

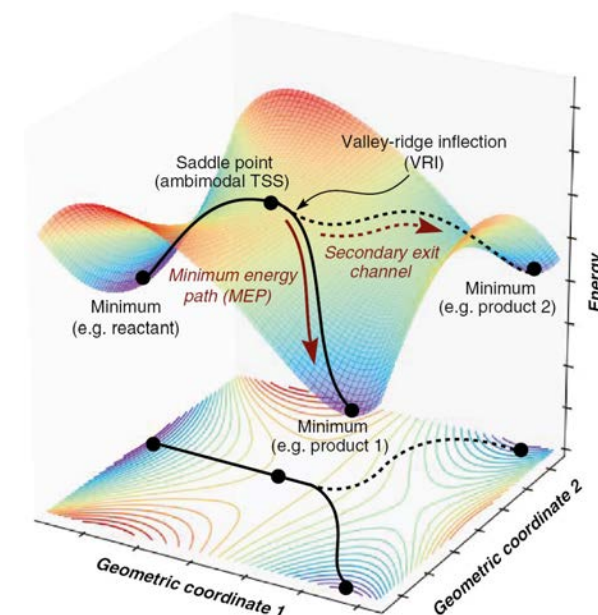
A Phase Space Structure Analysis of Chemical Reaction Dynamics Using Supervised Dimensionality Reduction

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Today's talk

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- **My subject of interest:**
 - **Chemical reactions** whose reactivity is affected by the **dynamics** on the potential energy landscape.
- **One of the difficulty in the subject:**
 - **The large dimension of the system** makes it difficult to handle.
- **My approach:**
 - **Extracting a few dimensions** that describe the reactivity of the chemical reaction system well
→ **Supervised dimension reduction**



A chemical reaction where transition theory does not hold 2/15

- **How to analyze reactivity in chemistry**
 - Transition state theory (TST)
 - rate constant depends on its barrier heights
- **Supposition in the TST**
 - micro canonical in the intermediate region
- **Collapse of the TST**
 - Dynamical trajectories (R→P, direct) affect the specific reactivity.
 - Previous studies have analyzed these reactions qualitatively and statistically.

Many reactions have been reported which are affected by the dynamics.

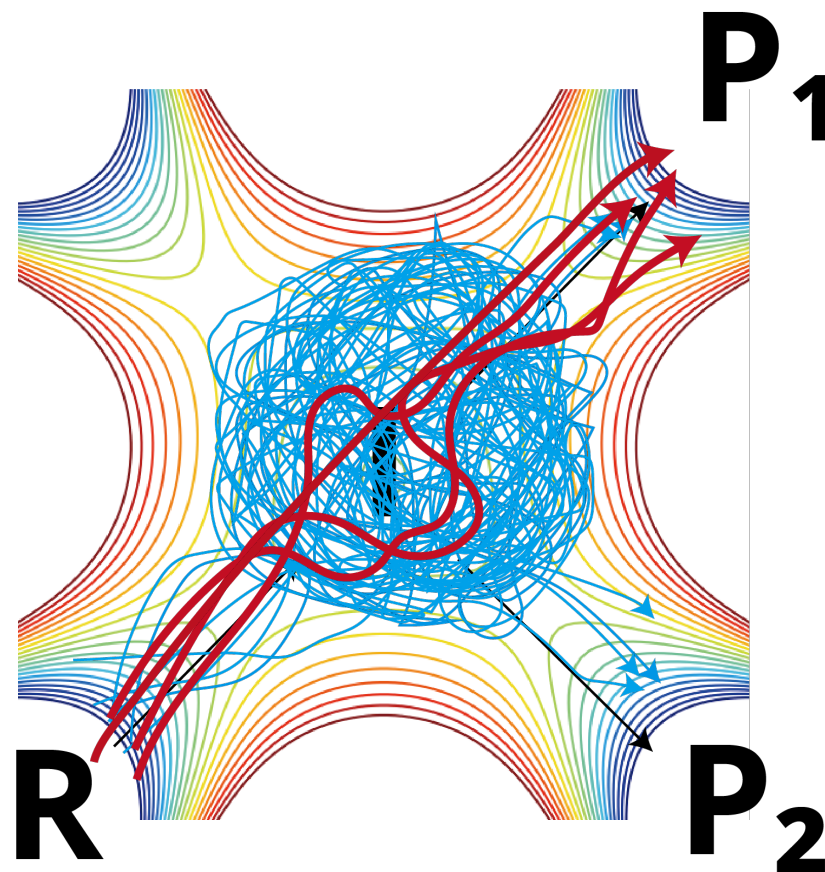
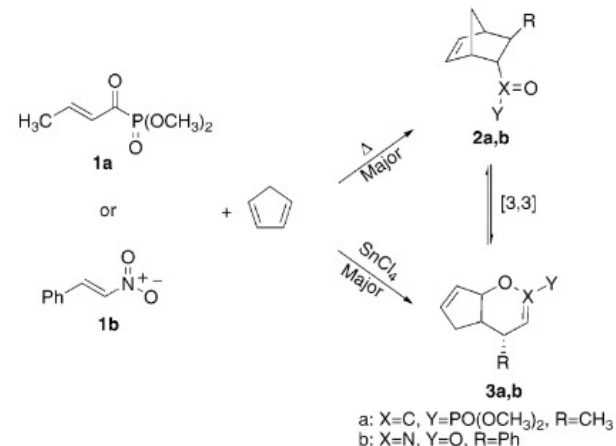
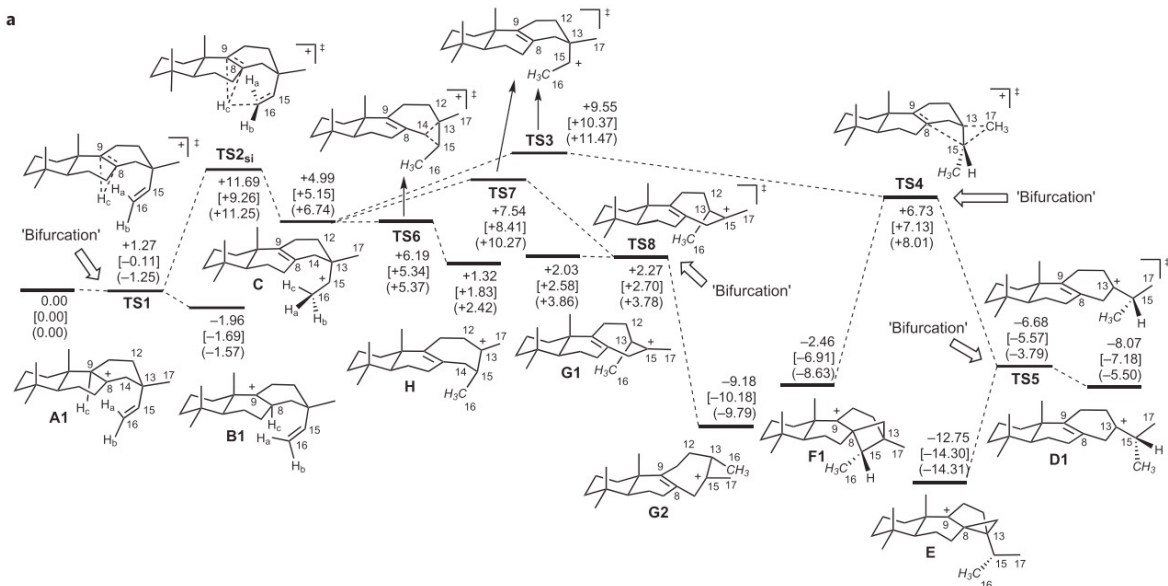
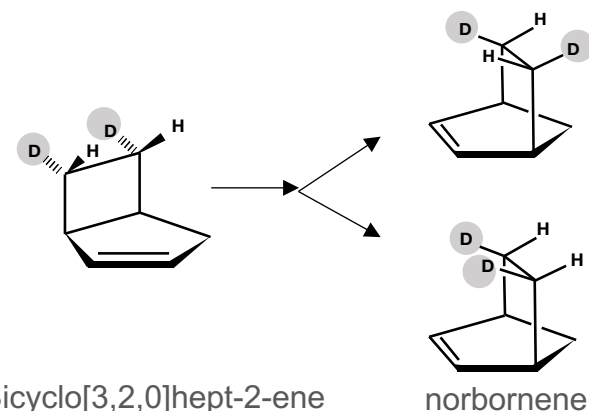


Fig. potential energy surface

Chemical reactions which reactivity is affected by the dynamics 3/15



A competition of Hetero / Diels-Alder reaction²⁾



A stereoselectivity of a gas phase reaction³⁾

There is **no systematic method** to analyze real chemical reaction dynamics with considering **momenta**.

1) Y. Hong, D. Tantillo, Nature Chemistry, (2014) 6, 2, 104-111.

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3) Carpenter B. K, J. Am. Chem. Soc. 117 (1995) 6336-6344.

● Problem:

- Many chemical reactions are reported whose reactivity are affected by dynamics²⁻³⁾
- The dynamical reactivity comes from the **contribution of momenta** in the reaction.
- Discussing the **dynamics in phase space** can be effective.

Phase space:

Comparing to the **configurational** space (only position), the phase space consists of not only **position but also momentum**.

- So far, the non-statistical behavior of chemical reaction have been studied **with few-degrees-of-freedom models**⁴⁻⁸⁾.
- However, discussing real chemical reaction systems in phase space is still the challenging problem.
- We are interested in applying **the reactive island theory** in the phase space.

5) N. De Leon, M. A. Mehta, and R. Q. Topper, J. Chem. Phys, 94, (1991) 8310.

6) T. Komatsuzaki, R. Stephen Berry, *Advances in Chemical Physics*, 130(A) (2005) 143-170.

7) S. Wiggins, L. Wiesenfeld, C. Jaffé, T. Uzer, Phys. Rev. Lett. 86 (2001) 5478-5481.

8) Y. Mizuno, M. Takigawa, S. Miyashita, Y. Nagahata, H. Teramoto, and T. Komatsuzaki, *Physica D: Nonlinear Phenomena* 428, 133047 (2021).

About Reactive island theory

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- One way to analyze chemical reaction dynamics in phase space.⁵⁻⁸⁾
- A trajectory corresponds to one point on cross-section in phase space.
- Points with the same reactivity cluster close together on the section.

