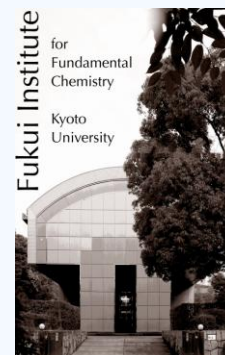


シミュレーションで分子の世界を探る

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NPO 科学カフェ京都
NPO 「あいんしゅたいん」 共催
京大湯川記念館 Panasonic 国際交流ホール
2010年7月10日



EMORY
UNIVERSITY

シミュレーション

- 実験・訓練を目的とし、複雑な事象・システムを定式化して行う模擬実験をいう。
- 「物理的シミュレーション」とは、何らかの物理的な物体（**モデル**）で実物を置き換えることを指す。置換する物体としては、実物よりも小さいものや安価なものが選ばれる。

原子・分子の世界



• 基本方程式＝量子力学

ポール・ディラックの言葉

「**物理の大部分と化学の全体**を数学的に取り扱うために必要な基本的法則は完全にわかっている。これらの法則を適用すると**複雑すぎて解くことのできない**方程式に行き着いてしまうことだけが困難なのである。」— Proc. Roy. Soc. (London) , A123, 714 (1929)

"The fundamental laws necessary for the mathematical treatment of large parts of physics and the whole chemistry are thus fully known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved."

原子核と電子の運動の分離

- ボルン-オッペンハイマー近似

原子核は電子に比べて重いので、電子の運動を記述する時は、近似的に原子核は静止していると考えることができる。

- 原子核の運動は主に古典力学（ニュートン力学）で解く。

”古典分子動力学” (Classical Molecular Dynamics, MD)

- 原子核の運動を量子力学で解くこともできる。

今の所、数値的に解けるのは、数原子まで。

”量子分子動力学”

電子の挙動には量子力学が必要

- シュレディンガー方程式を解く（非相対論）
（ディラック方程式（相対論））

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle$$

- 分子軌道法

要求される精度

物理的問題 $\sim eV \sim 96KJ/mol \sim 23kcal/mol$

化学的問題 $\sim 0.1eV \sim 10KJ/mol \sim 2.3kcal/mol$

”Dr. Gerhard Herzberg (Nobel Prize in chemistry, 1983) の挑戦
(1970後半)”

小さな分子の励起エネルギーを0.1eVの精度で計算できれば、理論を信用する

量子化学

ハートリーフォック法
数) 計算時間 $\sim N^3$ (N: 分子中の原子の

多体摂動(MP, MBPT)論 $\sim N^5$

配置間相互作用(CI)法 $\sim N^{6-7}$

クラスター結合(CC)法 $\sim N^{6-7}$ 20原子程度

小さい分子では、Herzbergの挑戦を達成(1980代後半)

計算精度は確保できる

N依存性が大きい Nが3倍、 N^6 は700倍

大きな分子に適用できない

(ムーアの法則：トランジスタの集積密度は2年に2倍; 1000倍になるのに10年かかる)

近似的方法

密度関数法(DFT) $\sim N^3$ 精度は落ちる、100原子程度⁶

50年前

福井謙一研究室でフロンティア理論の発展と応用
計算機の速度 $\sim 10^{15}$ 倍

Bull. Chem. Soc. Jpn. 32, 853 (1959)

*LCAO SCF Calculation on Anthracene and Reactivity
Indexes in SCF Method*

By Kenichi FUKUI, Keiji MOROKUMA and Tejiro YONEZAWA

PPP SCF calculation

Bull. Chem. Soc. Jpn. 34, 1178 (1961)

*An Attempt to Discuss Reactivities of Excited Molecules
by the Molecular Orbital Method*

By Kenichi FUKUI, Keiji MOROKUMA and Tejiro YONEZAWA

Hückel calculation

Bull. Chem. Soc. Jpn. 38, 1263 (1965).

A Molecular Orbital Treatment of Hydrogen Bonds.
I. Preliminary Results

By Keiji MOROKUMA, Hiroshi KATO, Tejiro YONEZAWA
and Kenichi FUKUI

1st extended Hückel calculation



Tiger (58-62)



Monroe (59-63)



KDC1(1st computer) (60-64)



IBM709@Japan IBM (61-64)

量子化学ポテンシャル

- 原子核の位置を固定して電子のエネルギーをシュレーディンガー方程式から計算
- エネルギーは原子核の座標の関数

$$V(x_1, y_1, z_1, x_2, y_2, z_2, \dots) = V(\mathbf{R})$$

ポテンシャルエネルギー面

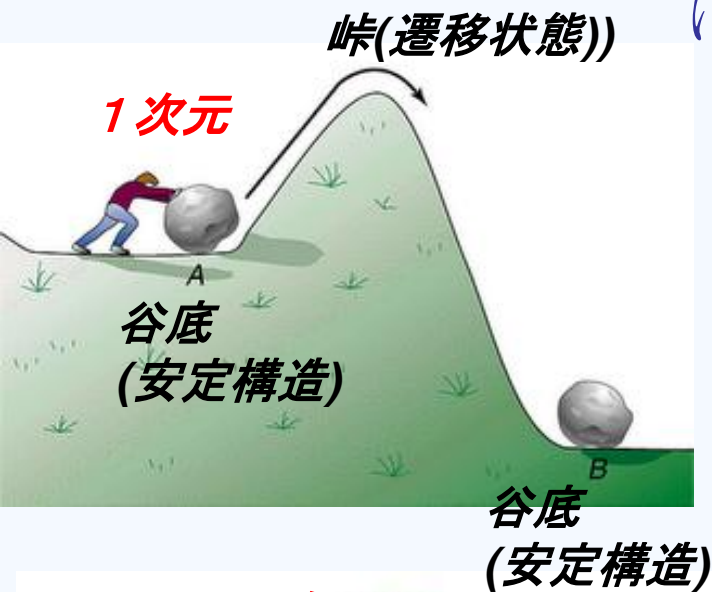
自由度=3N-6 N: 原子数

(2自由度だと、地図と同じ)

ポテンシャル面の谷底＝村落＝安定構造

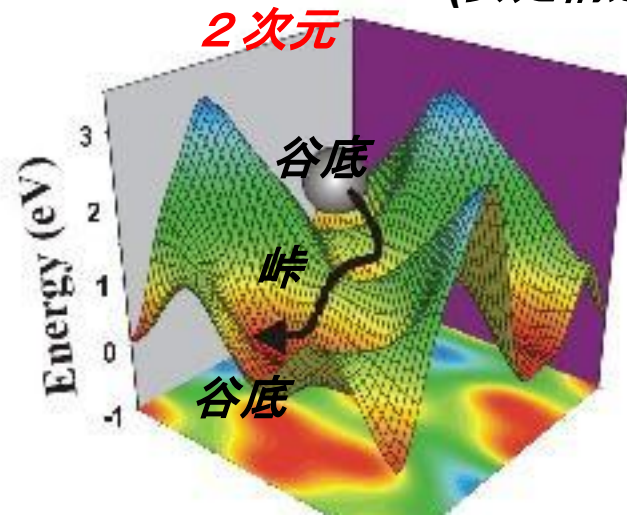
鞍点＝峠＝遷移状態

化学反応は安定分子が遷移状態をこえて別の安定分子
に変化する過程



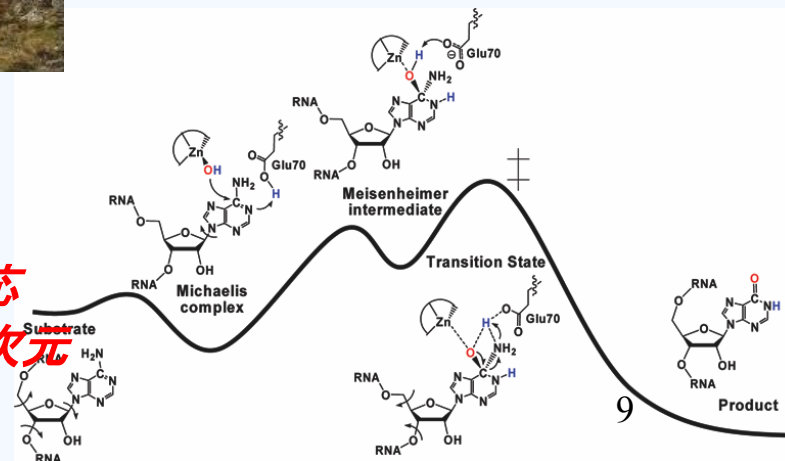
計算で安定構造や遷移状態を決めることが出来る。

実験で遷移状態を決めることは容易でない。



2次元

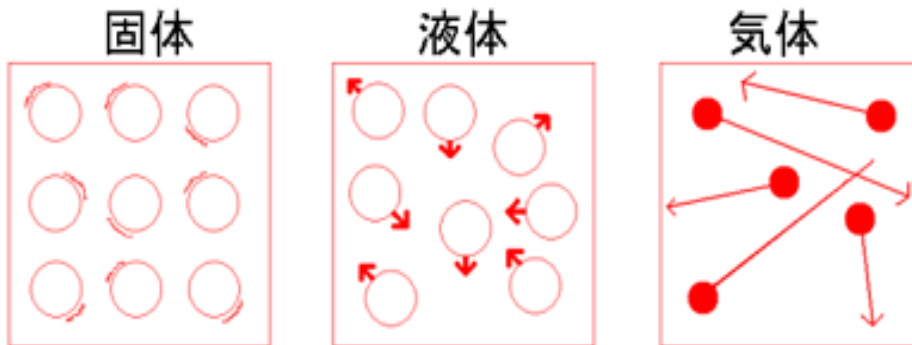
実際の化学反応
多次元だが1次元
に投影する



古典力学で原子核の運動を記述する (古典分子動力学、MD)

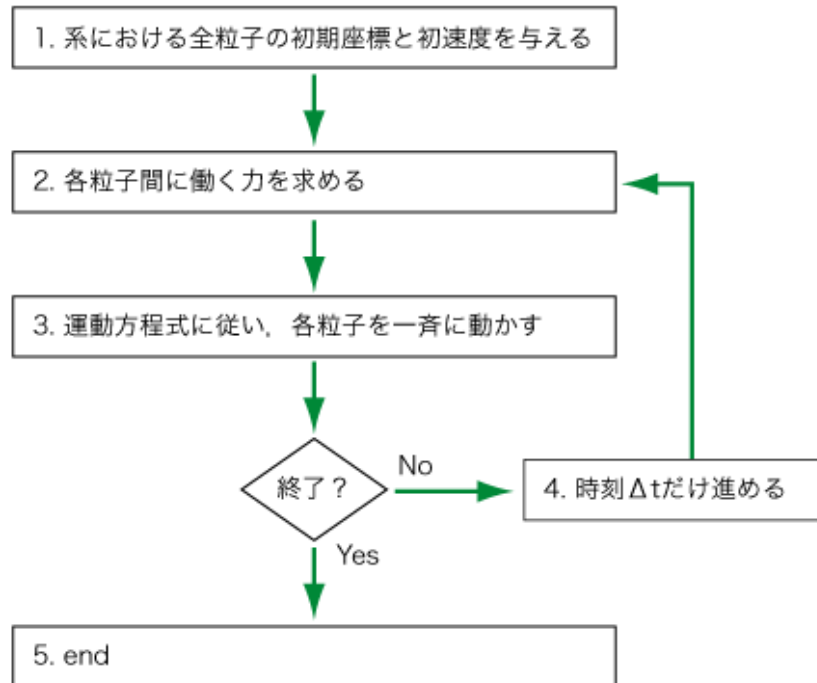
分子動力学法(Molecular Dynamics)

物質(固体・液体・気体) = 粒子の集合体



全粒子の動きを同時に追跡: **ミクロな現象**
(各粒子間に働く力 → 運動方程式)

↓
その物質特有の種々の**マクロな性質**が求まる。
(密度, 硬さ, 内部エネルギー, ...)



分子内、分子間に働くエネルギー (ポテンシャルエネルギー) を決める必要

分子力場 (Molecular Mechanics, MM)

いくつかの相互作用の和で表す簡単なポテンシャルが使われる
速い (量子力学の 10^6 - 10^9 倍の計算速度) 1秒の 10^6 - 10^9 倍=12日-32年

量子力学的効果含まれない (パイ電子の効果)
結合の切断不可能 (一応出来るように改良できる)

$$V = V_H + V_b + V_{tor-i} + V_{tor-p} + V_C + V_{vdW} \quad (1)$$

$$V_H = \frac{1}{2} \sum_n^{N_H} K_{Hn} (r_n - r_o)^2$$

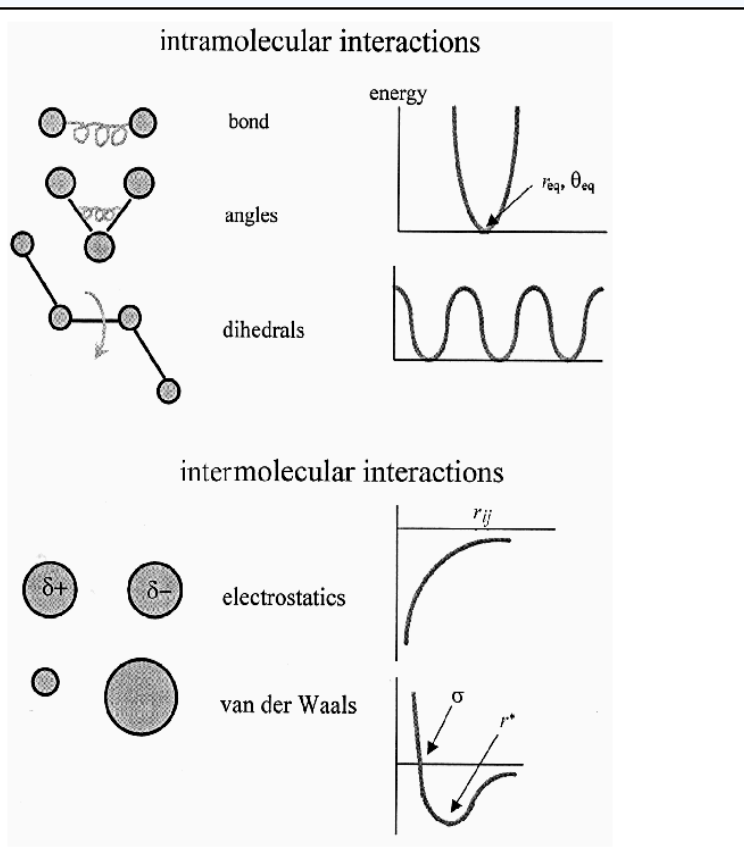
$$V_b = \frac{1}{2} \sum_n^{N_\theta} K_{\theta n} (\theta_n - \theta_o)^2$$

$$V_{tor-i} = \frac{1}{2} \sum_n^{N_\xi} K_{\xi n} (\xi_n - \xi_o)^2$$

$$V_{tor-p} = \frac{1}{2} \sum_n^{N_\phi} K_{\phi n} [1 + \cos(m\phi_n - \delta_n)]^2$$

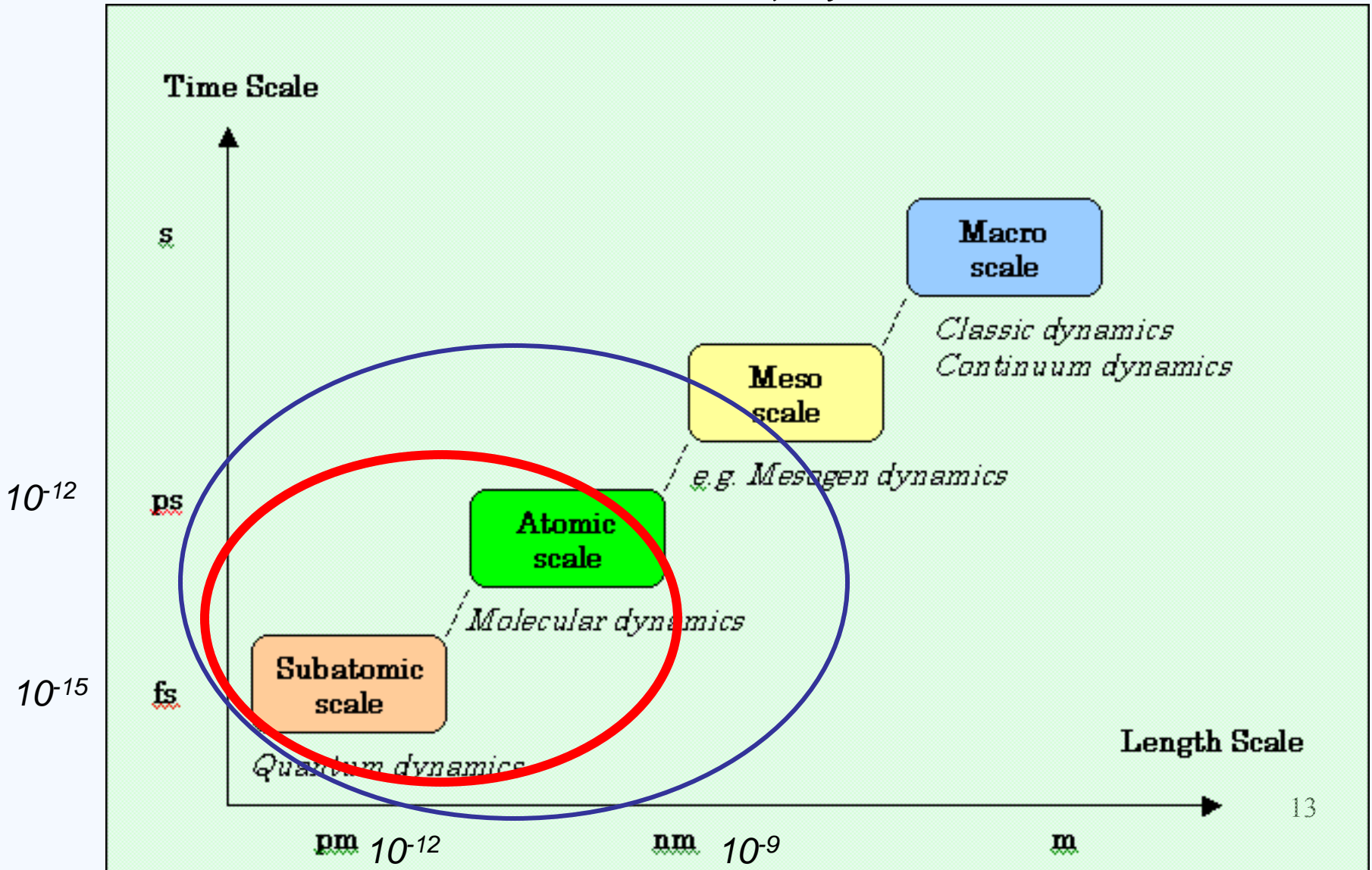
$$V_C = \frac{1}{4\pi\epsilon} \sum_{i < j}^{N_c} \frac{q_i q_j}{r_{ij}}$$

$$V_{vdW} = \sum_{i < j}^{N_v} \left[\frac{C_{12}(ij)}{r_{ij}^{12}} - \frac{C_6(ij)}{r_{ij}^6} \right]$$



分子力場を使った分子動力学の世界

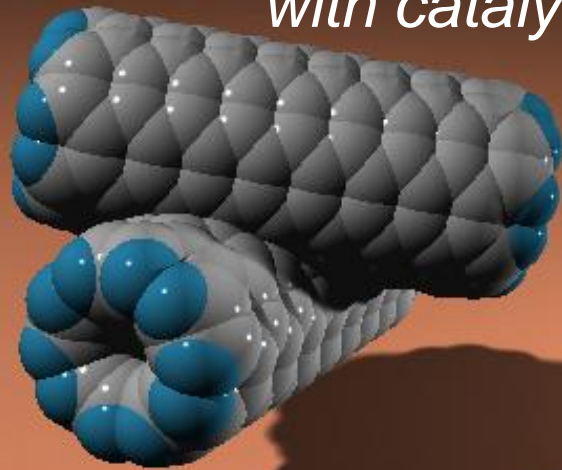
物質系のシミュレーションの長さスケールと時間スケール



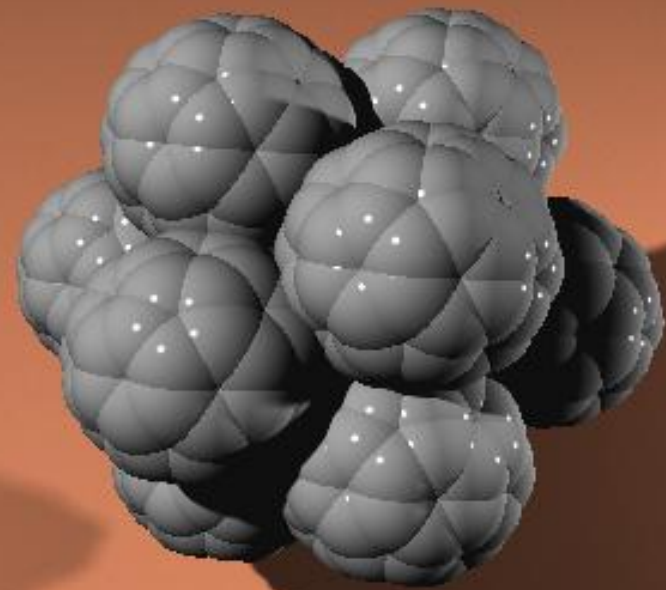
フラーレンと炭素ナノ構造の生成反応の機構

Ignis mutat res – 炎がすべてを変化させる

*800°C or higher
with catalysts*



1500°C or higher



炭素の同素体

ダイヤモンド

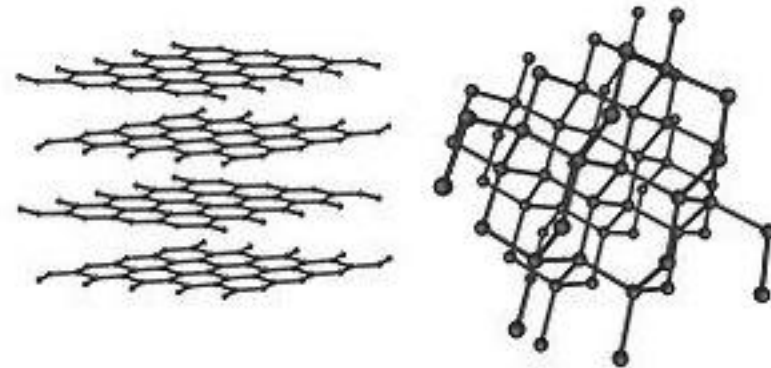
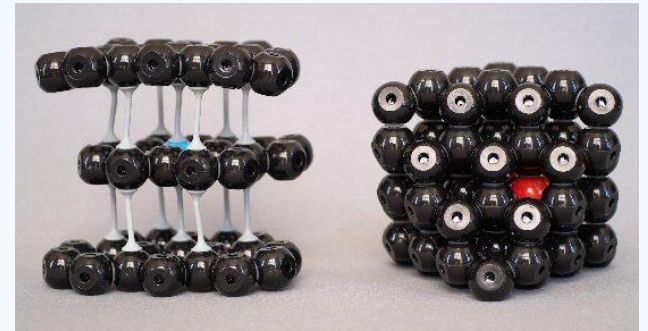
正四面体構造、炭素原子は4本の結合、 sp^3 炭素

グラファイト（黒鉛）

平面構造、炭素原子は3本のシグマ結合と1個の
パイ電子、 sp^2 炭素

パイ電子はエネルギーが
高く、反応に重要な寄与

グラファイト ダイヤモン



PO
E



フラーレン

sp²炭素のみから出来ているかご状化合物の総称

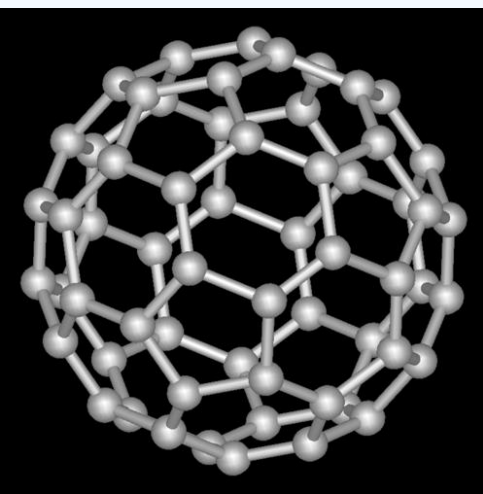
C_{60} 1985 Kroto, Smalley, Curlにより発見

1996 ノーベル化学賞

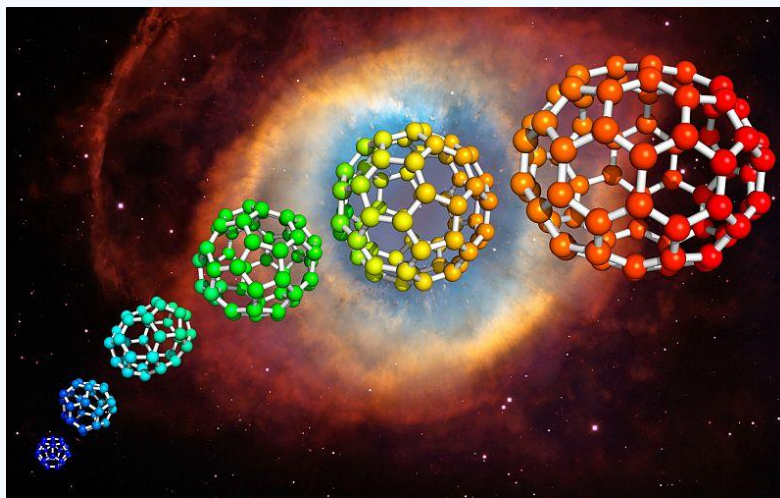
高次フラーレン $C_{70}, C_{76}, C_{78}, \dots$

- 安定なフラーレンでは、5員環の数は必ず12, 6員環の数は大きさにより変化 (オイラーの多面体定理)
- 安定なフラーレンでは、5員環は隣り合わない (独立5員環則)

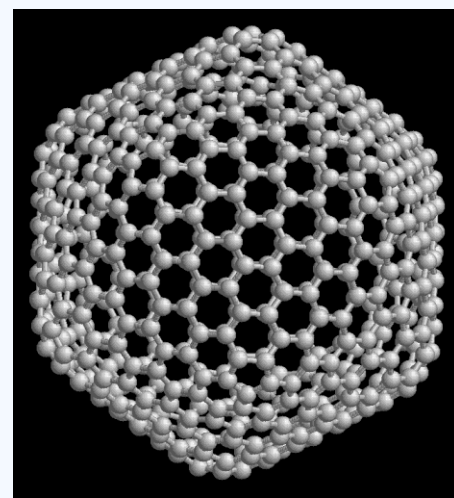
C_{60}



C_{60} - C_{86}



C_{540}

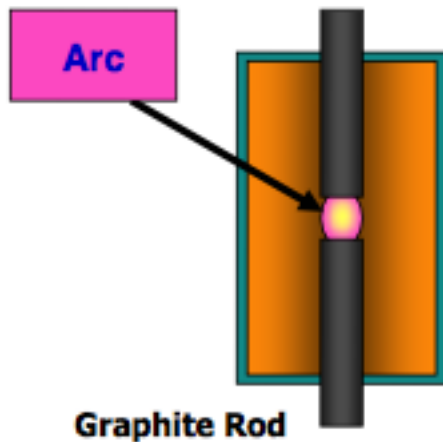


New Method for Fullerene Production

Mitsubishi: 40t/y now, 1500t/y 2007

Conventional Method (Arc Method)

Fullerenes produced in a batch system from graphite rods

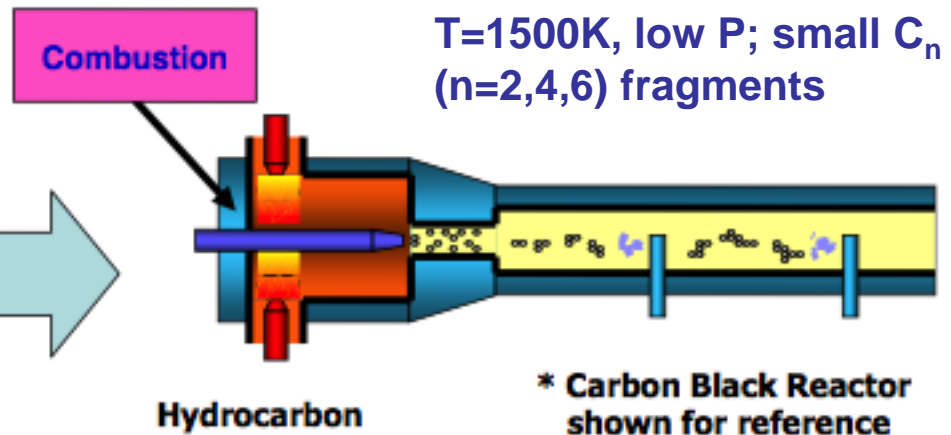


\$20,000/kg

- Expensive Process
- Batch Process Not Suitable for Mass Production

New Method (Combustion Method)

Fullerenes produced in a continuous system from hydrocarbon



\$200/kg

- Cost Efficient Process
- Continuous Process Suitable for Mass Production

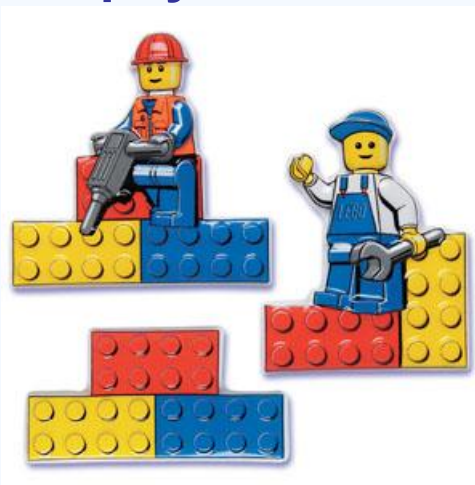
“Centrally managed” C_{60} formation models

Hypothetical mechanisms relying on more or less sound assumptions; **no intermediate species experimentally confirmed so far.**

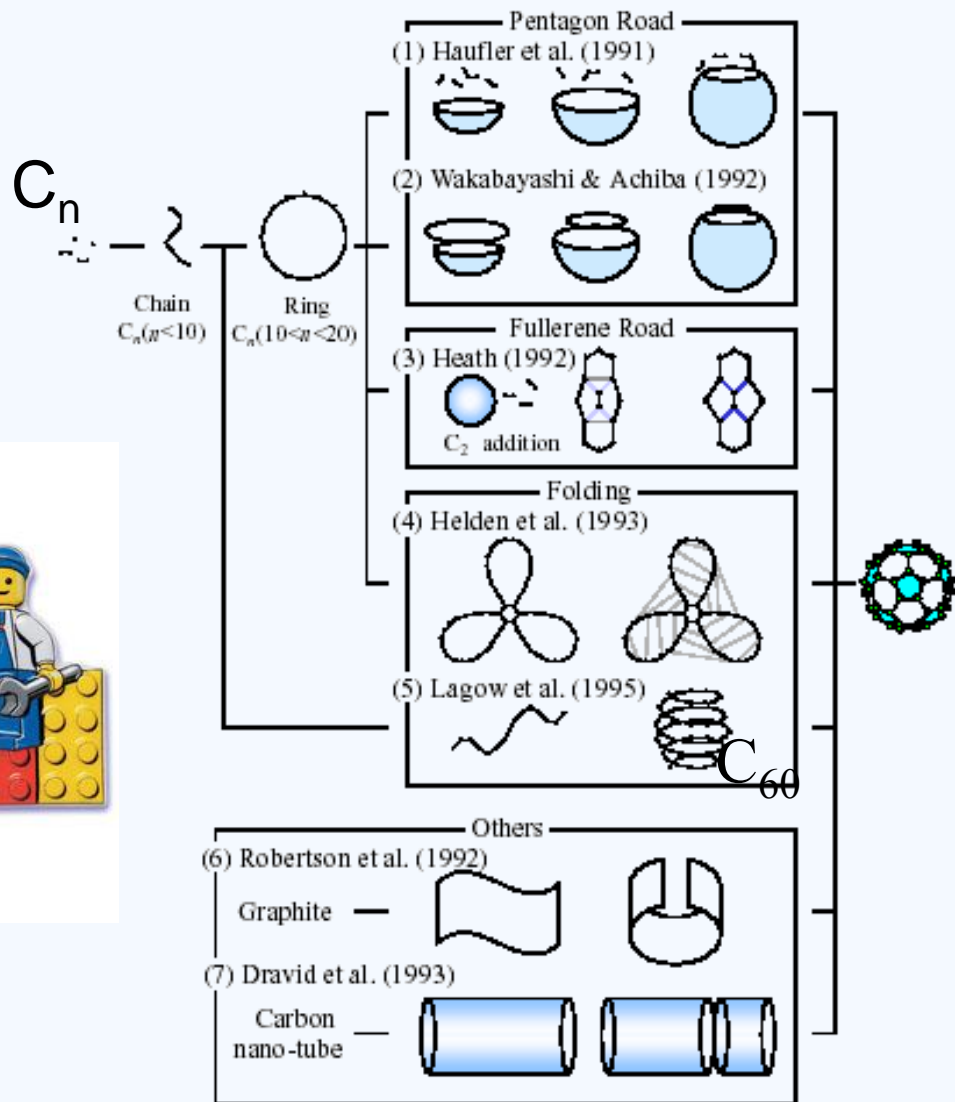
“Lego philosophy”



Buckminster Fuller 1895-1983

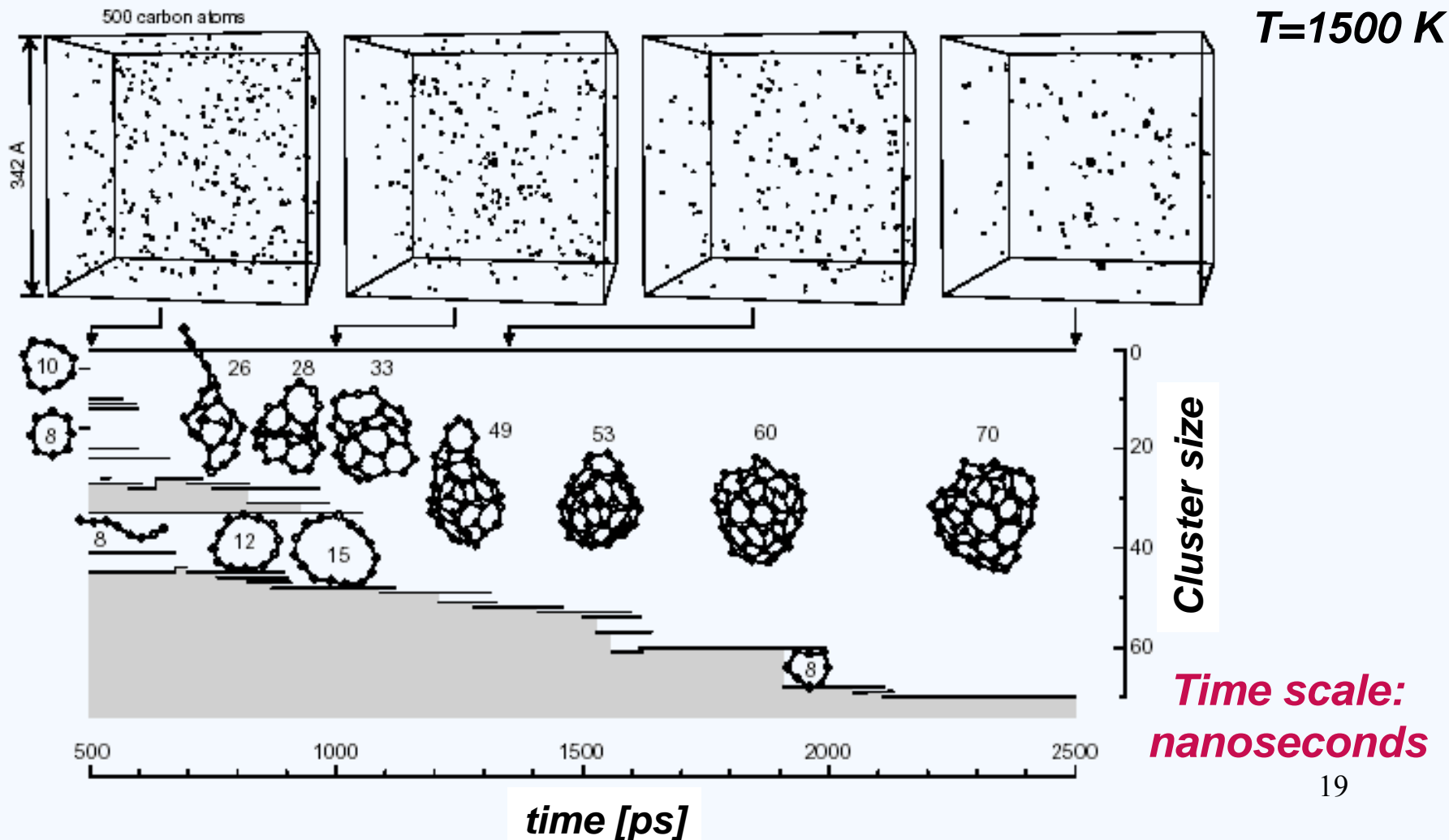


No experimental or theoretical verification !



Brenner-Potential MD Simulation of the Fullerene Formation Process - Time Scale

Yamaguchi, Y.; Maruyama, S. *Chem.Phys.Lett.*, **1998**, 286, 336-342



Formation of Fullerenes and Carbon Nanotubes

Quantum chemical molecular dynamics (QM/MD) studies

Chemistry of sp^2 carbons

π conjugation determines the reactivity

Need of quantum mechanics

(classical mechanics, i.e. force field is no good)

Need simulation of minimum of 100 ps–1 ns (10^4 - 10^5 calculations)

Force Field (MM)

relative speed ~ 1

Density functional tight-binding method (DFTB) $\sim 10^{2-3}$

Density functional method (DFT) $\sim 10^6$

We use DFTB.

Self-consistent-charge density-functional tight-binding (SCC-DFTB)

D. Porezag, Th. Frauenheim, T. Köhler, G. Seifert, R. Kaschner, *Phys. Rev. B* **51**, 12947 (1995)
 M. Elstner et al., *Phys. Rev. B* **58**, 7260 (1998)

Second order-expansion of DFT total energy with respect to **charge fluctuation**

TB-eigenvalue equation $\sum_v c_{vi} (H_{\mu\nu} - \varepsilon_i S_{\mu\nu}) = 0$ Single-zeta
STO basis set

$$E_{tot} = 2 \sum_i f_i \varepsilon_i + E_{rep} + \frac{1}{2} \sum_{\alpha\beta} \gamma_{\alpha\beta} \Delta q_\alpha \Delta q_\beta$$

~100 atoms
 ~100 ps

Finite temperature approach (Mermin free energy E_{Mermin})

M. Weinert, J. W. Davenport, *Phys. Rev. B* **45**, 13709 (1992)

$$f_i = \frac{1}{\exp[(\varepsilon_i - \mu)/k_B T_e] + 1}$$

T_e : electronic temperature

S_e : electronic entropy

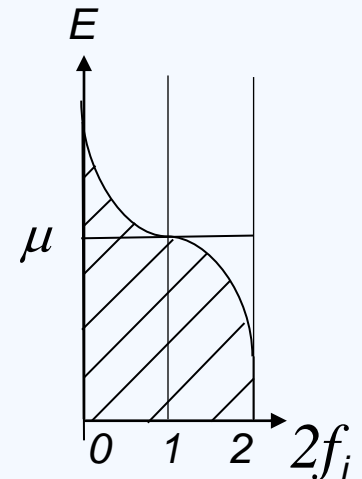
$$0 \leq f_i \leq 1$$

$$S_e = -2k_B \sum_i \left[f_i \ln f_i + (1 - f_i) \ln(1 - f_i) \right]$$

$$E_{Mermin} = E_{tot} - T_e S_e$$

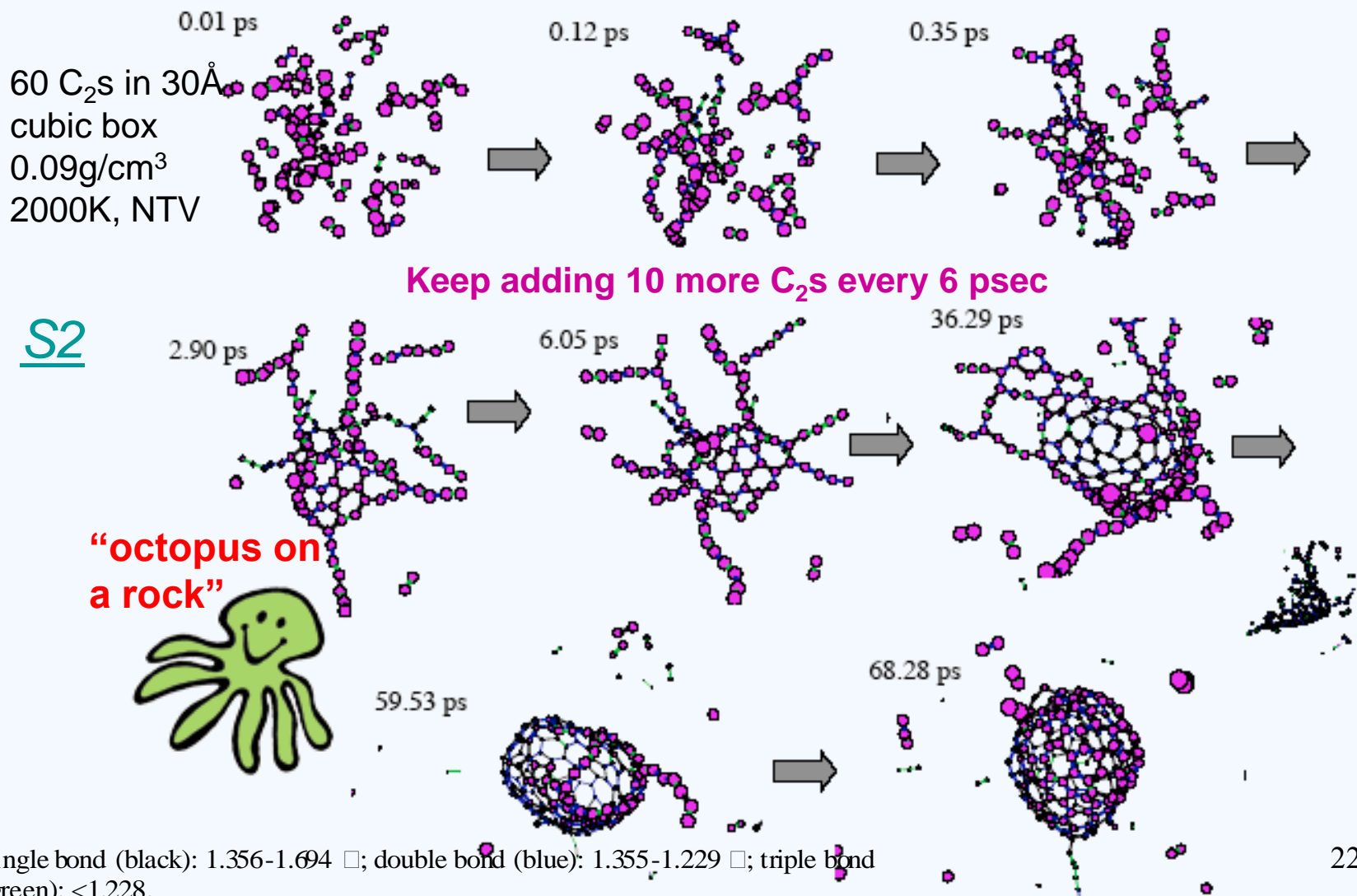
Atomic force

$$\vec{F}_\alpha = -2 \sum_i f_i \sum_{\mu\nu} c_{\mu i} c_{\nu i} \left[\frac{\partial H_{\mu\nu}^0}{\partial \vec{R}_\alpha} - \left(\varepsilon_i - \frac{H_{\mu\nu}^1}{S_{\mu\nu}} \right) \frac{\partial S_{\mu\nu}}{\partial \vec{R}_\alpha} \right] - \Delta q_\alpha \sum_\xi \frac{\partial \gamma_{\alpha\xi}}{\partial \vec{R}_\alpha} \Delta q_\xi - \frac{\partial E_{rep}}{\partial \vec{R}_\alpha}$$

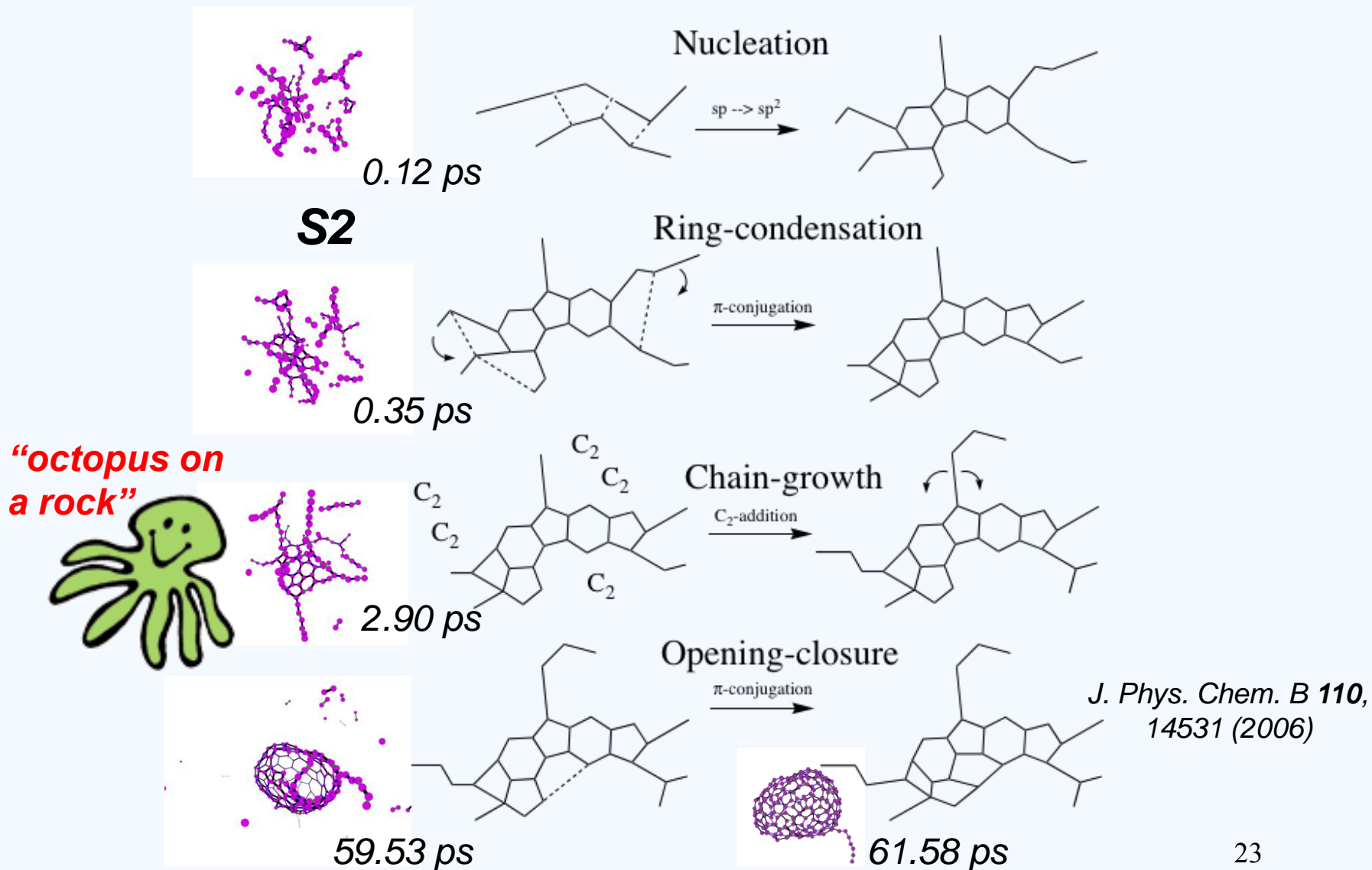


Tackling the *Fullerene* Formation Mechanism: DFTB/MD Study

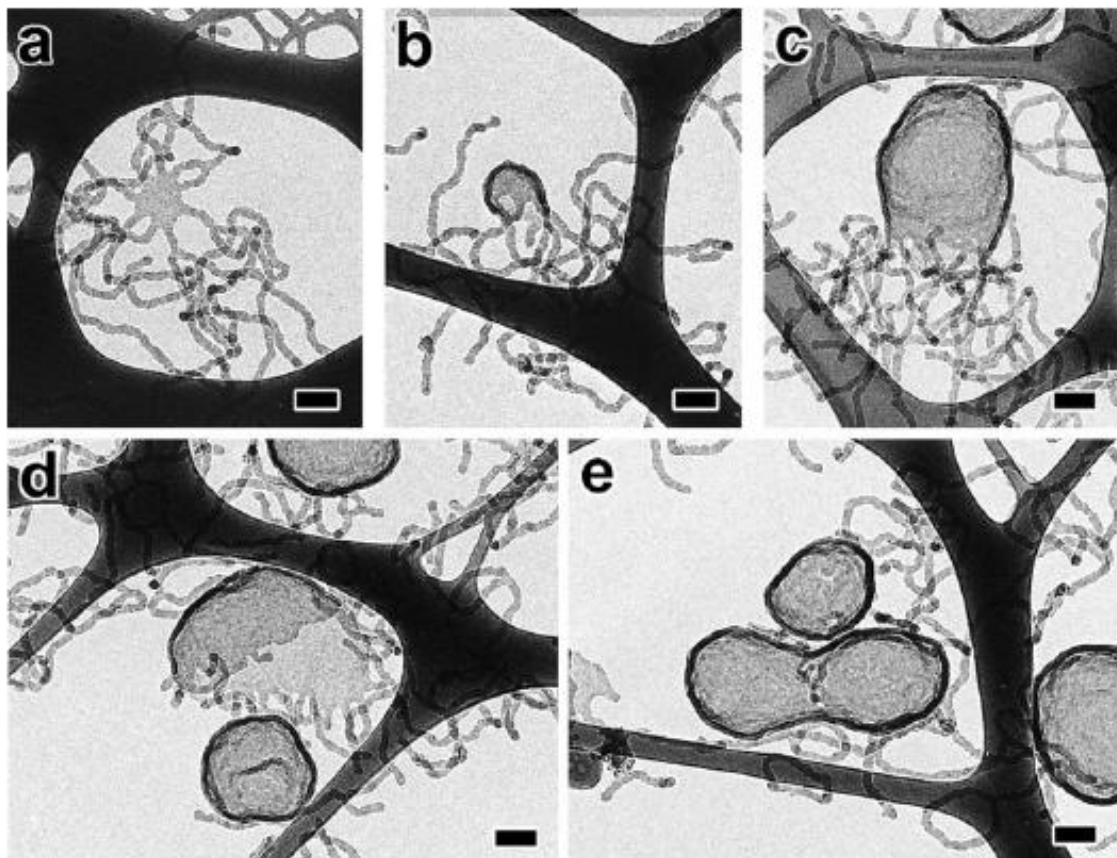
S. Irle, G. Zheng, M. Elstner, K. Morokuma, Nano Lett. **3**(12), 1657 (2003)



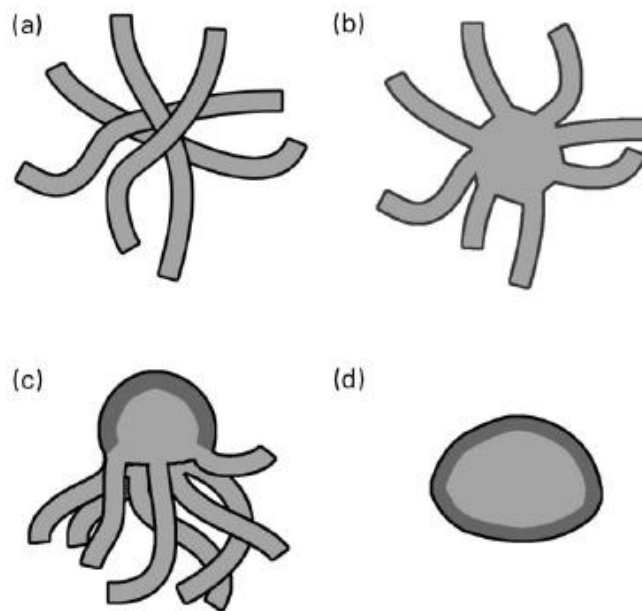
Schematics of “Size Up” approach - self-assembly through a sequence of irreversible processes



Comparison: Self-assembly of vesicles in diblock polymers



“octopus on a rock”



Putaux et al., *Farad. Discuss.* **128**, 163 (2004)

Dissipative structures vs the arrow of time

Ilya Prigogine et al., George M. Whitesides et al.

- Non-equilibrium and nonlinearity favor the spontaneous development of **self-organizing systems**, which maintain their **自己組織化** internal organization, regardless of the general increase in entropy, by expelling matter and energy into the environment

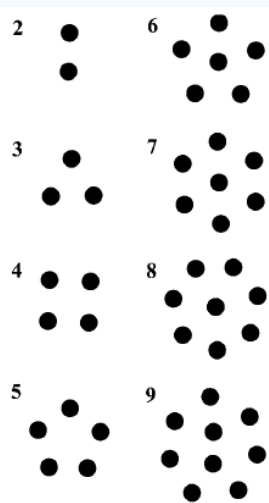
Examples for order created dynamically out of chaos: Dissipative structures without associated single potential energy function

Belousov-Zhabotinsky
chemical reaction cell

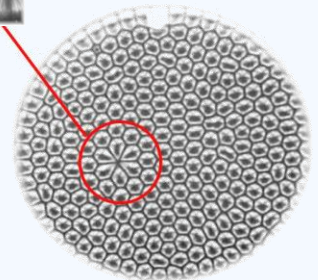
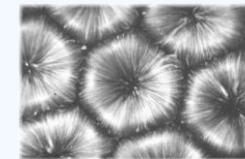
Driving force: $d[\text{Ce}^{\text{III/IV}}\text{ions}]/dx$



Biochemical systems: proteins and
nucleic acids



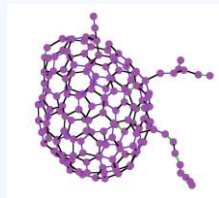
Whitesides
magnetic spinners
Driving force:
magnetic gradient/
hydrodyn. repulsion



Rayleigh-Benard
convection cells
Driving force: dT/dx

More original Size-Up Giant fullerene trajectories

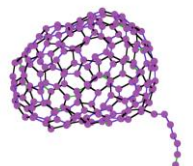
Original runs: fullerenes: 5 out of 25



S1

C146

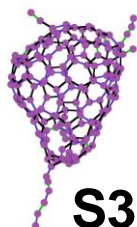
68.7 ps



S2

C185

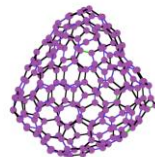
61.6 ps



S3

C147

43.8 ps



S4

C208

84.3 ps



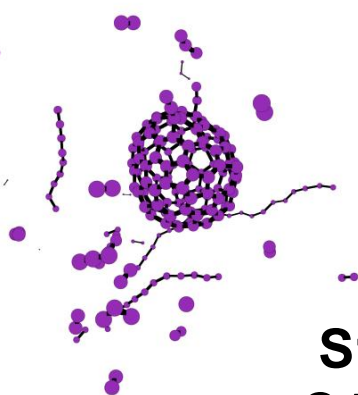
S5

C124

~45ps

**Time scale:
Picoseconds!
Growth to large n
cage directly!**

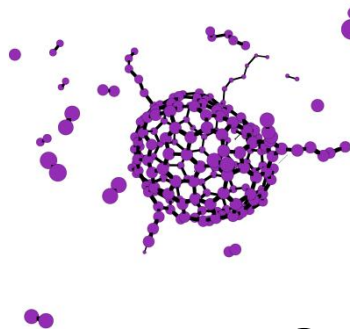
New runs fullerenes: 3 out of 10: “C₂ feeding” time now 12 ps.



S1z

C121

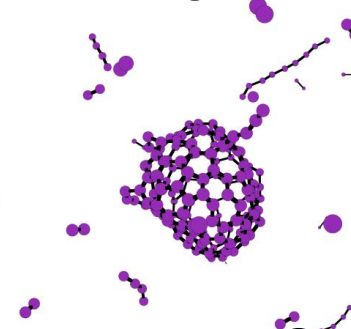
78.6 ps



S2z

C180

76.7 ps

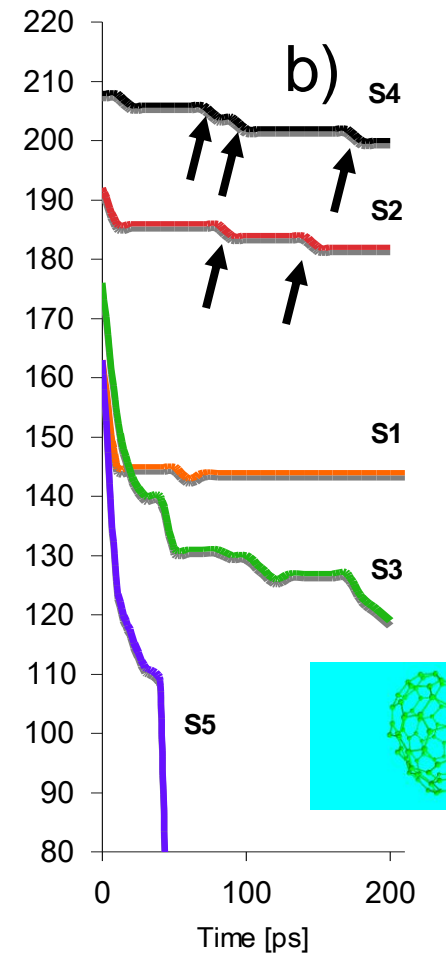
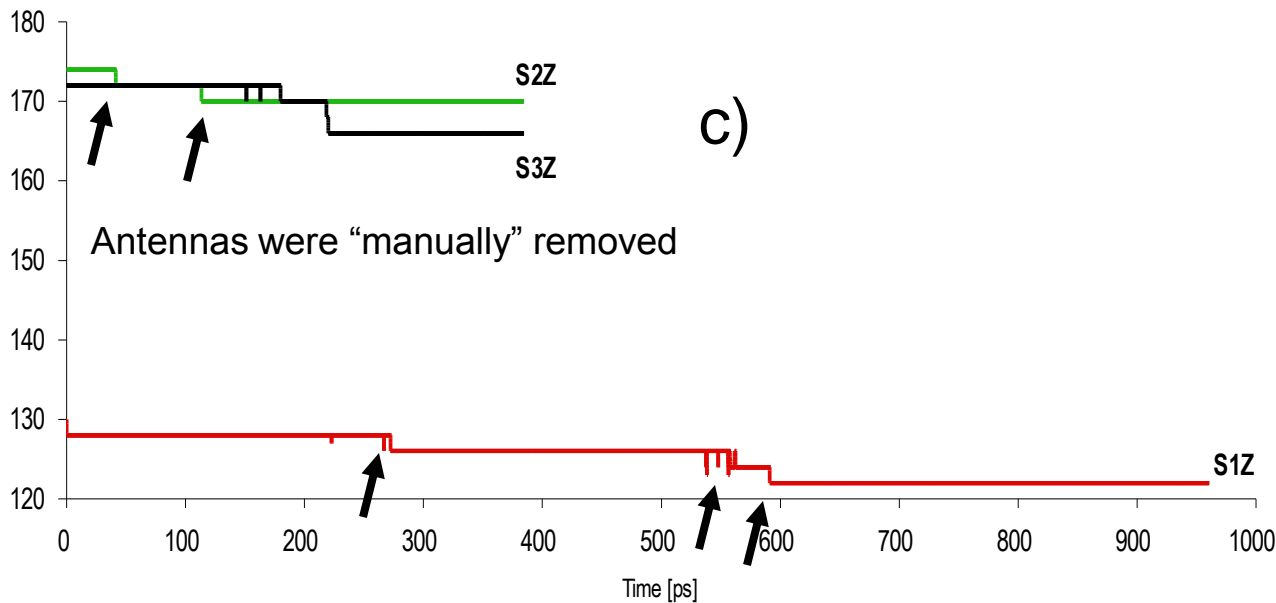
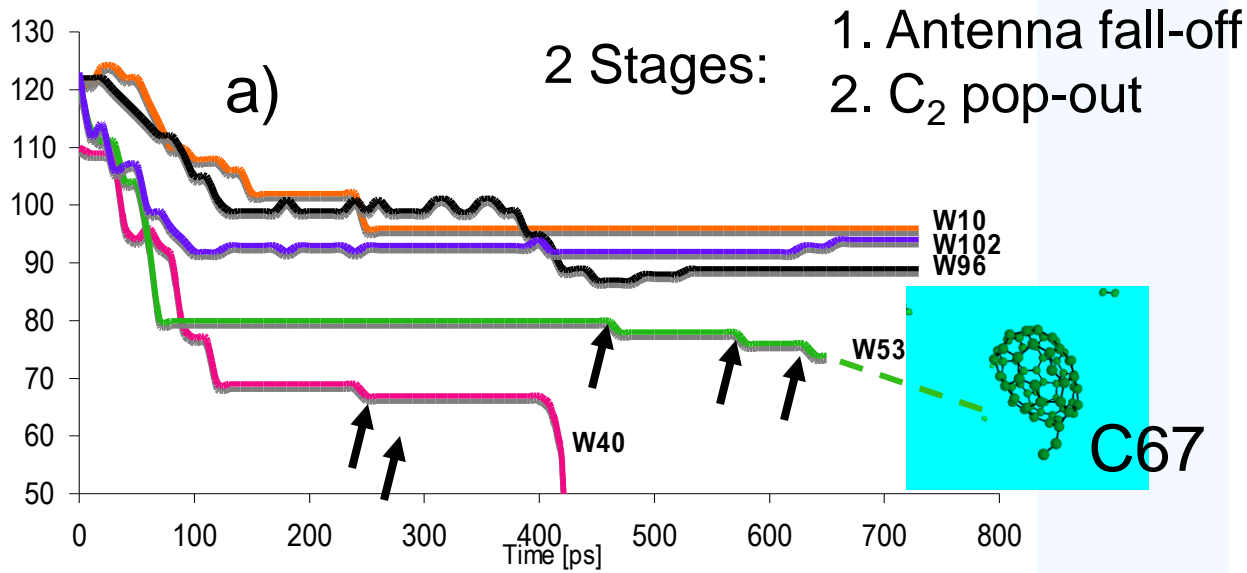


S3z

C169

107.8 ps

Shrinking of Giant Fullerenes at high temperatures: Size-Down



J. Nanosci.
Nanotechnol. (2007)

Indirect experimental evidences for giant fullerene shrinking

With annealing in He atmosphere

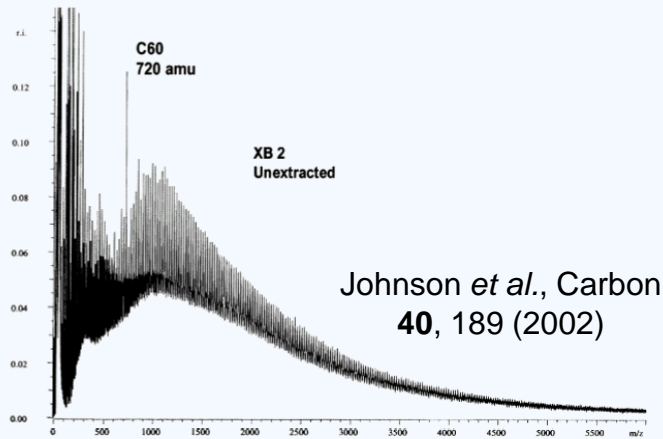
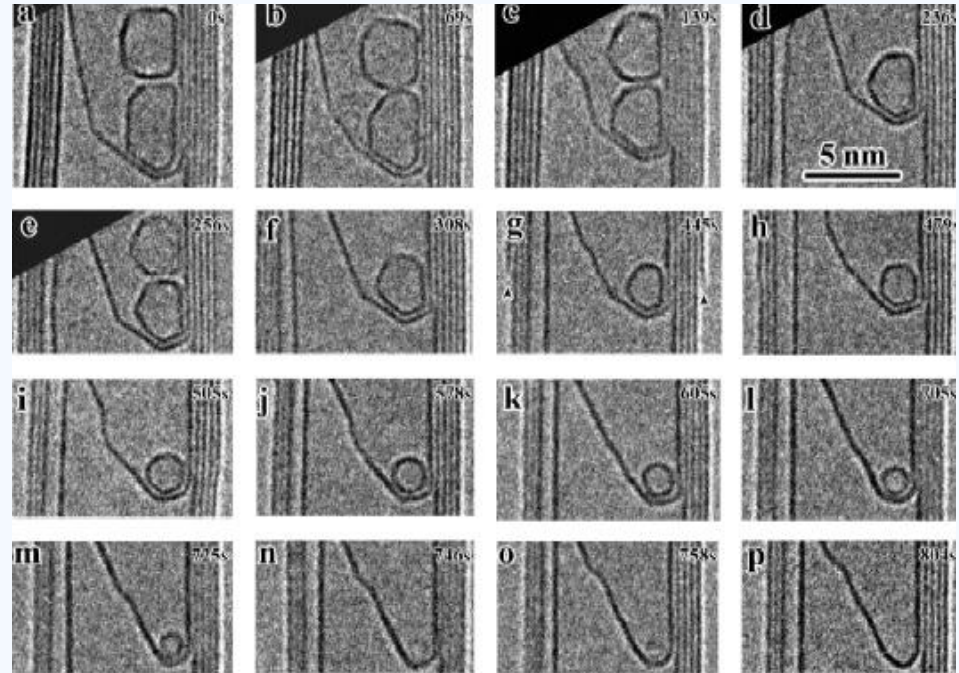
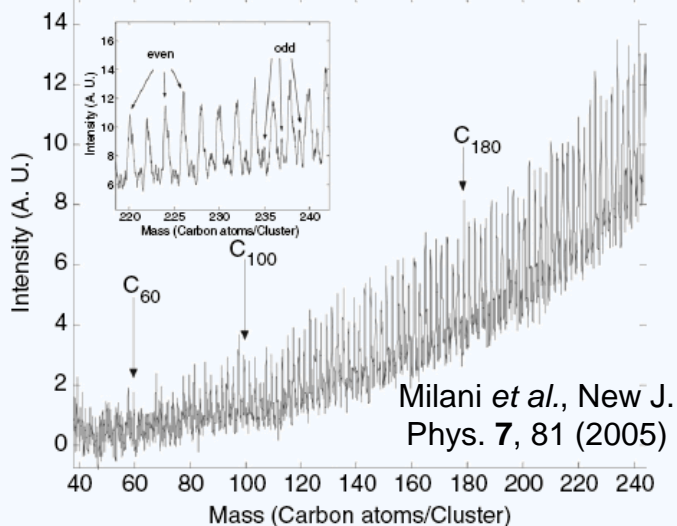


Fig. 4. XB2 MALDI mass spectrum showing C60 and higher fullerenes in carbon black soot.

Without annealing in vacuum



Continuous shrinkage of a giant fullerene (C₁₃₀₀) trapped inside the cavity of a MWCNT at high temperatures. The time elapsed (in seconds) is marked. Credit: Phys. Rev. Lett **99**, 175503 (2007).

カーボンナノチューブ

炭素によって作られる六員環ネットワーク (sp^2 炭素のグラフェンのシート) が単層あるいは多層の同軸管状になった物質。

単層のもの: シングルウォールナノチューブ (SWNT)

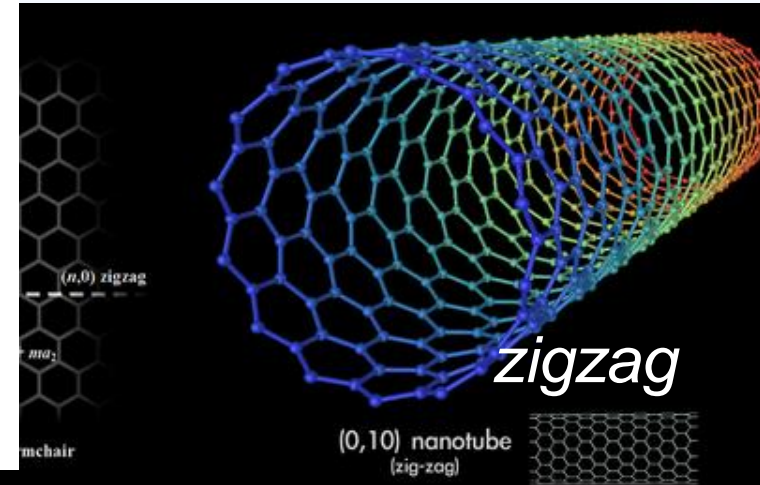
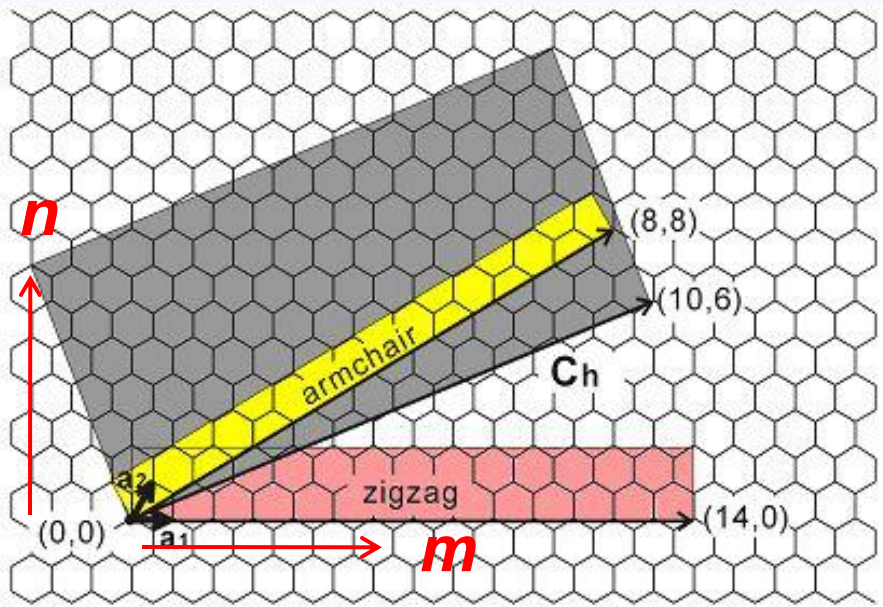
多層のもの: マルチウォールナノチューブ (MWNT)

1991 飯島澄夫により発見

作り方: アーク法 (黒鉛, 金属触媒)、レーザーアブレーション法 (黒鉛金属)、CDV (化学気相蒸着) 法 (アセチレン、メタンなどの熱分解, 金属粒子)、その他



カーボンナノチューブの構造



一般にカイラル指数(n, m)
で巻き方を表す。

Armchair (n, n)

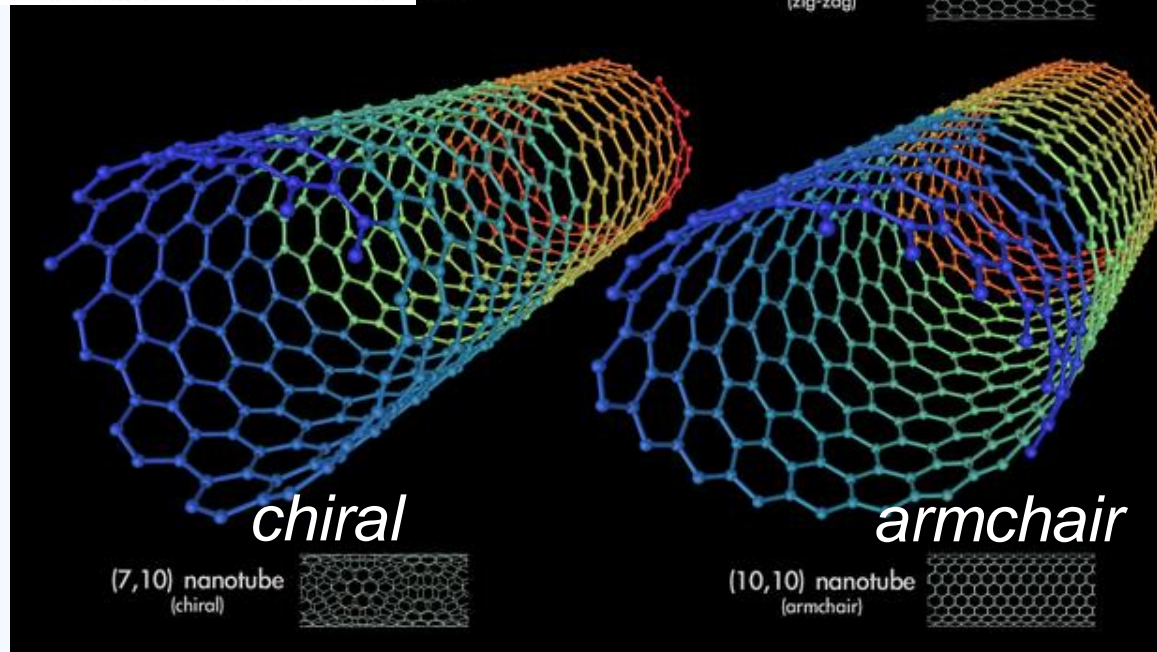
Zigzag ($n, 0$)

Chiral (n, m)

$n-m=3$ の倍数 金属

$n-m=3$ の倍数でない 半導

体



カーボンナノチューブの性質

細くて強い

同じ重さの鉄の
数百倍の強度がある

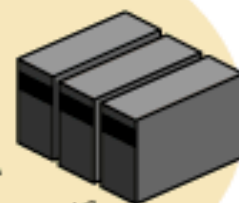
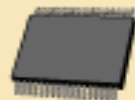
カーボン
ナノチューブ線
0.3mm



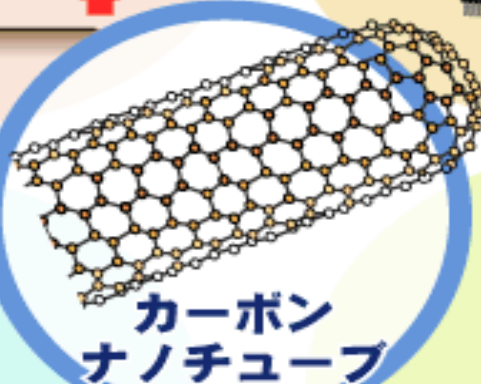
構造により半導体になる

究極の半導体として
利用が期待される

半導体



スーパー
コンピュータ

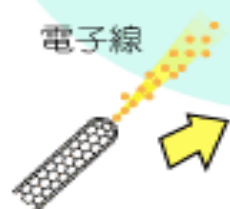


電気をよく通す

電気をよく通し、
低い電圧で電子を
放出するので、
テレビのディスプレイ
などに応用できる

高精細ディスプレイ

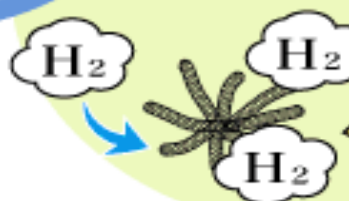
電子線



カーボン
ナノチューブ

ガスをよく吸着する

水素をよく吸着し、
水素吸蔵材料として
利用が期待できる



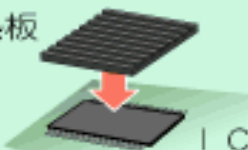
水素燃料電池
自動車



熱をよく伝える

熱伝導性に優れ、
ICの放熱板などに応用できる

放熱板



注) 図はイメージです。

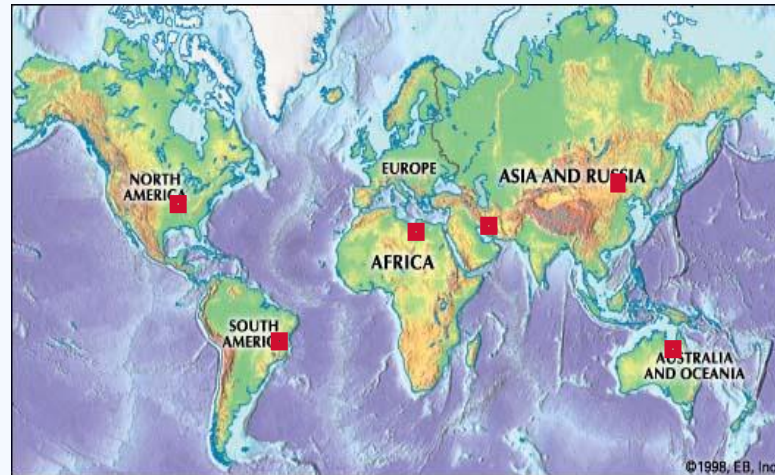
Unique physicochemical properties of SWNTs promise “mouthwatering” applications

Semiconductor/metallic wires	FET	FED
Transistor	Hydrogen storage	Conducting polymer
AFM tips	Fuel cell/electric capacitor/solar cell component	
Chemical sensor	Structural reinforcement	Loudspeaker



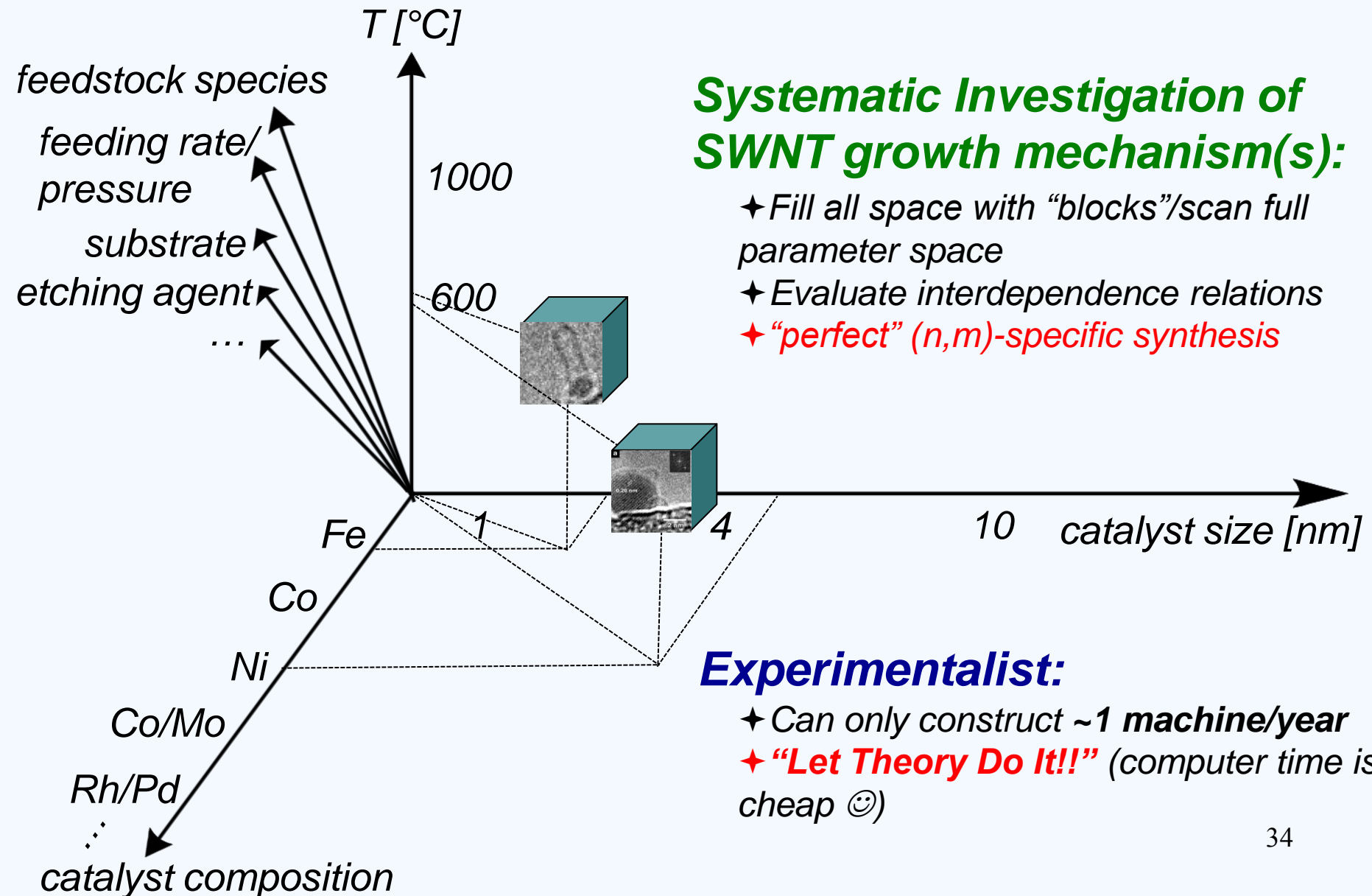
“Space Elevator”

Global *network* with solar cell farms:
 $6 \times (100\text{km})^2$ at 3.3 TW Each = 20 TW

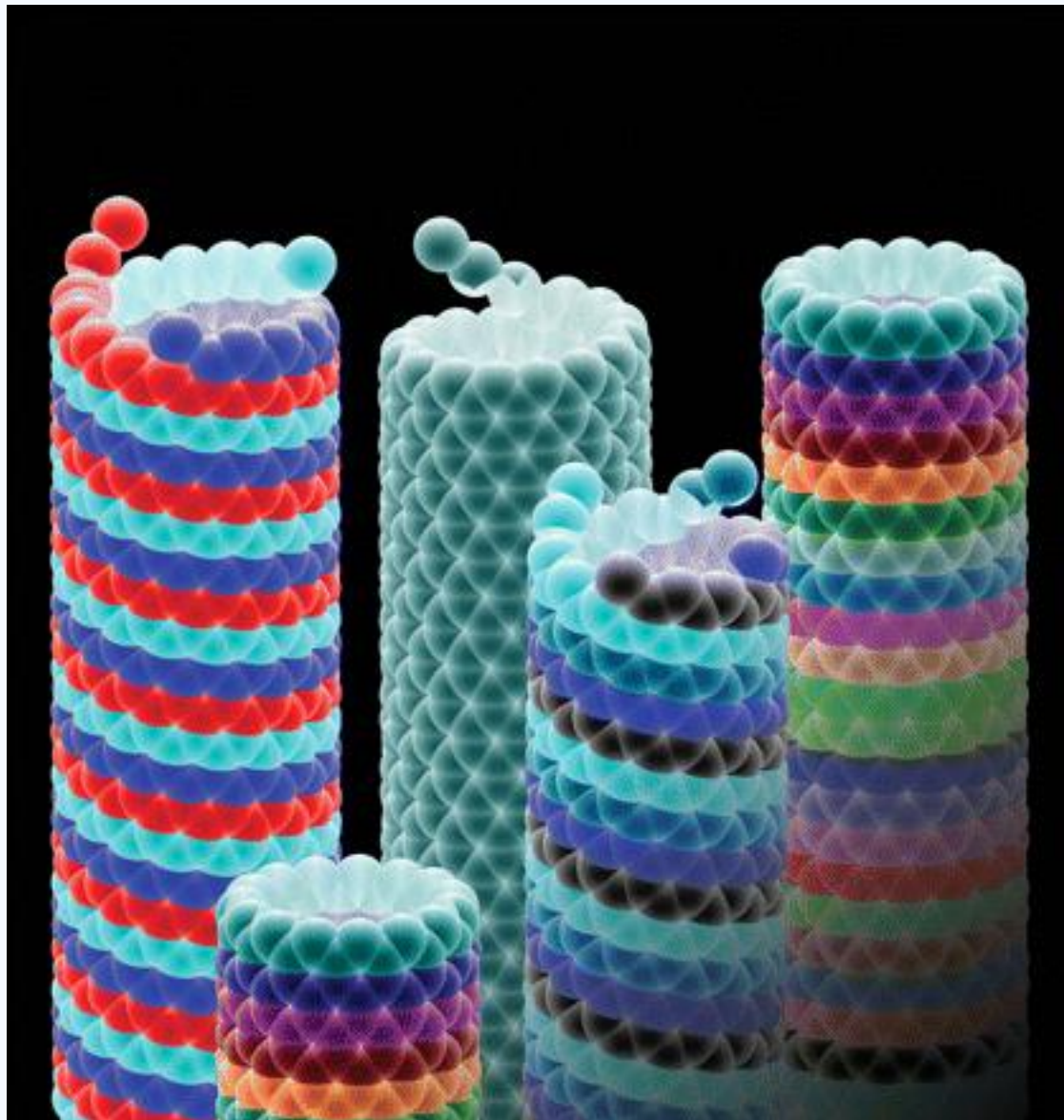


From R. E. Smalley’s talk: Our Energy Challenge, <http://smalley.rice.edu>

SWNT Growth N-dimensional "Parameter Space"



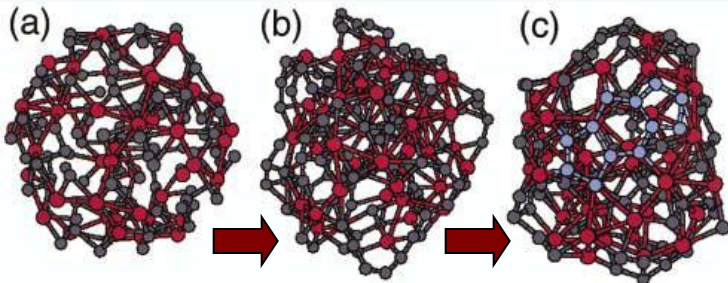
カーボンナノチューブの生長の漫画



Previous Car-Parrinello Molecular Dynamics (CPMD)

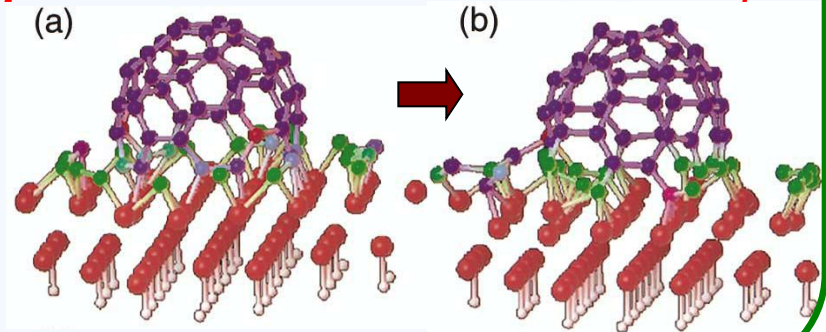
Heroic efforts on supercomputers, one-shot simulations!

J. Gavillet et al, Root-Growth Mechanism for SWNTs, Phys. Rev. Lett. **87**, 275504 (2001)

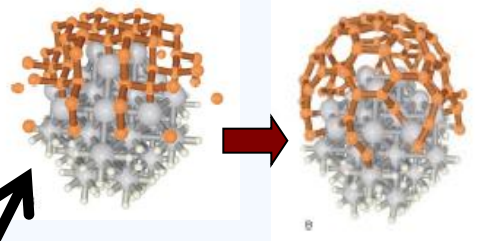


Carbon precipitation on Co carbide particle, 51 Co & 102 C atoms, **25 ps**
1 hexagon, 2 pentagons

$C_{30}+44C$ on Co surface at 1500 K, **15 ps**
5 carbon atoms diffused to cap



J.-Y. Raty et al, Growth of Carbon Nanotubes on Metal Nanoparticles: A Microscopic Mechanism from Ab Initio Molecular Dynamics Simulations, Phys. Rev. Lett. **95**, 096103 (2005)



Change from diamond structure (sp^3) to fullerene cap (sp^2) immediately!

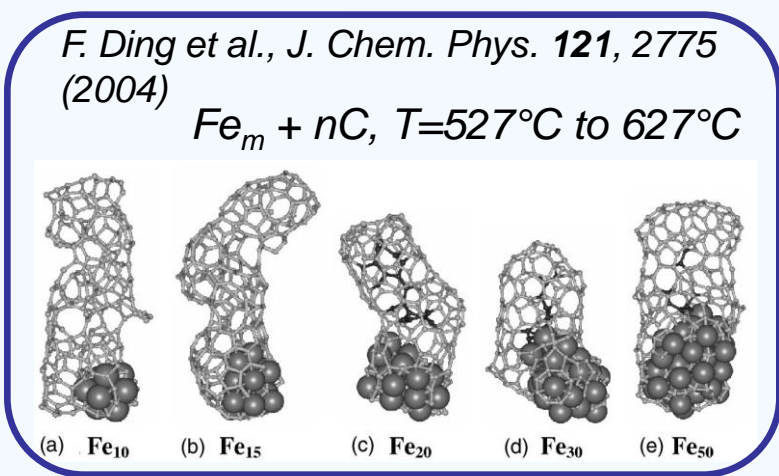
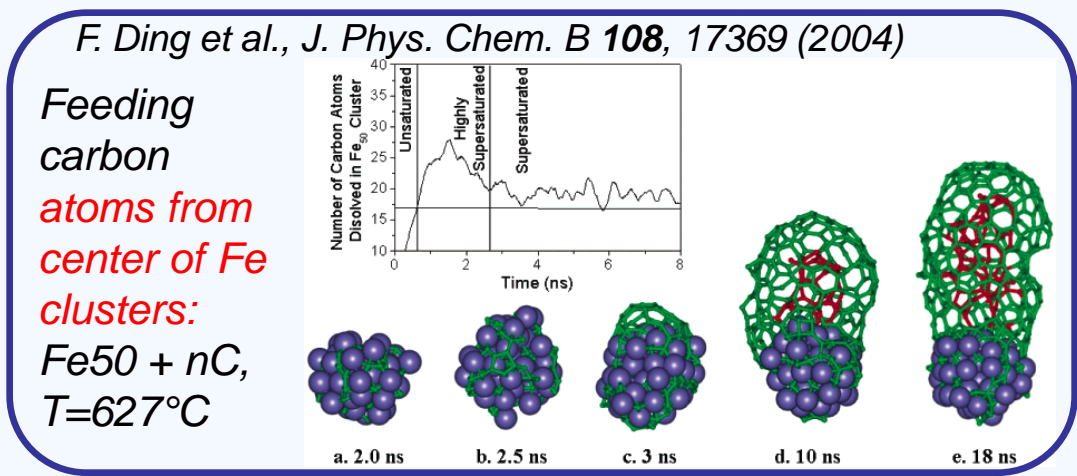
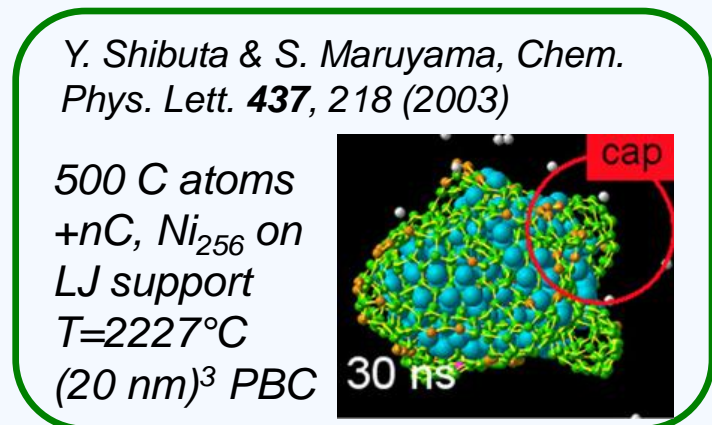
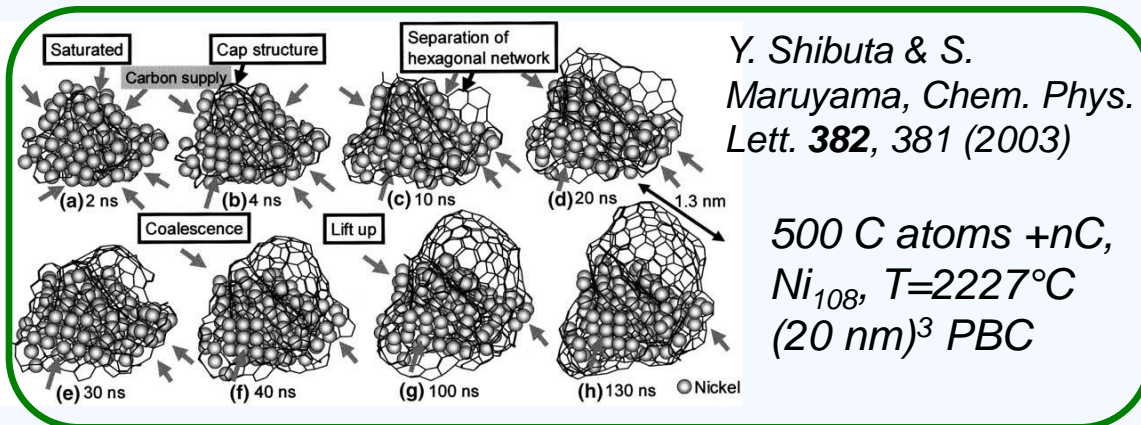
simulation time ~ **10 ps**
Too short to demonstrate self-assembly

Nano-diamond: **Inappropriate model!**

Reactive Empirical Bond Order (REBO) MD

Classical potential, cheaper, many long simulations!

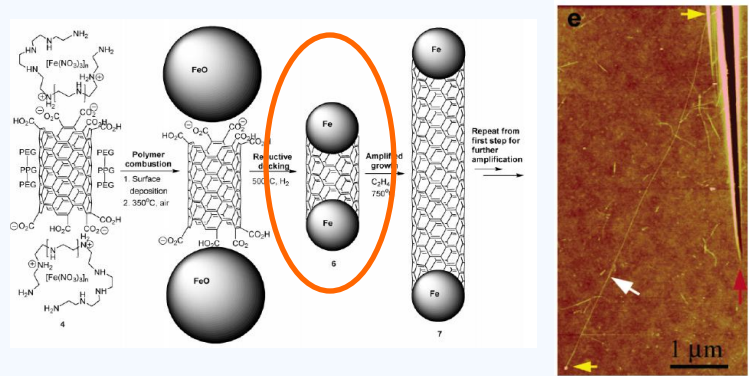
Bond order potential **allows bond breaking** via potential switching functions, but **does not include effects of π -conjugation or charge transfer**



Many more studies ...

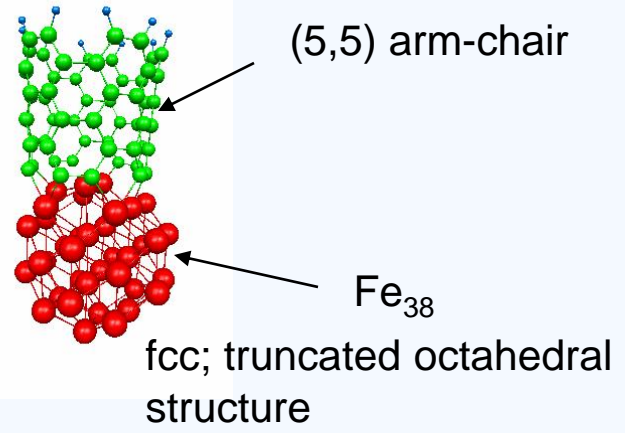
Growth of Single-Walled Carbon Nanotubes on Metal Cluster

Experiment of continued growth



[2] R.E. Smalley et al. JACS 128, 15824 (2006)

Model system

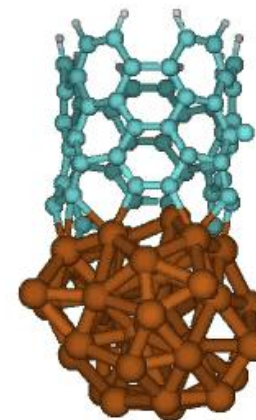
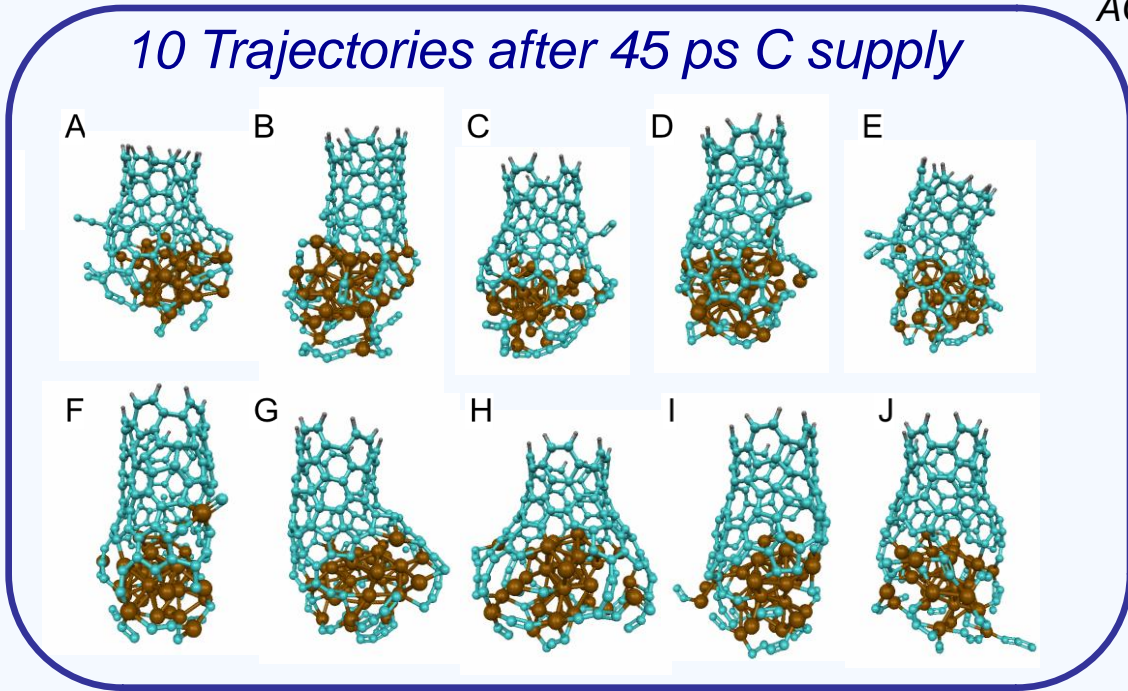


Molecular dynamics of nano-systems is a very challenging topic.

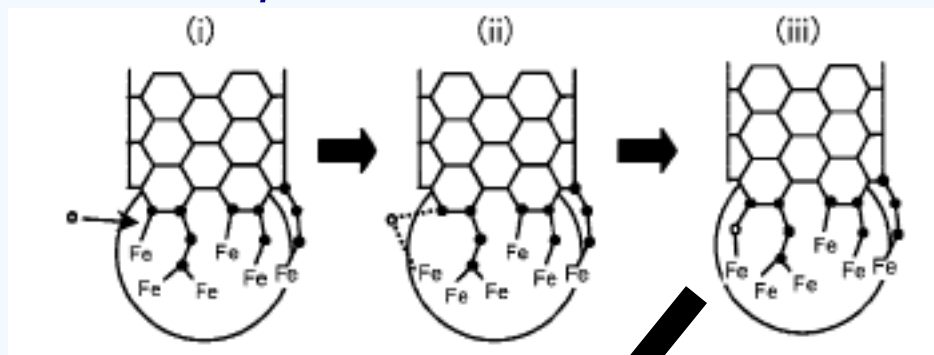
scc-DFTB/MD with **electronic temperature**

ACS Nano **2**, 1437 (2008)

10 Trajectories after 45 ps C supply

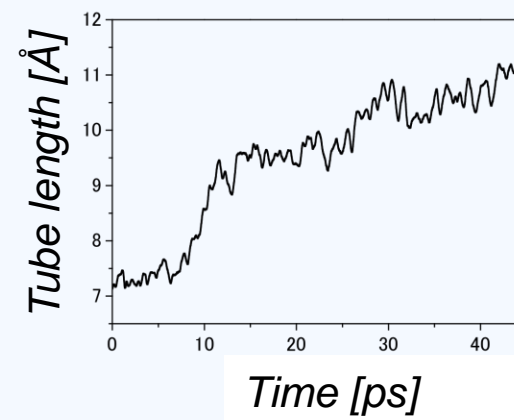


Schematic depiction of C atom insertion events



new 5-, 6-, 7-membered rings

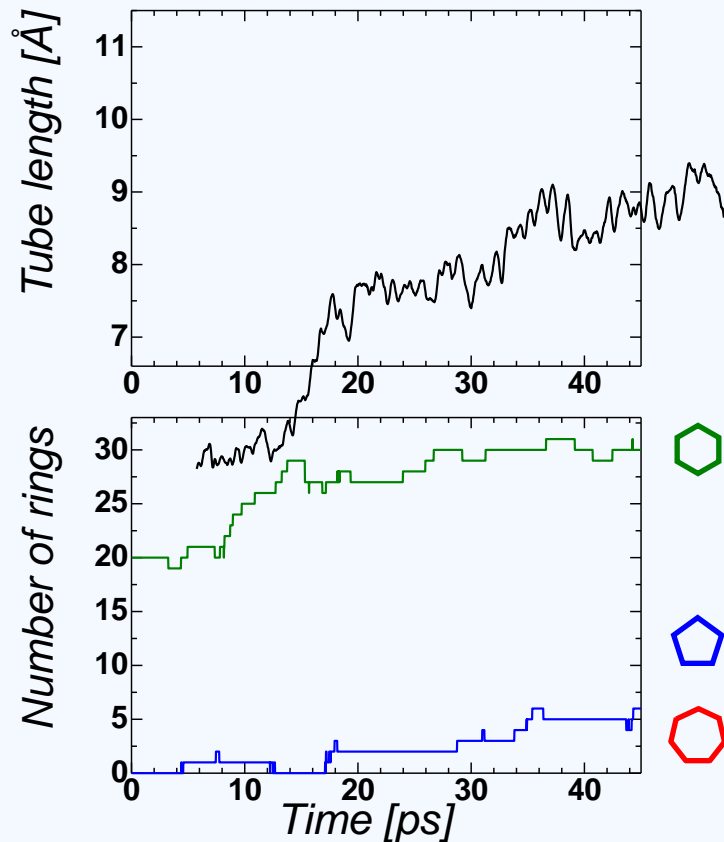
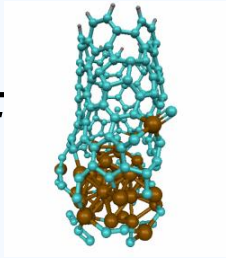
Trajectory F



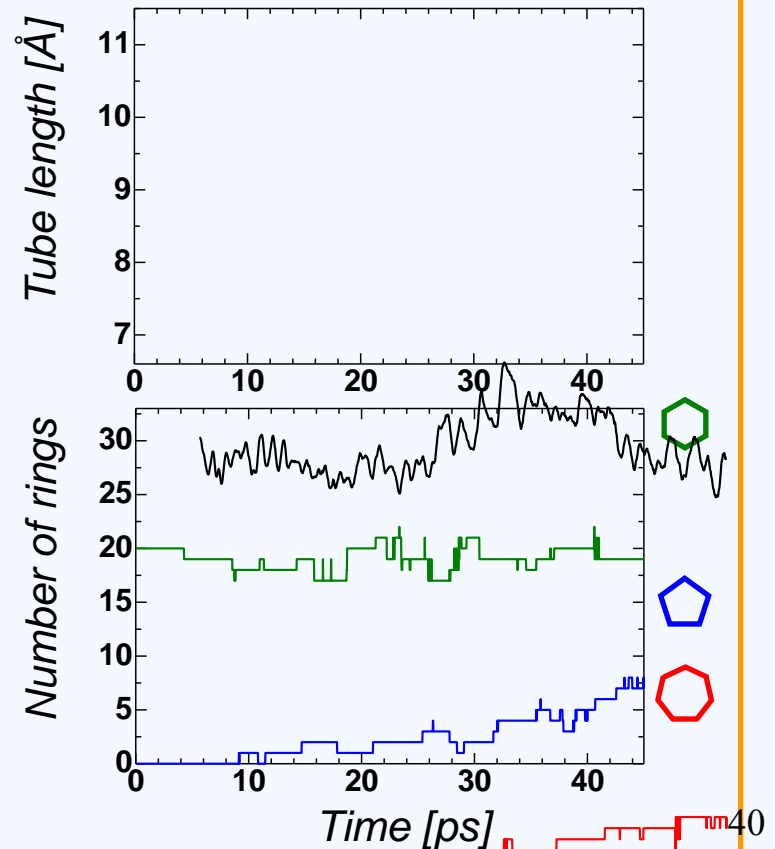
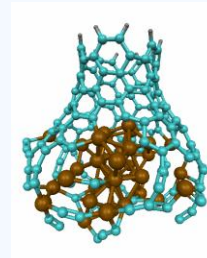
Growth rate: ~ 10 pm/ps³⁹

Relationship between ring type and length

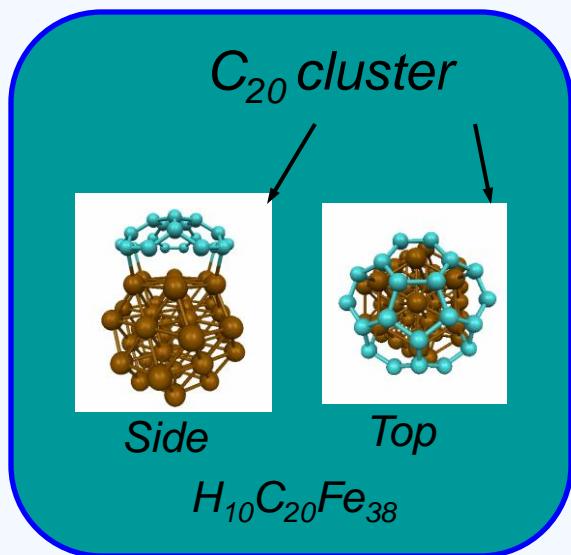
F



H

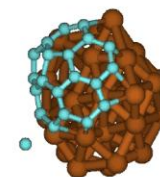
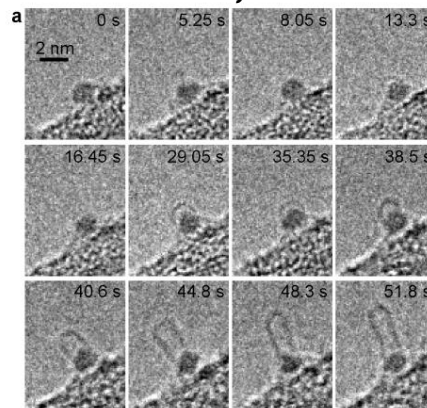


Y. Ohta, Y. Okamoto, S. Irlle, and K. Morokuma, *Phys. Rev. B* (2009)

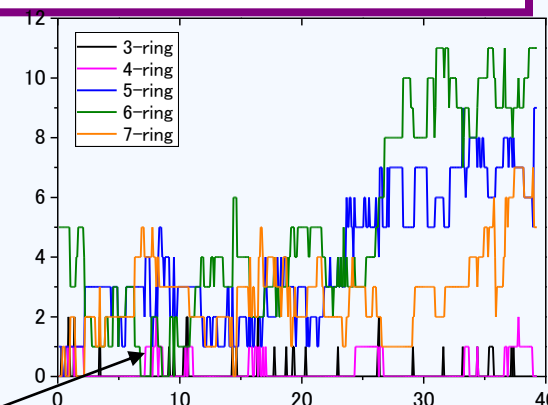
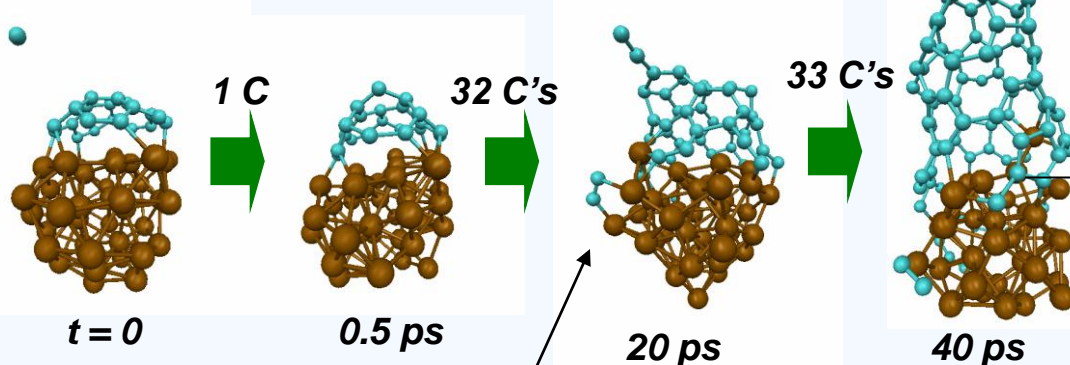


Experimental snapshots

H. Yoshida et al, *Nano Lett.* (2008).



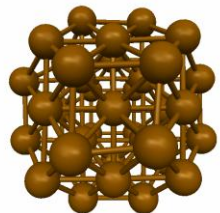
Nanotube 10 Å long was formed.



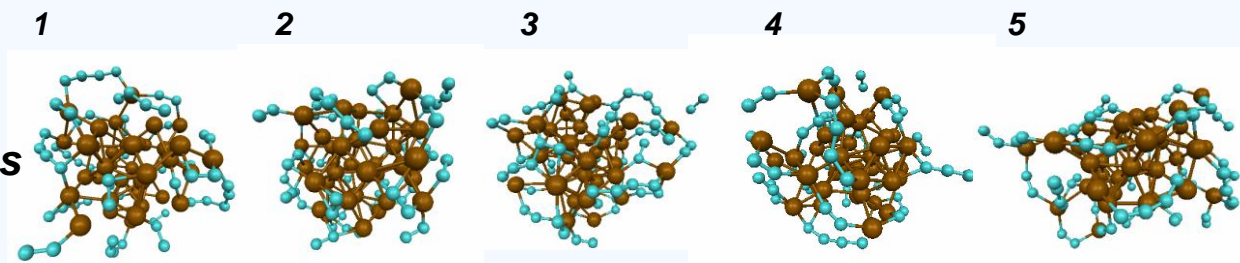
During growth, non-hexagonal rings and polyynes frequently formed and then rearrangement of sp^2 network occurs to construct carbon sidewall.

Y. Ohta, Y. Okamoto, A. J. Page, S. Irle, and K. Morokuma, ACS nano (2009)

Initial model: Fe_{38}



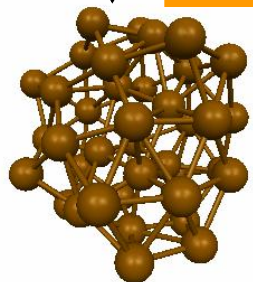
$t = 0$ ps



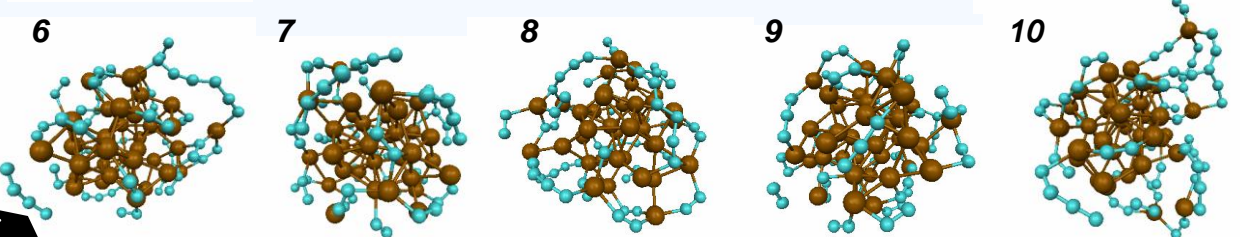
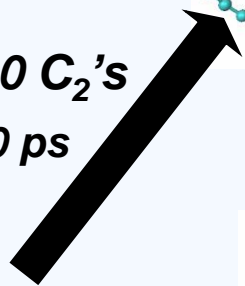
10 ps



Annealed at
1500 K



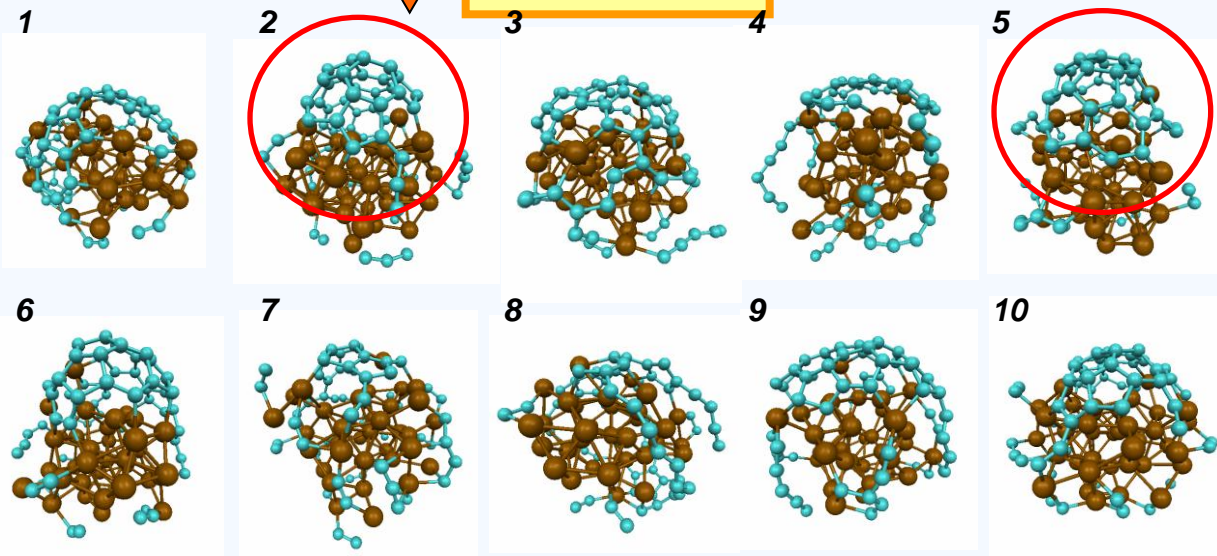
30 C_2 's
30 ps



410 ps



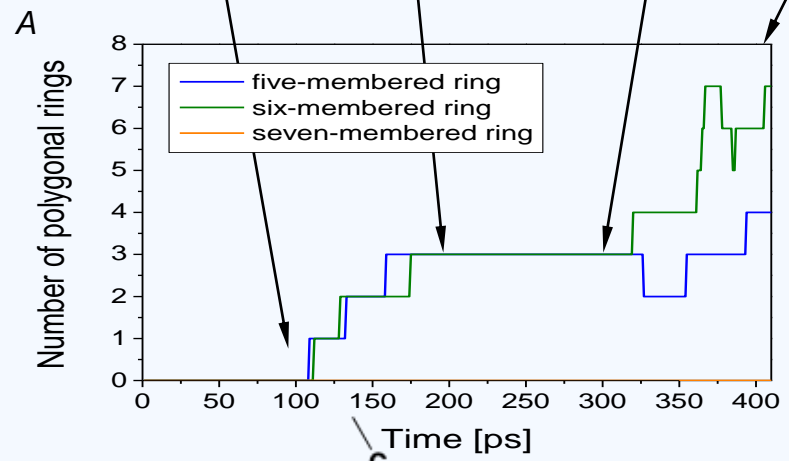
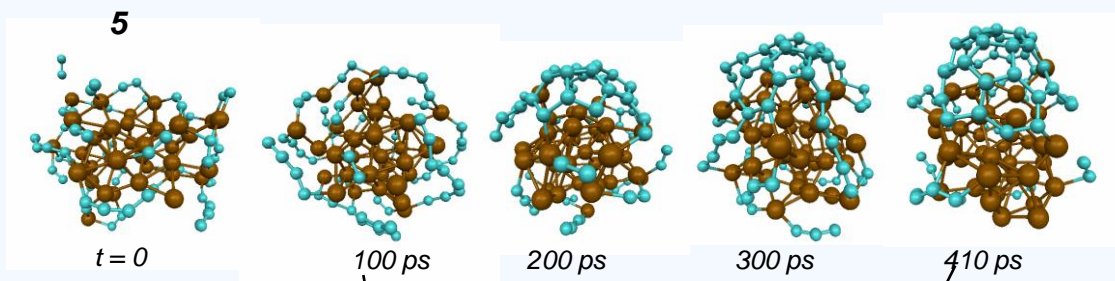
Annealed at
1500 K



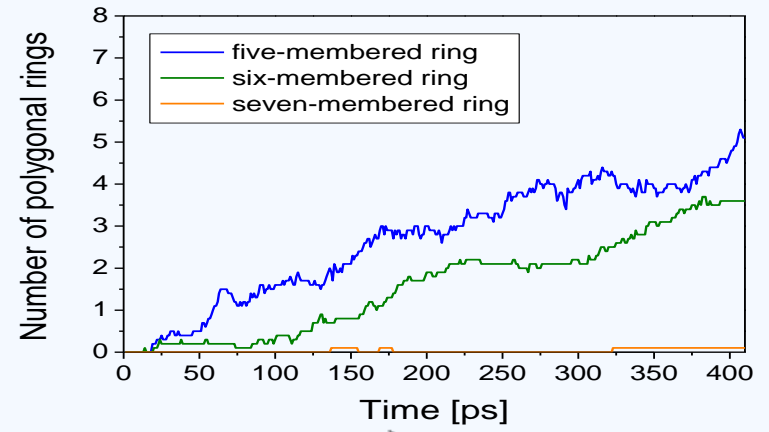
$t = 410$ ps

10 geometries are
randomly sampled
between 5 and 10 ps
for ten trajectories.

Y. Ohta, Y. Okamoto, A. J. Page, S. Irle, and K. Morokuma, submitted

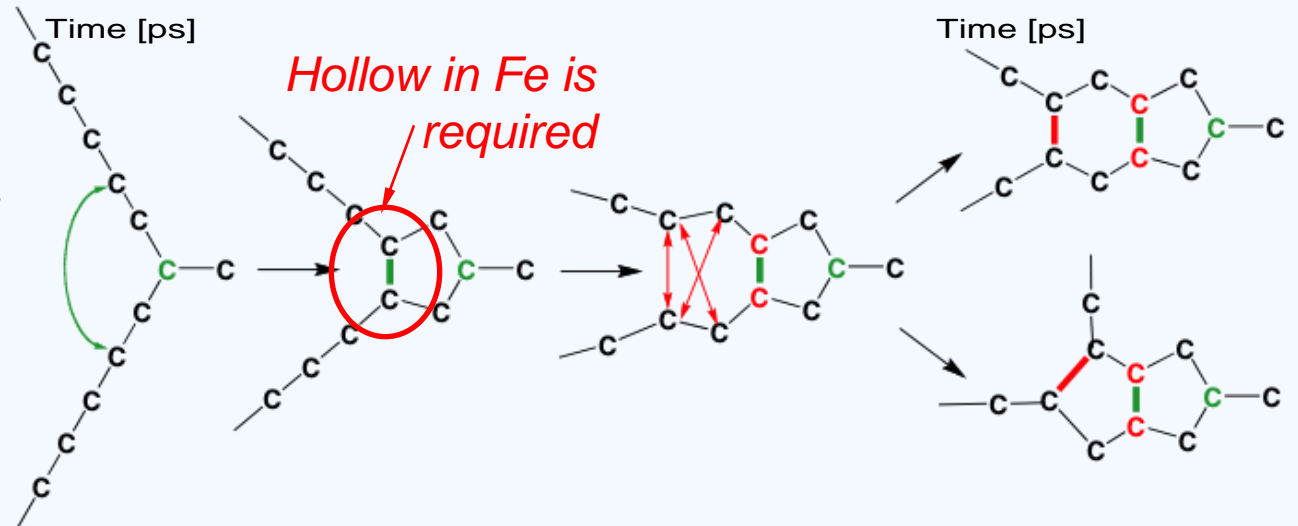


Average 5- and 6-ring counts over 10 annealing trajectories



Formation of first condensed 2-ring system (5/5 or 5/6)

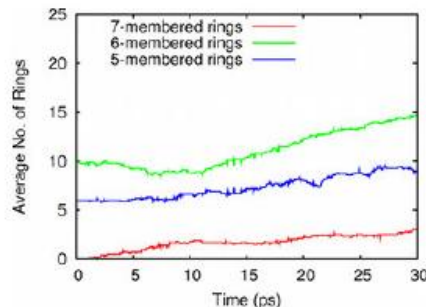
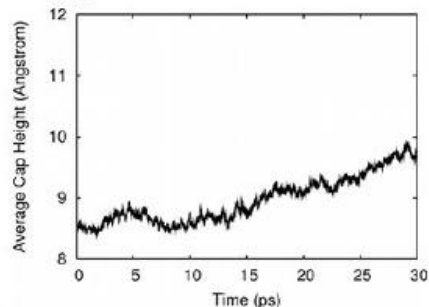
Always pentagon first!



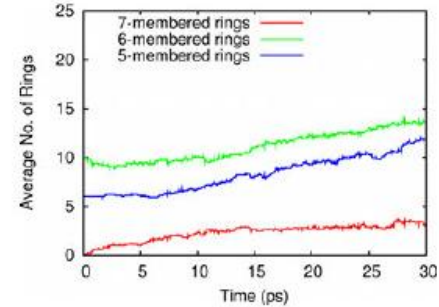
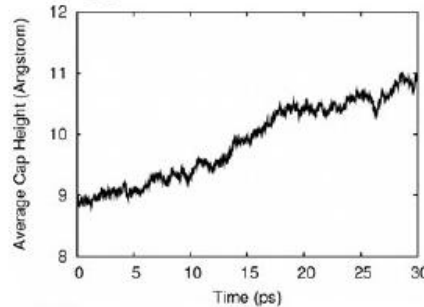
SCC-DFTB/MD Investigation of Metal & Size Effects on SWNT Growth (5)

Comparison of M_{38} - & M_{55} -catalyzed SWNT growth (M=Fe, Ni)

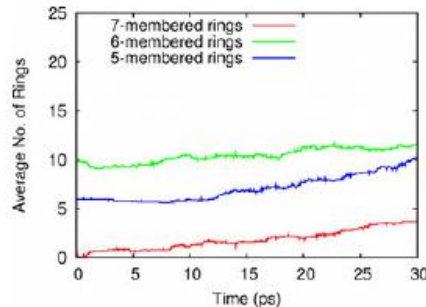
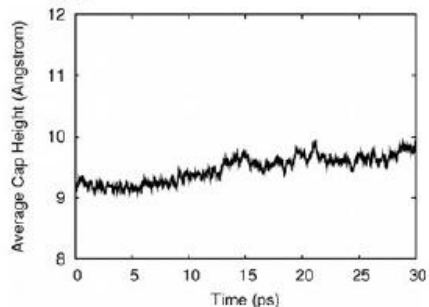
Fe_{38}



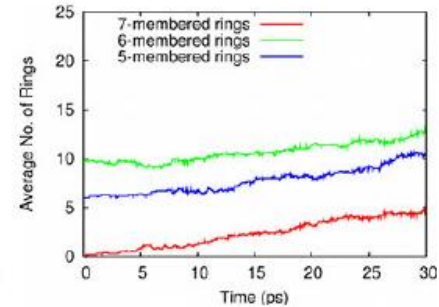
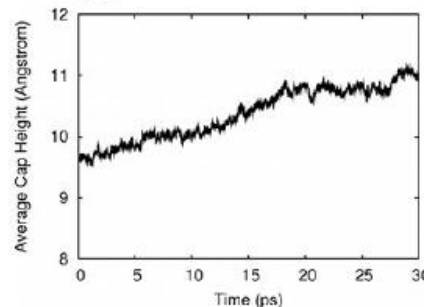
Ni_{38}



Fe_{55}



Ni_{55}



Size Effect: Average Growth (Average Growth Rates, $d\text{\AA}ps^{-1}$) using M_x Catalysts after 30 ps

	M=Fe	M=Ni
$x = 38$	1.229(4.10)	1.961(6.53)
$x = 55$	0.654(2.18)	1.302(4.34)
$M_{38}:M_{55}$	1.88:1	1.51:1

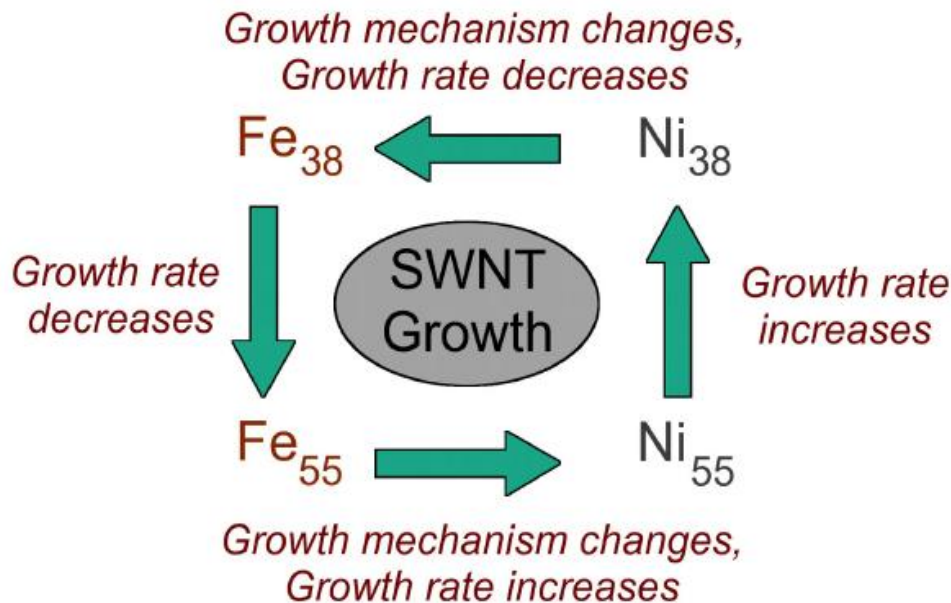
⇒ SWNT growth rate decreases with increasing catalyst size.

Larger catalyst particle ⇒ greater surface area + volume for the decomposed carbon to explore before contributing to the SWNT base.

SCC-DFTB/MD Investigation of Metal & Size Effects on SWNT Growth (6)

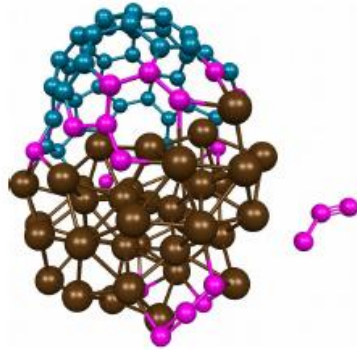
Summary

- SWNT growth simulated using M_x catalysts ($M = \text{Fe}, \text{Ni}; x = 38, 55$).
- Effect of catalyst composition and size determined.
- Correlations between SWNT growth rate/mechanism and TM-C adhesion energies observed.
- Ni-catalyzed SWNT growth mechanism established using QM/MD.

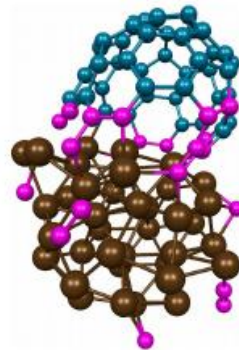


SCC-DFTB/MD Investigation of SWNT Healing (4)

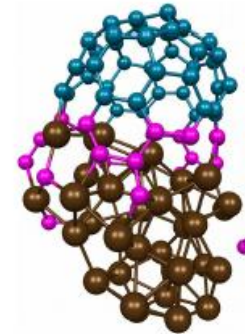
Slower Carbon Supply Rate Leads to Healing



Fast Supply
(11.0 ps)



Slow Supply
(220 ps)



Very Slow Supply
(440 ps)

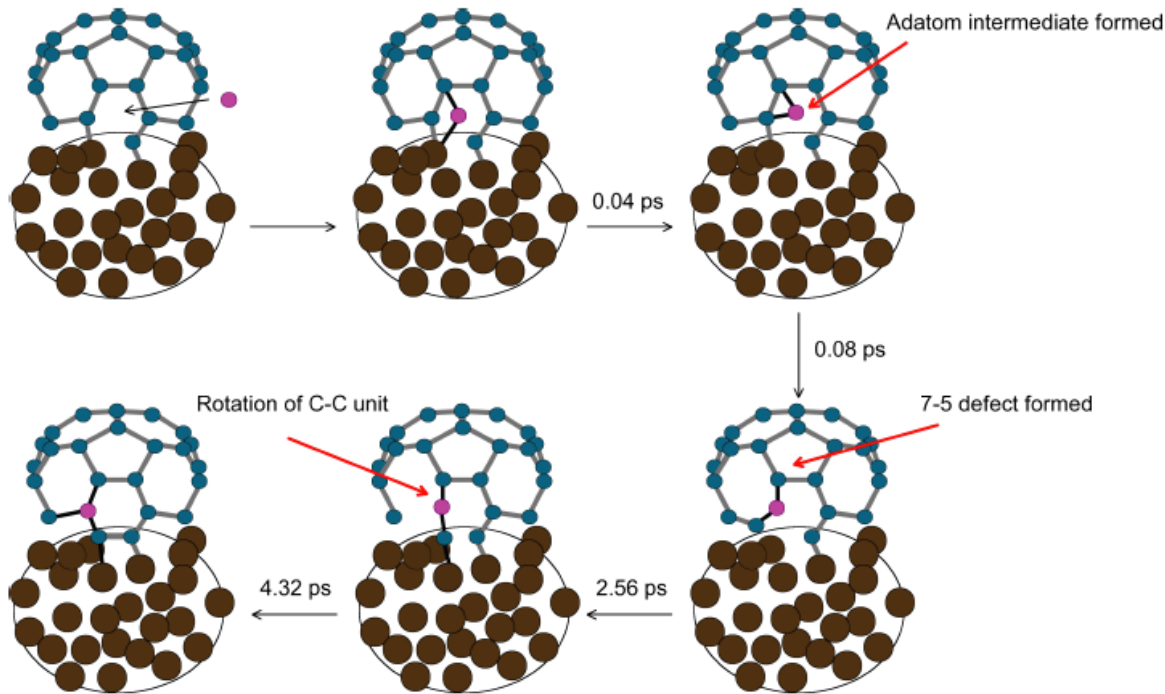
Average Ring Formation and Formation Rates for Fast/Slow/Very Slow Supply Simulations After Adding 22 Carbons.

Ring Type	Fast Supply		Slow Supply		Very Slow Supply	
	Rings Formed	Formation Rate ($\times 10^2 \text{ ps}^{-1}$)	Rings Formed	Formation Rate ($\times 10^2 \text{ ps}^{-1}$)	Rings Formed	Formation Rate ($\times 10^2 \text{ ps}^{-1}$)
5-membered	1.0	8.70	1.7	0.74	1.1	0.24
6-membered	-0.8	-6.96	1.7	0.74	1.5	0.33
7-membered	1.7	14.78	1.5	0.65	1.4	0.30

SCC-DFTB/MD Investigation of SWNT Healing (5)

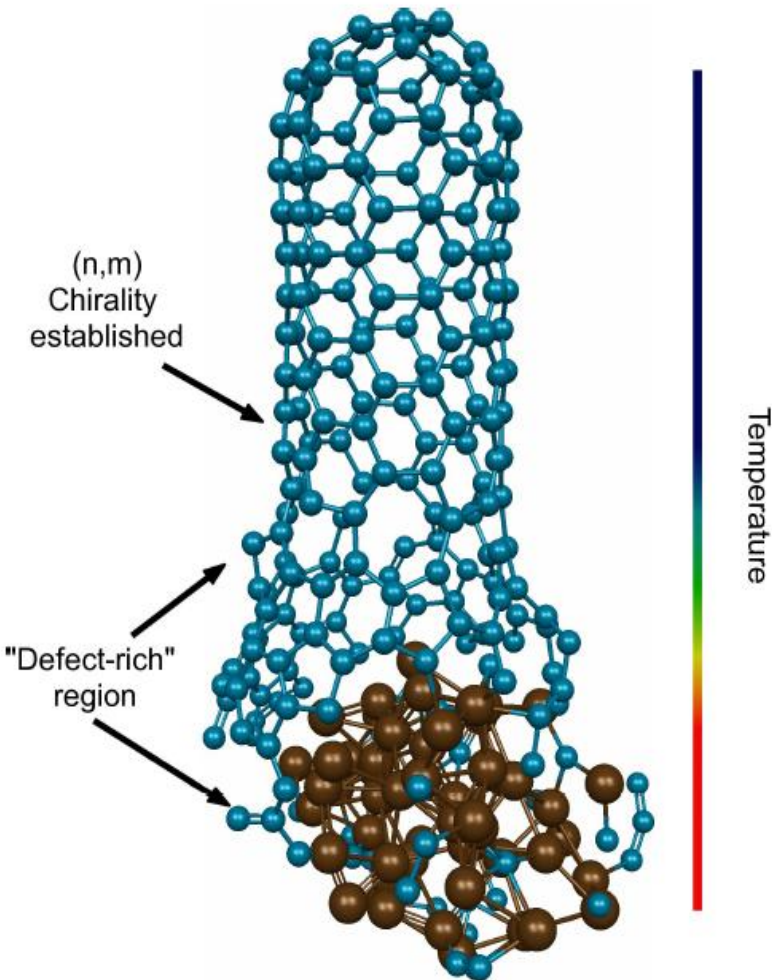
Healing Mechanism: 7+5-Ring \rightarrow 6+6-Ring Isomerisation

SWNT healing mechanisms require timescales of *ca.* 5-30 ps (or more...)
 \Rightarrow **SWNT healing driven by relative rates of defect formation/removal.**



SCC-DFTB/MD Investigation of SWNT Healing (7)

A Proposed Mechanism for Chirality-Controlled SWNT Growth



Throughout root-growth, the base of the SWNT remains defect rich. These defects ultimately isomerize, forming new 6-membered rings. These 6-membered rings are thermodynamically the most stable structure, and gradually lift away from the SWNT-catalyst region.

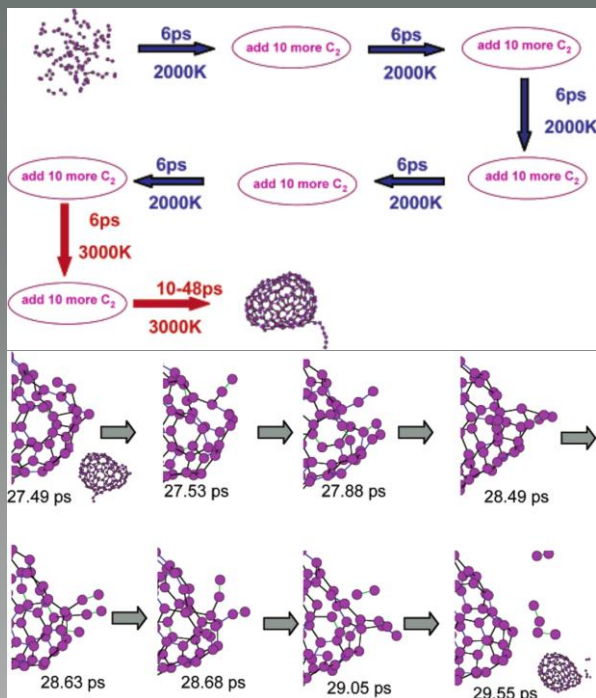
Chirality, imprinted on the SWNT cap during nucleation, is therefore maintained throughout growth by the addition of only 6-membered rings to the sidewall during the growth process *provided that carbon addition to the SWNT is slow enough.*

High Temperature Combustion & Formation of Fullerenes

SCC-DFTB/MD Simulations

Biswajit Saha

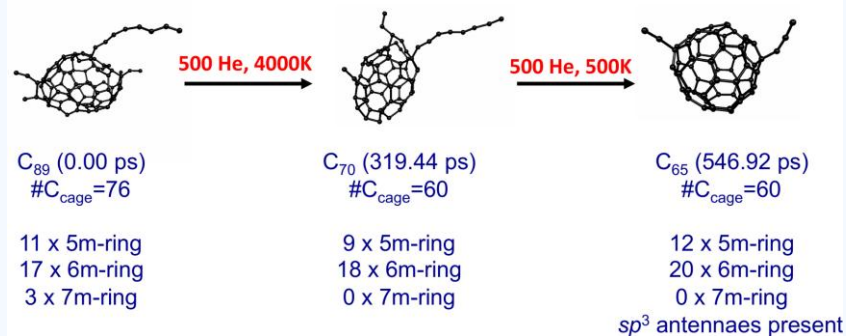
'Shrinking-Hot-Giant' Mechanism of Fullerene Formation



Irle et al., *J. Phys. Chem. B*, **110**, 14531, (2006);
 Irle et al., *Nano. Lett.*, **3**, 1657, (2003)

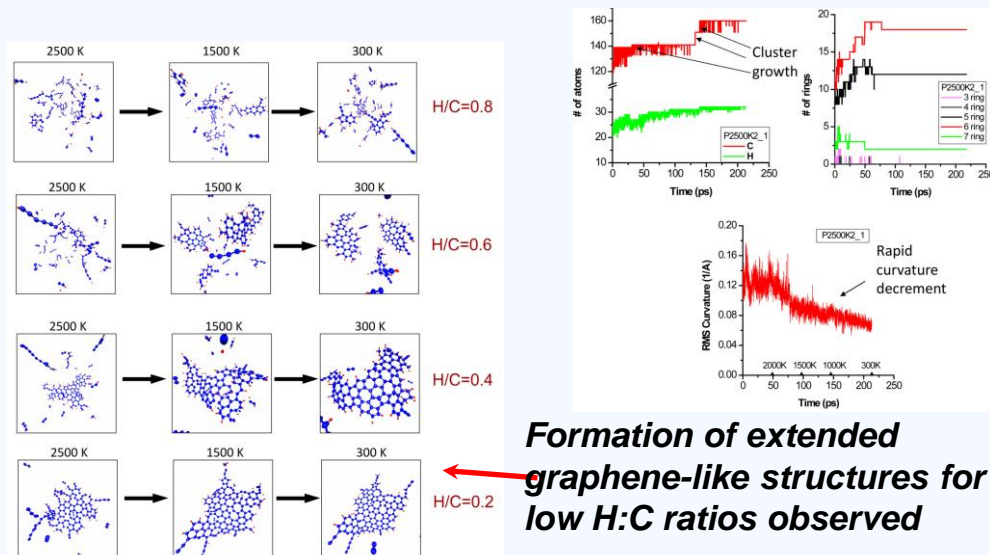
GF shrinking driven by fall off events of 'antennae' structures attached to the fullerene, and 'pop out' events of C₂ in the fullerene structure.

Effect of He Buffer Gas on SHG Mechanism?



GF shrinking rates increase in the presence of He buffer gas. C₂ removal from fullerene structures slows over time.

High Temperature Combustion: Formation of Extended PAH Structures

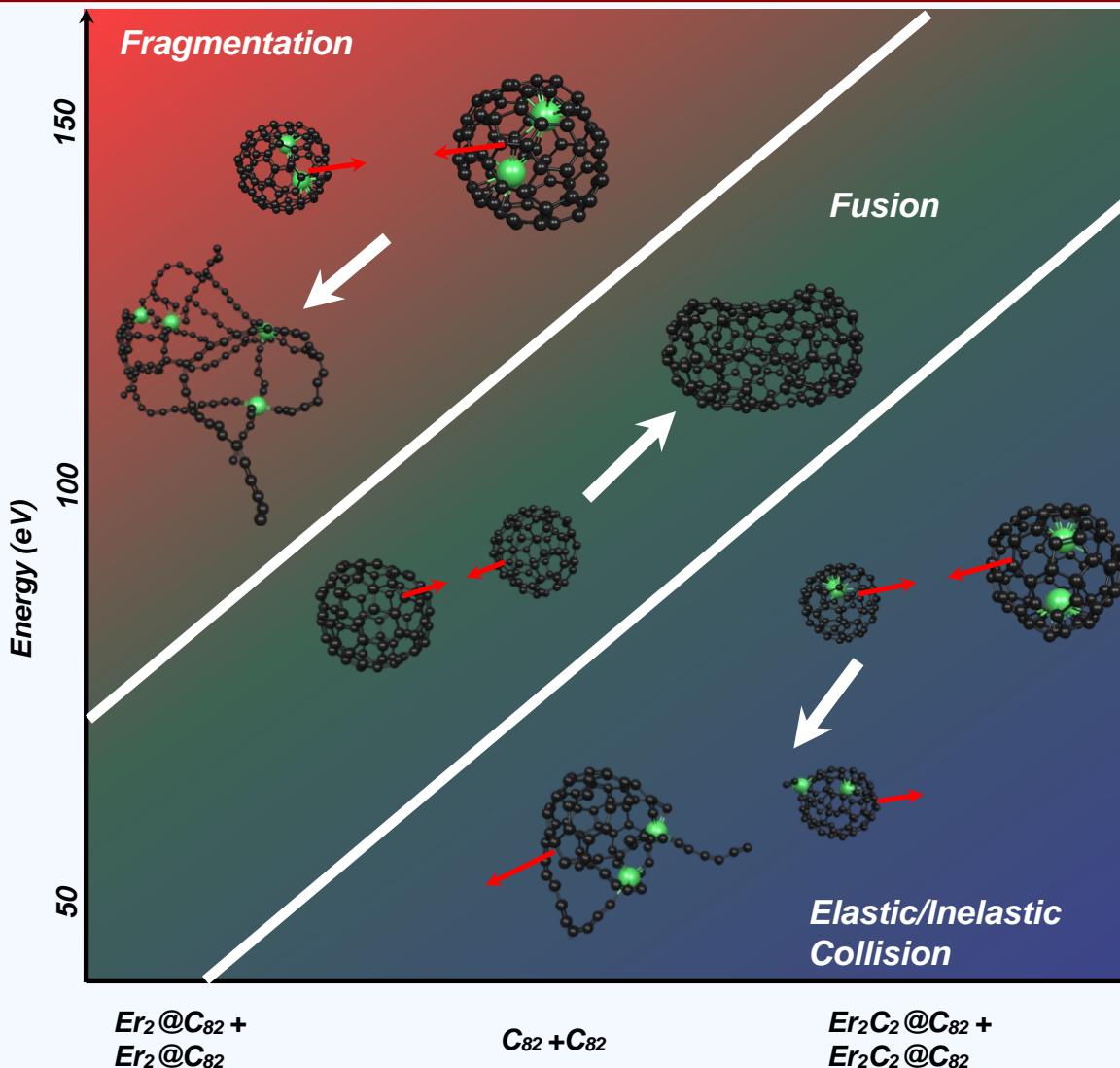


Formation of extended graphene-like structures for low H:C ratios observed

Saha et al., *J. Chem. Phys.*, **132**, 224303, (2010)

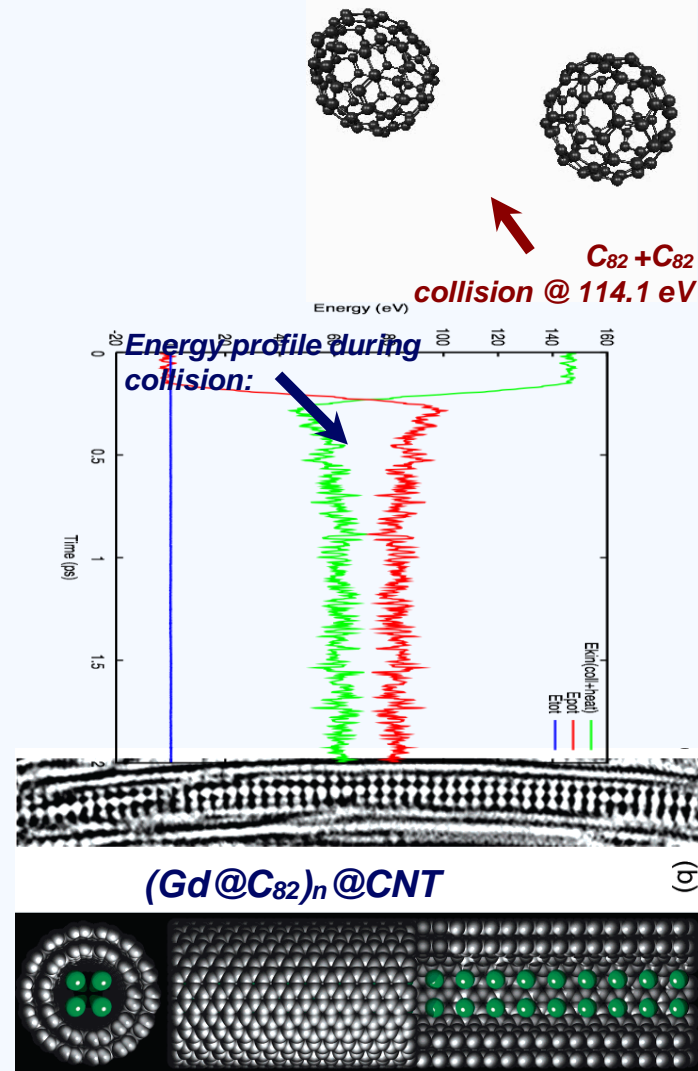
Metal Nanowire Formation

Collision Induced Fusion of C_{82} & $Er_xC_y@C_{82}$: SCC-DFTB/MD Simulations



Outcome of collision reaction determined by charge residing on fullerene cages!

Ramon Valencia



Kitaura et al., Nano. Lett. 8, 693, (2008)

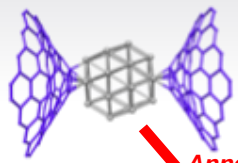
SWNH \leftrightarrow SWNT Transformations on Fe & Ni Catalysts

SCC-DFTB/MD Simulation

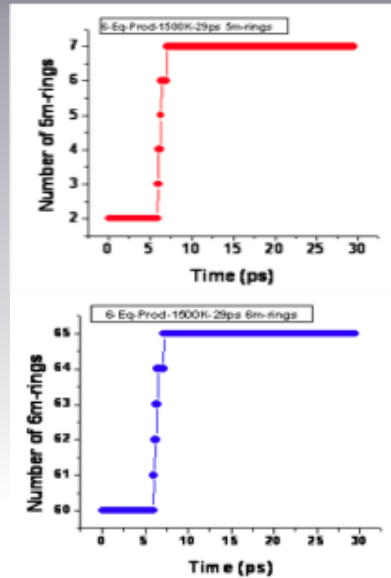
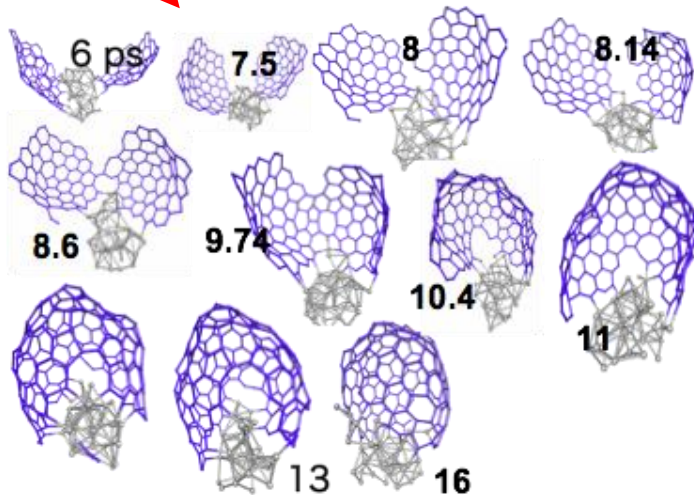
High-Temperature SWNH \leftrightarrow SWNT Conversion on Ni₃₈

RS Chandrakumar

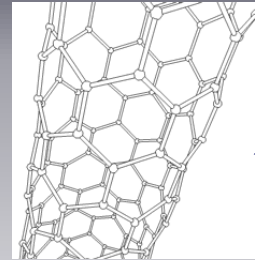
- Transformation occurs unassisted @ 1500 and 2500 K!
- Driven by formation of pentagons and hexagons in carbon structure.



Annealing at 2500 K



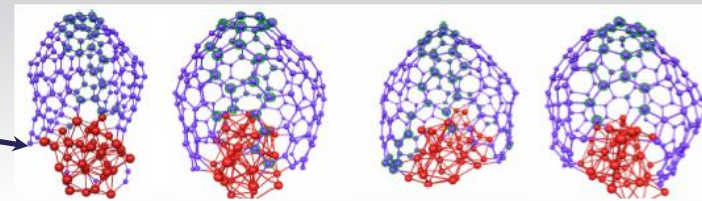
Is it Really A Single-Walled Nanotube??



A Perfect SWNT:
A hexagon-only tube connected to a cap/fullerene structure

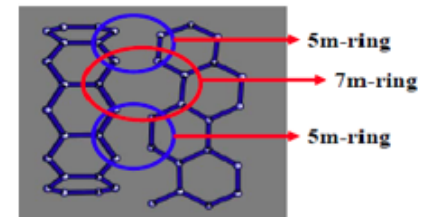
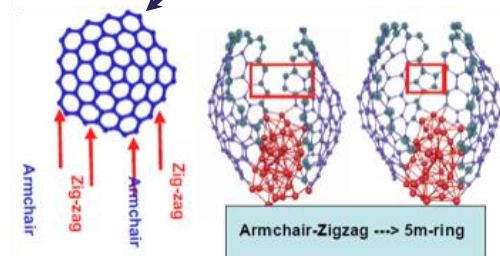
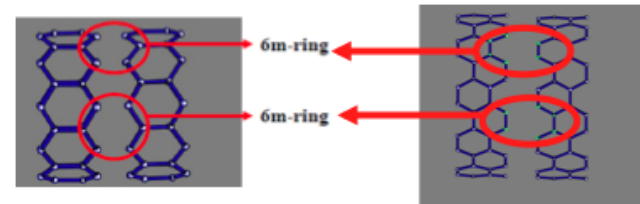
Converted SWNH's:
Structures contain several pentagons/heptagons

Final structures on Fe₃₈ @ 2500 K



Origin of Defect Structures?

Original nanocone contains both zigzag and armchair edges!

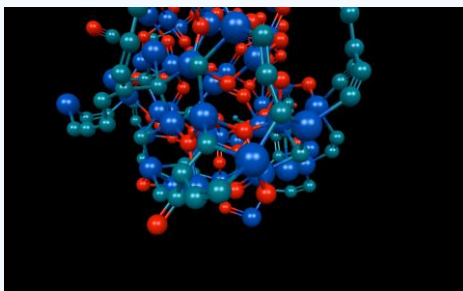


CVD Processes and SWNT Nucleation on SiO₂ Catalysts

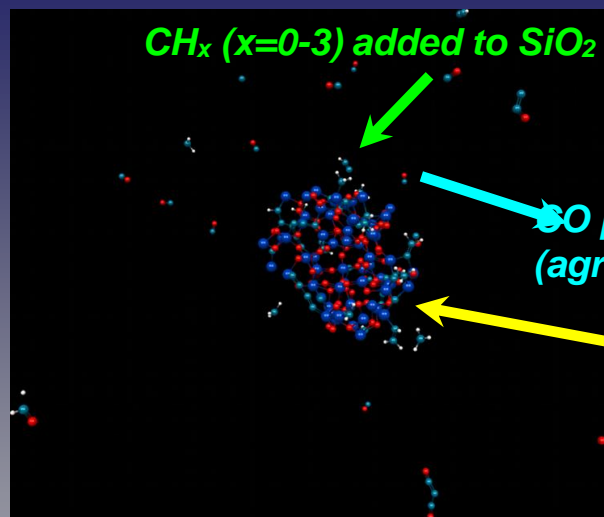
SCC-DFTB/MD Simulation

Alister Page

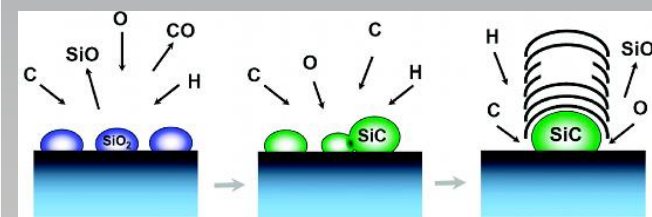
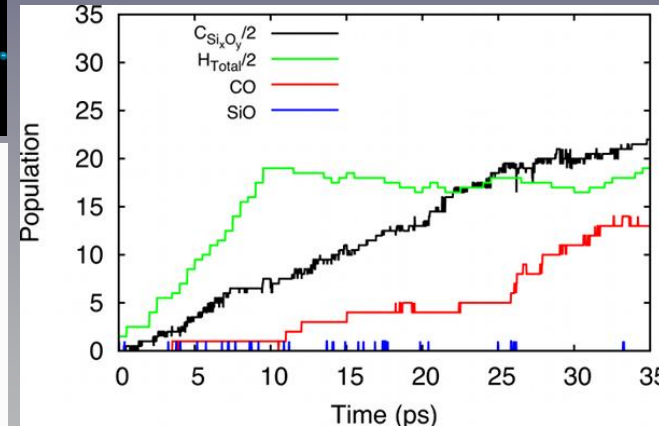
Carbon Ring Formation: The 1st Step to SWNT Nucleation



Simulated CH₄ CVD on SiO₂ Nanoparticles



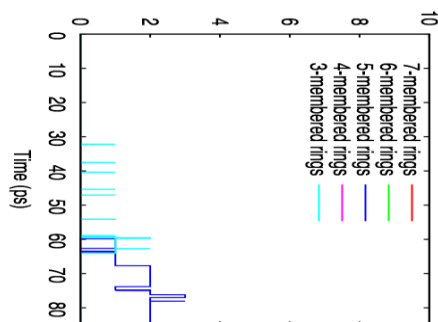
Outer regions of SiO₂ reduced to SiC



Bachmatiuk et al., ACS Nano 3, 4098, (2010)

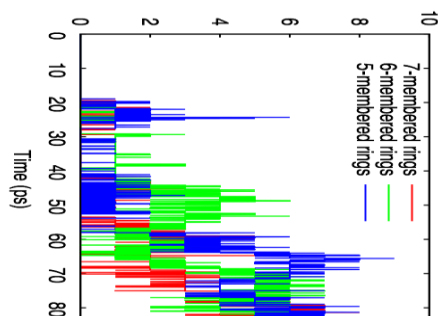
Carbon Ring Production

No. of Rings



Carbon-Silicon Ring Production

No. of Rings

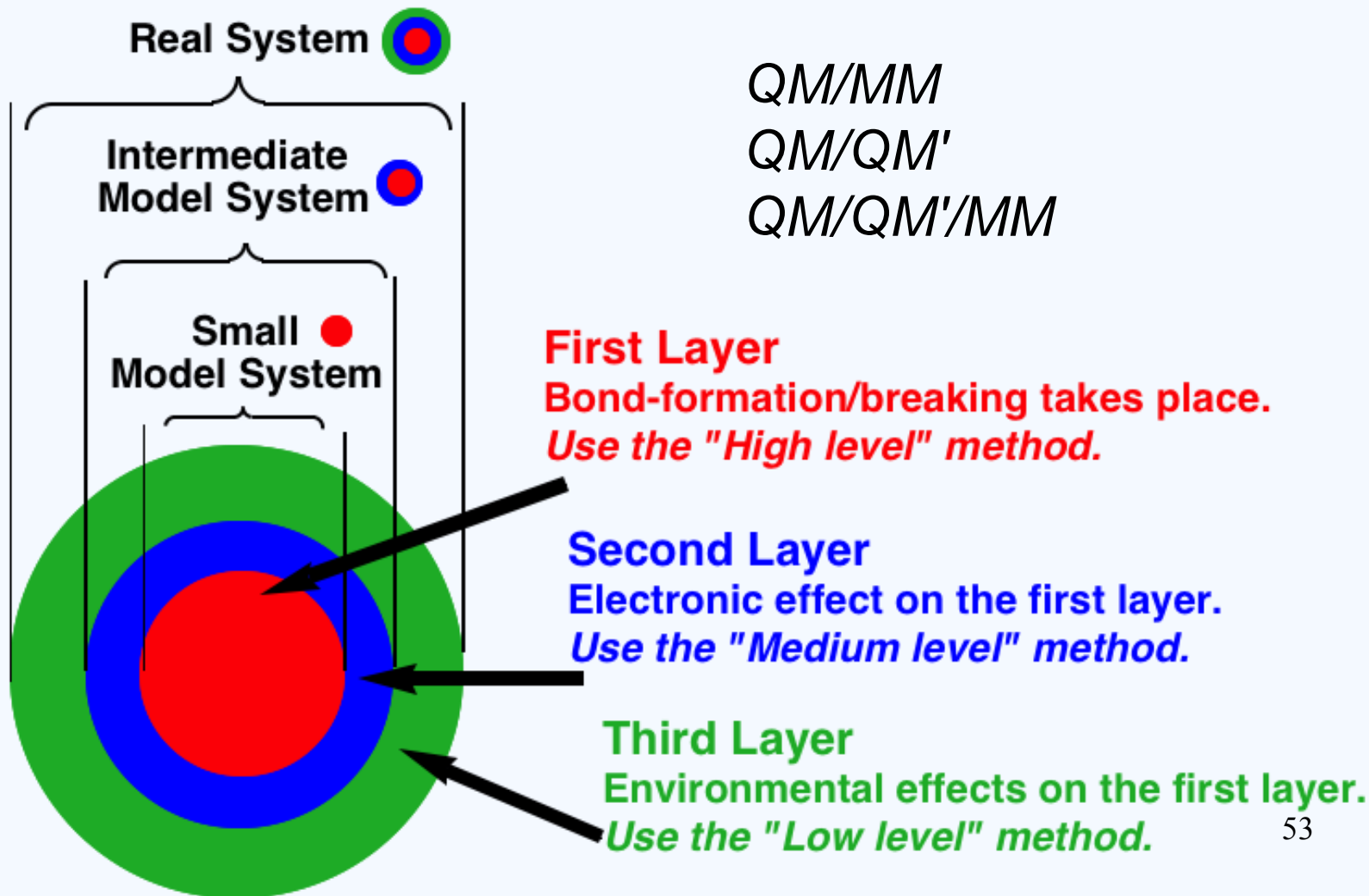


Cyan=C Blue=Si Red=O White=H

高精度量子化学で計算できないような大きな分子の計算

The ONIOM Method (an onion-skin method)

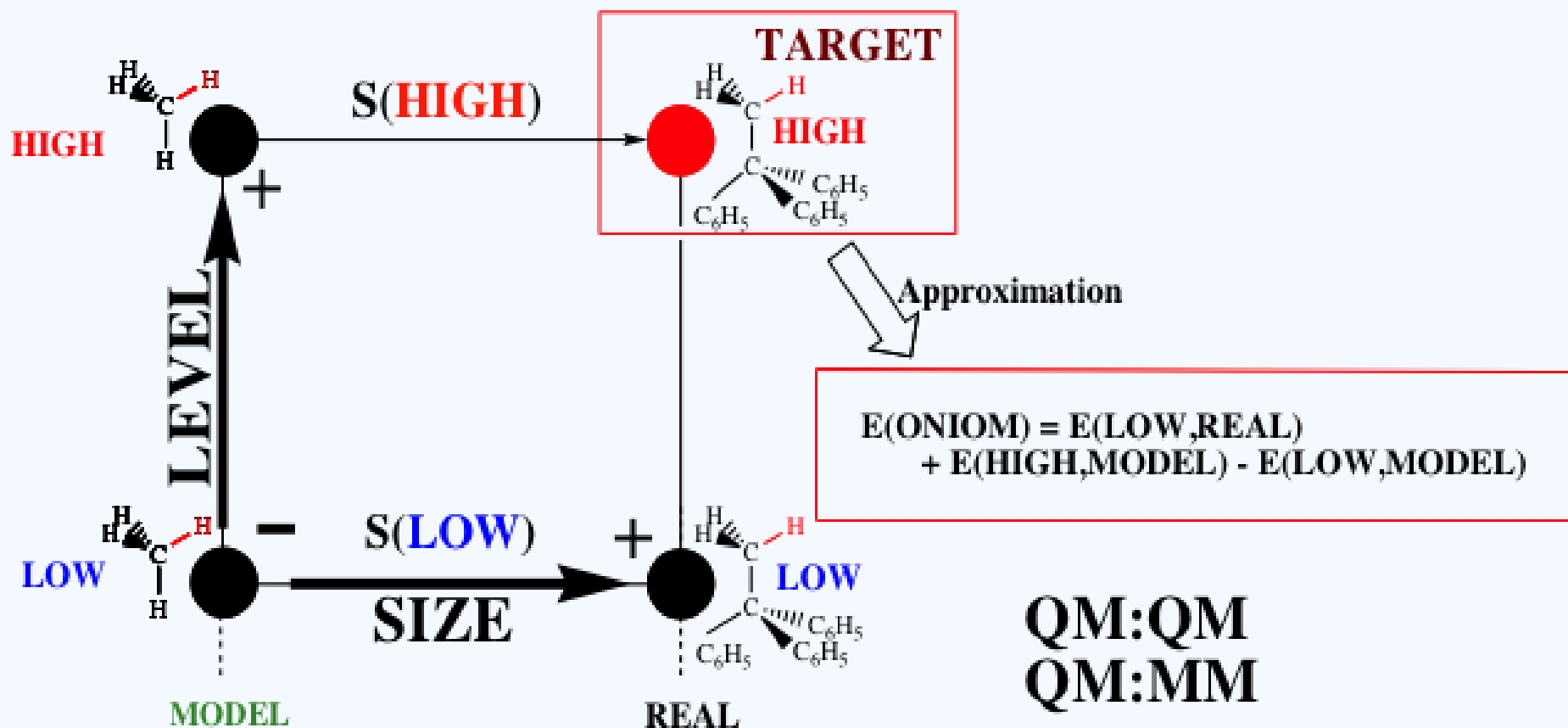
(Own N-layered Integrated molecular Orbital and molecular Mechanics)



ONIOM Energy:

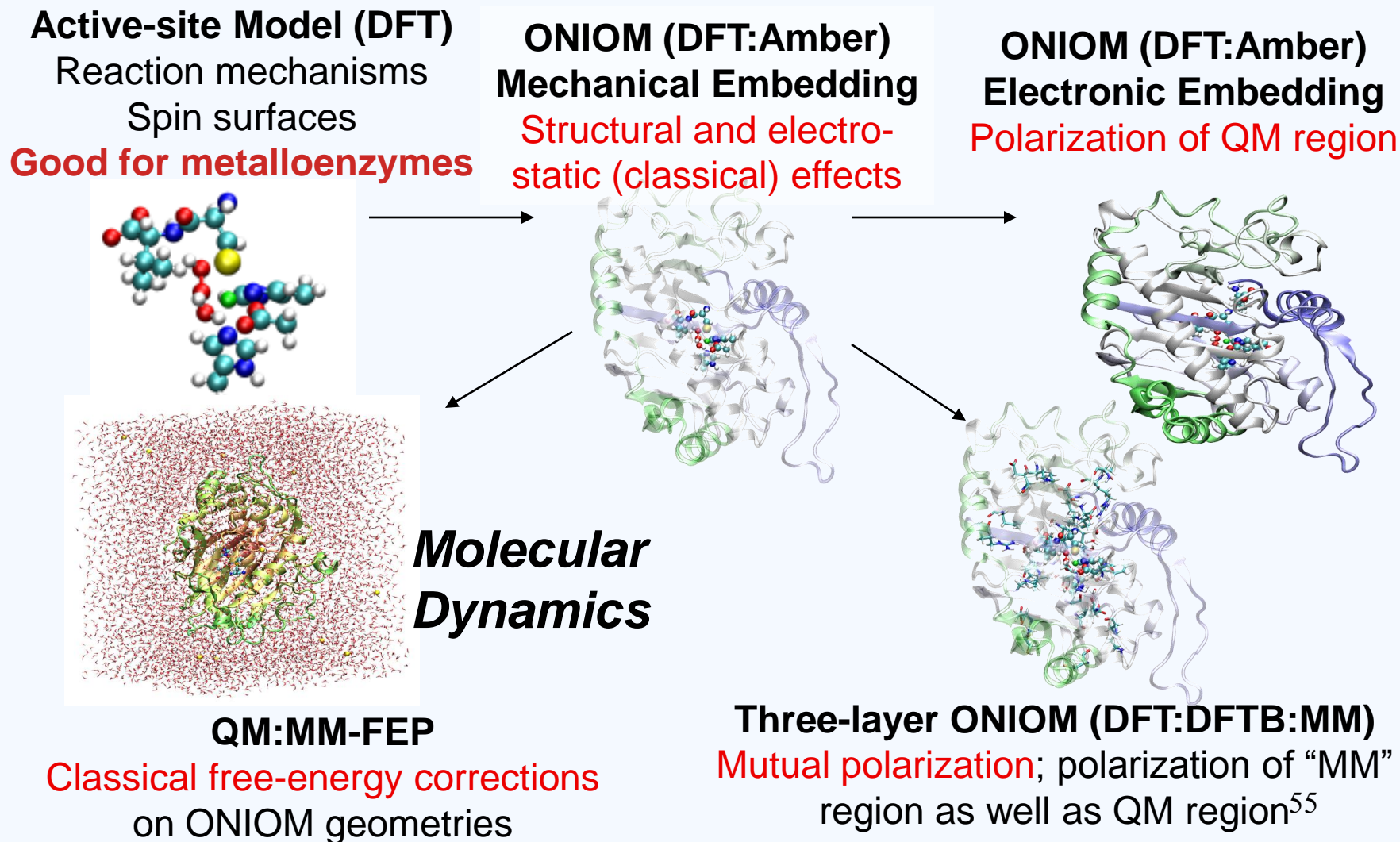
Approximation for the target (high,real) calculation

Level Effect and Size Effect assumed uncoupled



蛋白の中での化学反応 — 酵素反応

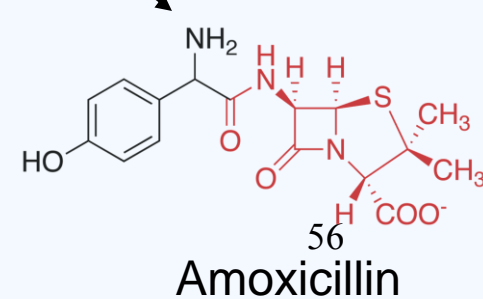
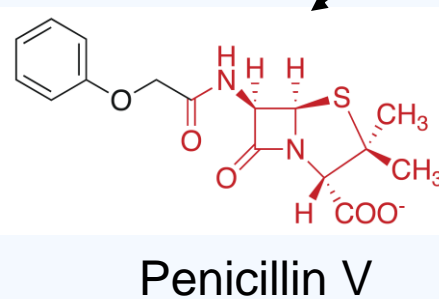
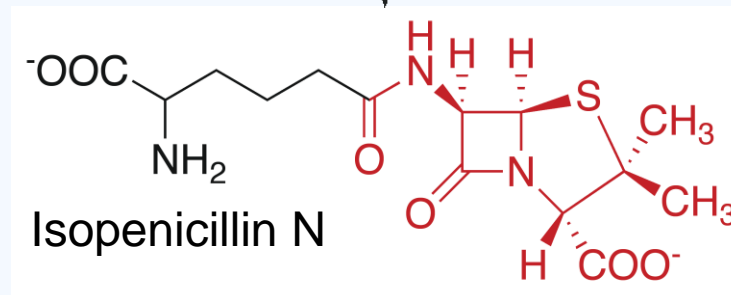
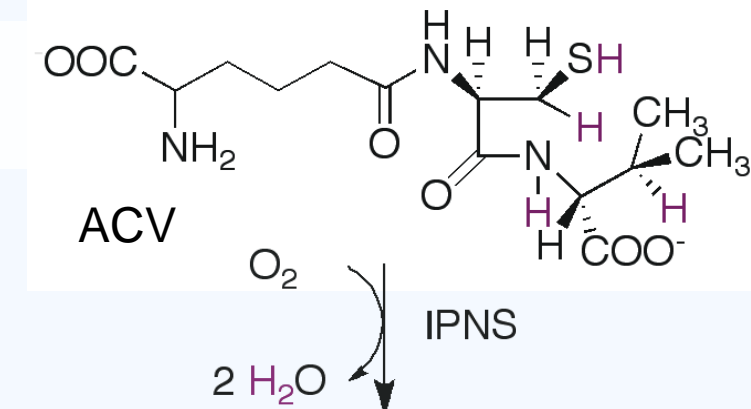
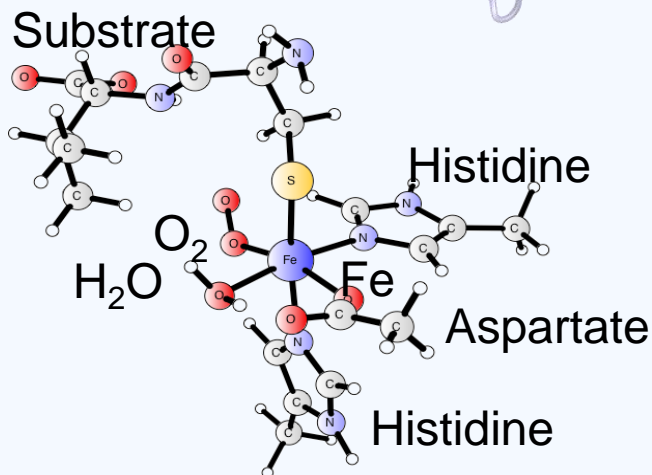
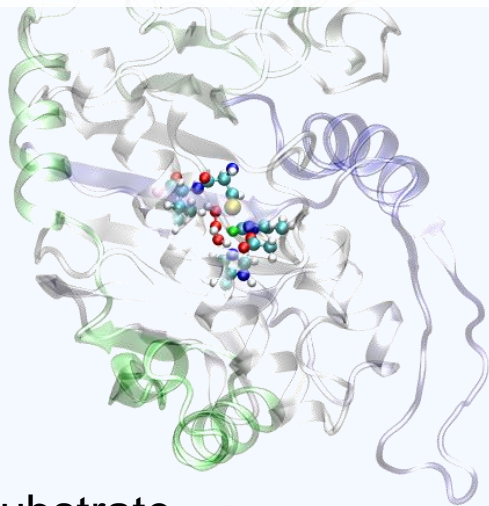
Strategy for Protein Effects in Enzymes



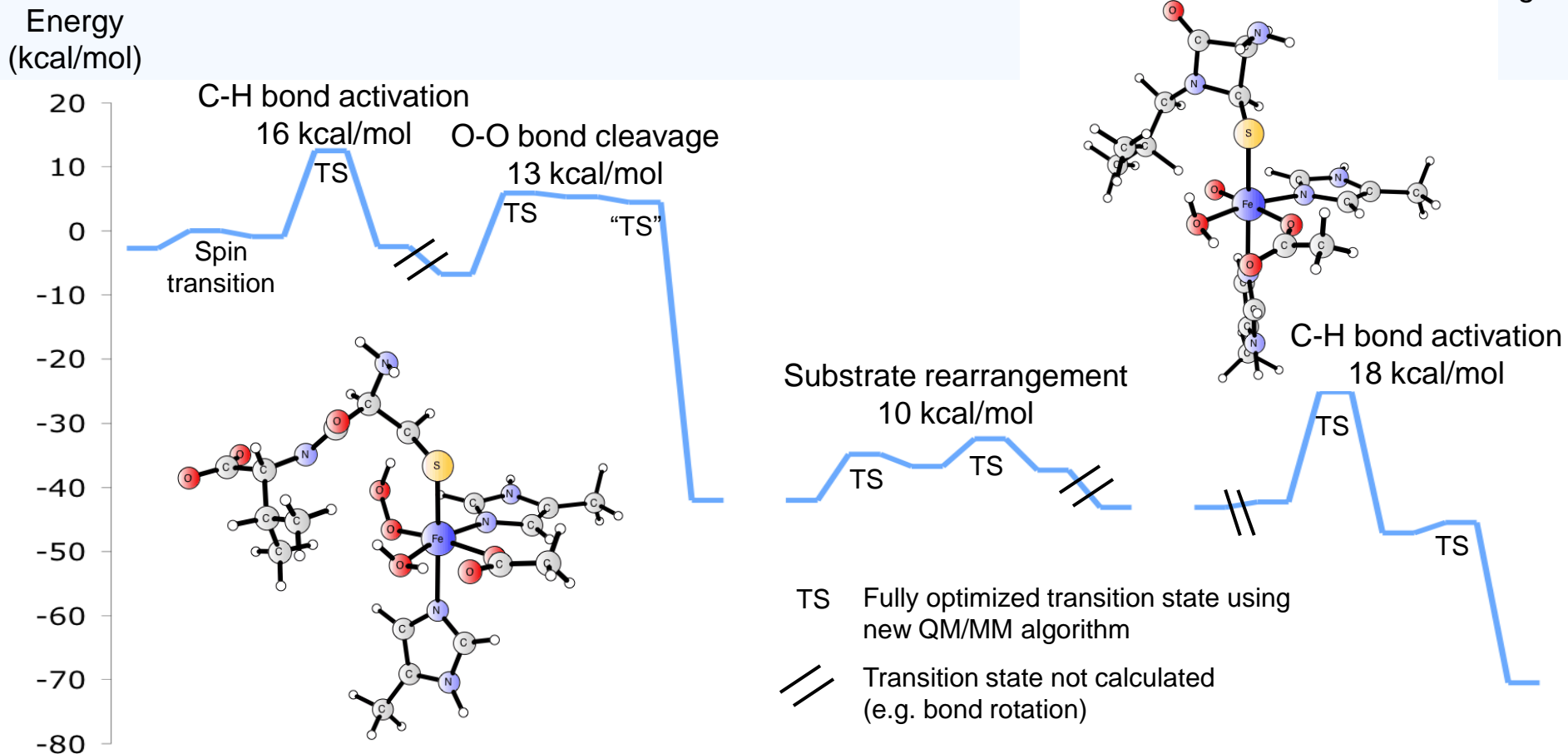
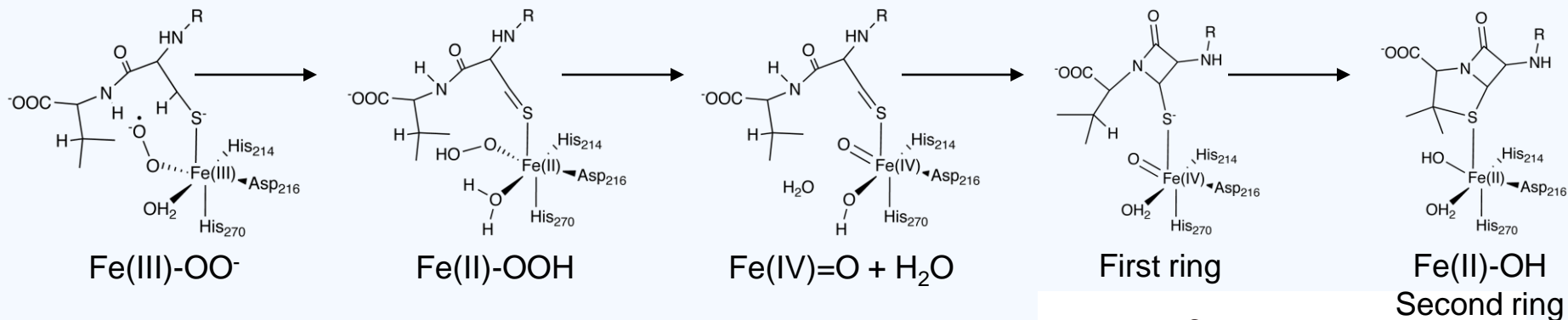
Biosynthesis of Antibiotics in Isopenicillin N Synthase (IPNS)

Lundberg, Kawatsu et al. (2007, 2008)

Oxygen-activated
non-heme iron enzyme



Proposed Reaction Mechanism - ONIOM Calculations

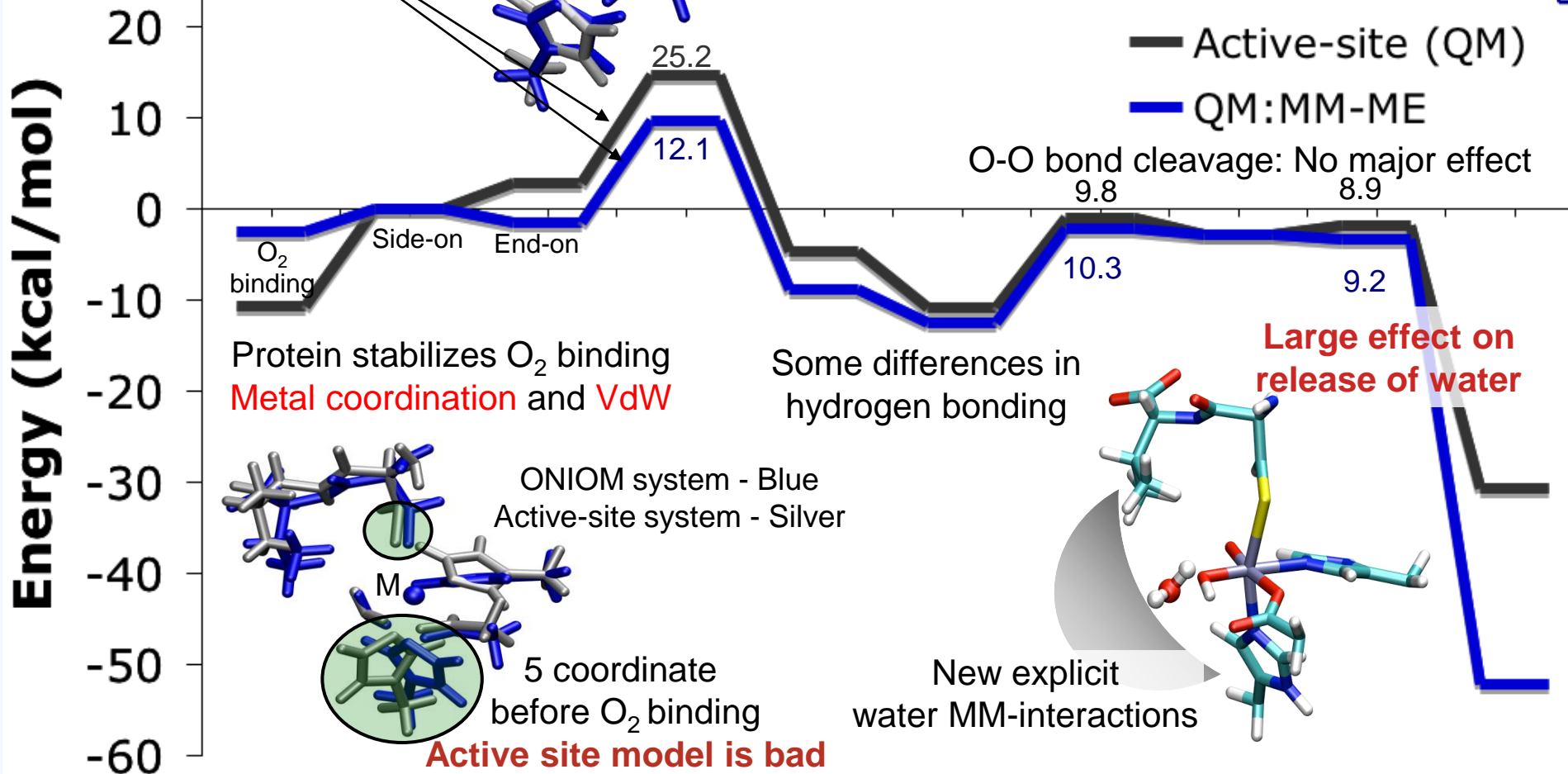
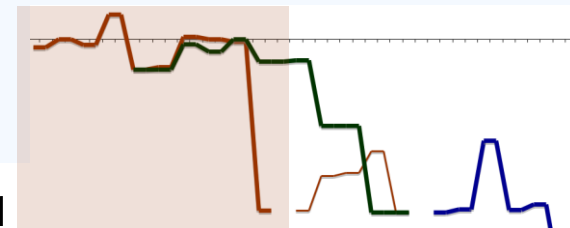


Comparing Active-Site and ONIOM-ME Models

C-H activation TS (6 coord) - No major effect vs. end-on O₂ (also suggested by Solomon)

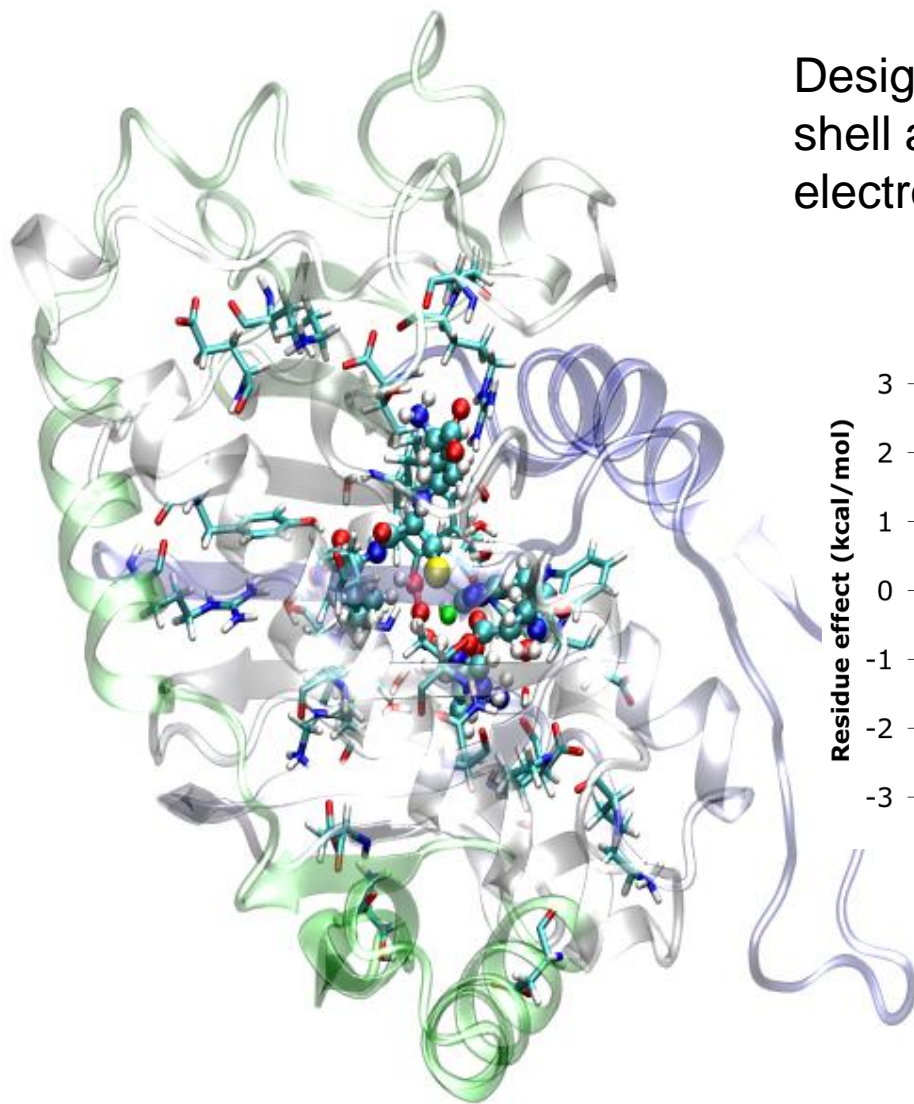
Ligand donor mechanism

Optimized with active-site and ONIOM Model 1

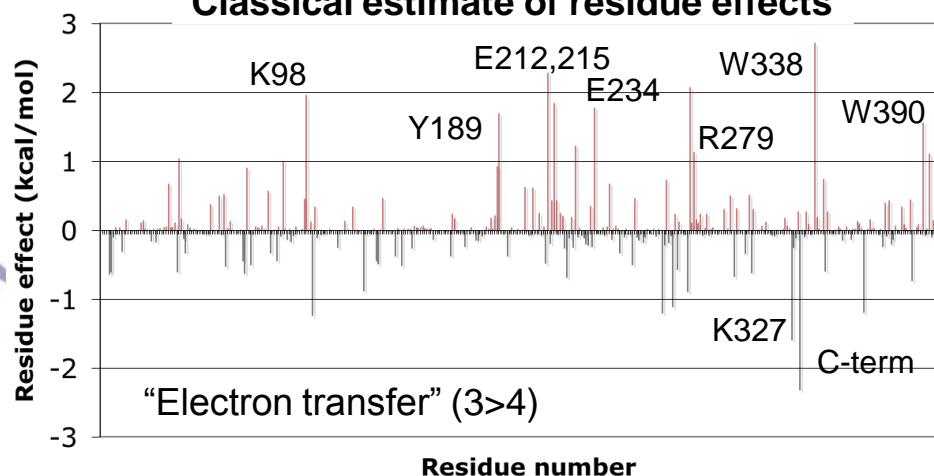


ONIOM DFT:DFTB:MM Model for IPNS

Design the DFTB layer by including second-shell amino acids and those with large electrostatic effects in a classical description.



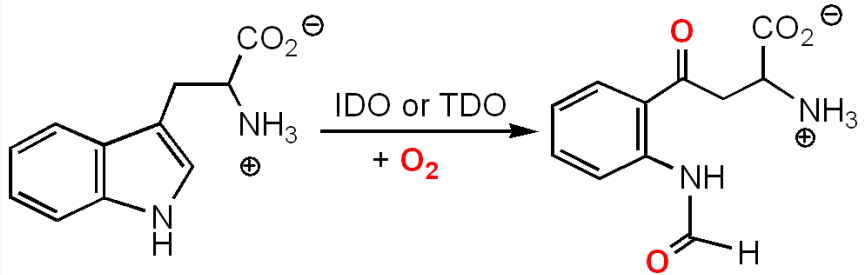
Classical estimate of residue effects



Layer	Atoms	Representation
High	65	Ball and stick
Low	5368	Cartoon

A missing mechanism of tryptophan 2,3-dioxygenase

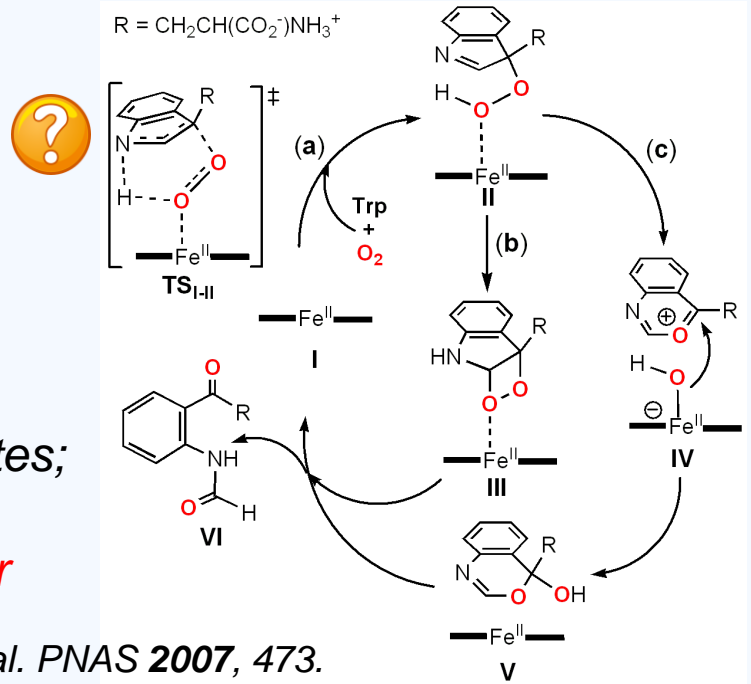
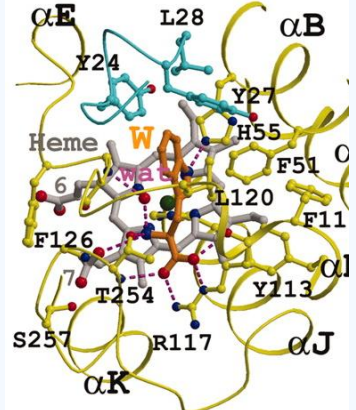
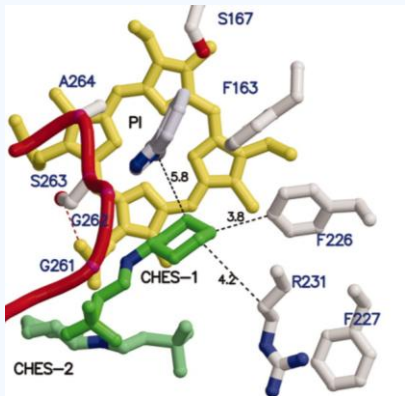
Chung, L. W.; Li, X.; Sugimoto, H.; Shiro, Y.; Morokuma, K. *JACS* **2008**, 130, 12298; unpublished.



TDO: Kotake, Y.; Masayama, I. Z. *Physiol. Chem.* **1936**, 243, 237.
IDO: Yamamoto, S.; Hayaishi, O. J. *Biol. Chem.* **1967**, 242, 5260.

Unlike P450, peroxidase, HO, **unclear mechanism** (deprotonation → electrophilic addition at C3 with Fe^{II}-O₂); physiological roles (e.g. suppress T cell proliferation)

X-ray structures of hIDO(left) & xcTDO (right) Recently-proposed mechanisms

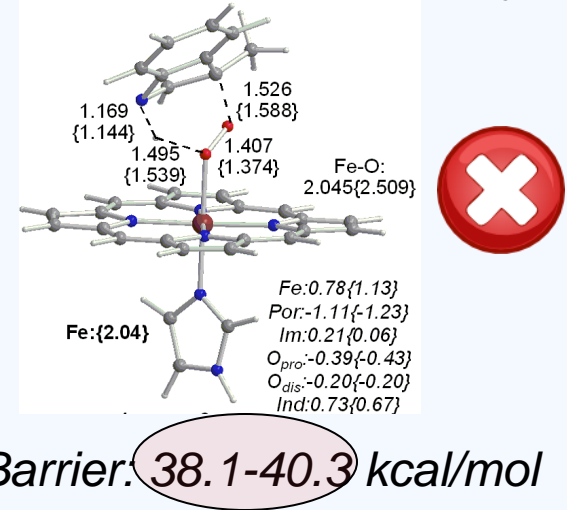
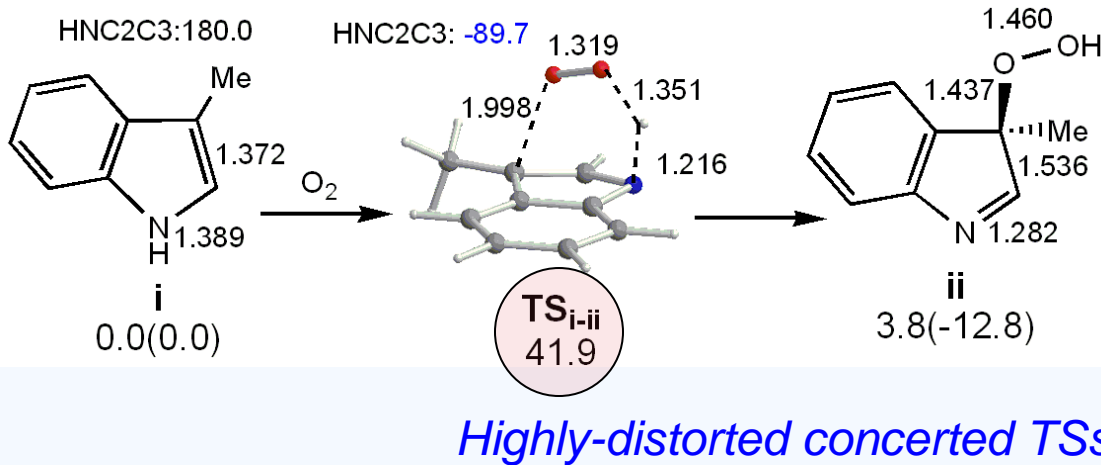


Unique active-site: highly hydrophobic active sites; unimportant polar residues (mutation);
 → No need external proton and electron donor

IDO: Sugimoto, H. et al. *PNAS* **2006**, 2611. **TDO:** Forouhar, E. et al. *PNAS* **2007**, 473.

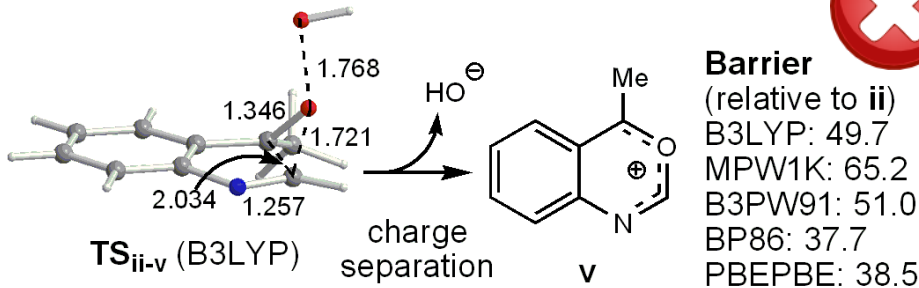
Active-site model (B3LYP Results)

The proposed **electrophonic addition concerted proton-transfer** pathway?

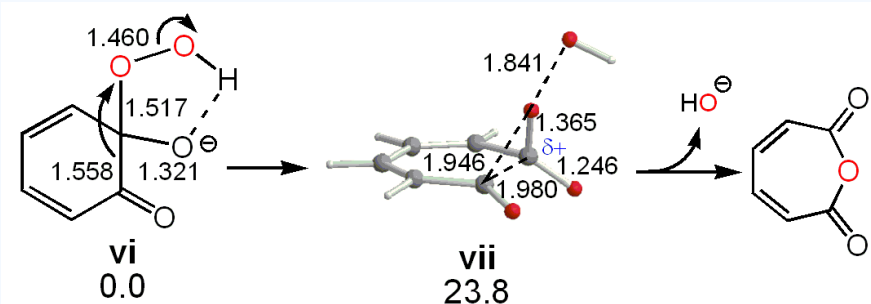


Commonly-accepted **Criegee-type Rearrangement** pathway?

High barrier for a neutral TDO substrate

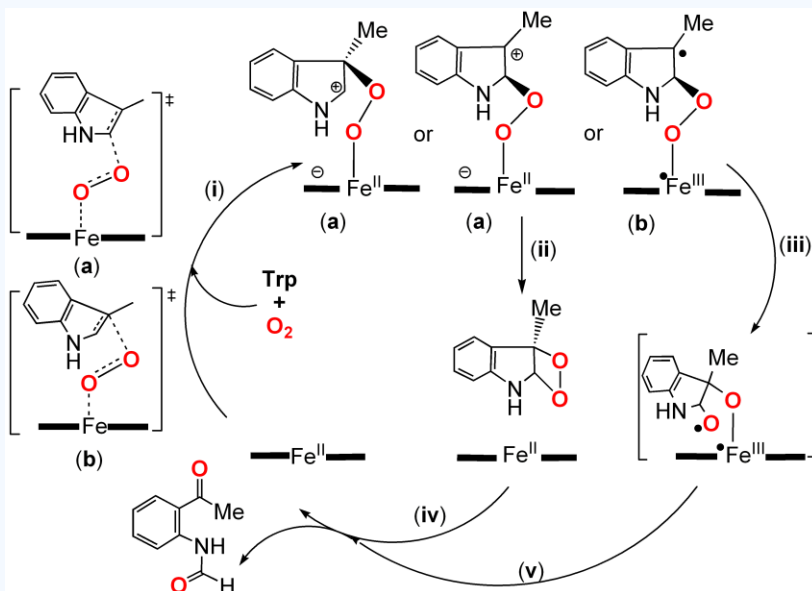


Low barrier for an anionic non-heme substrate



High-energy proposed pathways → Another operating mechanism!!

Summary of the most favorable pathways (active-site model)



- ❌ Concerted addition and proton-transfer
- ✅ **Direct** (a) electrophilic and (b) **radical addition** from Fe^{II}-O₂ and Fe^{III}-O₂⁻ species at either **C2** or C3
- ❌ Widely-believed Criegee rearrangement
- ✅ Formation of dioxetane intermediate pathway (ii) or O-O cleavage pathway to give **ferryl-oxo** followed by oxo-attack (iii & iv)

Chung, L. W.; Li, X.; Sugimoto, H.; Shiro, Y.; Morokuma, K. *JACS* **2008**, *130*, 12298.

Subsequent experimental findings

	L-Trp		1-Me-L-Trp	
	K _{cat} (s ⁻¹)	K _M (μM)	K _{cat} (s ⁻¹)	K _M (μM)
hIDO (wt)	1.7	21	0.027	150
hIDO (S167A)	1.95	-	0.032	31
xcTDO (wt)	19.5	114	-	-
xcTDO (H55A)	2.86	133	0.048	59

Deprotonation is not necessary

Chauhan, N. et al. *JACS* **2009**, *131*, 134186.

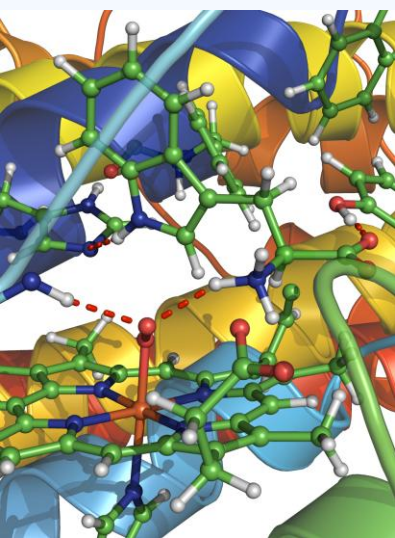
Observation of Fe^{III}-O₂⁻ and ferryl-oxo intermediates in hIDO by resonance Raman

Lewis-Ballester et al. *PNAS* **2009**, *106*, 17371;

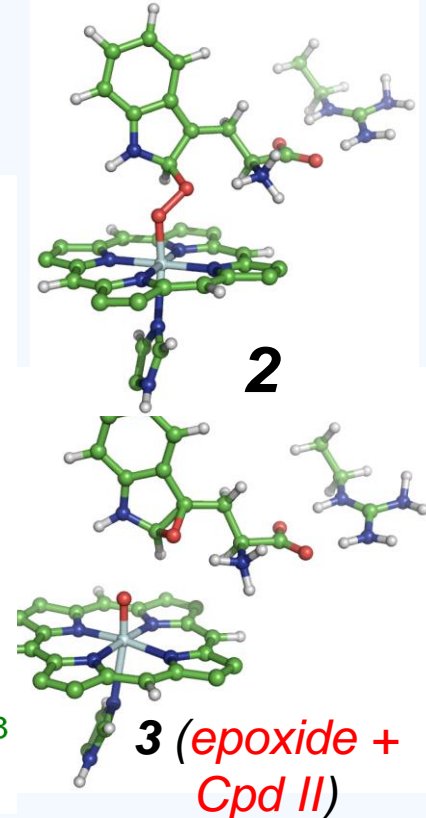
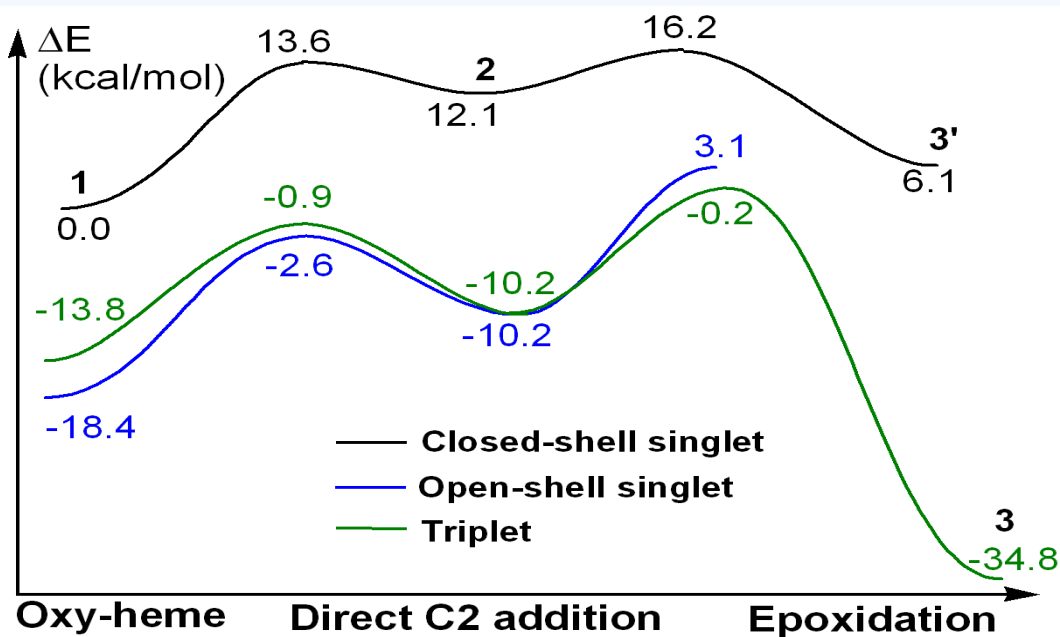
Yanagisawa et al. *Chem. Lett.* **2010**, *39*, 36

ONIOM(B3LYP:Amber) results for xcTDO

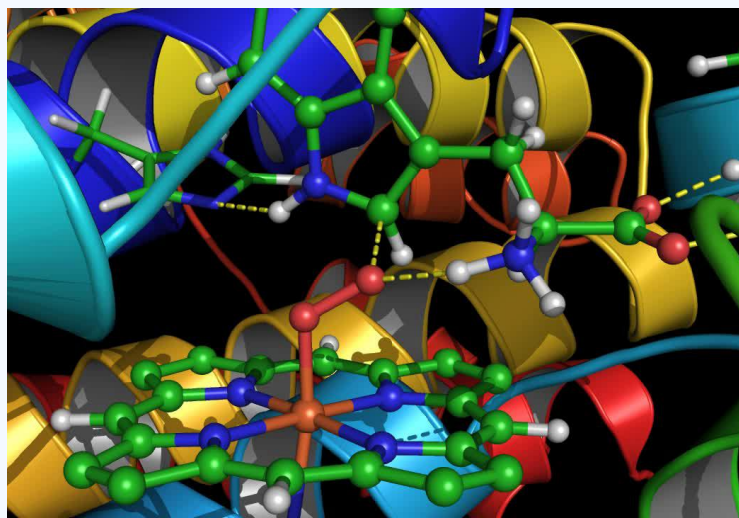
First oxygen incorporation processer



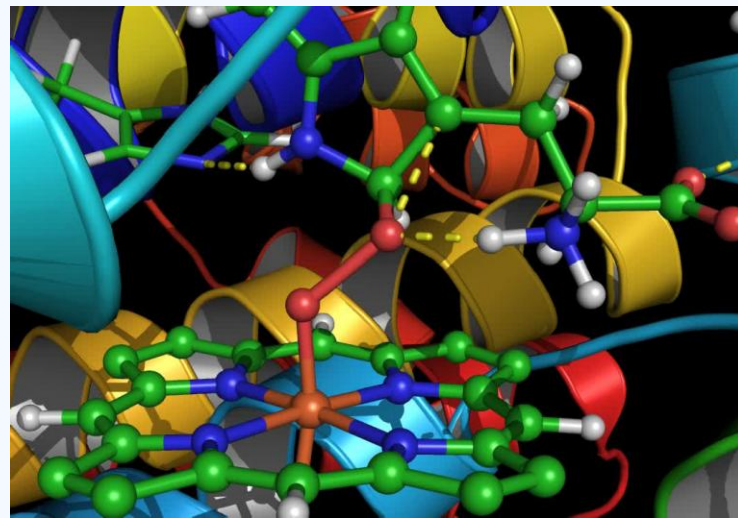
1



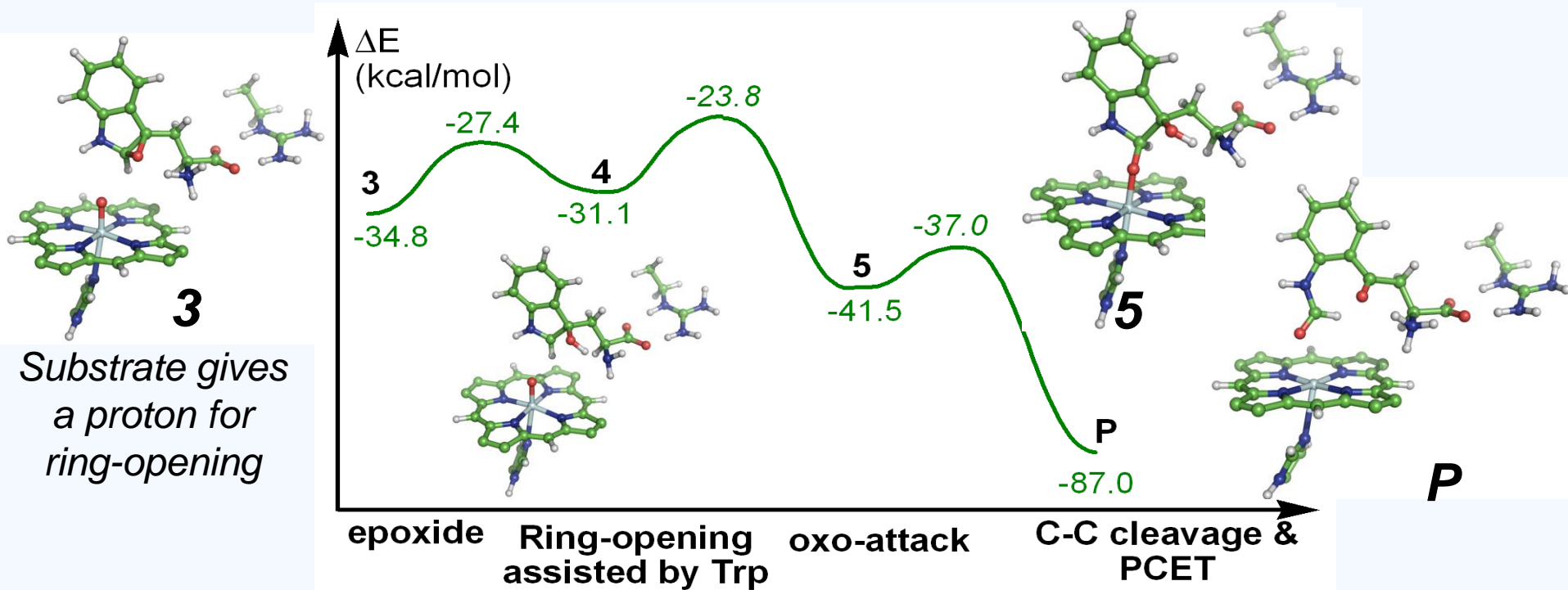
Direct radical addition TS at C2 only



Epoxidation TS



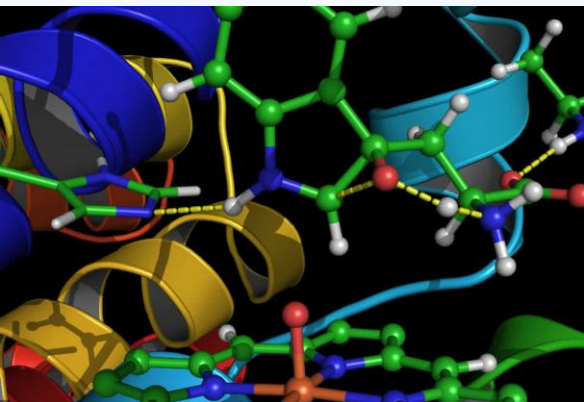
Second oxygen incorporation processes



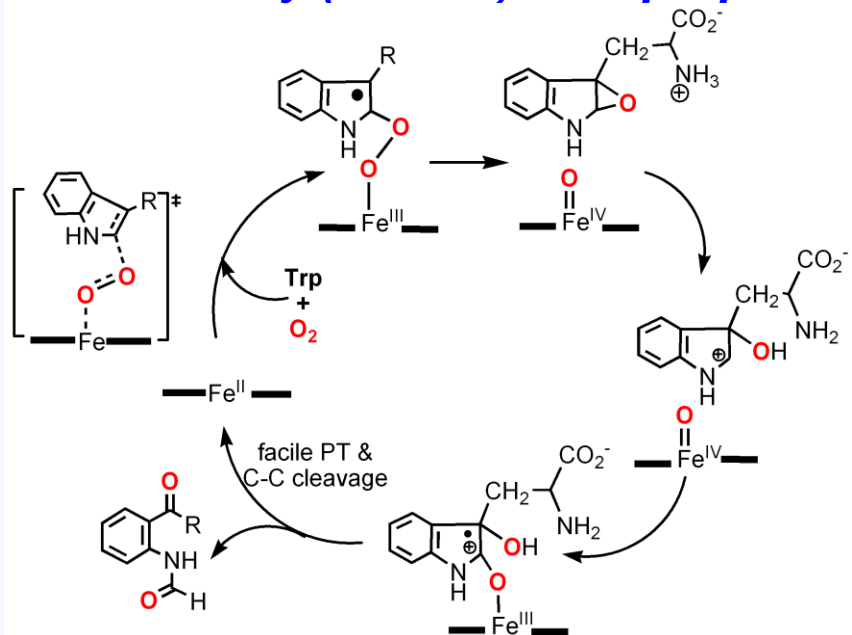
**PT-catalyzed
regioselective RO TS**

Oxo-attack TS

C-C cleavage TS

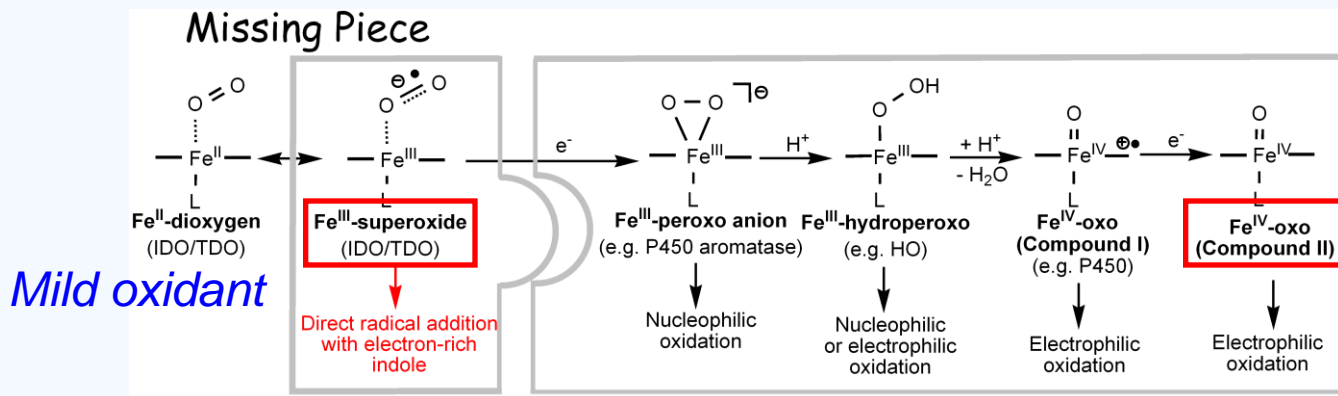


Summary (ONIOM): Our proposed exceptional pathway for xcTDO



Direct radical addition of Fe^{III}-O₂⁻ specie
at C2 of Trp
*Homolytic O-O cleavage and ring-
closure* to give ferryl-oxo and epoxide
Acid-catalyzed ring opening
Oxo-attack
C-C cleavage and back proton transfer

O₂ activation and oxidation process in heme systems: Dual oxidants in TDO



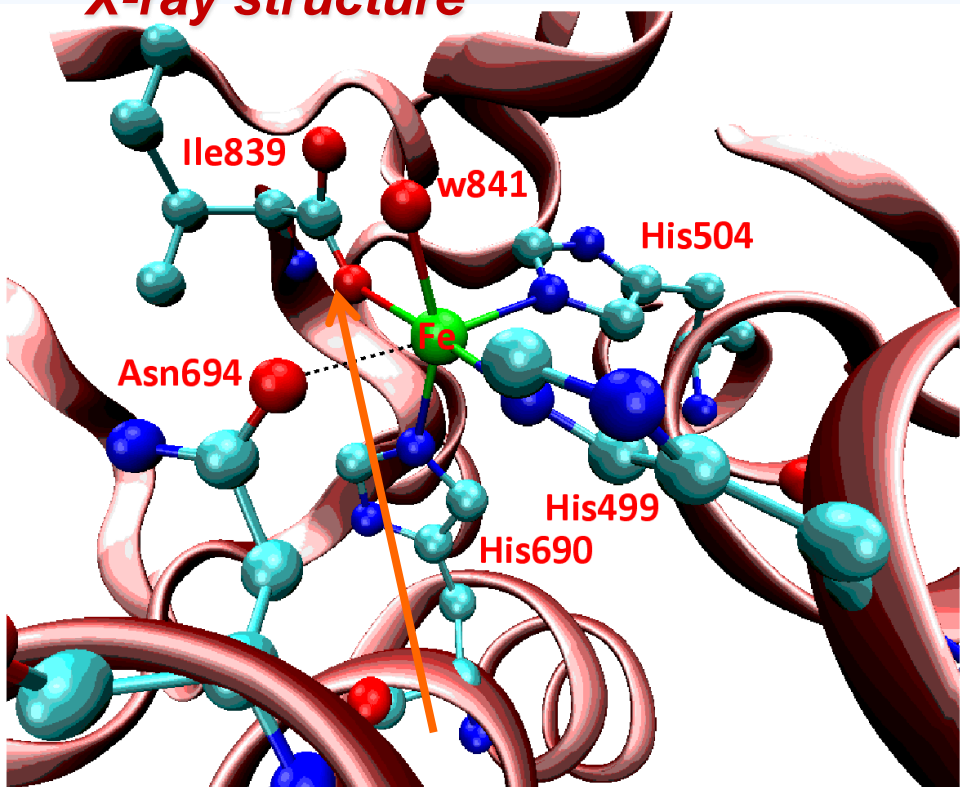
*Very strong oxidant
Cpd I & II*

Besides non-heme oxygenases, *not-well-recognized ferric superoxide and ferryl-oxo species* as the oxidants in heme-containing TDO
→ *Old heme oxygenase, New heme chemistry*

Ferrous soybean lipoxygenase (SLO-1)

Hajime Hirao and KM, *J. Phys. Chem. Lett.* (2010) 1, 901–906.

X-ray structure

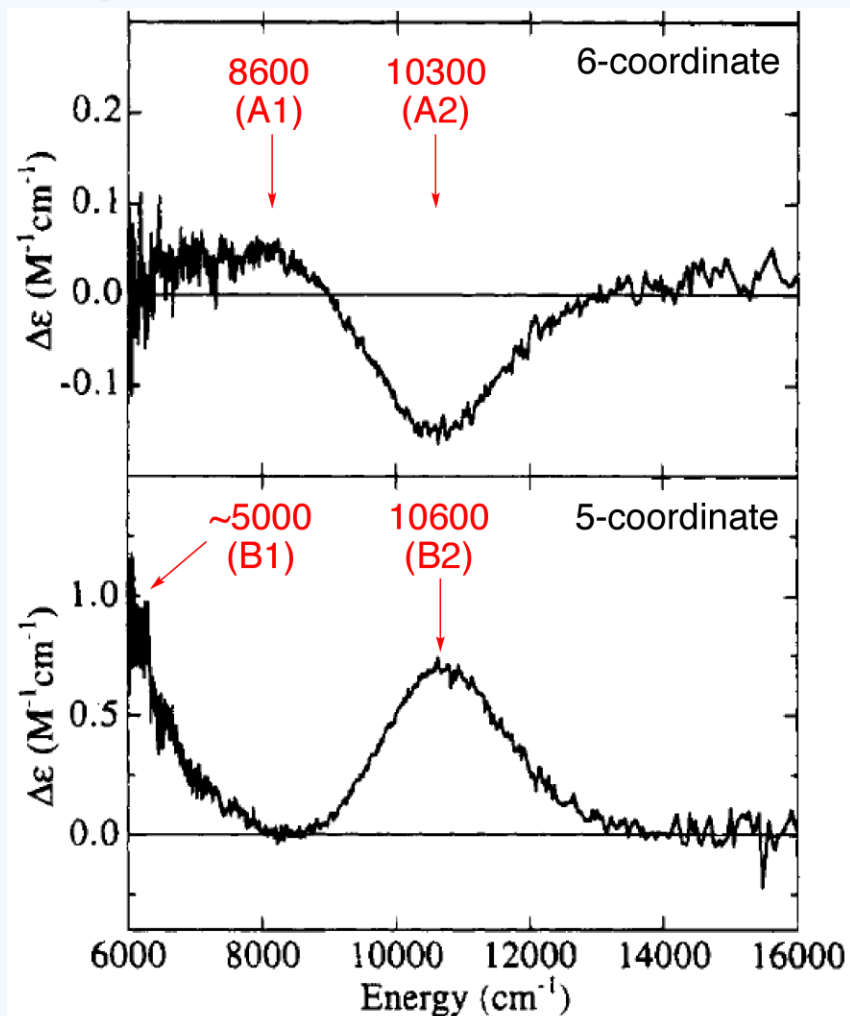


$R(\text{Fe}-\text{O}_{694}) = 3.05 \text{ \AA} (1\text{YGE})$
 $2.87 \text{ \AA} (1\text{F8N})$

Why is $R(\text{Fe}-\text{O}_{694})$ is so long?

Minor et al., *Biochemistry* 1996/2001.

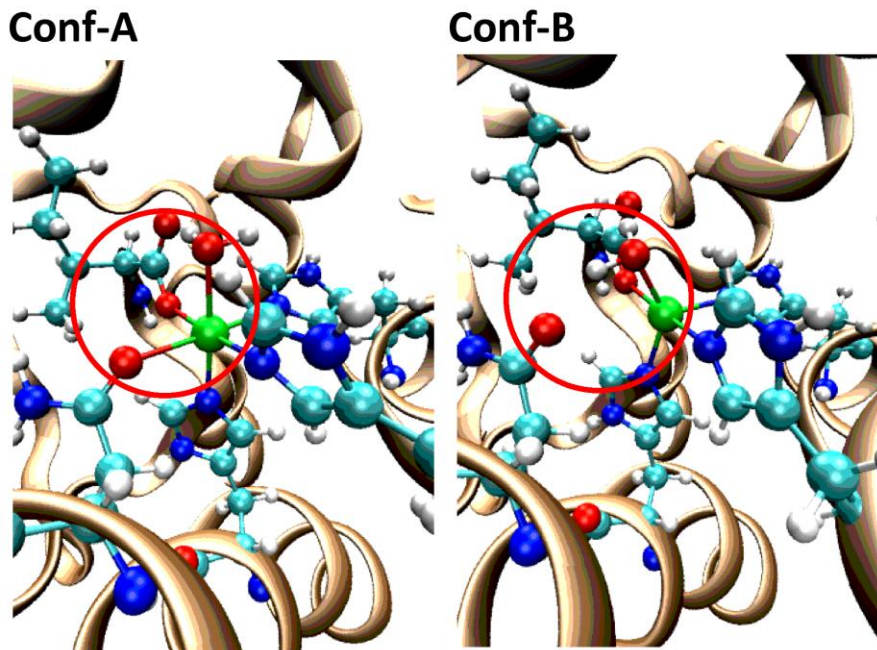
CD spectra



What are the two forms?

Solomon et al., *JACS* 1995; *Chem. Biol.* 1997.

Geometry



Conf-A: Short Fe-O₆₉₄ & large O-Fe-N

Conf-B: Long Fe-O₆₉₄ & small O-Fe-N

→ Different in water orientation.

→ Average agreed well with X-ray.

Key geometric parameters (Å or degrees)

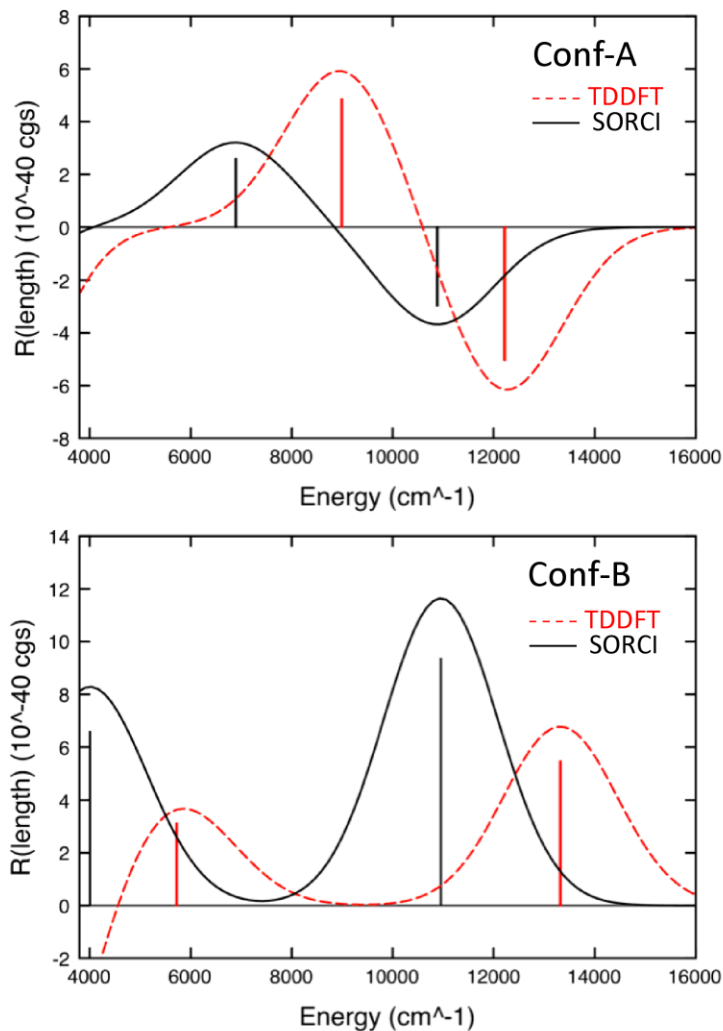
	Conf-A	Conf-B	Average(A/B)	Exptl (WT)	Exptl (Q697E)
$\angle O_W\text{-Fe-N}_{690}$	176.9	140.0	158.5	157.4	140.9
$r(\text{Fe-O}_{694})$	2.39	3.46	2.93	2.87	3.41

Our proposal: WT X-ray structure is a mixture of Conf-A and Conf-B.

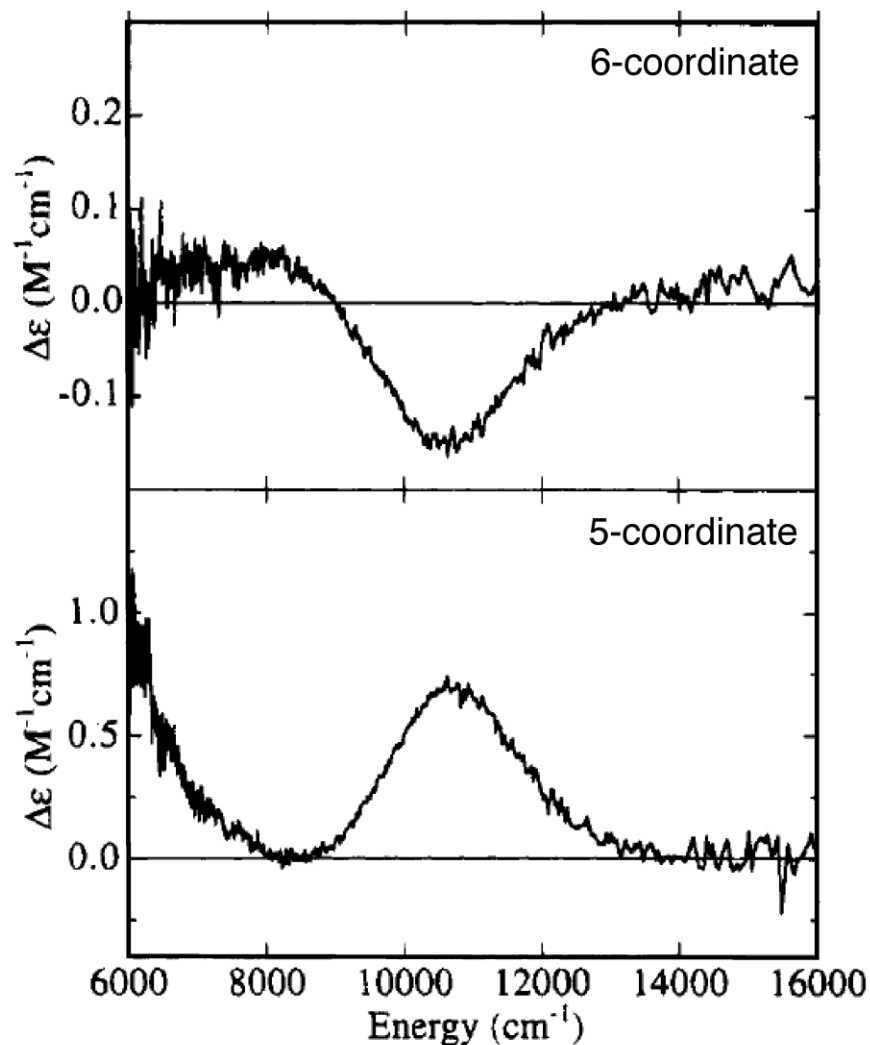
Q697E will contain only Conf-B.

CD spectra

(a) Theory



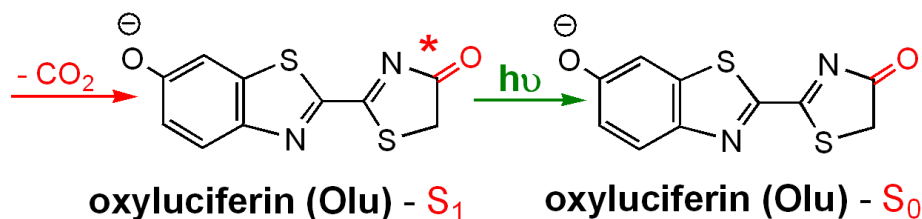
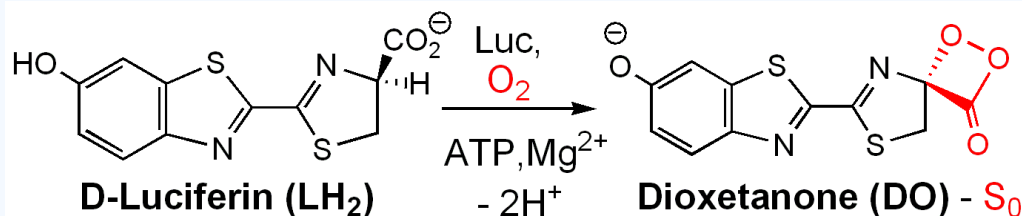
(b) Experiment



- **Good agreement with the experimental spectra.**
- **Two forms in experiment are Conf-A and Conf-B.**

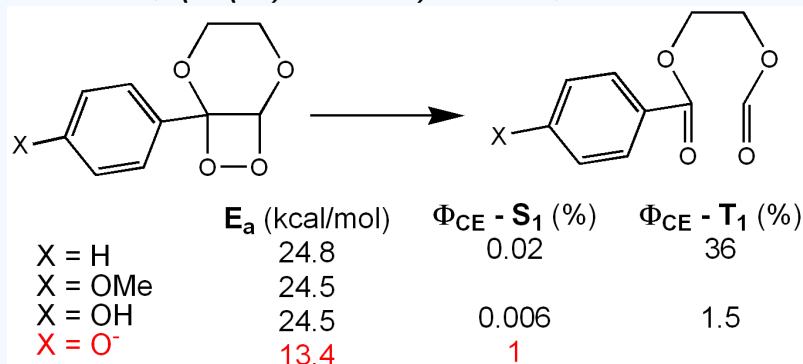
Mechanism of Efficient Firefly Bioluminescence via Adiabatic TS and Seam of Sloped Conical Intersection

Chung, L. W.; Hayashi, S.; Lundberg, M.; Nakatsu, T.; Kato, H.; Morokuma, JACS 2008, 130, 12880.



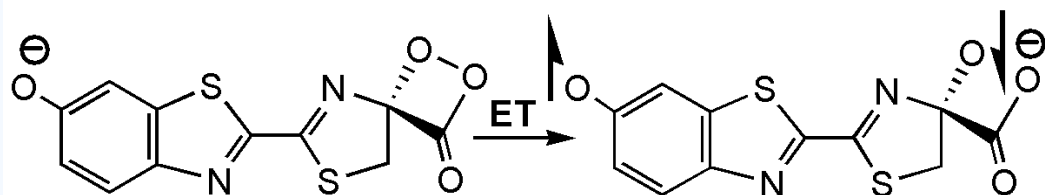
High efficient bioluminescence, ($\Phi(bl) = 0.42$): Ando, et al. Nature Photonics 2008, 2, 44.

Bio-imaging



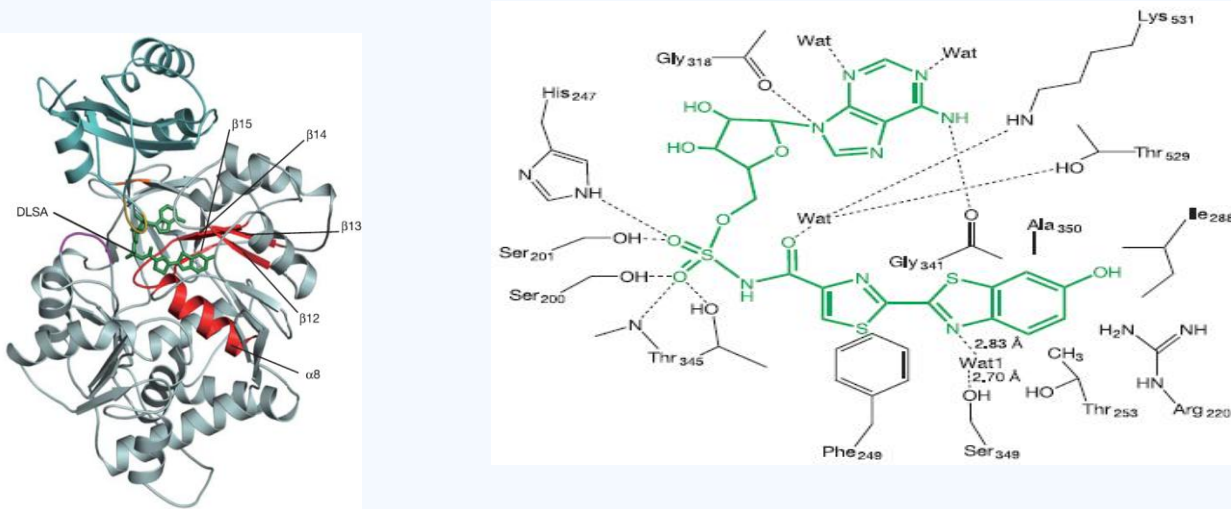
Schaap, A. P.; Gagnon, S. D. J. Am. Chem. Soc. 1982, 104, 3504

Intramolecular Chemically Initiated Electron-Exchange Luminescence



Koo, J.-Y.; Schmidt, S. P.; Schuster, G. B. Proc. Natl. Acad. Sci. U.S.A. 1978, 75, 30.

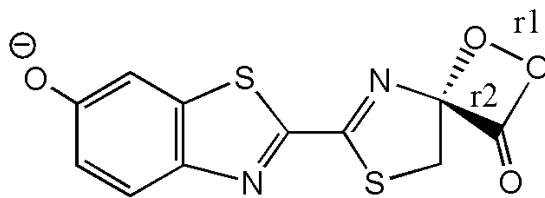
X-ray structures of the Japanese firefly



Nakatsu, T.; Ichiyama, S.; Hiratake, J.; Saldanha, A.; Kobashi, N.; Sakata, K.; Kato, H. *Nature* **2006**, 440, 372.

Computational Models & Methods

Bioluminescence of the firefly dioxetanone (DO)



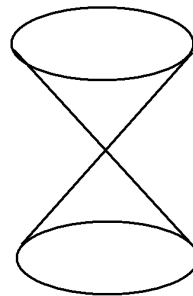
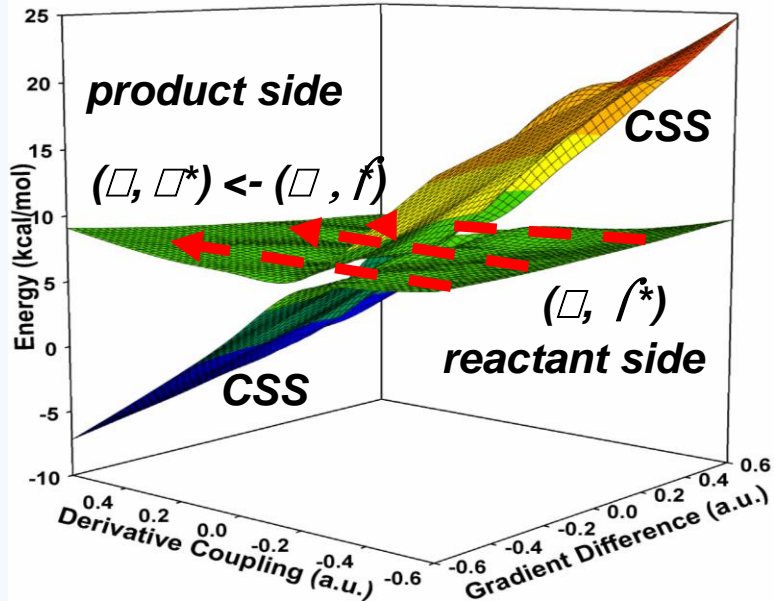
Ideal: (32e,26o)

Our practice active space:
(4e,4o) for C-C and O-O bonds
(8e,8o) for π -conjugated part

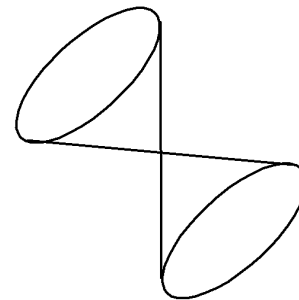
Active Site Model: Geometry optimization: SA-CASSCF(12e,12o)/6-31G* (S_0 , S_1)

Single-Point calculations: CASPT2(12e,12o)/6-31G*

Topology around MECI



(a) Peaked conical intersection

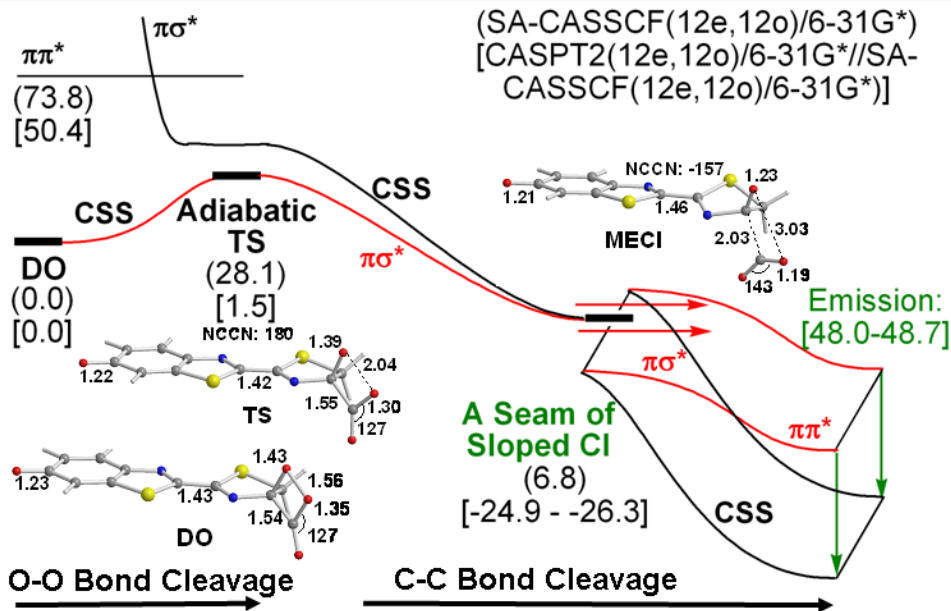
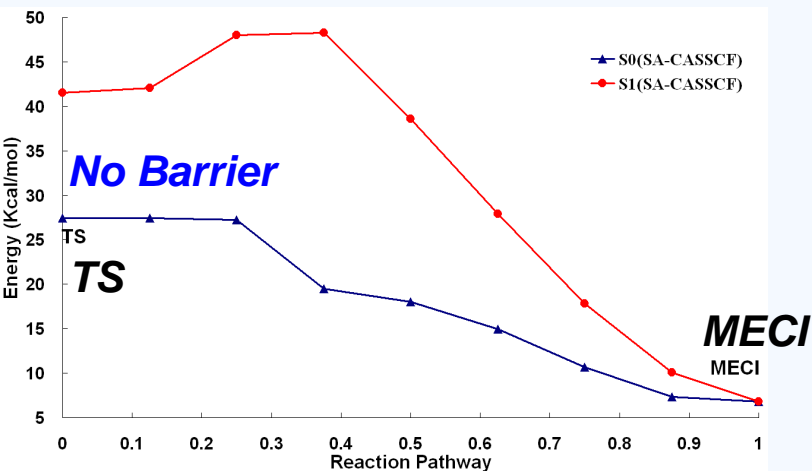


(b) Sloped conical intersection

Sloped MECI \rightarrow chemi-excitation
Extend seam \rightarrow Higher transition probability

Schematic overall mechanism

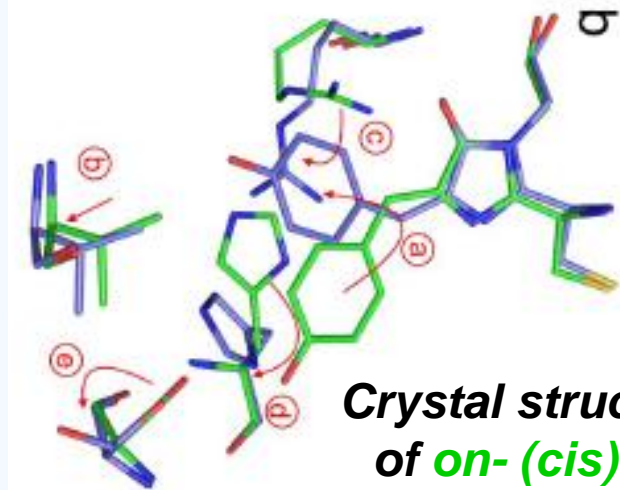
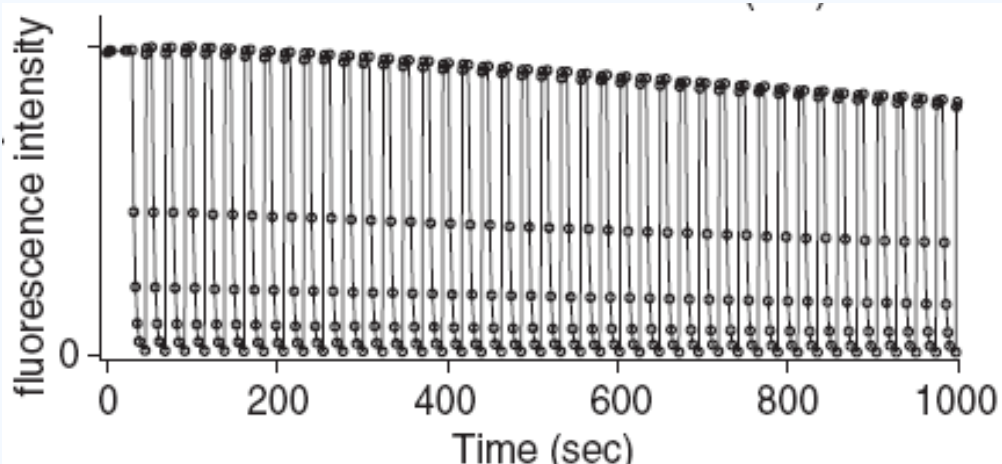
Linear interpolated pathway



Chung, L. W.; Hayashi, S.; Lundberg, M.; Nakatsu, T.; Kato, H.; Morokuma, JACS 2008, 130, 12880.

Dynamics in Protein Environment in Progress

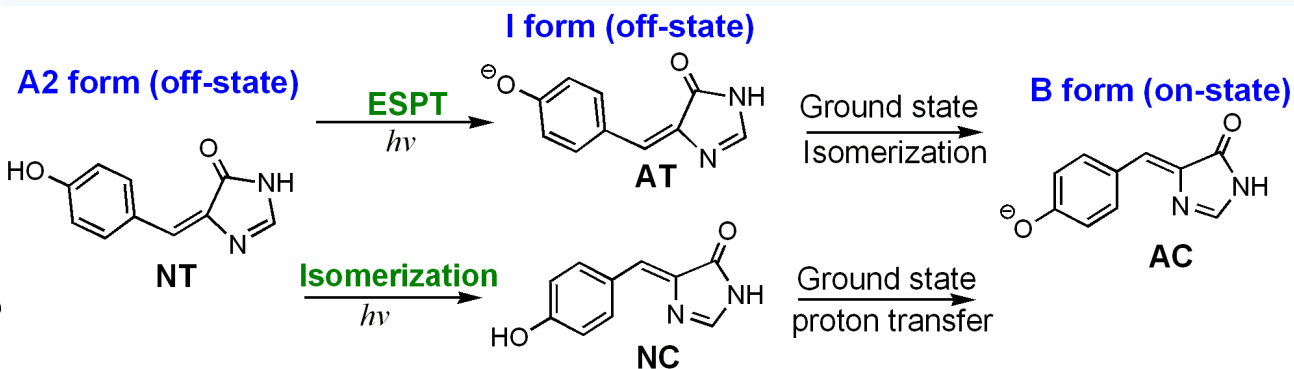
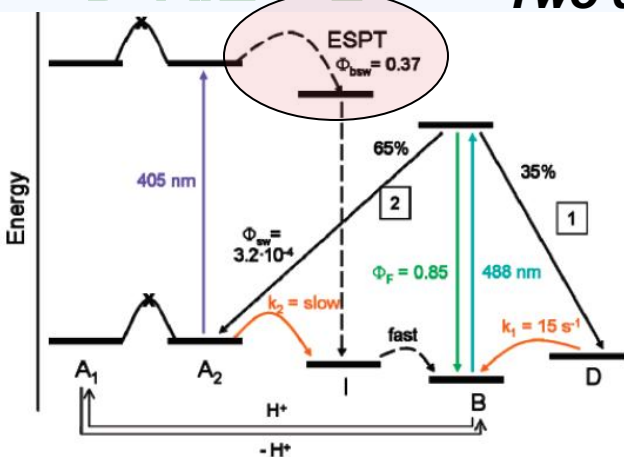
Dronpa (reversible photoactivation and photobleaching)



Crystal structures of **on- (cis)** and **off- (trans)** states

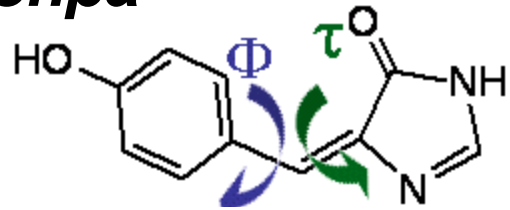
D-KIE ~ 2

Two different proposed reaction pathways



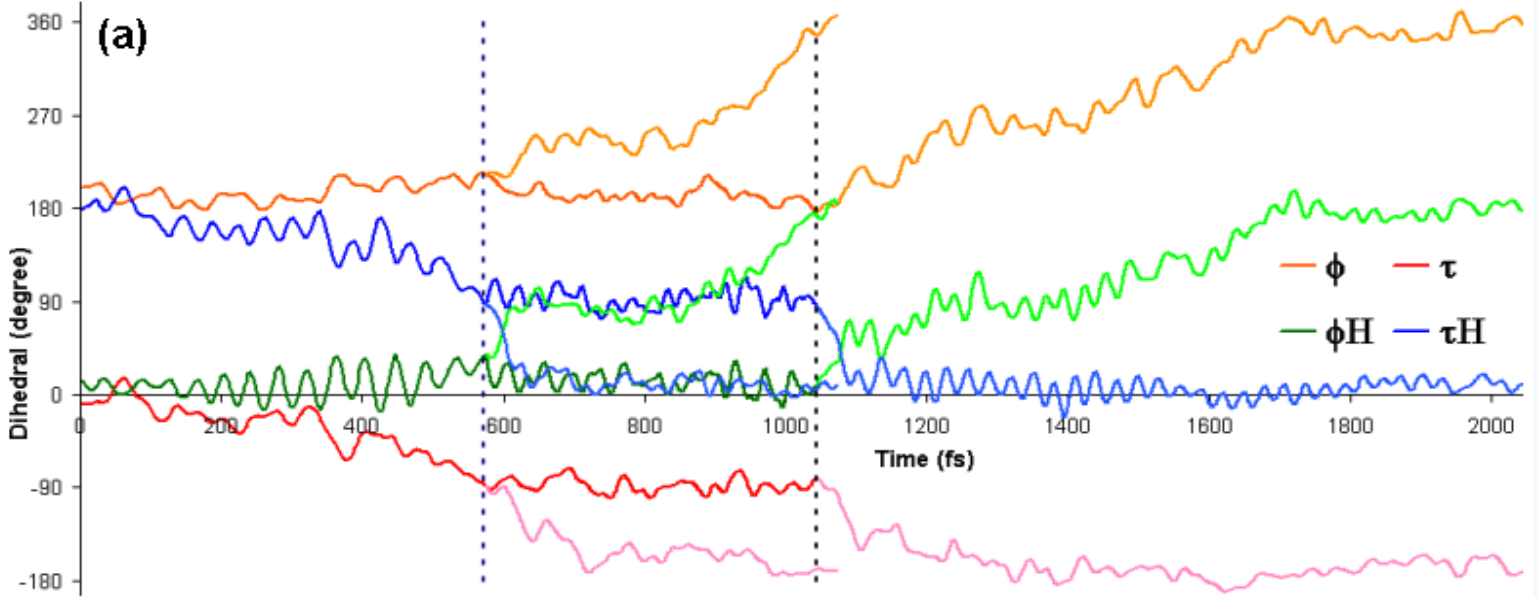
Ando, R.; Mizuno, H.; Miyawaki, A. *Science*, **2004**, 306, 1370. (2) Habuchi, S.; et al. *PNAS* **2005**, 102, 9511.
 (3) Andresen, M.; et al. *PNAS* **2007**, 104, 13005. (4) Fron, E.; et al. *JACS* **2007**, 129, 4870.

ONIOM(CASSCF(6e,6o)/3-21G:Amber)/MD of excited states of Dronpa

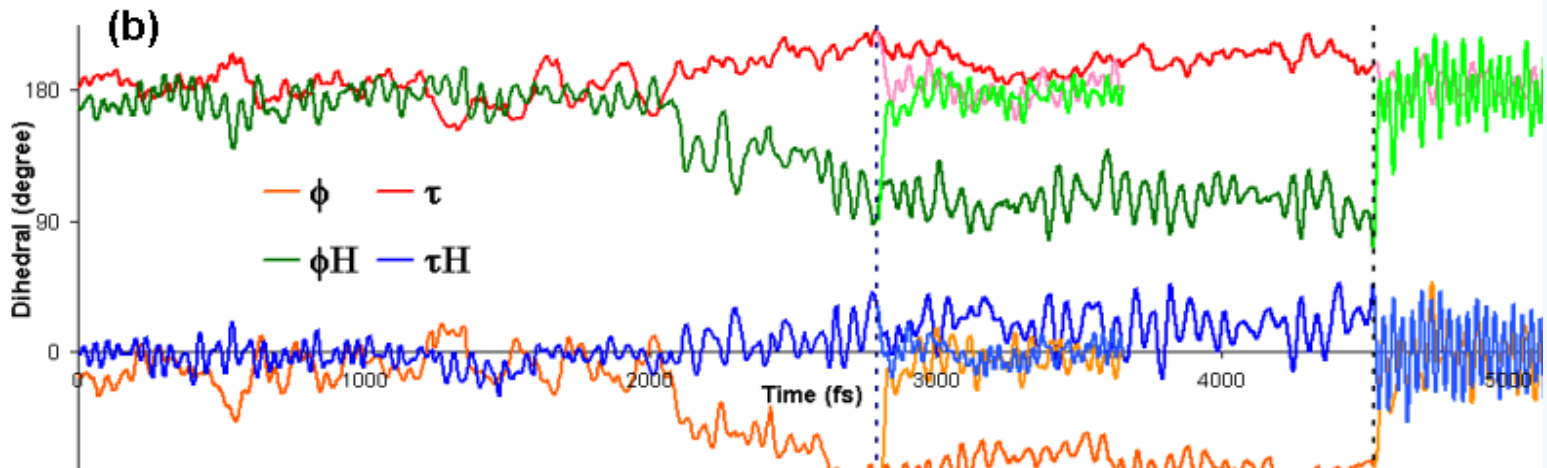


1. Calculate average life time, reaction probability
2. Comparison with dynamics in water solution

N_{trans}
(off state)

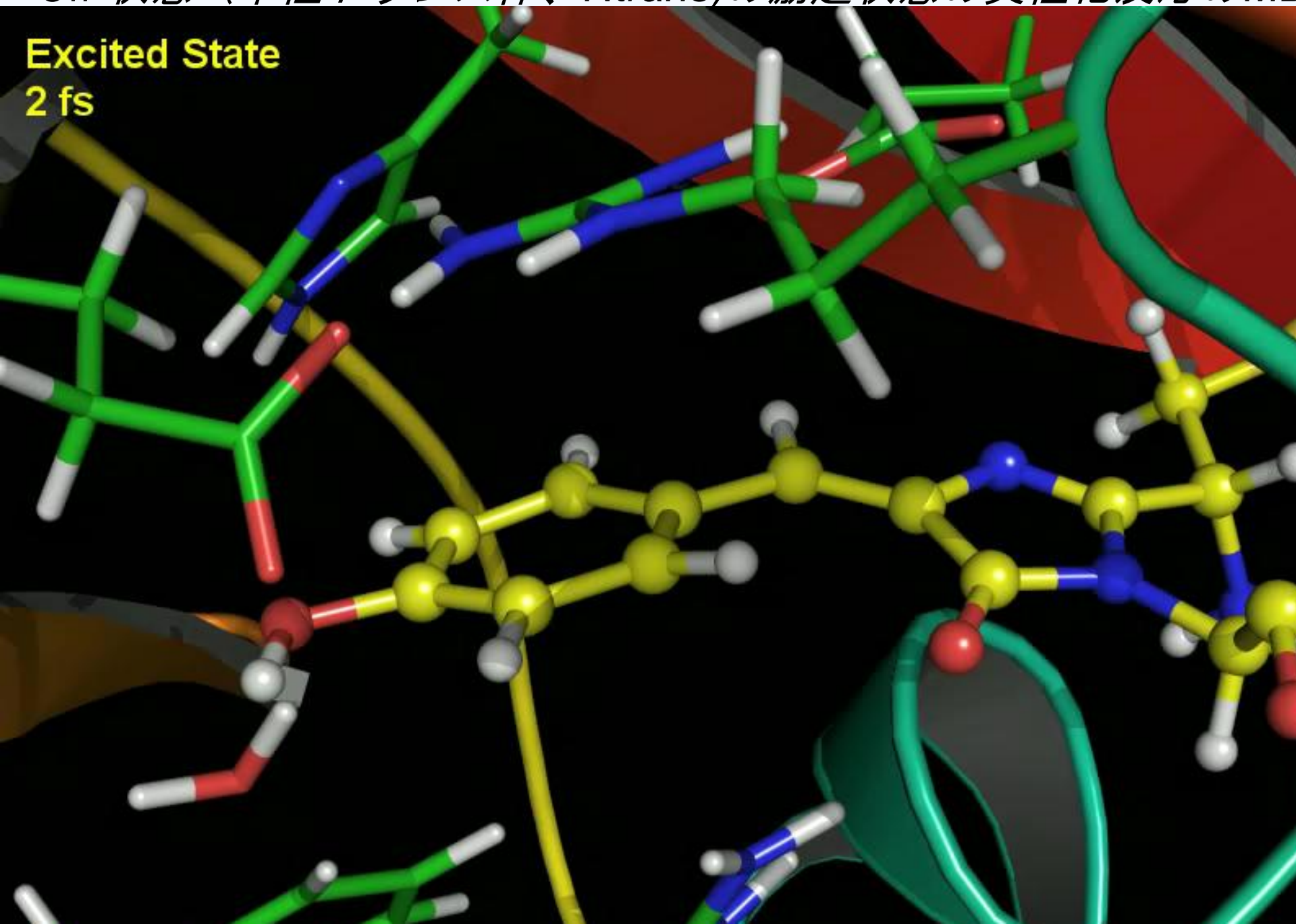


A_{cis}
(on state)



Off-状態 (中性トランス体、Ntrans) の励起状態の異性化反応のMD

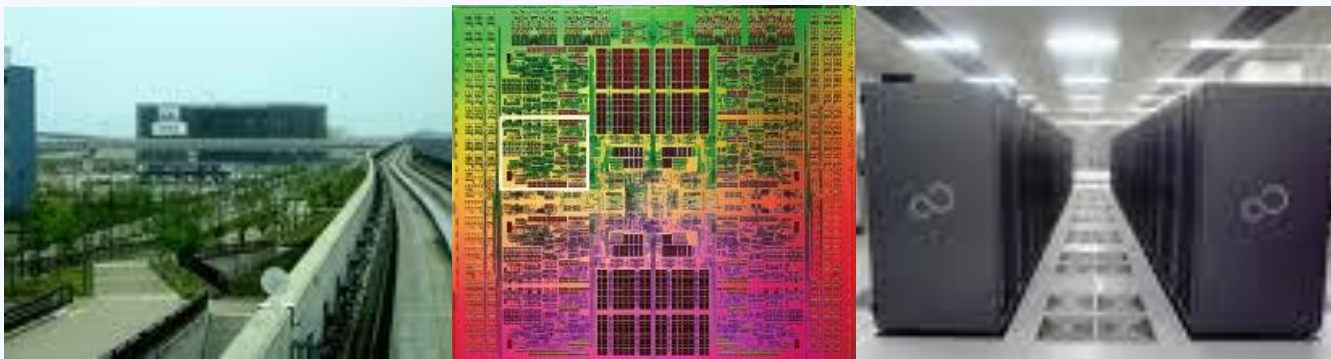
Excited State
2 fs



理論化学・計算化学による分子の構造、 機能、反応のシミュレーション

- 1。実験で得られない情報が得られる。
 - 2。実験の難しい系(未だ合成されたことのない化合物等)でも計算は出来る。
 - 3。計算の方が実験より速い。
- 今後ますます、分子シミュレーションが化学の発展に重要な役割をするようになる。

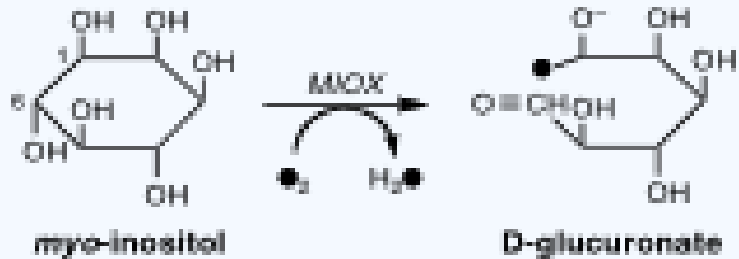
理研次世代スーパーコンピュータへの期待きわめて大きい



myo-Inositol oxygenase (MIOX)

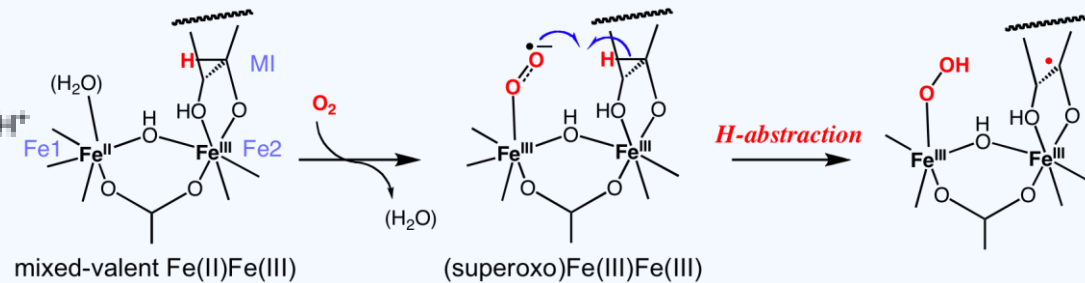
H. Hirao and K. Morokuma, *J. Am. Chem. Soc.* 131,17206–17214 (2009).

MIOX-catalyzed reaction



Charalampous et al.
*JBC*1950s/1960s.

Initial steps



Xing et al. *Biochemistry* 2006a, *Biochemistry* 2006b,
*PNAS*2006. Brown et al. *PNAS*2006.

C–C cleaved, one oxygen atom incorporated, etc.

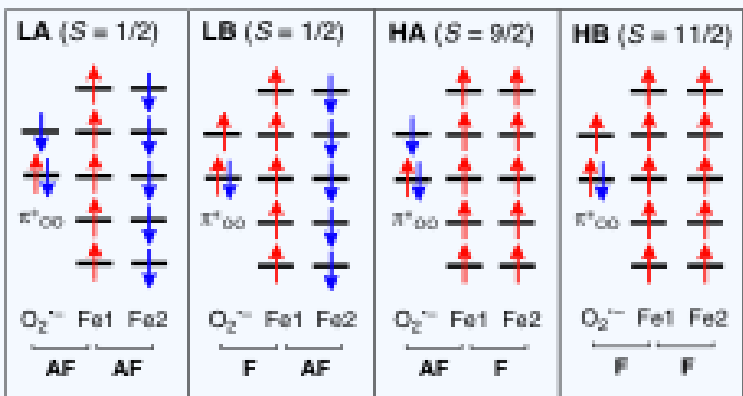
Overexpression of MIOX causes too much catalysis, leading to diabetic diseases.

A (**superoxo**)diiron(**III/III**) intermediate effects C–H activation.

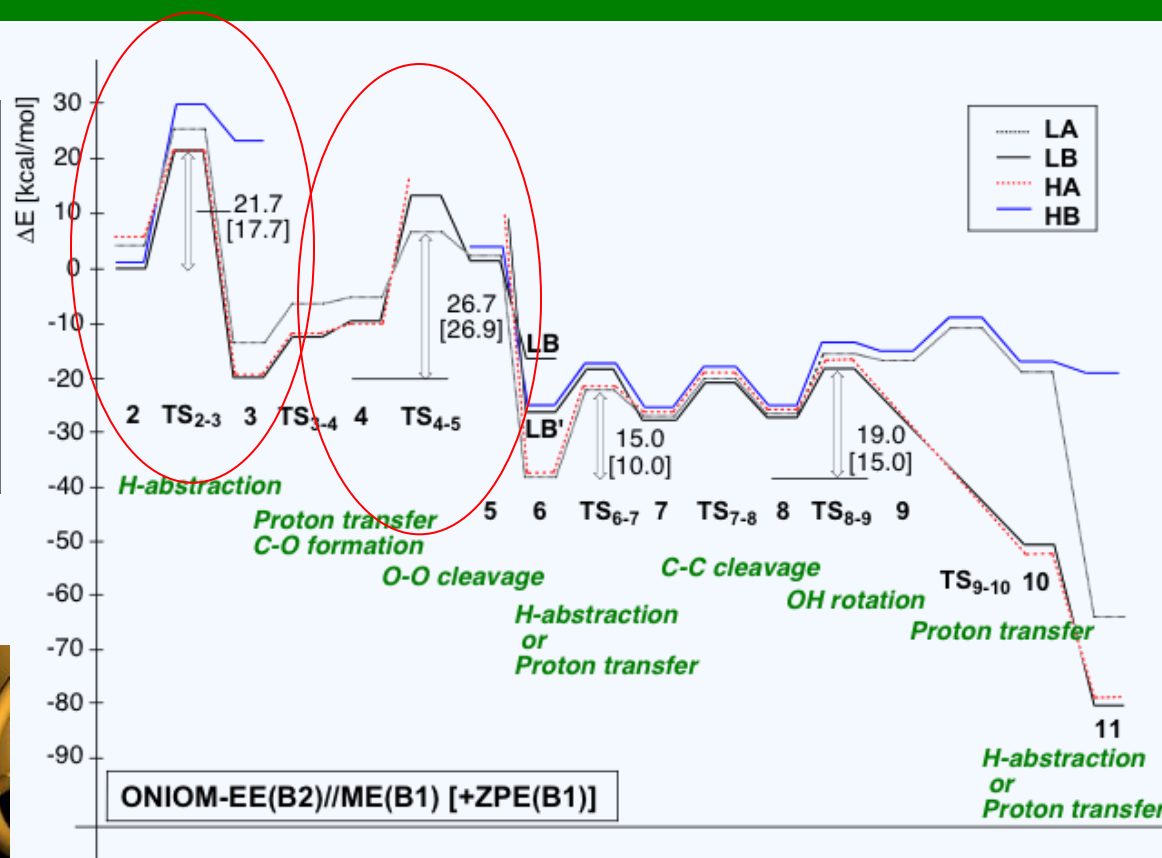
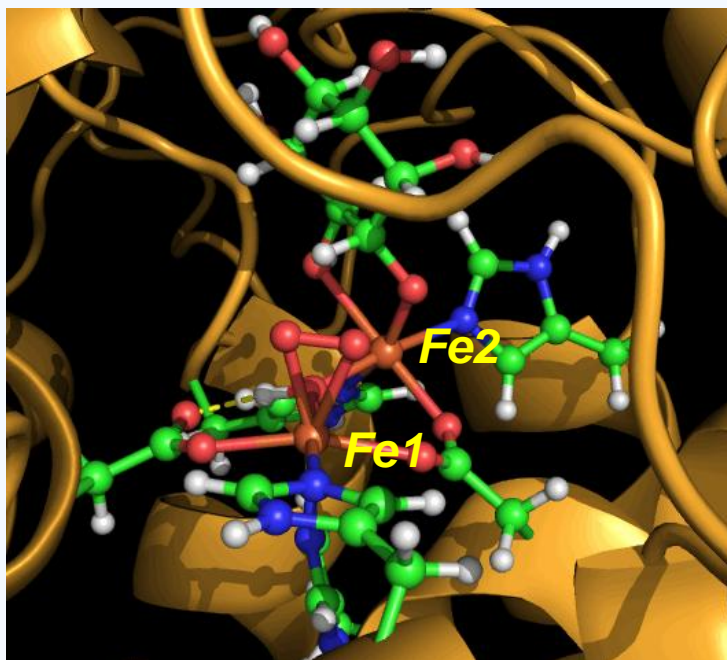
Still, the nature of the reactive species and reaction mechanism remain largely unclear.

We computationally addressed these issues.

Reaction profile



H-abstraction

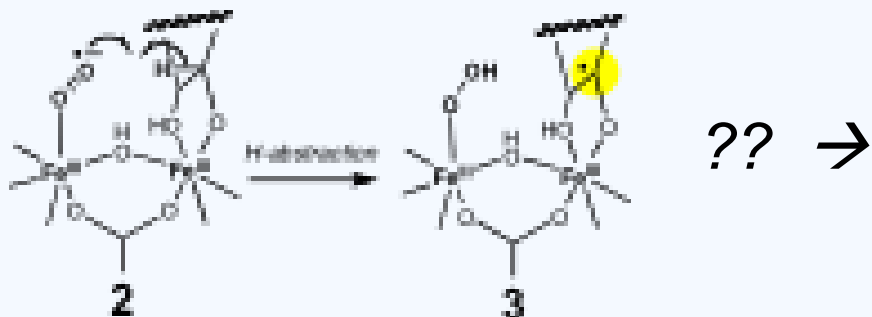


In the reactant, **LB** and **HB** are the ground states. O-O cleavage has the highest barrier (rate-limiting step).

Theoretical KIE for H-abstraction agreed well with experiment.

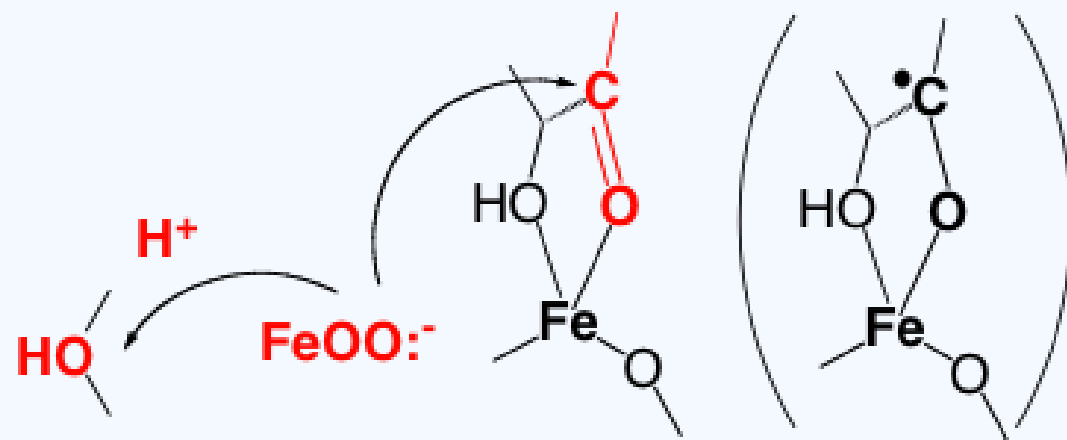
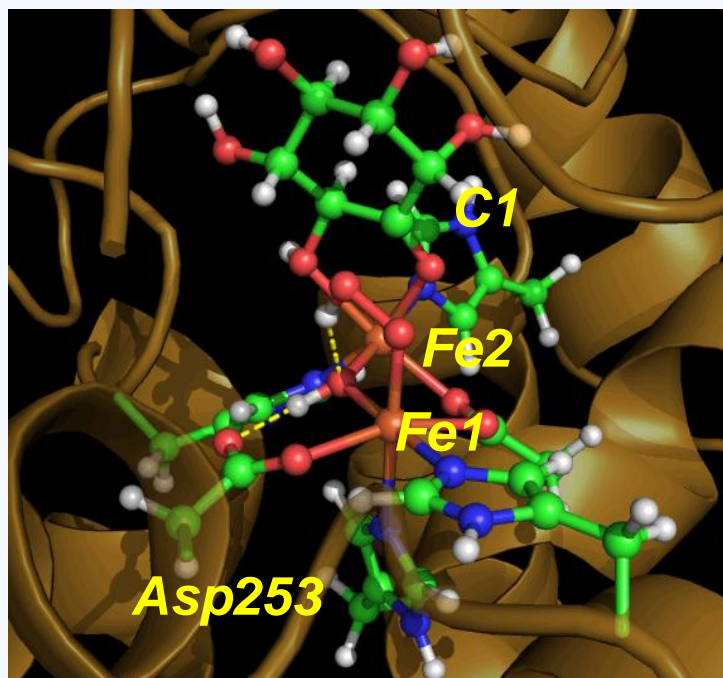
All but **HB** have similar stability in **3** (H-addition product).

Important role of bridging hydroxide



Spin NOT localized on C1, but goes down to Fe2

*CO part better viewed as carbonyl.
Nucleophilic attack by FeOO^- , rather than by $\text{FeOO}\cdot$, is more favorable.*



The bridging hydroxide acts as a catalytic base that facilitates the nucleophilic attack of FeOO^- on carbonyl.