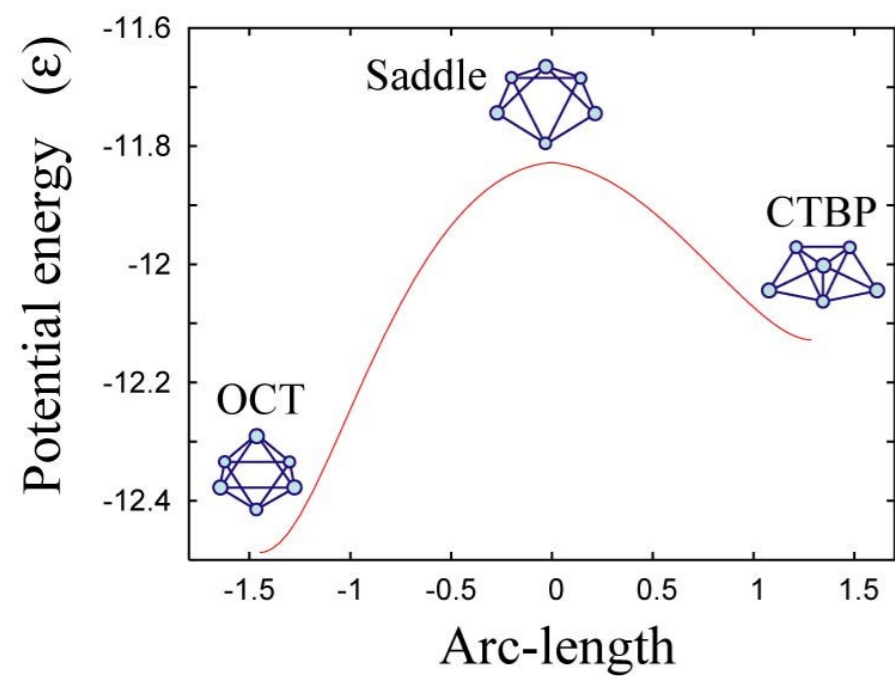


Abstract

We present a novel mechanism for the onset of large-amplitude conformational transitions of molecular systems. We first develop a methodology to scrutinize **intramolecular vibrational energy transfer** using the framework of **hyperspherical coordinates**. This method makes it possible to extract a small number of predominant **reactive modes** out of all vibrational modes of a molecule. It is shown that a large amount of kinetic energy must flow into the reactive modes in order for the system to undergo conformational transitions. We clarify the mechanism of this energy transfer in terms of **mode coupling**, and show a general mechanism for molecular reactions.

1. Prototypical Model (Ar₆ Cluster)

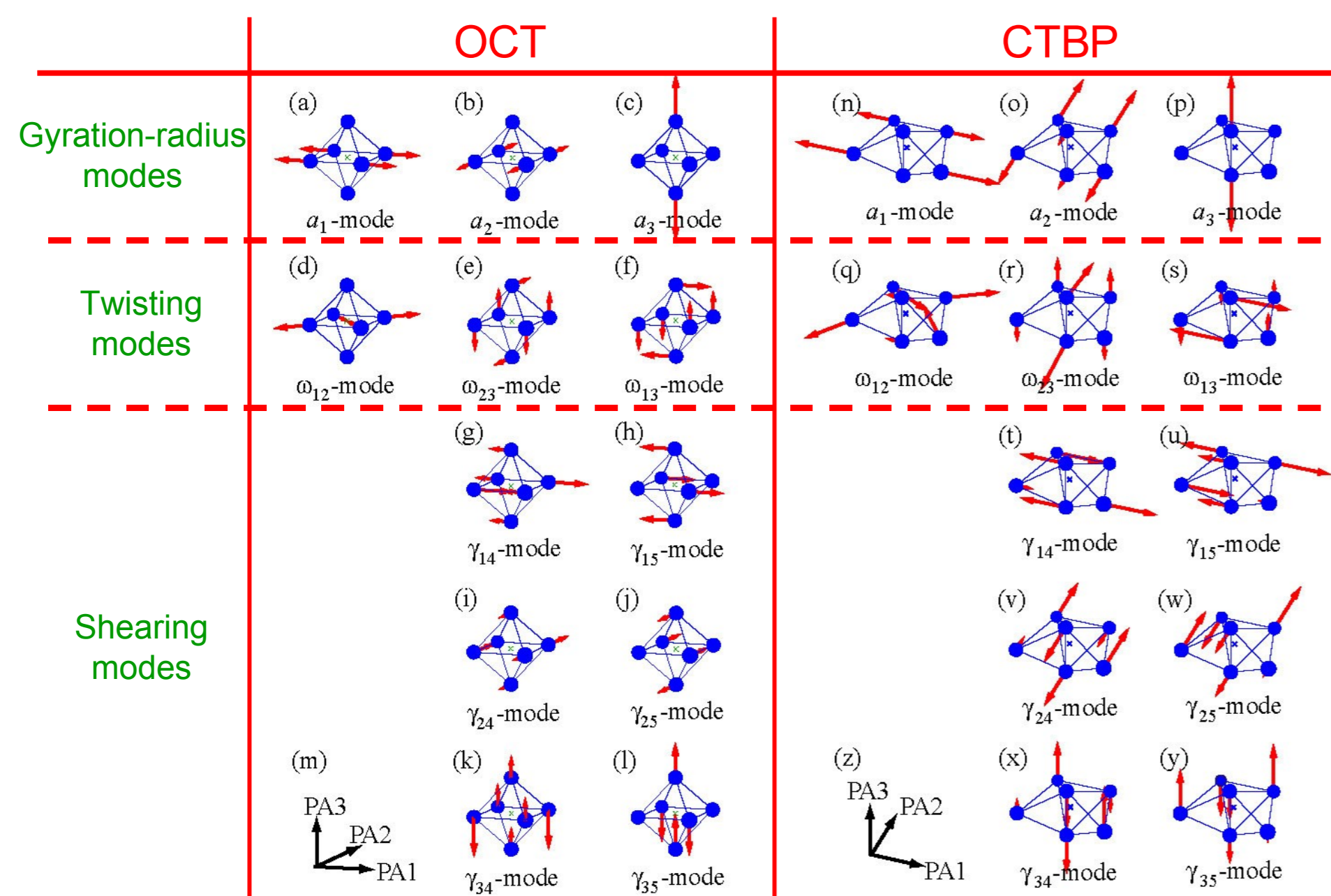


Hamiltonian

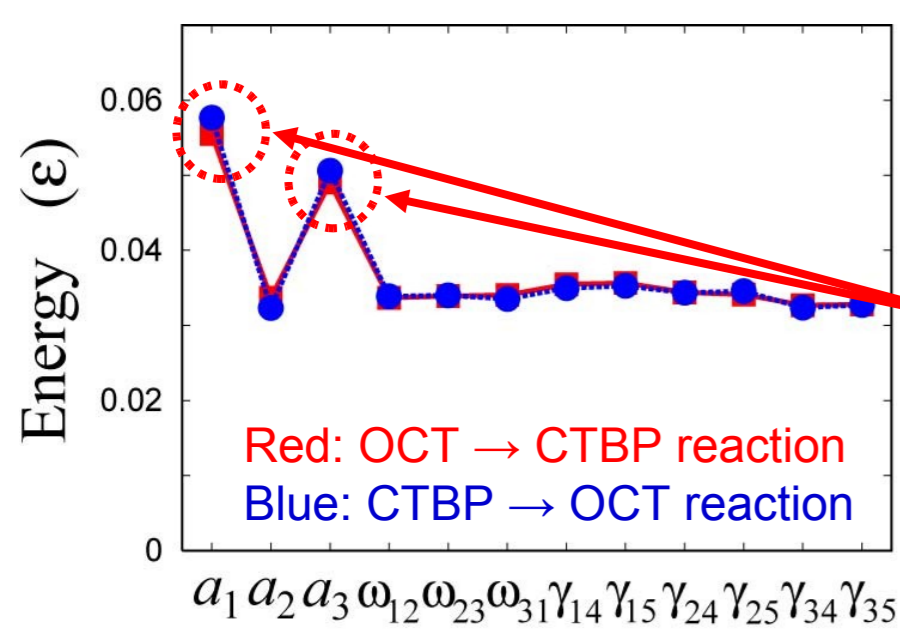
$$\frac{H}{\varepsilon} = \frac{1}{2} \sum_{i=1}^6 \dot{x}_i^2 + \sum_{kk'} \left[\exp\{-2(d_{kk'} - d_0)\} - 2 \exp\{-(d_{kk'} - d_0)\} \right]$$

- Microcanonical molecular dynamics.
- The cluster undergoes structural transition between the OCT and CTBP isomers.

2. Hyperspherical Modes



3. Predominant modes in Reaction

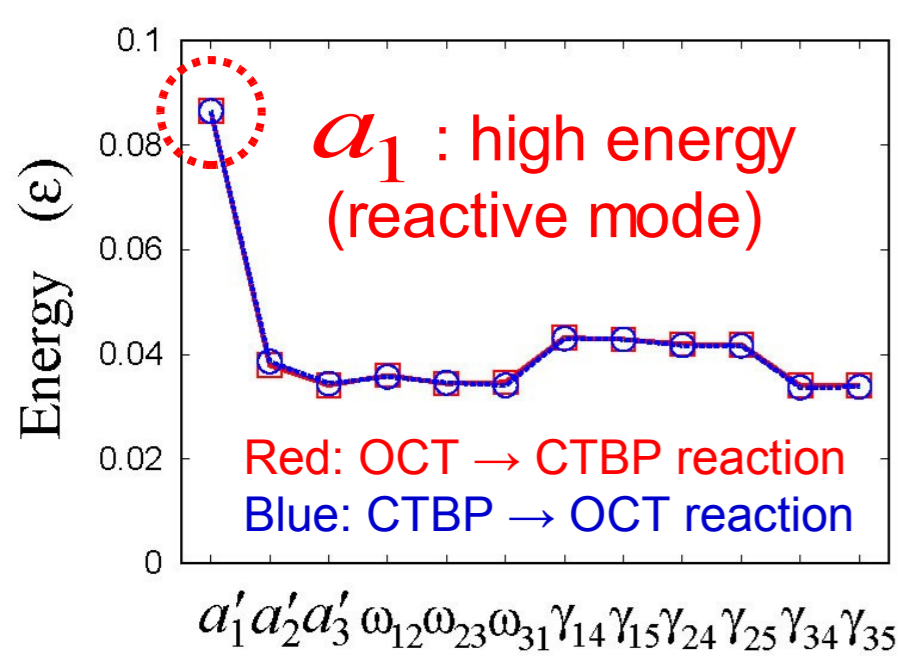


Average distribution of kinetic energy over the 12 internal modes in reactive trajectories.

These two gyration-radius modes occupy a large amount of kinetic energy.

➔ Predominant modes

4. Reaction Coordinate



Coordinate transformation:

Two reactive modes
 $a_1, a_2, a_3, \omega_{12}, \omega_{23}, \omega_{31}, \gamma_{14}, \gamma_{15}, \gamma_{24}, \gamma_{25}, \gamma_{34}, \gamma_{35}$

Principal component analysis

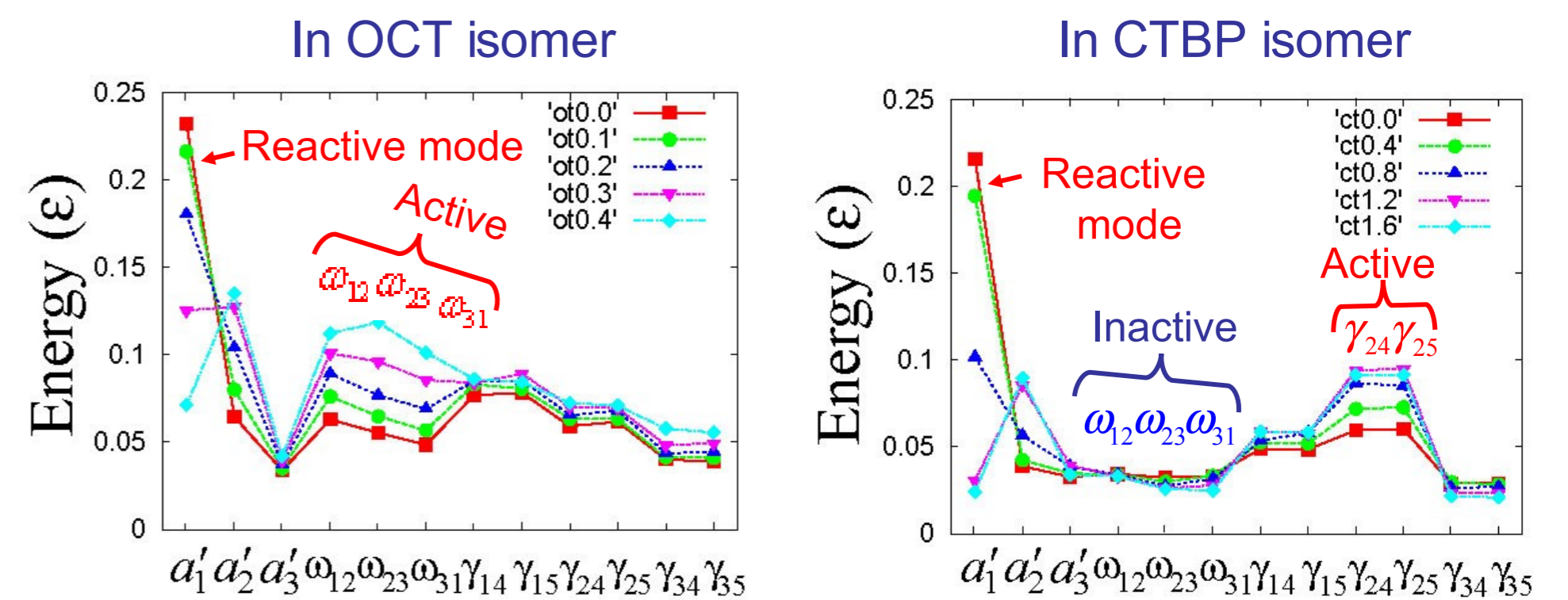
$$\begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} = \begin{pmatrix} 0.801 & -0.292 & 0.523 \\ -0.045 & 0.841 & 0.539 \\ -0.597 & -0.455 & 0.660 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}$$

Single reactive mode

$a_1, a_2, a_3, \omega_{12}, \omega_{23}, \omega_{31}, \gamma_{14}, \gamma_{15}, \gamma_{24}, \gamma_{25}, \gamma_{34}, \gamma_{35}$

$\begin{cases} a_1: \text{Reaction coordinate} \\ a_2, a_3: \text{"bath" modes} \end{cases}$

5. Critical Energy Transfer before Reactions



6. Forces on the Reaction Coordinate

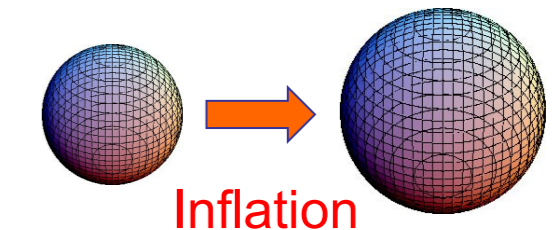
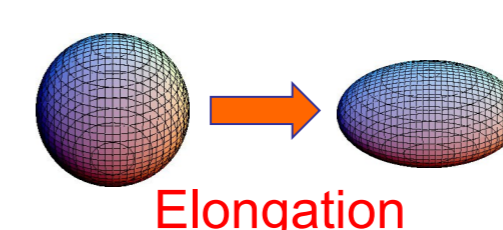
Equations of motion for radii of gyration

$$\ddot{a}_1 = \frac{a_1(a_1^2 + 3a_2^2)(a_1^2 - a_2^2)}{(a_1^2 + a_2^2)^2} \omega_{12}^2 + \frac{a_1(a_1^2 + 3a_3^2)(a_1^2 - a_3^2)}{(a_1^2 + a_3^2)^2} \omega_{13}^2 + a_1 \sum_{k=4}^{n-1} \gamma_{1k}^2 - \frac{\partial V}{\partial a_1}$$

$$\ddot{a}_2 = \frac{a_2(a_2^2 + 3a_1^2)(a_2^2 - a_1^2)}{(a_2^2 + a_1^2)^2} \omega_{21}^2 + \frac{a_2(a_2^2 + 3a_3^2)(a_2^2 - a_3^2)}{(a_2^2 + a_3^2)^2} \omega_{23}^2 + a_2 \sum_{k=4}^{n-1} \gamma_{2k}^2 - \frac{\partial V}{\partial a_2}$$

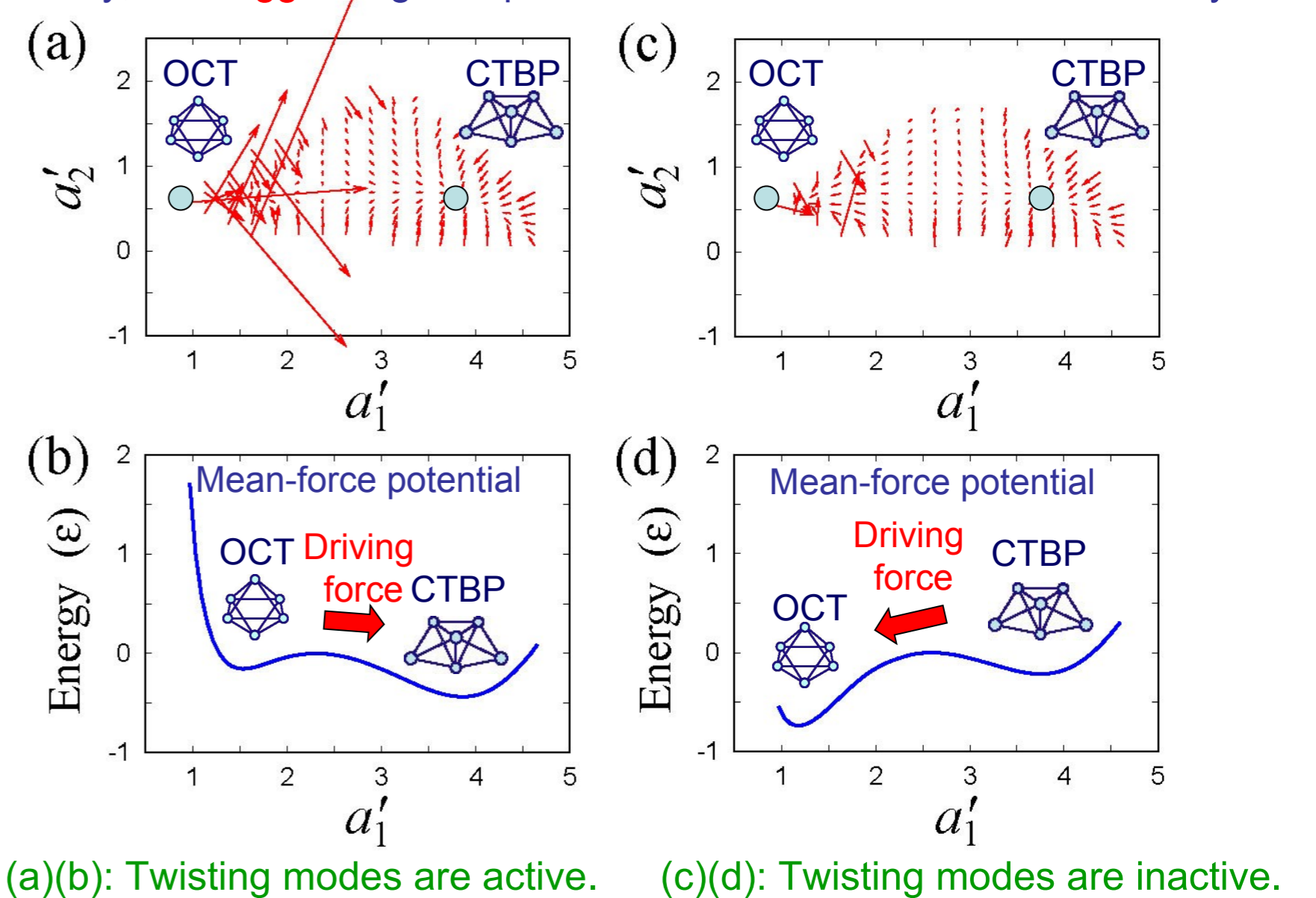
$$\ddot{a}_3 = \frac{a_3(a_3^2 + 3a_2^2)(a_3^2 - a_2^2)}{(a_3^2 + a_2^2)^2} \omega_{32}^2 + \frac{a_3(a_3^2 + 3a_1^2)(a_3^2 - a_1^2)}{(a_3^2 + a_1^2)^2} \omega_{31}^2 + a_3 \sum_{k=4}^{n-1} \gamma_{3k}^2 - \frac{\partial V}{\partial a_3}$$

Internal centrifugal force (coupling with twisting modes) Internal centrifugal force (coupling with shearing modes) Potential force



7. Driving Mechanism for Reactions

Activation and inactivation of the twisting modes **change the average force field** effectively, and **trigger** large-amplitude conformational transition of the system.



(a)(b): Twisting modes are active. (c)(d): Twisting modes are inactive.

8. Conclusions

- We have developed a novel method to scrutinize **intra-molecular energy transfer** based on the framework of **hyperspherical coordinates**.
- Due to mode coupling, activation and inactivation of the "twisting" modes **mediate** the effective force field acting on the reaction coordinate, and **trigger** molecular reactions.