Energy Barrier between the Conformations of Gaseous and Crystalline Rubrene

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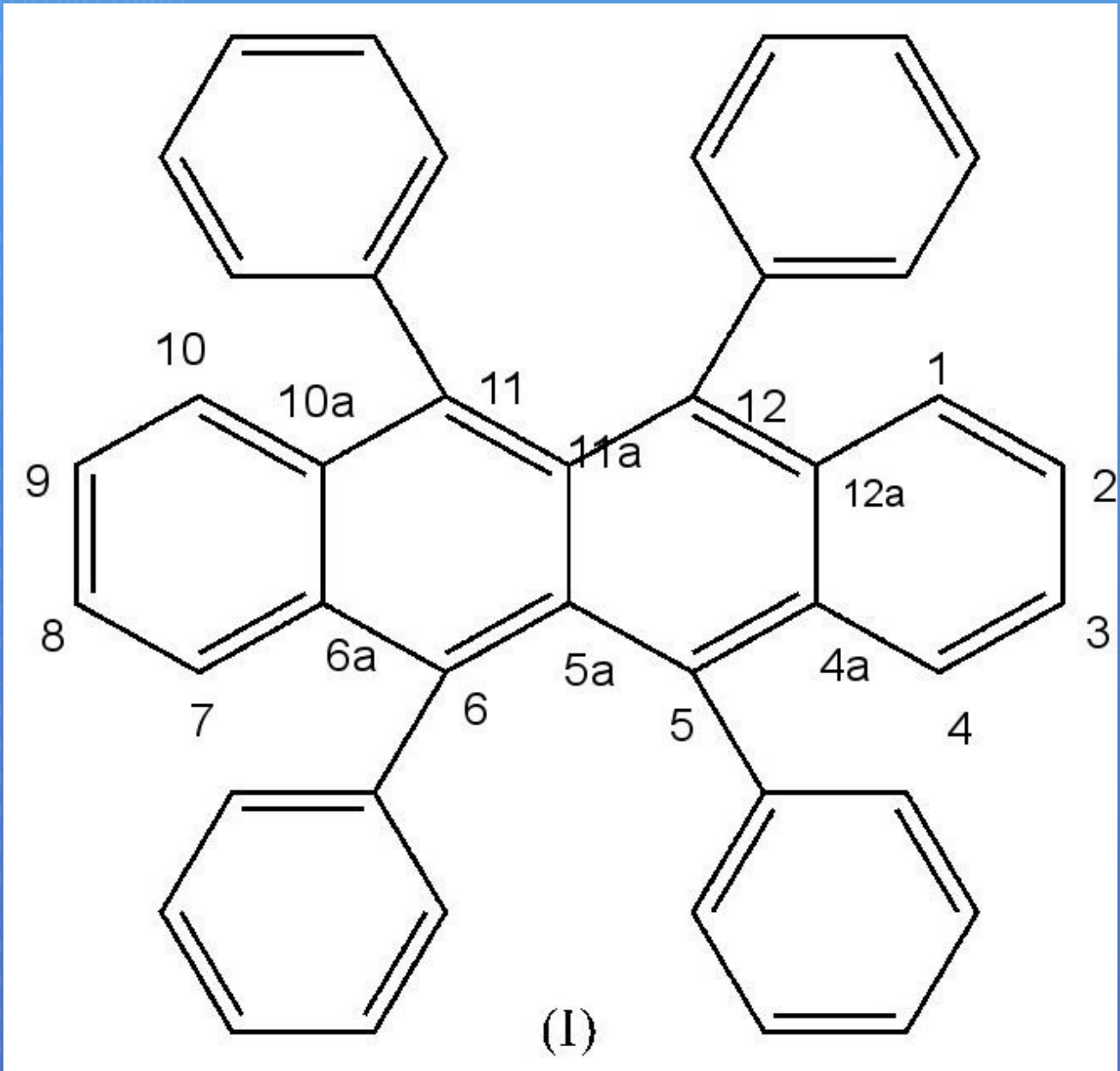
Outline

- Introduction and motivation
- Results and discussion
- Future perspective

Introduction and Motivation

Chemical Formula

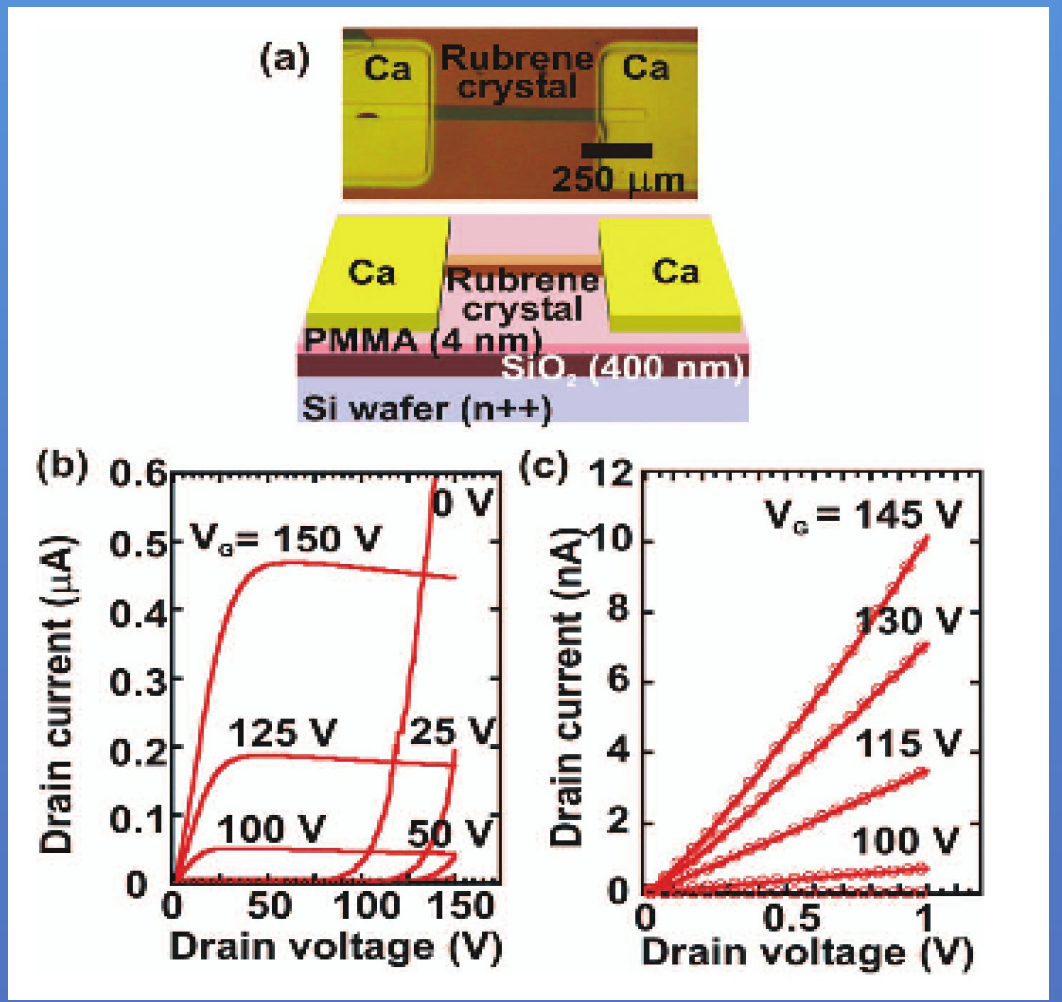
- Rubrene: 5,6,11,12-tetraphenyltetracene ($C_{42}H_{28}$)



(I)

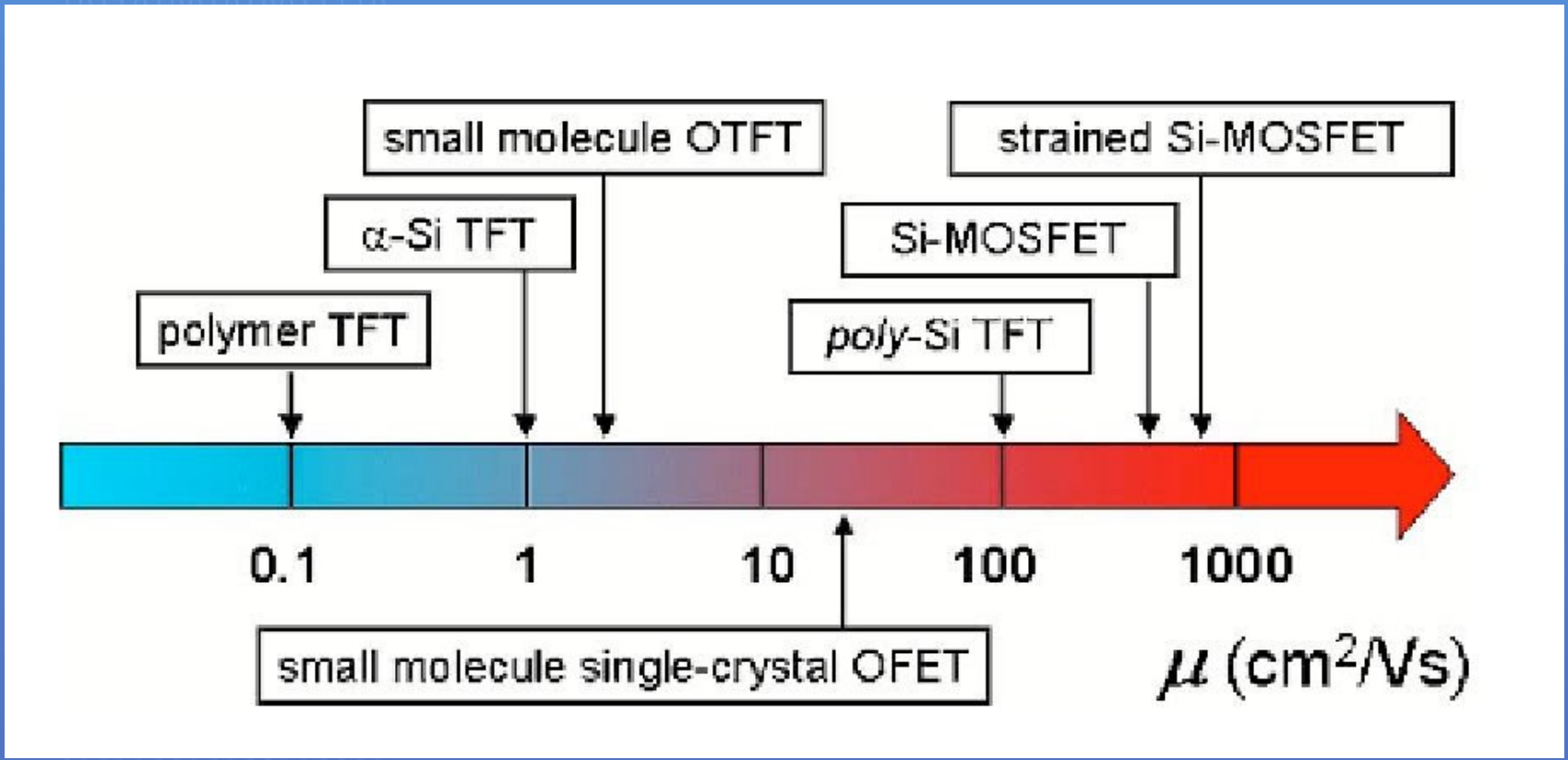
Application

- Plastic electronics
- Organic field effect transistor (OFET)
- Organic photovoltaic devices



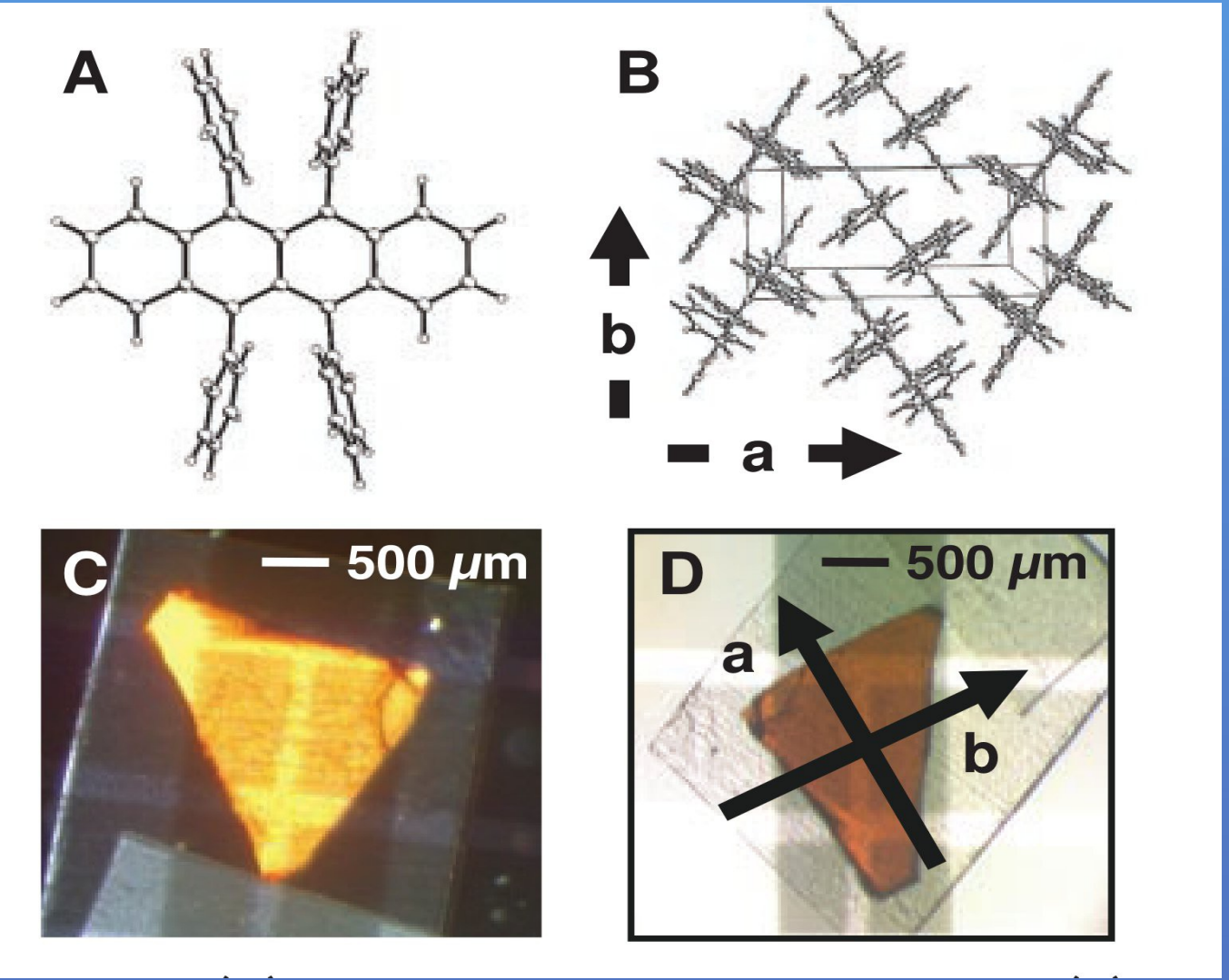
Mobility

- Organic semiconductor
- Single crystal rubrene: 15-20 cm2/V s
- Comparable to polysilicon



Single Crystal Rubrene

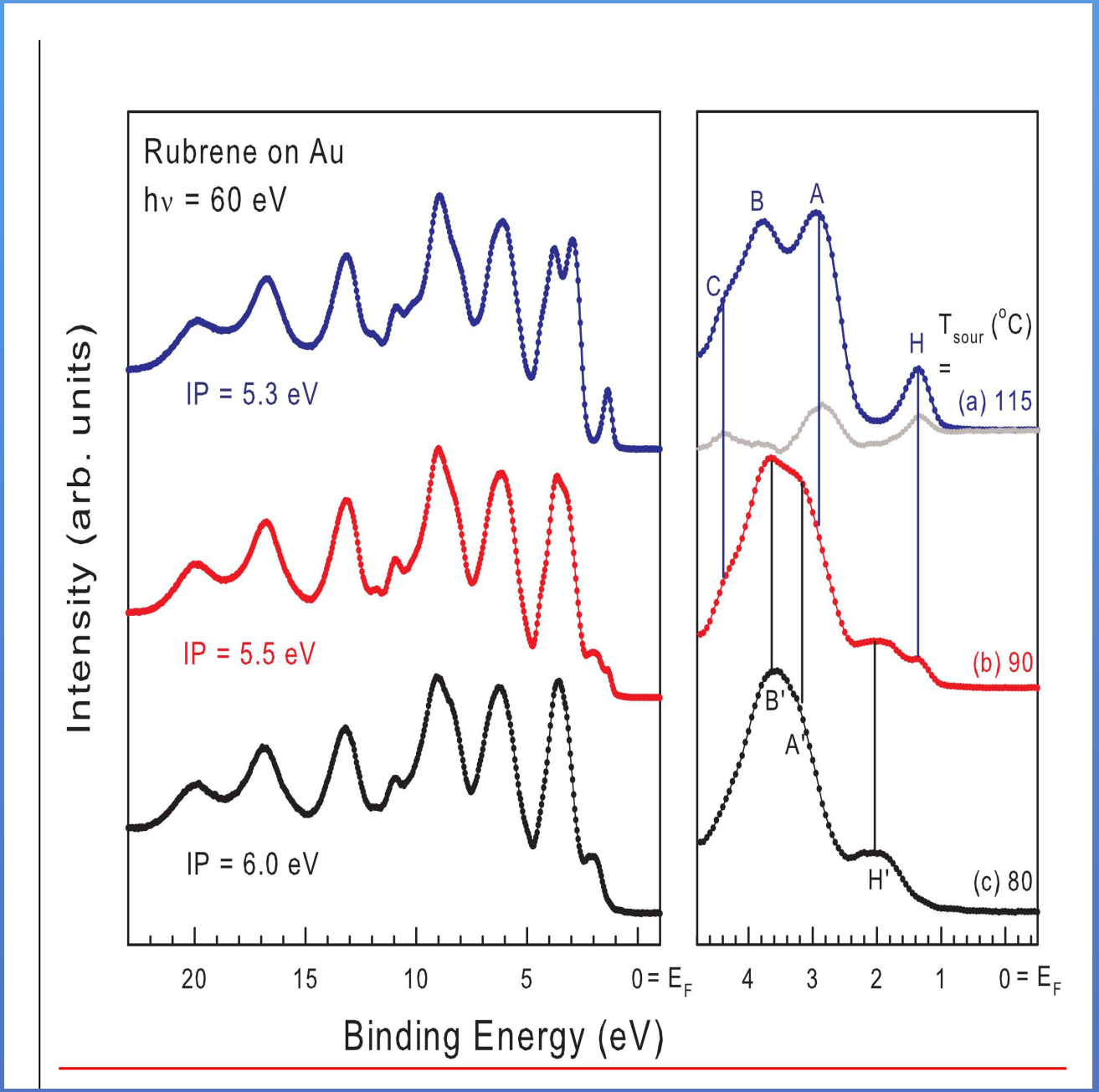
- Orthorhombic
- Pi-pi overlap along b direction → anisotropic conductivity



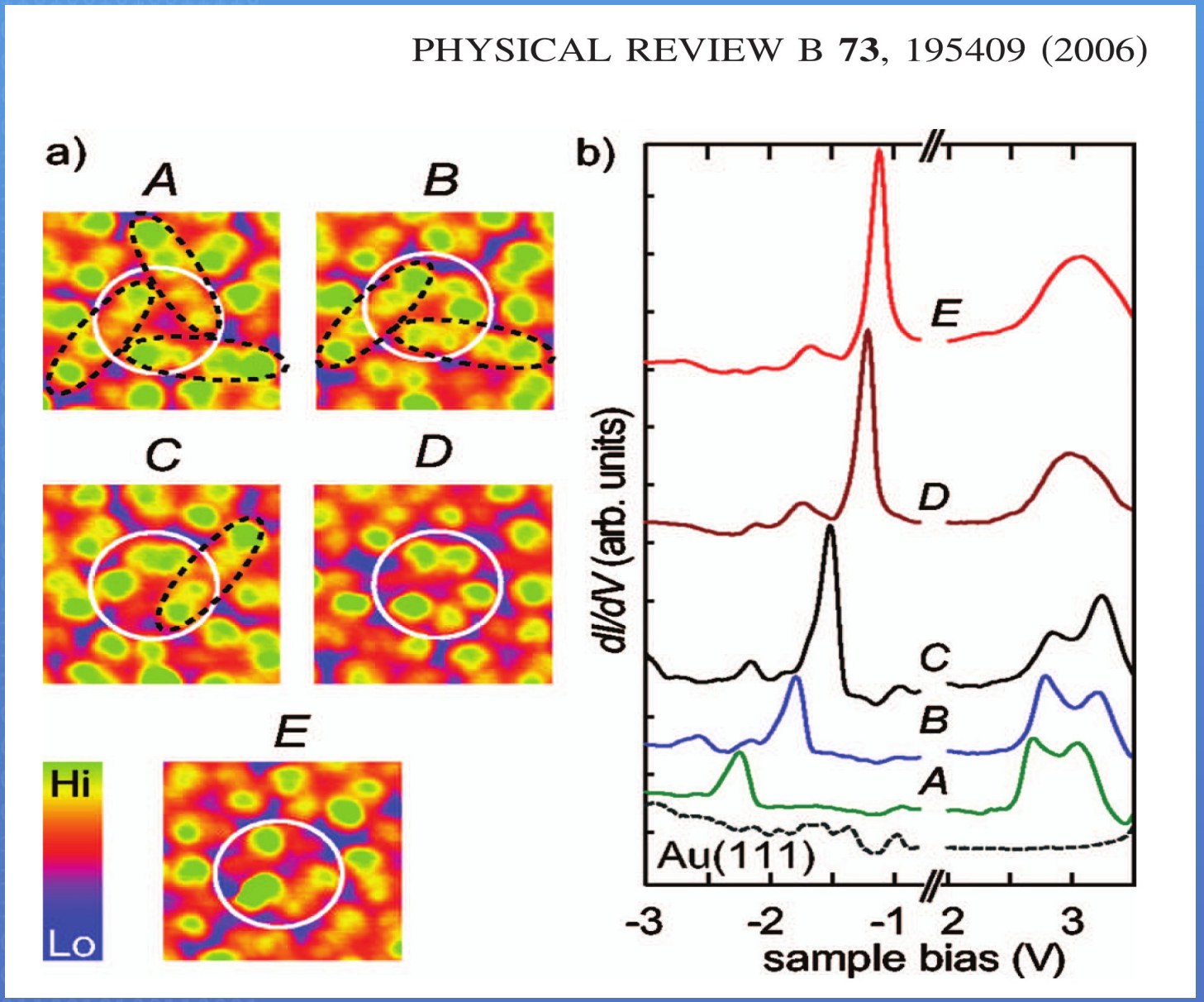
Photoemission Spectra (PES)

- Depends on temperature only
- Indep. of thickness and substrate
- HOMO:

  High T(115 C) > Low T(80 C) by ~0.8 eV
- Data obtained by Prof. C. P. Cheng, NCYU

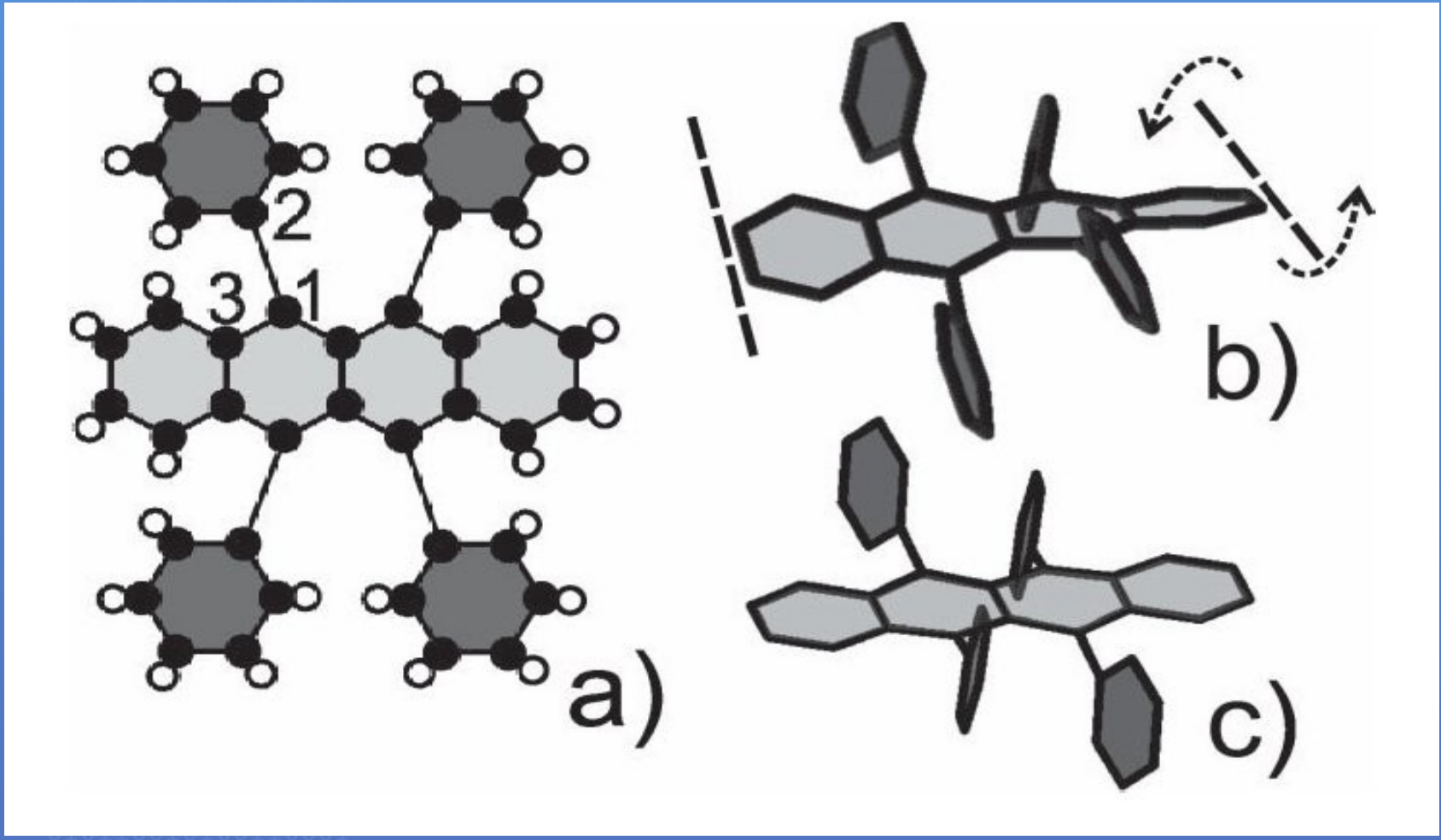


HOMO Shifting Observed with STM



Conformations

- Gaseous: D2 symmetry; twisted backbone (Fig. b)
- Crystalline: C2h symmetry; planar backbone (Fig. c)



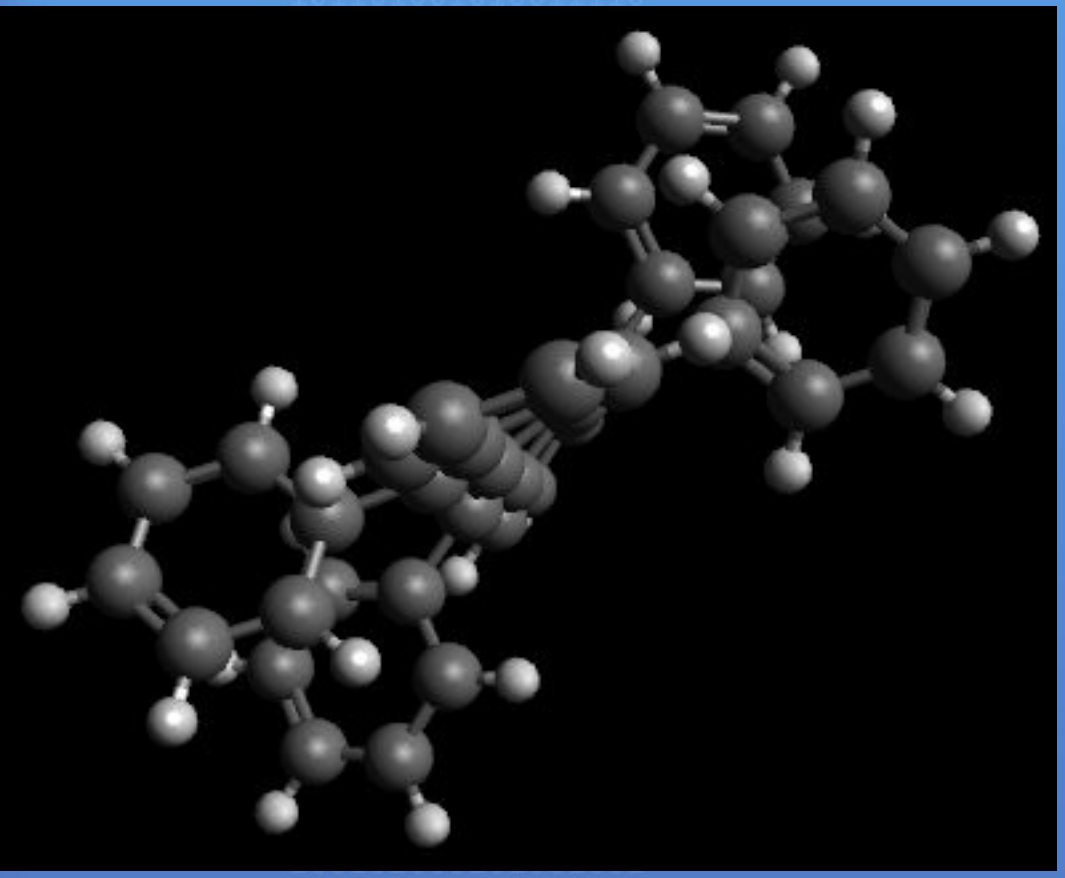
Results and Discussion

Simulation Package GAMESS-US

- GAMESS-US: General Atomic and Molecular Electronic Structure System
- Quantum chemistry (HF and DFT)
- Free and Fortran source available
- Parallelized by DDI or MPI
- Can be queued by PBS Torque (and others)

Conformation Simulation

- Theory level: B3LYP/6-31G

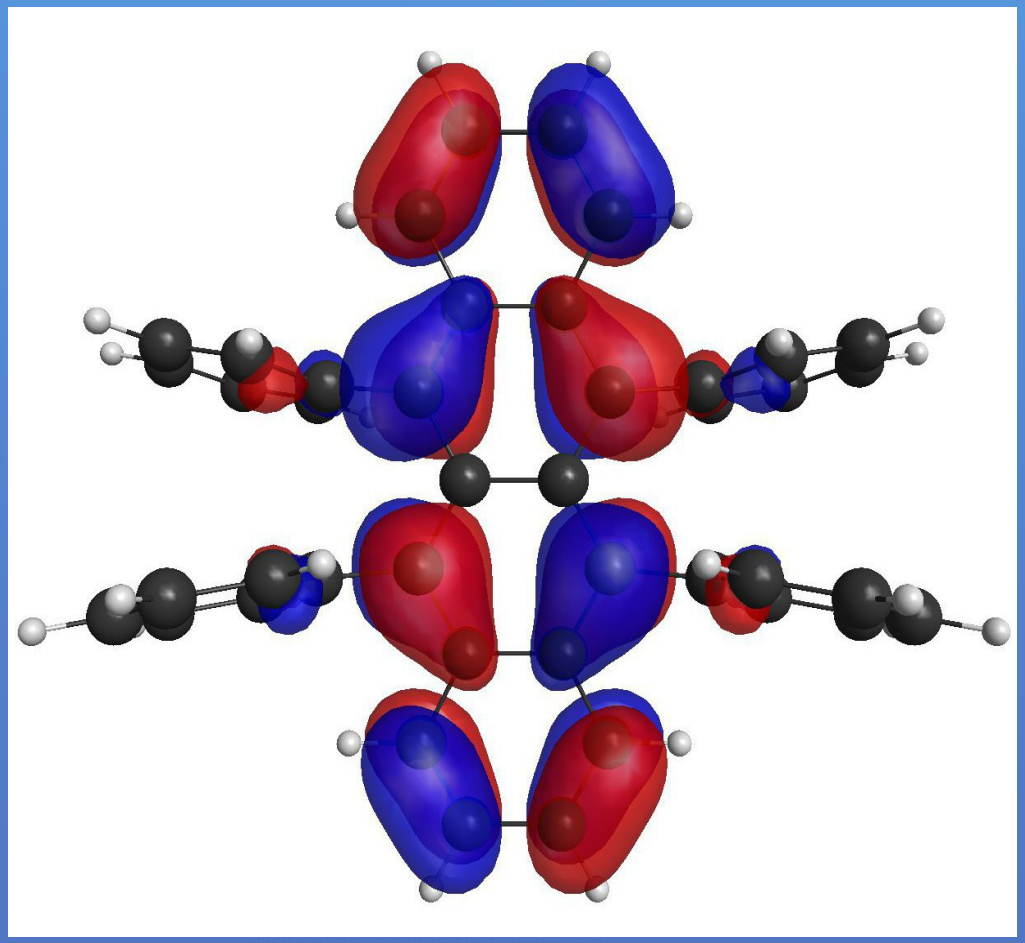


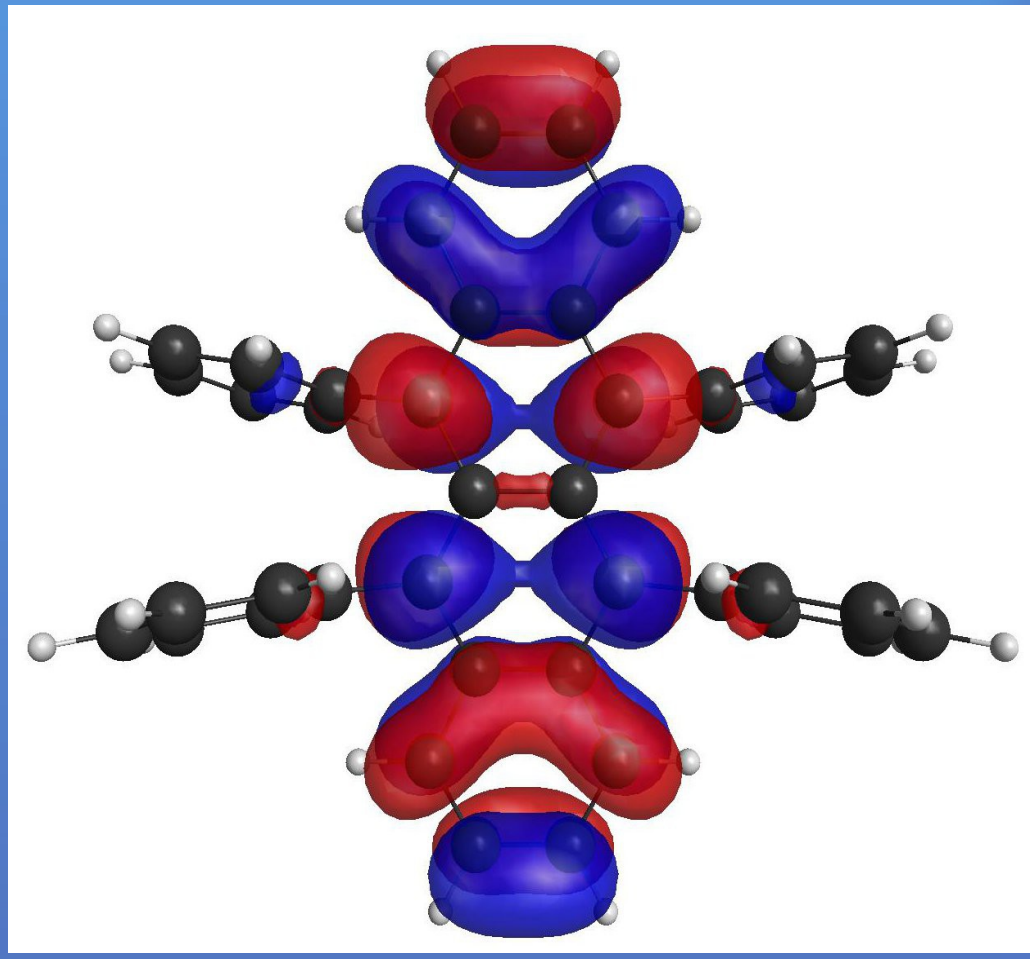
D2 Symmetry
(Twisted backbone;
44.4 degrees)

C2h Symmetry
(Planar backbone)

Molecular Orbitals – C2h

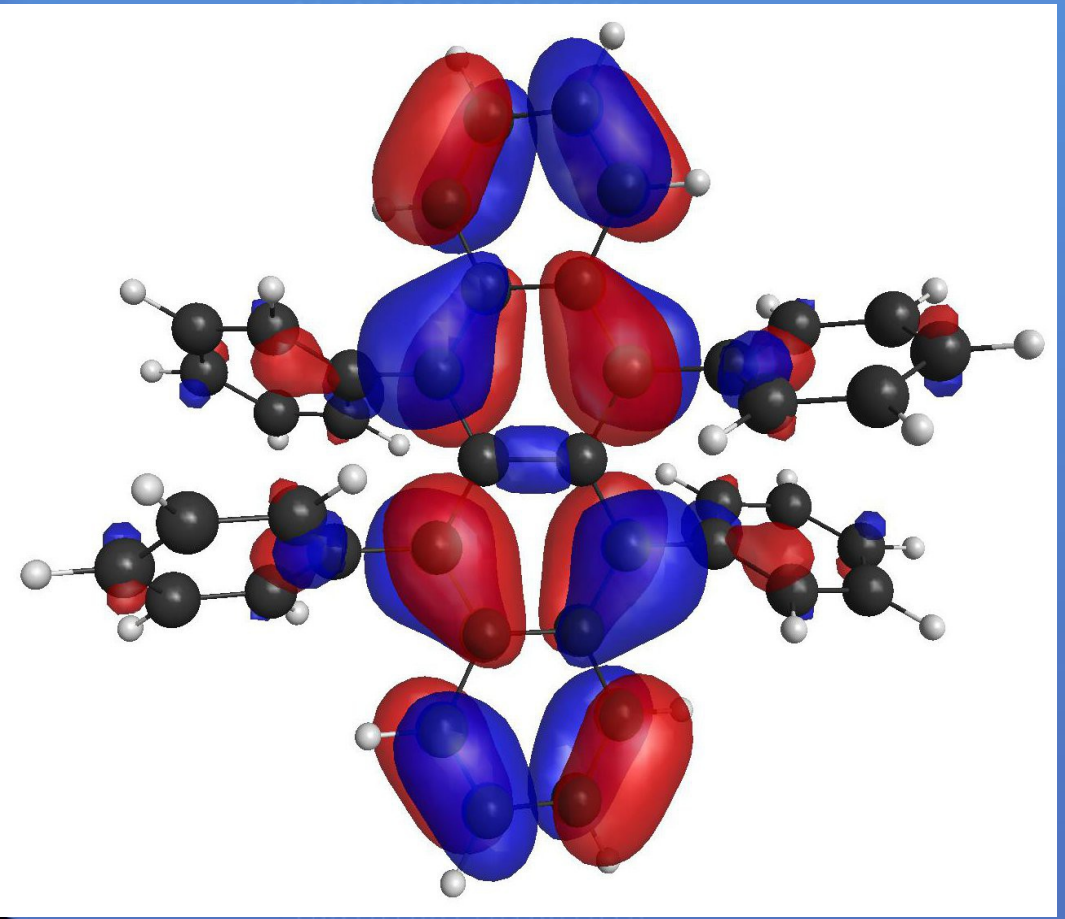
- Theory level: B3LYP/6-31G
- HOMO(Au) LUMO(Ag)

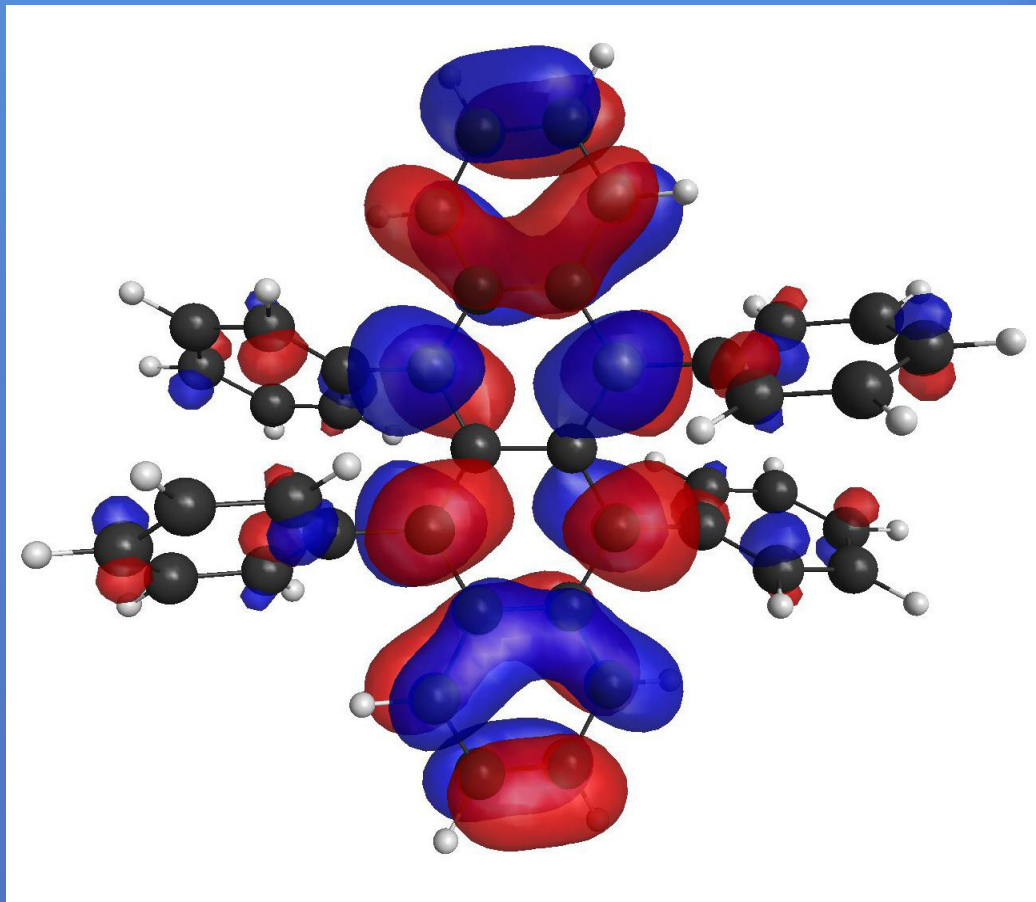




Molecular Orbitals – D2

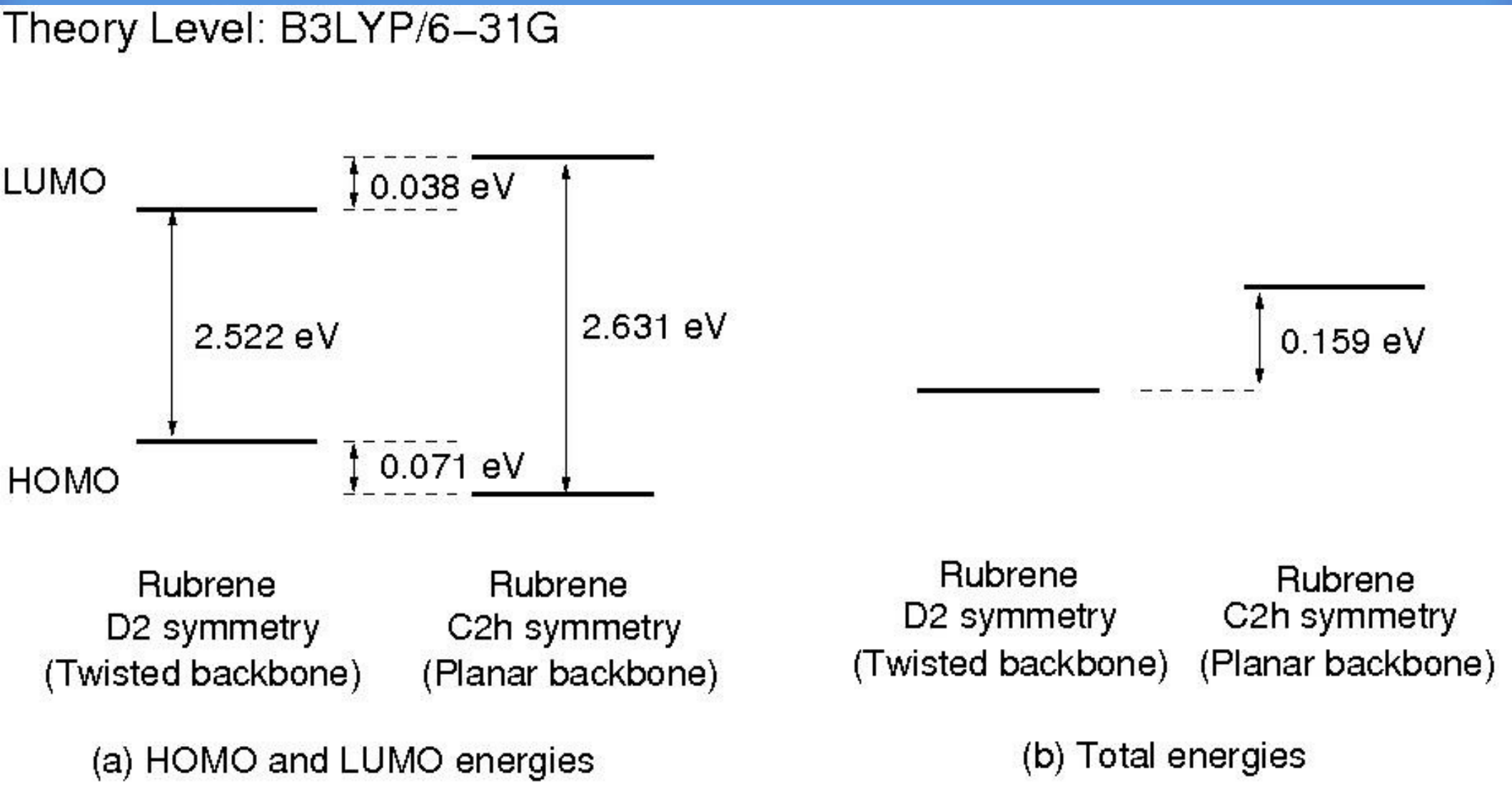
- Theory level: B3LYP/6-31G
- Backbone twisting ~
  w.f. not much change around nuclei
- HOMO(A) LUMO(B1)





Energy and HOMO (DFT)

- Theory level: B3LYP/6-31G

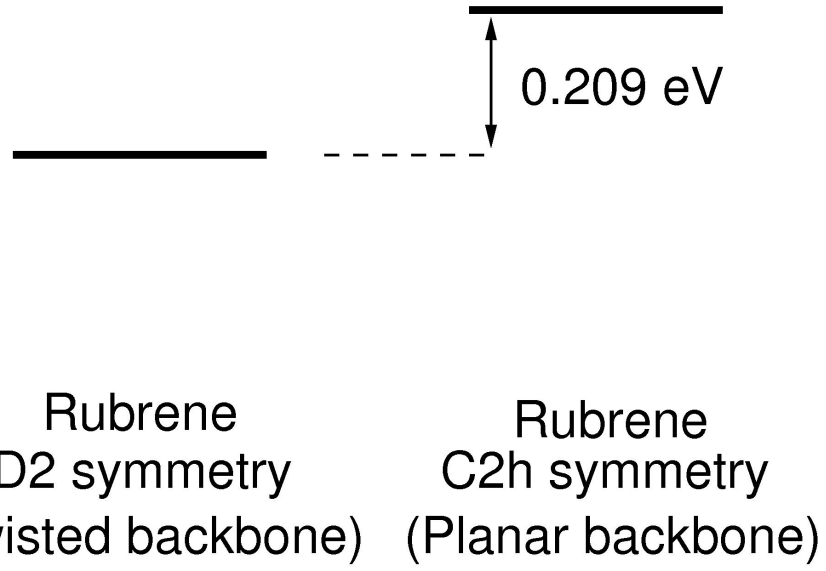


Energy and HOMO (HF/6-31G)

- Qualitatively(or semi-quantitatively) agrees with DFT
- HOMO shift: close to DFT; one order of mag. < exp.

Theory Level: HF/6–31G

(a) HOMO and LUMO energies



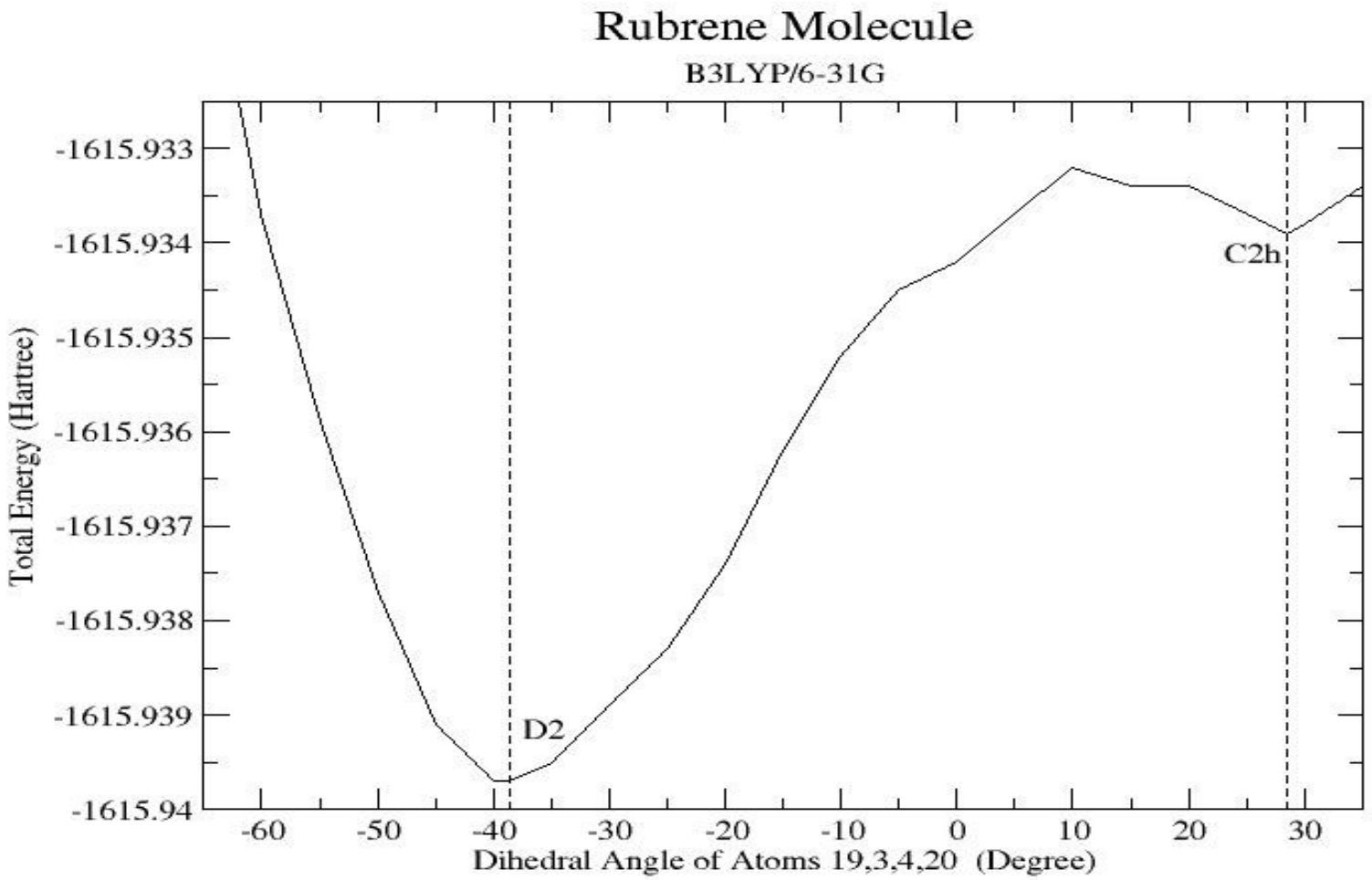
(b) Total energies

Transition – Total Energy

- Energy barriers

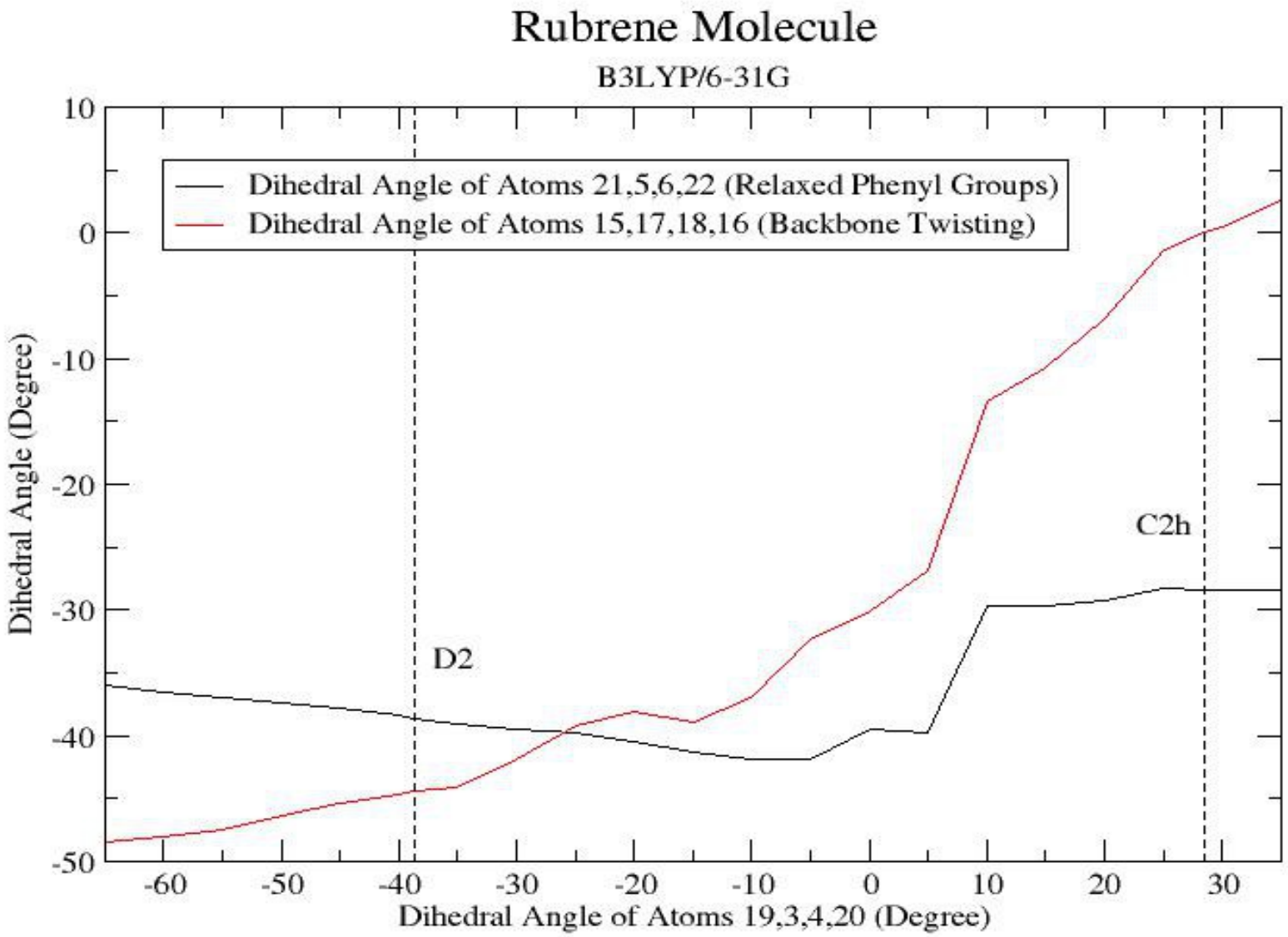
  C2h → D2 0.018 eV (209 K)

  D2 → C2h 0.177 eV (2055 K)



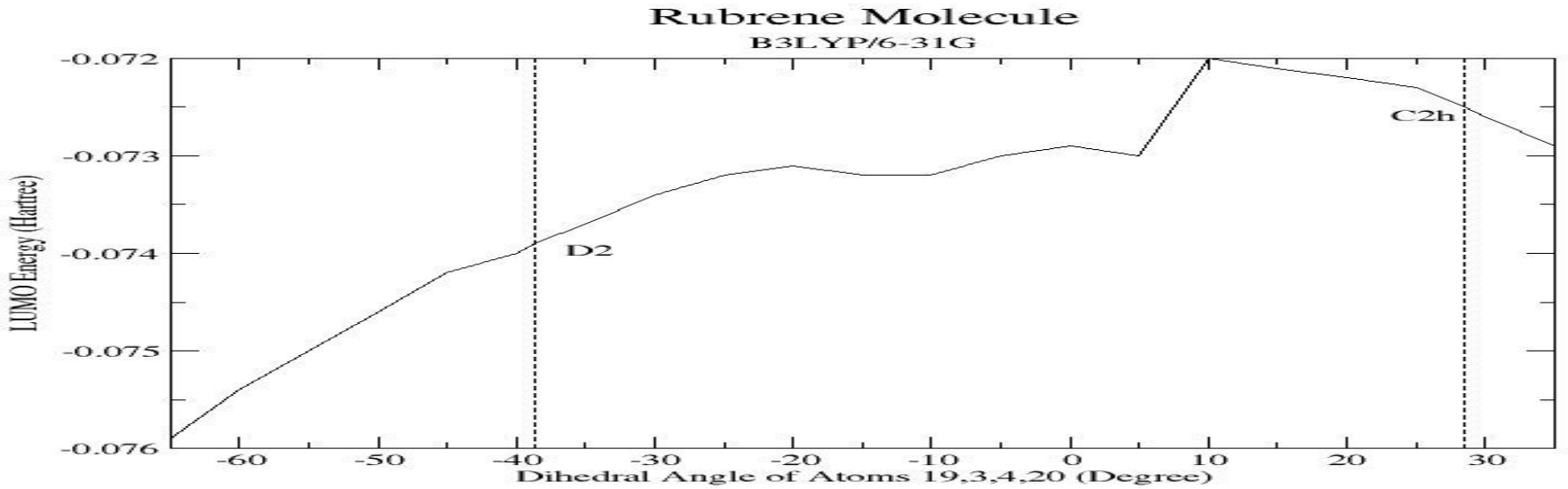
Transition – Geometry

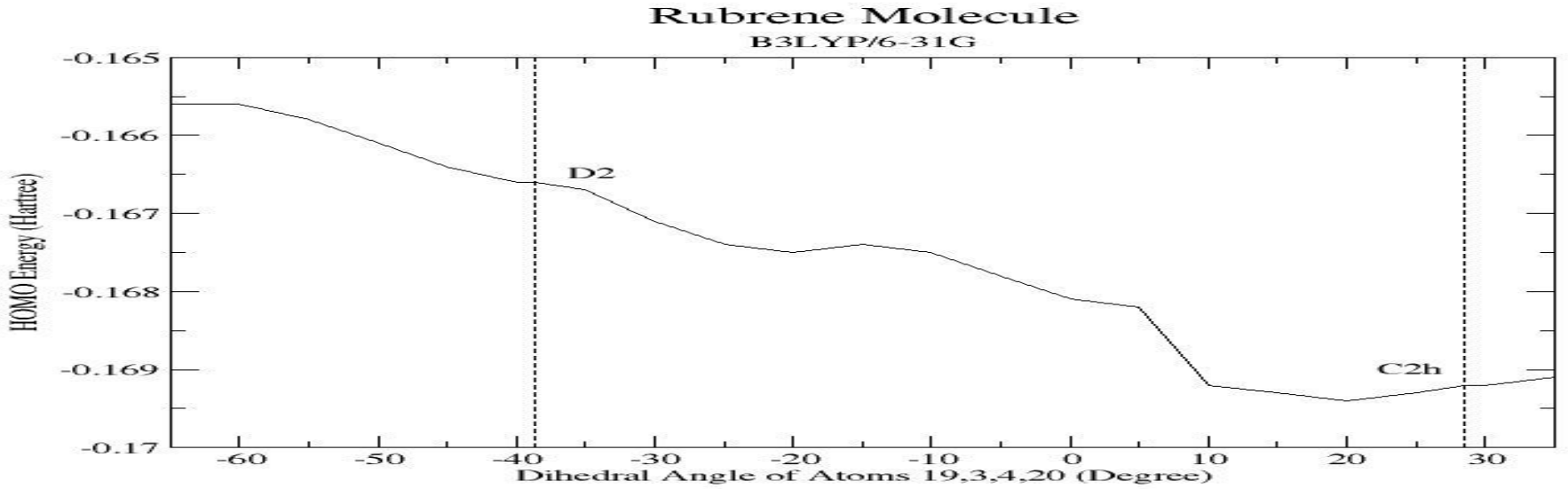
- Largest twist angle adjustment near max. energy



Transition – HOMO & LUMO

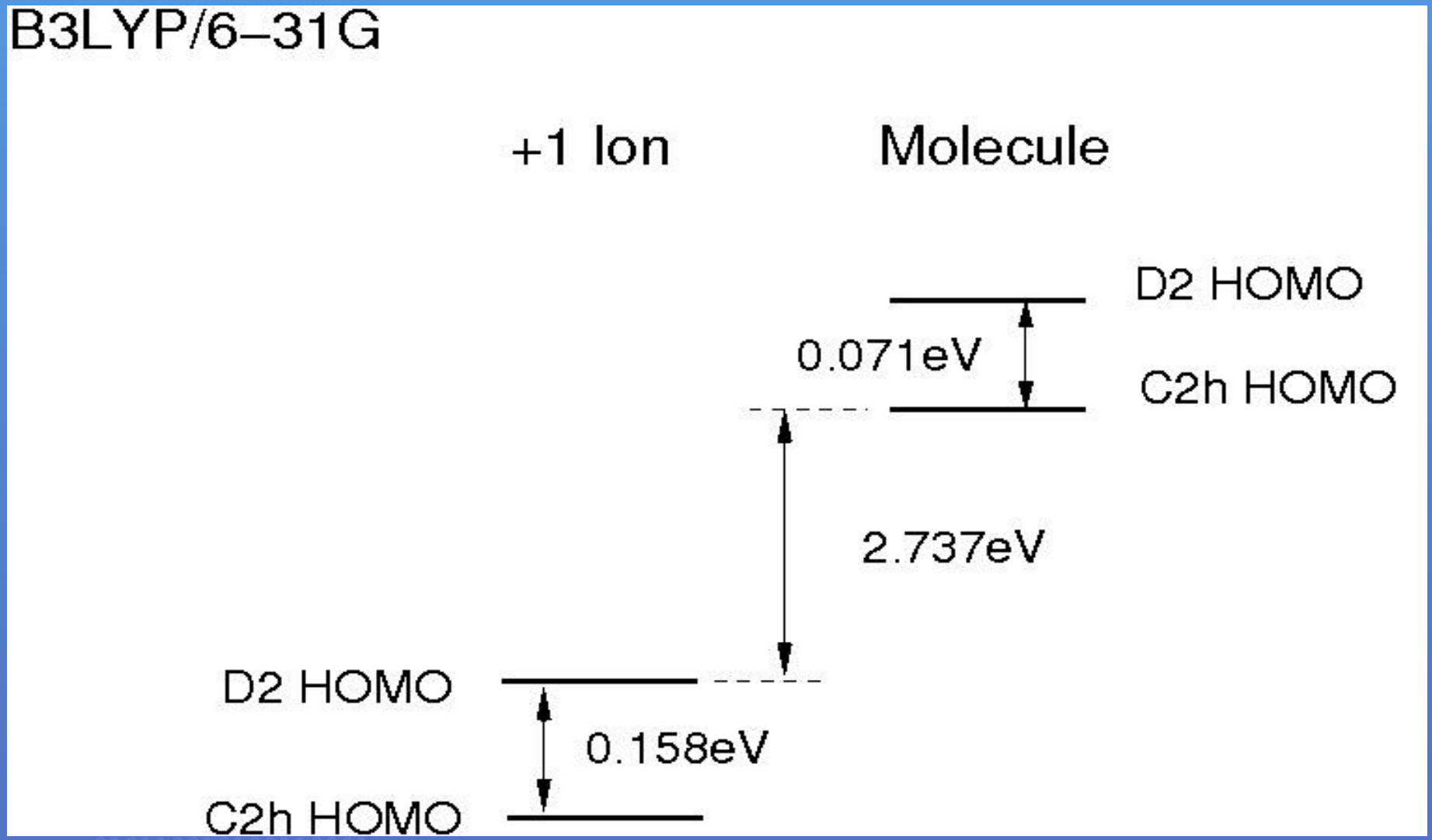
- HOMO change C2h → D2: 0.08 eV << exp. (0.8eV)





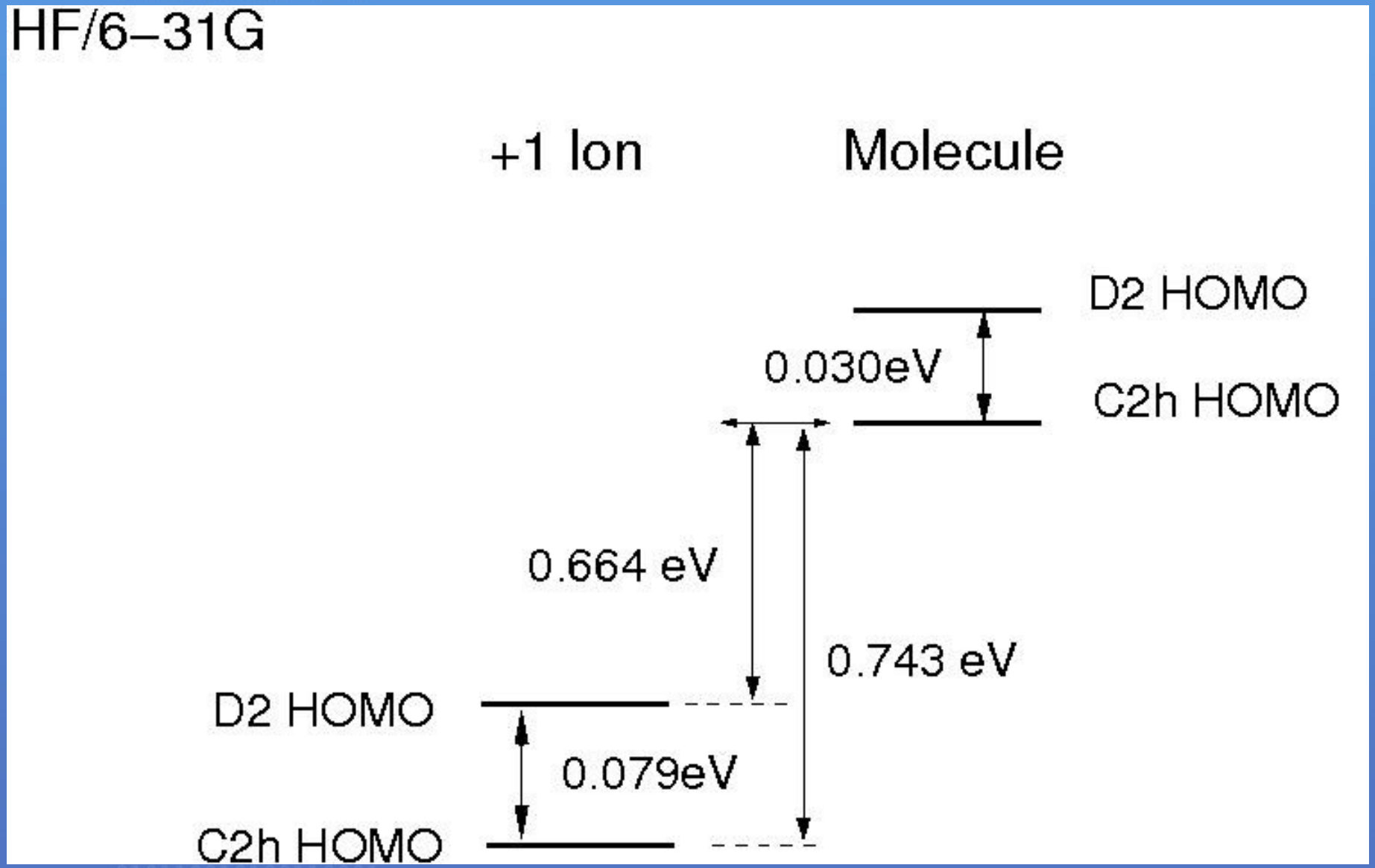
Rubrene Ion (DFT) – HOMO

- E(C2h Rub) – E(D2 Ion) = 2.737 eV = (3~4)*0.8 eV
- eg. Loss of 2 electrons/6-rubrene cluster



Rubrene Ion (HF) – HOMO

- E(C2h Rub) – E(D2 Ion) = 0.664 eV ~ 0.8 eV



Possible Reasons to Observe Ions

- Low temperature deposition
  → Not single crystal
  → Poor conductivity
  → Sample ionization
- Can be verified by conductivity experiment

Concluding Remarks

- Energy barriers between conformations of rubrene are reported
- HOMO shift of ~0.8 eV can not be due to conformation, most likely due to ionized rubrene (to be checked by conductivity experiment)
- HOMO shifts predicted by DFT and HF differ by 3 times. Which to trust in?

Ongoing Work

- Present work based on 6-31G
- Need to use more complete basis sets
  - ➔ Trajectory of conformation change: 6-31+G(2d,p)
  - ➔ Molecule and ion(C2h and D2): 6-31++G(3df,3p) or aug cc-pVnZ family to extrapolate the CBS
- HF → CCSD or CCSD(T) to include correlation
- Double check PES data

Thank you for your attention.