5th Users' Conference of IT4Innovations, November 9 – 10, 2021, Ostrava, Czechia

Theoretical study of sublimation, local disorder and strain energies of crystalline caged hydrocarbons

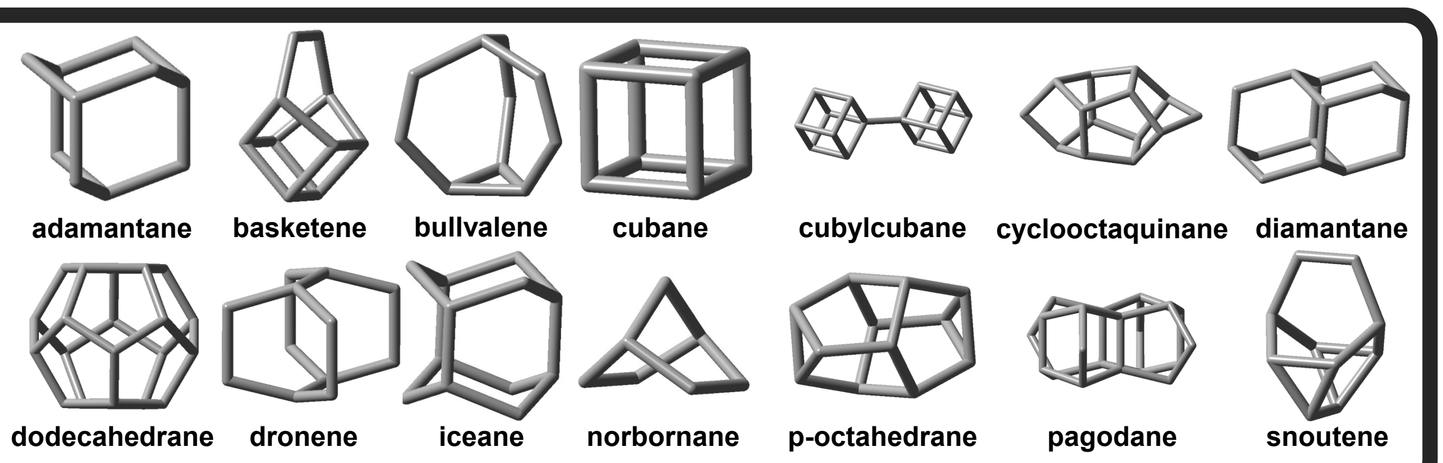
Petr Touš, Ctirad Červinka

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY PRAGUE

Department of Physical Chemistry, University of Chemistry and Technology, Prague, Technická 5, CZ-166 28 Prague 6, Czech Republic, tousp@vscht.cz, cervinkc@vscht.cz

IT4I

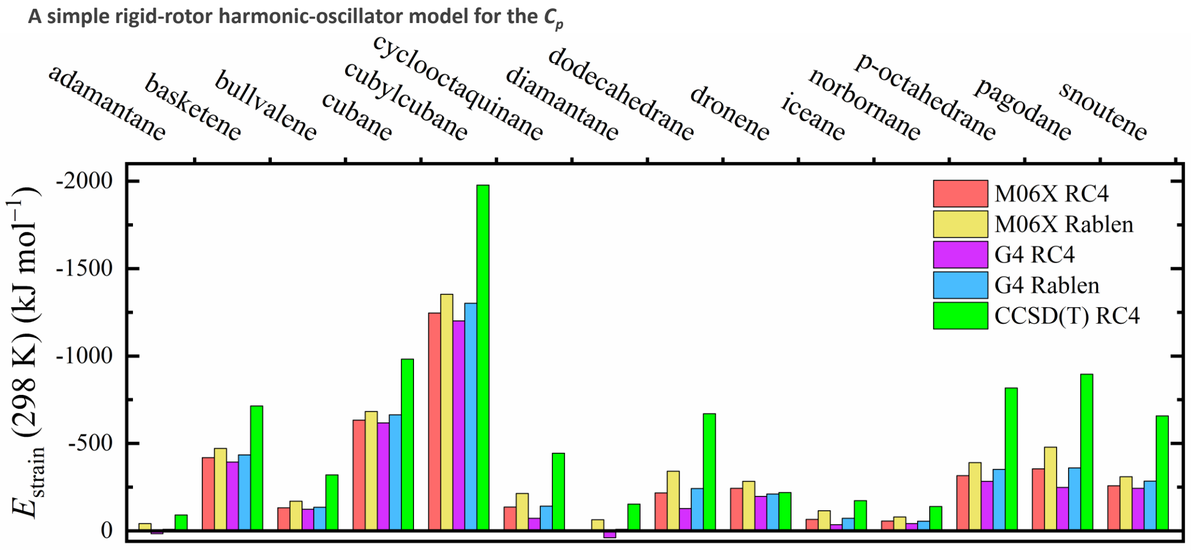
- **Caged hydrocarbons**
  - Compact carbon skeleton
  - High strain of various types
  - High symmetry
  - Highly customizable
  - Efficient crystal packing
  - Prone to disorder
- **Reasons for study?**
  - Great variety of shapes and sizes
  - Relatively overlooked
  - Unresolved thermodynamic data
  - Theorized uses
    - Energy storage, pharmaceuticals…



Strain energy

- **Fuzzy concept – various types of strain**
  - Bayer, torsional (Pitzer)…
- **Enthalpies of homodesmotic (RC4) reacitons[1]**
  - Error cancellation, use for strain energies limited
  - CCSD(T)/CBS, G4, and M062X/6-31+G(2df,p)
- **Rablen's[2] non-strained increments**
  - Easy to use, defined for use in strained species
  - G4 and M062X/6-31+G(2df,p)
- **Temperature dependence of enthalpies**
  - A simple rigid-rotor harmonic-oscillator model for the C_p
- **Expected trends achieved**
  - e.g., E(cubylcubane) ≈ 2E(cubane)
  - Unnatural bond angles → high strain
- **Rablen's increments vs. Reaction enthalpies**
  - Comparable results and computational resources usage

[1]Wheeler, S. E.; Houk, K. N.; Schleyer, P. v. R.; Allen, W. D. *Journal of the American Chemical Society* **2009**, *131 (7),* 2547-2560
[2]Rablen, P. R. *Chemistry* **2020**, *2 (2)*, 347-360



Fragmentation-additive calculations (FAC) scheme

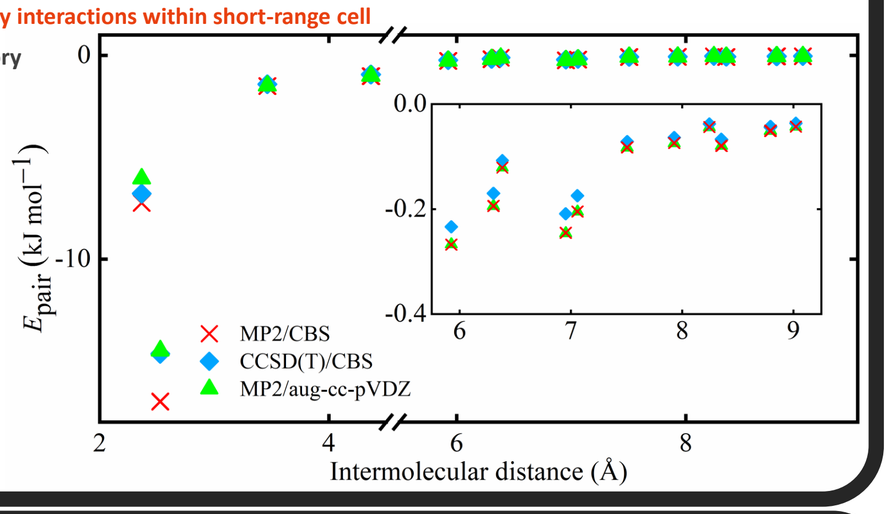
- **Computational scheme for bulk properties**
- **General idea**
  - Perform a cheaper (low-tier) calculation with PBC
  - Correct proximate pairwise (or many-body) interactions with an expensive (high-tier) method
- **Long-range regime at low level of theory**
  - Force field, low-tier quantum-mechanical method…
- **Creation of a short-range region within lattice**
  - Reasonable cut-off distance – convergence of two-body/many-body energies
- **Computation of two-/many-body interactions within short-range cell**
  - Both low and high level of theory

THIS SCHEME USED FOR:

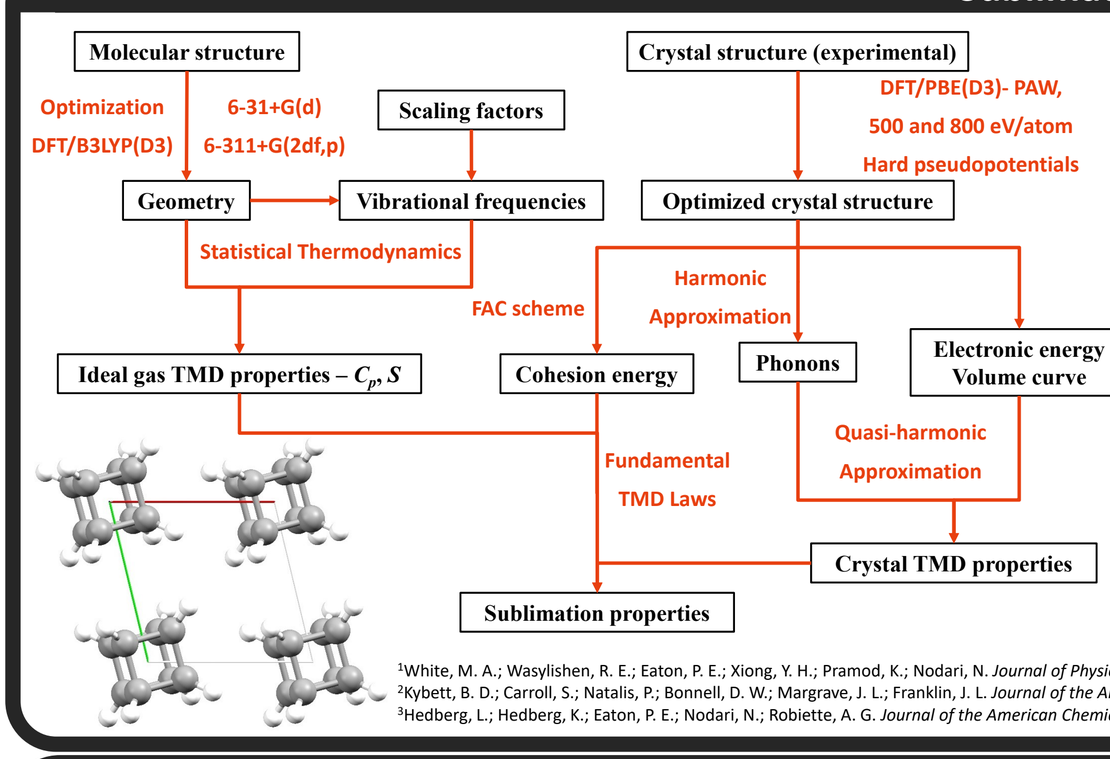
- **Cohesion energy**
  - Only two-body interactions assumed in the short-range regime
  - Many-body interactions in the long-range regime
- **Rotational perturbation energy differences**
  - Many terms cancel out in the short-range regime

Advantages

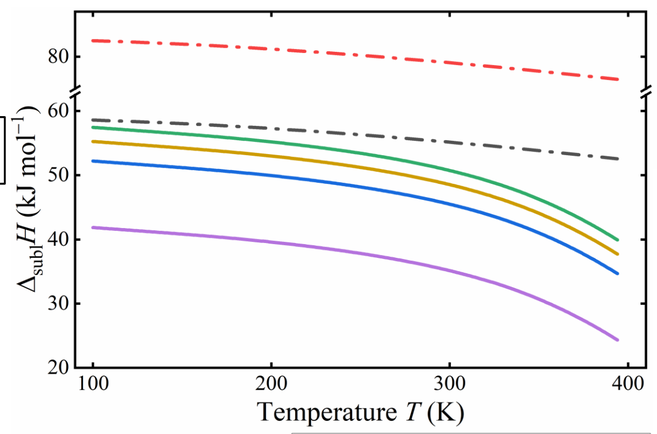
- Possible to use high levels of theory otherwise unachievable for big systems
- Many terms may cancel out – less computational resources

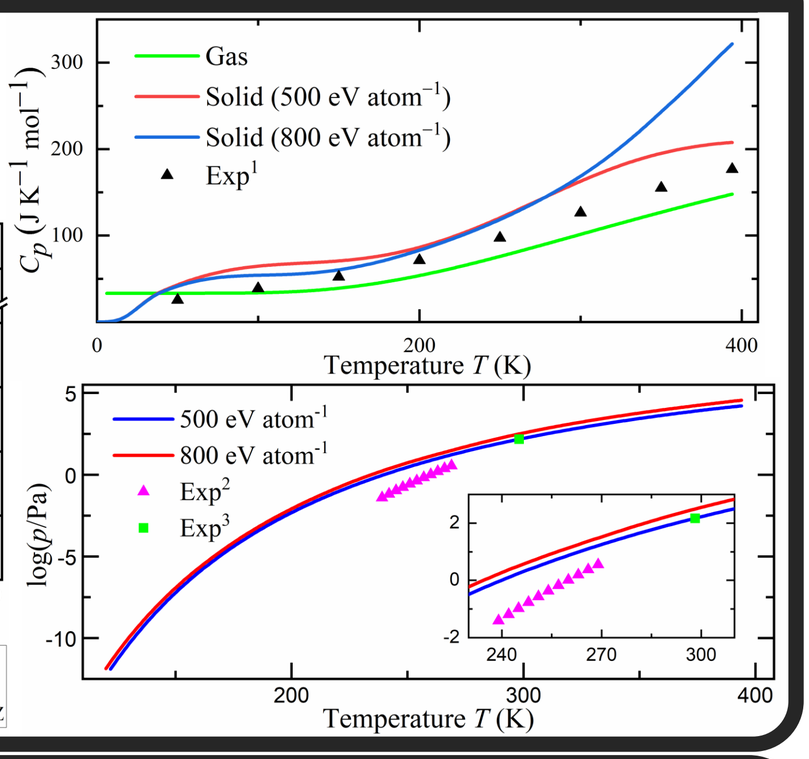


Sublimation properties – e. g. cubane



- **Cubane**
  - Two sets of incompatible experimental sublimation data
  - Close correspondence of one data set to computed values
  - Validation of computational scheme for other caged hydrocarbons

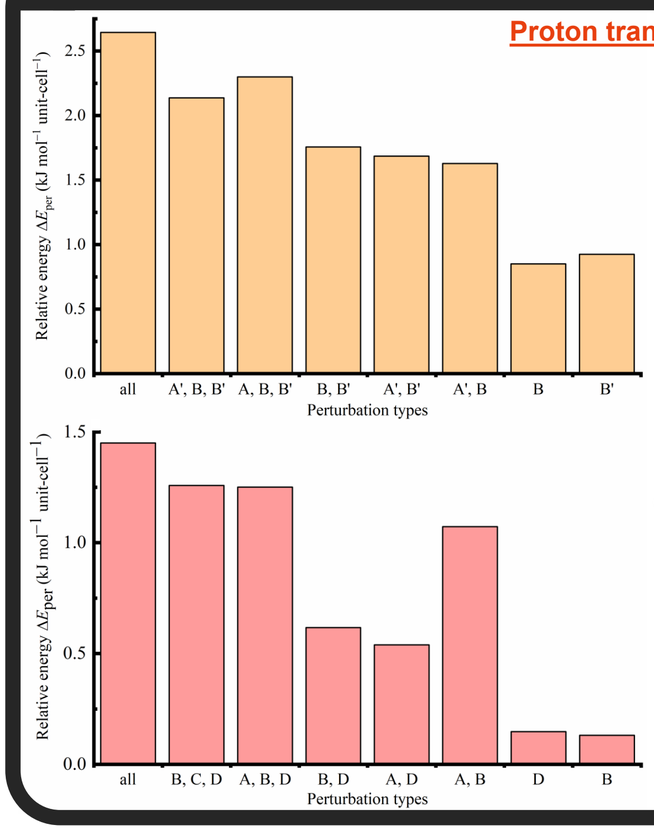


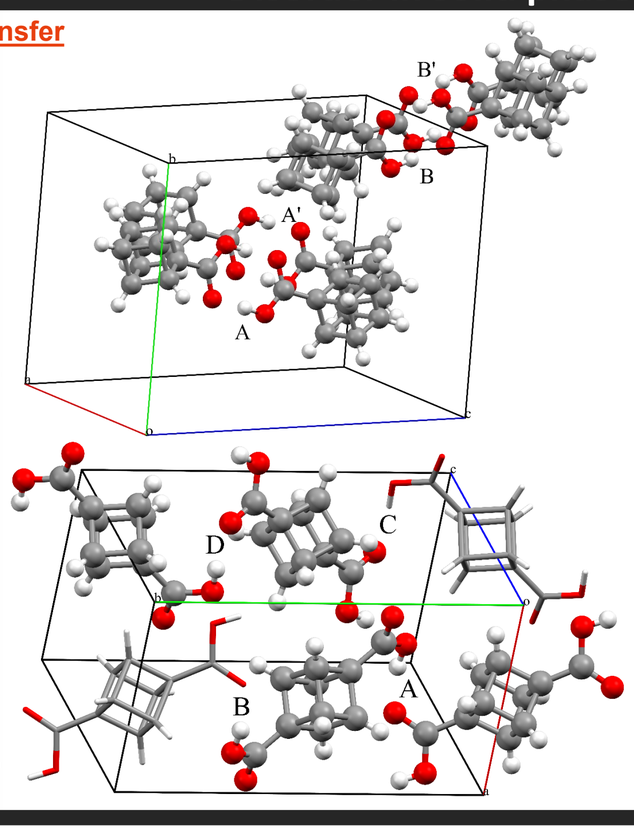


[1]White, M. A.; Wasylishen, R. E.; Eaton, P. E.; Xiong, Y. H.; Pramod, K.; Nodari, N. *Journal of Physical Chemistry* **1992**, *96*, 421–425
[2]Kybett, B. D.; Carroll, S.; Natalis, P.; Bonnell, D. W.; Margrave, J. L.; Franklin, J. L. *Journal of the American Chemical Society* **1966**, *88*, 626
[3]Hedberg, L.; Hedberg, K.; Eaton, P. E.; Nodari, N.; Robiette, A. G. *Journal of the American Chemical Society* **1991**, *113*, 1514–1517

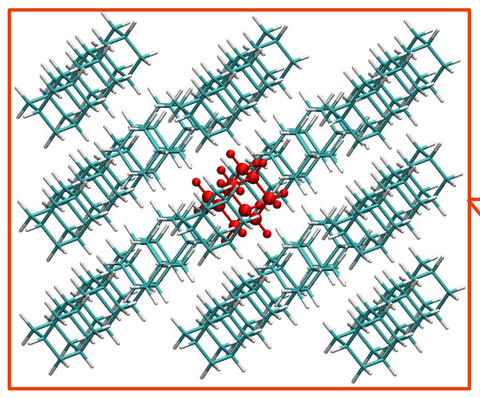
Disorder in solid phases of caged hydrocarbons

Proton transfer

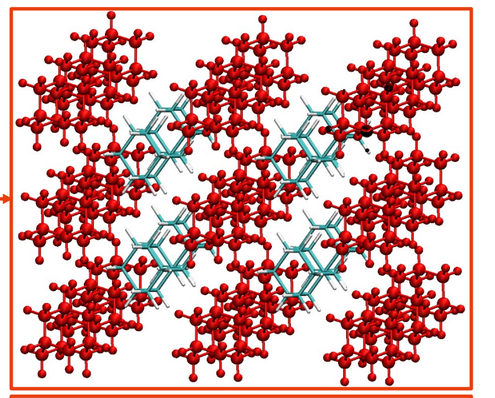




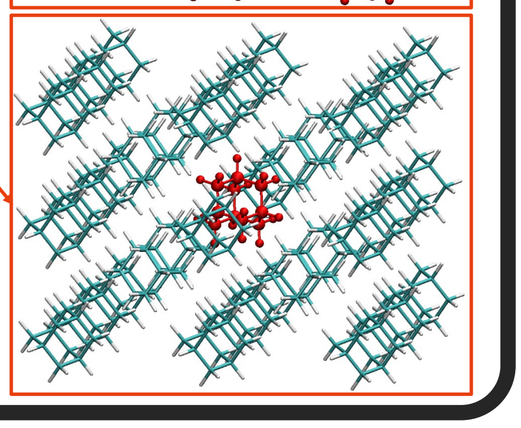
Rotational disorder



DFT/PBE
Periodic boundary conditions
ΔE = -12.94 kJ mol^{-1}
Periodic rotation



Point defect rotation
FAC Scheme
ΔE = 30.75 kJ mol^{-1}



- High symmetry → rotation of nearly spherical molecules
- e.g., adamantane
  - Rotation in periodic lattice → lower energy
  - Rotation as a point defect → higher energy
  - One unresolved polymorph
    Possibility for more?
- Metastable phase?
  Unrealistic geometry?
  Computational artifact?

Acknowledgements
Gregory Beran, University of California Riverside – Development of the Hybrid many-body interaction model

This work has received financial support from The Ministry of Education, Youth and Sports of the Czech Republic from the Project No. LTAUSA18011 as a part of the INTER-EXCELLENCE program.

MINISTRY OF EDUCATION, YOUTH AND SPORTS