figs. 5 and 6, respectively. All the calculations were performed using the Gaussian09 program.

Fourier power spectrum of $q\Delta S_{residual}(q, t)$

The Fourier power spectrum at each q value was obtained by Fourier transform of $q\Delta S_{residual}(q, t)$ at later times (>360 fs), and each spectrum was normalized at its maximum value. All the normalized spectra at various q values were averaged to yield the averaged Fourier power spectrum shown in Fig. 4c.

Data availability

The datasets generated and analysed here are available from the corresponding author on reasonable request.

Code availability

The codes used for the analysis here are available from the corresponding author on reasonable request.

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Author contributions H.I. supervised the project; S.-i.A. and H.I. designed the experiment; J.G.K. and H.I. developed the data analysis strategy; J.G.K., S.N., H. Kim, E.H.C., T.S., T.W.K., K.H.K., H. Ki, Jungmin Kim, M.C., Y.L., J.H., K.YO., K.I., R.F., J.H.L., J.P., I.E., S.H.C., S.K., M.K., T.K., S.O., M.Y., S.J.L., S.L., C.W.A., S.C., Jeongho Kim, S.-i.A. and H.I. performed the experiments; J.G.K., H. Kim, E.H.C., K.H.K., D.-S.A. and T.J. analysed the data; J.M. and Joonghan Kim performed quantum chemical calculations; J.G.K., S.N., Jeongho Kim, S.-i.A. and H.I. wrote the manuscript with contributions from all authors.

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Additional information

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Correspondence and requests for materials should be addressed to H.I. Peer review information Nature thanks Richard A. Mathies, Martin Meedom Nielsen and the other, anonymous, reviewer(s) for their contribution to the peer review of this work. Reprints and permissions information is available at http://www.nature.com/reprints.



Extended Data Fig. 1| Schematic of photoinduced bond formation in

 $[Au(CN)_2]_3$, Upon laser excitation (with energy represented by hv), wavepackets are created in both of the ground and excited states. The excited-state wavepacket in the T'_1 state is prepared in the FC region after the ultrafast intersystem crossing from the initially excited singlet state (S_1) to a triplet excited state (T'_1). The excited-state wavepacket created in the FC region should move towards the equilibrium structure of T'_1 , which has two equivalent covalent Au–Au bonds between adjacent gold atoms (right inset, yellow spheres; blue and white spheres denote N and C atoms, respectively). The trajectory of the wavepacket from the FC region to the equilibrium structure of T'_1 eventually determines the reaction trajectories of the ultrafast bond formation and hints towards its reaction mechanism. Three candidate reaction mechanisms of bond formation (paths 1, 2 and 3), described in the text, are represented by blue arrows on the nuclear coordinates of R_{AB} versus R_{BC} . In short, path 2 represents a concerted bond formation mechanism and path 1 and path 3 represent asynchronous bond formation mechanism. Path 1 and path 3 are distinct, depending on which bond is formed first between the A–B pair and the B–C pair. The initial motion of the excited-state wavepacket affects the initial motion of the ground-state wavepacket in the S₀ state, because impulsive Raman scattering generating the ground-state wavepacket can occur non-impulsively, owing to the finite pulse duration (-100 fs), as described in Supplementary Information. After the initial motions of the wavepackets in the ground and excited states, the wavepackets oscillate around their equilibrium structures.





 $q\Delta S(q, t)$ measured at PAL-XFEL and their fits (red lines) using an exponential 1.1-ps time constant convoluted with an IRF with a FWHM of 170 fs. **d**, The first five RSVs resulting from the SVD analysis on the data measured at PAL-XFEL, multiplied by their corresponding singular values s_1 , s_2 , s_3 , s_4 and s_5 .



Extended Data Fig. 3 | **Results of the structural analysis using residual difference scattering curves. a**, Experimental residual difference scattering curves, $q\Delta S_{\text{residual}}(q, t)$, measured from -1,040 fs to 2,235 fs. **b**-e, Theoretical fits of $q\Delta S_{residual}(q, t)$ obtained from the structural analyses considering wavepacket motions in the S_0 state (**b**), the T'_1 state (**c**), the T_1 state (**d**), or both the S_0 and T'_1 states (**e**). Only the last analysis (using S_0 and T'_1) gives a satisfactory fit quality.



Extended Data Fig. 4 | Assignment of vibrational modes using vibrational frequencies and vibrational motions. Each vibrational normal mode has a specific structural motion with a characteristic frequency. For example, a simple nonlinear triatomic molecule has three vibrational modes named after specific structural motions: symmetric stretching, asymmetric stretching and bending. The characteristic frequency v_n of a vibrational mode vibrating along a normal coordinate Q_n corresponds to the energy gap between adjacent vibrational states of each mode, where $n = \{a, b, c\}$ for symmetric stretching, asymmetric stretching, asymmetric stretching and bending, respectively. Vibrational frequencies are routinely measured by static or time-resolved spectroscopy that can probe vibrational transitions via infrared absorption or Raman scattering. Atomic motions themselves are not directly detected by spectroscopy, and thus the assignment of the observed frequencies to specific vibrational modes requires quantum chemical calculations that provide the connection between the vibrational frequencies and their corresponding atomic motions.

By comparing the vibrational frequencies determined from experiment (v_{exp}) and quantum chemical calculation, the measured vibrational frequency can be assigned to a specific normal mode. Direct characterization of vibrational motions requires a tool with structural sensitivity, for example TRXL, as presented in this work. In a TRXL measurement, photoexcitation with a coherent optical laser pulse creates vibrational wavepackets of certain vibrational modes, and scattering of an X-ray pulse directly probes the resultant time-dependent structural changes that are characteristic of the activated vibrational modes—such as the temporal changes of the interatomic distances (R_{AB} , R_{BC} and R_{AC}) in [Au(CN)₂⁻]₃. On the basis of direct information of both vibrational motions and vibrational frequencies obtained with TRXL, vibrational assignments can be made more accurately, and even the locations of vibrational wavepackets and the trajectories of their motions in multidimensional nuclear coordinates can be determined.



Extended Data Fig. 5 | Normal modes of the S0 state. Normal modes of the S0 state. Normal modes of the S0 state with frequencies in a range from 20 cm⁻¹ to 170 cm⁻¹, obtained from DFTshown. Displacement vectors of each normal mode are indicated by red arrows
for the Au atoms (yellow) and blue arrows for the other atoms (C, grey spheres).calculations. The frequency and atomic motions of each normal mode areN, blue spheres).

Au-Au-Au asymmetric stretching



 $Extended Data Fig. 6 | Normal modes of the T_1 state. Normal modes of the T_1 state, as in Extended Data Fig. 5.$



T₁_#4 mode Frequency: 53 cm⁻¹ Au-Au-Au bending + C-Au-C rocking



T₁_#8 mode Frequency: 79 cm⁻¹ C-Au-C bending



T₁_#12 mode Frequency: 92 cm⁻¹ Au-Au-Au symmetric stretching



Extended Data Fig. 7 | **SVD analysis on the TRXL data of [Au(CN)**₂⁻]₃ **measured in the previous TRXL study.** See ref.⁹. Shown are the first four RSVs multiplied by their corresponding singular values.



Extended Data Fig. 8 Solvent heating contribution to the TRXL signal. a, Experimental difference scattering curves, $q\Delta S(q)$, of FeCl₃ solution measured at time delays from -740 fs to 2,260 fs. **b**, The first four LSVs multiplied by their corresponding singular values. **c**, The first four RSVs multiplied by their corresponding singular values. Only the first LSV and RSV

contain meaningful signals, and so a single difference scattering curve (that is, the first LSV) accounts for the contribution to solvent heating on the scattering data measured with a water solvent. In the structural analysis, the first LSV was used as a scattering intensity change upon increase in temperature of the water solvent, $\Delta S_{heat}(q)$.

	Symmetric stretching of T ₁ '	Asymmetric stretching of T_1	Bending of T_1'	Considering all the structural parameters of T ₁ '
q∆S _{residual} (q,t) (a.u.)	a	b 360 fs	C 360 fs	d 360 fs
	410 fs	410 fs	410 fs	410 fs
	460 fs	460 fs	460 fs	460 fs
	510 fs	510 fs	510 fs	510 fs
	560 fs	560 fs	560 fs	560 fs
	610 fs	610 fs	610 fs	610 fs
	660 fs	660 fs	660 fs	660 fb
	710 fs	710 fs	710 fs	710 fs
	760 fs	760 fs	760 fs	760 fs
	810 fs	810 fs	810 fs	810 fs
	860 fs	860 fs	860 fs	860 fs
	910 fs	910 fs	910 fs	910 fs
	960 fs	960 fs	960 fs	960 fs
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	2 3 4 5 6	2 3 4 5 6 $\alpha(^{\text{A}-1})$	2 3 4 5 6	2 3 4 5 6
	$\mathcal{G}(\mathbf{A}^{*})$	Y (\(\(\))	$q(\mathbf{A}^{*})$	$\mathbf{Y}(\mathbf{A}^{*})$

Extended Data Fig. 9 | **Structural analysis of the three types of vibrational motions of the T₁ state.** Experimental residual difference scattering curves (black lines) at several time delays after 360 fs and their theoretical fits (red lines), obtained from the structural analysis. **a**-**c**, For the structural analysis, vibrations of T'₁ at later times (>360 fs) were classified into three types of vibrational motions (symmetric stretching, asymmetric stretching and bending). We performed the structural analysis for each of the three cases considering symmetric stretching motions (**a**), asymmetric stretching motions (**b**) and bending motions (**c**) of T'_1 . **d**, For comparison, all the three structural parameters of T'_1 were used for the structural analysis.



Extended Data Fig. 10 | Structural analysis using asymmetric and symmetric structures of S₀. Experimental residual difference scattering curves (black lines) at selected time delays and their theoretical fits (red lines) obtained from the structural refinements considering the asymmetric bent S₀.

structure (left) or symmetric bent S_0 structure (right). The asymmetric case gives superior fit qualities compared to the symmetric case, indicating that the equilibrium structure of S_0 is asymmetric and bent.