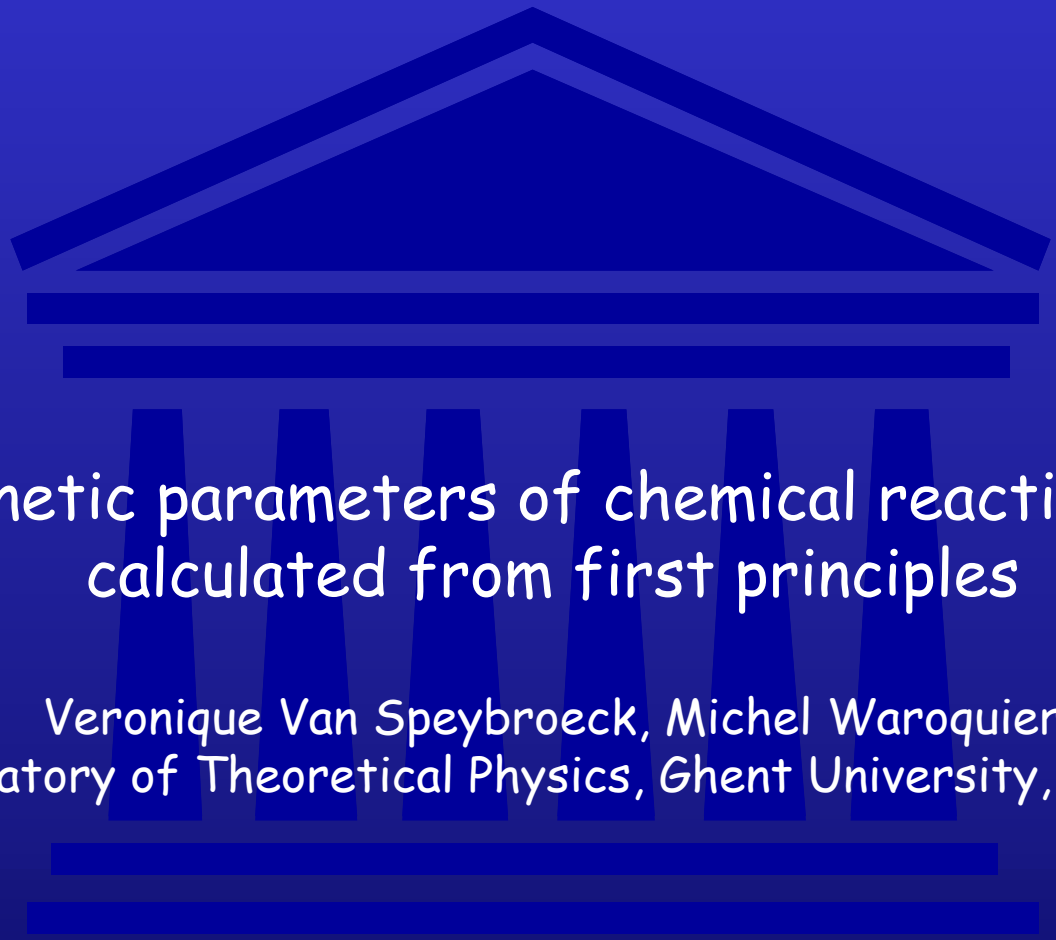


Kinetic parameters of chemical reactions calculated from first principles

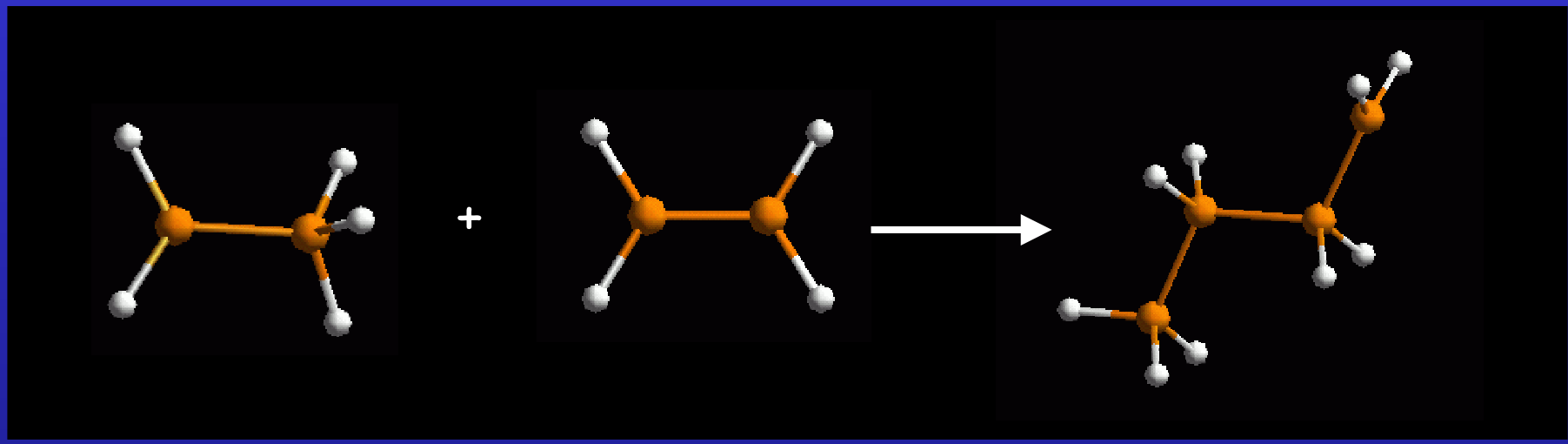
Veronique Van Speybroeck, Michel Waroquier
Laboratory of Theoretical Physics, Ghent University, Belgium

Eurokin – Louvain-La-Neuve, 18/19 february 2002

Outline

- Theoretical procedures on addition of ethylradical to ethene
- Cyclization of primary ethylbenzene radical : coupled internal rotations
- Hydrogen abstraction reactions : Free rotor approach
- Application on other reaction of coke formation

Chemical Reaction : A+B -> C



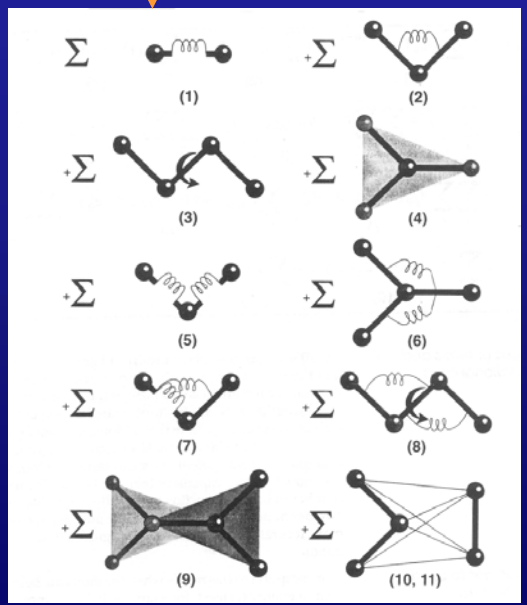
Experimental information :
reaction enthalpies, reaction entropies, kinetic parameters,...

Macroscopic quantities

?
Microscopic information on chemical reaction

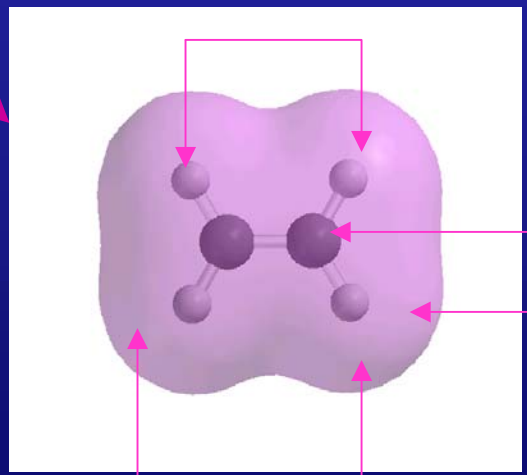
Theoretical calculations

	Static	Dynamic
Ab initio	Hartree-Fock Density Functional Theory	Car Parrinello MD
Semi-empirical Empirical		Molecular Mechanics



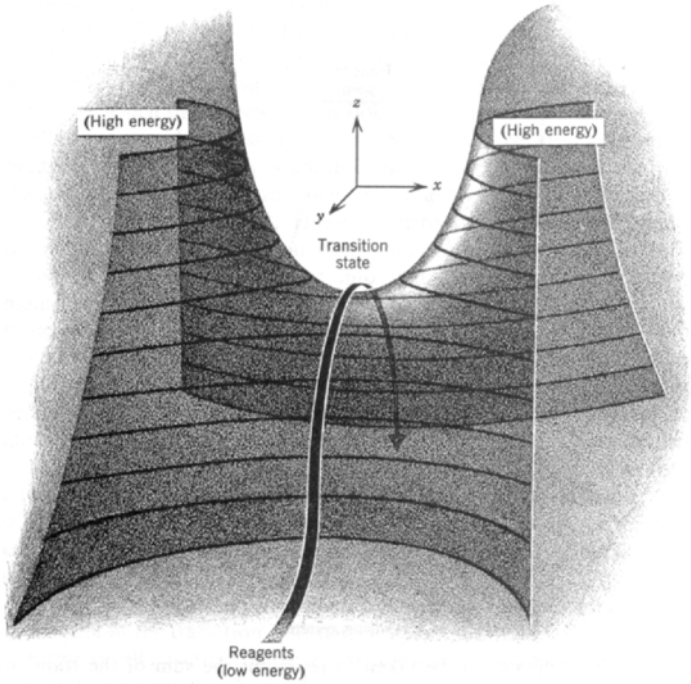
Interactions are described by empirical Force Fields

Interactions between nuclei



Interactions between electrons

Interactions between electrons

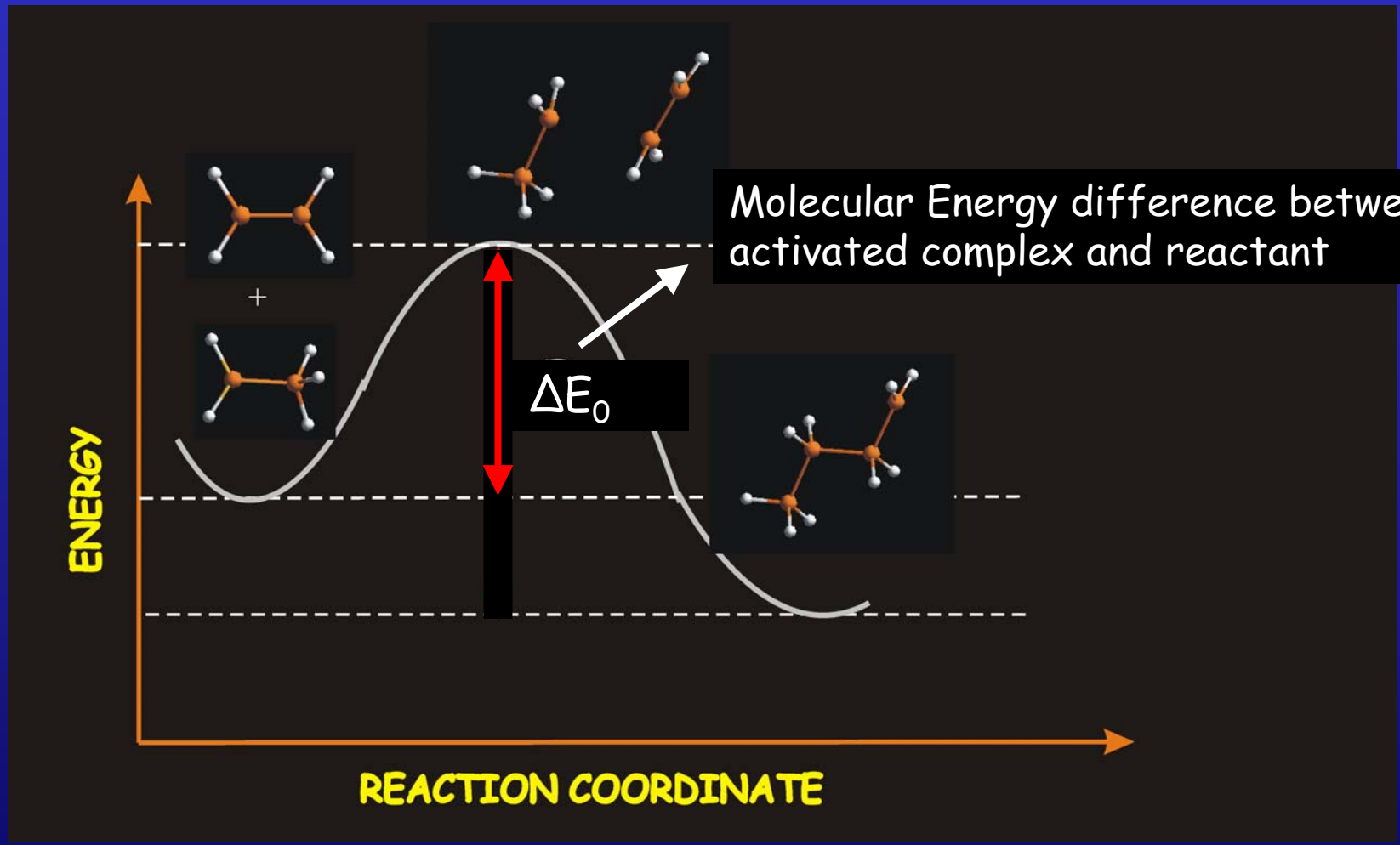


Transition State Theory

Rate equation : $k(T) = \frac{k_B T}{h} \frac{q_{\pm}}{q_A q_B} e^{-\frac{\Delta E_0}{k_B T}}$

$-\frac{\Delta E_0}{k_B T}$ → *Molecular Energy difference at absolute zero between activated complex and reactant*

$\frac{q_{\pm}}{q_A q_B}$ → *Microscopically determined partition function*

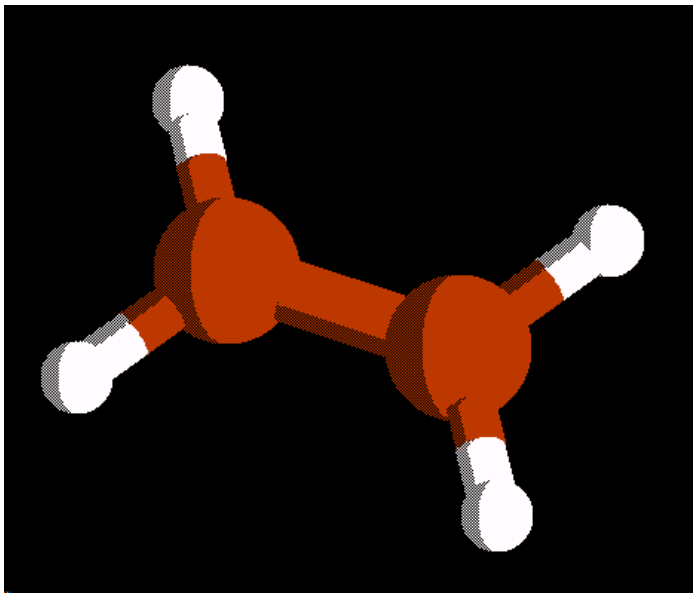

Molecular Energy difference between activated complex and reactant
ΔE_0
ENERGY
REACTION COORDINATE

Partition function q :

$q = q_{trans}\, q_{vib}\, q_{rot}\, q_{electronic}$

- translational : global translation of the molecule
- rotational : global rotation of the molecule
- electronic = 1 (Electrons are in groundstate)
- vibrational :

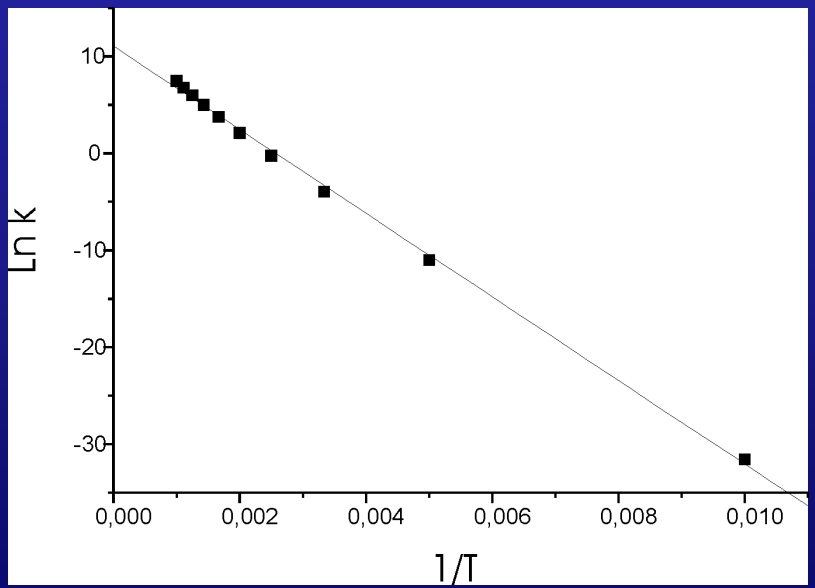
$$q_{vib,i} = \frac{e^{-\frac{h\nu_i}{2k_BT}}}{1 - e^{-\frac{h\nu_i}{k_BT}}}$$



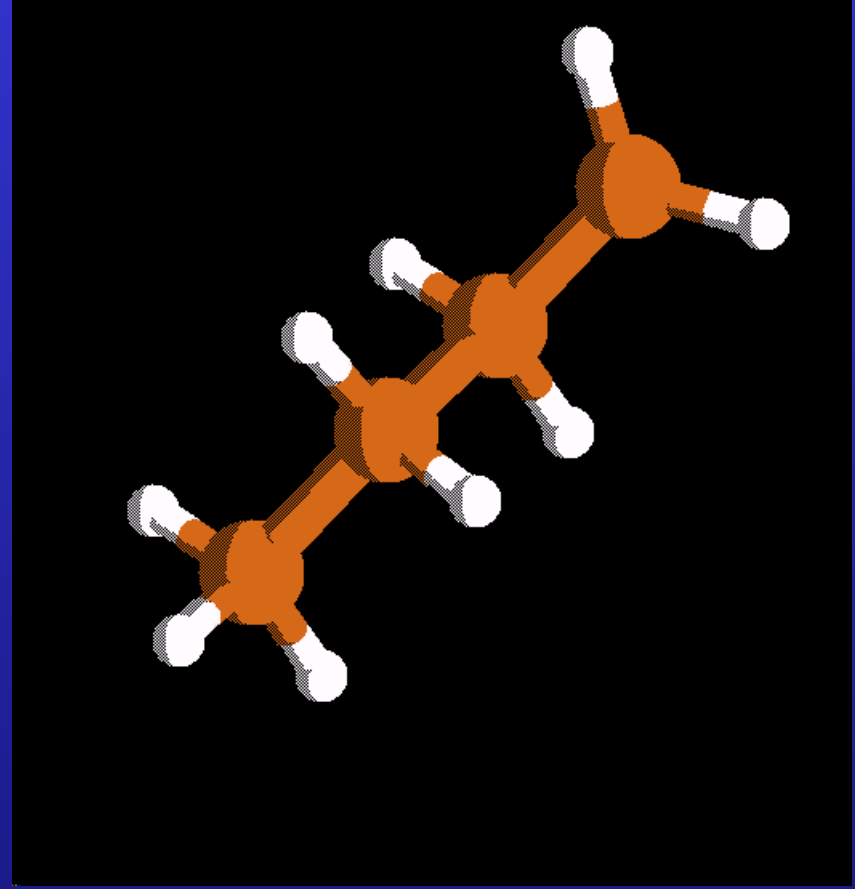
$$k(T) = \frac{k_B T}{h} \frac{q^{\ddagger}}{q_A q_B} e^{-\frac{\Delta E_0}{k_B T}}$$

Arrhenius rate law

$$k(T) = A\, e^{-\frac{Ea}{RT}}$$

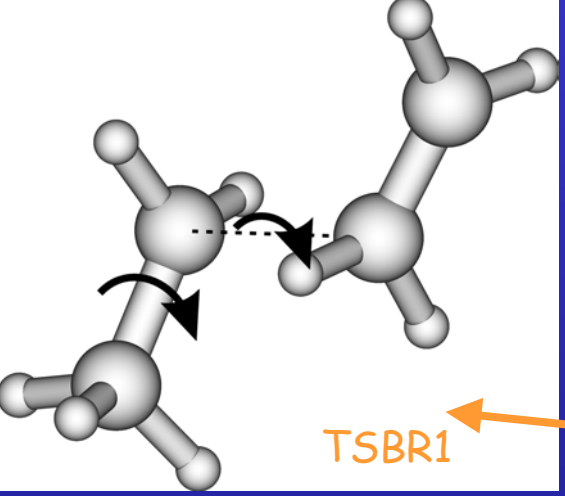


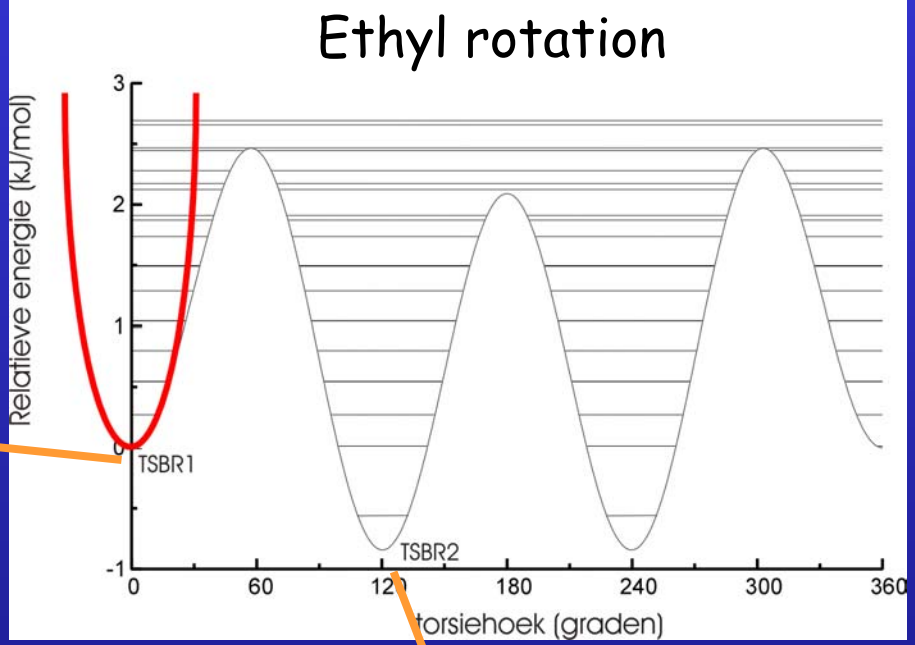
Exp : Ea = 30.5 kJ/mol



Kinetic parameters
(DFT/B3LYP/6-311G**)

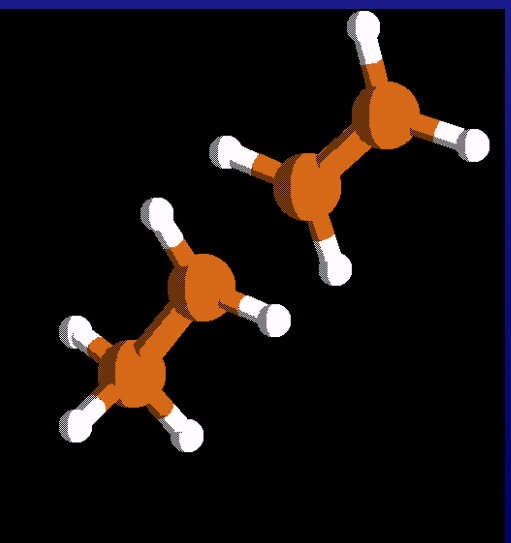
ΔE_0= 34.9 kJ/mol
Ea = 36.81 kJ/mol
A = 9.75 E7 dm^3/mol.s



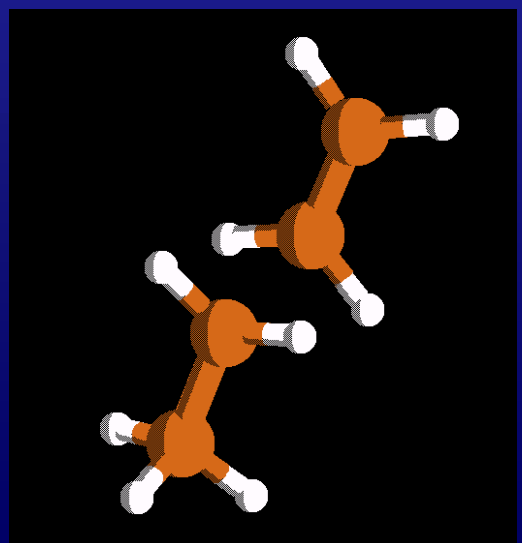


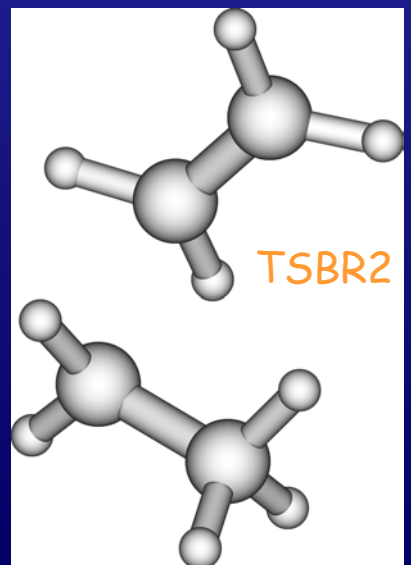
More transition states come into play

HO

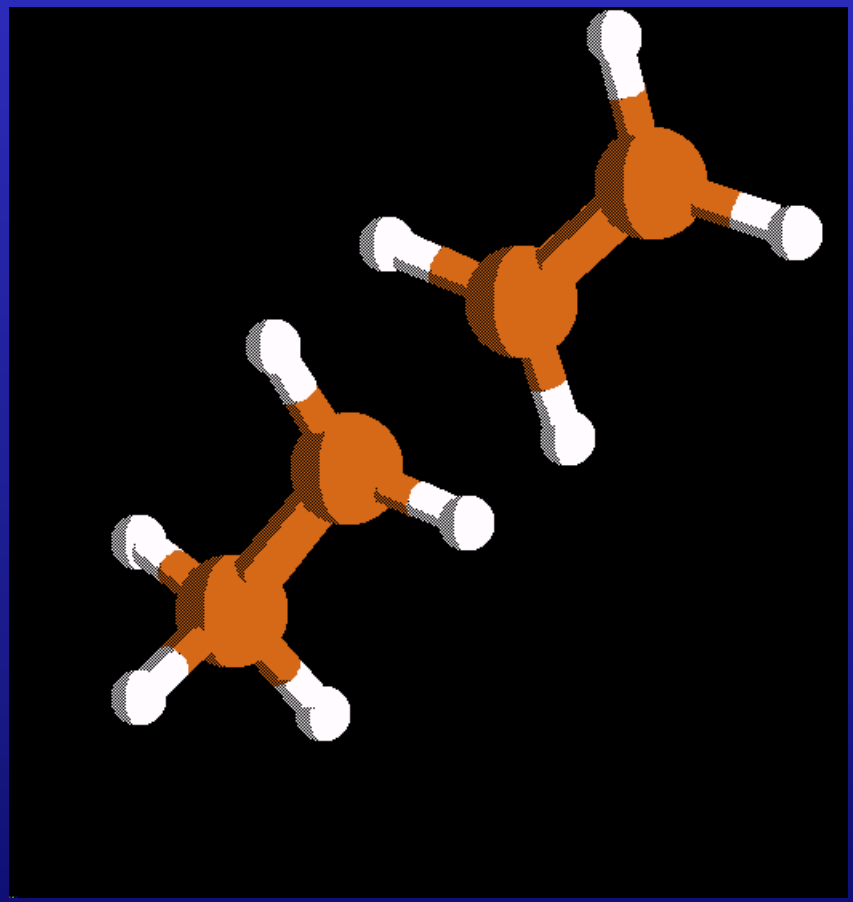


IR

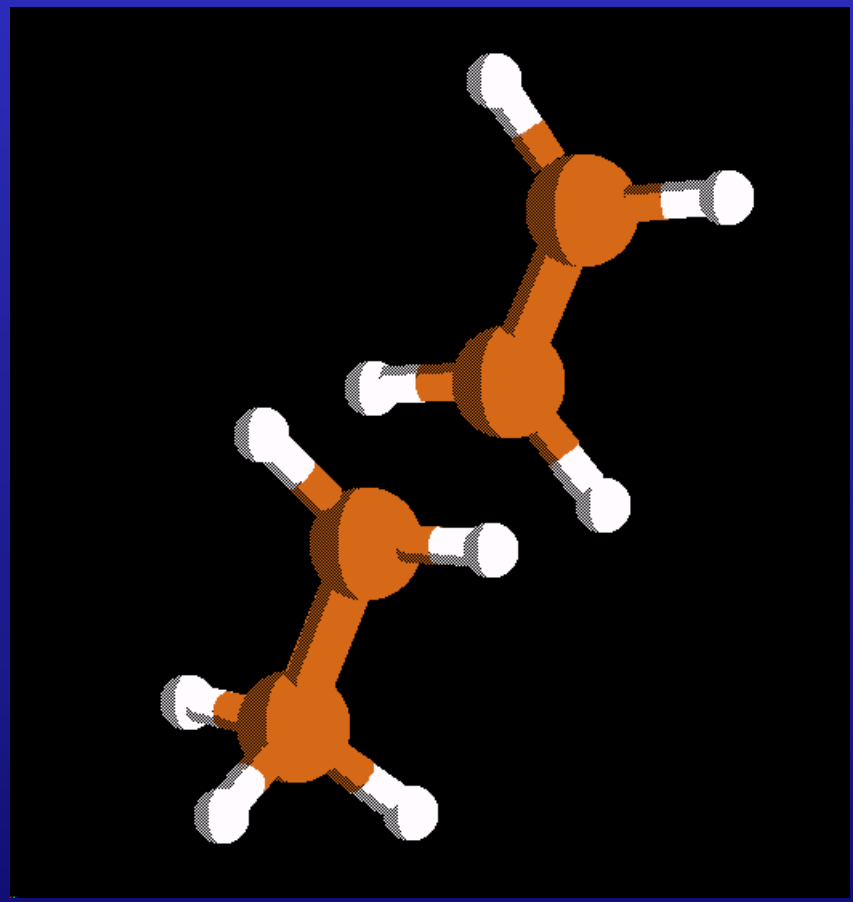


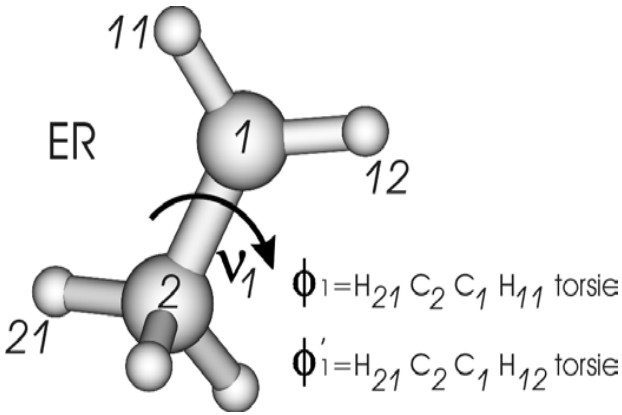


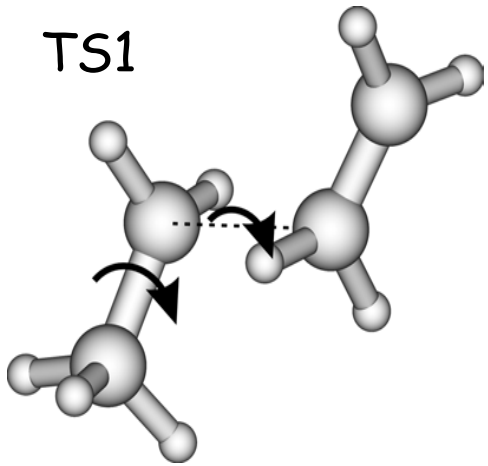
HO

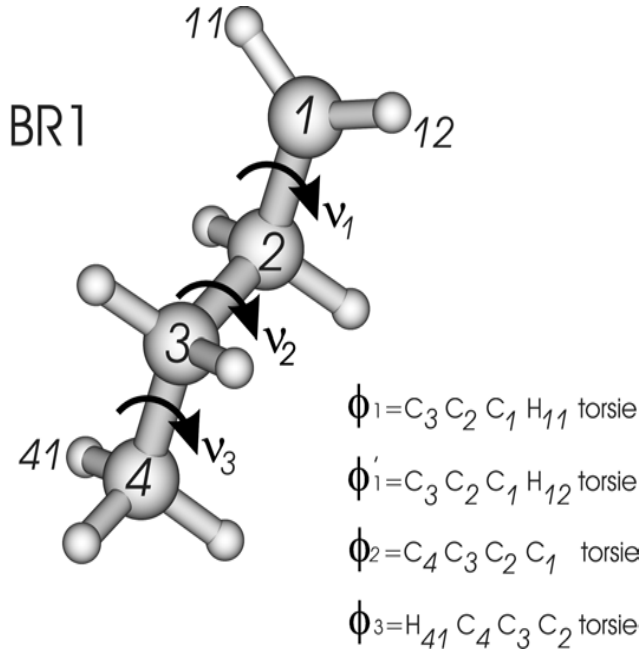


IR




ER
11
1
12
2
21
ν_1
$\phi_1 = H_{21}\, C_2\, C_1\, H_{11}$ torsie
$\phi'_1 = H_{21}\, C_2\, C_1\, H_{12}$ torsie


TS1


BR1
11
1
12
2
3
41
4
ν_1
ν_2
ν_3
$\phi_1 = C_3\, C_2\, C_1\, H_{11}$ torsie
$\phi'_1 = C_3\, C_2\, C_1\, H_{12}$ torsie
$\phi_2 = C_4\, C_3\, C_2\, C_1$ torsie
$\phi_3 = H_{41}\, C_4\, C_3\, C_2$ torsie

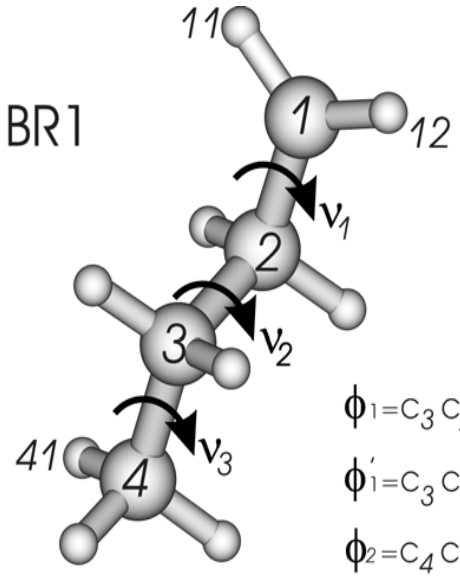
Partition function q :

$q = q_{trans}\, q_{vib}\, q_{rot}\, q_{electronic}$

$$q_{vib,i} = \frac{e^{-\frac{h\nu_i}{2k_BT}}}{1 - e^{-\frac{h\nu_i}{k_BT}}}$$

Some low vibrational modes correspond with internal rotations

$$q_{rot,int,m} = \frac{1}{\sigma_{int}} \sum_k g_k(m) \exp\left(-\frac{\varepsilon_k(m)}{k_BT}\right)$$



In principle all internal rotations are coupled

Approximation : All internal rotations are decoupled with a rotational multidimensional rotational potential

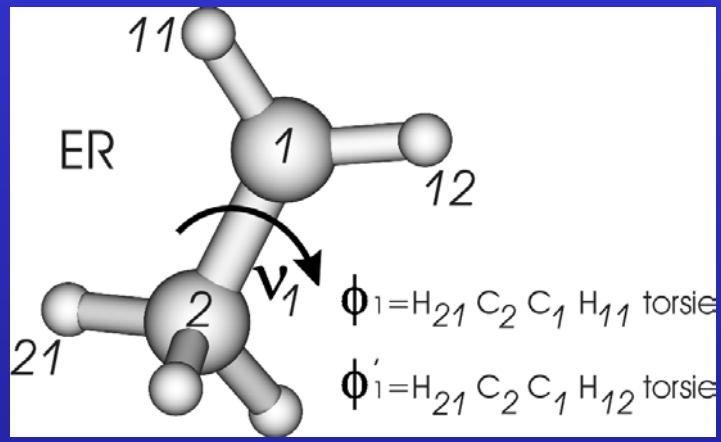
$$-\frac{\hbar^2}{2Im}\frac{\partial^2 \psi_{km}(\phi_m)}{\partial \phi_m^2} + V(\phi_m)\psi_{km}(\phi_m) = \varepsilon_k^{(m)}\psi_{km}(\phi_m)$$

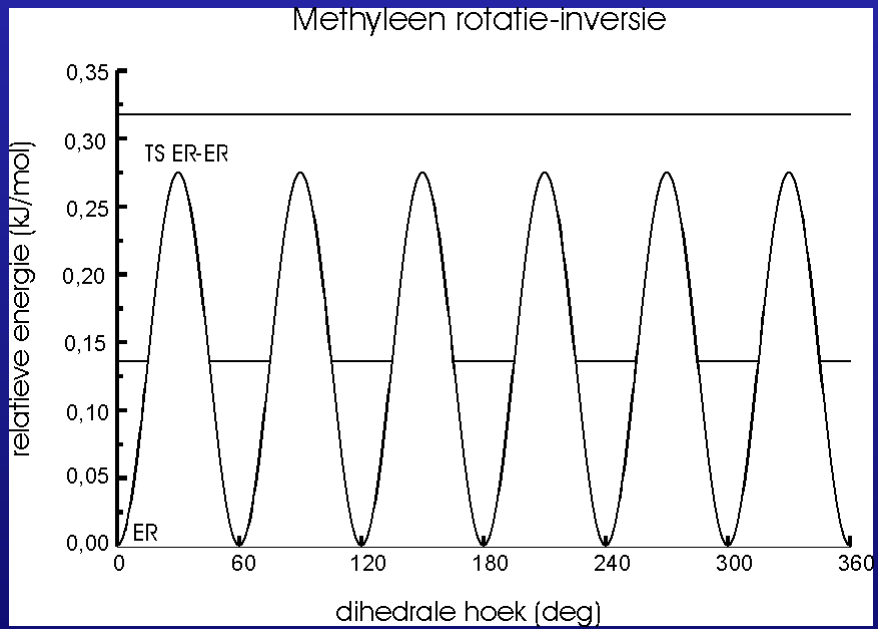
Reduced moment of inertia

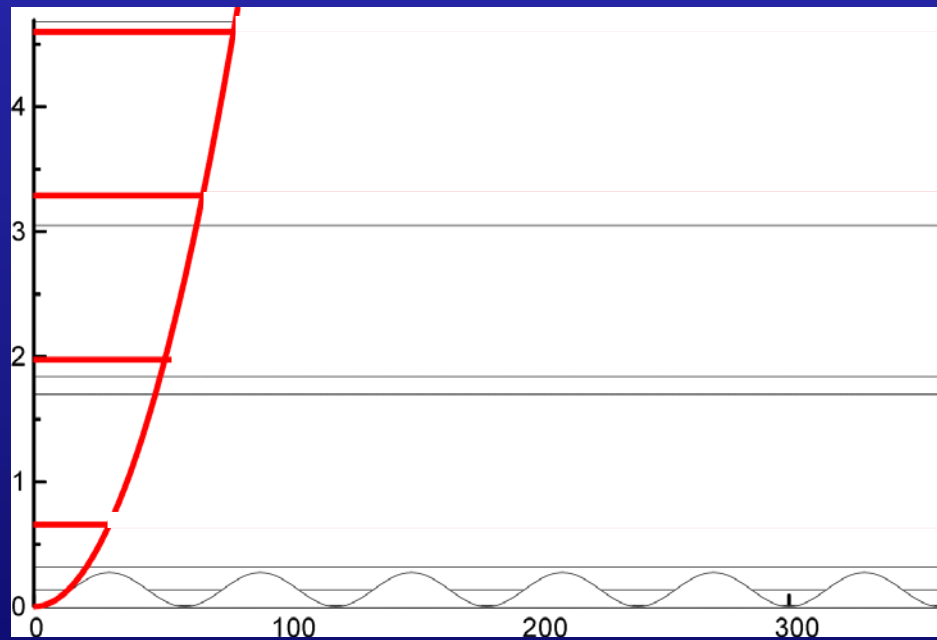
$$Im = Am\left(1 - \sum_{I=X,Y,Z} Am\lambda^2_{mi}/Ii\right)$$

Energy Eigenvalues

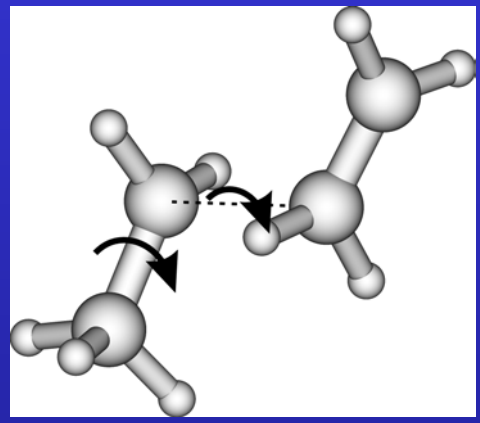
Rotational wave function

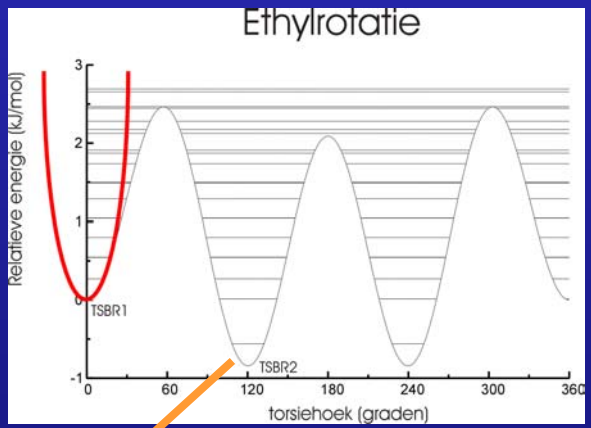


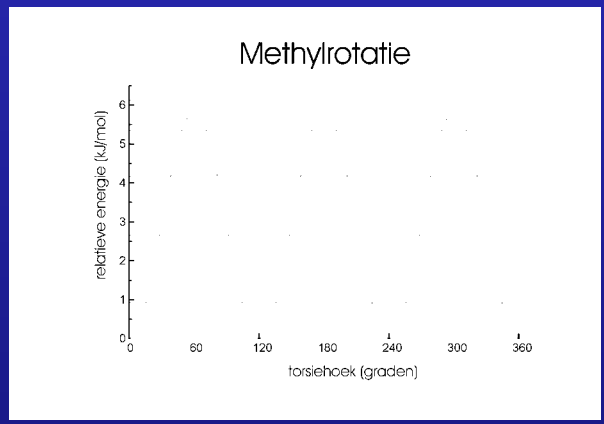


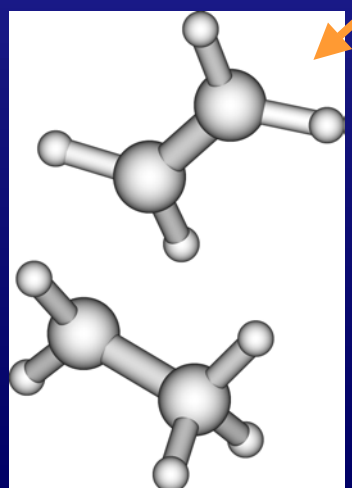


No extra conformers come into play,
but the density of states increases,
partition function increases



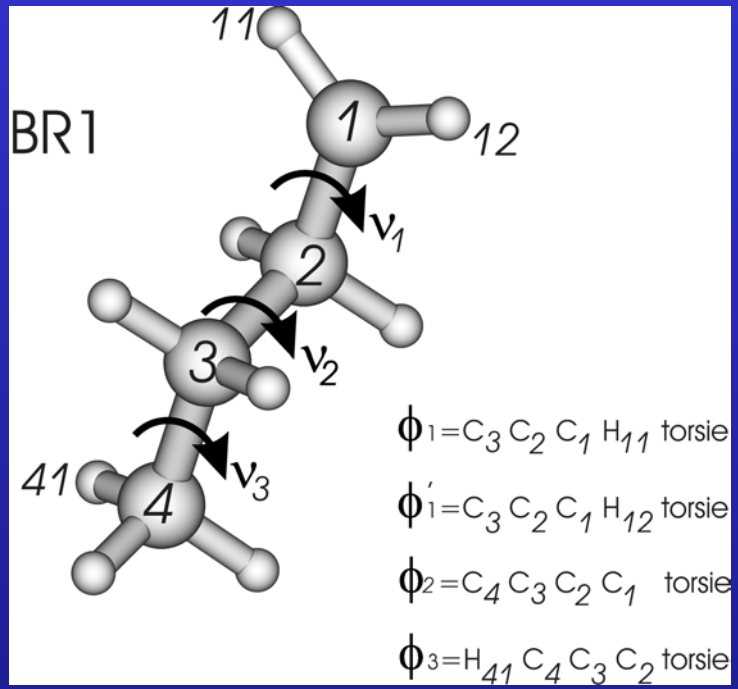


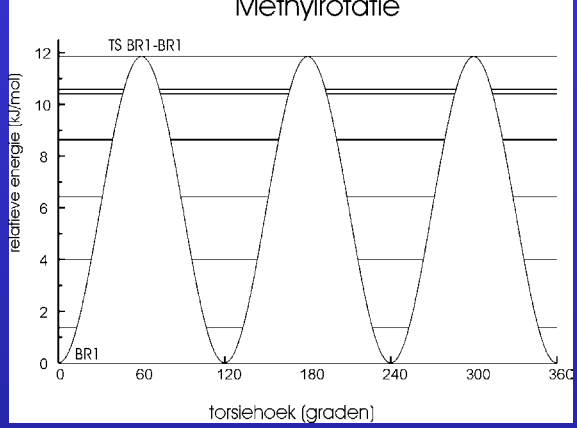


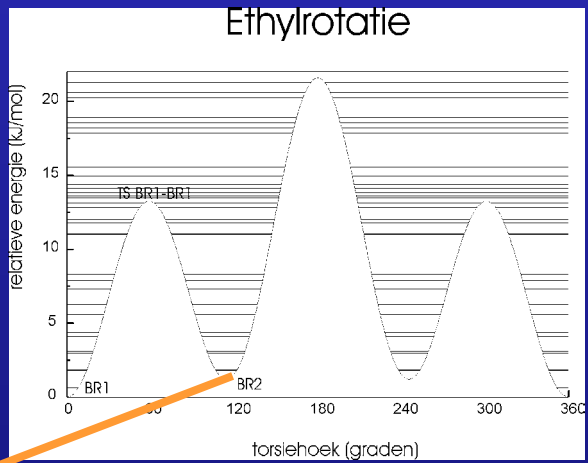


More conformers come into play

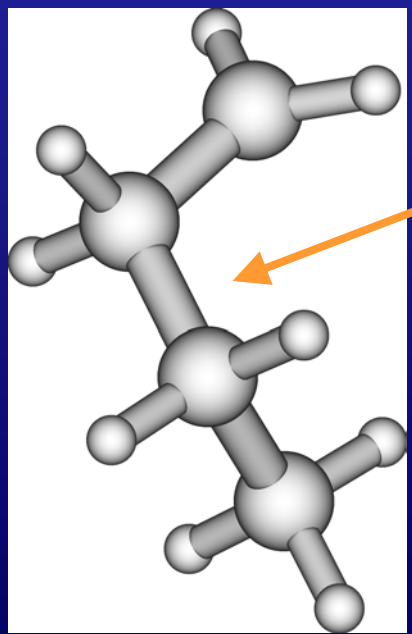
Addition reaction :
gauche attack is energetically preferred

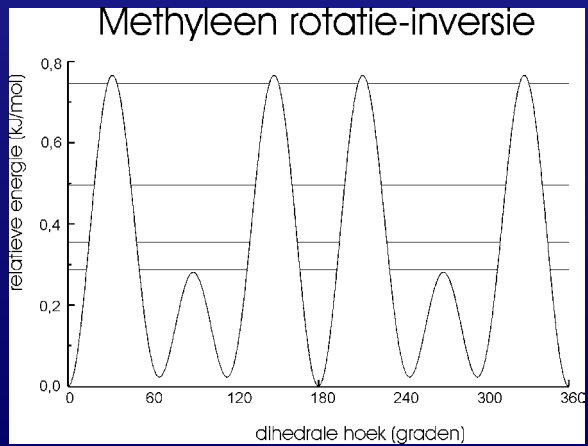

BR1
11
1
12
2
3
41
4
ν_1
ν_2
ν_3
$\phi_1 = C_3\ C_2\ C_1\ H_{11}$ torsie
$\phi'_1 = C_3\ C_2\ C_1\ H_{12}$ torsie
$\phi_2 = C_4\ C_3\ C_2\ C_1$ torsie
$\phi_3 = H_{41}\ C_4\ C_3\ C_2$ torsie


Methylrotatie
TS BR1-BR1
BR1
relatieve energie (kJ/mol)
torsiehoek (graden)


Ethylrotatie
TS BR1-BR1
BR1
BR2
relatieve energie (kJ/mol)
torsiehoek (graden)

BR2




Methyleen rotatie-inversie
relatieve energie (kJ/mol)
dihedrale hoek (graden)

Kinetic parameters with internal rotations for forward addition reaction

	Ea	A
HO	36.81	9.8 E7 dm3/mol.s
IR	37.06	9.8 E8 dm3/mol.s

Slight influence on activation energy

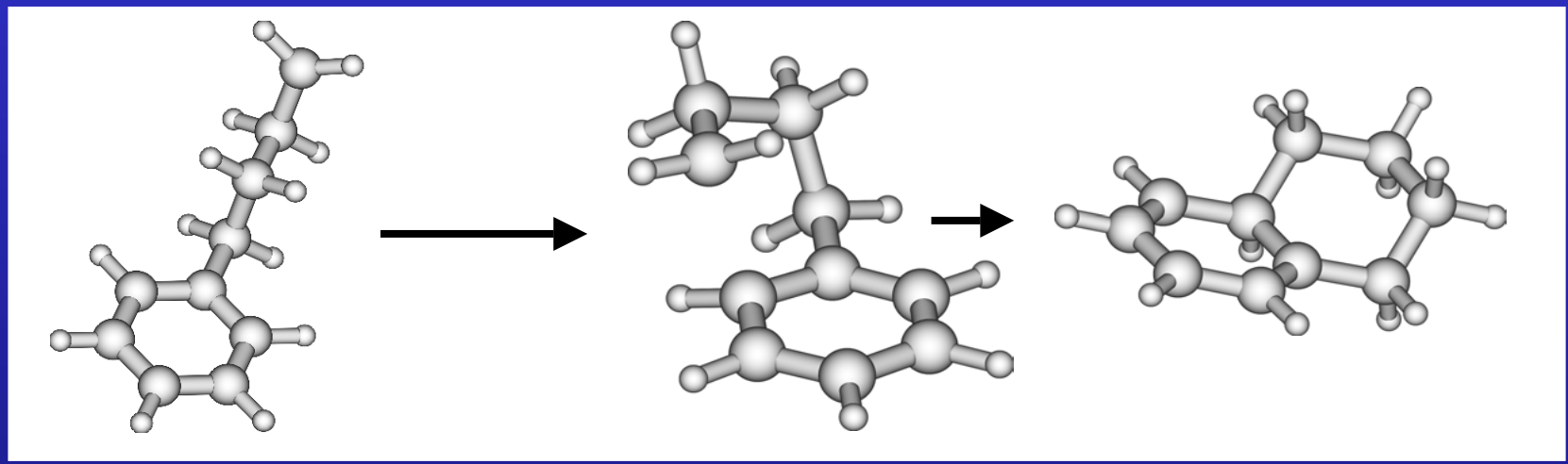
$$\frac{A_{IR}}{A_{HO}} = 10$$

- More conformers
- Density of states increases

Outline

- Theoretical procedures on addition of ethylradical to ethene
- Cyclization of primary ethylbenzene radical : coupled internal rotations
- Hydrogen abstraction reactions : Free rotor approach
- Application on other reaction of coke formation

Cyclization of the butylbenzene radical



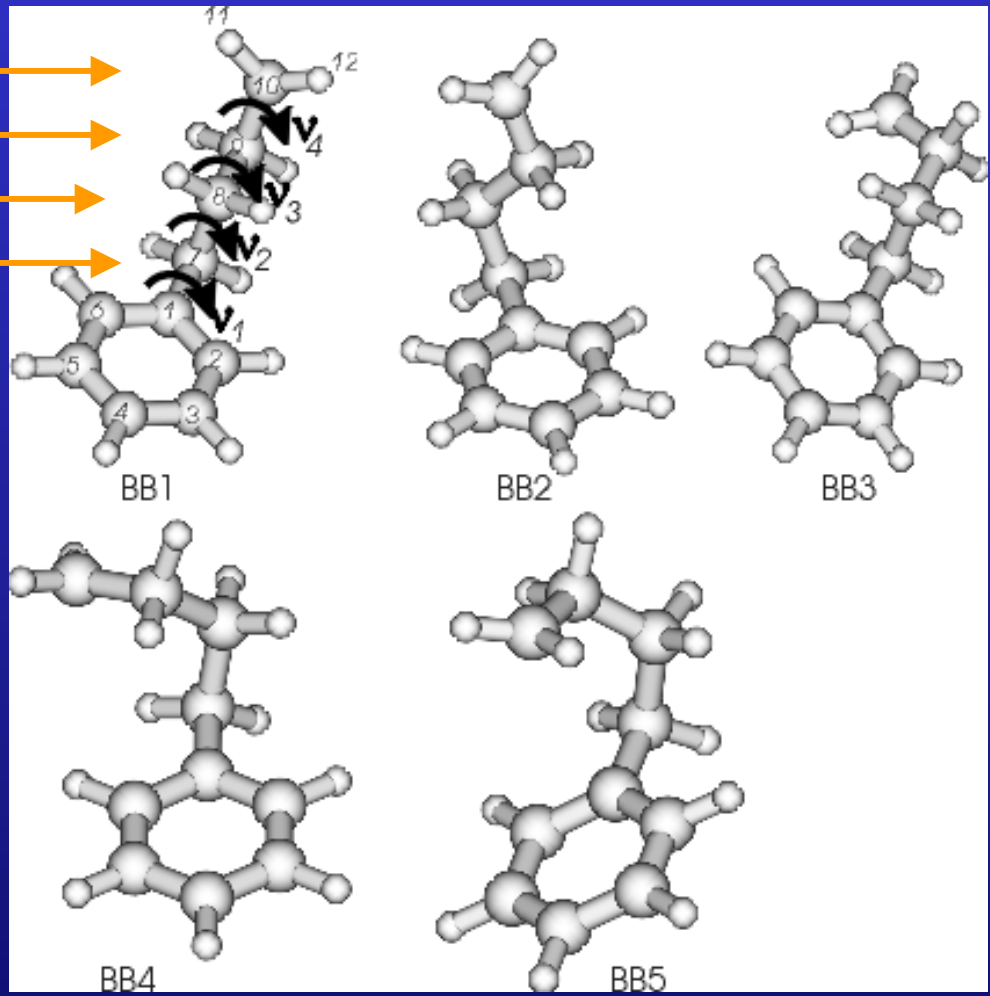
More internal rotations must
be activated to reach the transition state

methylene rotation-inversion

ethylene rotation

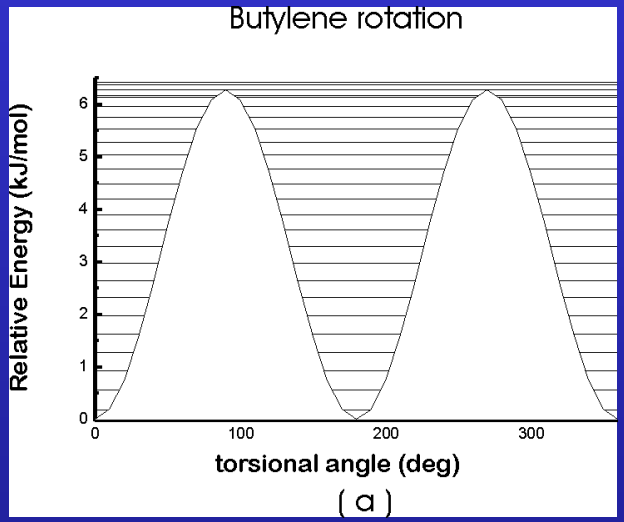
propylene rotation

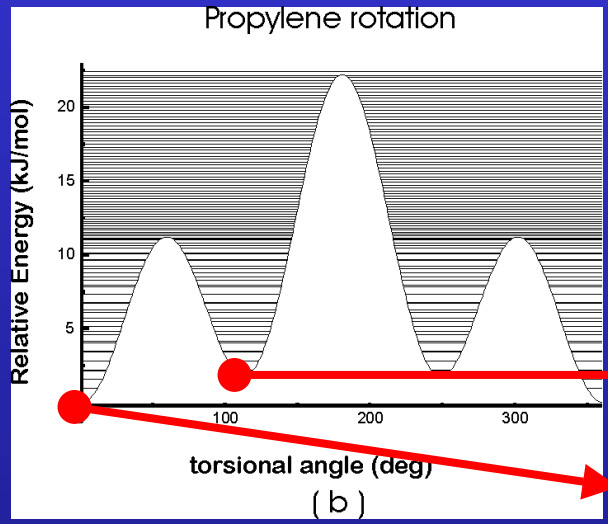
butylene rotation



Conformational Analysis :

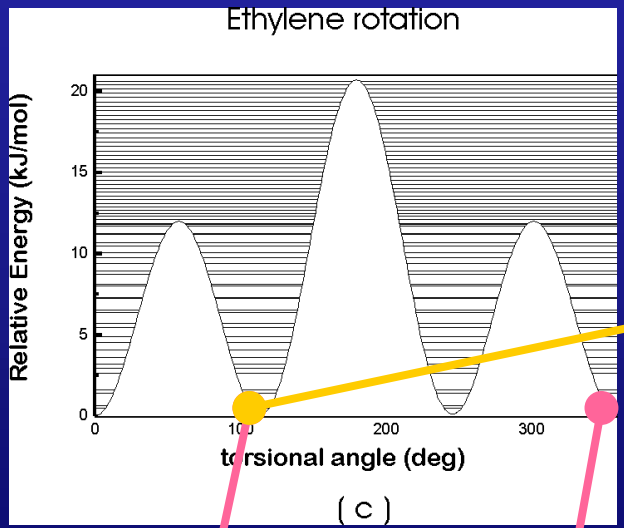
- *orthogonal conformation of butylchain*
- *combinations of gauche and anti orientations of CCCC torsional angles*

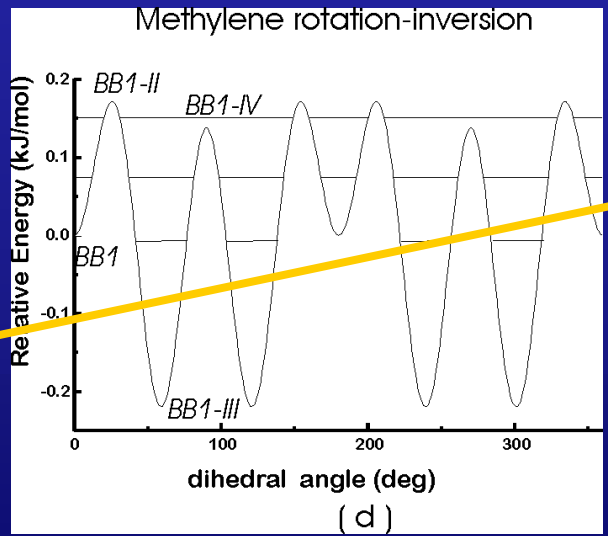




BB2

BB1





BB3

gauche

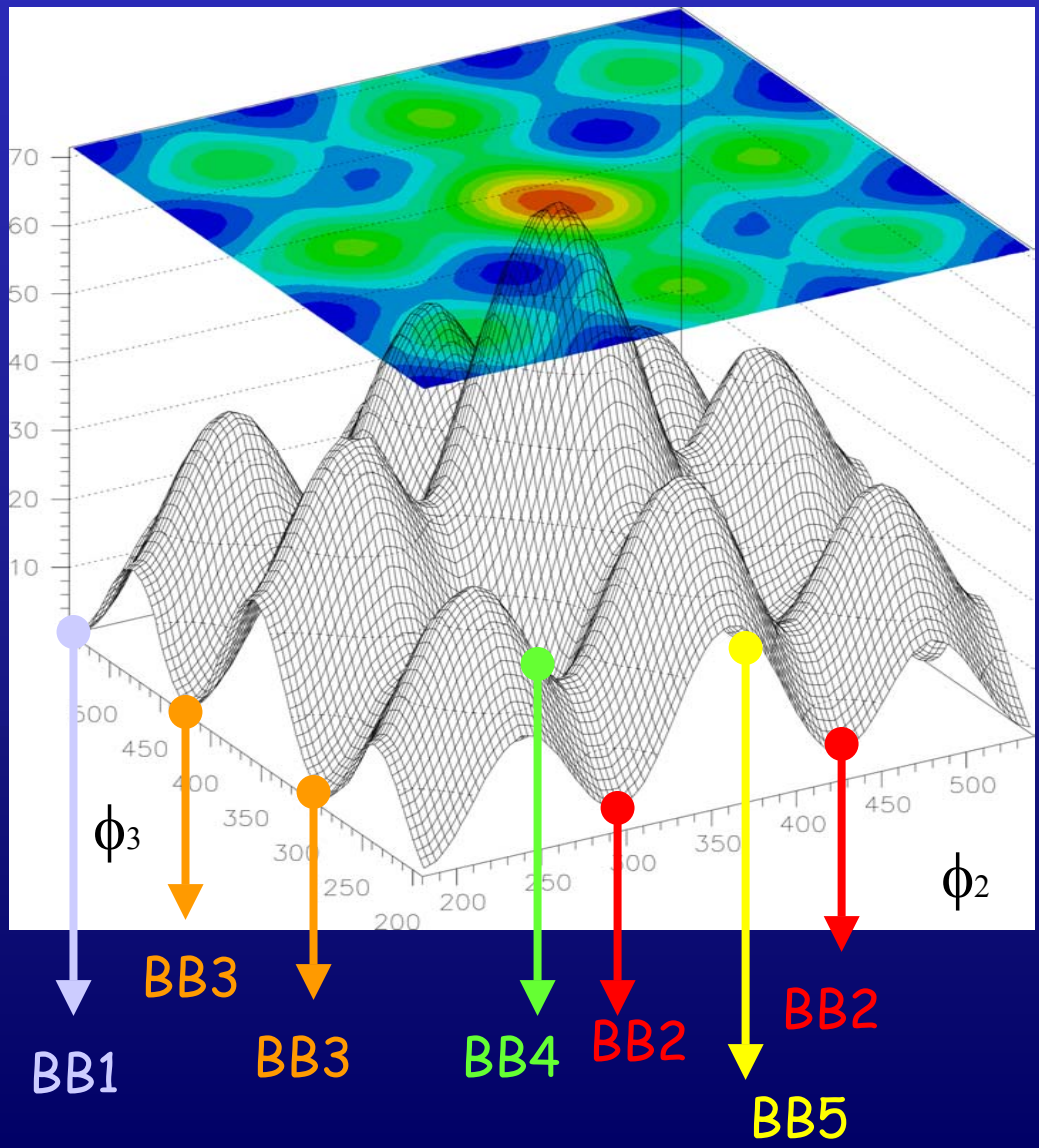
trans

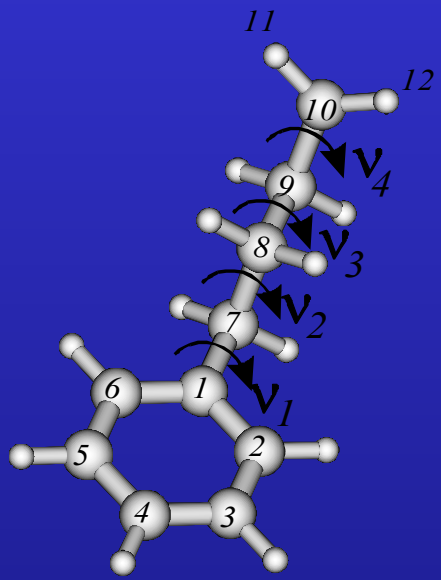
All conformers that can be reached by one internal rotation are taken into account correctly

How are other conformers like BB4,BB5 taken into account ?

Some conformers are only accessible by a path on the 2-dimensional PES

Correctly described by coupled internal rotations





The global and all internal rotations are coupled

Rotational Hamiltonian : $H = H_R + H_T + H_{RT}$

- Global rotation
- Internal rotation
- Coupling between total and internal rotation

Coupled internal rotations

$$H_T = \frac{1}{2} A J_2^2 + \frac{1}{2} B J_3^2 + C J_2 J_3 + V(\phi_2, \phi_3)$$

$$-\hbar^2 \frac{\partial^2}{\partial \phi_2^2} \qquad -\hbar^2 \frac{\partial^2}{\partial \phi_3^2}$$

$$\longrightarrow \quad \psi_k \ (\phi_2, \phi_3)$$

$$\varepsilon_k$$

Uncoupled internal rotation

$$V(\phi_2, \phi_3) \longrightarrow V(\phi_2) + V(\phi_3)$$

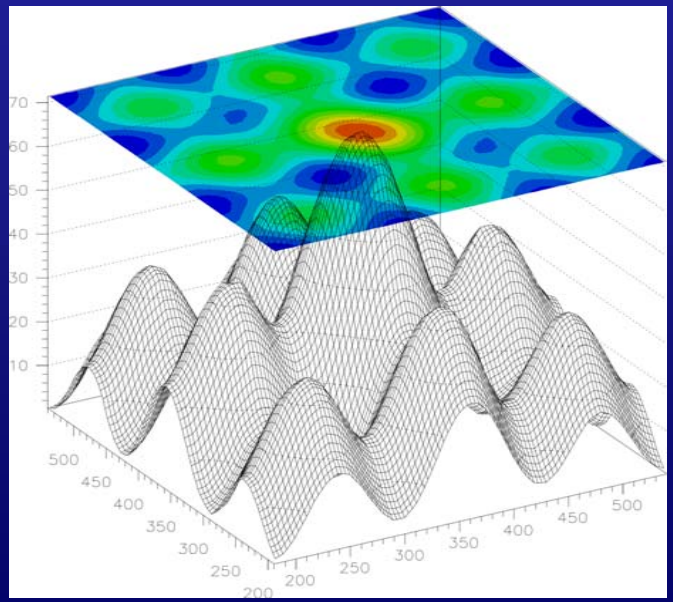
$$-\frac{\hbar^2}{2I_2} \frac{\partial^2 \psi_k(\phi_2)}{\partial \phi_2^2} + V(\phi_2)\psi_k(\phi_2) = \varepsilon_k \psi_k(\phi_2)$$

Influence of coupled internal rotations on partition functions

Ethylene and propylene internal rotation in butylbenzene radical

	ethylene	propylene	
q HO (300K) =	2.38	3.00	
q IR,uncoupled (300K)=	7.71	* 7.83 =	60.36
q IR,coupled(300K)=			23.93

Density of states is larger in IR rotor case versus HO case
More conformers can be accessed



Partition function decreases, due to large bump in potential energy surface, energy levels are shifted up

Influence of coupled internal rotations on the kinetic parameters

Cyclization Reaction :

Ea (HO)	= 49.53	A(HO)	=1.5E10
Ea (IR,uncoupled)	= 49.25	A(IR,uncoupled)	=1.6E9
Ea (IR,coupled)	= 49.21	A(IR,coupled)	=3.0E9

Activation energy is primarily determined by difference in groundstate energies between transition state and reactant

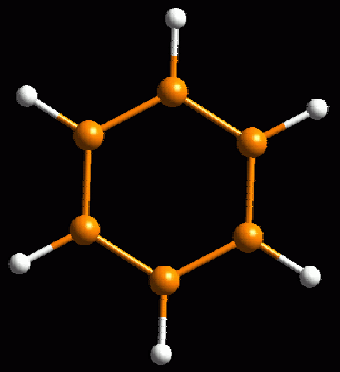
Influence of coupled internal rotations is rather small on A for this particular reaction

Work is in progress to test the approach on other reaction and on other thermodynamic quantities

Outline

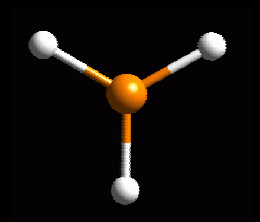
- Theoretical procedures on addition of ethylradical to ethene
- Cyclization of primary ethylbenzene radical : coupled internal rotations
- Hydrogen abstraction reactions : Free rotor approach
- Application on other reaction of coke formation

Hydrogen abstraction reactions

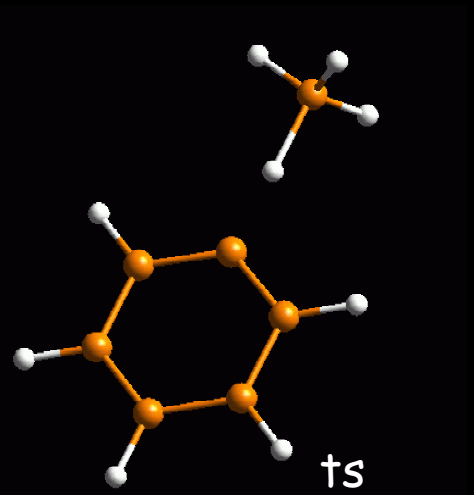


Benzene

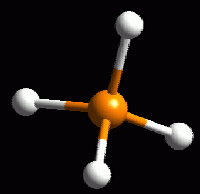
+



methylradical

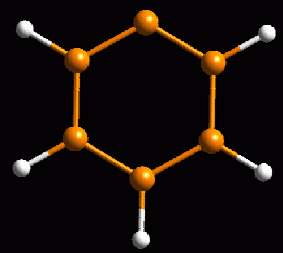


ts



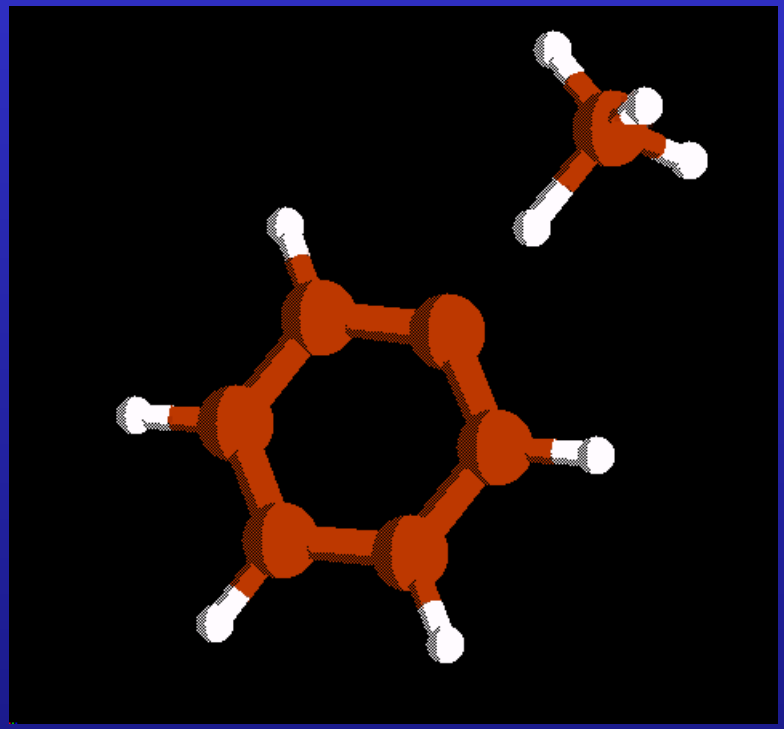
Methane

+

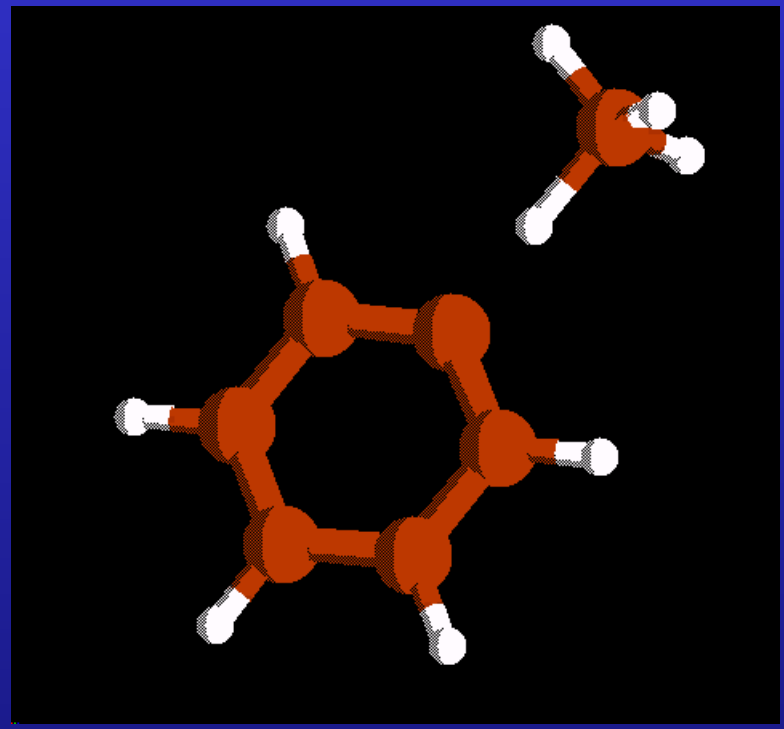


Fenylradical

One imaginary frequency corresponding with reaction coordinate



Internal rotation with very loose potential
Frequency 8.39 1/cm



Standard from ab initio packages : All vibrations in HO approximation

$q_{vib1}(300K)_{HO}$ = 25.8

$q_{vib1}(300K)_{Free\ Rotor}$ = 11.1

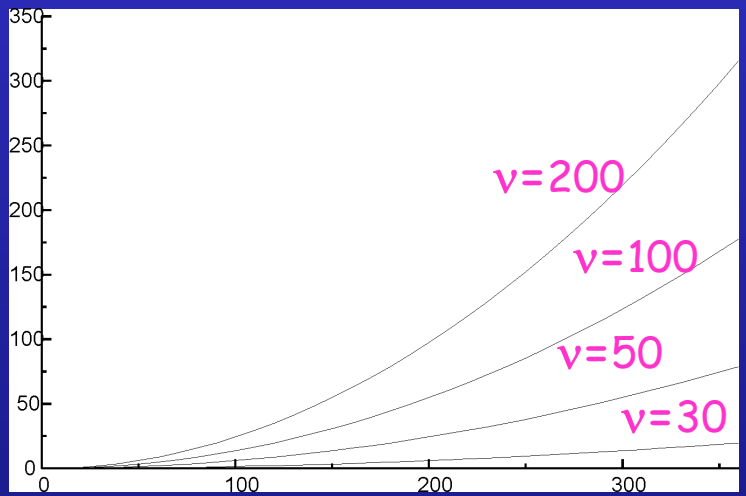
HO description is not physical in this case

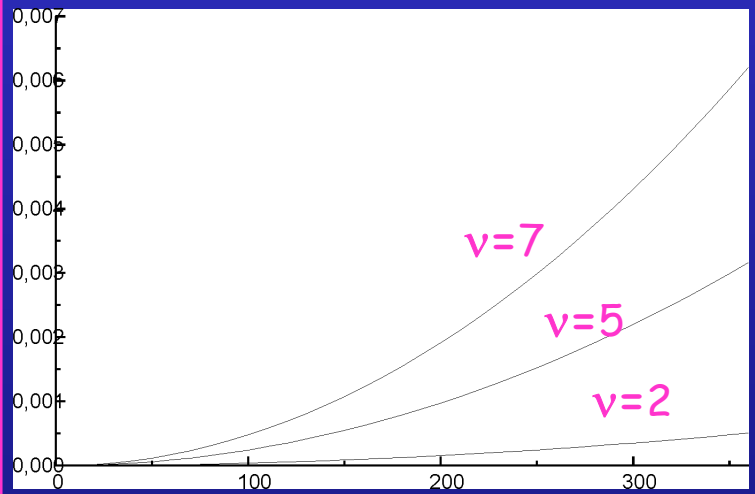
HO description :

ν

force constant : k= Im ω^2

HO potential : V= 0.5*k*Θ^2





Describe as free rotor

Not a realistic representation as HO.

HO description is only valid

if the potential causes serious hindering

Partition function of transition state :

q(HO, 700K) = 60.26

q(Free rotor, 700 K) = 17.04

Kinetic parameters :

Ea (HO) = 79.68 kJ/mol

Ea (free rotor) = 76.05 kJ/mol

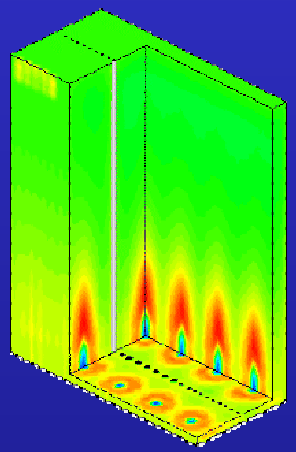
A(HO) = 3.36 E9 m^3/mol s

A(free rotor) = 5.14 E8 m^3/mol s

For hydrogen abstractions, serious overestimation of partition functions of transition state in HO approximation

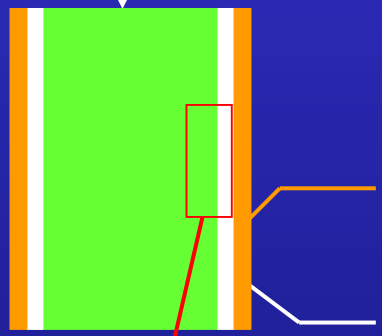
Outline

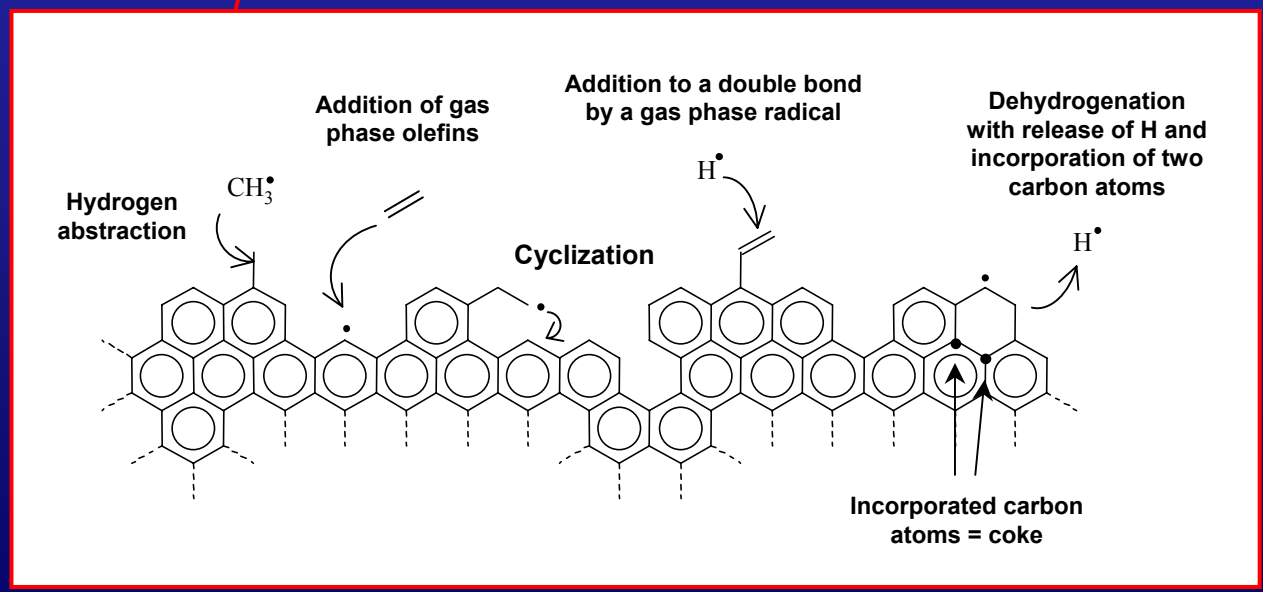
- Theoretical procedures on addition of ethylradical to ethene
- Cyclization of primary ethylbenzene radical : coupled internal rotations
- Hydrogen abstraction reactions : Free rotor approach
- Application on other reaction of coke formation



3-dimensional view of
a thermal cracking furnace

Process gas :
Hydrocarbon mixture





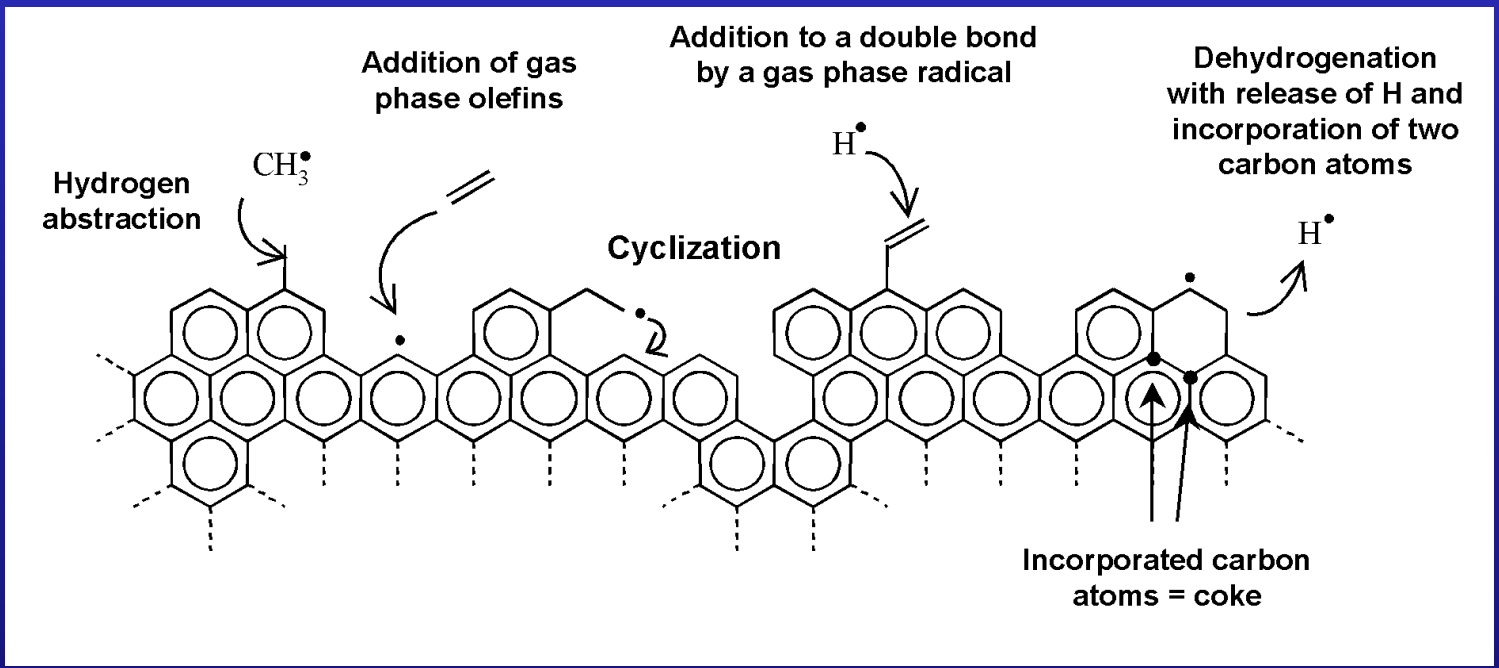
Thermal cracking network with more than 1000 reactions

?

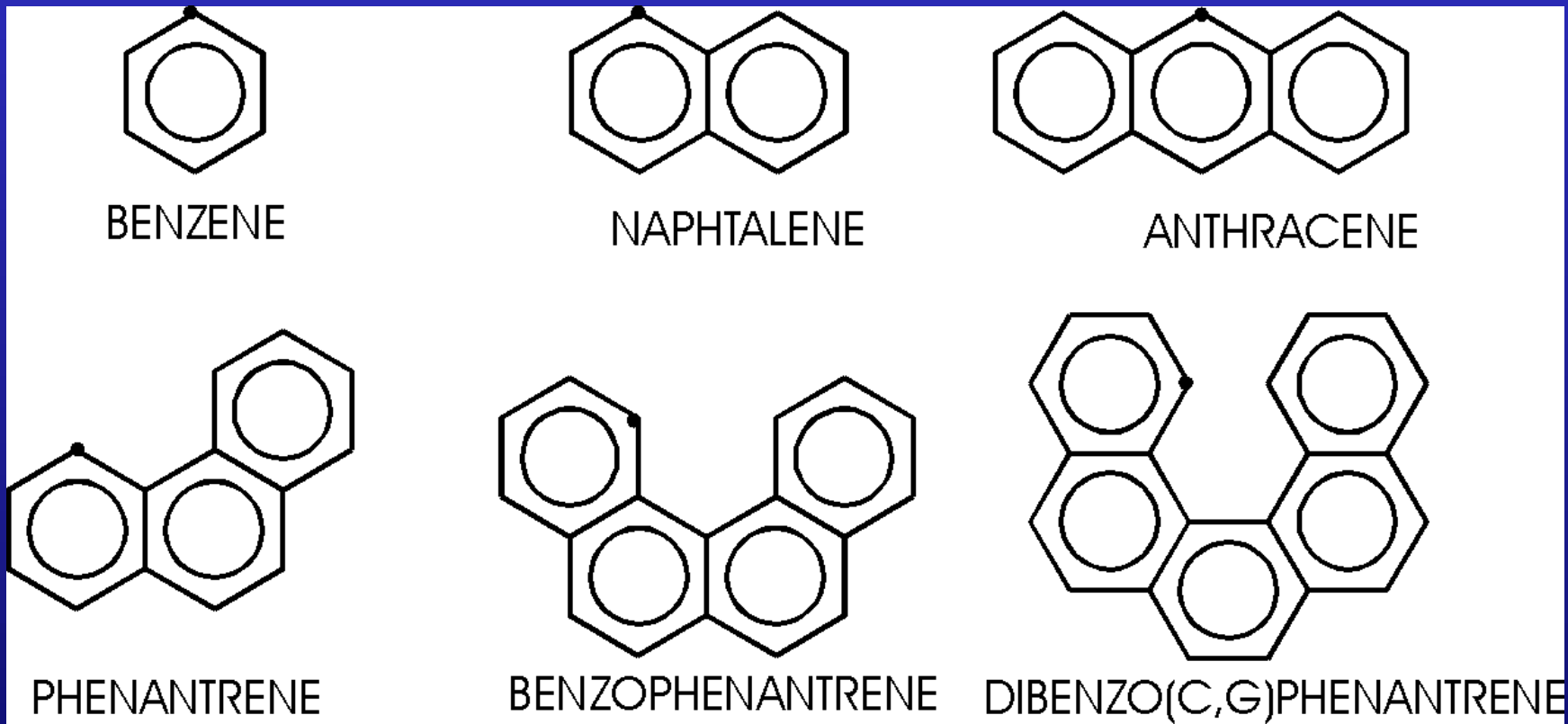
Information on kinetic and mechanistic aspects
of elementary reactions of the network

Ab initio calculations on elementary reactions of the network

Elementary Reactions

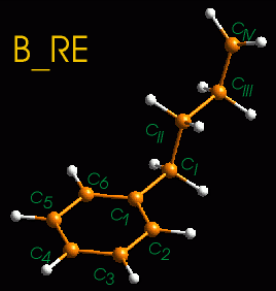


Influence of the local coke matrix on the kinetic parameters.

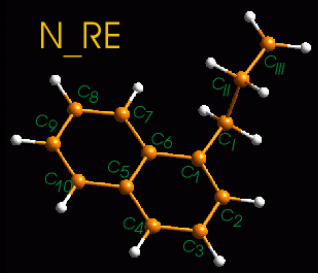


REACTANTS

B_RE

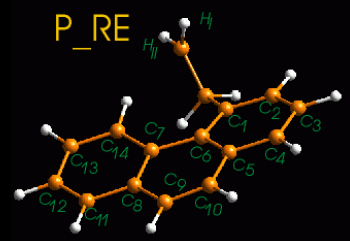


N_RE

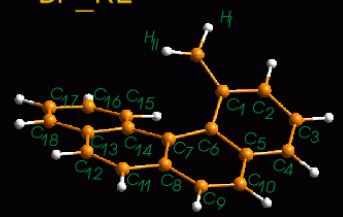


A_RE

P_RE

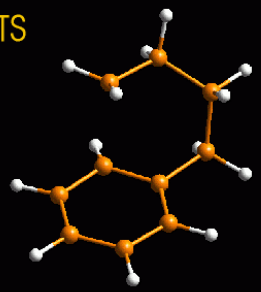


BP_RE



TRANSITION STATES

B_TS



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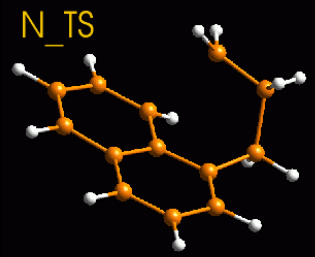

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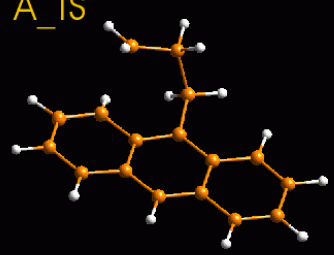

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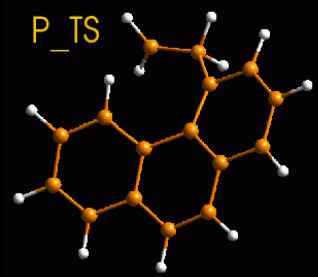

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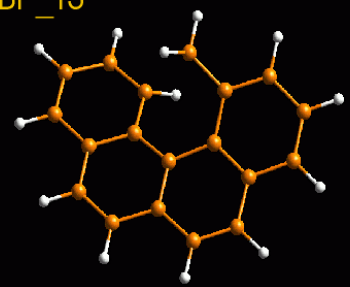
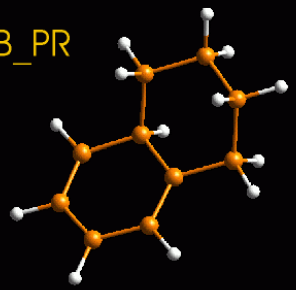


PRODUCTS

B_PR



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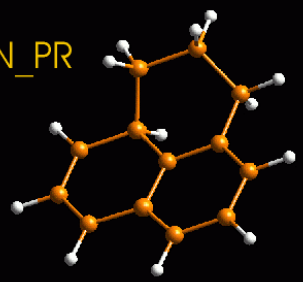

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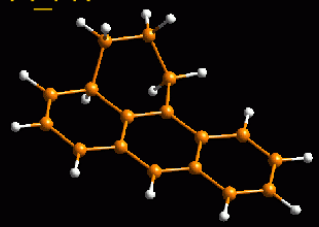

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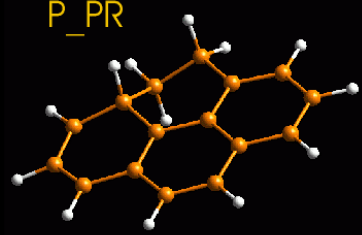

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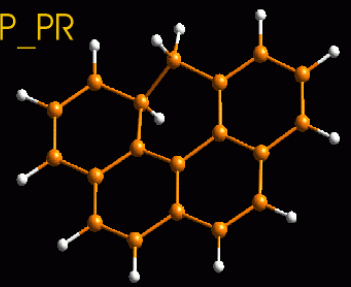
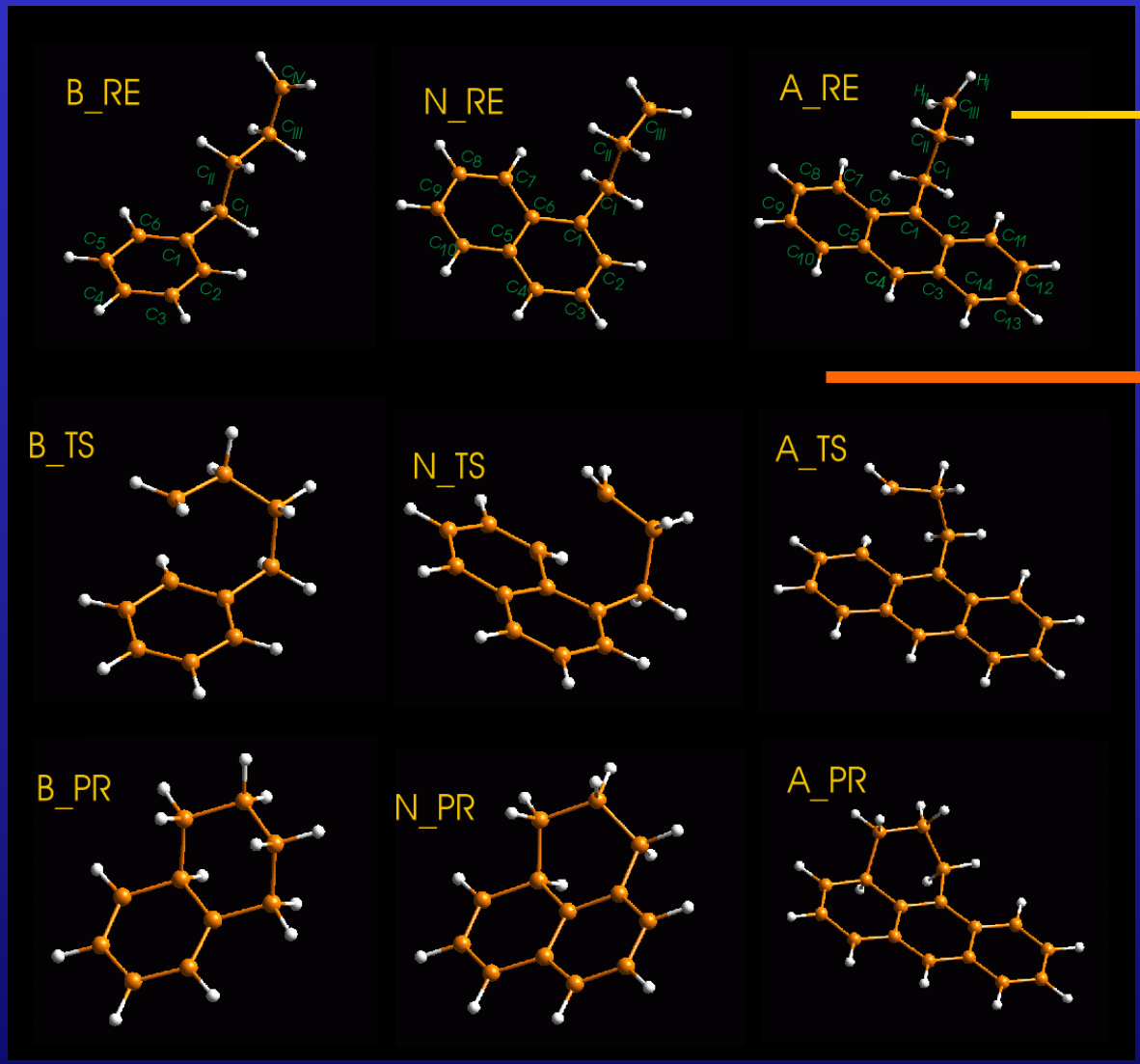
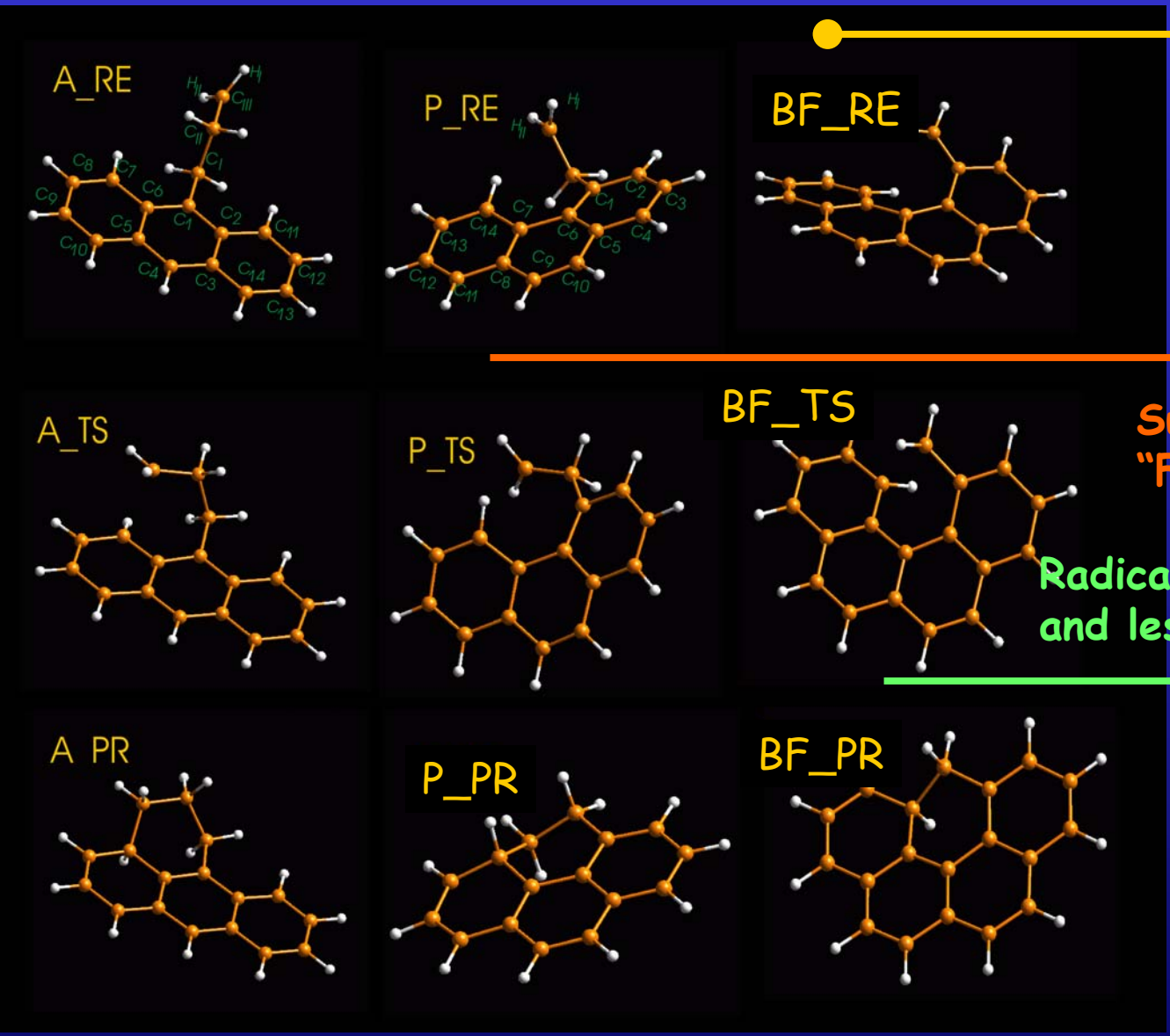




Aromaticity is preserved in reactant

Transition state is stabilized by resonance stabilization

	Ea	A
B	49.53	1.5 E10
N	47.79	1.3 E11
A	40.38	2.4 E11



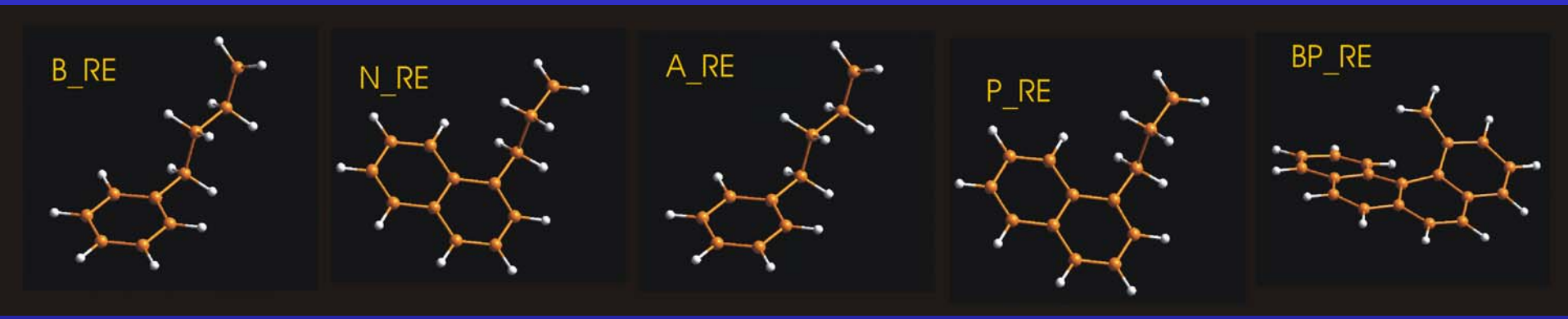
Aromaticity is partly broken in reactant

Substrate is more reactive "Folded cluster"

Radical is of the benzylic type and less reactive

	Ea	A
A	40.38	2.4E11
P	32.64	3.8E11
BP	50.35	1.9E12

Preexponential factor



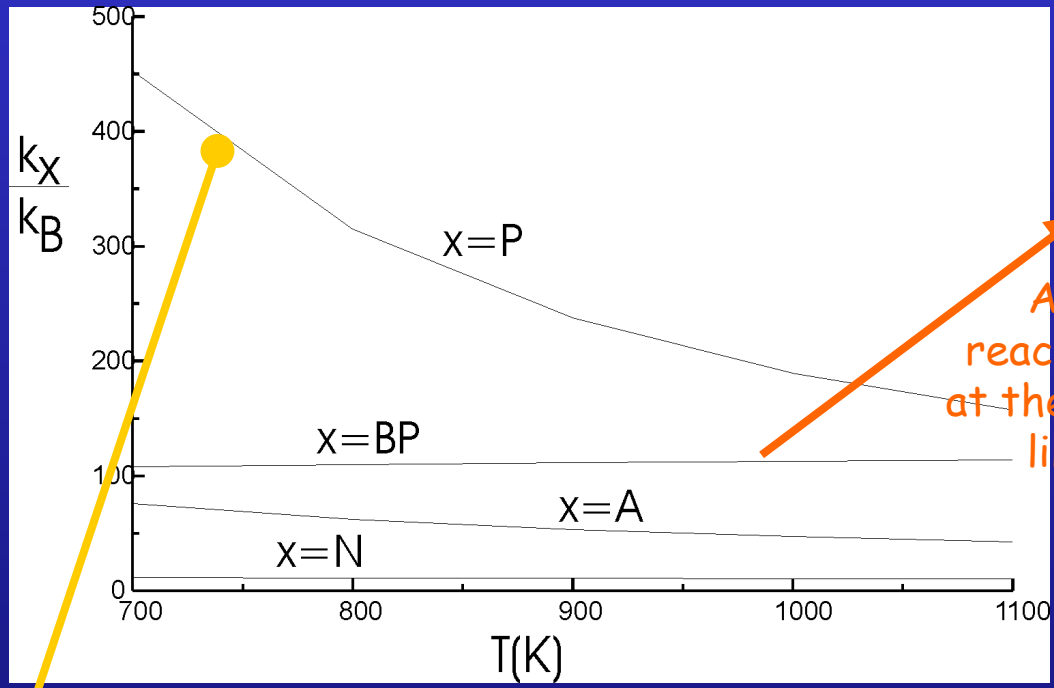
1.5 E10 1.3E11 2.4E11 3.8E11 1.9E12

The alkylchain is longer, the conformational flexibility increases

The probability that a the reactant molecule resides in a conformation suitable for cyclization decreases

Not a pure effect of the structure of the coke matrix

Influence of the local structure of the coke matrix on the reaction kinetics



At the end of the reactor also cyclization at the benzophenantrene-like site becomes important

Temperatures in a typical cracking unit
700K-1100K

Ring closure at "folded" clusters is much faster than at cluster in which aromaticity is preserved in reactant.

Coke formation is autocatalytic : Larger macroradicals, react faster than the smaller ones they originate from

Conclusions

- Rate constants can be calculated from first principles
- Microscopic insight into the factors that govern reaction barrier and preexponential factor
- Influence of correct theoretical description of internal rotations is large

Collaborators

- K. Van Cauter, D. Van Neck, M.Waroquier (RUG, Laboratory of Theoretical Physics)
- M.Saeys, M.F. Reyniers, G.B.Marin (RUG, Laboratory of Petrochemical Engineering)

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