*Global Reaction Route Mapping on the Potential Energy Surface via the **Anharmonic Downward Distortion** Following*

Koichi Ohno

Graduate School of Science,

Tohoku University, JAPAN

Global Mapping of the World

← **Ptolemaios's map**

Discovery of New Routes

1492 Christpher Columbus
1498 Vasco da Gama
1497 Sebastien Gabbot
1499 Amerigo Vespucci
1519 Ferdinand Magellan

Captain James Cook →

1728-1779

Exploration
of the Unknown World!

How to Explore the Chemical World?

Global Map?

Tool for Exploration?

Fundamental Problems of Chemistry?

for a given Chemical Formula, such as $C_NH_MO_L$.

1) What kinds of chemical species (isomers) exist?

2) How are they converted each other?

3) How do they dissociate into smaller species?

To solve These Problems Theoretically,

Global Mapping of Potential Energy Surfaces (PES)

is required to be made.

Minima:

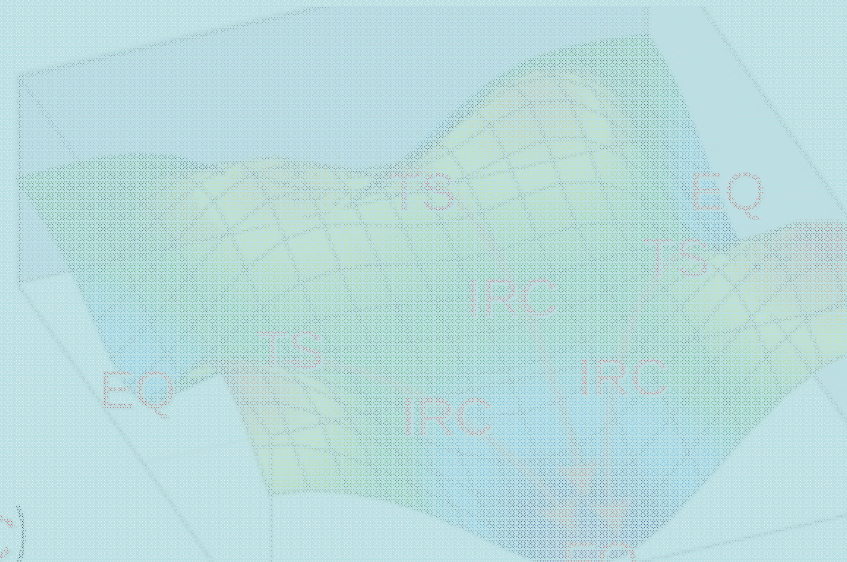
Equilibrium Structures (*EQ*)

Saddle points:

Transition Structures (*TS*)

Valleys:

Intrinsic Reaction Coordinates (*IRC*)

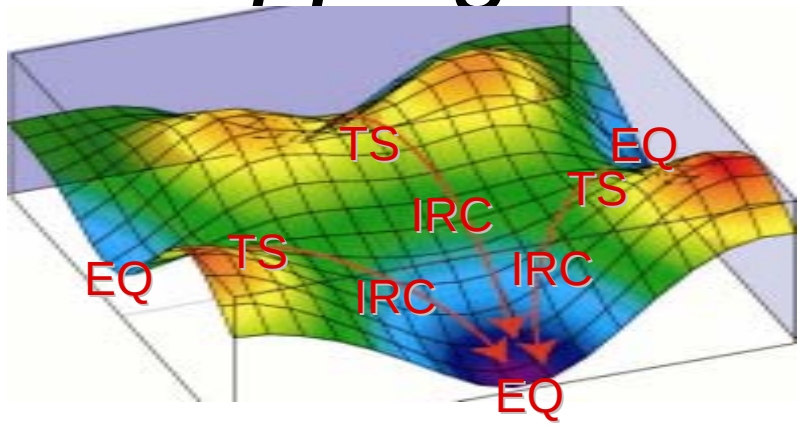


$H\Psi = E\Psi$ *yields Potential Energy Surface.*

Schrödinger / Heisenberg / Dirac • Pople / Kohn • Nakatsuji

In order to study PES,
you need to solve
Schrödinger's equation,
many ・・・ times!

Algorithms for PES Mapping



EQ: Geometry Optimization

Problem Depend on the initial guess!

Numerous Try-&-Errors!

TS: Transition Structure Search

Eigen Vector Following (*EVF*) : Cerjan & Miller (1981)

SEAM ： Jensen (1992)

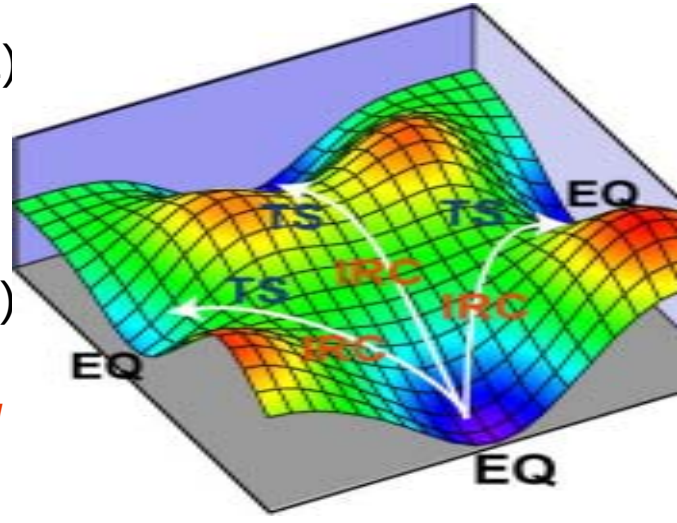
αBB ： Floudas et al. (1992)

Gradient Extremal (*GE*) : Sun & Ruedenberg (1993)

Sphere Optimization (*SO*) : Abashkin & Russo (1994)

Nudged Elastic Band (*NEB*) ： Jonsson et al. (1998)

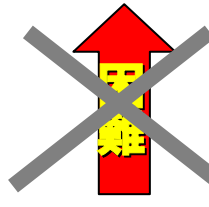
Problem Partially possible, but *generally impossible!*



IRC: Reaction Pathway Search

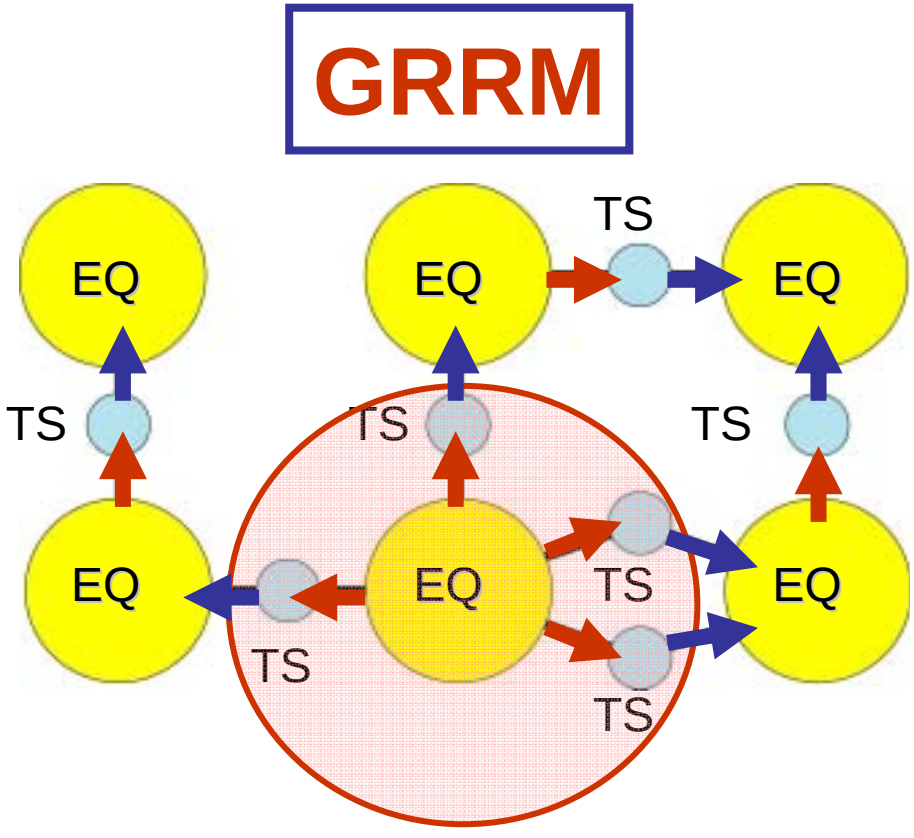
Downhill walks from TS are easy along steepest decent paths!

Problem *Uphill walks along reaction paths are impossible!*

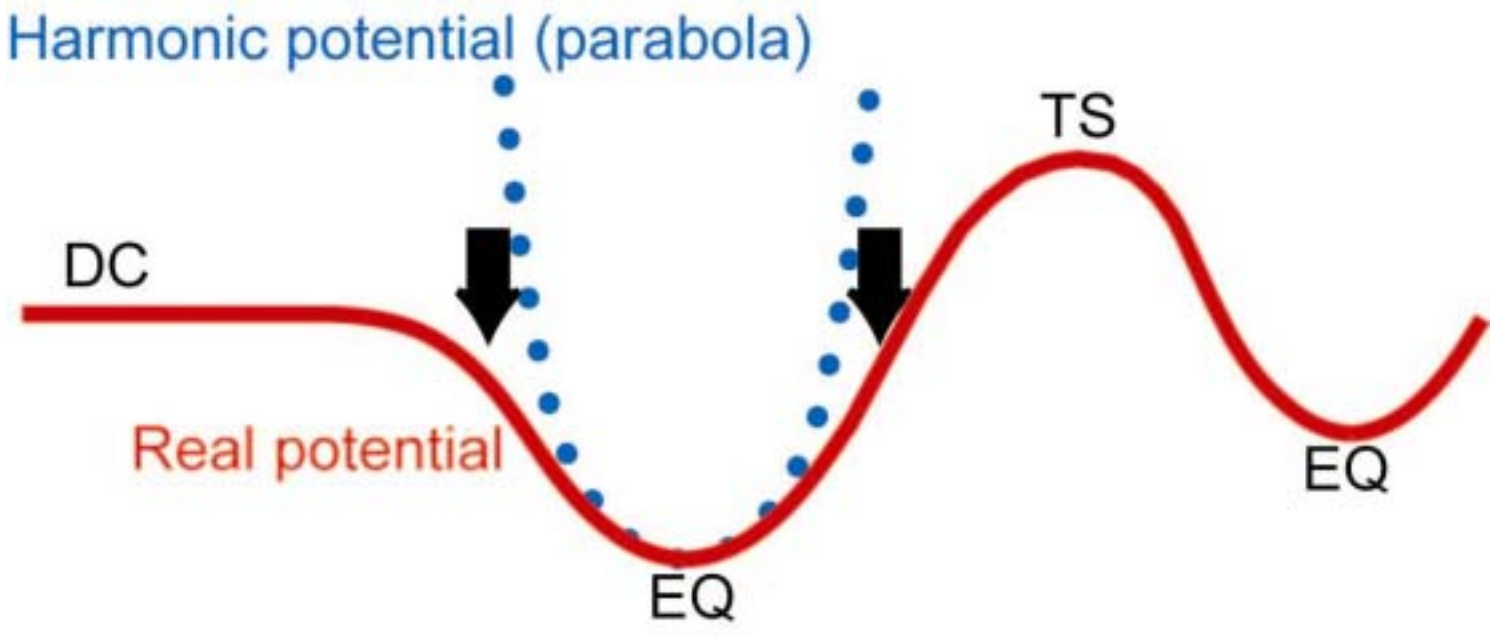


No Algorithm for Uphill Walk along Reaction Path!

Uphill walks along reaction paths make it possible to perform Global Reaction Route Mapping without wondering on PES!



How to find reaction routes from EQ?

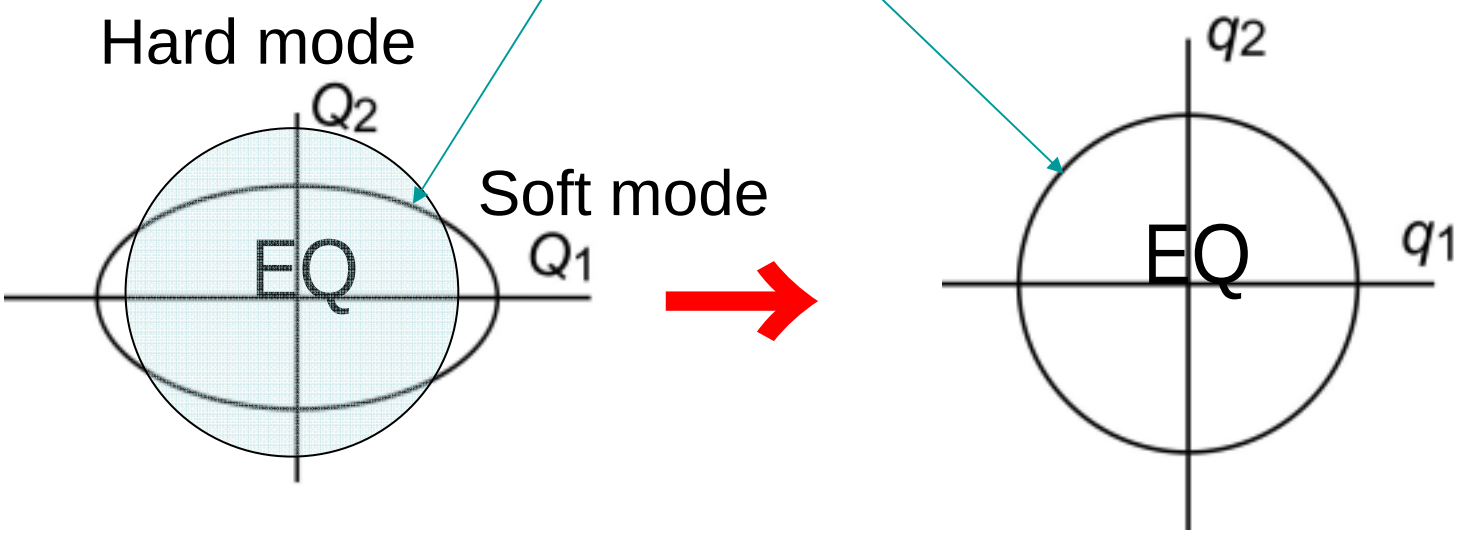


***A**nharmonic **D**ownward **D**istortion* **(ADD) indicates Reaction Routes*!**

（↓ ADD ： Compass to the Unknown Chemical World ）

How to Find ADDs?

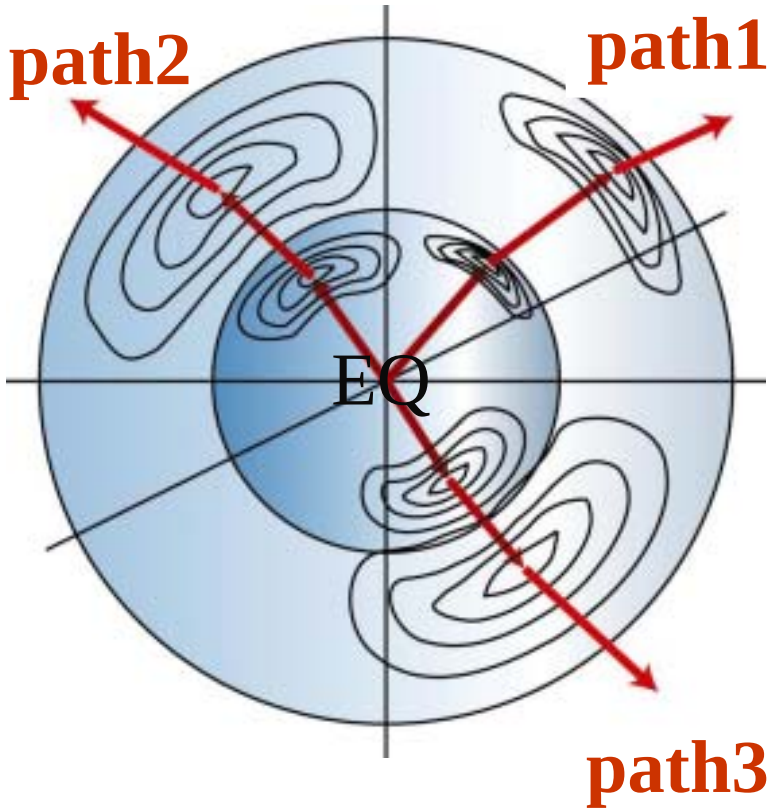
- Use the Iso-Energy Harmonic Hyper-Surface.
- *Scaled Normal Coordinate* : $q_i = \boldsymbol{\lambda}_i^{1/2} Q_i$



Optimization on Sphere Surface!

How to Find & Follow ADD?

- ADD can be found as real energy minima on a scaled hyper-sphere.
- Reaction pathways can be followed by expanding the size of hyper-spheres.



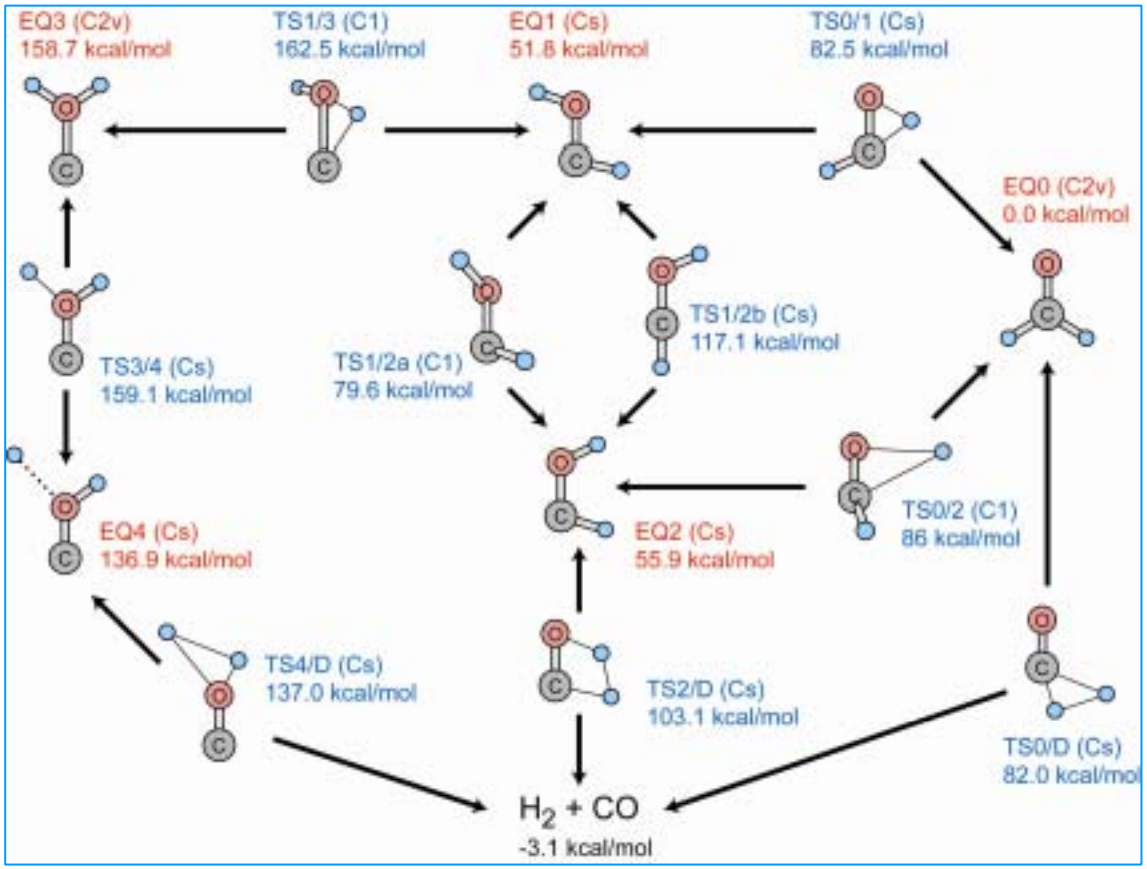
Scaled Hypersphere Search(SHS) Method

K.Ohno & S.Maeda, *Chem. Phys. Lett.*384,277(**2004**).

- ***GRRM* 1.00** is the first computer program based on the **SHS (*ADD following*)** algorithm for an ***automated exploration*** of chemical reaction pathways by using energies obtained from solutions of $H\Psi = E\Psi$.
- ***GRRM* 1.00** copes with long standing fundamental problems in chemistry by automated exploration of chemical reaction pathways.
- O ***GRRM* 1.00 automatically explores unknown isomers.**
- O ***GRRM* 1.00 automatically explores unknown synthetic routes.**
- O ***GRRM* 1.00 automatically explores unknown dissociation channels.**
- ***GRRM* 1.00** develops an unexplored world of chemistry by elucidating unknown chemical reaction networks.
- ○ ***GRRM* 1.00 is useful for production of the Atlas for the chemical world.**
- ○ ***GRRM* 1.00 is useful for design of new chemical compounds and reactions.**
- ○ ***GRRM* 1.00 is useful for designing new tactics for energy / environment problems.**
- ○ ***GRRM* 1.00 is useful for elucidation of catalysis and design of new catalysts.**
- ***GRRM* 1.00** is an epoch-making program of potential analyses for the following problems.
- ● **Normal coordinate analysis** Normal coordinate calculations can be made at arbitrary structures. Optionally, enthalpy and Gibbs energies can also be obtained.
- ● **Optimization of equilibrium structures** Equilibrium structures can be optimized by **SIRFO** and **BFGS** methods**.**
- ● **Optimization of transition structures** Transition structures can be optimized by **SIRFO** and **Bofill's** methods**.**
- ● **IRC search IRC** can be traced by **Page** and **McIver** methods**.**
- ● **GRRM search** Global reaction route mapping (**GRRM**) can be made for the potential surface of a given chemical formula. Starting from an equilibrium structure, automated search of dissociation and isomerization can be performed to explore **GRRM** corresponding to the Atlas of chemical reaction routes. Optionally, exploration of reaction routes can be made for the limited region around a particular structure.
- ● **One step TS search** An efficient search of the reaction pathway connecting a reactant and a product can be made to determine the transition structure (**TS**). This procedure can be done automatically without initial guess, and this technique is much more rapid and applicable than any other methods, such as the **NEB** method.
- ● **Intermediate search** Intermediates between a pair of isomers can be found, even if they are far apart. The **SHS** method in the hypersphere-contraction-mode enables us to explore multi-step reaction pathways, even if they amount to several tens of steps.
- ***Program Package & Requirement for GRRM* 1.00**
- ***GRRM* 1.00** utilizes energies obtained by **Gaussian03**.
- ***GRRM* 1.00**, a 64-bit or a 32-bit version, can be used under a Linux / Unix environment.
- ***GRRM* 1.00** can be used for research and education, after application to the following address by E-mail.
ohnok@qpcrkk.chem.tohoku.ac.jp
- Further information for ***GRRM* 1.00** is available at the following page.
- http://qpcrkk.chem.tohoku.ac.jp/

GRRM for H_2CO

5 EQ 9 TS



Gradient **E**xtremal Method(**HF/STO-3G**): **Bodensgard & Jensen**, *J.Chem.Phys.*104, 8025 (**1996**).

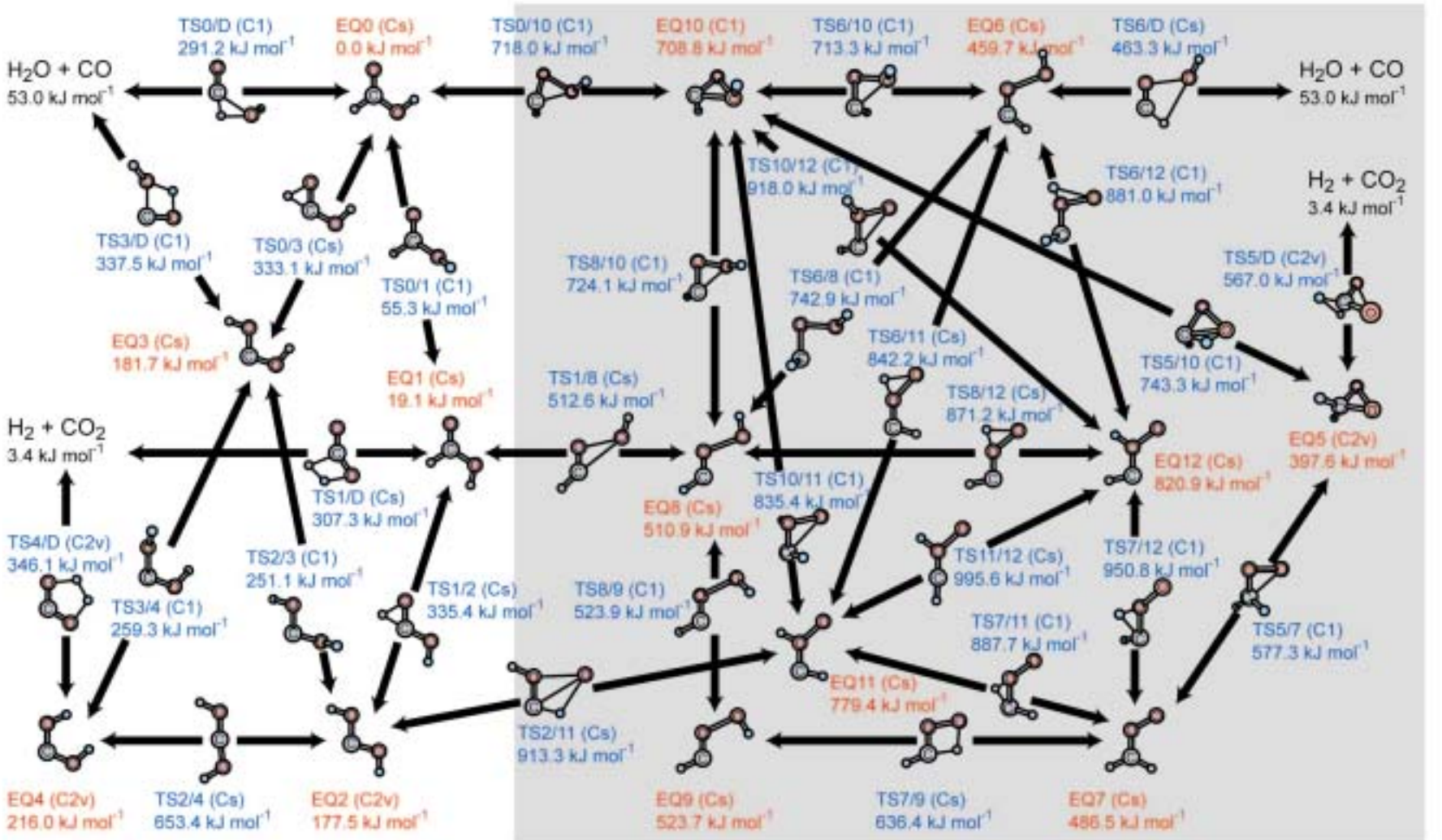
Reduced **G**radient **F**ollowing Method(**HF/STO-3G**): **Quapp et al**. *J.Compt.Chem.*19,1087 (**1998**).

Scaled **H**ypersphere **S**earch Method(**MP2/3-21G**): **Ohno & Maeda**, *Chem. Phys. Lett.*384,277(**2004**).

Scaled **H**ypersphere **S**earch Method(**B3LYP/6-31G**): **Maeda & Ohno**, *J.Phys.Chem.A* 109,5742(**2005**).

GRRM for H_2CO_2

13 EQ 30 TS

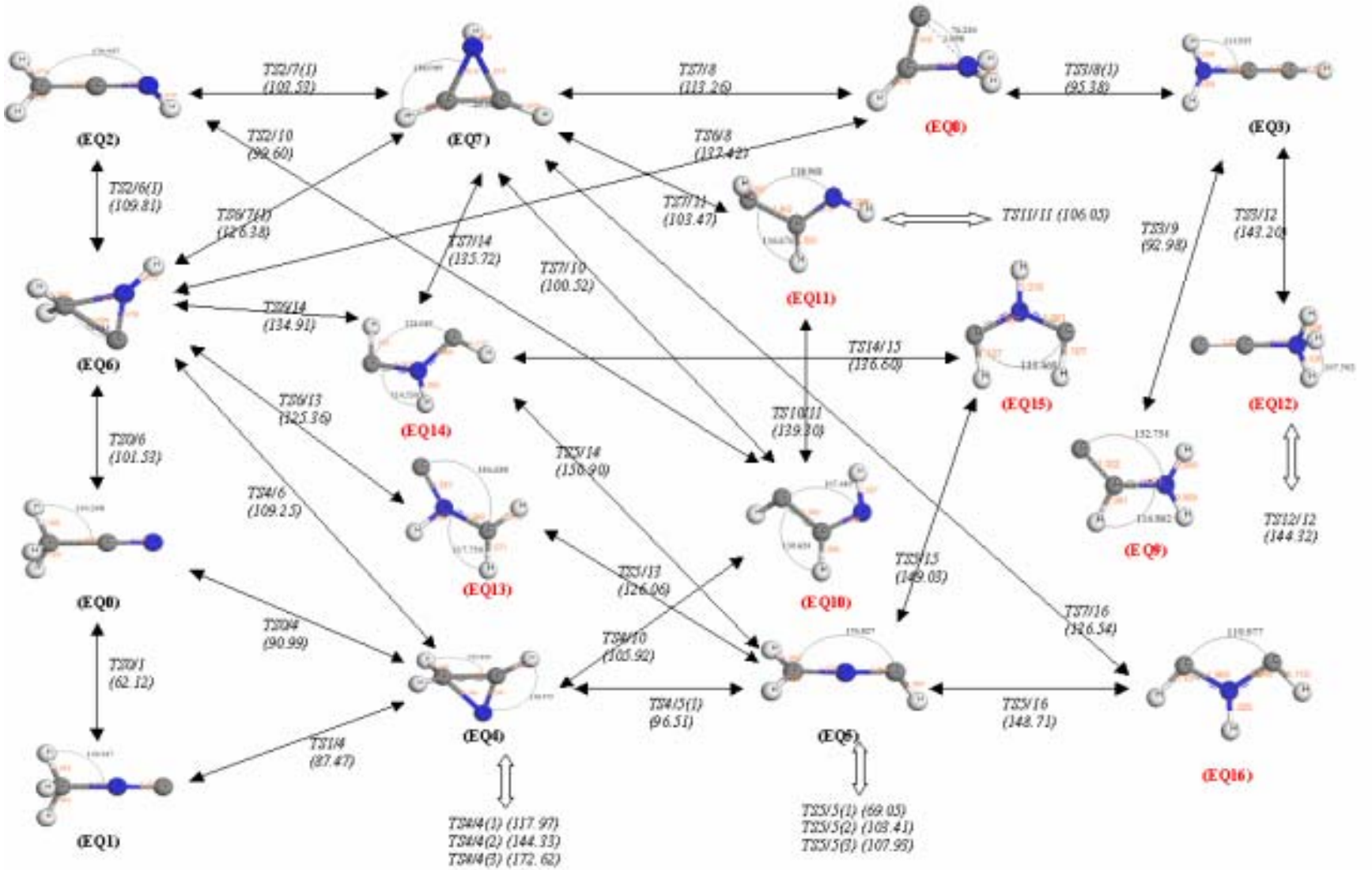


K. Ohno, S. Maeda, *J.Phys.Chem. A*, 110, 8933 (2006).

GRRM for C_2H_3N

17 EQ 59 TS

9 EQ & 41 TS were newly found!



X. Yang, S. Maeda, and K. Ohno, *J. Phys. Chem. A* 109, 7319 (2005)

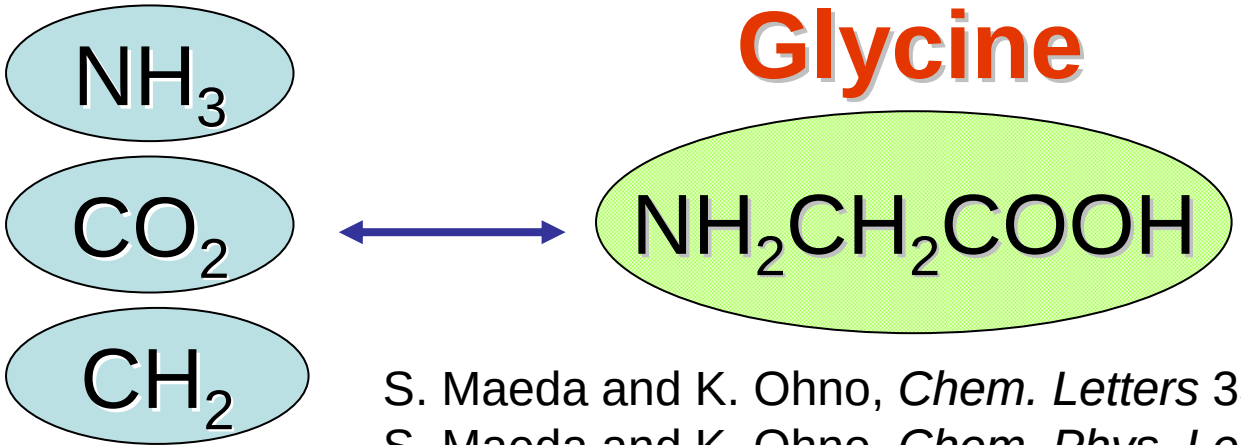
Application to finding
a new synthetic route with no byproducts
recommended by economy and environments

- Find Dissociation Channels starting from the aimed compound (*A*)

$$A \rightarrow B + C$$

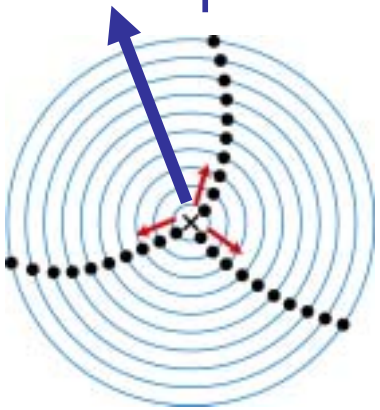
$$\leftarrow$$

- Trace back to the initial compounds (A) from the dissociation products (*B* and *C*)

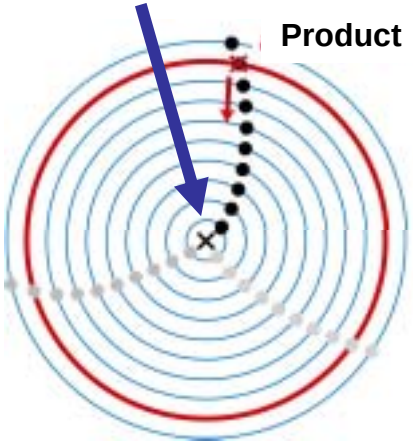


S. Maeda and K. Ohno, *Chem. Letters* 33, 1372 (2004).

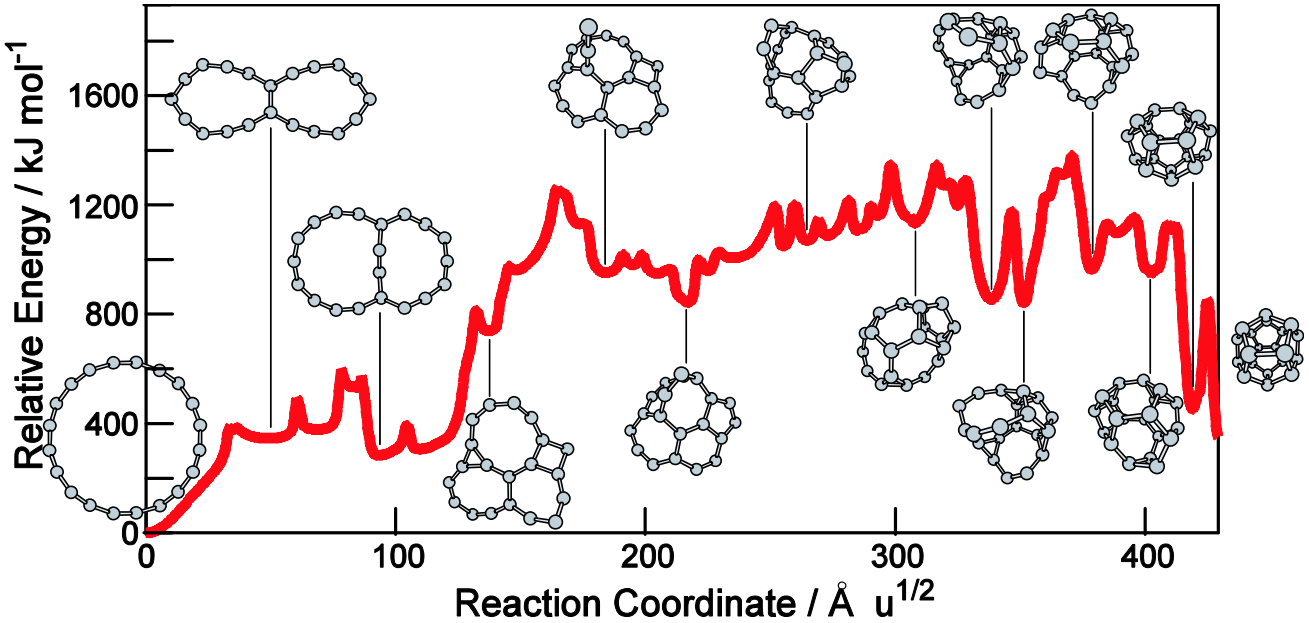
Sphere Expansion



Sphere Contraction

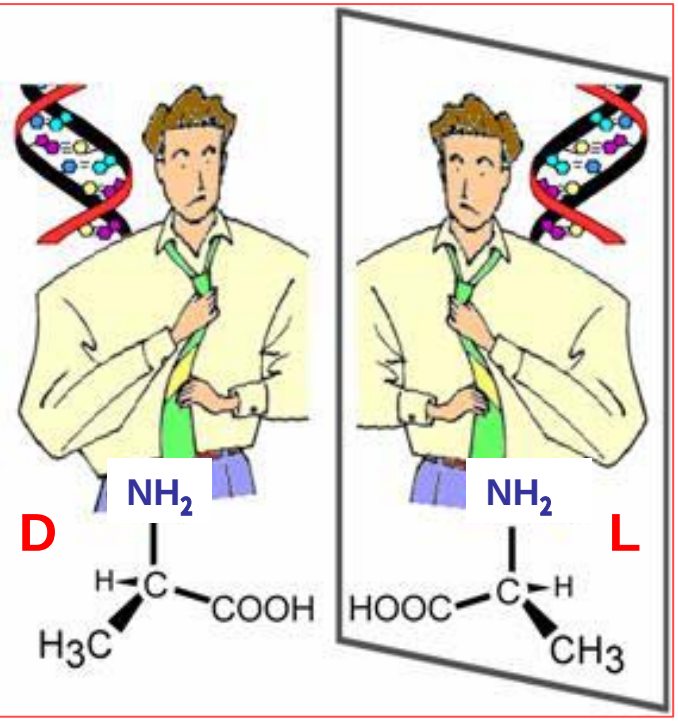


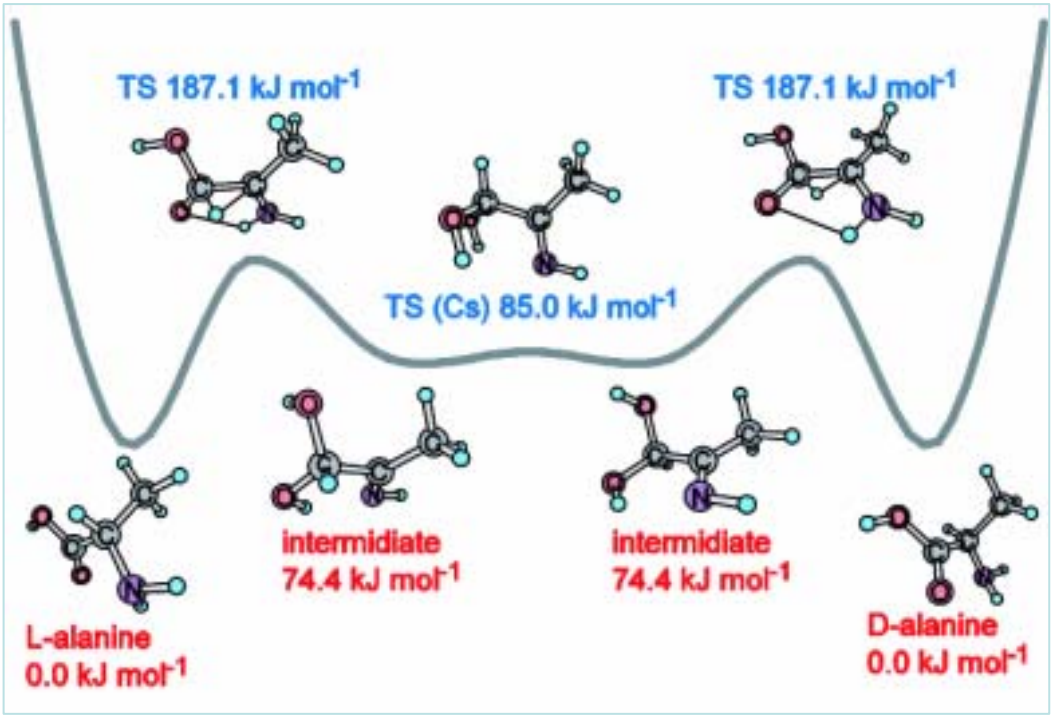
Multi-step Conversion Routes of C_{20} Clusters

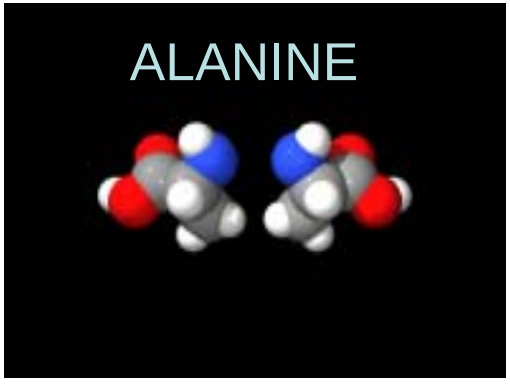


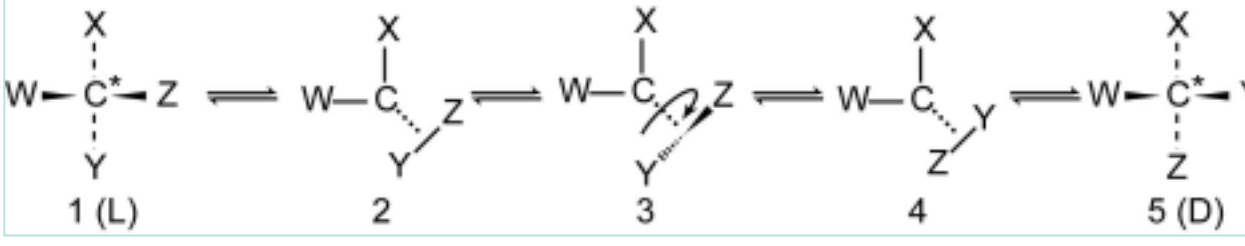
S. Maeda and K. Ohno, *J. Chem. Phys.* 124, 174306 (2006)

D-L Conversion Routes for Optical Isomers









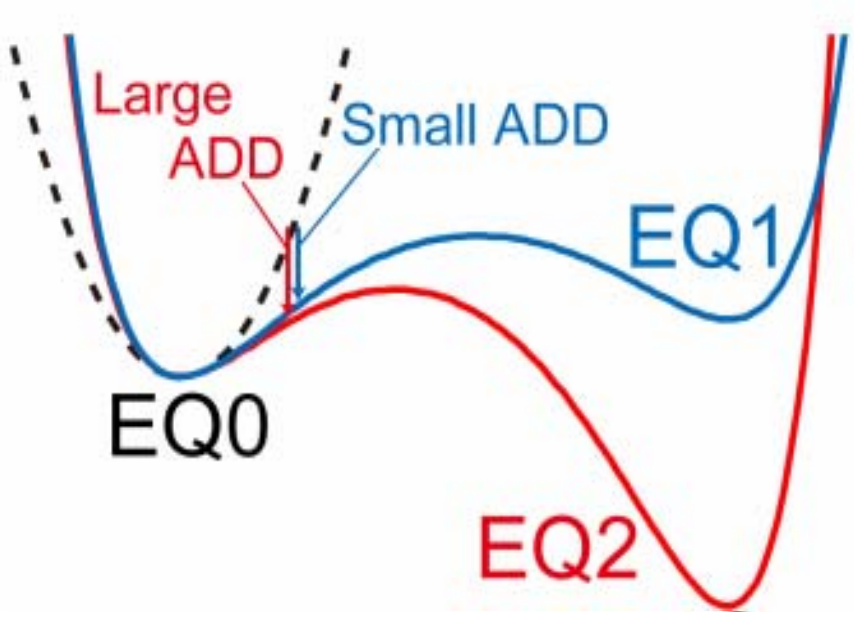
K. Ohno and S. Maeda, *Chem. Letters* 35, 492 (2006)

Large ADD Following

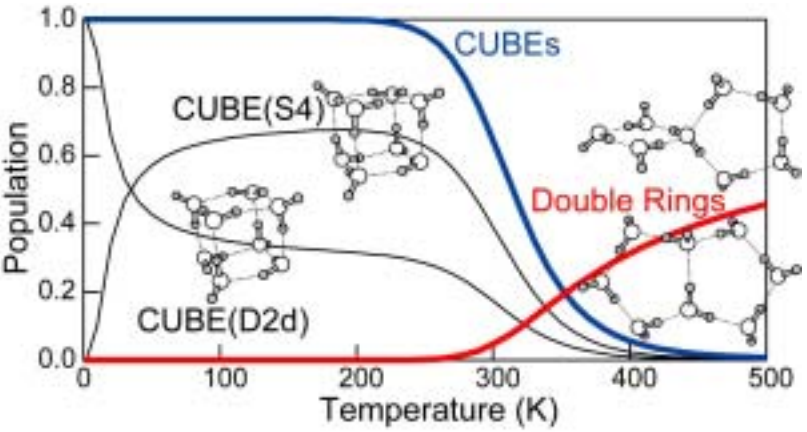
- Full ADD (FADD) ⇔ Full CI
- Large ADD (**LADD**) ⇔ Limited CI

- Large ADD finds Lower Barrier leading to Lower EQ.

→ *Lower Energy Regions connected by Lower Barriers can be Searched Efficiently.*

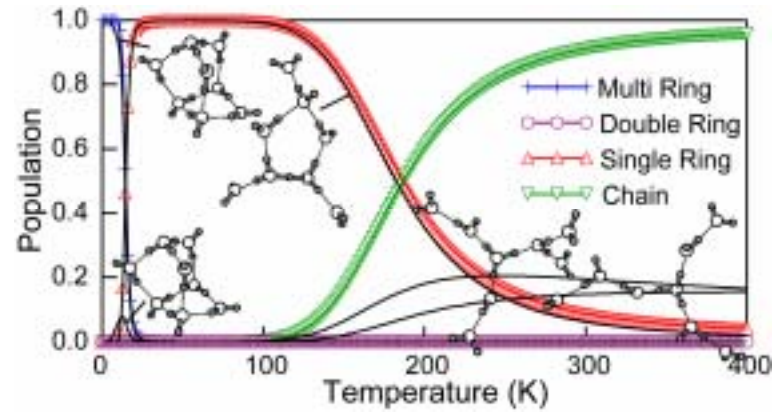


Thermodynamic Analyses for Clusters : $(H_2O)_8$

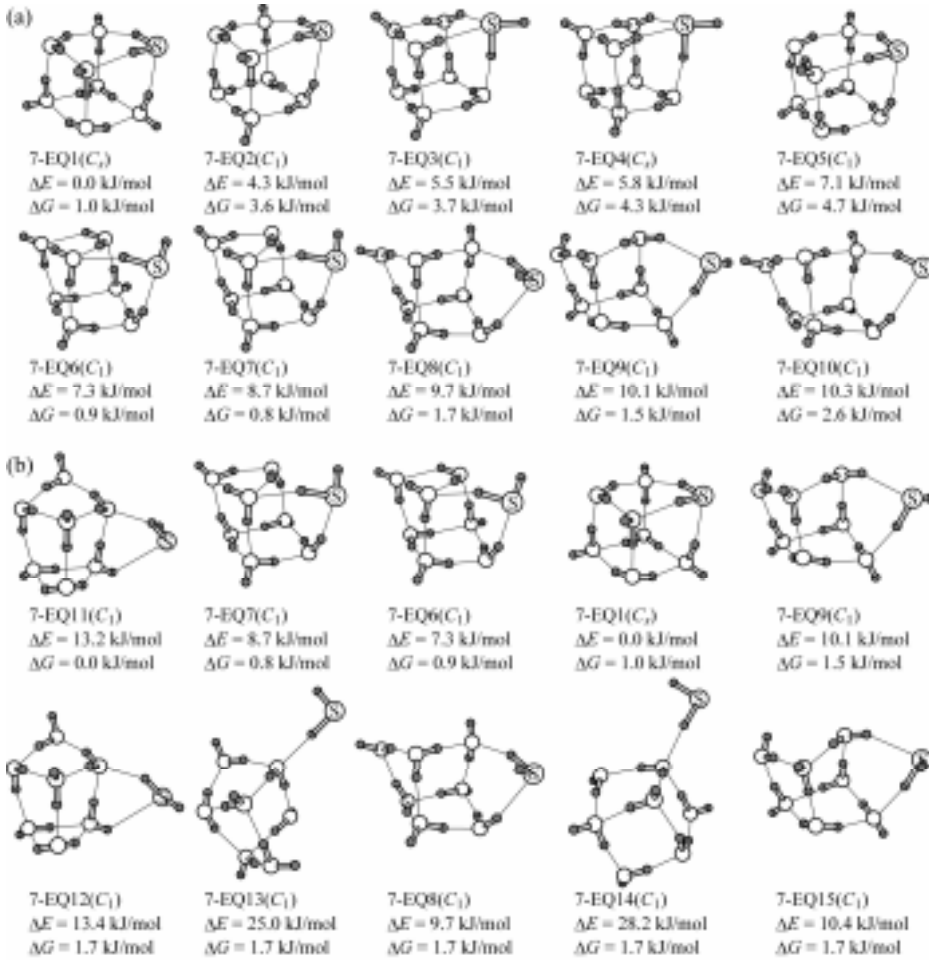


S. Maeda and K. Ohno,
J. Phys. Chem. A 111, 4527 (2007)

$H^+(H_2O)_8$



Micro Solvation of H_2S in Water

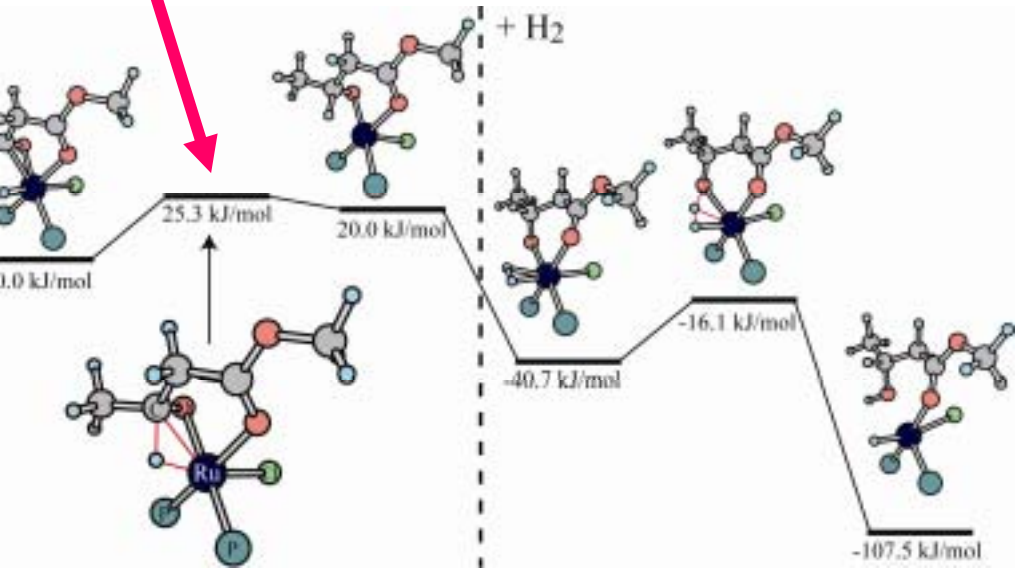


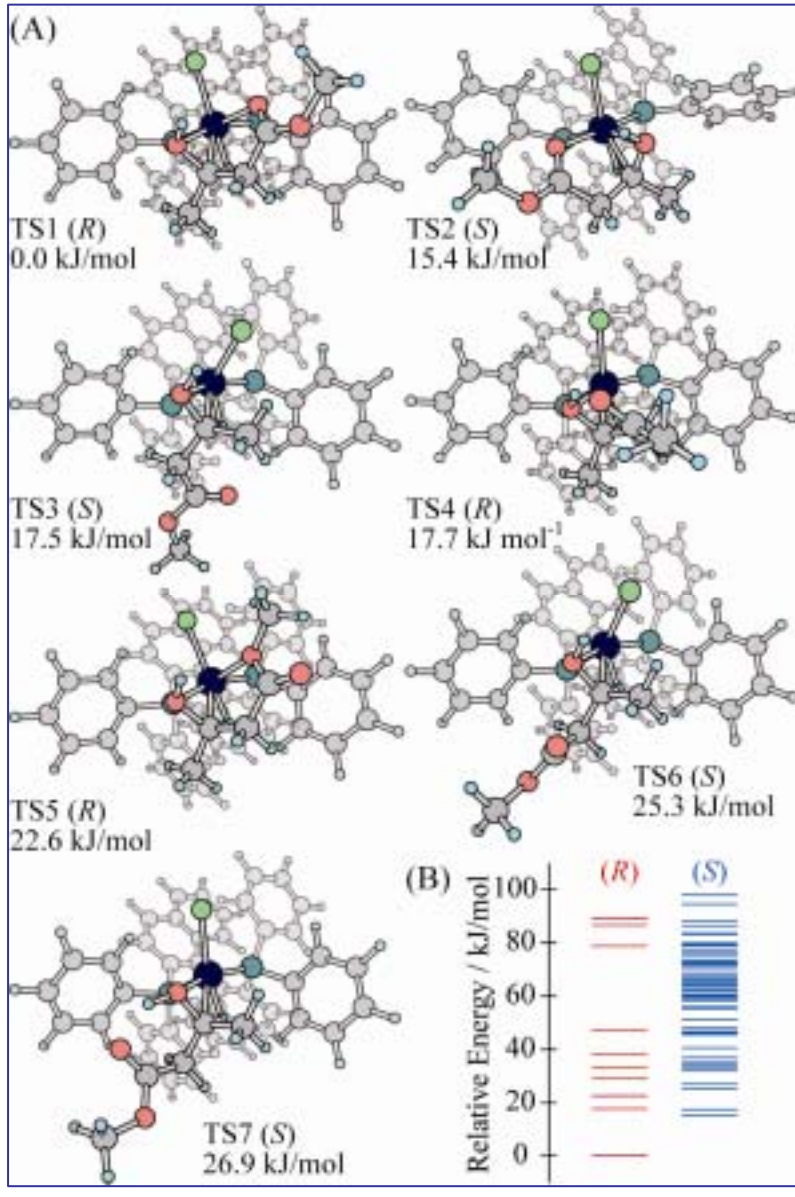
S. Maeda and K. Ohno,
J. Phys. Chem. A 111,13168 (2007)

Asymmetric Catalyst :
RuHCl-BINAP

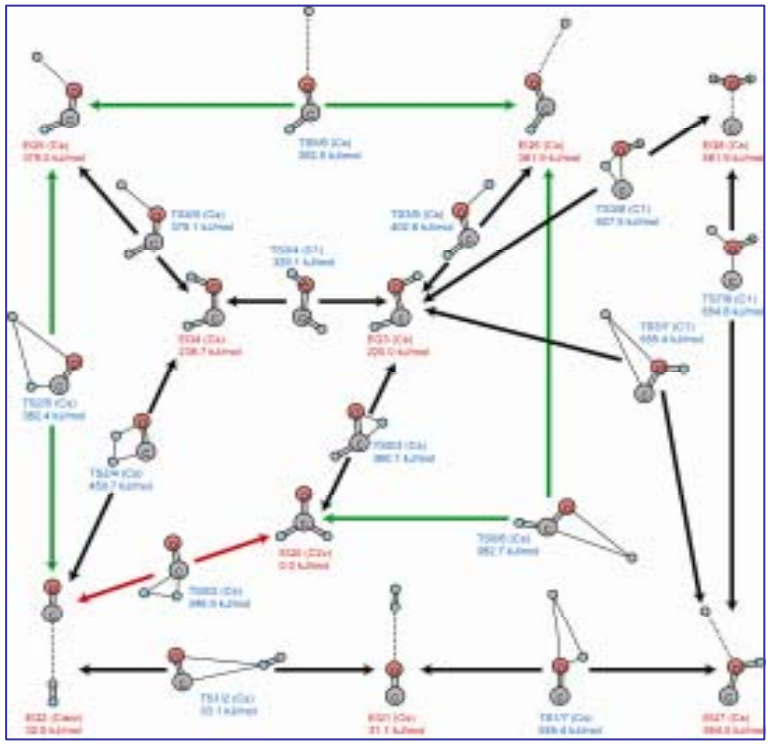
$CH_3COCH_2COOCH_3 + H_2 \rightarrow CH_3C^*HOHCH_2COOCH_3$

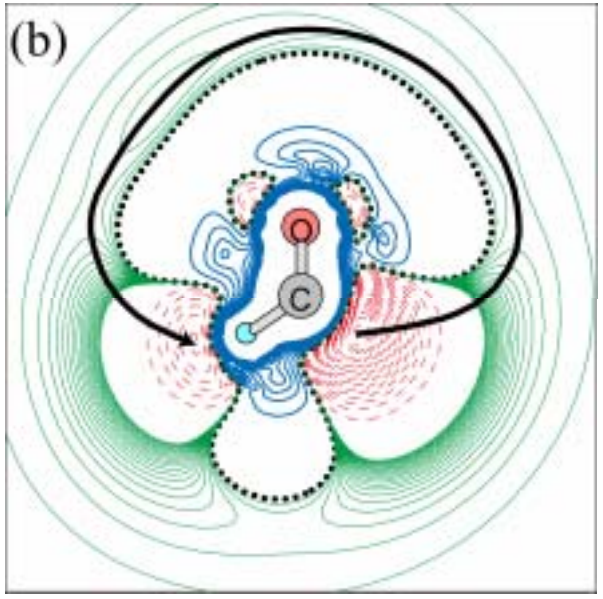
Chirality Determining Step





A New GRRM for H_2CO

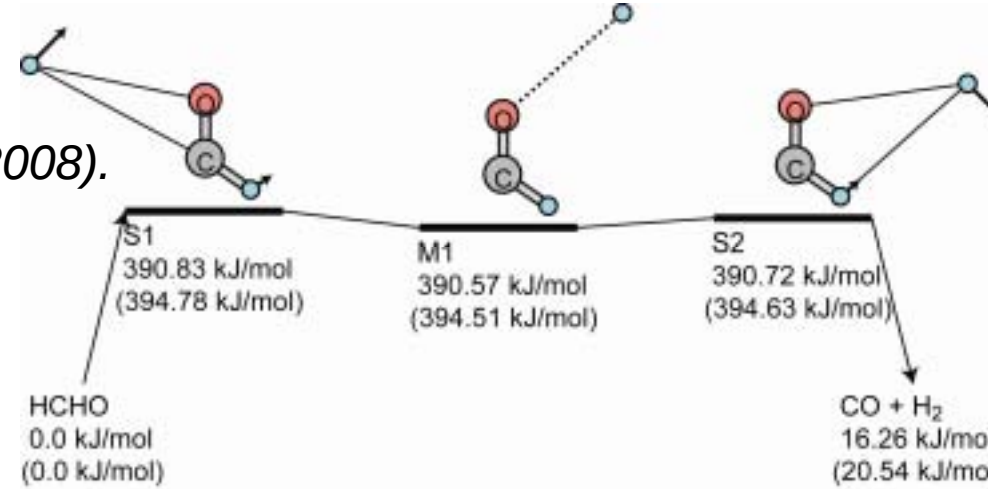




UCCSD(T)/6-311++G(2df,2p)

(UCCSD(T)/aug-cc-pVTZ//6-311++G(2df,2p))

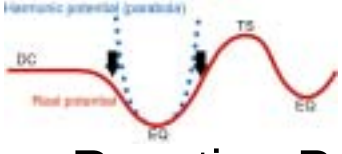
S. Maeda and K. Ohno,
Chem. Phys.Lett. 460, 55 (2008).



ownsend, et al.
cience **306**, 1158 (2004)

Summary

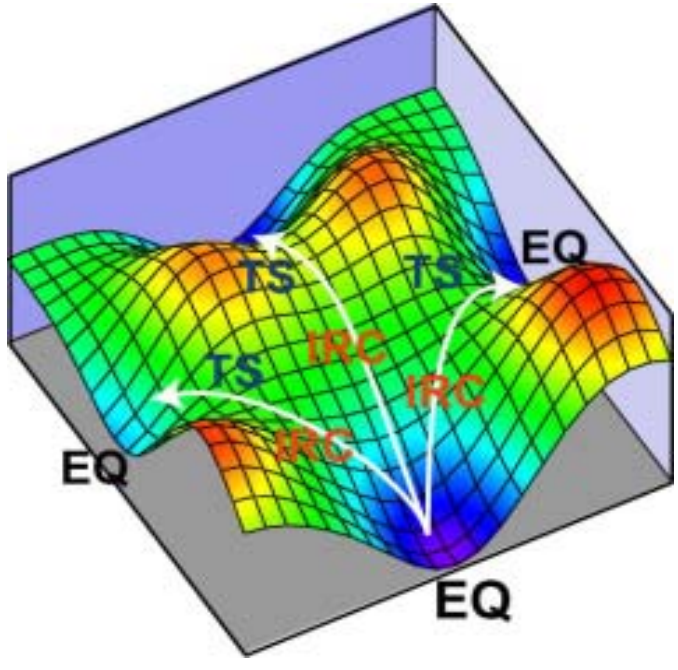
Anharmonic Downward Distortion (ADD) has been discovered as a Compass indicating Directions of Reaction Paths.



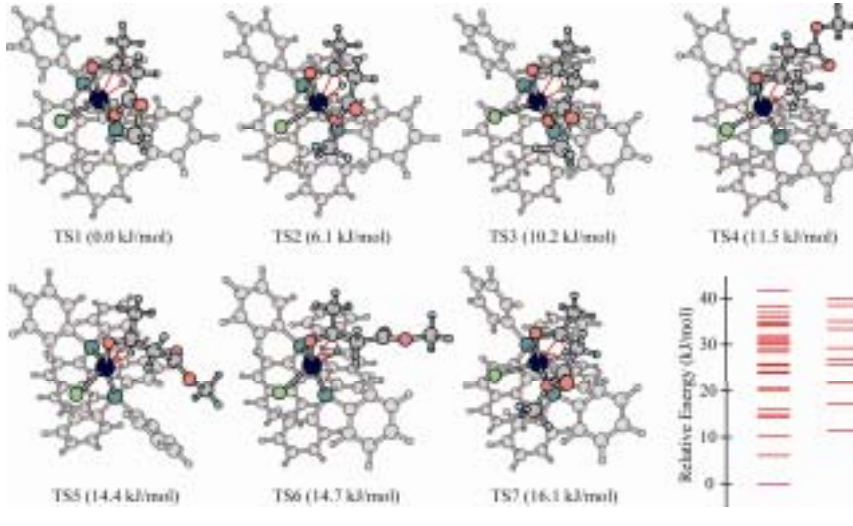
Uphill-Walks along Reaction Paths become possible by following ADD.

Scaled Hypersphere Search (SHS) Algorithm has been developed for Global Reaction Route Mapping on the Potential Energy Surface (PES).

Uphill-Walks on PES enables us to discover Unexplored Chemistry.



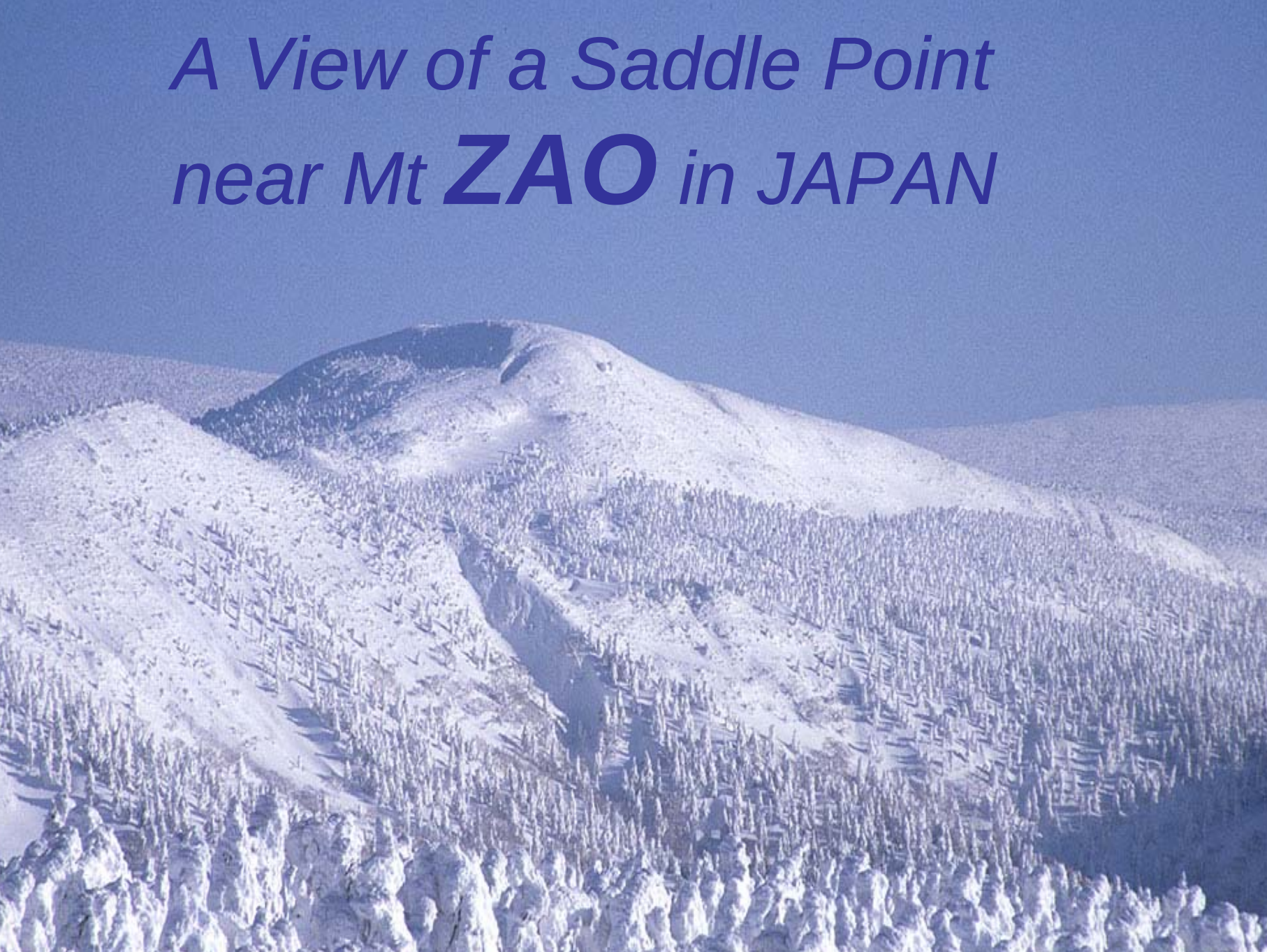
Uphill walks become possible



R S

Collaborators

○ for this work


A View of a Saddle Point
near Mt ZAO in JAPAN