

Femtosecond X-ray liquidography captures the birth of molecular vibrations mediating bond formation

Trajectories of wavepackets along reaction coordinates, which determine real-time atomic motions in molecules during reactions, are often drawn in calculated or imagined potential energy surfaces (PES). However, it is still challenging to experimentally determine the trajectories of wavepackets on multidimensional nuclear coordinates. In our recent work, we succeeded in achieving this goal using photoinduced bond formation of a gold trimer complex (GTC), [Au(CN)2-]3, in an aqueous solution [1]. The equilibrium structure of GTC in the ground state (S₀) determines the position of the Franck-Condon (FC) region and the structure in the FC region, where the excited-state wavepacket is initially created, can be considered as the reactants (A+B+C) of the reaction. This wavepacket moves toward the equilibrium structure of T₁', which is the product (A-B-C) with two equivalent covalent Au-Au bonds. Regarding the bond formation process of GTC, the three candidate reaction mechanisms can be considered: (i) the concerted bond formation mechanism where two covalent bonds, A-B and B-C, are formed synchronously, and the asynchronous bond formation mechanism where (ii) A-B is formed first or (iii) B-C is formed

first. To determine the reaction mechanism among the three candidate mechanisms, it is required to directly observe the initial motions of the wavepacket starting from the FC region on multidimensional PES.

To accomplish this task, we performed femtosecond time-resolved X-ray liquidography (TRXL) experiments [2] using X-ray free electron lasers (XFELs) at SACLA BL3 [3] and the X-ray Scattering and Spectroscopy (XSS) beamline of PAL-XFEL [4]. Structural analyses were performed against the TRXL data, and the best fits shown in Fig. 1(a) were obtained when both of the ground and excited states, S_0 and T_1 ', were considered, indicating that wavepacket motions in PESs of both S_0 and T_1 ' contribute to the TRXL signal. Using the time-dependent changes of structural parameters, R_{AB} , R_{BC} , R_{AC} , and Au–Au–Au angle (θ), shown in Figs. 1(b)-1(c), we reconstructed the trajectories of the excited-state (Figs. 2(a) and 2(c)) and ground-state [1] wavepackets in multidimensional nuclear coordinates, R_{AB} vs R_{BC} vs θ .

As shown in Fig. 2(a), the excited-state wavepacket generated in the FC region (R_{AB} =3.13 Å and R_{BC} =3.38 Å, θ = 119°) moves on the PES of T₁' toward the equilibrium structure of T₁' (R_{AB} =2.82 Å



Fig. 1. (a) Experimental TRXL signal (left), and their theoretical fits (right) obtained from the structural analysis. (b) $R_{AB}(t)$, $R_{BC}(t)$, and $R_{AC}(t)$, and Au–Au–Au angle, θ , of T₁' are represented by black, red, blue, and cyan dots, respectively. (c) The Au–Au distances in the late time range (>360 fs) for T₁' are represented by black open circles with their fits by a sum of two damping cosine functions (red lines).

and $R_{BC} = 2.82 \text{ Å}, \theta = 180^{\circ}$). Specifically, R_{AB} 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 $R_{\rm BC}$ is still much longer than the covalent bond length (2.82 Å) at those time delays, as shown in Fig. 2(a). The earlytime trajectory reveals that the two covalent bonds are formed in an asynchronous manner, in which the covalent bond is formed earlier in the shorter Au-Au pair of the ground state. With respect to θ , the excited-state wavepacket starts from the FC region $(\theta = 119^{\circ})$ and reaches the equilibrium value of T₁' $(\theta = 180^{\circ})$ in 335 fs, giving the time scale of bentto-linear transformation. After the initial motions, the wavepacket oscillates around their equilibrium

structures in the late time range (> 360 fs), as can be seen in Fig. 1(c). The trajectory of the wavepacket in T₁' in the late time range (> 360 fs) is shown in Fig. 2(c). For T₁', a sum of two symmetric stretching modes with 79 cm⁻¹ and 125 cm⁻¹ frequencies give satisfactory fits (Fig. 1(c)), and for S₀, a symmetric stretching mode with 32 cm⁻¹ frequency and an asymmetric stretching mode with 44 cm⁻¹ frequency gives satisfactory fits [1].

In summary, the trajectories of nuclear wavepackets were visualized using femtosecond TRXL and unambiguously provides a direct view of the vibrational motion that drives an asynchronous bond formation. Femtosecond TRXL can be used as a fundamental tool to visualize atomic motions and reveal reaction pathways in many chemical reactions.



Fig. 2. (a, c) The trajectory of the wavepacket in T_1 ' in (a) the early time range (<360 fs) and (c) the late time range (>360 fs) is represented in the coordinates of R_{AB} versus R_{BC} versus θ and R_{AB} versus R_{BC} , respectively. In (a), the positions of the wavepacket at measured time delays are indicated by dots using a color scheme shown at the bottom of each panel. For several time delays, the time delays in femtoseconds units are shown. (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 are indicated by black solid lines. The changes of interatomic distance and angle are indicated by red arrows and blue arrows, respectively. The trajectory of the wavepacket in S_0 is now shown due to space limitation. In (c), the wavepacket positions at several time delays in femtoseconds units are shown. The normal coordinates of the equilibrium structures are represented by gray spheres. The red arrows indicate the displacement vectors of Au atoms.

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