Simulating thermally activated processes using metadynamics technique: Dissociation of gas-phase carbonic acid

Padma Kumar Padmanabhan
Department of Physics
Indian Institute of Technology Guwahati

Plan of the talk

- Introduction
  - Molecular Dynamics (MD): Classical & *ab initio*
- Simulating Thermally Activated Processes (Rare Events)
  - Metadynamics technique (MTD)
  - Particle in 1-D potential
  - Conformational Changes of H_2CO_3
  - Dissociation of Carbonic Acid, $H_2CO_3 \Rightarrow CO_2 + H_2O$

Molecular Dynamics (MD) Basics

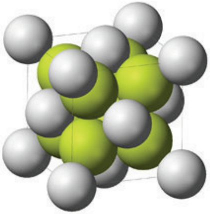
MD: A technique to recreate the natural atomic motion in a computer!!!

- ❑ Calculate using Newton's Law,

$$F_{ij} = -\nabla U_{ij}$$

$$F_i = \sum_{j \neq i} F_{ij}$$

$$a_i = F_i / m_i$$



- ❑ Integrate the equations of motion

$$v(t+\Delta t) = v(t) + \Delta t \frac{f(t)}{m}$$

$$r(t+\Delta t) = r(t) + v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2$$

Structural Model
Periodic Boundary Conditions

- **Better schemes available!**
  Velocity Verlet, Predictor correction

- ❑ Compute statistical and dynamical properties from stored trajectories

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Classical Vs *ab initio* MD...

😐 **Inter-Atomic Potentials -the important ingredient!**

❑ Classical MD: uses "pre-defined" potentials

- Lennard-Jones (6-12), $\mathcal{U}(r_{ij}) = 4\,\epsilon\,\left((\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}\right)$
- Born-Mayer-Huggins, $\mathcal{U}(r_{ij}) = \frac{q_i\,q_j}{r_{ij}} + A_{ij}\,exp(-r_{ij}/\rho_{ij}) - \frac{C_{ij}}{r_{ij}^6} - \frac{D_{ij}}{r_{ij}^8}$

  - **Parameters are "tuned" to reproduce experimental data!**
  - **Quality Matters! Transferability not guaranteed!**

❑ *ab initio* MD: computes potentials "on the fly"

- Density Functional Theory (DFT)
- GS ***e***$^-$ wavefunctions for every atomic configuration, $x_i(t)$, $y_i(t)$, $z_i(t)$
- Plane wave basis sets
- Hellmann-Feynmann Forces

All within the Born-Oppenheimer Approximation,

Trajectories are still Newtonian!

ab initio (Car-Parrinello) MD

Advantages Over Classical MD:

- ☺ Free of empirical inputs
- ☺ Many body interactions and atomic polarizabilities are accounted for!
- ☺ Capable of describing chemical changes of matter including the **making** and **breaking** of **chemical bond**

Disadvantages:

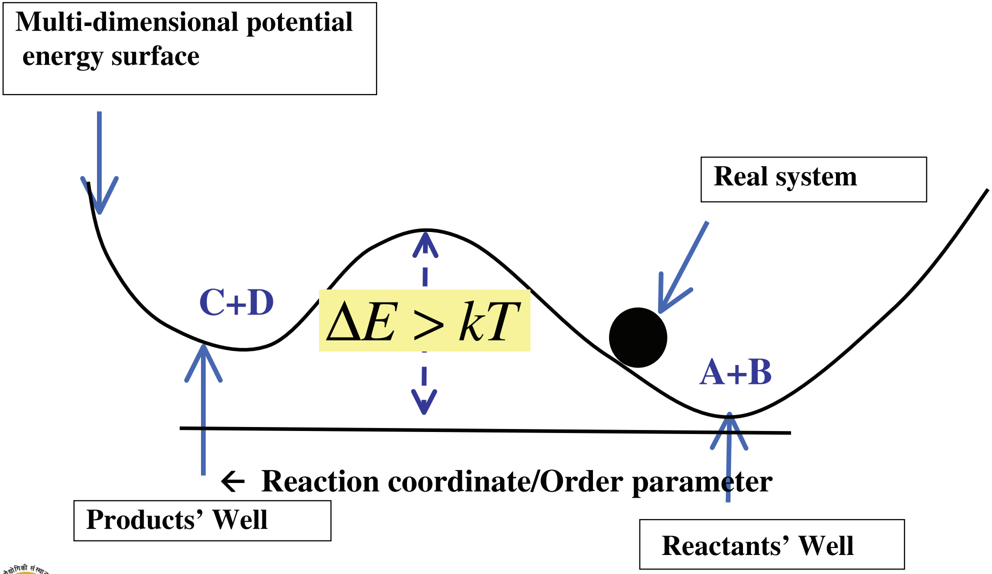
- ☹ Computationally expensive
- ☹ Small system size (few hundred atoms/few hundred electrons)
- ☹ **Short duration** (~few tens of picoseconds) of runs

Too short to study many (activated-) physical and chemical processes ("rare events") in nature!!

- The need for improvements!

Simulating Chemical Reaction

$A+B \Leftrightarrow C+D$



Multi-dimensional potential energy surface

Real system

C+D

$$\Delta E > kT$$

A+B

← Reaction coordinate/Order parameter

Products' Well

Reactants' Well

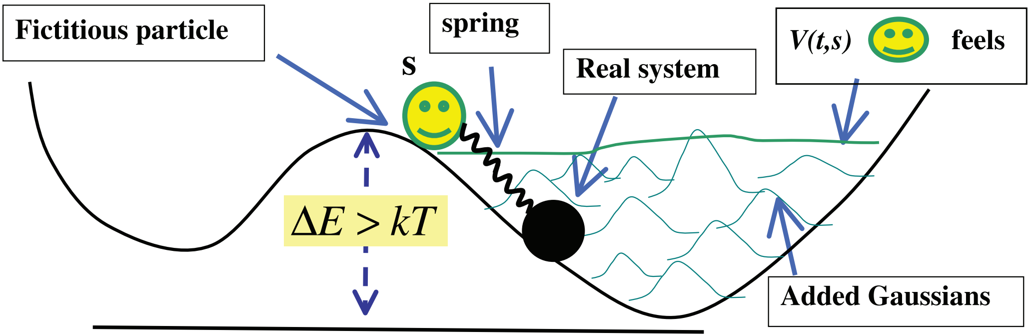
Metadynamics – The idea!

Laio & Parrinello, *PNAS*, 99, 12562 (2002).

$$\mathcal{L}_{MTD} = \mathcal{L}_{CP} + \frac{1}{2}\mu\dot{s}^2 - \frac{1}{2}k(S(R)-s)^2 - V(t,s)$$

S(R)- collective (dynamical-) variable

$$V(t,s) = H \sum_{t_i \le t} \exp\left\{-\frac{(s-s(t_i))^2}{2\Delta s^2}\right\}$$



← Reaction coordinate/Order parameter, s

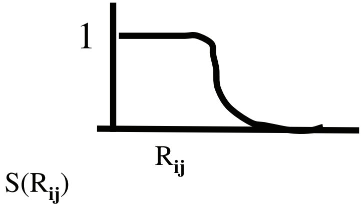
Self (~~avoiding~~) discouraged walk!!

Choice of Collective Variables

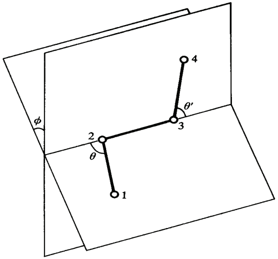
The choice of the collective (dynamical-) variable, ***S(R):***

- distances/bond lengths
- bond angles
- **smooth ‘coordination numbers’**

$$\mathbf{S(R_{ij}) = (1 - (R_{ij}/R_0)^6) / (1 - (R_{ij}/R_0)^{18})}$$

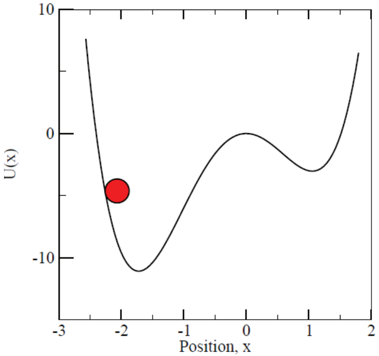


- **dihedral angles**



Metadynamics: An illustration

Particle in 1-D potential: $U(x) = -6.2\,x^2 + 1.5\,x^3 + 1.7\,x^4$



Langevin-type forces,

$$m\frac{dv}{dt} = -\nabla U_{eff}(x) - \gamma v + F(t)$$

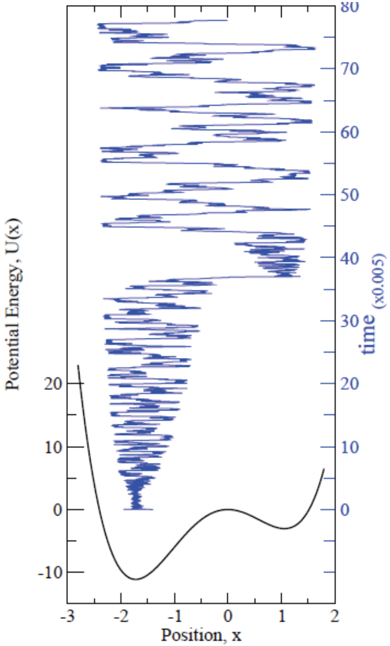
with, $F(t) = \rho * (2\xi - 1);\ \overline{F(t)} = 0$

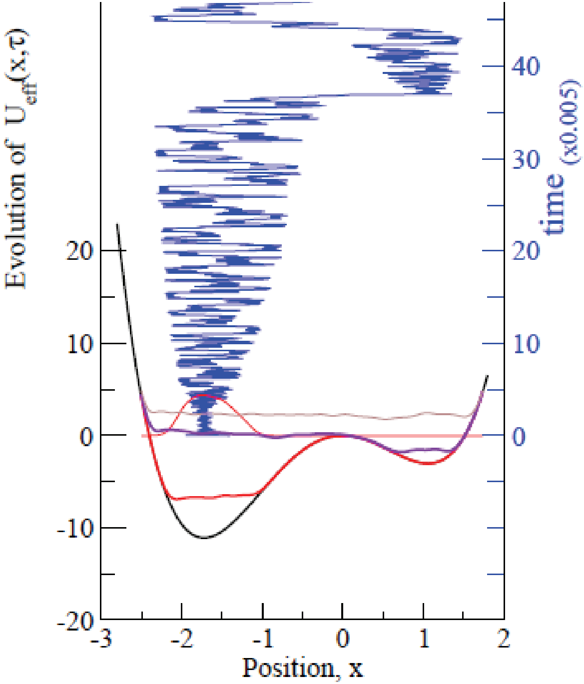
$$G(x,t) = H \exp\left\{-\frac{(x - x(t))^2}{2\Delta s^2}\right\}$$

$$U_{eff}(x,t) = U(x) + H \sum_{t_i \le t} \exp\left\{-\frac{(x - x(t_i))^2}{2\Delta s^2}\right\}$$

$m=10$; $kT=1$; $\gamma=5$; $\rho=15.81$; $dt=1$; $\xi=(0\text{-}1)$; $H=0.05\text{-}0.6$; $\Delta s=0.05\text{-}0.6$; $t_{i+1}-t_i=300$;

...MTD Illustration: Evolution of the effective potential

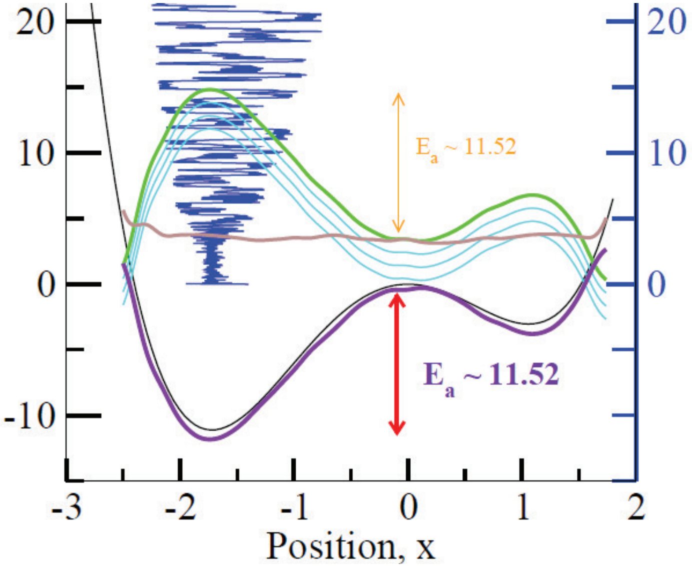




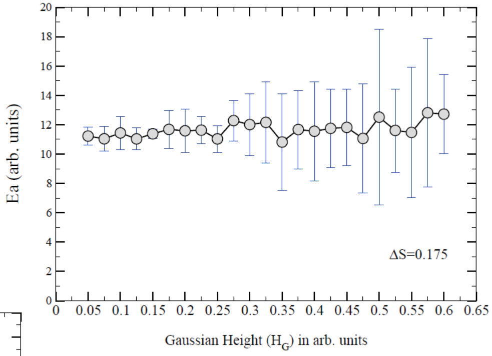
...MTD Illustration: Free Energy Estimation

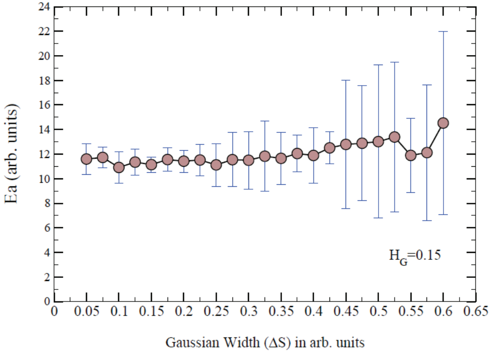
$$F(s) = -\lim_{t\to\infty} V(t,s)$$

Bussi *et. al*. *PRL*, 96, 090601(2006

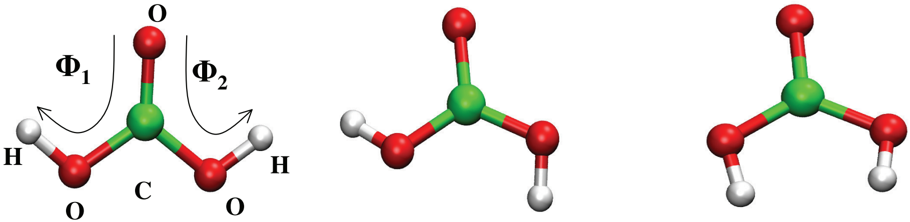


…MTD Illustration: Convergence of estimates with H & ΔS





Conformations of Carbonic Acid



$\Delta E = 0$ **$\Delta E \sim +1.5$ kcal/mol** **$\Delta E \sim +9.0$ kcal/mol**

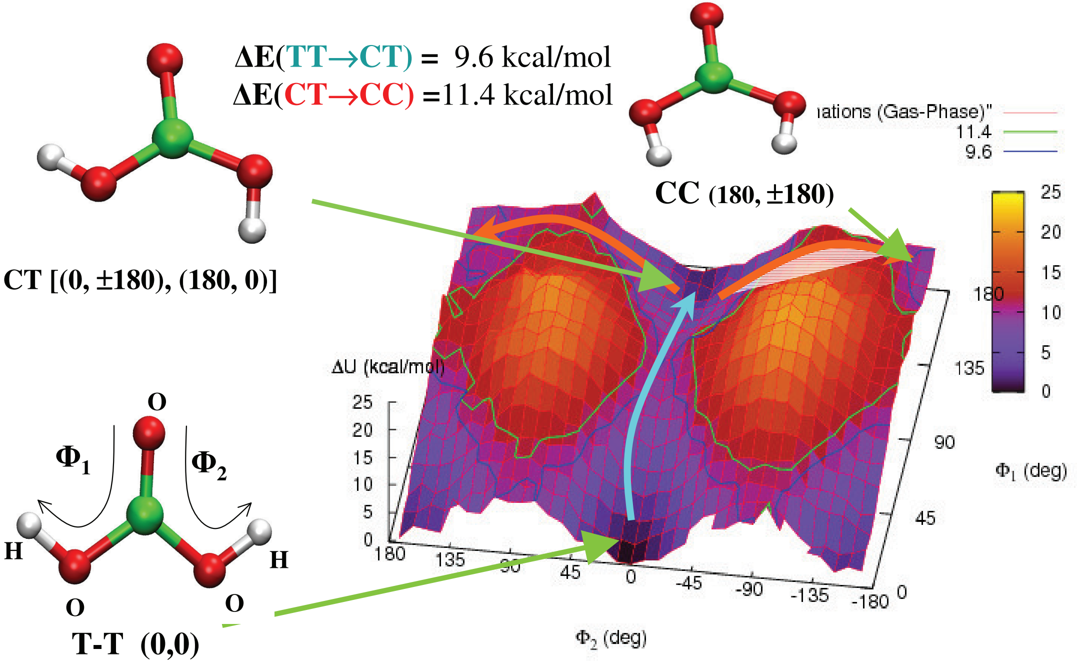
Trans – Trans (TT) **Cis – Trans (CT)** **Cis – Cis (CC)**

These conformers are related by changes in the two **O=C–O–H** dihedral angles, **Φ_1 & Φ_2** (Hence **good** CVs (S(R))!

Height and width of Gaussians: W=0.627 kcal/mol; $\Delta s \sim 10^{o}$;

Interval at which Gaussians added: 20 MD steps. (a bit hard driven!)

Potential energy surface for conformational changes…



ΔE(TT→CT) = 9.6 kcal/mol
ΔE(CT→CC) =11.4 kcal/mol

CT [(0, ±180), (180, 0)]

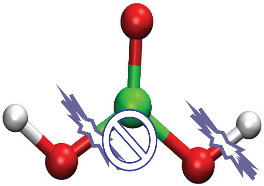
CC (180, ±180)

T-T (0,0)

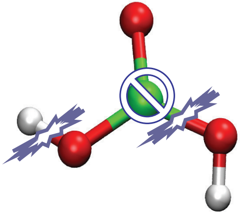
Kumar et al. *J. Chem. Phys.* 126, 204315 (2007)

Dissociation of H_2CO_3

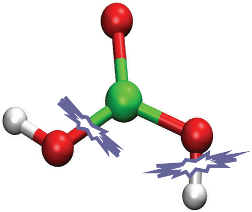
$H_2CO_3 \Leftrightarrow H_2O + CO_2$



Trans-Trans



(1)



(2)

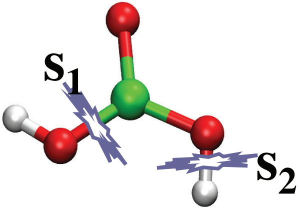
Cis-Trans

Cleaving Chemical bonds employing **coordination number** as the CV

$$S(R_{ij}) = (1 - (R_{ij}/R_0)^6) / (1 - (R_{ij}/R_0)^{18}$$

- **Who is most / least stable against dissociation to carbon dioxide ?**
- **What's the mechanism?**

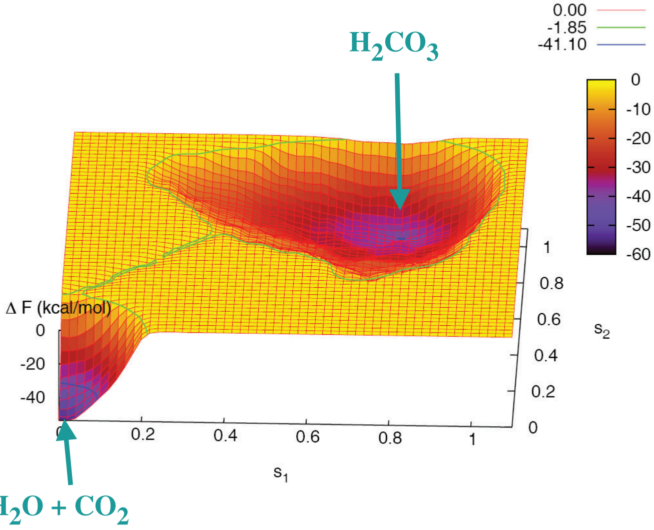
Free- energy surfaces for dissociation of the **Cis-Trans(2)** - *H_2CO_3 in gas-phase*



$$F(s) = -\lim_{t\to\infty} V(t,s)$$

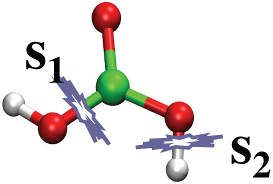
Bussi *et. al*. *PRL*, 96, 090601(2006)

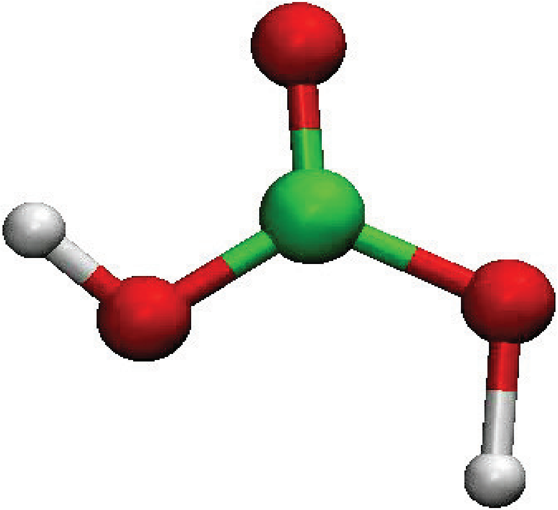
$\Delta F_a = 37.05$ kcal/mol



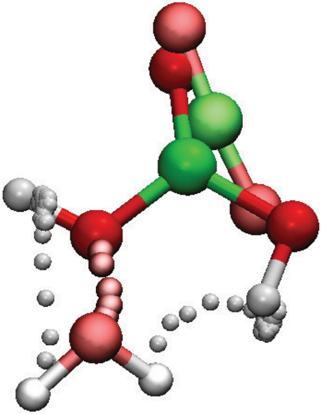
Kumar et al. *J. Chem. Phys.* 126, 204315 (2007)

Mechanism of H_2CO_3 dissociation in gas-phase

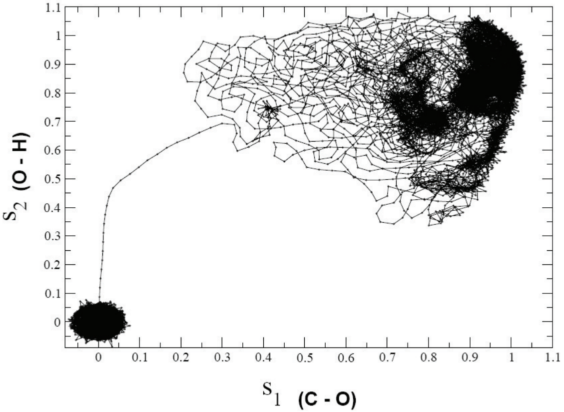




Mechanism of H_2CO_3 dissociation in gas-phase

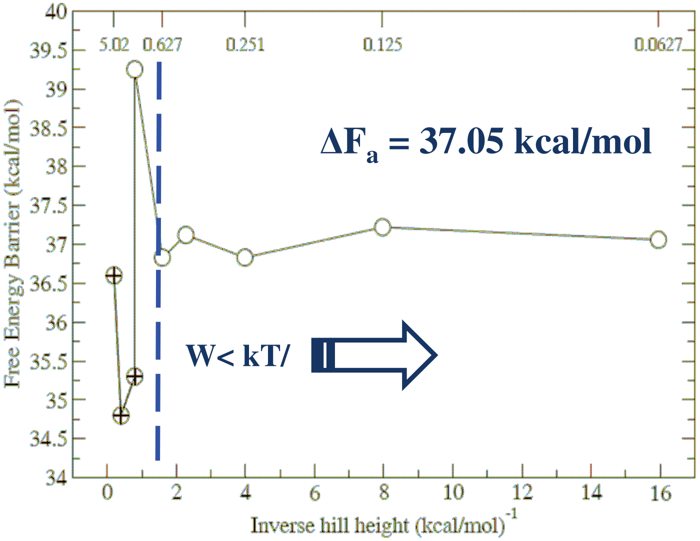


The real space trajectory.
(Superimposed snap shots from metadynamics)



The meta-space trajectory.

Hill Tuning



Good Convergence of Free- energies with Hill Height

Kumar et al. *J. Chem. Phys.* 126, 204315 (2007)

Conclusion

Metadynamics Offers a very promising technique to study activated physical/chemical processes!

Advantages:

☺ Efficient exploration of reaction pathways

☺ Provides insights in to the mechanism

☺ Allows (Landau-) Free Energy Estimation

- require less physical intuition
- finite temperature effects included

😐 Comes with ***little*** additional computational overhead

Disadvantage:

☹ Temporal information/Kinetics is unavailable!

Acknowledgement

Collaborators:

Prof. R. J. Kirkpatrick
(UIUC/MSU)

Dr. A. G. Kalinichev
(UIUC/MSU)

Mr. Pritam Ganguly
IITG

Discussion: Dr. Nisanth Nair (IITK) Dr. Axel Kohlmayer (PSU)

Funding: Department Of Energy (DOE), USA.

Infrastructure: **IITG,** NCSA @ UIUC, NERSC, SDSC, PSC – USA

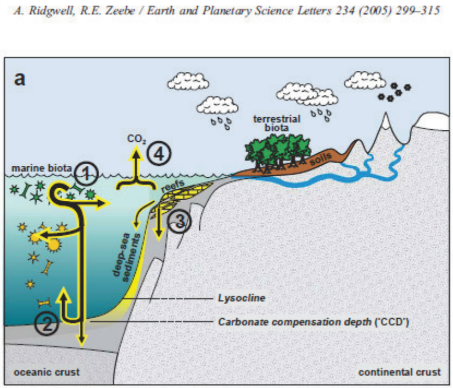
Software: CPMD, VMD

Thanks: Prof. S. B. Santra & Organizers of SCMP

Thank you!

Thank you!

Metadynamics investigation of Reactivity of Carbonate



A. Ridgwell, R.E. Zeebe / Earth and Planetary Science Letters 234 (2005) 299–315

- **Ridgwell & Zeebe, *Earth and Planet. Sci. Lett.*, 234, 299 (2005).**

Significance:

Aqueous Carbonate species: H_2CO_3, HCO_3^-, CO_3^{2-}, CO_2 (aq.), important in many chemical, biological, geological processes. Particularly, **Global Warming** and **CO_2 sequestration**

System-Setup

Car-Parrinello MD:

- A single H_2CO_3 in cubic box of 11.0 Å.
- DFT: GGA, BLYP functional employed.
- Ultra soft pseudo potentials (Vanderbilt) used.
- Plane wave cut off used: 35 ryd.
- μe =600 a.u; fictitious KE of e^- 0.0018 a.u.
- Time step used: ~ 0.1 fs.
- Ions and electrons are thermostated (Nose-Hoover method).
- All simulations are carried out at ~ 315 K.
- Over all translation and rotation are corrected for at every MD step.

Kumar & Marx, *Phys. Chem. Chem. Phys.*, 8, 573 (2006).

Ab initio MD study of aqueous carbonates

-Equilibrium study

Kumar et. al., J. Phys. Chem. (2009).