Applications of stochastic surface walking method in molecular crystal structure prediction

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Workshop of "Bridging-Time Scale Techniques and their Applications in Atomistic Computational Science"
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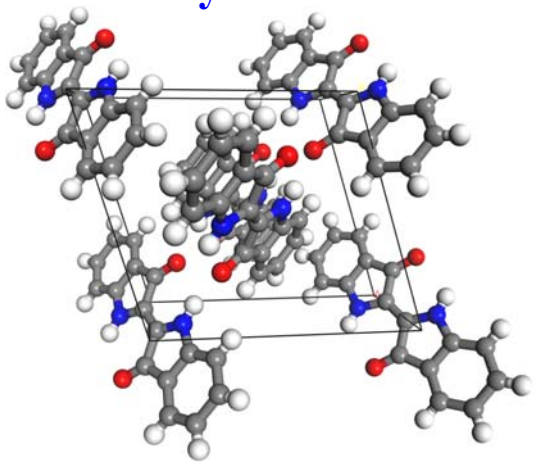
12-15 Sep, 2016, Dresden

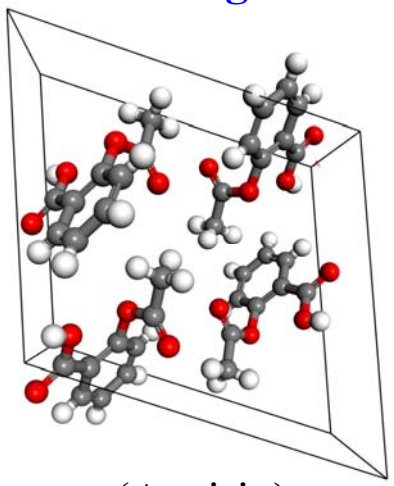
◆ Solid form of organic compound

Dye



(Indigo dye)

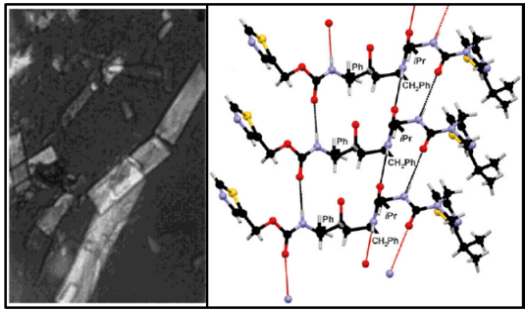
Drug



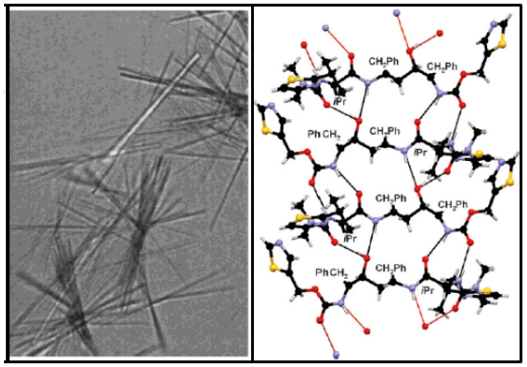
(Aspirin)

◆ HIV Treatment Ritonavir

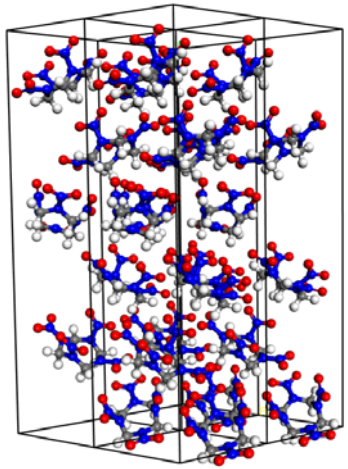
Synthesized phase



Stable phase



Dynamite

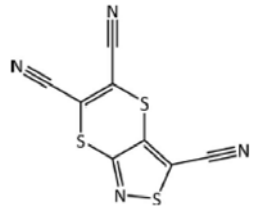


(HMX)

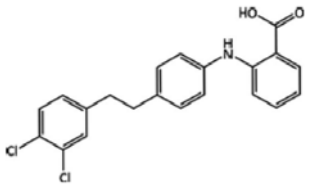
◆ CCDC Crystal Structure Prediction Blind Test

(The Cambridge Crystallographic Data Centre)

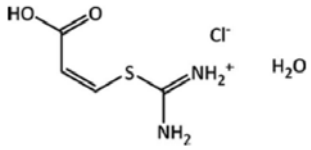
(XXII)



(XXIII)



(XXIV)



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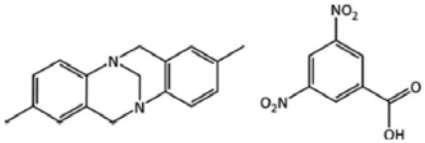
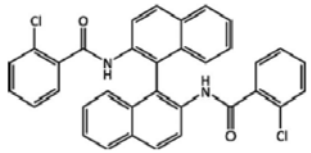


(XXVI)



Acta Crystallogr. Sect. B: Struct. Sci. **(2016).** B72, 439–459

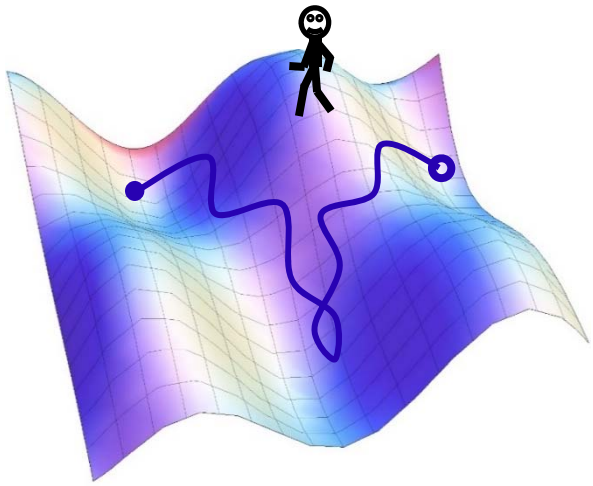
Team	Members	Generation method
1	Chadha,* Singh	MC simulated annealing
2	Cole,* McCabe, Read, Reilly, Shields	CSD analogues
3	Day*, Bygrave, Campbell, Case, Gee, McMahon, Nyman, Pulido, Taylor, Yang	Quasi-random search (Sobol')
4	Dzyabchenko	Grid search
5	van Eijck	Random search
6	Elking, Fusti-Molnar	Random generation
7	de Jong, van den Ende,* de Gelder, de Klerk, Bylsma, de Wijs, Meekes, Cuppen	Random search
8	Lund, Pagola, Orendt, Ferraro, Facelli*	Genetic algorithm
9	Obata, Goto*	Grid search
10	Hofmann,* Kuleshova	Random search
11	Lv, Wang, Ma*	Random search
12	Curtis, Li, Schober, Cosburn, Lohani, Vacarro, Oberhofer, Reuter, Bhattacharya, Vázquez-Mayagoitia, Ghiringhelli, Marom*	Genetic algorithm
13	Mohamed	MC simulated annealing
14	Neumann, Kendrick, Leusen	MC parallel tempering
15	Sugden, Gatsiou, Vasileiadis, Adjiman,* Pantelides*	Quasi-random search (Sobol')
16	Pickard,* Monserrat, Misquitta, Needs	Random search
17	Jankiewicz, Metz, Podeszwa,* Szalewicz	Grid search
18	S. L. Price,* Hylton, L. S. Price, Guo, Watson, Iuzzolino	Quasi-random search (Sobol')
19	Metz, Hylton, S. L. Price, Szalewicz*	Quasi-random search (Sobol')
20	Vogt, Schneider, Metz, Tuckerman,* Szalewicz*	Random search
21	Zhu,* Oganov, Masunov	Evolutionary algorithm
22	Boese	Re-ranking 10
23	Brandenburg, Grimme	Re-ranking 18
24	Metz, Guo, Szalewicz	Re-ranking 18
25	Hoja, Ko, Car, DiStasio Jr, Tkatchenko*	Re-ranking 18

◆ **Questions remaining:**

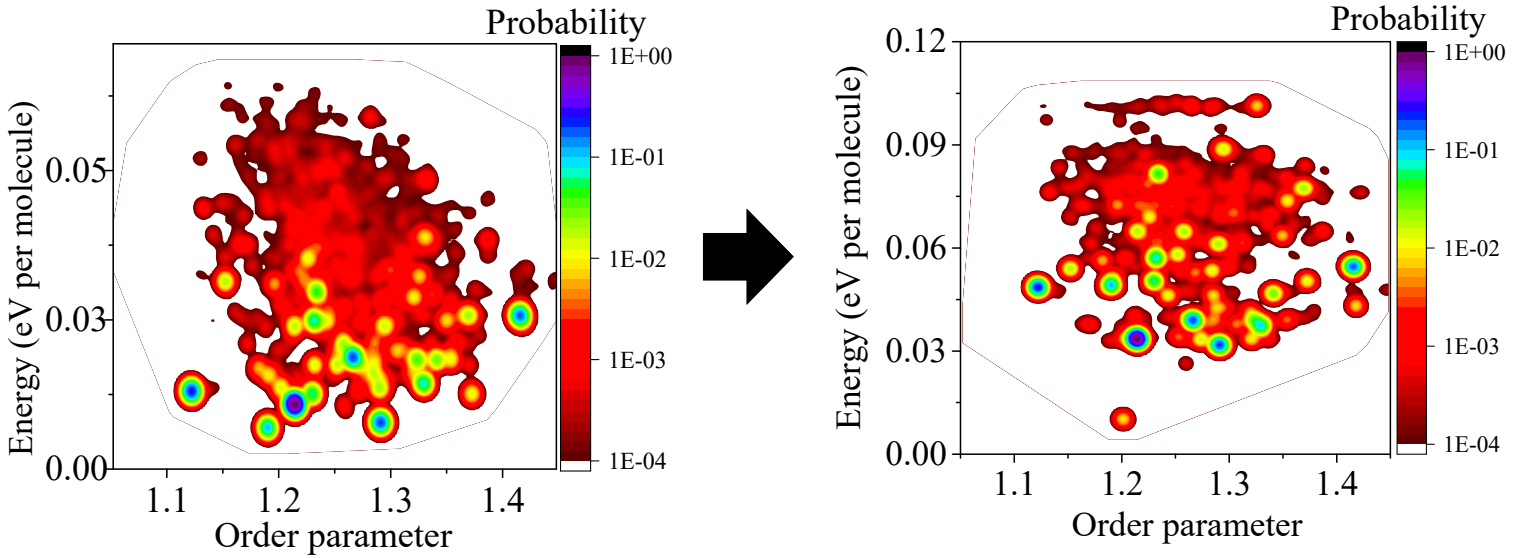
1. **What does the potential energy surface (PES) look like?**

2. **How does the phase transition affect the experimental observation?**

◆Calculation details



- ◆ Stochastic Surface walking method (SSW)
- ◆ Rigid body constrains
- ◆ Double-Ended Surface Walking
  - ◆ Amber force field (GAFF) (Lammps) + DFT (PBE +D3) (VASP)



Steinhardt Q6 order parameter

◆Method: Stochastic Surface walking

Biased rotation + Biased translation to climb

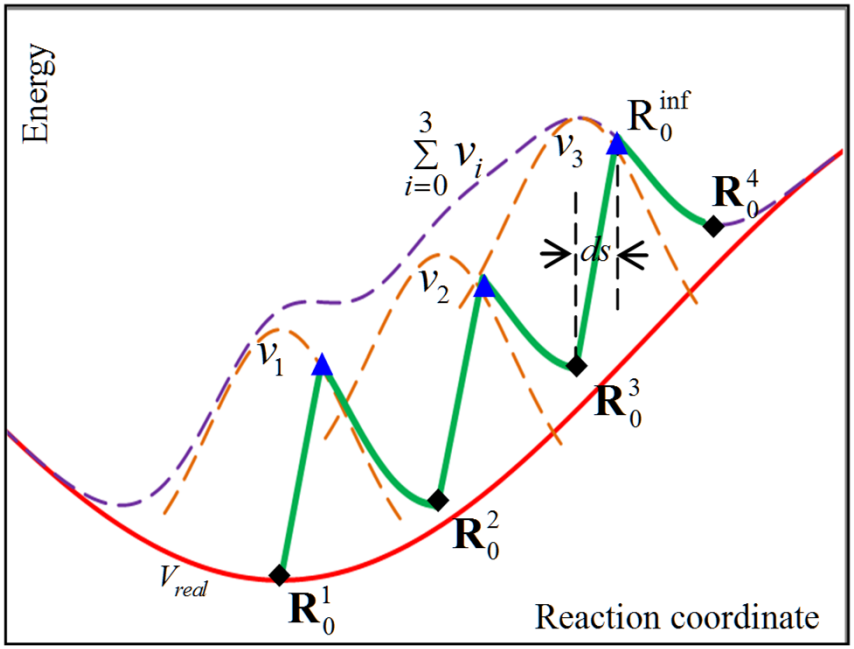
$$V_{R0} = V_{real} + V_G$$

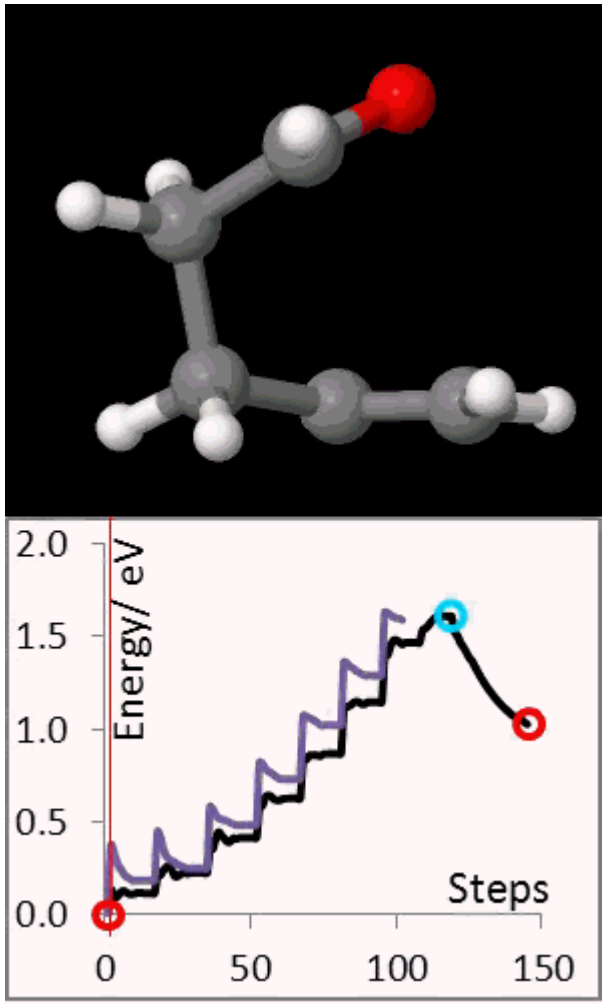
$$V_G = \sum_i v_i \qquad (i = 1, 2, 3 \cdots k)$$

$$v_i = w_i \times \exp\left[-\frac{\left(s_t^i - s_0^i\right)^2}{2 \times ds^2} \right]$$

$$s_t^i = \mathbf{R}_0^t \bullet \mathbf{N}_i$$

$$s_0^i = \mathbf{R}_0^i \bullet \mathbf{N}_i$$



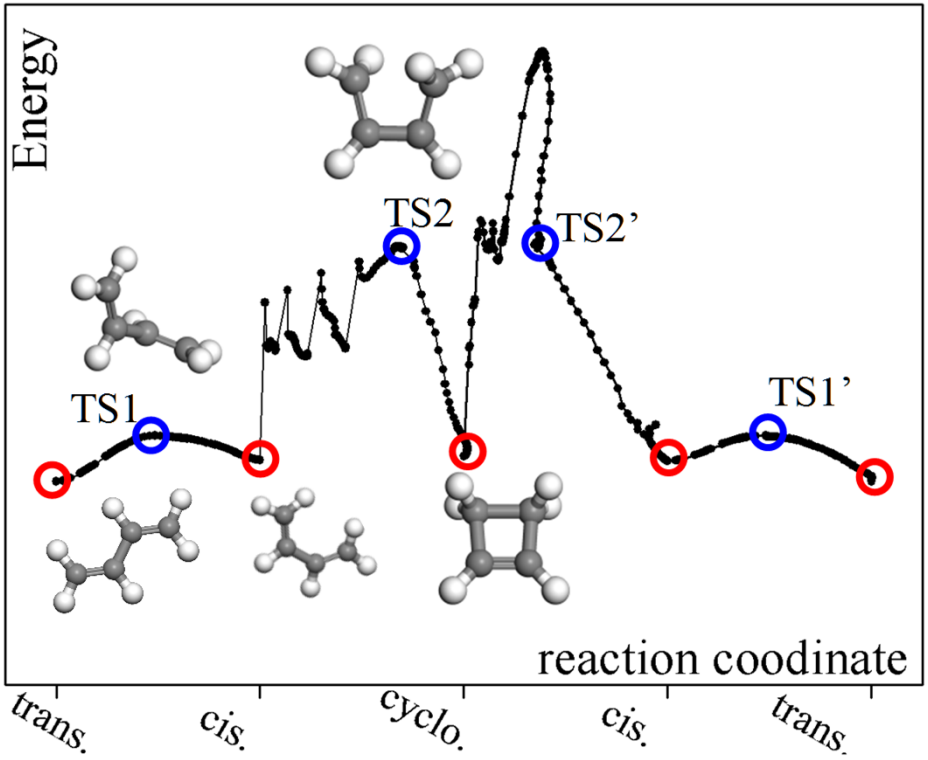


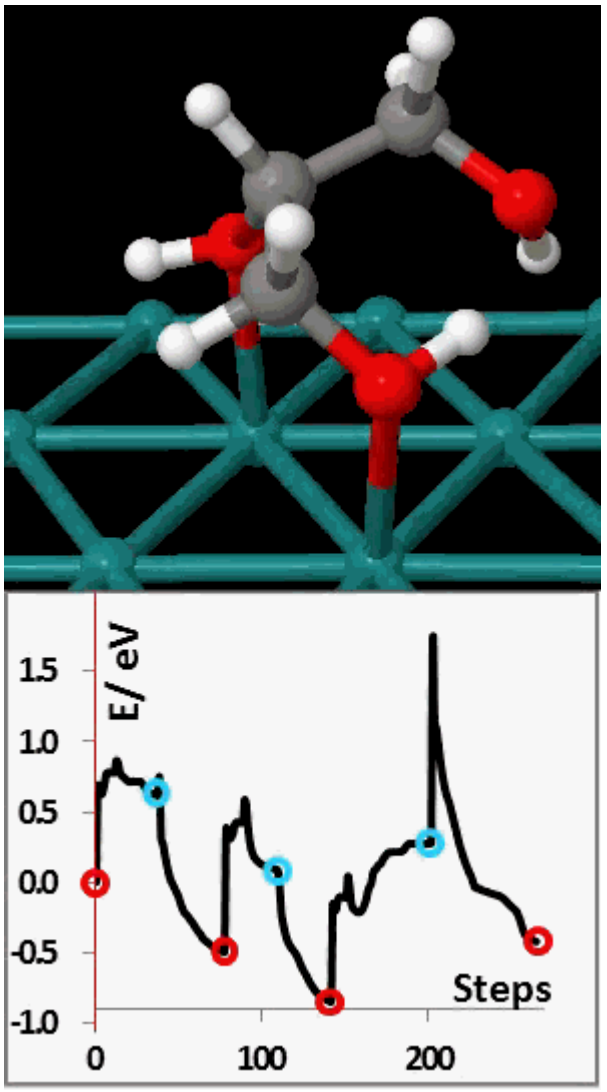
C Shang and Z-P Liu *JCTC* **2010**

C Shang and Z-P Liu *JCTC* **2012**

◆Method: Stochastic Surface walking

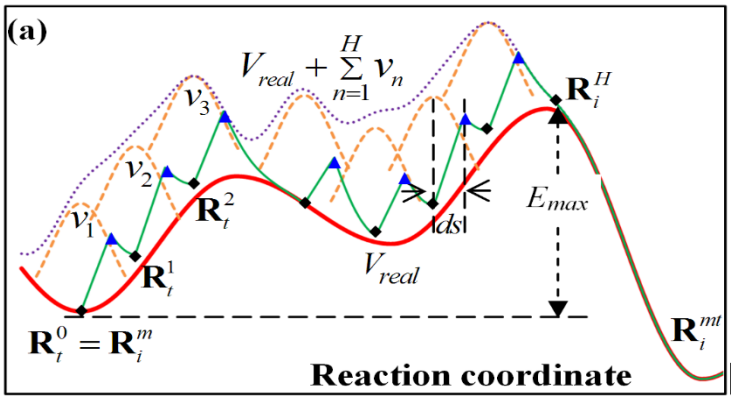
Continuous TS searching process

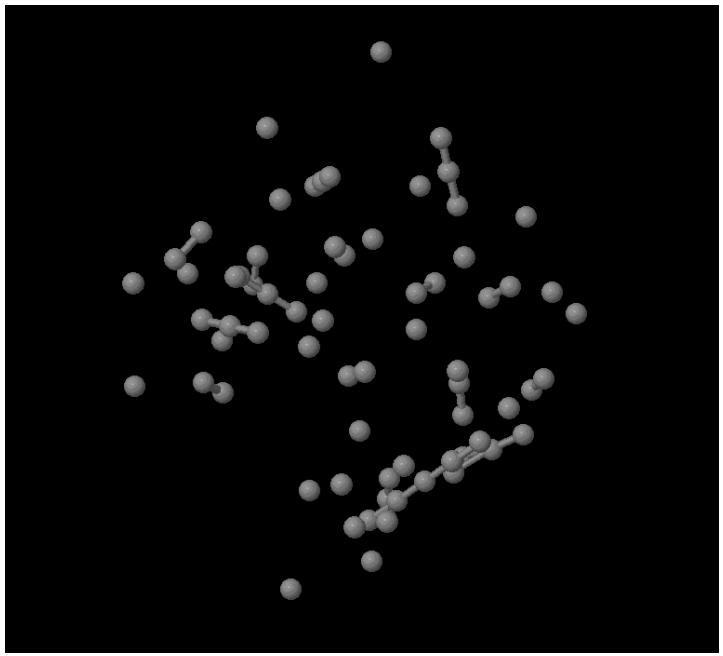




◆Method: Stochastic Surface walking

1. Never stop to locate TSs
2. Fix the size and the number of bias potential
3. Generate mode randomly (move class)
4. Metropolis Monte Carlo





C Shang and Z-P Liu *JCTC* **2013**

X-J Zhang, C Shang and Z-P Liu *JCTC* **2013**

C Shang, X-J Zhang and Z-P Liu *PCCP* **2014**

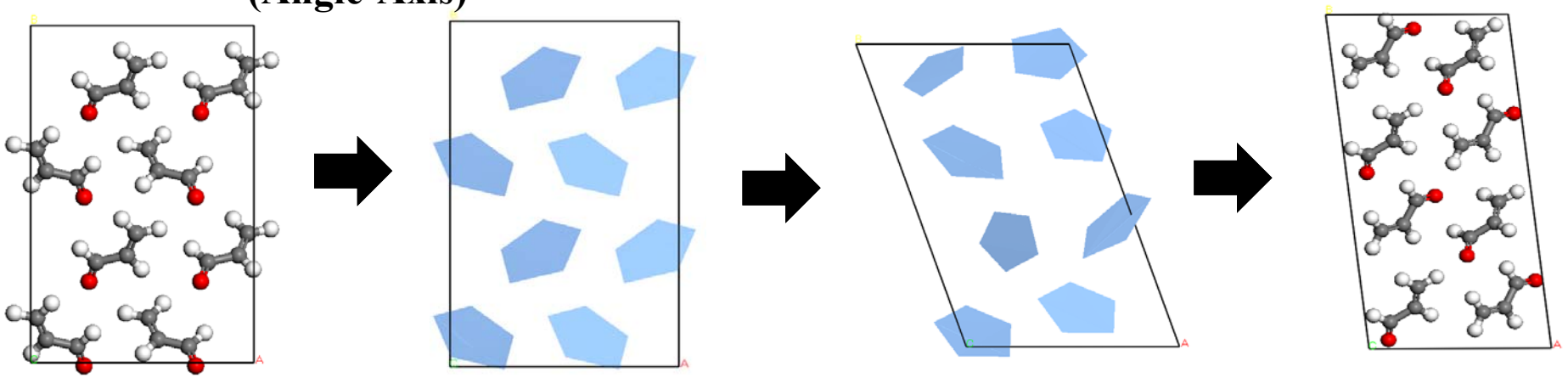
◆ Coarse-grained SSW

Rigidify

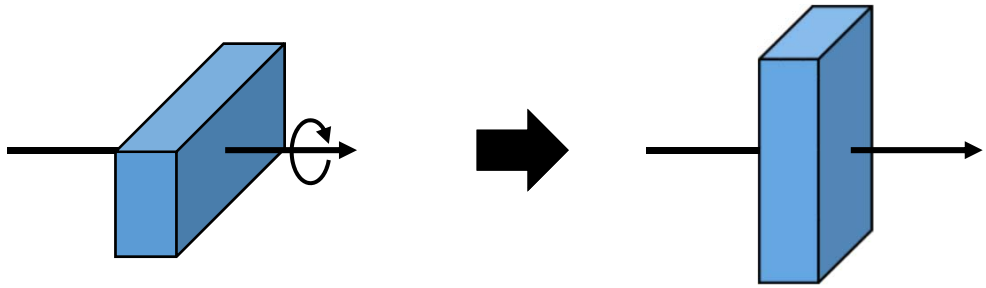
(Angle-Axis)

SSW climb

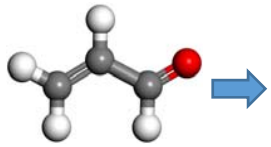
Fully relax

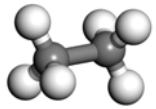


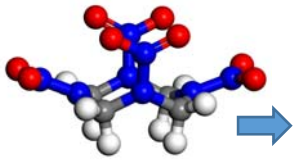
Angle-Axis: $\mathbf{R}_I = \mathbf{I} + (1 - \cos\theta_I)\tilde{\mathbf{p}}_I\tilde{\mathbf{p}}_I + \sin\theta_I\tilde{\mathbf{p}}_I$



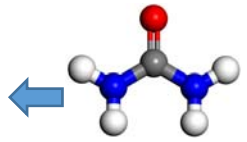
◆ Efficiency of global minimum locating

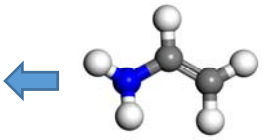


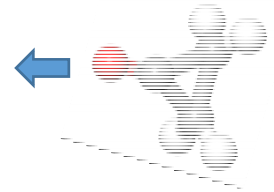




	Success ratio in 10^4 steps	Average SSW steps	Average force calculation
2D (64 atoms / 8 molecules)			
urea	10	234	2.7×10^5
acrolein	10	3923	4.8×10^6
ethenamine	2	>21500	$>2.2\times10^7$
3D (64 atoms / 8 molecules)			
ethane	10	1436	1.37×10^6
Acetic acid	8	5382	4.88×10^6
tetrahedrane	6	8560	9.75×10^6
cyclopropanone	0	>27000	
3D (168 atoms / 6 molecules)			
HMX	6		



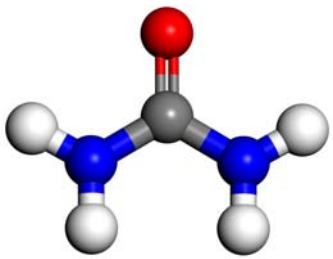


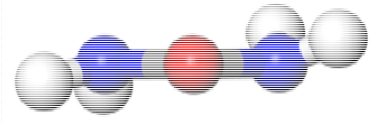


Difficulty: (1) 3D >2D (2) non-polar > polar (hydrogen-bonded)

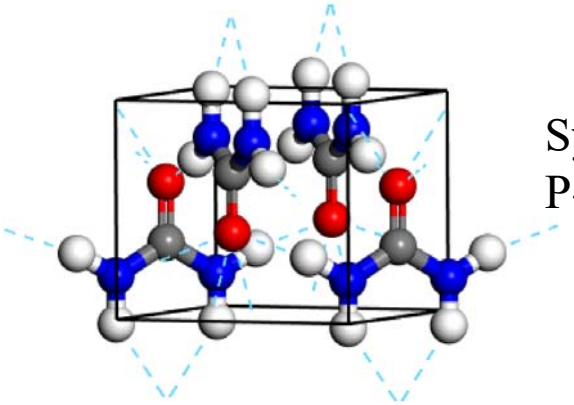
	Success ratio in 10^4 steps	Average SSW steps	Average force calculation
urea	10	234	2.7×10^5
acrolein	10	3923	4.8×10^6

Urea





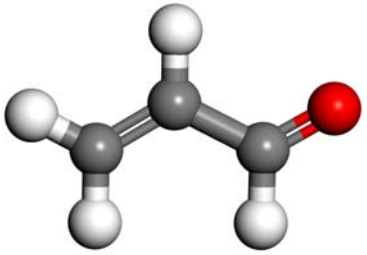
Symmetry: C2

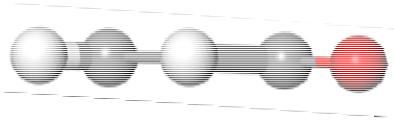


Symmetry:
$P\bar{4}2_1m$ (#113)

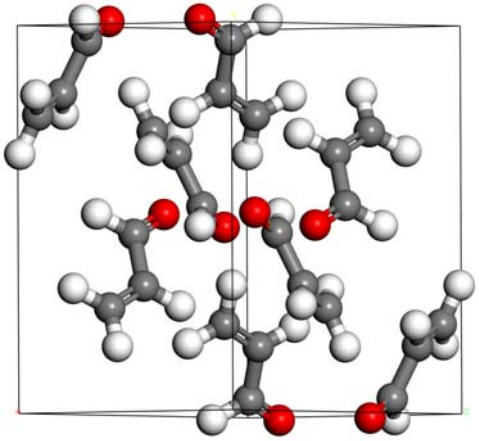
Grow from aqueous solution by slow evaporation of the solvent at 43℃. The structure wad determined in early 19th.

Acrolein





Symmetry: Cs

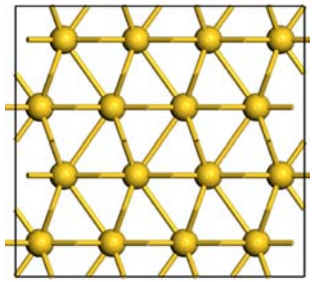


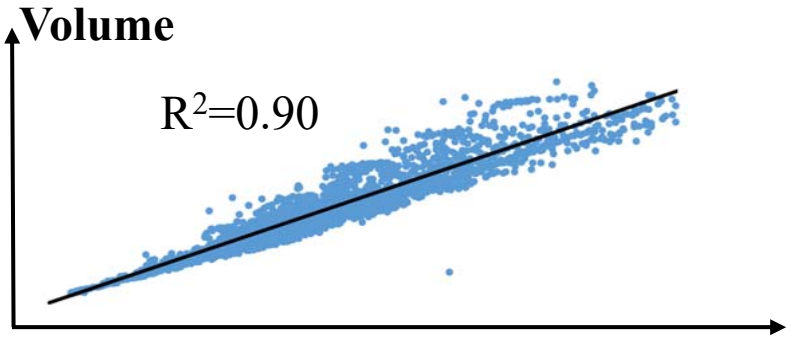
Symmetry:
Pbca (#61)

Grow at 178 K in situ by laser-assisted zone refinement (Boese & Nussbaumer, 1994). The crystal structure was solved in 2007 by Forster et al.

Close packing versus Orientation

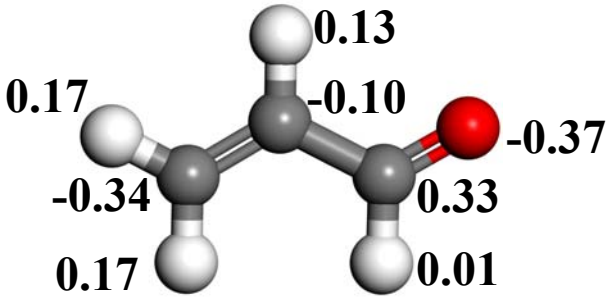
Lennard-Jones

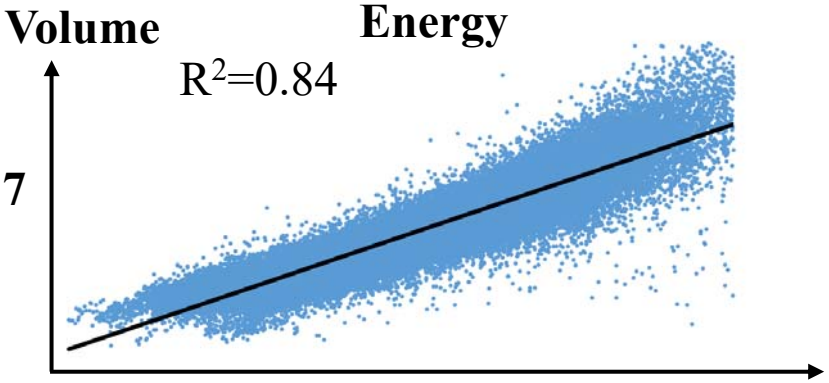




Acrolein

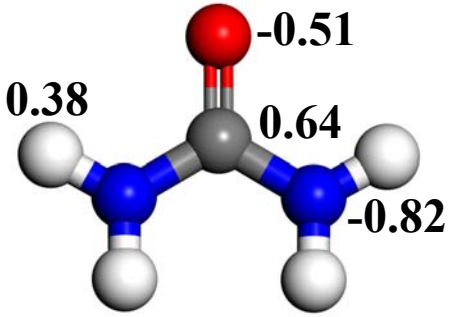
(Non-polar)

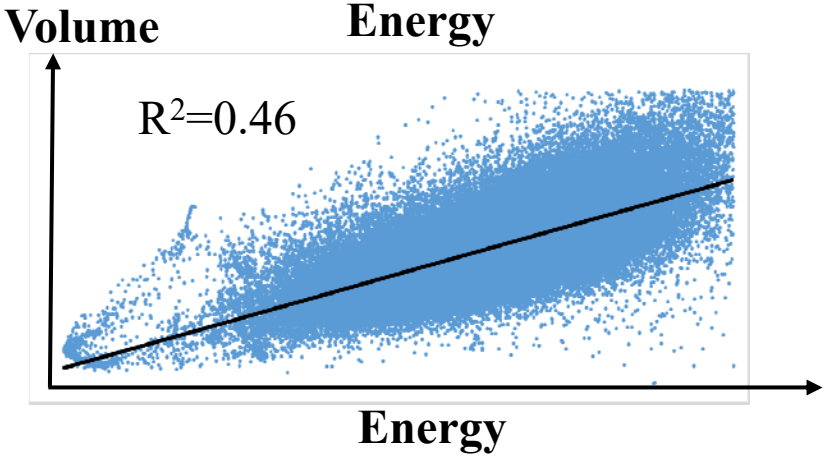




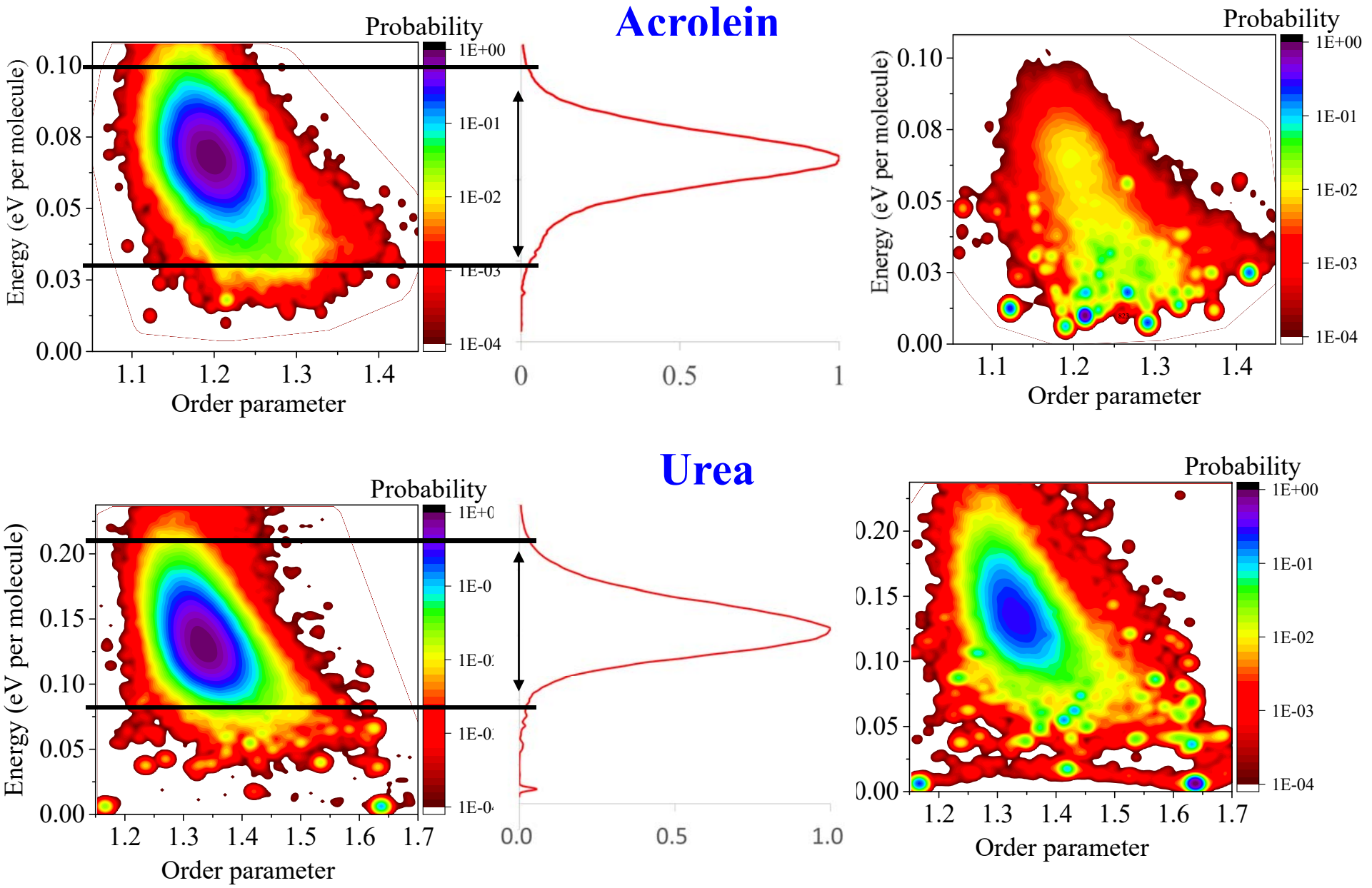
Urea

(Hydrogen-bonded)



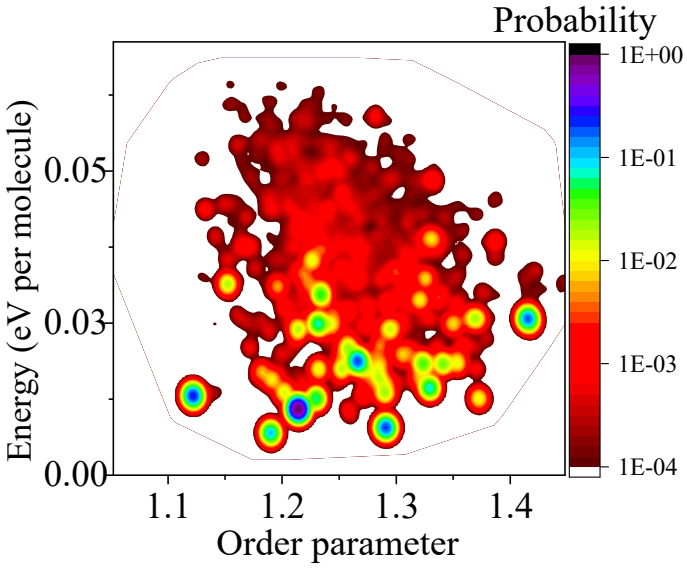


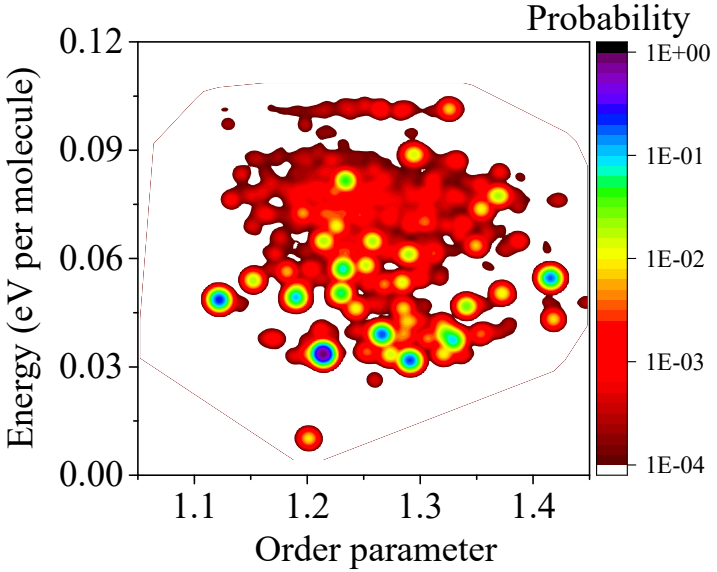
◆ Potential energy surface of acrolein and urea



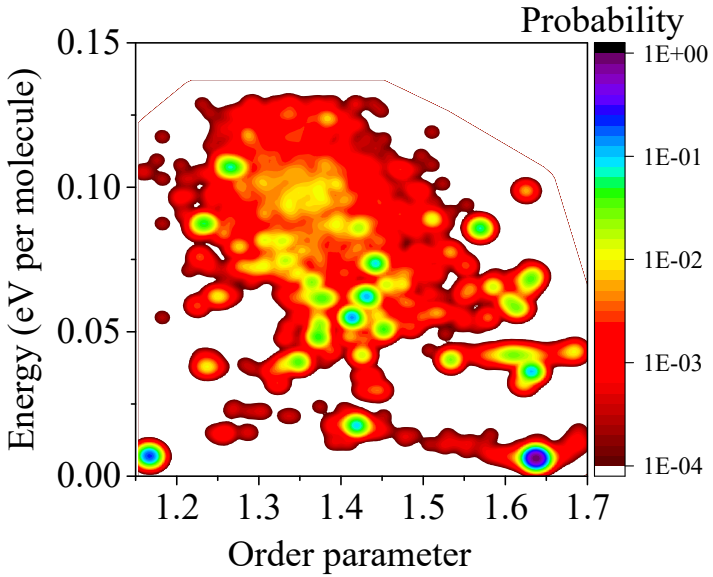
◆ DFT refinement

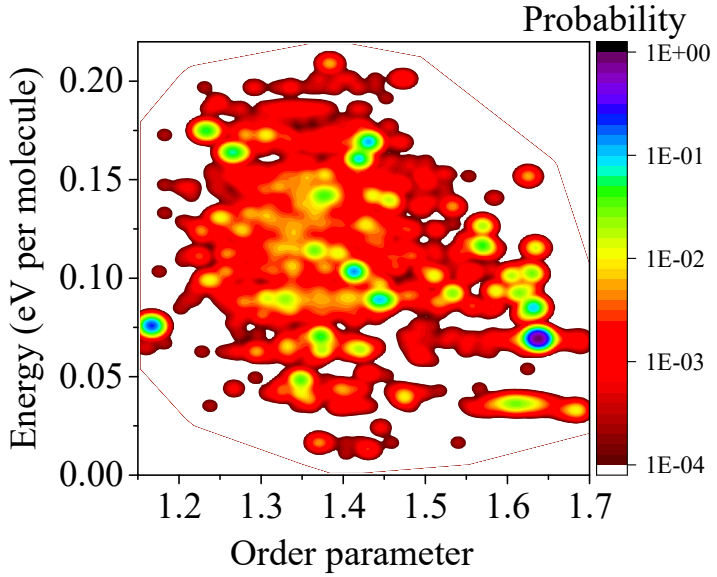
Acrolein



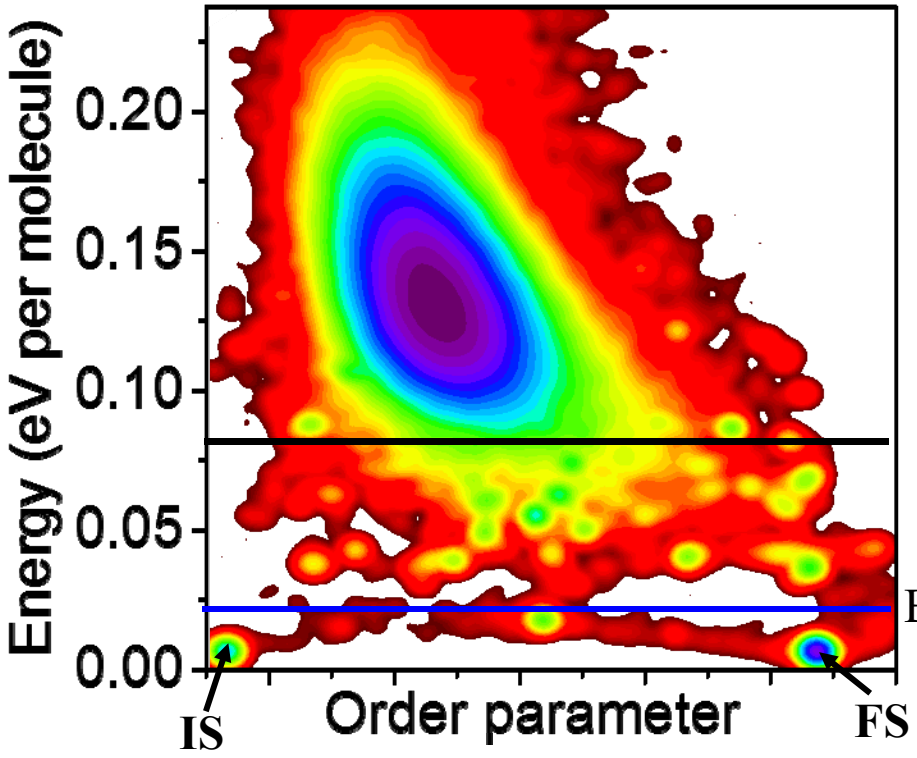


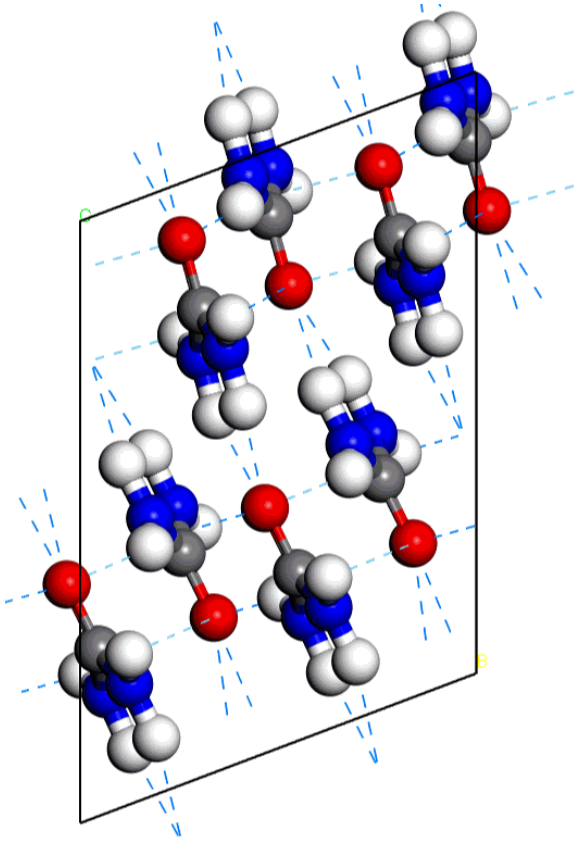
Urea

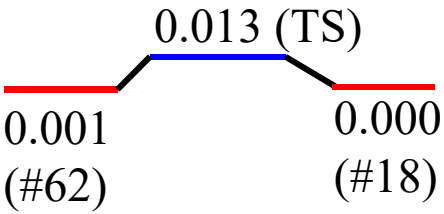




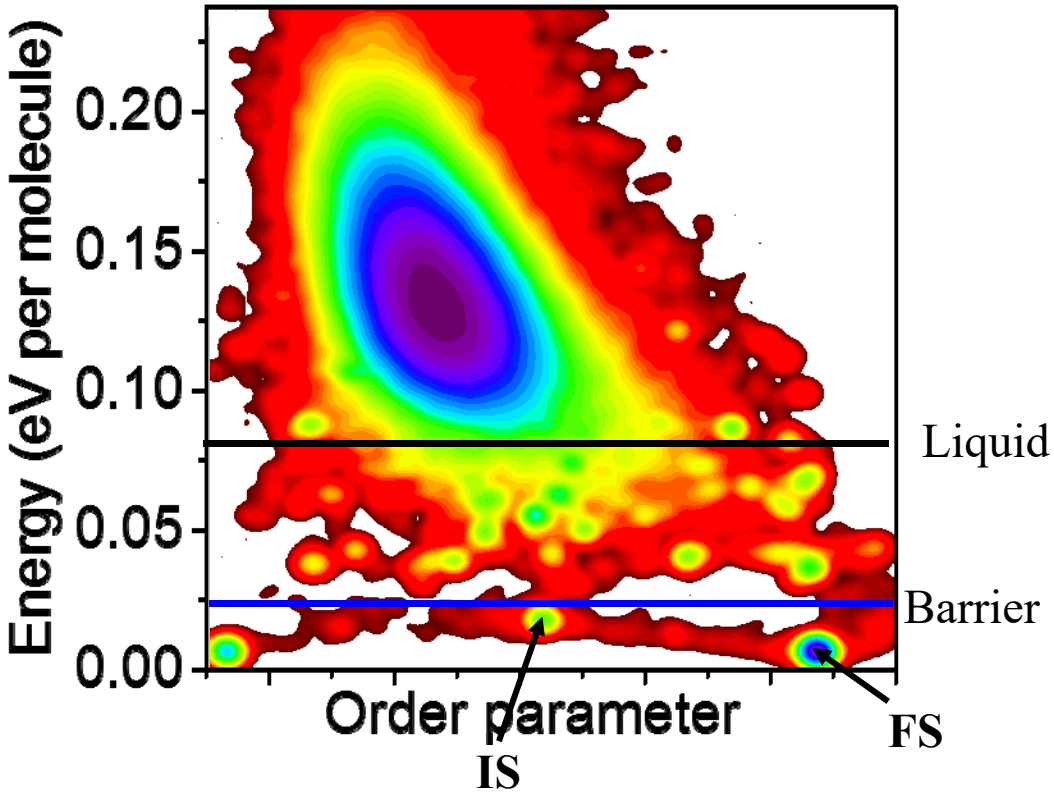
◆ Phase transition of urea

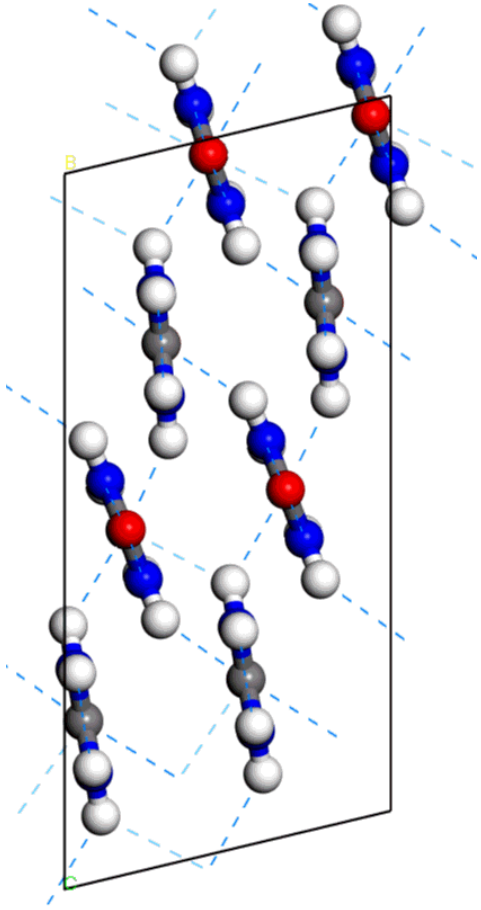


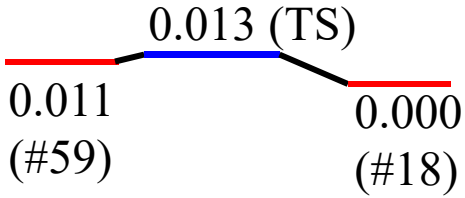




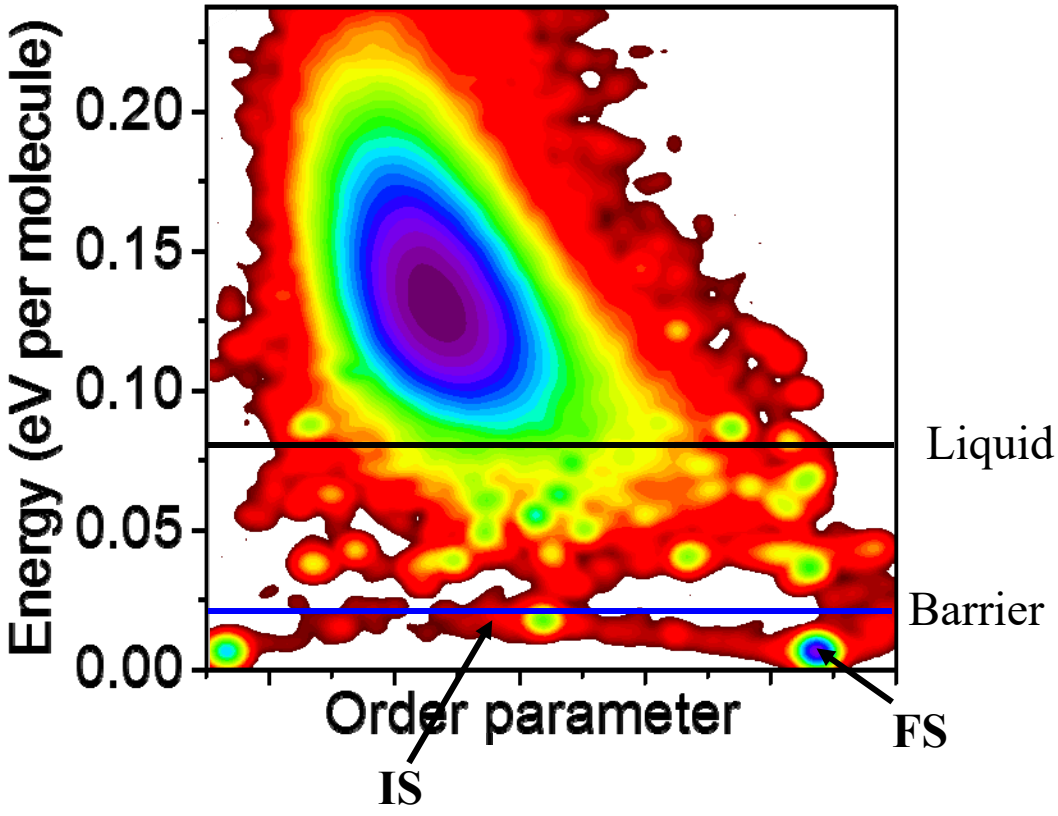
◆ Phase transition of urea

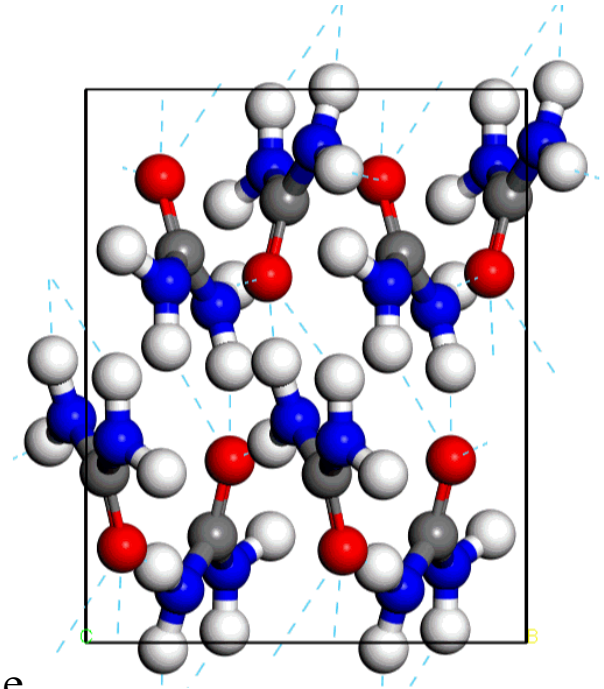


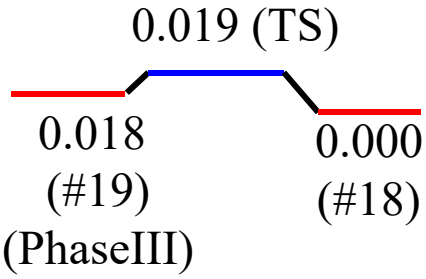




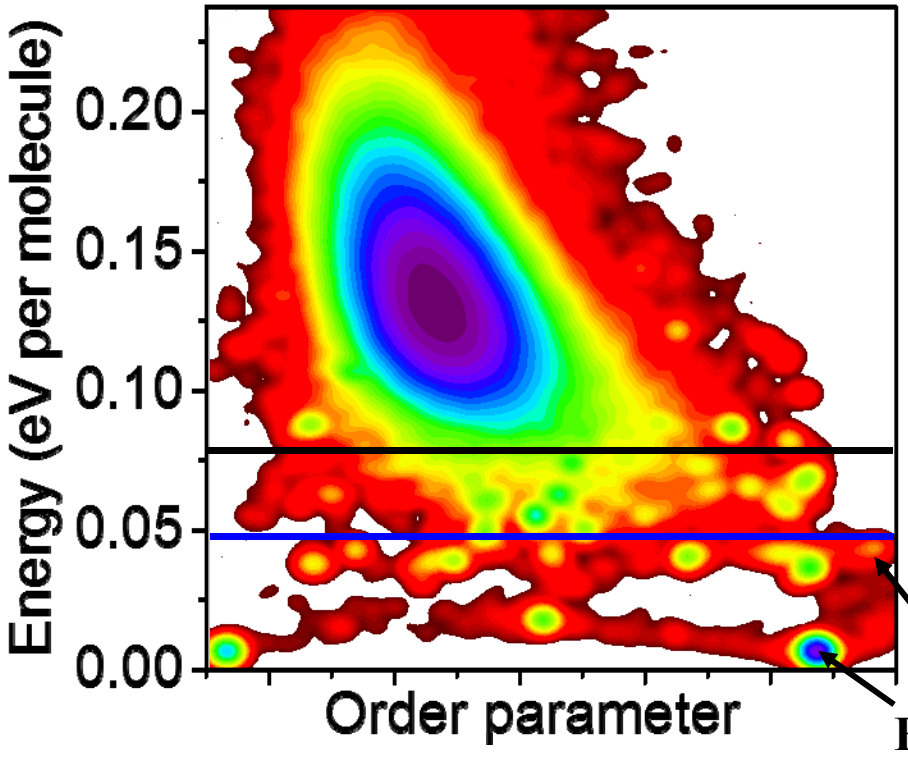
◆ Phase transition of urea







◆ Phase transition of urea

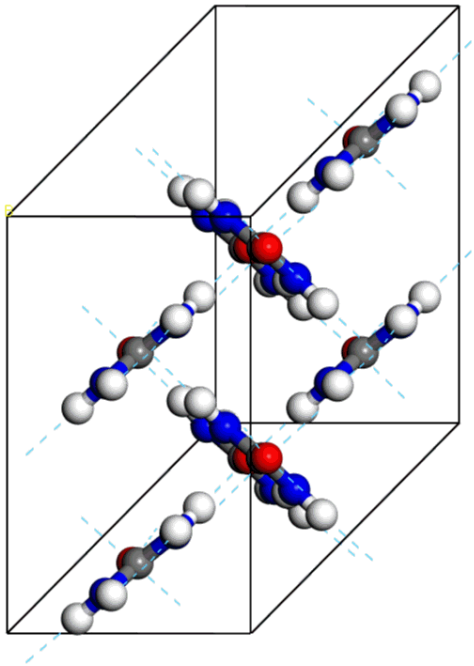


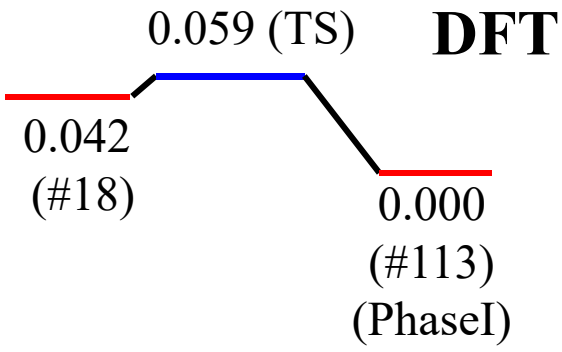
Liquid zone

Barrier

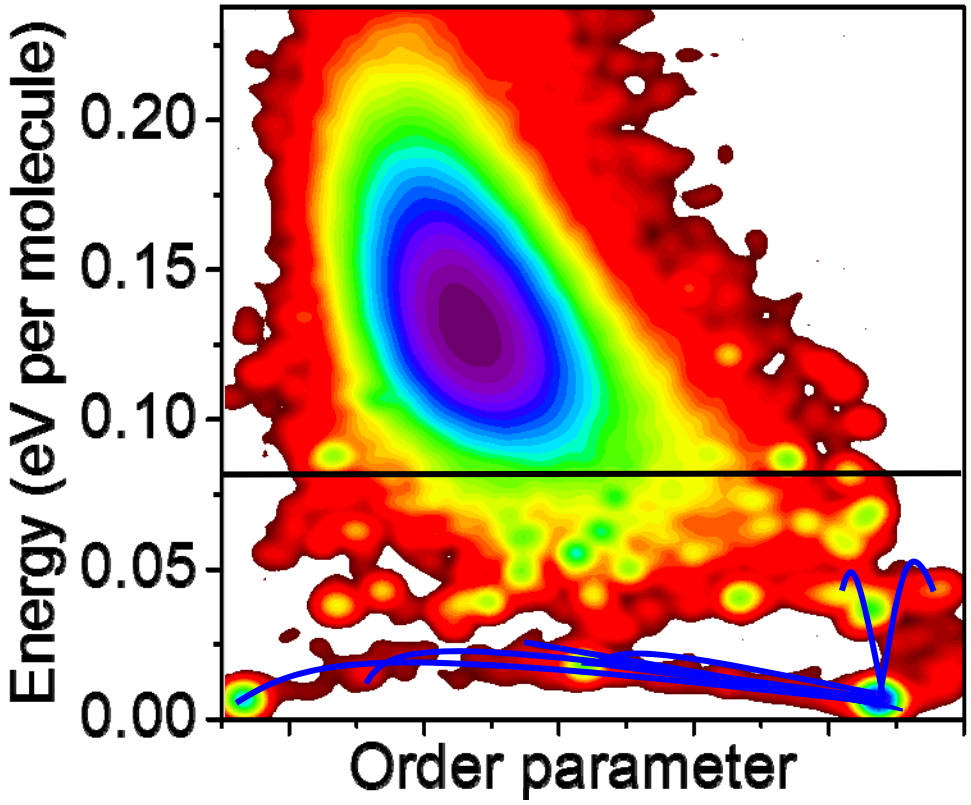
IS

FS



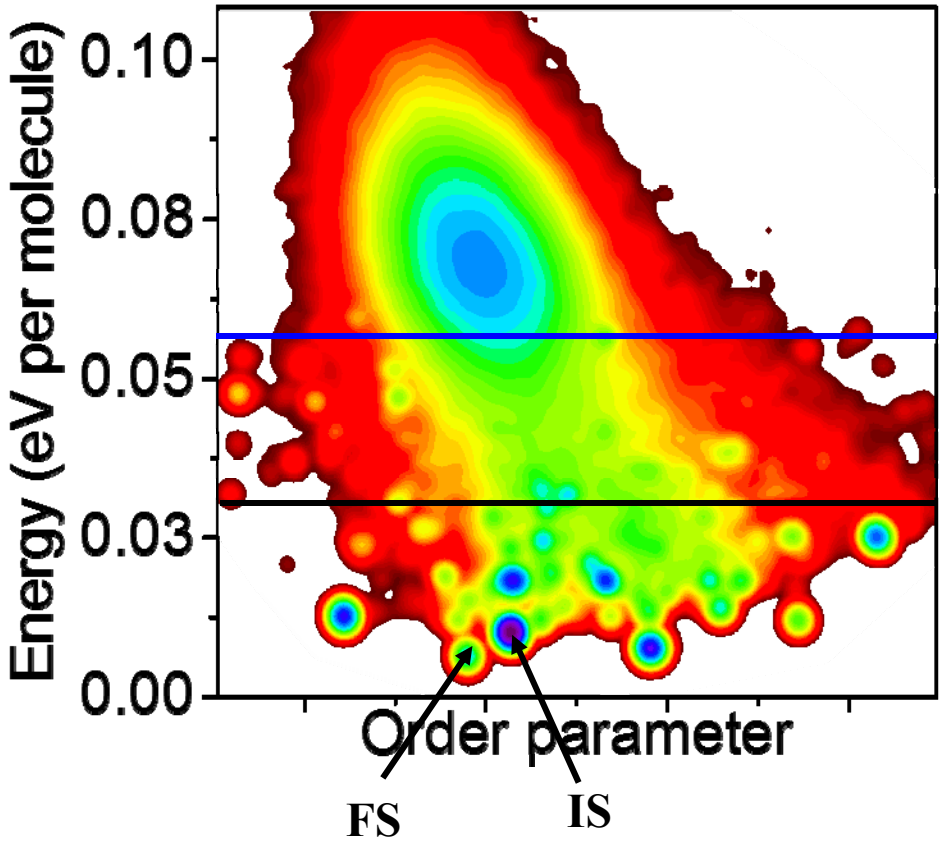


◆ Phase transition of urea



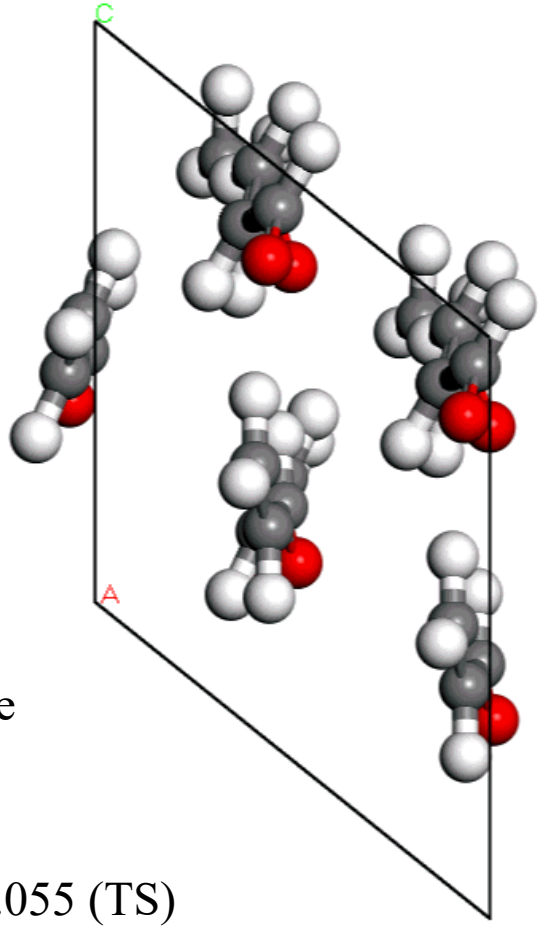
◆ H-bond network is kept during phase transition

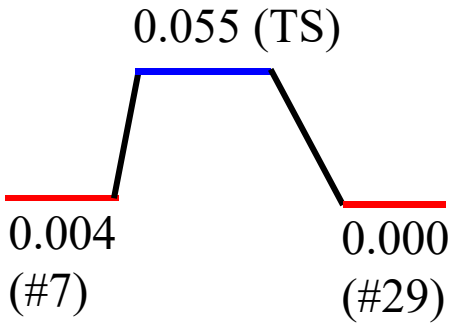
◆ Phase transition of acrolein



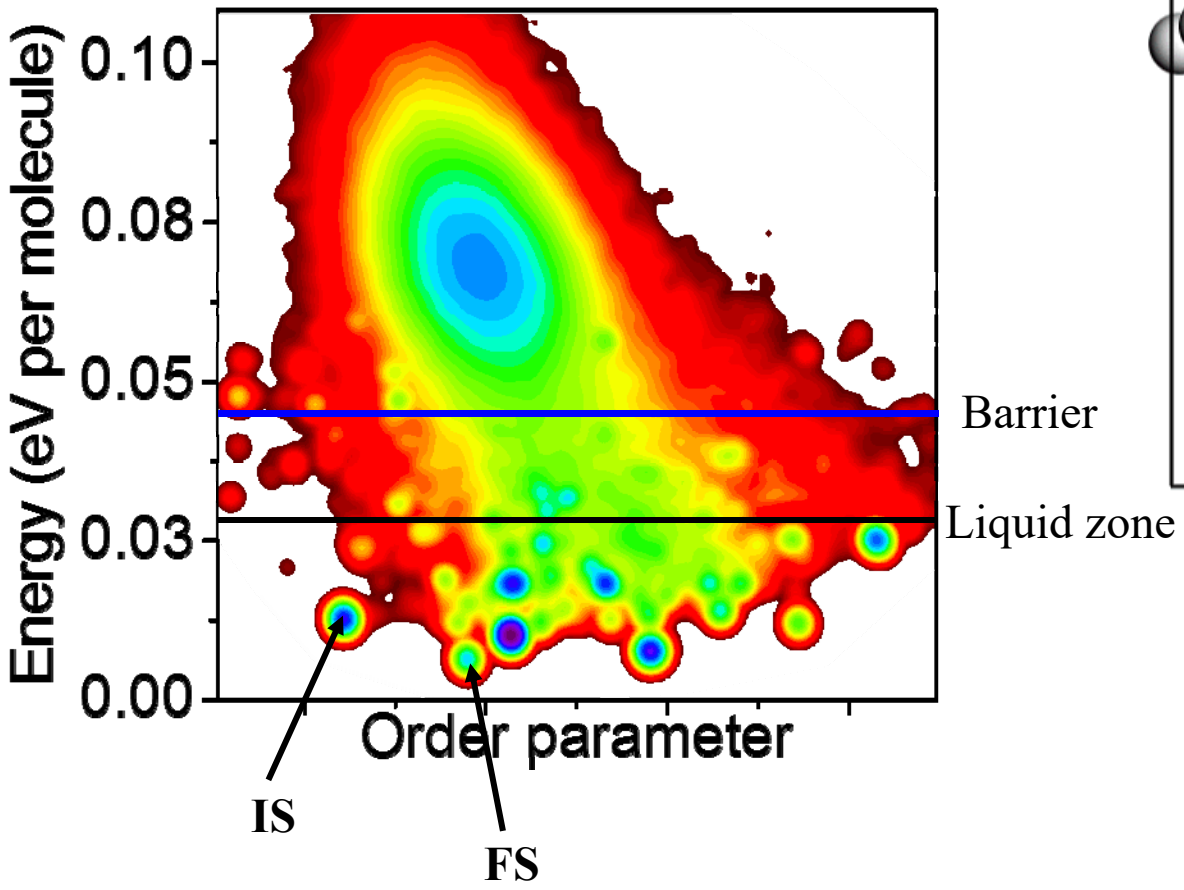
Barrier

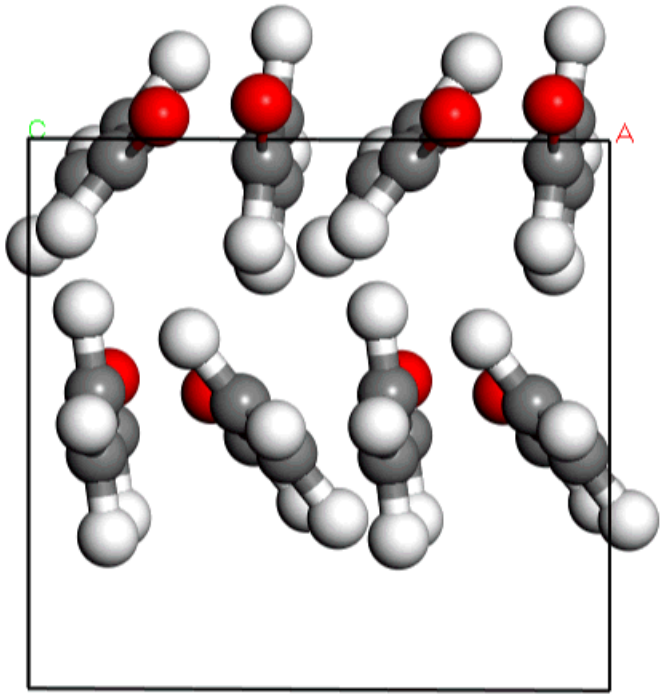
Liquid zone

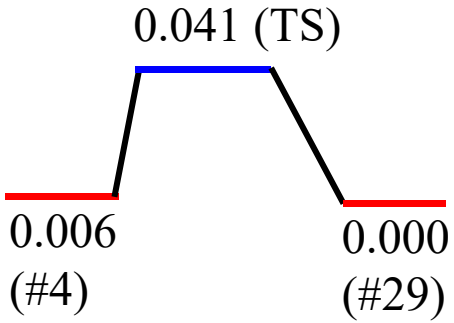




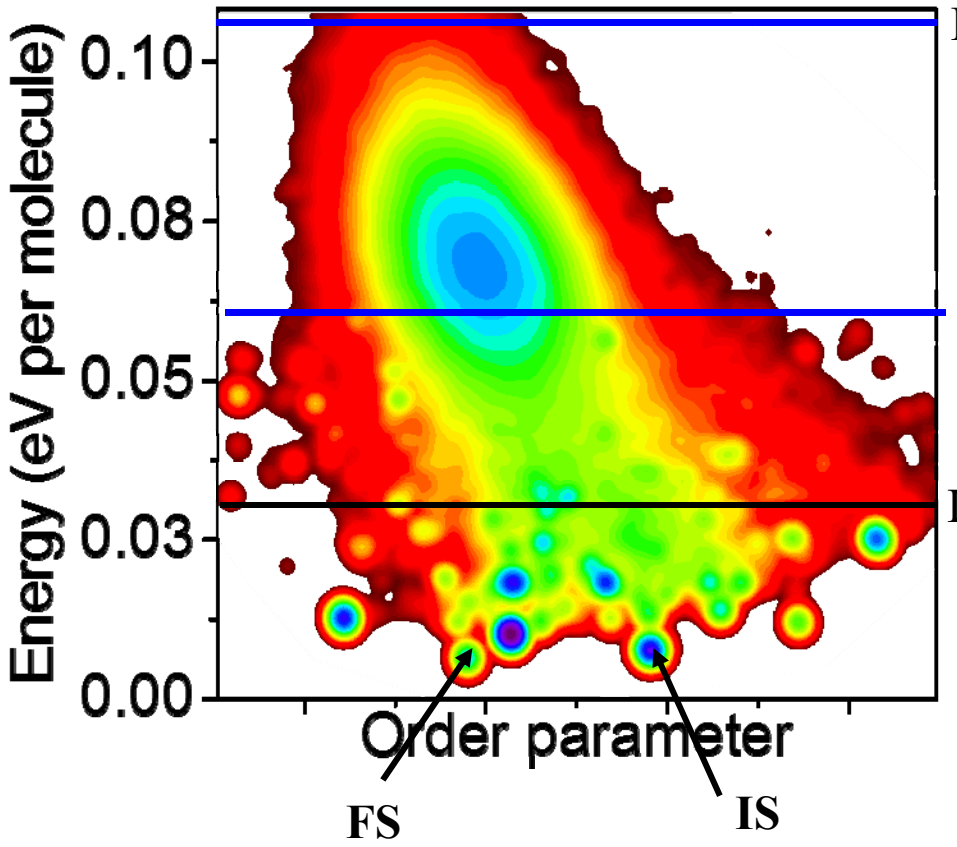
◆ Phase transition of acrolein







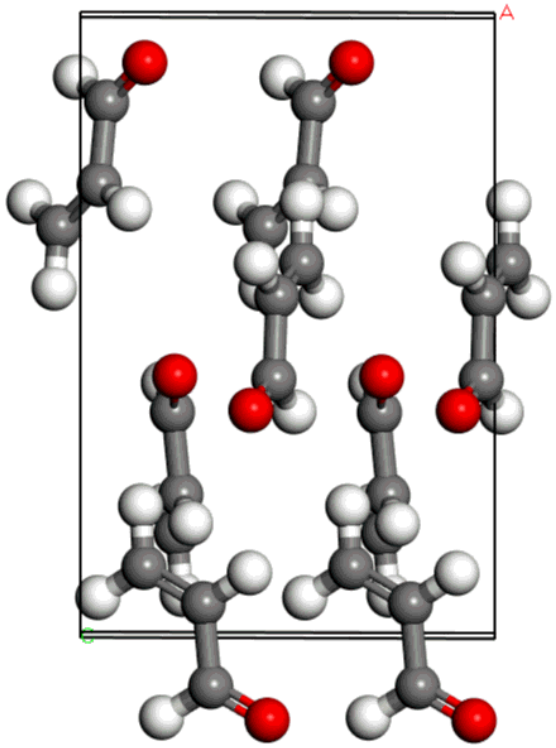
◆ Phase transition of acrolein

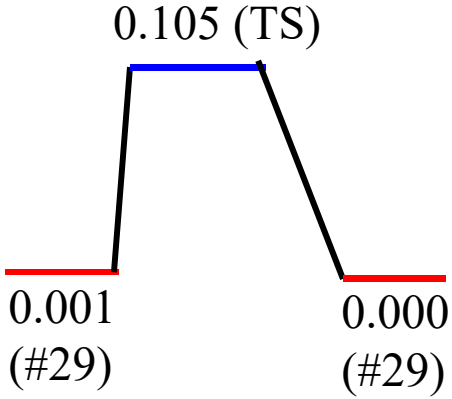


Barrier

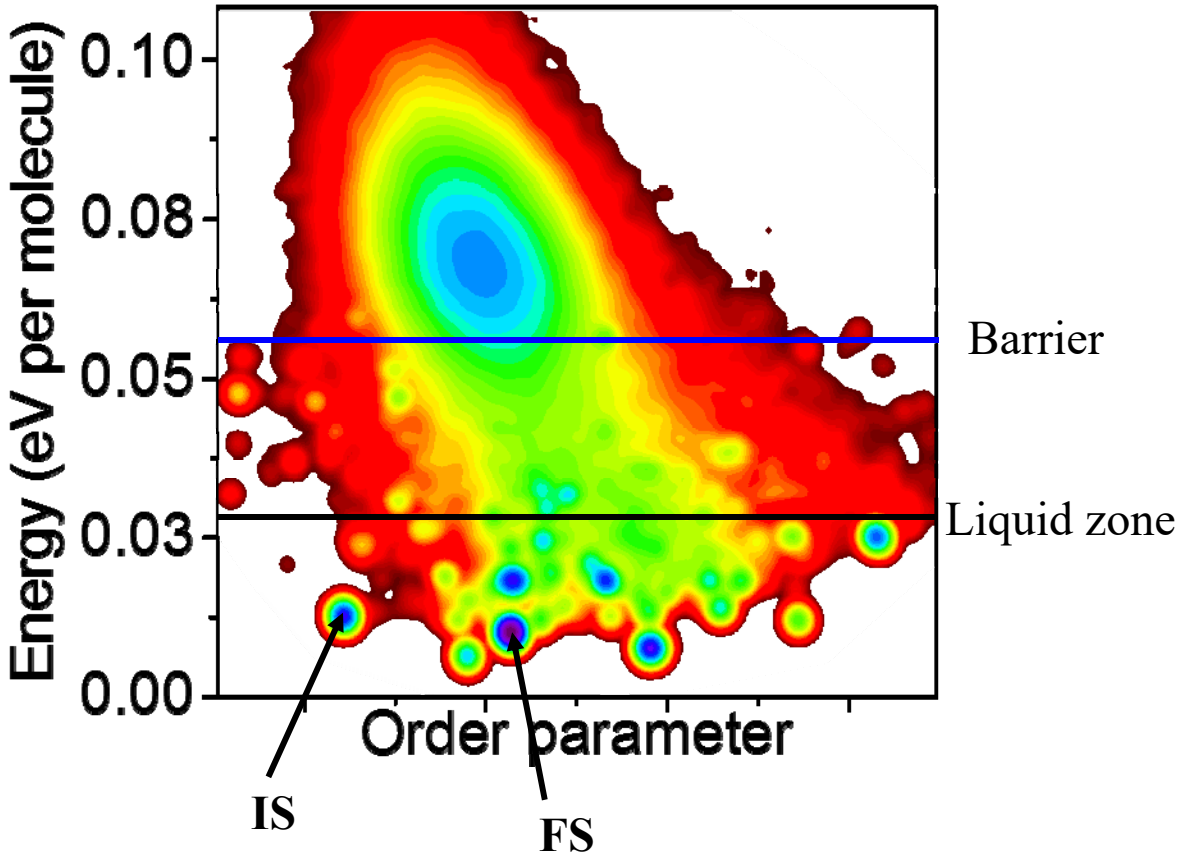
Barrier
(multi-step)

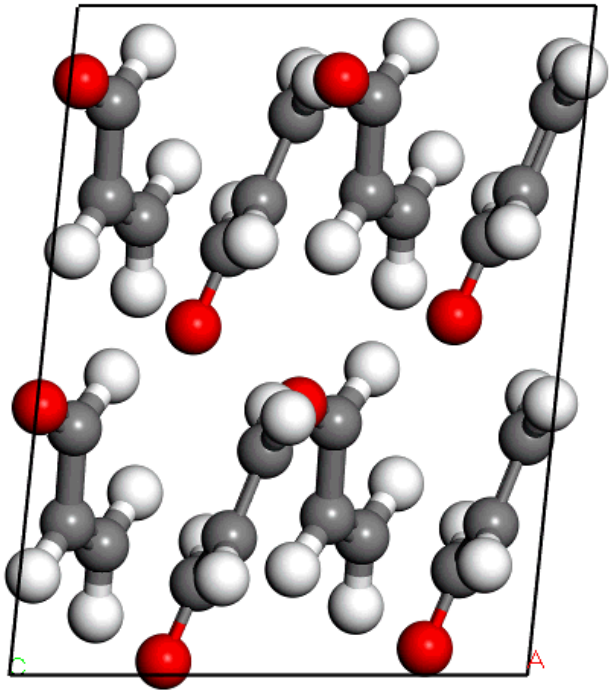
Liquid zone

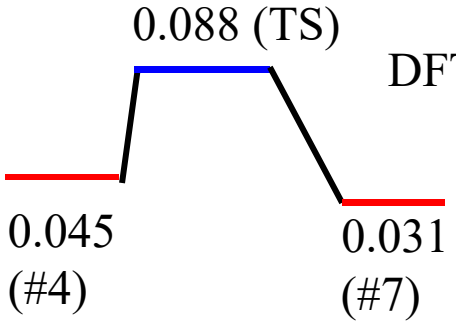




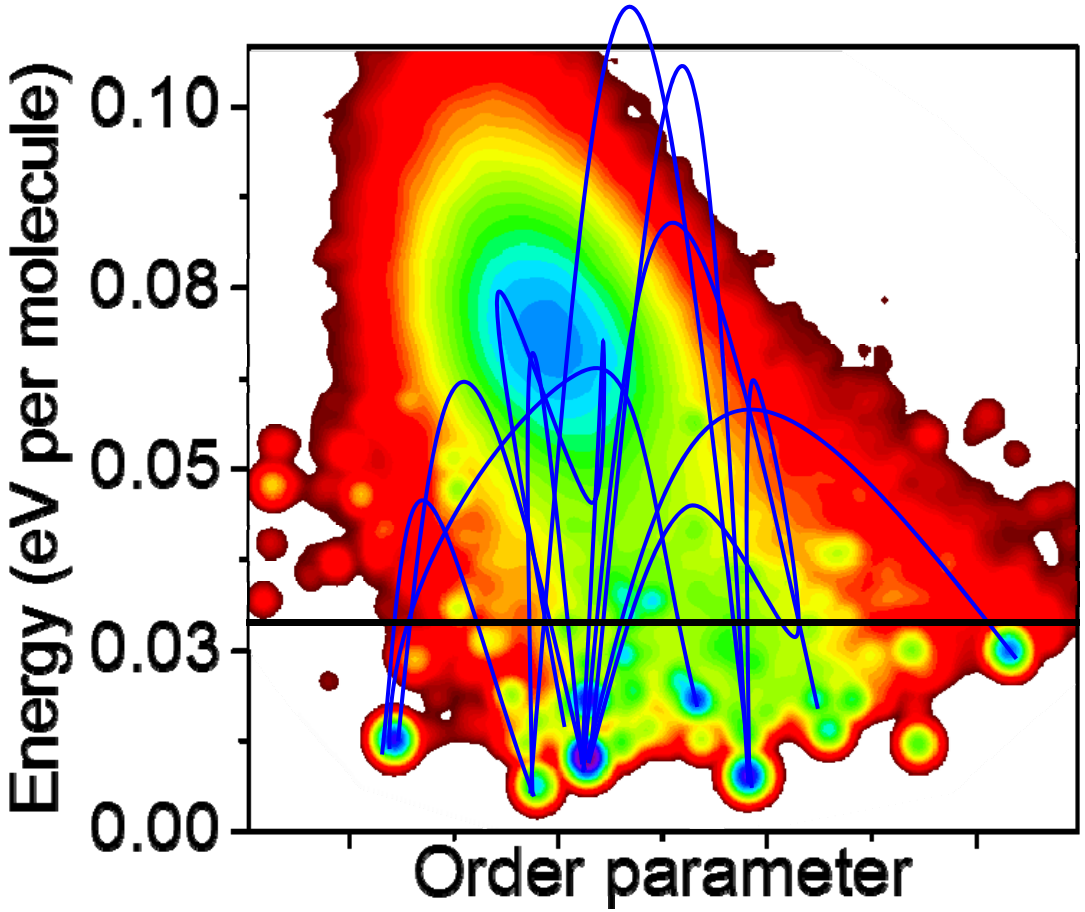
◆ Phase transition of acrolein







◆ Phase transition of acrolein



Liquid zone

◆ No preferred orientation in solid forms.

◆ High barrier is resulted from ,mlecules flipping during phase transition

◆ Summary:

◆ Identified the liquid-like zone and the distance between the GM and the lower boundary of the liquid-like zone.

◆For non-polar molecules, the barrier of possible phase transition is high, making the transition from any stable phase to the GM difficult.

◆ Acknowledgement

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