## Photoinduced Charge Transfer versus Fragmentation Pathways in Lanthanum Cyclopentadienyl Complexes

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In TDESMD calculations, the geometry optimized model was used as a starting point. We assume that the molecule cools down before it gets irradiated by the laser pulse. If we believe that the optimized geometry is not sufficient for adequate modeling and thermalized initial conditions are necessary, we can take more samples from MD trajectory as inputs for TDESMD simulations. Such calculation would require much more computational resources.

We have performed the investigation of how the distribution of products depends on initial position and momenta of ions in the reactant molecule as well as on presence or absence of average over ensemble of trajectories. Here we compare the simulated mass spectra extracted from TDESMD simulations by using the optimized geometry with those by using thermalized initial conditions. Interestingly, it is observed that the simulated mass spectra by using optimized geometry are different from those by using thermalized initial conditions. Figure S1 shows the simulated mass spectra with the starting point of  $La(Cp)_3$ . It is found that all simulated mass spectra clearly show features of  $La(Cp)_3^+$ ,  $La(Cp)_2^+$ , and  $La(Cp)^+$ . However, only few features in the low mass region have been reproduced. Figure S2 and S3 show the simulated mass spectra with the starting point of La(Cp).

In **Figure S2**, spectrum *b* provides better agreement with *a* in terms of position and relative intensities of the peaks, while spectra *c*, *d*, and *e* predict additional peaks around m/z = 151 corresponding to LaCH<sub>x</sub> fragments, not seen in the experiment. It indicates that the thermalization of the model prior to TDESMD facilitates additional pathway of the reaction, not seen in experiment. Since the equilibrium initial geometry gives better coincidence with experiment than thermalized initial geometry, one can draw two conclusions: (i) modeling is done at the temperature higher than the one in experiment; (ii) the experimental environment of vacuum (low pressure) leads to cooling of the injected precursor samples down to temperatures lower than the

sublimation temperature. Such cooling upon injection of higher pressure gas into vacuum or lowpressure chamber leads to instantaneous condensation. Since we have difficulty in determining the exact temperature in experiments, the use of optimized geometry as a single reference approach is a compromise. A single trajectory approach also uses reduced computational resources.



**Figure S1.** Comparison between experimental PI–TOF mass spectrum of  $La(Cp)_3$  (blue) and simulated mass spectra extracted from TDESMD simulations by using optimized geometry (black), initial MD geometry (red), and final MD geometry (green) of  $La(Cp)_3$  as a starting point. The average ensemble of trajectories of the red and green is shown as pink. The duration of the simulation is 1000 fs. In TDESMD simulation electrons are hopping between orbital pair of (HO–3, LU+10).



**Figure S2.** Comparison between experimental PI–TOF mass spectrum of  $La(Cp)_3$  (blue) and simulated mass spectra extracted from TDESMD simulations by using optimized geometry (black), initial MD geometry (red), and final MD geometry (green) of La(Cp) as a starting point. The average ensemble of trajectories of the red and green is shown as pink. The duration of the simulation is 600 fs. In TDESMD simulation electrons are hopping between orbital pair of (HO–2, LU+2).



**Figure S3.** Comparison between experimental PI–TOF mass spectrum of  $La(Cp)_3$  (blue) and simulated mass spectra extracted from TDESMD simulations by using optimized geometry (black), initial MD geometry (red), and final MD geometry (green) of La(Cp) as a starting point. The average ensemble of trajectories of the red and green is shown as pink. The duration of the simulation is 600 fs. In TDESMD simulation electrons are hopping between orbital pair of (HO–1, LU+5).



**Figure S4**. (a, b) Nonadiabatic relaxation dynamics of  $La(Cp)_3$  for the initial condition corresponding to feature a' (HO-1  $\rightarrow$  LU) in **Figure 3**. The color codes red, green, and blue represent the distribution for gain, no change, and loss, respectively, relative to the equilibrium distribution. Panel a shows distribution of charge as a function of energy and time. Dashed and solid lines indicate expectation values for energy, calculated in an energy space distribution for unoccupied and occupied bands, respectively. Panel b shows spatial distributions of charge as a function of time. (c) The structure of  $La(Cp)_3$  scaled with Z in panel b.



**Figure S5**. (a, b) Nonadiabatic relaxation dynamics of  $La(Cp)_3$  for the initial condition corresponding to feature  $b'(HO-3 \rightarrow LU+3)$  in **Figure 3**. The color codes red, green, and blue represent the distribution for gain, no change, and loss, respectively, relative to the equilibrium distribution. Panel a shows distribution of charge as a function of energy and time. Dashed and solid lines indicate expectation values for energy, calculated in an energy space distribution for unoccupied and occupied bands, respectively. Panel b shows spatial distributions of charge as a function of time. (c) The structure of  $La(Cp)_3$  scaled with Z in panel b.



**Figure S6.** (a, b) Nonadiabatic relaxation dynamics of  $La(Cp)_3$  for the initial condition corresponding to feature c' (HO-1  $\rightarrow$  LU+10) in **Figure 3**. The color codes red, green, and blue represent the distribution for gain, no change, and loss, respectively, relative to the equilibrium distribution. Panel a shows distribution of charge as a function of energy and time. Dashed and solid lines indicate expectation values for energy, calculated in an energy space distribution for unoccupied and occupied bands, respectively. Panel b shows spatial distributions of charge as a function of time. (c) The structure of  $La(Cp)_3$  scaled with Z in panel b.



**Figure S7.** (a) Total energies of relaxed intermediates in **Table 2**. The atomic model is geometry optimized by PBE to get the total energy without kinetic energy of bond contraction and bond elongation (red). The single point energy calculation of geometry optimized intermediate is performed by MP2 (blue). (b) Total energies computed by MP2 as a function of total energies computed by PBE. The green indicates a linear fit with a function of y = 1.79x - 0.86.

In general, a major challenge is in simultaneous propagation of electronic and nuclear degrees of freedom whose Hamiltonians do not commute. Hamiltonian of light-to-matter interaction evolution reads

$$H' = -\sum_{mn} |m\rangle \langle n| \,\vec{\mu}_{mn} \cdot \vec{E} + h. \, c. \tag{S1a}$$

$$H^{ph} = \sum_{m} |m\rangle \langle m|H_m(R).$$
 (S1b)

The exact evolution operator can be cast in the interaction picture

$$\widetilde{U} = e^{-\frac{i}{\hbar} \int_0^{\Delta t} dt' (H^{ph} + H')} = U' \cdot U^{ph} \cdot U^{BCH}$$
(S2)

where  $U' = e^{-\frac{i}{\hbar}\int_0^{\Delta t} H'(t')dt'}$ ,  $U^{ph} = e^{-\frac{i}{\hbar}\Delta t\sum_m |m\rangle\langle m|H_m(R)}$ , and  $U^{BCH} = e^{-\frac{i}{2\hbar}\int_0^{\Delta t} dt'[H',H^{ph}]}$  due to

Baker-Campbell-Hausdorff theorem. The pulse area is defined as the integral of pulse envelop

$$\theta = \int_{t_1}^{t_2} dt' \frac{\vec{\mu} \cdot \vec{E}}{\hbar}.$$
(S3)

Under resonance condition  $\hbar\Omega = \varepsilon_m - \varepsilon_n$ , the light-driven time evolution operator determined by single parameter can be recast in the form

$$U' = e^{-i\theta(|m\rangle\langle n| + |n\rangle\langle m|)}.$$
 (S4)

During each Rabi half cycle the evolution of the electron nuclear wave function is given by,

$$\Psi(r, R, t + \Delta t) = \widetilde{U}(\Delta t)\Psi(r, R, t).$$
(S5)

Density matrix propagation is written as

$$\rho = \begin{pmatrix} \rho_{gg} & \rho_{ge} \\ \rho_{eg} & \rho_{ee} \end{pmatrix} = U'^+ \cdot \rho(0) \cdot U'.$$
(S6)

In each half period  $n\pi < \theta < (n + 1)\pi$ , the evolution consists of the electronic state flip due to laser perturbation by Eq. (S4). We approximate this flip to occur instantaneously and neglect effects related to continuous change of state occupation probability. Between the flips the nuclear degrees of freedom evolve according to nuclear Hamiltonian  $H_m(R)$ . Then all evolution is represented as sequence of such half-period propagators.



**Figure S8.** Total energies of relaxed intermediates in **Table 2**. The atomic model is geometry optimized by PBE to get the total energy without kinetic energy of bond contraction and bond elongation (red). Total energies of intermediates are processed according to equation 29, resulting in the following regression coefficients A = -0.1, B = 3.5, C = 2.0, and D = -4.4 (blue).



**Figure S9.** Total energies of relaxed intermediates in **Table 3**. The atomic model is geometry optimized by PBE to get the total energy without kinetic energy of bond contraction and bond elongation (red). Total energies of intermediates are processed according to equation 29, resulting in the following regression coefficients A = 0.6, B = 1.0, C = 0.2, and D = -1.0 (blue).



**Figure S10**. (a) Total density of states (DOS) and projected density of states (PDOS) of La(Cp). The black lines, green long dashes, blue short dashes, and red dots indicate the total density of states, the partial density of states component on C 2p, La 5d, and La 4f, respectively. The partial charge density for selected Kohn–Sham orbitals is illustrated on the top. Positions in the DOS indicate intervals of energy containing certain orbitals. The blue, gray, and white spheres represent La, C, and H, respectively. Isosurfaces are in yellow. (b) Calculated absorption spectrum of La(Cp). Features *a'* and *b'* correspond to transitions HO–2  $\rightarrow$  LU+2, and HO–1  $\rightarrow$  LU+5, respectively. These transitions are typical ligand–to–metal charge–transfer (LMCT) transitions.