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Femtosecond X-ray Liquidography Visualizes Wavepacket Trajectories in Multidimensional Nuclear Coordinates for a Bimolecular Reaction

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dynamics of photoinduced reactions. The motions of vibrational wavepackets are often discussed in the interpretation of observables measured with various time-resolved vibrational or electronic spectroscopies but mostly in terms of the frequencies of wavepacket motions, which are approximated by normal modes, rather than the actual positions of the wavepacket. Although the time-dependent positions (that is, the trajectory) of wavepackets are hypothesized or drawn in imagined or calculated potential energy surfaces, it is not trivial to experimentally determine the trajectory of wavepackets, especially in multidimensional



nuclear coordinates for a polyatomic molecule. Recently, we performed a femtosecond X-ray liquidography (solution scattering) experiment on a gold trimer complex (GTC), $[Au(CN)_2^-]_3$, in water at X-ray free-electron lasers (XFELs) and elucidated the time-dependent positions of vibrational wavepackets from the Franck–Condon region to equilibrium structures on both excited and ground states in the course of the formation of covalent bonds between gold atoms.

Bond making is an essential process in chemical reactions, but it is challenging to keep track of detailed atomic movements associated with bond making because of its bimolecular nature that requires slow diffusion of two reaction parties to meet each other. Bond formation in the solution phase has been elusive because the diffusion of the reactants limits the reaction rate of a bimolecular process, making it difficult to initiate and track the bond-making processes with an ultrafast time resolution. In principle, if the bimolecular encounter can be controlled to overcome the limitation caused by diffusion, the bond-making processes can be tracked in a time-resolved manner, providing valuable insight into the bimolecular reaction mechanism. In this regard, GTC offers a good model system for studying the dynamics of bond formation in solution. Au(I) atoms in GTC exhibit a noncovalent aurophilic interaction, making GTC an aggregate complex without any covalent bond. Upon photoexcitation of GTC, an electron is excited from an antibonding orbital to a bonding orbital, leading to the formation of covalent bonds among Au atoms. Since Au atoms in the ground state of GTC are located in close proximity within the same solvent cage, the formation of Au–Au covalent bonds occurs without its reaction rate being limited by diffusion through the solvent.

Femtosecond time-resolved X-ray liquidography (fs-TRXL) data revealed that the ground state has an asymmetric bent structure. From the wavepacket trajectory determined in three-dimensional nuclear coordinates (two internuclear distances and one bond angle), we found that two covalent bonds are formed between three Au atoms of GTC asynchronously. Specifically, one covalent bond is formed first for the shorter Au–Au pair (of the asymmetric and bent ground-state structure) in 35 fs, and subsequently, the other covalent bond is formed for the longer Au–Au pair within 360 fs. The resultant trimer complex has a symmetric and linear geometry, implying the occurrence of bent-to-linear transformation concomitant with the formation of two equivalent covalent bonds, and exhibits vibrations that can be unambiguously assigned to specific normal modes based on the wavepacket trajectory, even without the vibrational frequencies provided by quantum calculation.

KEY REFERENCES

Kim, J. G.; Nozawa, S.; Kim, H.; Choi, E. H.; Sato, T.; Kim, T. W.; Kim, K. H.; Ki, H.; Kim, J.; Choi, M.; Lee, Y.; Heo, J.; Oang, K. Y.; Ichiyanagi, K.; Fukaya, R.; Lee, J. H.; Park, J.; Eom, I.; Chun, S. H.; Kim, S.; Kim, M.; Katayama, T.; Togashi, T.; Owada, S.; Yabashi, M.; Lee, S. J.; Lee, S.; Ahn, C. W.; Ahn, D. S.; Moon, J.; Choi, S.; Kim, J.; Joo, T.; Kim, J.; Adachi, S. I.; Ihee, H. Mapping the emergence of molecular vibrations mediating bond formation. *Nature* **2020**, 582, 520–524.¹ The trajectories of the nuclear wavepackets were visualized in multidimensional nuclear

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(a) Q₁. Can we determine the equilibrium structure of a van der Waals complex in solution?



(b) Q₂. Is it possible to track the wavepacket trajectories in multidimensional nuclear coordinates?



(c) Q_3 . Can the vibrational modes be determined via directly visualizing the motion?



Figure 1. Three major questions $(Q_1, Q_2, and Q_3)$ represented in panels a, b, and c, respectively, are relevant to structural dynamics of photochemical reactions. (a) The equilibrium structure of a van der Waals complex in the liquid solution phase needs to be determined, but experimentally determining the structure is not trivial. In GTC, the equilibrium structure of the ground state determines the structure at the FC region, which is the starting point of the bond formation reaction. (b) Tracking the wavepacket trajectories in multidimensional nuclear coordinates can provide a decisive clue for revealing the reaction pathway and reaction mechanism. A scheme for wavepacket motions in the ground and excited states and photoinduced bond formation process in GTC is represented. The PES of T₁ is not shown for simplicity. (c) Molecular vibrations characterized by either vibrational frequencies or vibrational motions. By directly visualizing the vibrational motions, as well as obtaining the vibrational frequencies, more unambiguous assignments of the molecular vibrations are possible. Reproduced with permission from ref 1. Copyright 2020 Springer Nature.



Figure 2. Sensitivity map for the bond formation reaction of GTC. The TRXL signal is more sensitive to the position of the atom with the larger radius and the internuclear distance with the darker color. The sensitivity was evaluated by the degree of change of the difference X-ray scattering curve upon shifting each atomic position or internuclear distance. The sensitivity was scaled to yield the relative sensitivity by setting the maximum sensitivity for the atomic position or internuclear distance to be unity. Internuclear distances with sensitivities below a certain threshold are not shown for simplicity. The sensitivity of the solute–solvent cage term is indicated by the circle labeled " H_2O ".

coordinates by femtosecond X-ray liquidography, thereby revealing an asynchronous bond formation mechanism in $[Au(CN)_2^{-1}]_3$.

• Kim, K. H.; Kim, J. G.; Nozawa, S.; Sato, T.; Oang, K. Y.; Kim, T. W.; Ki, H.; Jo, J.; Park, S.; Song, C.; Sato, T.; Ogawa, K.; Togashi, T.; Tono, K.; Yabashi, M.; Ishikawa, T.; Kim, J.; Ryoo, R.; Kim, J.; Ihee, H.; Adachi, S.-i. Direct observation of bond formation in solution with femtosecond X-ray scattering. Nature 2015, 518, 385–389.² The formation of a gold trimer complex, [Au(CN)₂⁻]₃, was visualized in real time using femtosecond X-ray liquidography, and the three-dimensional structures of the subsequently formed reaction intermediates were also determined.

■ INTRODUCTION

Molecular vibrations play an important role in the progress of chemical reactions by providing atomic motions on the reaction coordinates and are often discussed as key parameters in the interpretation of reaction dynamics measured with various time-resolved spectroscopies^{3–27} and femtosecond X-ray or electron techniques.^{1,28–41} In femtosecond time-resolved experiments, an ultrashort laser pulse creates a coherent superposition of molecular vibrations, that is, vibrational wavepackets, and the

motions of wavepackets are often used to describe the molecular dynamics. Nevertheless, it is not trivial to experimentally track such trajectories of wavepackets, especially for polyatomic molecules, which have to be described in multidimensional nuclear coordinates. In fact, in most of the previous experimental studies on ultrafast dynamics of wavepackets, the vibrational wavepackets exhibiting oscillatory behaviors were interpreted in terms of the frequencies of their periodic motions that were approximated by normal modes, not their actual time-dependent positions. Even with correct assignments of the activated normal modes based on the frequency information, it is not trivial to experimentally map out the details of vibrational motions, for example, the relative amplitudes, phases, and displacement vectors of all relevant normal modes, which determine the trajectories of wavepackets. It is important to identify trajectories of wavepackets along reaction coordinates since they can provide a decisive clue for revealing reaction mechanisms. To address this issue, we performed femtosecond time-resolved X-ray liquidography (fs-TRXL) experiments^{1,2,28,33,42-44} at X-ray free-electron lasers (XFELs)^{45,46} and revealed such trajectories of vibrational wavepackets in both ground and excited states of a gold trimer complex (GTC), $[Au(CN)_2^{-}]_3$, in aqueous solution. Furthermore, based on the wavepacket trajectories, we identified the molecular vibrations

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involved in the photoreaction unambiguously, purely based on the experimental data.

For several decades, ultrafast bond-breaking processes of various molecular systems have been studied intensively using time-resolved techniques.^{33–35,47–53} Contrary to the case of a bond-breaking process, which is essentially a unimolecular process and therefore can be initiated by femtosecond optical excitation in a synchronized manner, bond making is in most cases a bimolecular process that requires two reactant parties to meet each other in order to form a chemical bond. Because slow diffusion of the reactants through the solvent, which usually takes about 10 ns at about 1 mM concentration.^{54,55} limits the reaction rate of a bimolecular process, it is difficult to synchronize laser excitation with the moment of the encounter of two parties. In this regard, the GTC offers an excellent model system for studying the dynamics of bond formation in solution. Due to aurophilicity, GTCs without any covalent bond are formed by van der Waals interactions between Au atoms, and after absorbing photons, the GTC forms covalent bonds among Au atoms.^{1,2,42,56-61} Since Au atoms in the ground state of GTCs are located in close proximity within the same solvent cage, the formation of Au-Au covalent bonds occurs without being limited by slow diffusion through the solvent. Therefore, ultrafast time resolution can be achieved for probing this bondmaking process as in typical unimolecular reactions synchronized with femtosecond optical excitation, but the ensuing reaction is of the nature of the bimolecular reaction between $Au(CN)_2^-$ monomers.

WAVEPACKET TRAJECTORIES: EQUILIBRIUM STRUCTURE, BOND FORMATION MECHANISM, AND VIBRATIONAL MODE ASSIGNMENT

General Reaction Scheme

The GTC, upon the irradiation with ultraviolet light, is excited from the ground state (S_0) to the singlet state (S_1) . A triplet excited state (T_1') is reached with 20 fs by intersystem crossing from S_1 , completing the covalent bond formation and the bentto-linear structural transformation. Subsequently, further contraction of the Au–Au bonds was observed in the transition from initially formed T_1' to another triplet excited state (T_1) with a time constant of 1–2 ps. Nevertheless, it was not possible to track the time-dependent positions of all atoms during the ultrafast bond formation process, whose schematic scenarios are illustrated in Figure 1.

Sensitivity of the TRXL Signal to Atomic Positions and Internuclear Distances

The TRXL signal is sensitive to the structural changes associated with a reaction of interest. Each atom in the molecule of interest contributes to the TRXL signal to a different degree depending on its X-ray scattering factor, and consequently the sensitivity of the internuclear distance to the TRXL signal also varies depending on the corresponding atoms. To aid in visualizing the sensitivity of atomic positions and internuclear distances to the TRXL signal, we checked how the atomic position and the internuclear distances quantitatively affect the TRXL signal and plotted the results, that is, a sort of a sensitivity map, in Figure 2. The detailed procedures to obtain the sensitivity map are described in the Supporting Information (SI). The sensitivity map is drawn such that the position of the atom and the internuclear distance contributing the TRXL signal more are indicated with larger radius and darker color, respectively. The sensitivity map visually demonstrates that the atomic positions

of CN ligands in the GTC do not affect the TRXL signal whereas only those of the three gold atoms have significant contributions. In other words, the GTC can be considered as a triatomic molecule made of three gold atoms as far as the TRXL signal is concerned. The map also shows that the shorter distances, R_{12} and R_{23} , have higher sensitivities than the longer distance, R_{13} (where R_{12} , R_{23} , and R_{13} refer to Au₁-Au₂ distance, Au₂-Au₃ distance, and Au₁-Au₃ distance, respectively).

(Q_1) Equilibrium Structure in the Ground State and at the Franck–Condon Region

The relevant issues with respect to the wavepacket trajectories are 3-fold; (i) the structure of the ground state, (ii) the bond formation mechanism, and (iii) the assignment of vibrational modes. First, the structure of the GTC in the ground state, which determines the structure at the Franck–Condon (FC) region, needs to be determined. It is not trivial to determine the structure of the van der Waals complex in the liquid solution phase (see Figure 1a). Basically, four general candidates, (i) symmetric linear, (ii) symmetric bent, (iii) asymmetric linear, and (iv) asymmetric bent, are possible for a triatomic molecule. Although the details are not discussed here, the fit quality of $q\Delta S(q,t)$ against calculated $q\Delta S(q,t)$ improved meaningfully when the structure has $R_{12} = 3.13$ Å, $R_{23} = 3.38$ Å, and $\theta = 119^{\circ}$ (θ refers to the Au₁–Au₂–Au₃ angle).

(Q₂) Bond Formation Mechanism: Asynchronous versus Synchronous

Second, the trajectory of the wavepacket from the FC region to the equilibrium structure of T_1' determines the reaction pathway of the ultrafast bond formation in the multinuclear coordinates of R_{12} vs R_{23} vs θ . While the route connecting the FC region and the equilibrium structure of T_1' in a straight line (path 2 in Figure 1b), corresponding to the synchronous bond formation, is the most straightforward pathway, other pathways can be imagined as well such as the cases of asynchronous bond formation where one covalent bond is formed first, and thereafter another covalent bond is formed (path 1 and path 3 in Figure 1b). The difference in the two pathways is the order in which covalent bonds are formed, where path 1 represents a pathway in which the covalent bond in the shorter Au–Au pair is formed earlier, and in contrast, path 3 represents the case of the longer Au–Au pair being formed earlier.

(Q₃) Assignment of Vibrational Modes

After forming the covalent bonds, the newly born GTC in the excited state should have vibrational motions just as the GTC in the ground state should. Vibrational motions involve a periodic change of molecular structure in various patterns such as stretching, bending, and wagging, and such motions are characterized by their oscillating frequencies, which can be measured in frequency or time domain using various spectros-copies (see Figure 1c).³⁻²⁶ However, it is difficult to directly identify the specific motion, that is how constituent atoms move, of a vibrational mode associated with the observed vibrational frequency. Figure 1c shows a simple triatomic molecule that has three modes of vibrational motions (symmetric stretching, asymmetric stretching, and bending), as an example. Each mode can be characterized by either how fast the molecule vibrates (that is, vibrational frequency) or how the molecule changes its structure over time (that is, vibrational motion). When assigning the measured vibrational frequencies to specific molecular vibrations, one commonly performs quantum chemical

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Semi-classical (SC) description for wavepackets



Figure 3. SC description of wavepacket dynamics. Under the SC treatment, a wavepacket can be described as a distribution of molecular structures. After excitation, a "particle" in the excited state (ES) is generated and the corresponding "hole" in the ground state (GS) on top of the existing distribution is generated. The difference obtained by subtracting the scattering signal before excitation from that after excitation is made of the particle in the ES and the hole in the GS. For conceptual convenience, the motion of the hole can be also treated as a particle in GS moving in the opposite direction to the hole.

calculations to obtain vibrational frequencies linked with vibrational normal modes for optimized molecular structures and then compares the experimentally obtained frequencies with the calculated normal-mode frequencies. However, the assignment of molecular vibrations based on such simple numerical comparison of only vibrational frequencies may lead to misinterpretation because polyatomic molecules can have many different vibrational modes of indistinguishably similar frequencies. Even with correct assignments, it is practically impossible to map out the details of vibrational motions, for example, their amplitude and phase, which determine the trajectories of vibrational wavepackets.

NUCLEAR WAVEPACKET MOTION

General Description

A femtosecond optical pulse can generate a wavepacket, which is the coherent superposition of wave functions. For a typical molecular vibration whose frequency is much higher than the thermal energy, kT, and for which the Huang–Rhys (HR) factor is much smaller than 1, after the interaction with a pump pulse that is resonant with the electronic excitation from the ground state, the wave function is $|\psi\rangle_{g(e)} \cong c_0|0\rangle_{g(e)} + c_1|1\rangle_{g(e)}$, where 0 and 1 are the vibrational quanta and g(e) represents the electronic ground (excited) state (see Figure 3D,E of ref 62). Here, the wave function represents the wavepacket for the vibrational mode, and the HR factor is a dimensionless factor proportional to the square of the displacement between potential energy surfaces (PESs) of the ground and excited states. This is the wavepacket for the vibrational mode. All the molecules within the excitation volume perform the same vibrational motion coherently with the same phase and amplitude according to the wave function. The vibrational wavepacket can also be created for nontypical cases, where higher vibrational quanta are involved and PESs of the ground

and excited states are displaced from each other (that is, a nonzero ${\rm HR}$ factor) as in this work.

The Case with the GTC

In the case of the GTC, because the structural difference between the ground and excited states is large, that is, the HR factors are large, and the frequencies of probed vibrational modes are small, one can think nearly classically. Right after the pump excitation, the molecule experiences a kick in the direction toward shorter bond length (larger bond angle), so the molecule starts to vibrate. Although there are broad distributions of bond lengths and bond angles, the wavepacket described above can still be applicable because of the large HR factors. Whereas in ordinary time-resolved optical spectroscopies this nuclear motion is probed spectroscopically (indirectly), in TRXL this is probed directly by X-ray scattering.^{63,64} Compared with the time-resolved spectroscopic signal expressed as a function of time (*t*), the TRXL signal contains additional information on the wavepacket motion in one extra dimension (*q*).

Semiclassical versus Quantum Mechanical Descriptions and Particle versus Hole

The nuclear wavepacket motion observed in a pump-probe experiment generally stems from vibrational wavepackets on both ground and excited states. We can understand these wavepacket dynamics in two different pictures: semiclassical (SC) and quantum mechanical (QM) treatments. The former case treats the molecular system as a distribution of molecular structures (Figure 3). When an impulsive optical pump pulse excites a molecule to an electronically excited state, a localized wavepacket on the excited state distribution via an absorption process is generated as a "particle" (that is, positive contribution to the scattering signal) and a corresponding "hole" (that is, negative contribution to the scattering signal) in the ground state distribution is generated. These wavepackets move and spread over time on their own electronic states. On the other hand, in the QM treatment, the same process is described based

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on wave functions or, more conveniently, the density matrix formalism. The wavepacket dynamics can be understood by two concomitant processes during interaction with an optical pulse, absorption and impulsive stimulated Raman scattering (ISRS). In spite of the different viewpoints between SC and QM treatments, they give very similar or, in some cases, identical results for the vibrational wavepacket dynamics.⁶⁵ While the SC treatment adopts a classical picture of describing the groundstate wavepacket as a hole, the hole generated in the ground state is exactly equivalent to the vibrational coherence generated in the ground state by ISRS in the quantum mechanical picture. Accordingly, we interpreted the experimental data based on the SC treatment, which is more intuitive and easy to understand.

We simulated the scattering curves by considering the elastic scattering component exclusively and applying the independent atom model (IAM). This assumption reduces the cost for simulating scattering curves, but at the same time fails to account for more detailed signals such as scattering due to bonding electrons and scattering change caused by the change of electronic charge distribution due to electronic transitions and coherent superposition of electronic states by electronic coherence.⁶⁶ The missing parts of the signal, however, should be relatively insignificant and mostly negligible in the TRXL signal for the molecules containing heavy atoms.⁶⁷ Analysis of TRXL data under the SC treatment and IAM has been successful not only for the GTC but also for some other metal complexes including $[Co(terpy)_2]^{2+}$ and $[Pt_2(P_2O_5H_2)_4]^{4-.28,29}$

In the SC treatment, the wavepackets can be described by structural distributions in the ground and excited states. Before excitation, the ground state has a structural distribution centered at its equilibrium structure and the excited state is empty. The scattering intensity before excitation, $S^{\text{Off}}(q)$, can be described as follows:

$$S^{\text{Off}}(q) = S_{S_0^{\text{eq}}}(q) \tag{1}$$

, where $S_{S_0^{eq}}(q)$ is the scattering curve of the equilibrium S_0 structure.

After excitation, part of the structures in the ground state absorb the light and transit into the excited state, generating a structural distribution in the excited state, which can be represented as a "particle" in the excited state. In contrast, the corresponding part of the structural distribution in the ground state disappears as a result of the transition, generating a "hole" in the ground state on top of the original distribution. Accordingly, the scattering intensity after excitation, $S^{On}(q)$, can be described as follows:

$$S^{\text{On}}(q, t) = \alpha \times [c_{\text{T}'_{1}}(t)S_{\text{T}'_{1}(t)}(q) + c_{\text{T}_{1}}(t)S_{\text{T}_{1}(t)}(q)] + S_{S_{0}^{\text{eq}}}(q) - \alpha (c_{\text{T}'_{1}}(t) + c_{\text{T}_{1}}(t))S^{\text{gs,hole}}(t)$$
(2)

where $S_{T'_1(t)}(q)$ and $S_{T_l(t)}(q)$ are the scattering curves of the transient structures of T_1' and T_1 states, respectively, and $S^{\text{gs,hole}}(t)$ is the scattering curve arising from the ground-state hole. $c_{T'_1(t)}(q)$ and $c_{T_l}(t)$ represent the time-dependent relative populations of the T_1' and T_1 states. α is the fraction of the population removed from the ground state.

In our analysis, we use the difference scattering intensity, $\Delta S(q,t)$, obtained by subtracting $S^{\text{Off}}(q)$ from $S^{\text{On}}(q,t)$. Plugging in eqs 1 and 2 yields the following equation.

$$\Delta S(q, t) = \alpha \times [(c_{T_{1}'}(t)S_{T_{1}'(t)}(q) + c_{T_{1}}(t)S_{T_{1}(t)}(q)) - (c_{T_{1}'}(t) + c_{T_{1}}(t))S^{gs,hole}(t)] = \alpha \times [c_{T_{1}'}(t)(S_{T_{1}'(t)}(q) - S_{S_{0}^{eq}}(q)) + c_{T_{1}}(t)(S_{T_{1}(t)}(q) - S_{S_{0}^{eq}}(q)) + (c_{T_{1}'}(t) + c_{T_{1}}(t))(S_{S_{0}^{eq}}(q) - S^{gs,hole}(t))]$$
(3)

We note that the relative contributions of the excited and ground states to $\Delta S(q,t)$ are equal, as can be seen in eq 3.

In the SC treatment of wavepacket dynamics, the ground state wavepacket is described as a movement of a "hole", but here we replaced the "hole" with a "particle" moving toward the opposite direction, and this is why we have the opposite sign for the ground state wavepacket component in $\Delta S_{\text{residual}}(q,t)$ compared to, for example, that in the TRXL study on $[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]^{4-29}$ Our approach of using the particle picture instead of the hole picture for the ground-state wavepacket is conceptually more convenient because the wavepackets can be described as particles regardless of the states (whether the excited state or the ground state).

The following is the equation that we used to simulate the TRXL data of GTC.

$$\begin{split} \Delta S(q, t) &= c_{T_{1}'}(t)(S_{T_{1}'(t)}(q) - S_{S_{0}^{eq}}(q)) \\ &+ c_{T_{1}}(t)(S_{T_{1}(t)}(q) - S_{S_{0}^{eq}}(q)) \\ &+ (c_{T_{1}'}(t) + c_{T_{1}}(t))(S_{S_{0}(t)}(q) - S_{S_{0}^{eq}}(q)) \\ &+ \Delta S_{heat}(q, t) \end{split}$$
(4)

where $S_{S_0(t)}(q)$ is the scattering curve of the transient structure of S_0 states (treated as a particle). $\Delta S_{heat}(q,t)$ is the scattering signal from the temperature change of the bulk solvent. We note that α is omitted in eq 4 for simplicity, but this fraction was taken into account by using a scaling factor as a fitting parameter in the structural analysis. To focus on wavepacket dynamics, we decomposed eq 4 further as follows.

$$\Delta S(q, t) = \Delta S_{\text{transit}}(q, t) + \Delta S_{\text{residual}}(q, t) + \Delta S_{\text{heat}}(q, t)$$
(5)

where

$$\Delta S_{\text{transit}}(q, t) = c_{T_1'}(t)(S_{T_1'^{\text{eq}}}(q) - S_{S_0^{\text{eq}}}(q)) + c_{T_1}(t)(S_{T_1^{\text{eq}}}(q) - S_{S_0^{\text{eq}}}(q))$$
(6)

$$\Delta S_{\text{residual}}(q, t) = (c_{\text{T}_{1}'}(t) + c_{\text{T}_{1}}(t))(S_{\text{S}_{0}(t)}(q) - S_{\text{S}_{0}^{\text{eq}}}(q)) + c_{\text{T}_{1}'}(t)(S_{\text{T}_{1}'(t)}(q) - S_{\text{T}_{1}^{\text{eq}}}(q)) + c_{\text{T}_{1}}(t)(S_{\text{T}_{1}(t)}(q) - S_{\text{T}_{1}^{\text{eq}}}(q))$$
(7)

Now the wavepacket dynamics are confined in $\Delta S_{\text{residual}}(q,t)$, while the population dynamics are separated as $\Delta S_{\text{transit}}(q,t)$. In other words, $\Delta S_{\text{residual}}(q,t)$ contains the structural changes with reference to the equilibrium structure of each electronic state during the wavepacket dynamics on both excited and ground states. Since the only difference between "hole" and "particle" is the direction, both equations are describing the same phenomenon, the motions of the ground-state wavepacket, but from different points of view. We note that our study probed



Figure 4. Femtosecond TRXL data and results of structure analysis using residual difference scattering curves. (a) Femtosecond TRXL curves, $q\Delta S(q,t)$, of $[Au(CN)_2^{-1}]_3$ in water measured at PAL-XFEL. (b) Experimental residual difference scattering curves, $q\Delta S_{residual}(q,t)$, measured from -1040 to 2235 fs. (c) Theoretical fits for $q\Delta S_{residual}(q,t)$ shown in panel b obtained from the structure analysis performed by considering both wavepacket motions in S₀ and T₁' and fitting residuals. (d, f) (left) Time-dependent Au–Au distances, $R_{12}(t)$, $R_{23}(t)$, and $R_{13}(t)$, and Au–Au–Au angles, θ , of T₁' (d) and S₀ (f) determined from the structure analysis are represented by black, blue, cyan, and magenta dots, respectively. The $R_{12}(t)$, $R_{23}(t)$, and $R_{13}(t)$ measured in the late time range (>360 fs) are fit by sums of two damping cosine functions (red lines) whose frequencies are shown in the panel. (right) Contributions of the normal modes assigned to wavepacket motions in T₁' (d) and S₀ (f) to the fits shown in the left panel. For T₁', the contributions of T₁_#6 and T₁_#12 modes are shown in green and brown curves, respectively, and for S₀, the contributions of S₀_#6 and S₀_#5 modes are shown in green and brown curves, respectively. (g) Theoretical displacement vectors of a symmetric stretching mode, S₀_#6, and an asymmetric stretching mode, S₀_#5, of S₀ assigned to the 32 and 44 cm⁻¹ oscillations, respectively. See the SI for details on the assignment of vibrational modes. Reproduced with permission from ref 1. Copyright 2020 Springer Nature.

the excited-state wavepacket in addition to the ground-state wavepacket whereas the TRXL study on $[Pt_2(P_2O_5H_2)_4]^{4-}$ probed only the ground-state wavepacket due to the special situation of the molecular system and the excitation wavelength used in the study. We note that the generation and initial motion of wavepackets can be affected by the condition of the excitation pulse such as temporal width, chirp and wavelength.^{29,68} For example, a linearly chirped pump pulse can enhance or reduce the amplitude of wavepacket motions of either the ground state "hole" or excited state "particle".⁶⁹ On a final note, investigating

the wavepacket dynamics in both the ground and excited states simultaneously by time-resolved spectroscopic tools generally becomes more complicated when the PESs of the ground and excited states are significantly different, which results in the difference in their symmetry groups and makes the reaction coordinates complicated. In contrast, since the wavepacket motion is tracked in terms of structure using TRXL, it is easier to distinguish the motion of the ground- and excited-state wavepackets, even when the PESs of the ground and excited states are quite different as in the case of the GTC.



Figure 5. Trajectories of the excited-state wavepackets determined from TRXL data. (a) Motions of the excited-state wavepacket on the PES of T₁ starting from the FC region of S₁ in an early time range (<360 fs) represented in the multidimensional nuclear coordinates of R_{12} vs R_{23} vs θ . The projection of wavepacket motion onto the $R_{12}-R_{23}$ plane is also shown at the bottom. The positions of the wavepacket at measured time points are indicated by dots, whose colors represent time delays based on a color scheme shown at the bottom. (b) Transient structures of T_1' at representative time delays. The Au atoms at each time delay are represented by yellow dots while the Au atoms in the FC region are represented by gray dots. Covalent bonds formed in the excited state are indicated by black solid lines. The changes in interatomic distance and angle are indicated by red arrows and green arrows, respectively. The ligands are omitted for simplicity. Structural changes are exaggerated for clear comparison. (c) Late time-range (>360 fs) trajectories of the excited-state wavepacket in T_1' represented in the multidimensional nuclear coordinates of R_{12} vs R_{23} vs time. The normal coordinates of the two symmetric stretching modes, $Q(T_1_{\pm})$ and $Q(T_1_{\pm})$ for T_1' are indicated by red arrows. At the end of each arrow, the representative structure with Au atoms as yellow spheres is shown to indicate displacements of three Au atoms according to the corresponding normal coordinate while the positions of Au atoms in the equilibrium structures are represented by gray spheres. The red arrows in representative structures indicate the displacement vectors of Au atoms, which are exaggerated for clarity, for each mode. The normal coordinates, which are exactly on the diagonal direction of the $R_{12}-R_{23}$ plane, are displaced a bit to show the normal coordinates clearly. In panels a and c, the equilibrium distances of R_{12} and R_{23} in T_1' are indicated by the blue dashed lines. For several representative time delays, the time delays in femtoseconds are shown next to the corresponding wavepacket position. The black curves connecting the dots in the order of time correspond to the trajectory of the wavepacket over time. Reproduced with permission from ref 1. Copyright 2020 Springer Nature.

ASYNCHRONOUS OR SYNCHRONOUS, THAT IS THE PROBLEM

TRXL experiments were performed for GTC in solution. The sample solution of GTC was excited by an optical laser pulse of 267 nm wavelength to initiate the photoinduced bond formation of GTC, and a time-delayed X-ray pulse was used to probe the structural change. TRXL signal is $q\Delta S(q,t)$, for the momentum-

transfer vector $q = (4\pi/\lambda)\sin(2\theta/2)$, where λ is the X-ray wavelength (12.7 keV) and 2θ is the scattering angle, and a measurement time *t*. More details are described in the SI and previous publications.^{1,2} Figure 4a shows $q\Delta S(q,t)$ measured at time delays from -1040 to 2235 fs. The temporal change of $q\Delta S(q,t)$ can be determined from the first two right singular vectors (rSVs) obtained from the singular value decomposition of $q\Delta S(q,t)$. Those two vectors are well fit by an exponential (a)

Bond angle, θ (°)

135

130

125

120

115

2.8

3.0

R₁₂ (A)

3.2

3.4





110 85 💑

60

Figure 6. Trajectories of the ground-state wavepackets determined from TRXL data. (a) Motions of the excited-state wavepacket on the PES of S_0 in an early time range (<360 fs) represented in the multidimensional nuclear coordinates of R_{12} vs R_{23} vs θ . The projection of wavepacket motion onto the $R_{12}-R_{23}$ plane is also shown at the bottom. (b) Transient structures of S_0 at representative time delays. The meanings of dots, colors, lines, and arrows are the same as Figure 5b. (c) Late time-range (>360 fs) trajectories of the excited-state wavepacket in S_0 represented in the multidimensional nuclear coordinates of R_{12} vs R_{23} vs time. The normal coordinates of the symmetric and asymmetric stretching modes, $Q(S_0=#6)$ and $Q(S_0=#5)$, for S_0 are indicated by red arrows. The meanings of dots, colors, lines, and arrows are the same as Figure 5c. Reproduced with permission from ref 1. Copyright 2020 Springer Nature.

function with 1.1 ps time constant, which is related to the T_1' -to- T_1 transition,^{1,2} convoluted with the instrument response function (IRF). To analyze these oscillations in more detail, we extracted the oscillating components from the experimental $q\Delta S(q,t)$ by subtracting the contributions of T_1' -to- T_1 transition and solvent heating, yielding residual difference scattering curves, $q\Delta S_{residual}(q,t)$. The two dimensions of $q\Delta S_{residual}(q,t)$ (q-axis and t-axis) provide direct information on time-dependent molecular structure, and thus they eventually enable us to track the wavepacket motions in multidimensional nuclear coordinates.

Figure 4b shows $q\Delta S_{residual}(q,t)$. The best fits shown in Figure 4c were obtained when both ground and excited states, S_0 and

 T_1' , were considered, indicating that the residual difference scattering curves arise from wavepacket motions in PESs of both S_0 and T_1' . In Figure 4e,f, the time-dependent changes of structural parameters, R_{12} , R_{23} , R_{13} , and Au–Au–Au angle (θ), obtained from the structural analysis are shown for both the ground and excited states. From the time evolution of these structural parameters, the trajectories of the excited-state (Figure 5a,c) and ground-state (Figure 6a,c) wavepackets can be reconstructed in multidimensional nuclear coordinates, R_{12} vs R_{23} vs θ , where the relative positions of all three Au atoms in the gold trimer complex can be described. We note that such trajectories can be obtained purely based on the experimental

Article

data, without relying on any theoretical calculation thanks to the structural sensitivity of TRXL.

The trajectories of wavepackets can be described in two separate time ranges, that is, (i) initial motions of the wavepackets on the PES of T₁' starting from the FC region of S_1 in an early time range (<360 fs) and (ii) subsequent harmonic oscillations around the equilibrium structures of T_1' in a late time range (>360 fs). In the early time range (<360 fs), each of the excited-state and ground-state wavepackets moves on its PES to approach its own equilibrium structure. The trajectory of the excited-state wavepacket reveals that the formation of two covalent bonds does not occur in a concerted, synchronous manner (for example, path 2 in Figure 1b). R_{12} decreases rapidly down to the covalent Au–Au bond length of the equilibrium T_1 (2.82 Å) at 35 fs time delay and becomes even shorter at 60 fs to reach the minimum length along the entire trajectory, whereas R_{23} stays much longer than the covalent bond length (2.82 Å) at those time delays (Figure 5a). This early time trajectory indicates that the shape of the PES around the FC region is steeper along the R_{12} axis than along the R_{23} axis. Subsequently, R_{23} keeps decreasing and R_{12} oscillates around the equilibrium bond length with a frequency of 97 cm⁻¹ until R_{23} eventually reaches the equilibrium bond length at 360 fs, supporting the mechanism of asynchronous bond formation (path 1 in Figure 1b). Detailed structural changes associated with the initial

wavepacket motion on the PES of T_1' are shown in Figure 5b. In previous TRXL studies,^{28,29,31} vibrational motions of $[Co(terpy)_2]^{2+}$, $[Pt_2(P_2O_5H_2)_4]^{4-}$, and $[Fe(bpy)_3]^{2+}$ were investigated, but wavepacket motions were explained only in terms of a single nuclear coordinate (an Fe-N distance for $[Fe(bpy)_3]^{2+}$, a Co-N distance for $[Co(terpy)_2]^{2+}$, a Pt-Pt distance for $[Pt_2(P_2O_5H_2)_4]^{4-}$, and an Fe-N distance for $[Fe(bpy)_3]^{2+}$, rather than multidimensional nuclear coordinates, because the studied polyatomic molecules were regarded as pseudo-diatomic molecules thanks to their high symmetry. The study on $[Fe(bpy)_3]^{2+}$ does mention the multidimensional PES, but in reality, only a single coordinate of the Fe-N distance was experimentally probed. Regarding the observation of the initial motion from the FC region, unless the location of the FC region is identified in multidimensional coordinates, such a motion provides any extra information since the initial motion presented in the study of $[Fe(bpy)_3]^{2+}$ is quite predictable as an extension of the subsequent motion in the late time delays. In contrast, the initial motion we observed for the GTC is quite different from the movement in the late time delays and consequently provides the special meaning of determining specific reaction mechanisms, that is, the asynchronous bond formation.

Figure 6a displays the trajectory of the ground-state wavepacket in S₀ and its projection onto the $R_{12}-R_{23}$ plane. The ground-state wavepacket moves in the direction of decreasing R_{12} and increasing θ within 100 fs. Such initial motion of the ground-state wavepacket should reflect the early time structural changes occurring in the excited state, that is, ultrafast bond formation and the slower bent-to-linear transformation. Figure 6b shows detailed structural changes associated with the initial wavepacket motion on the PES of S₀.

ASSIGNING VIBRATIONAL MODES

In the late time range after the initial motions (<360 fs), the wavepackets oscillate around their equilibrium structures. Figure 4d,f shows the temporal changes of structural parameters of T_1 ' and S_0 after 360 fs time delay, respectively. All the structural

parameters simply oscillate around their own equilibrium values, without any significant changes as observed in the early time wavepacket motion. To characterize the temporal oscillations of the structural parameters of T_1' and S_0 in the late time range, we fitted $R_{12}(t)$, $R_{23}(t)$, and $R_{13}(t)$ of T_1' and S_0 obtained from the structural analysis with various combinations of vibrational normal modes, for example, symmetric stretching, asymmetric stretching modes. For T_1' , a sum of two symmetric stretching modes with 79 and 125 cm⁻¹ frequencies gives satisfactory fits to the temporal changes of Au–Au distances (Figure 4d). Similarly, the fitting of the temporal changes of the structural parameters of S_0 is consistent with a symmetric stretching mode with 32 cm⁻¹ frequency and an asymmetric stretching mode with 44 cm⁻¹ frequency (Figure 4f).

The trajectories of the wavepackets in T_1' and S_0 in the late time range (>360 fs) are shown in the nuclear coordinates of R_{12} vs R_{23} in Figures 5c and 6c, respectively. The displacements of the wavepackets from the equilibrium structures are represented by a sum of structural changes along the two normal coordinates of the activated vibrational modes (T_1 _#6 and T_1 _#12 for T_1' and S_0 _#6 and S_0 _#5 for S_0 where the numbers indicate the orders of appearance in the DFT frequencies). Importantly, these harmonic oscillations manifested by the motions of wavepackets can be assigned to specific normal modes unambiguously because the TRXL signal contains the information on the vibrational frequency as well as the atomiclevel movement pattern of a vibrational mode.

It is worth comparing our assignment with the one made based on only the frequencies of normal modes. The oscillation frequencies can be easily extracted from the Fourier power spectrum of $q\Delta S_{residual}(q,t)$ in the late time range (>360 fs). The FT spectrum (not shown) shows a major peak at 32 cm⁻¹ and minor peaks at 79 and 125 cm⁻¹. If one follows the normal practice to choose the normal mode with the most similar frequency as the 32 cm⁻¹ oscillation among the 11 modes identified by DFT calculations for S₀ and T₁, a bending mode of T_1 with the frequency of 33 cm⁻¹ would be incorrectly chosen. Also, the additional mode (an asymmetric stretching mode with 44 cm⁻¹ frequency) discovered by TRXL data analysis would not be identified in the FT spectrum. Therefore, the result of this work showcases that the assignment of the observed oscillations to specific vibrational modes based on a simple numerical comparison of vibrational frequencies is susceptible to misinterpretation for polyatomic molecules that have many normal modes

Our data show no normal modes associated with bending motion in both the ground and excited states. DFT calculations predict bending modes at 20 cm⁻¹ in S₀ and 33 and 53 cm⁻¹ in T_1' . A possible reason why the bending modes were not identified from the TRXL data is as follows. The structural changes following the bending mode will be mostly reflected in $R_{13}(t)$, which is affected also by the symmetric or asymmetric stretching modes at the same time, meaning that too much information on various vibrational modes is intermingled in $R_{13}(t)$. Moreover, $R_{13}(t)$ is longer than $R_{12}(t)$ and $R_{23}(t)$, and thus $R_{13}(t)$ inherently has a worse signal-to-noise ratio than $R_{12}(t)$ and $R_{23}(t)$. This is because the longer the distance, the more blurred in the scattering signal, especially when the thermal motion, which is taken care of by using the Debye-Waller factors in the scattering equation, is high. As a consequence, the current signal-to-noise ratio, especially for $R_{13}(t)$, may not be high enough to resolve the bending motion in both the ground and excited states.

Accounts of Chemical Research

PERSPECTIVE

In this Account, we showed a successful example of fs-TRXL studies where the real-time trajectories of vibrational wavepackets were tracked based on the atomic-level characterization of ultrafast changes of molecular structure. The direct information on temporal changes of the molecular structure of GTC revealed by fs-TRXL allows us to achieve the following tasks that have not been possible: (i) determining the exact structure of the ground state, (ii) visualizing the trajectories of the nuclear wavepacket motions in multidimensional nuclear coordinates, which reveals the asynchronous bond formation, and (iii) unambiguously assigning the coherent oscillations observed in the scattering data to specific normal modes in the ground and excited states without relying on any quantum chemical calculations.

An unambiguous and direct look at the vibrational motion that drives a bond-forming reaction by precisely timing the mechanistic components of the reaction uncovered the reaction mechanism. While only the motions of highly scattering gold atoms were monitored in this work, it is possible, in principle, to visualize the motions of lighter atoms such as carbon and nitrogen,^{32,34} especially once the next-generation X-ray sources such as LCLS-II HE are developed as demonstrated by the simulation on O₃.¹ Regarding the limit of the complexity of molecular systems of which the nuclear motions can be resolved with our approach, we are studying a number of other molecular systems using fs-TRXL, and their data analysis is underway. In all of those cases, when we analyzed the data using the same method reported in this Account, we found that the reaction dynamics are governed by only two or three key nuclear coordinates, meaning that the method can still address the reaction dynamics of many molecular systems of importance.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.accounts.0c00812.

Details of time-resolved X-ray liquidography experiment, sensitivity map, quantum mechanical description for the wavepacket dynamics in TRXL signals, assignment of normal modes of ground and excited state wavepackets, and schematic of the TRXL experiment (PDF)

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