Mitzel Group
inorganic & structural chemistry

The seminar of three XMas fairy tales

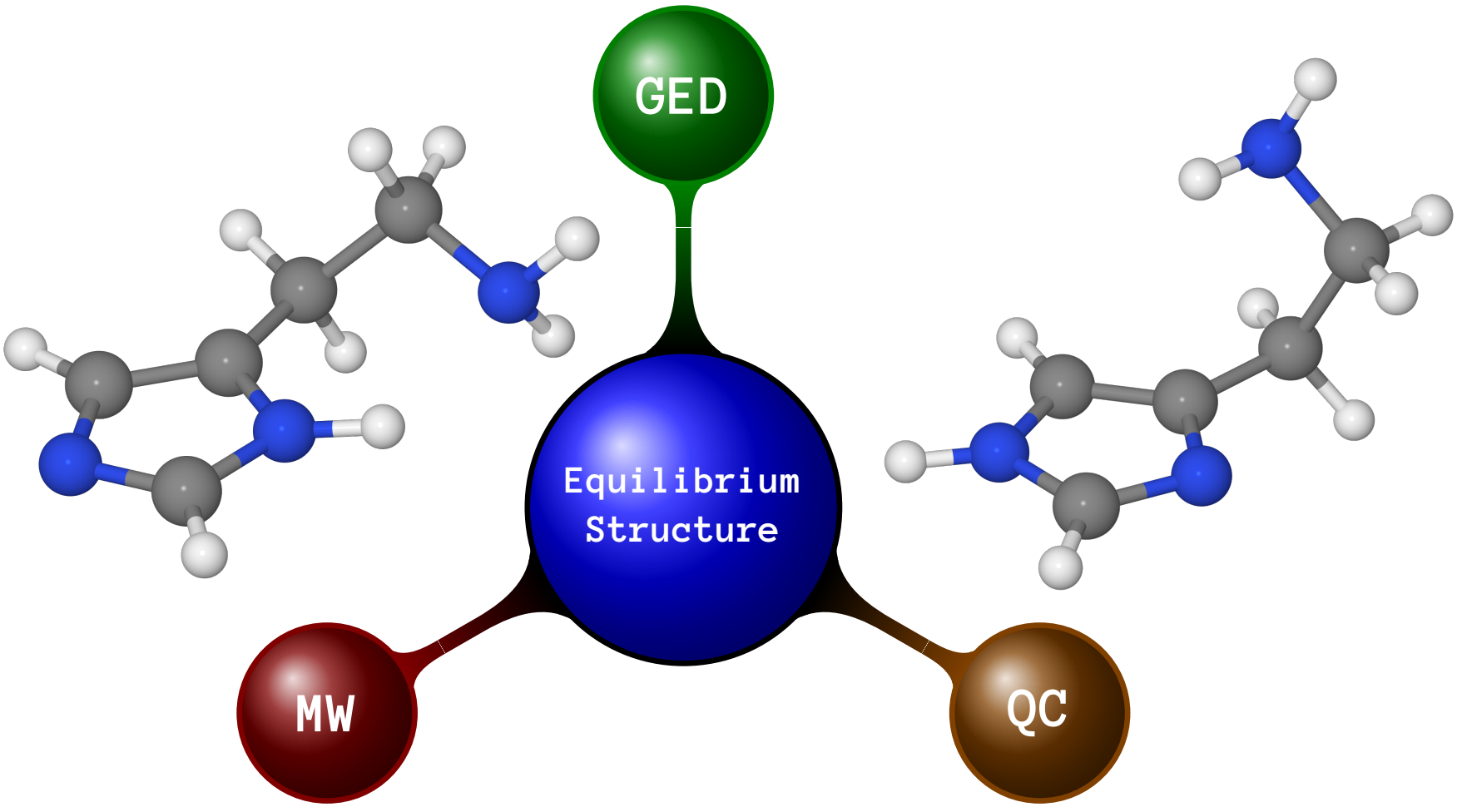
Denis T.

★★ 21-12-2015 ★★

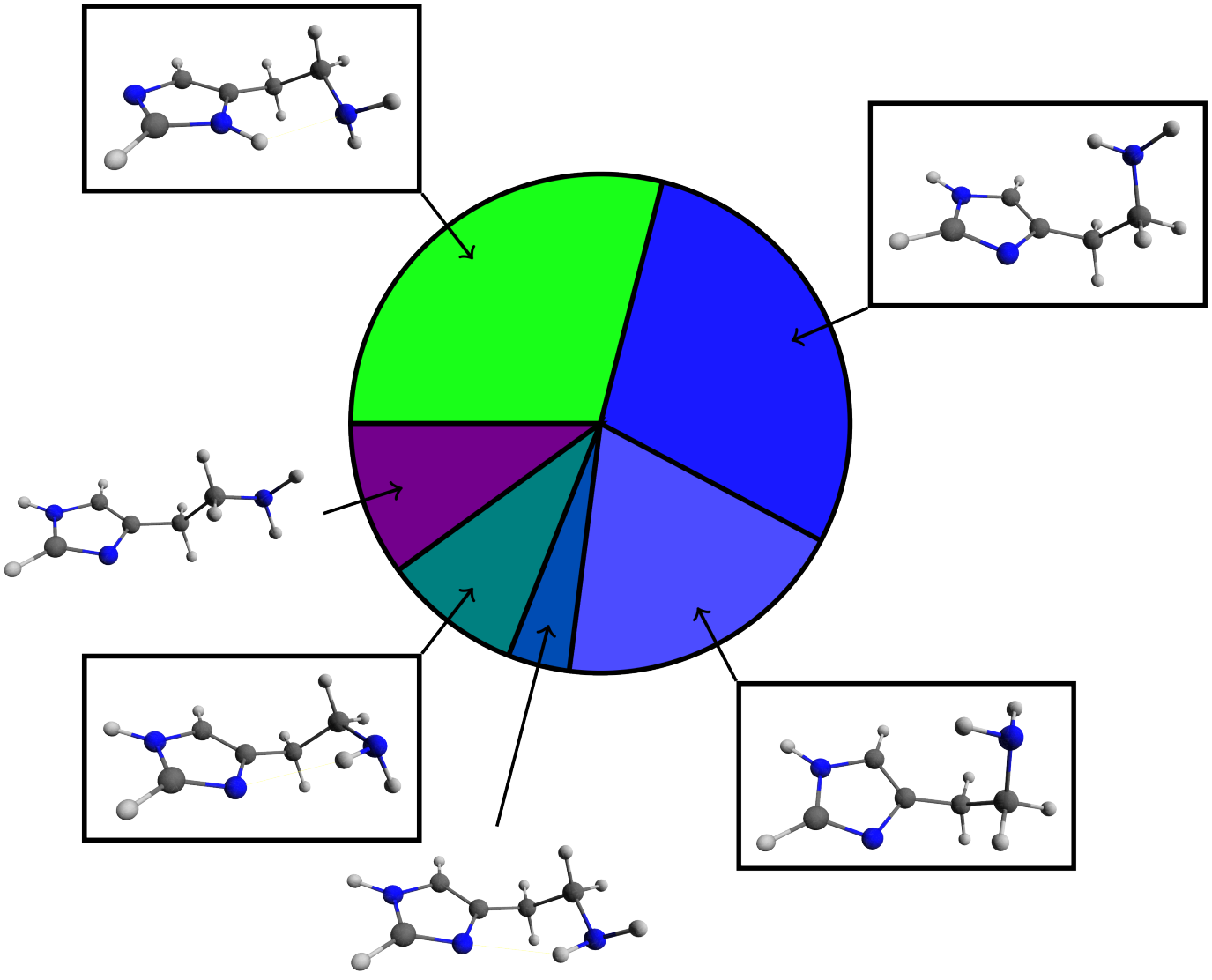
Featuring...

- ★ The saga of Histamine
- ★ The ballad of Pyrazinamide
- ★ The legend of Qassandra

The saga of Histamine



Histamine: Vapor composition

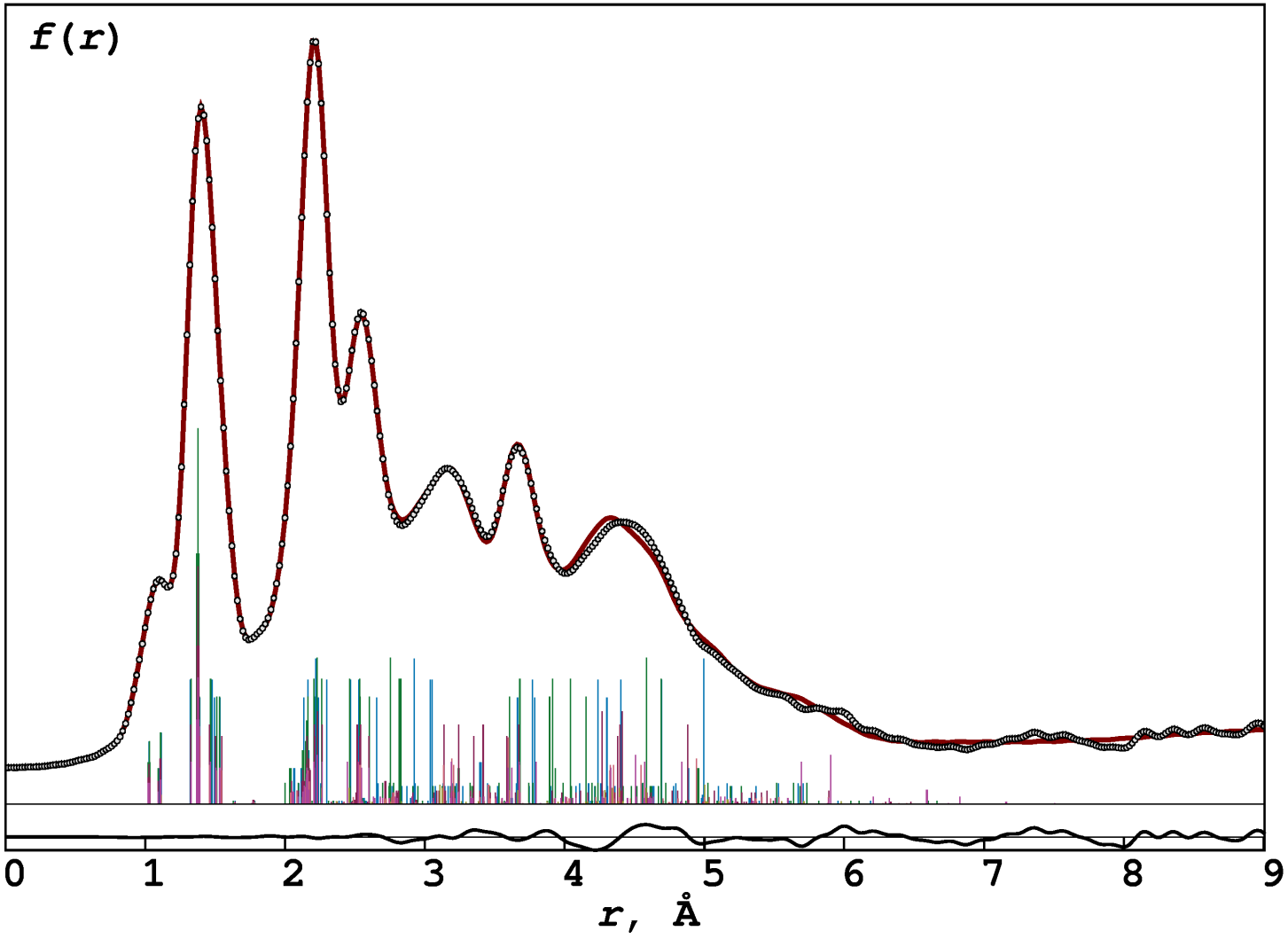


Vogelsanger B. et al., *JACS*, 1991, **113**, 7864–7869

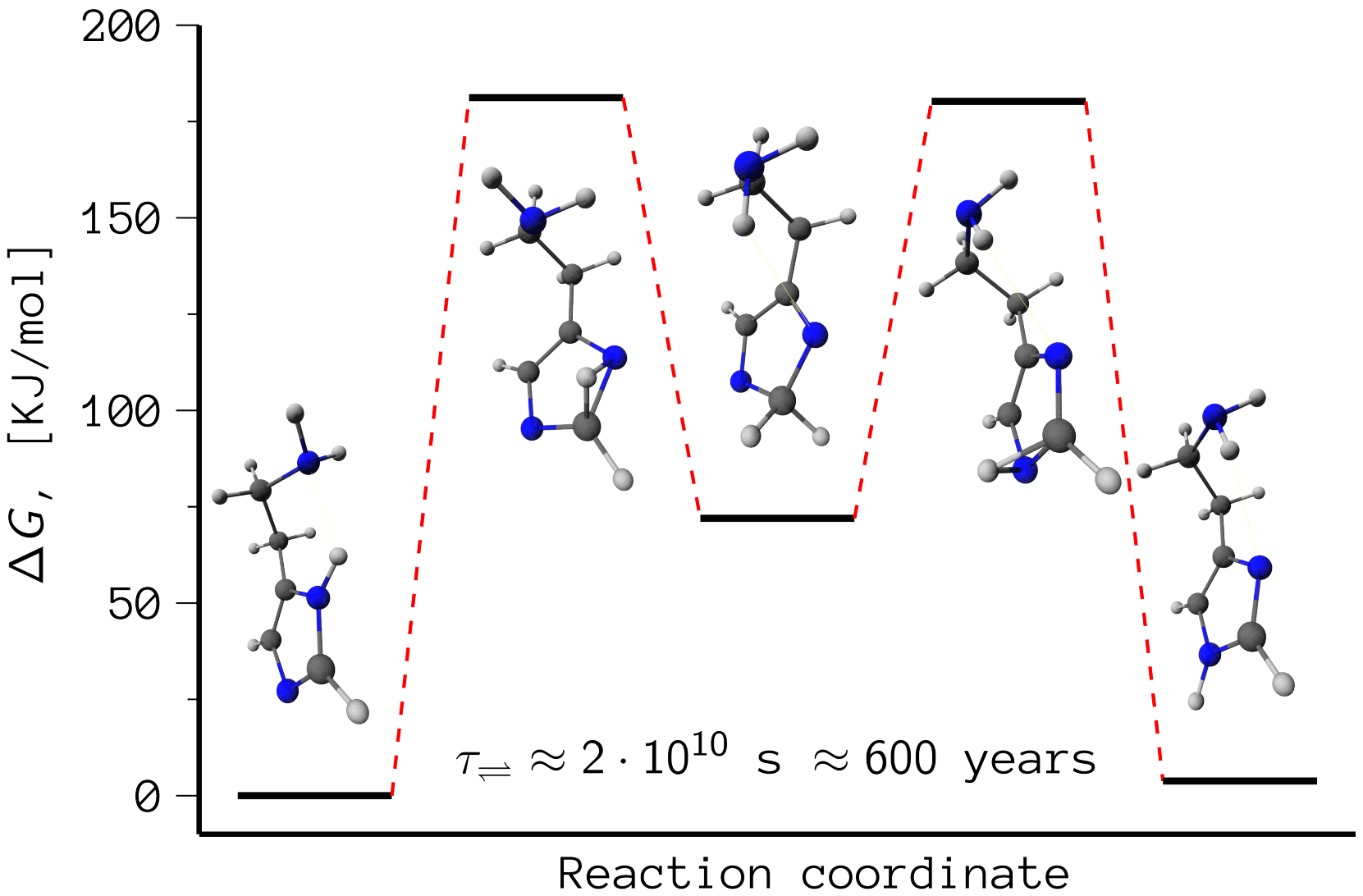
Godfrey P. et al., *JACS*, 1998, **120**, 10724–10732

Histamine: GED+MW+QCReg refinement

$R_f = 3.1\%$



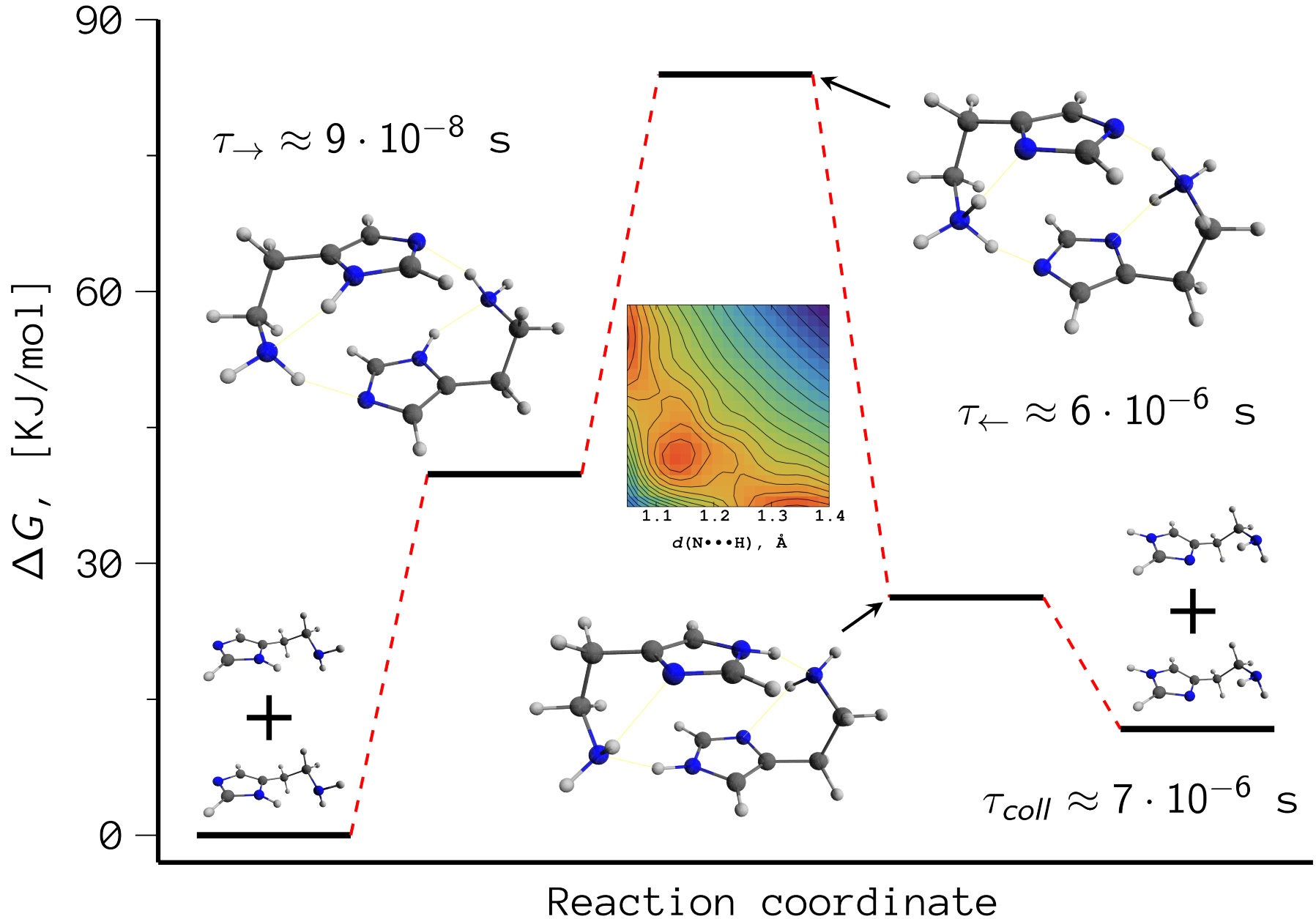
Histamine: intramolecular tautomerization



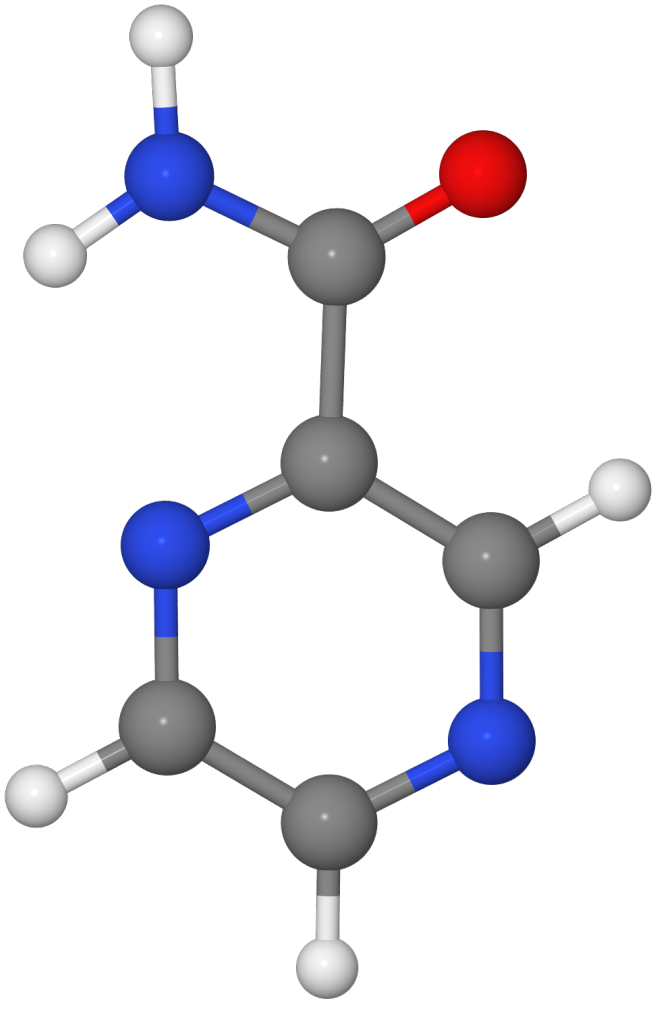
Borisov Y. et al., *Bull. of the Acad. of Sc. of USSR, Chem.*, **1988**, 37, 2504–2507

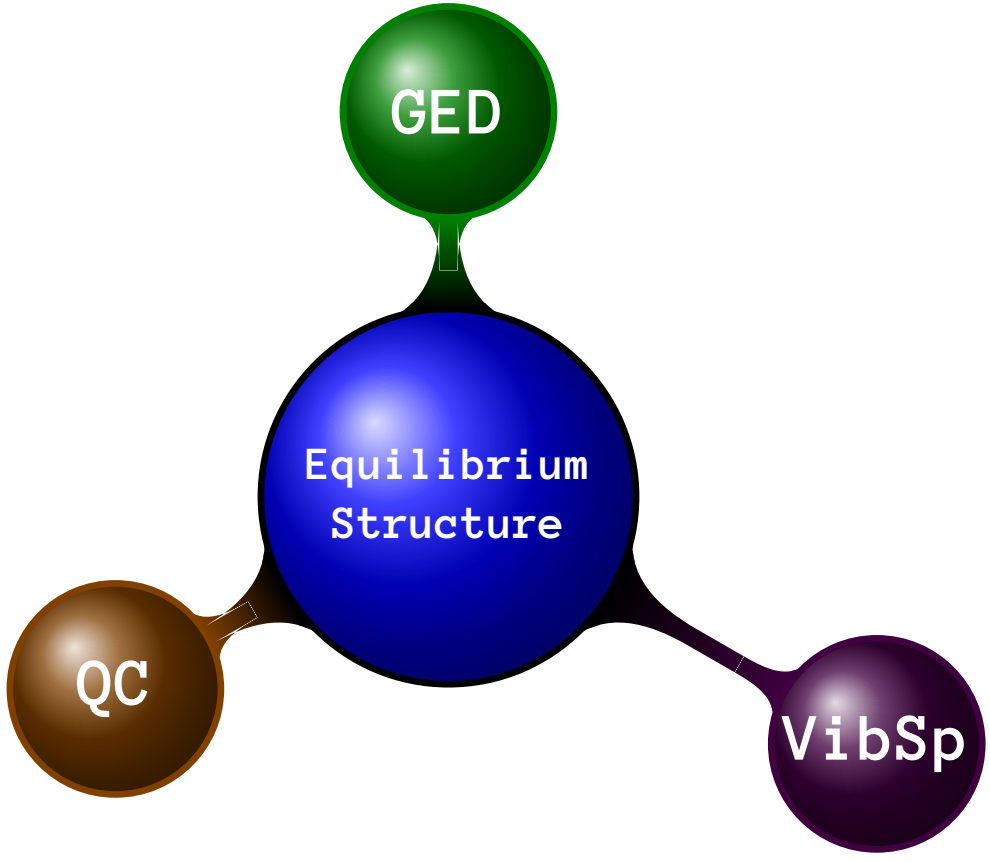
Nagy P. et al., *J. Phys. Chem. B*, **2005**, 109, 22588–22602

Histamine: intermolecular tautomerization

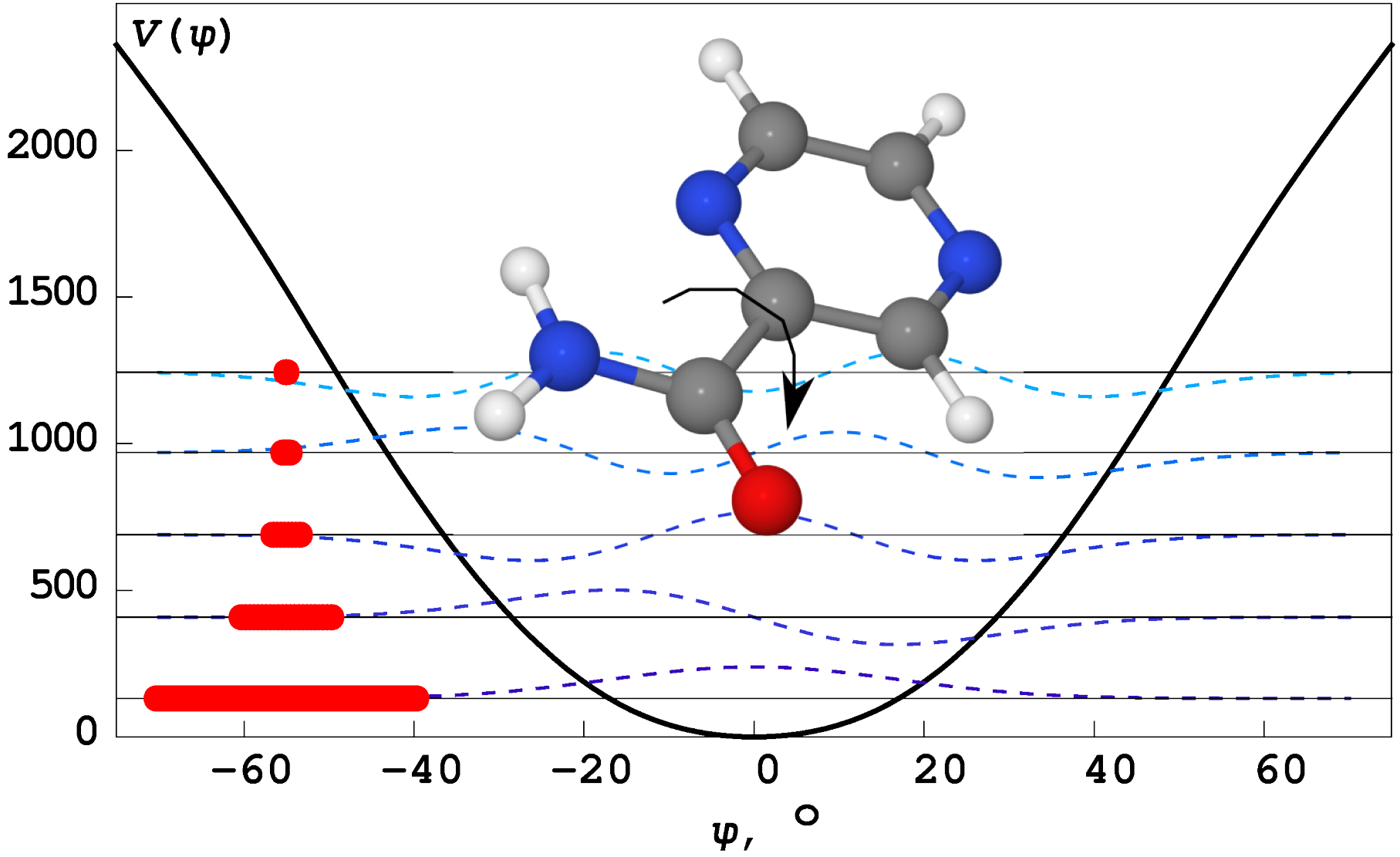


The ballad of Pyrazinamide (PZA)

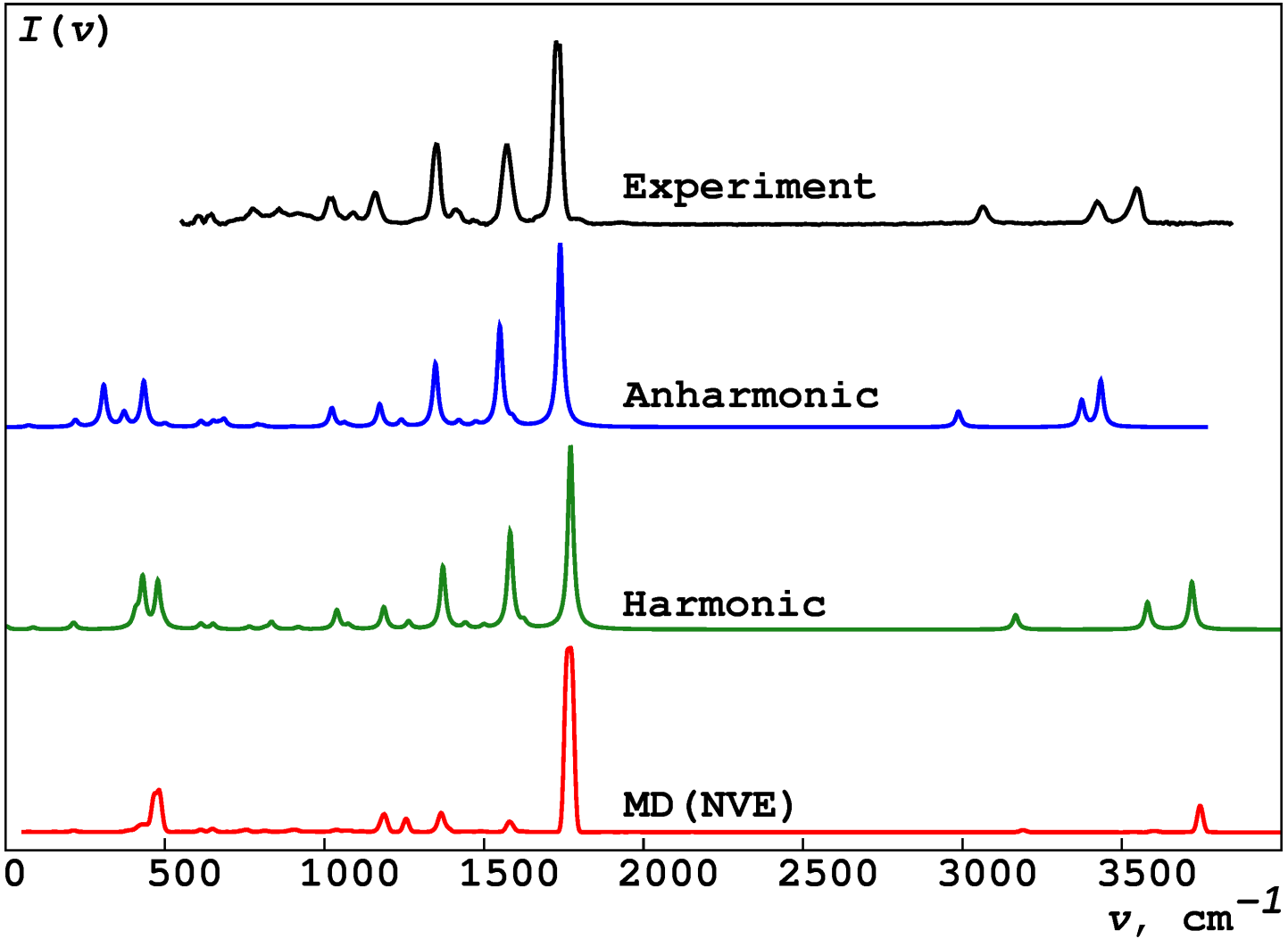




PZA: large amplitude motion



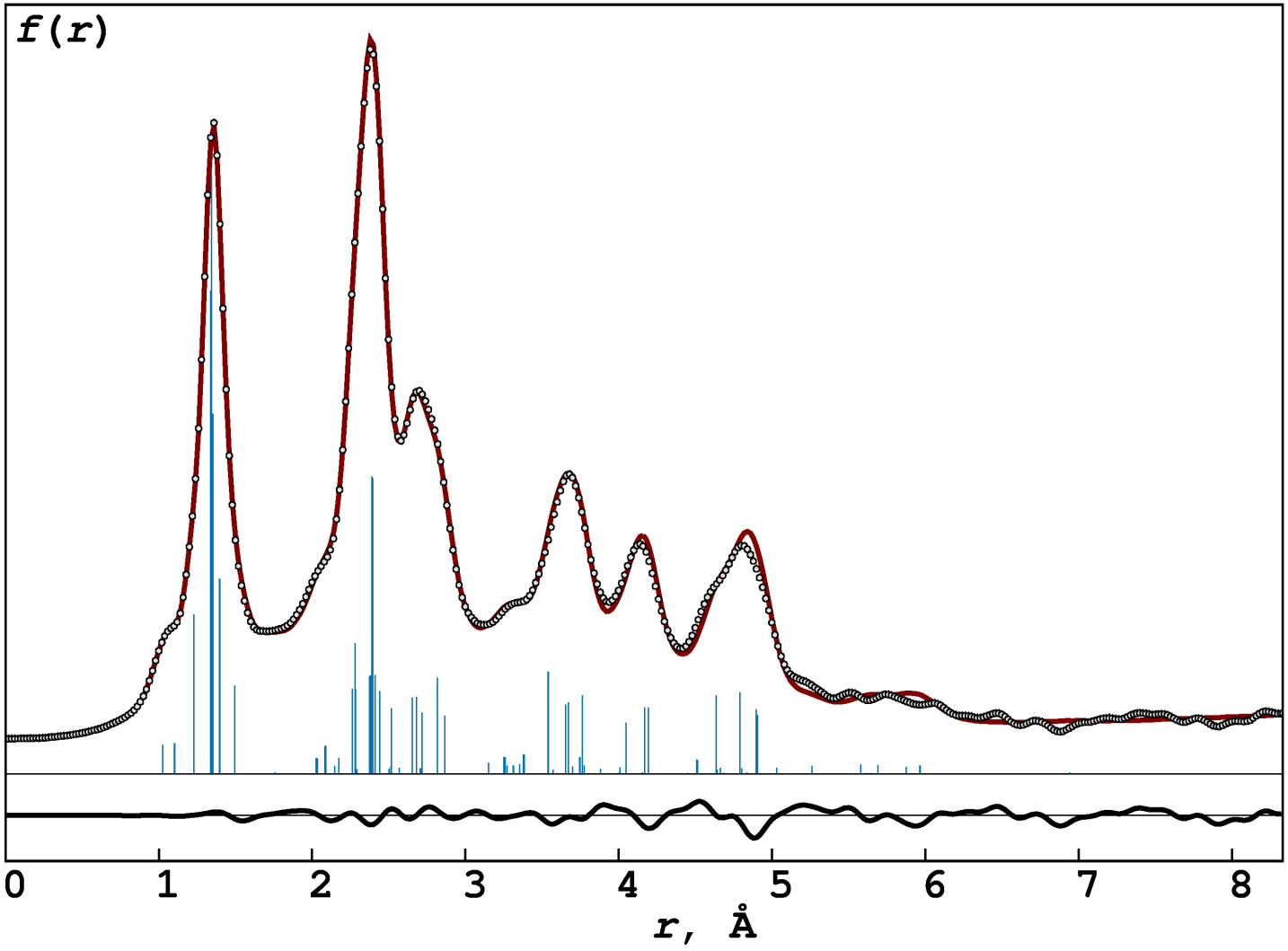
PZA: comparison with VibSp



http://webbook.nist.gov/chemistry/

PZA: GED+QCReg refinement

$R_f = 3.4\%$

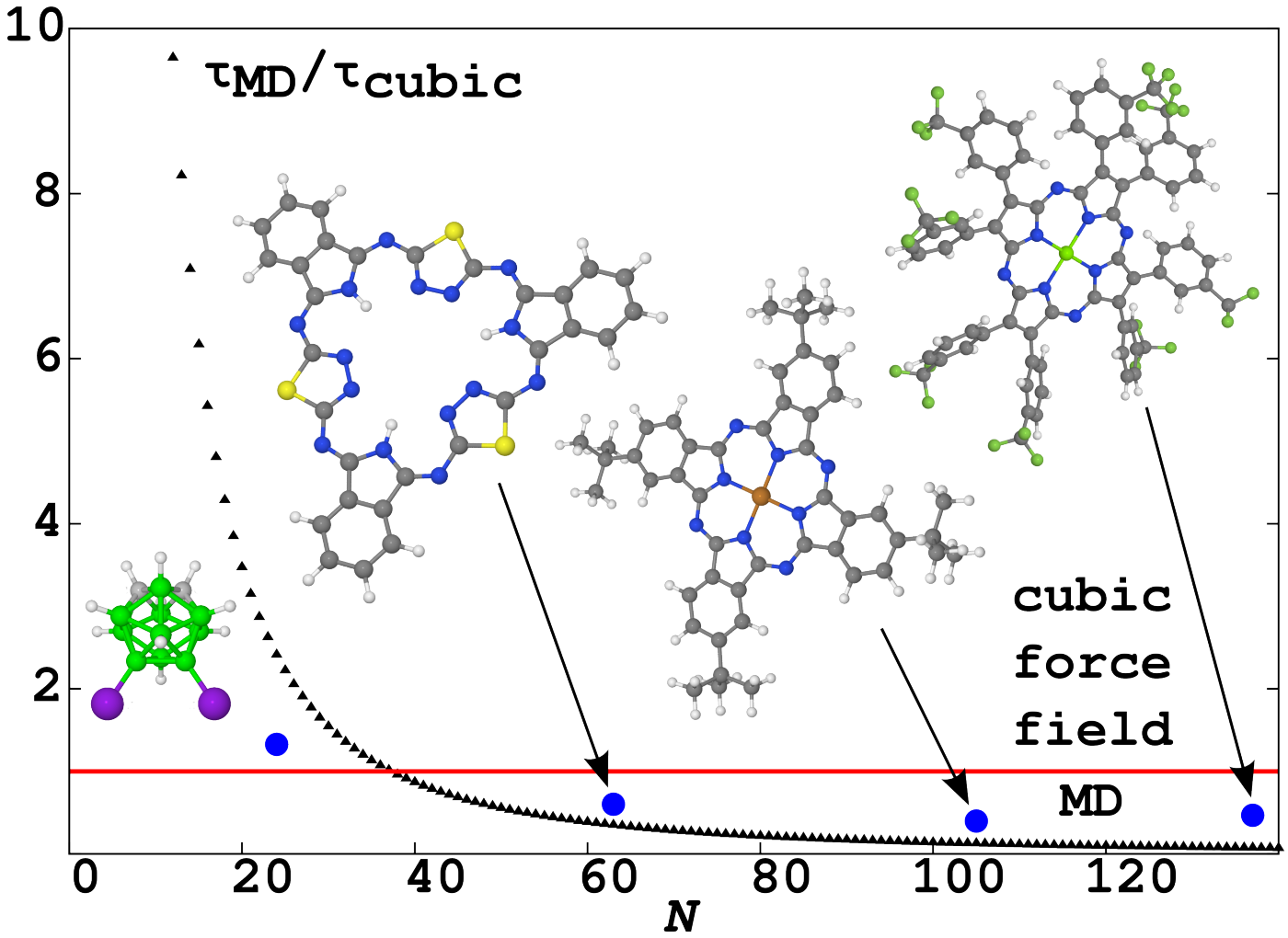


Qassandra

(**Qu**A**ntum** corrections to cla**SS**ical p**A**rameters for gas electro**N** Diff**RA**ction)

Qassandra: Why MD?

MD vs. Cubic force field calculation



Zhabanov Yu. et al., *J. Mol. Struct.*, **2015**, 1092, 114–112

Pimenov O. et al., *Struct. Chem.*, **2015**, 26, 1531–1541

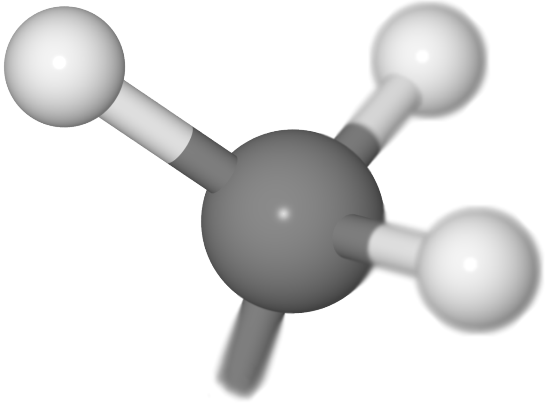
Qassandra: Problems of MD

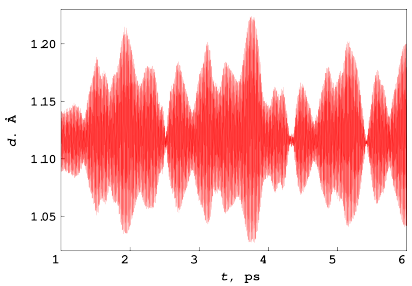
Classical Behavior

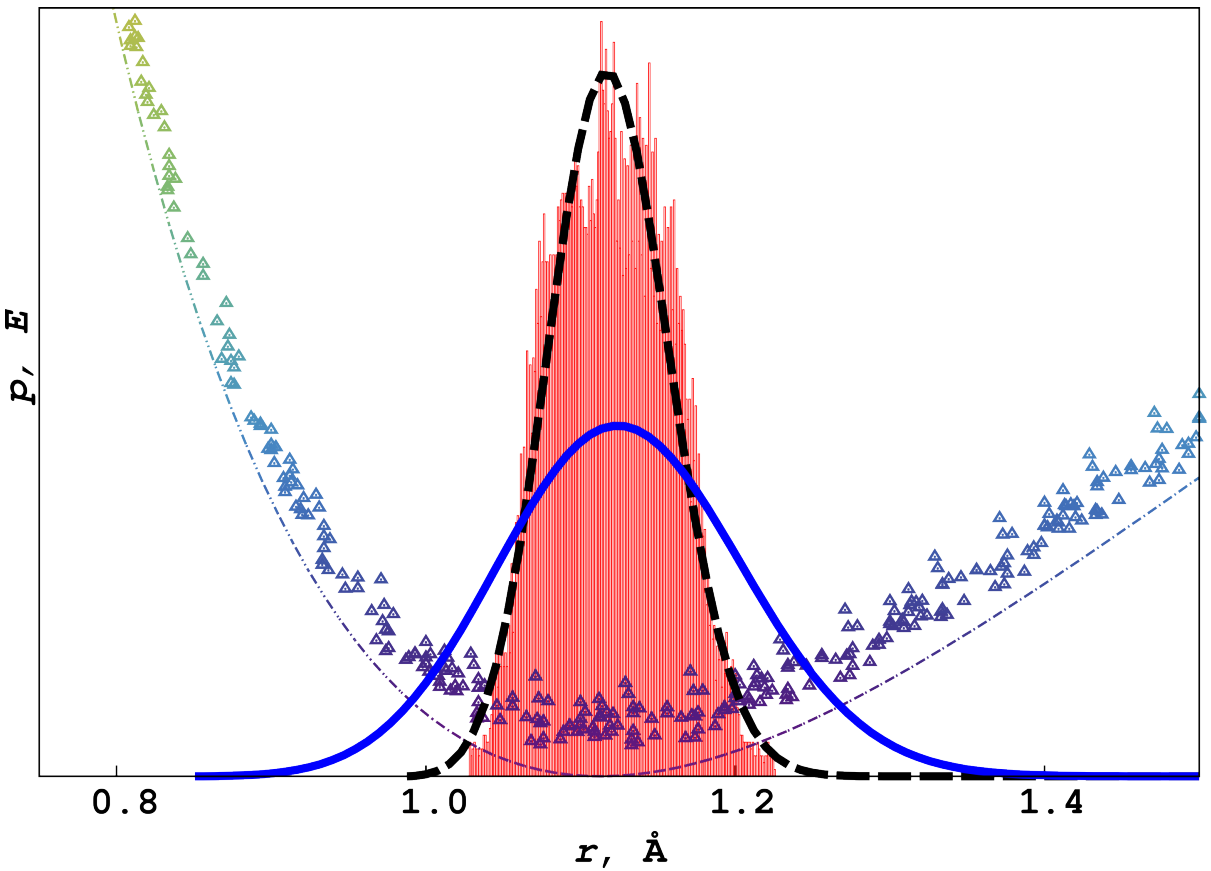
"Flying Ice Cube" Effect

Harvey S. et al., *J. Comput. Chem.*, **1998**, 19, 726–740

Qassandra: How does it work?

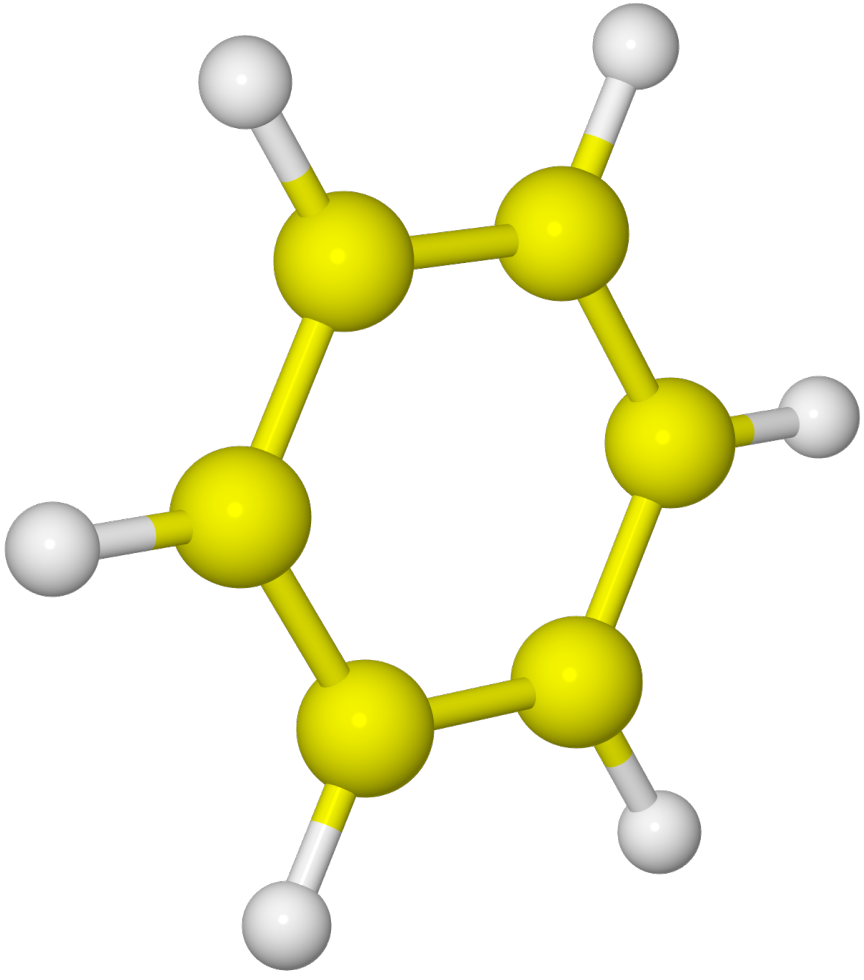






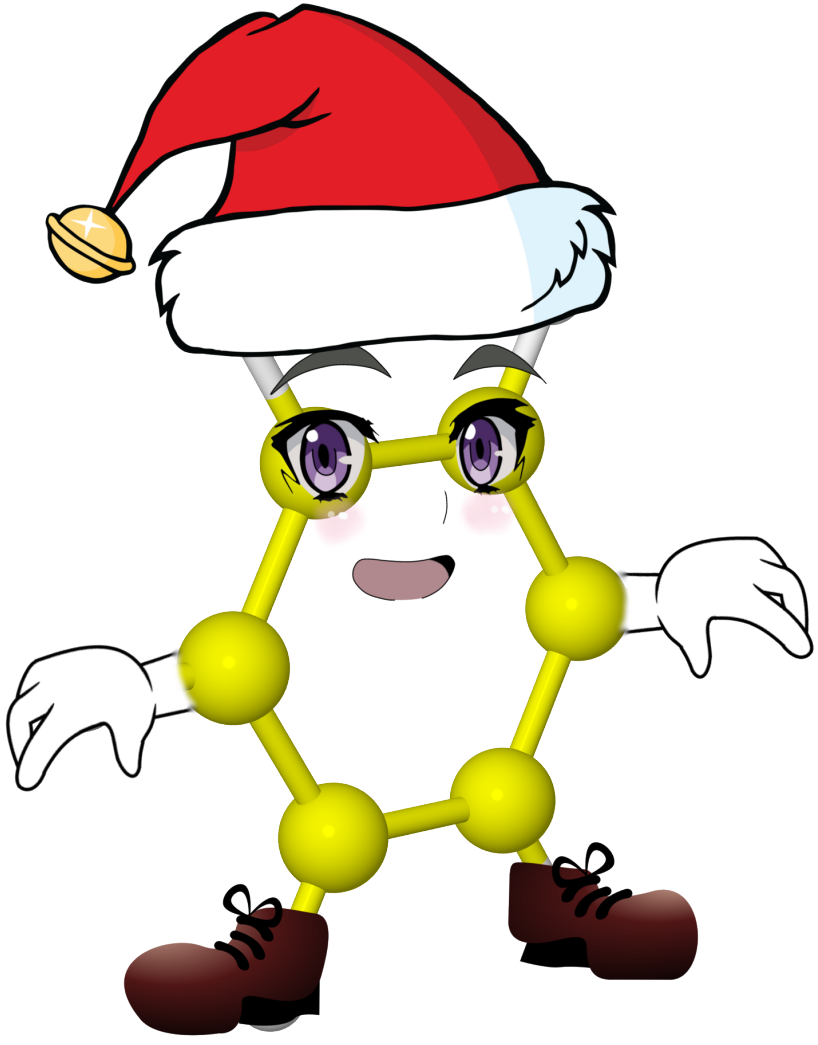
C–H term in ethane

Qassandra: applicability check



Benzene

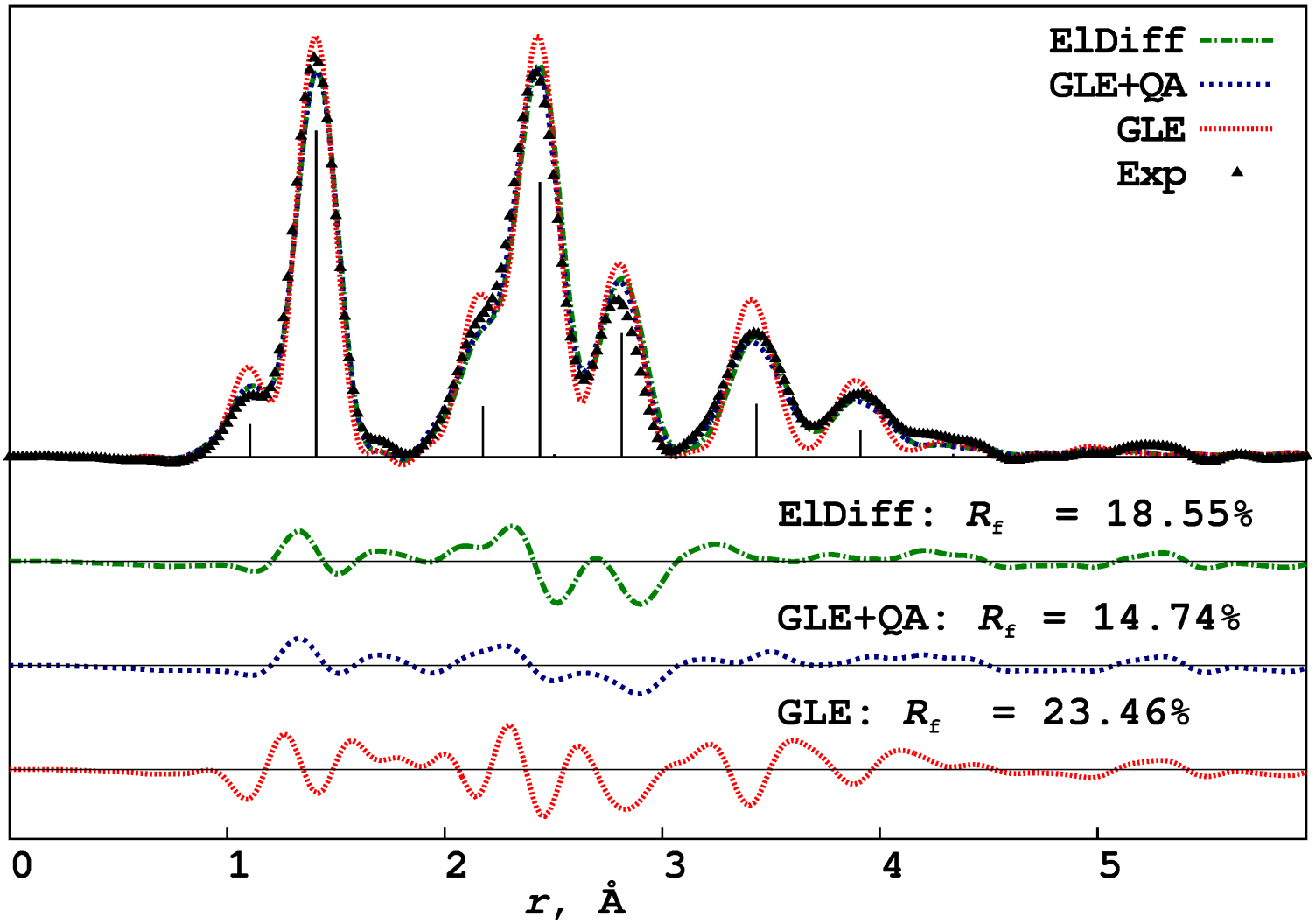
Qassandra: applicability check



XMas Benzene

Qassandra: applicability check

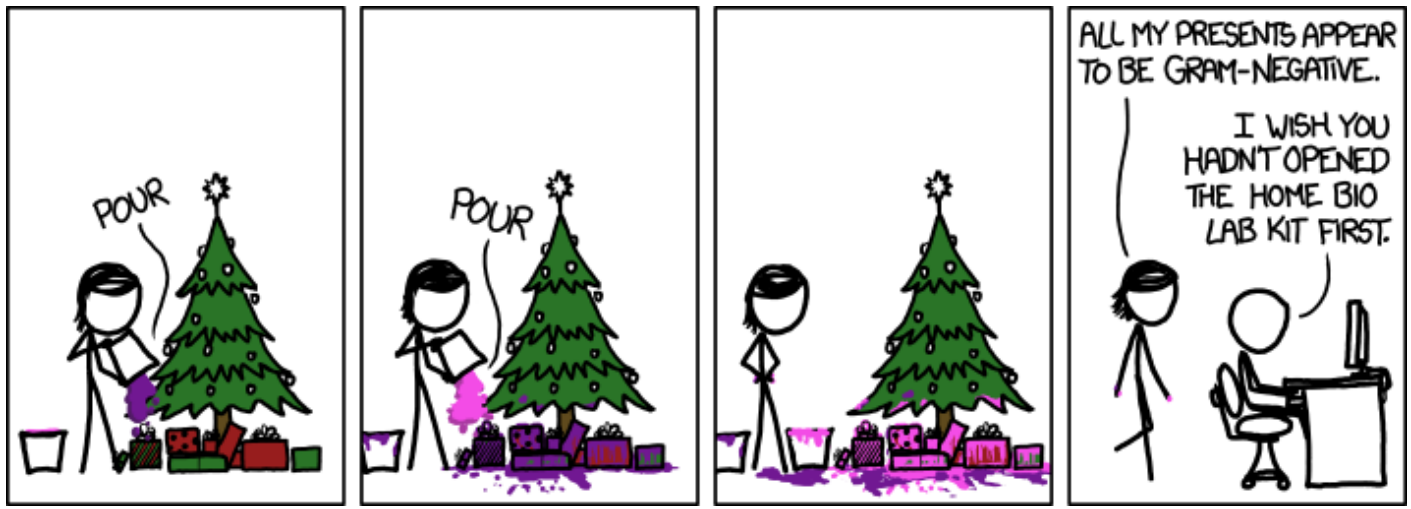
Benzene: experiment vs. theory



Conclusions

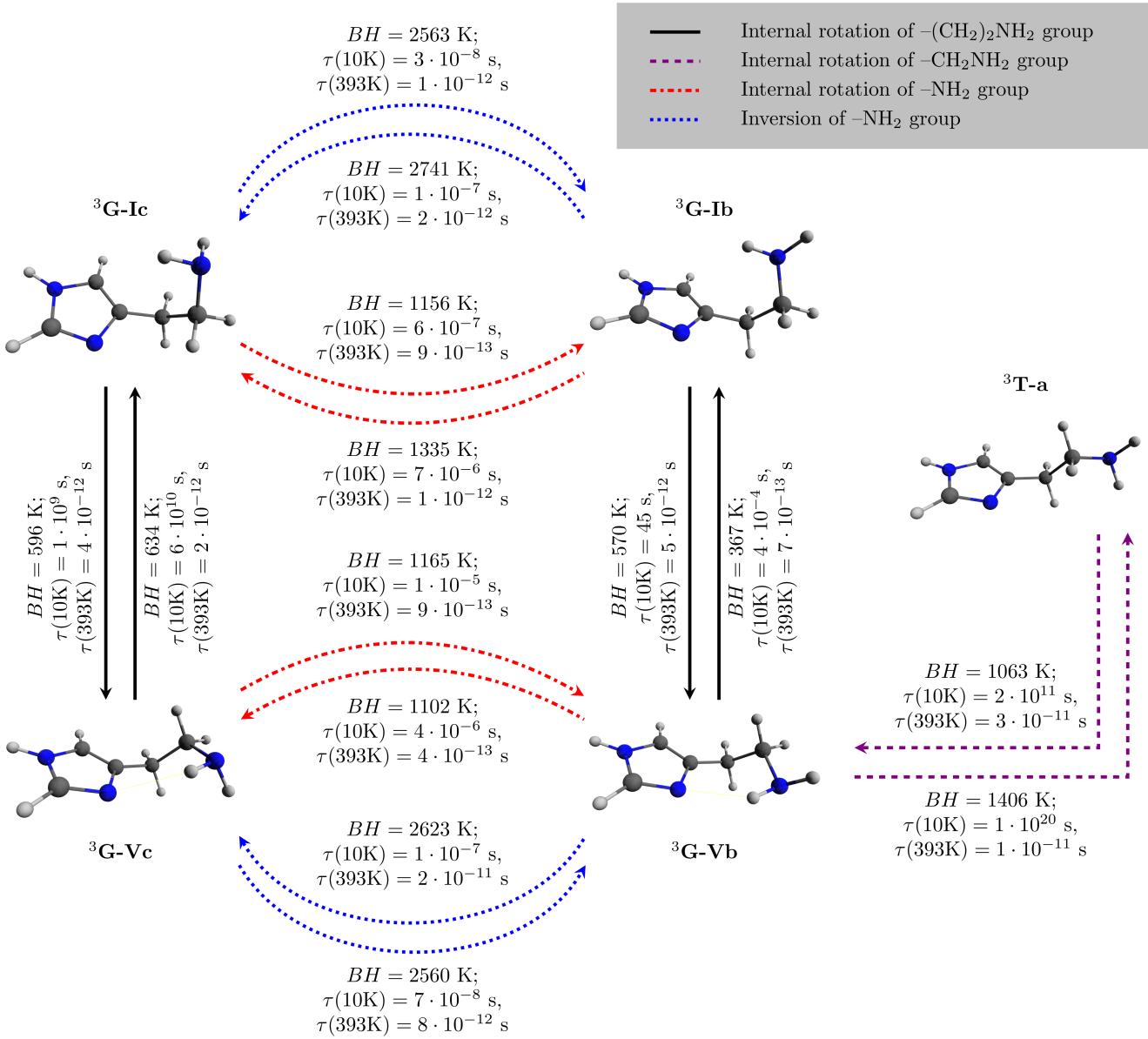
- ★ MOAR r_e STRUCTURES! (Histamine and PZA)
- ★ The gas of histamine reaches tautomeric equilibrium
- ★ Qassandra is alive!

Thank You for the attention!



© En3rgy

Histamine: conformational equilibrium



Types of systems in thermodynamics

Isolated system = *NVE*

Heat exhange ··· ✗

Matter exhange ··· ✗

Types of systems in thermodynamics

Closed system = *NVT*

Heat exhange ··· ✓

Matter exhange ··· ✗

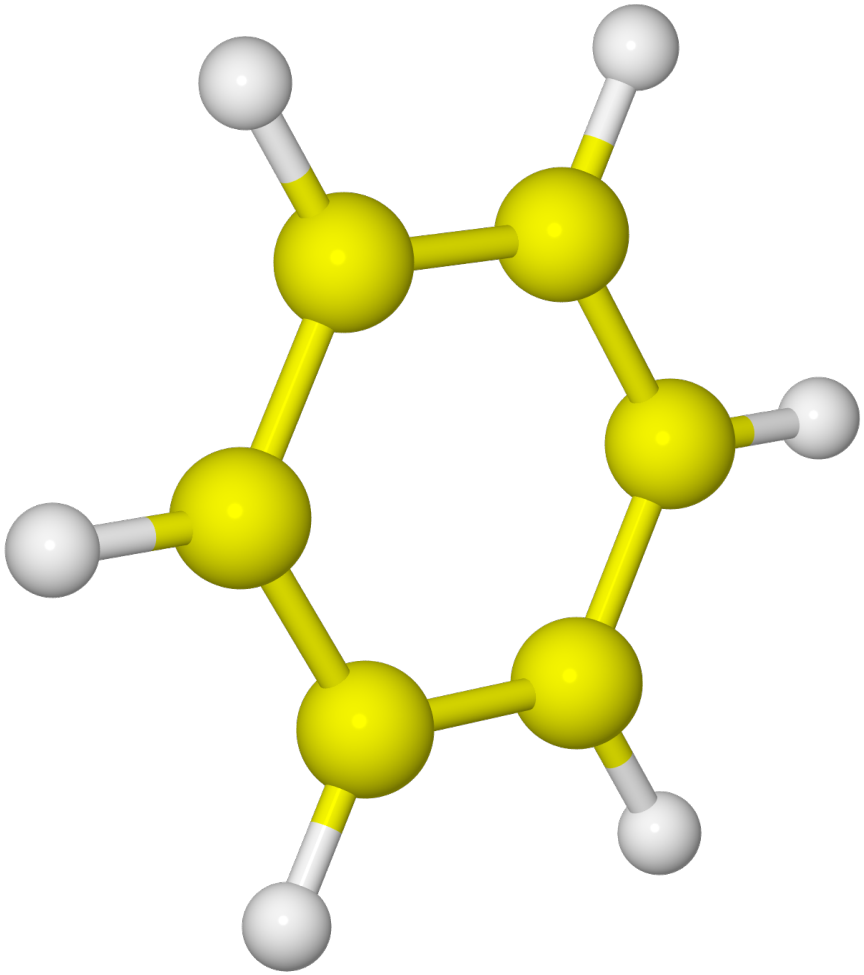
Types of systems in thermodynamics

Open system = μVT

Heat exhange ··· ✓

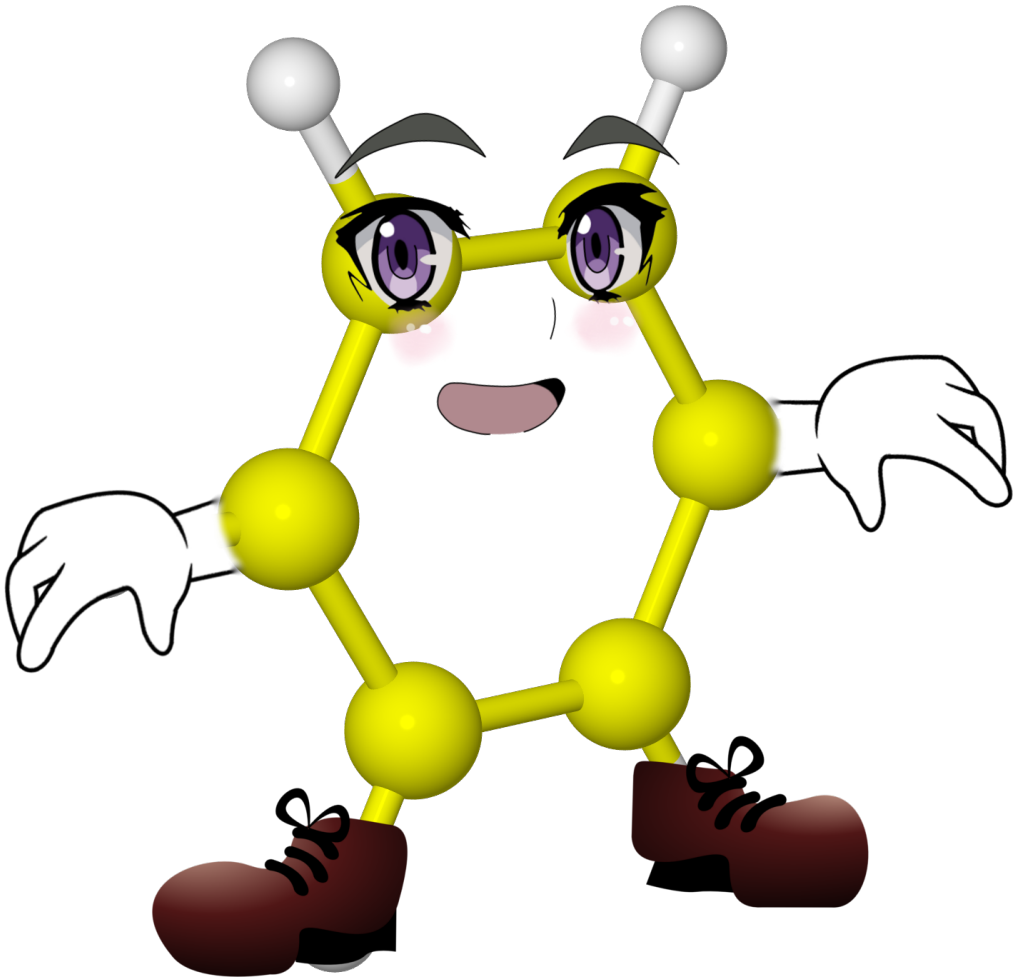
Matter exhange ··· ✓

Molecular dynamics simulations (MD)



System = molecule

Molecular dynamics simulations (MD)

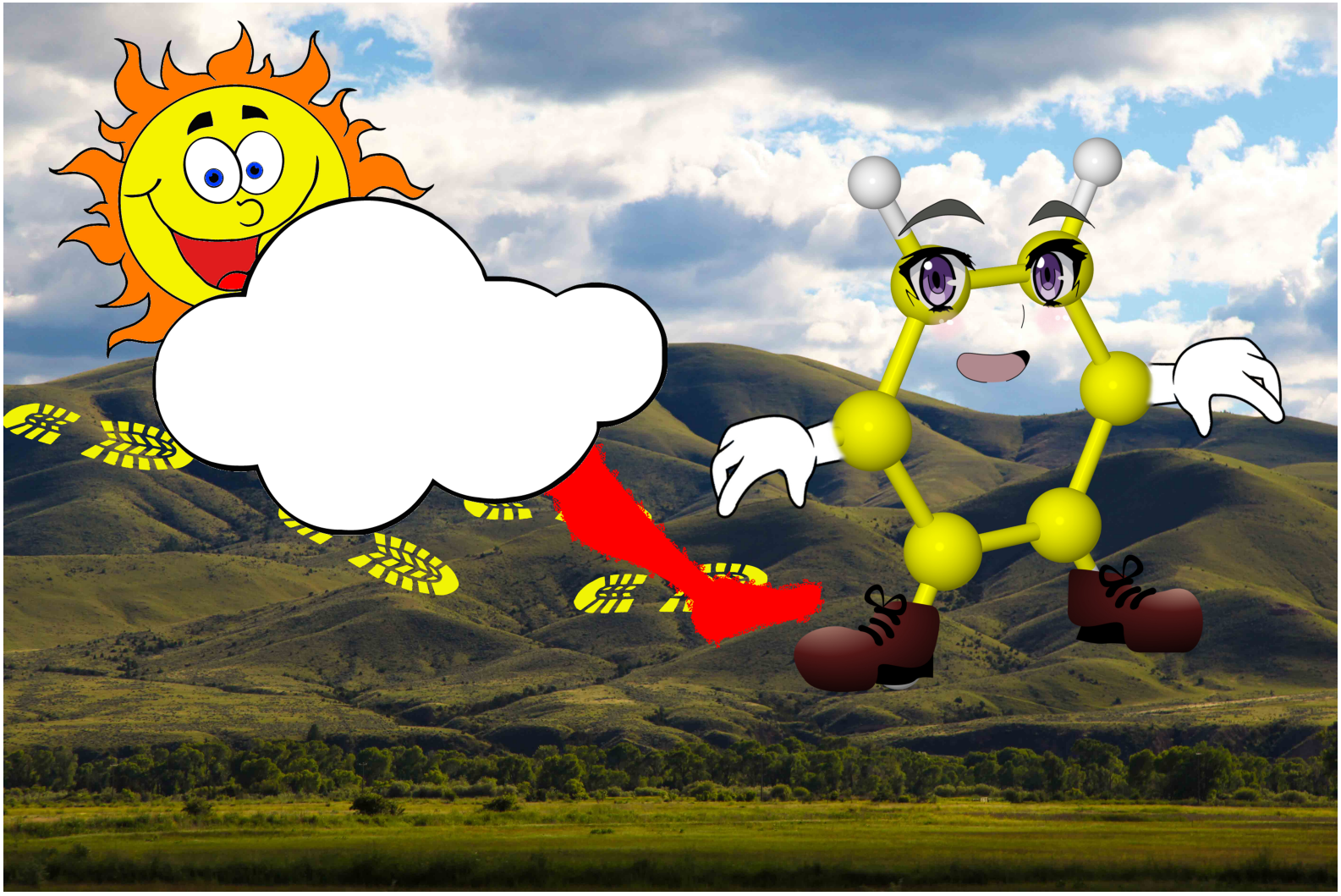


System = molecule

NVE MD

Classical motions on the PES

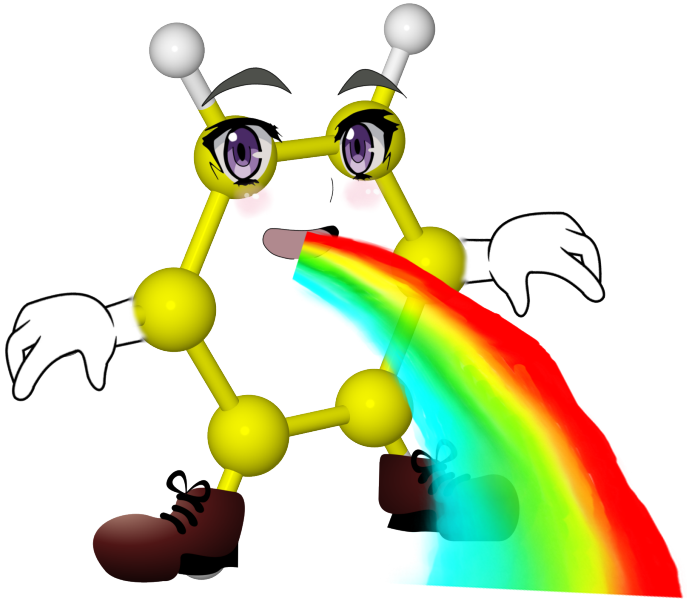
NVT MD



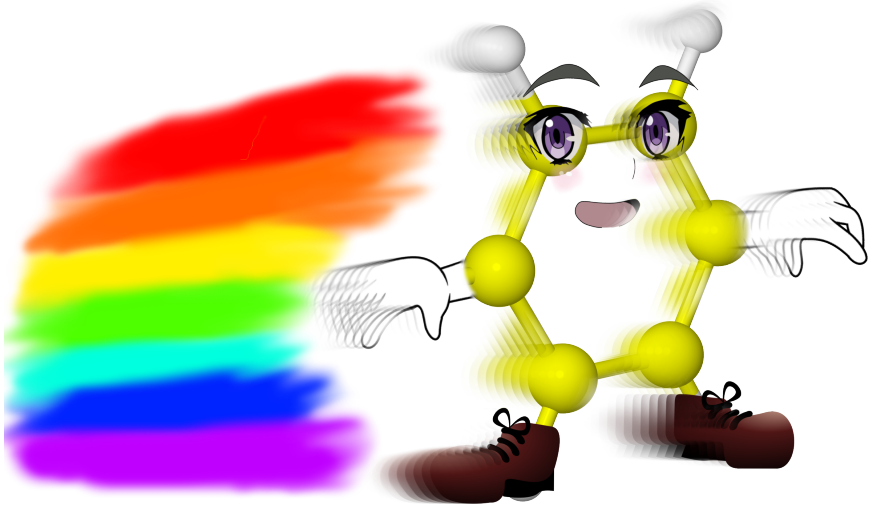
Classical motions on the PES with thermostat

NVT MD: thermostating

Energy loss ($E_{kin} \downarrow$)



Energy gain ($E_{kin} \uparrow$)



Problems in MD simulations: "Flying Ice Cube Effect"

Non-equilibrium distribution of energy for the degrees of freedom

Solution: better thermostats

Problem of the solution: limited availability

Problems in MD simulations: classical behavior

The lighter the atom - the more of quantum behavior

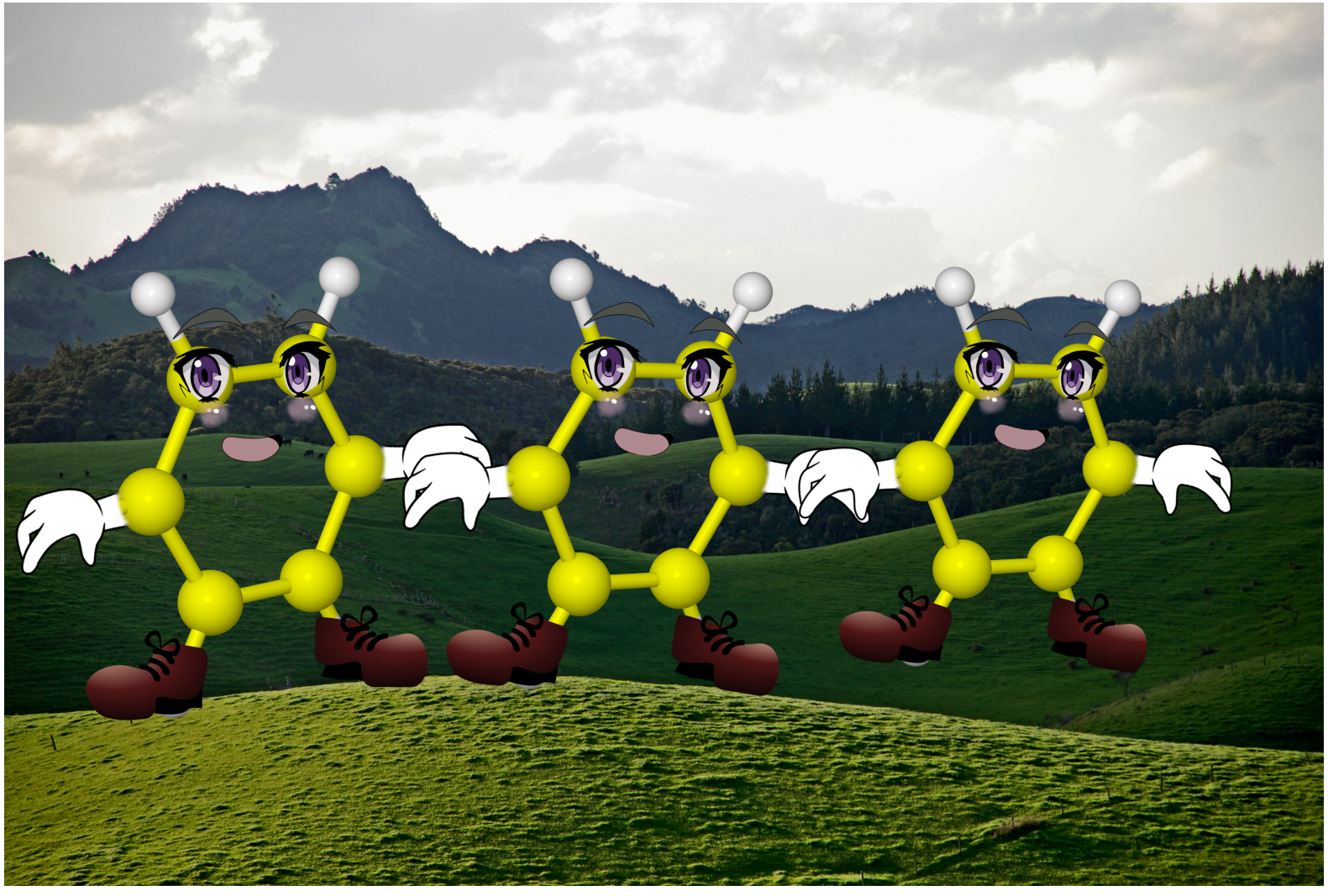
Solution #1: PIMD

Problems of solution #1: computational costs increase, limited availability

Solution #2: colored-noise thermostats

Problem of solution #2: limited availability

PIMD



Accounting quantum motions using path-integral approach