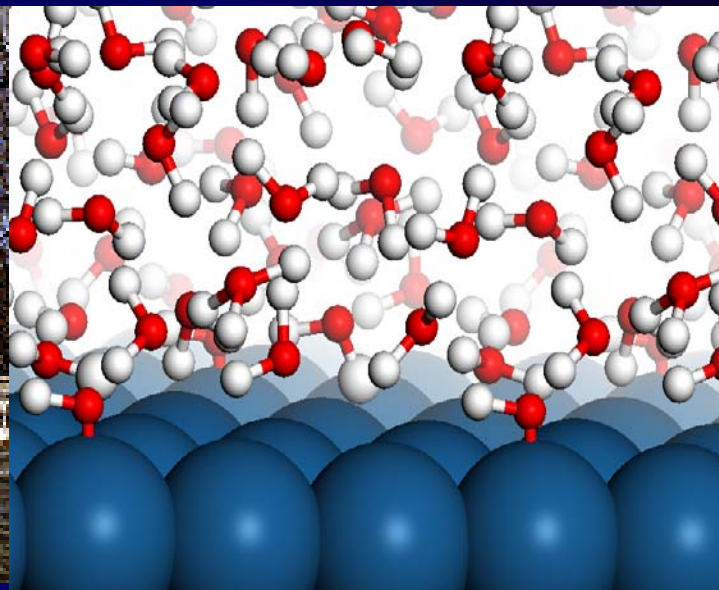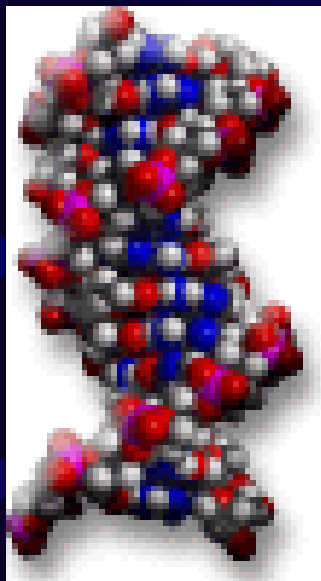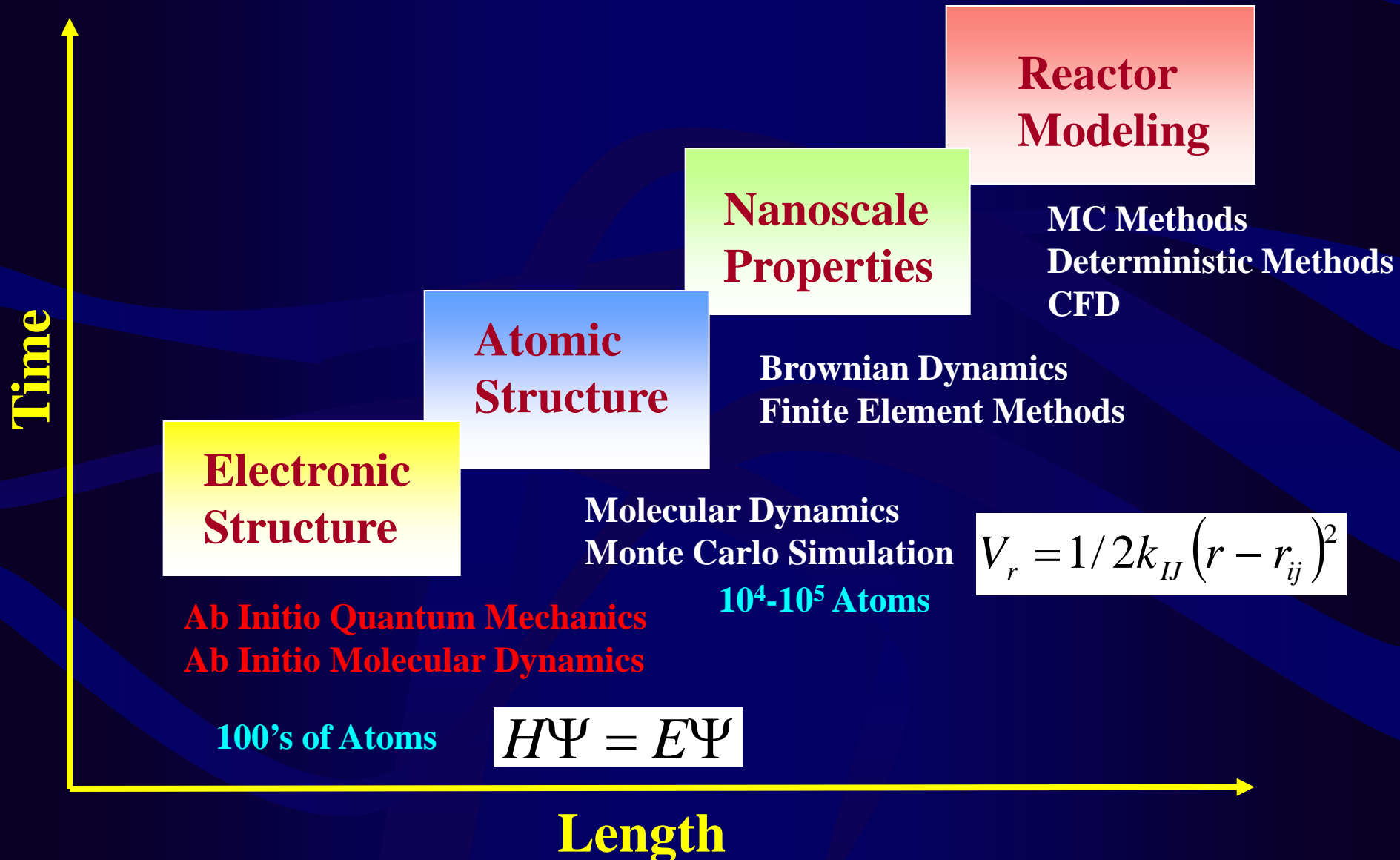# Atomistic and Molecular Simulation Methods

Matthew Neurock

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University of Virginia

Computational Chemistry

A suite of methods which range from highly empirical models
to ab initio electronic structure calculations that enable the prediction
of structure and properties of an N atom system.

Ab initio QM	Semiempirical QM	Molecular Mechanics
Rigorous Solution of Schrödinger's Equation	Approximate Solution to Schrödinger's Equation	Empirical Potential Function
Electronic Structure	Empirical information used to solve computationally demanding integrals	Prediction of Structure and Conformational Energies
Full range of properties		
10^2-10^{-3} Atoms	10^3-10^4 Atoms	10^5-10^7 Atoms

Increasing Empiricism $\longrightarrow$

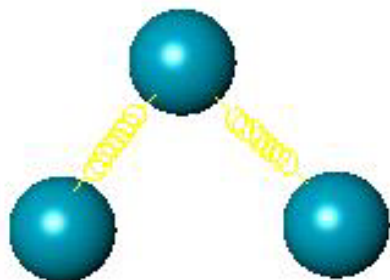$\longleftarrow$ **Increasing Computational Demand**

Basic Methods in Computational Chemistry

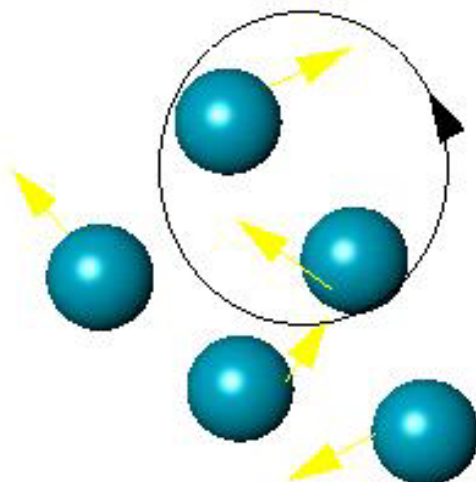**Fundamental Entity = Atom**   **Fundamental Entity = electron**

Molecular Mechanics

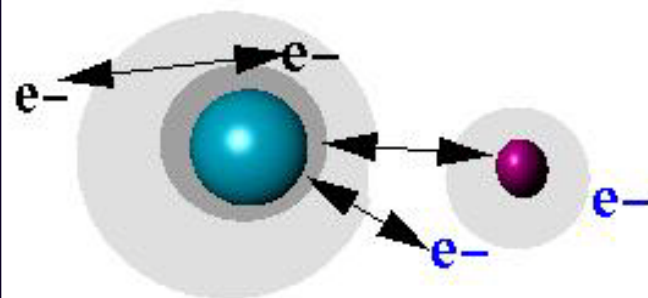*Optimize Structure and Conformation*

Molecular Dynamics

Newton's Equations of Motion

Simulate Dynamic Movement of Particles.

Classical forces and force fields.

Quantum Mechanics

Force Balance on Electrons

$$H\Psi = E\,\Psi$$

Required for Modeling ' Reactivity

$$H = K.E. + V_{ne} + V_{ee}$$

Methods for Predicting Properties

Properties/Methods	MM	MC	MD	QM
Structural	Yes	Yes	Yes	Yes
Electronic	No	No	No	Yes
Spectroscopic	No	No	No	Yes
Chemical	Some	Some	Some	Yes
Magnetic	No	No	No	Yes
Optical	No	No	No	Yes
Thermochemical	Some	Some	Some	Yes
Thermophysical	Few	Some	Some	Some
Reactivity	No	No	No	Yes
Mechanical	Some	Some	Some	Some
Biological	No	No	No	Difficult
Catalytic	Few	Few	Few	Yes

Quantum Mechanical Methods

Time Dependent Schrödinger Equation

$$\hat{H}\Psi = i\hbar\frac{d\Psi}{dt}$$

$$\hat{H}(r,t) = \hat{H}(r)$$

$$\Psi(r,t) = \Psi(r)e^{-iEt/\hbar}$$

Wave-Particle Duality

*Electrons are too light
To be described by
Classical mechanics.*

*QM equation corresponding
To Newton' second law
Concerning how the system
Evolves with time.*

H operates on the
Function and returns the
Observable quantity (energy)

Time Independent Eq.

$$\hat{H}\Psi = E\Psi$$

$$|\Psi|^2 =$$ **Probability of finding the N particle system in a particular configuration.**

Goal of Quantum Mechanical Methods

Predict the Structure, Energy and Properties of an N Particle System,
**(Electrons & Nuclei)**

Energy is a direct function of the exact position of all of the atoms, and the forces that act upon these atoms.

Predicting Properties

- **Structural**
- **Electronic**
- **Spectroscopic**
- **Chemical**
- **Magnetic**
- **Optical**
- **Thermochemical**
- **Thermophysical**
- **Reactivity**
- **Mechanical**
- **Biological**
- **Catalytic**

In theory, all of the these properties can be predicted if we know how the fundamental geometric and electronic structure control them. In practice, simulating some of these systems is a best a very difficult challenge.

Schrödinger Equation
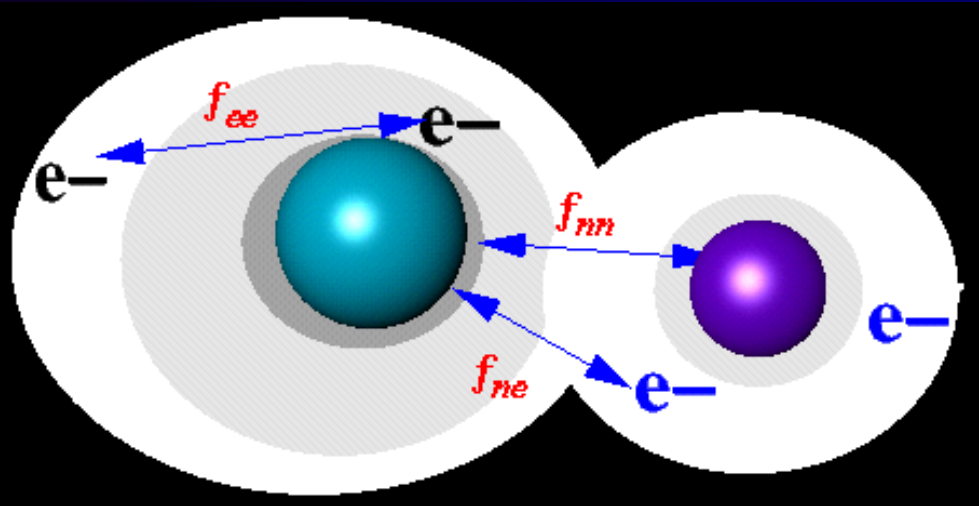
Electronic Force Balance
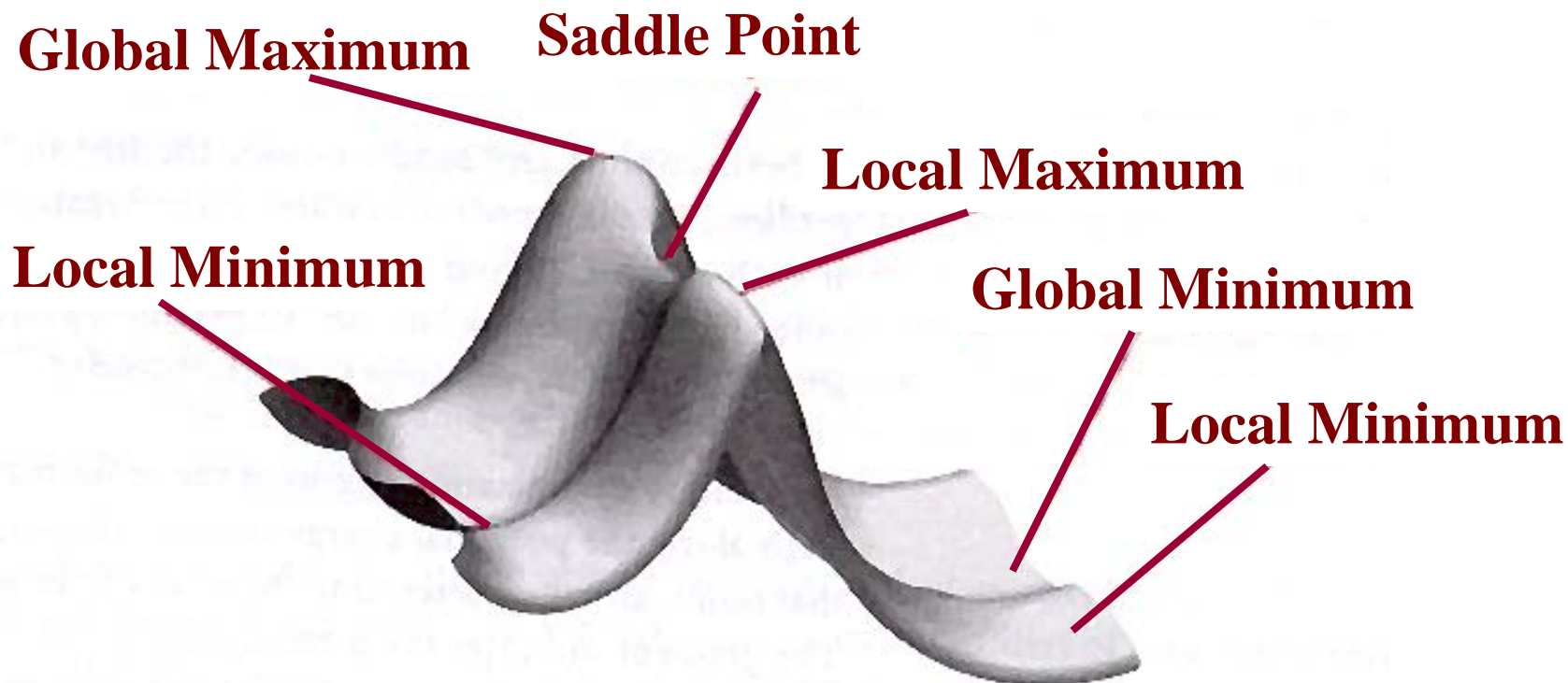
Kinetic Energy

Electron/Electron Repulsion

$$\hat{H}(r_i, R_a) = -\sum_i^n \frac{\hbar}{2m_i} \nabla_i^2 - \sum_i^n \sum_a^N \frac{Z_a}{\left| r_i - R_a \right|} + \sum_i^n \sum_{j>i}^n \frac{1}{\left| r_i - r_j \right|} + \sum_a^n \sum_{b>a}^n \frac{Z_a Z_b}{\left| R_a - R_b \right|}$$

Nuclear/Electron Attraction

Nuclear/Nuclear Repulsion
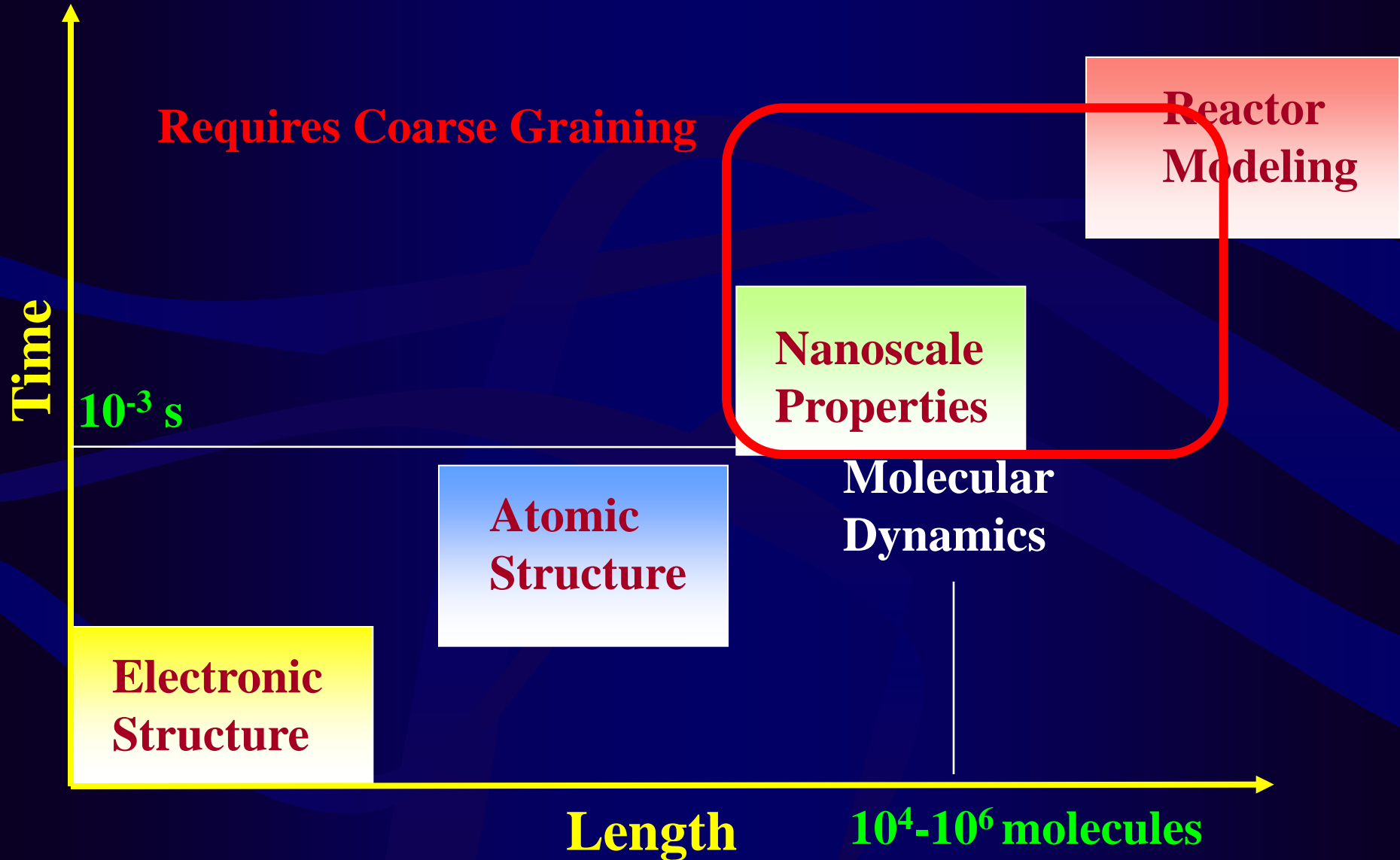
Multidimensional Potential Energy Surface

3N-6 Dimensions

Global Maximum

Saddle Point

Local Maximum

Local Minimum

Global Minimum

Local Minimum

Multiple energy minimum

Simulating Longer Time and Length Scales

Time

Requires Coarse Graining

10^{-3} s

Reactor Modeling

Nanoscale Properties

Molecular Dynamics

Atomic Structure

Electronic Structure

Length

10^4-10^6 **molecules**

Monte Carlo Simulation

"Monte Carlo Method" – Probabilistic approach involving stochastic sampling.

1940's Origin Ulam and von Neumann – to determine the distance a neutron would travel in a material before colliding with a nucleus. Named after Monte Carlo Casino in Monaco.

Define a domain of possible inputs
Generate inputs randomly from the domain using a specified
   Probability distribution
Perform deterministic computations using the inputs
Aggregate the results of individual computations into final result

Analogous to the game "Battleship"

Monte Carlo Simulation
Configurational Integral & MC Integration

$$Z = \int dr^N \exp\left[-U(r^N)/k_B T)\right]$$

Monte Carlo Simulation is used to stochastically sample random configurations to carry out the integration.

$$Z = \frac{V}{N_{MCsteps}} \sum_{i=1}^{N_{MCsteps}} \exp\left[-U(r^N)/k_B T\right]$$

Average property A

$$\langle A \rangle = \frac{\int A(r^N) \exp\left(-\dfrac{U(r^N)}{k_B T}\right) dr^N}{\int \exp\left(-\dfrac{U(r^N)}{k_B T}\right) dr^N} = \frac{\sum\limits_{i=1}^{M} A_m}{\sum\limits_{i=1}^{M} 1} = \frac{1}{M} \sum_{i=1}^{M} A_m$$

Monte Carlo Simulation Methods

Canonical Ensemble (NVT) MC Simulation

Minimize Helmholtz Free Energy

Determine P, Optimized Structure and Lowest Energy

Metropolis algorithm used to stochastically sample the system.

System maintains constant number of molecules, volume, and temperature

Isothermal-Isobaric simulations can also be performed in order to calculate volume.

Grand Canonical Ensemble (μVT) MC

Number of particles are allowed to change.

Useful in simulating phase behavior

Sorption isotherms, phase diagrams, etc.

Simulation enables stochastic trial moves along with particle insertion and deletion moves.

$$P_{Accept} = \frac{fV}{k_B T (N+1)} \exp(-\Delta U / k_B T)$$ Insertion

$$P_{Accept} = \frac{N k_B T}{fV} \exp(-\Delta U / k_B T)$$ Deletion

Monte Carlo Simulation Methods

Configurationally Biased Monte Carlo Simul.

Allows larger molecules to insert "atom-by-atom" thus avoiding the difficulty in sampling the low probability for molecular insertion.

Acceptance rules are changed in order to reflect the bias introduced in allowing these low probability acceptances.
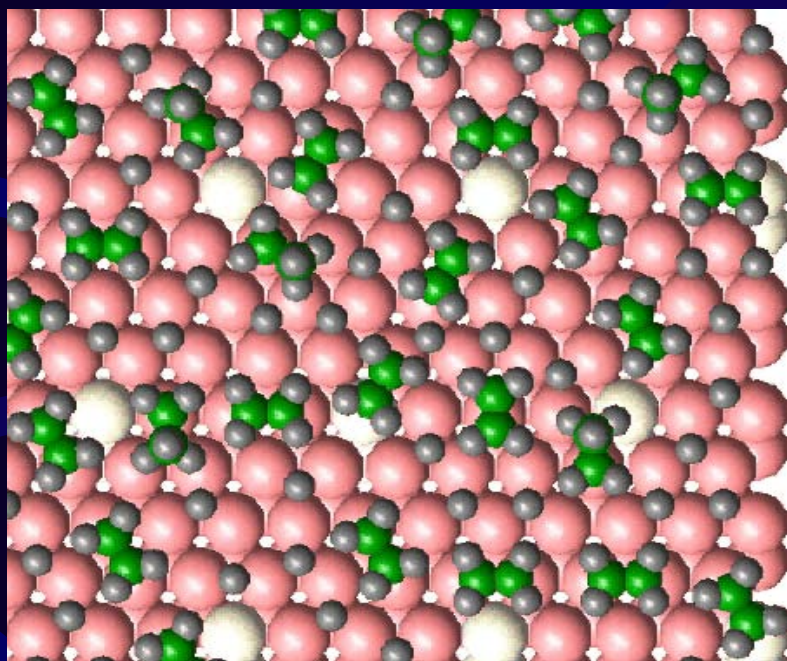
Significant reduction in the CPU costs.

Gibbs Ensemble Monte Carlo Simulation

Used to simulate phase equilibrium for fluids and mixtures.

Particles allowed to move between two phases.

Simulating Intricate Atomic and Molecular Kinetic Processes for Engineering Applications

Non-Equilibrium Kinetic Processes
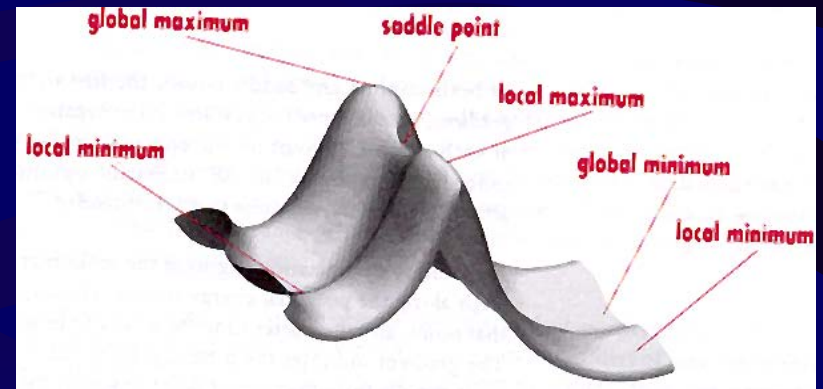
Reaction
Diffusion
Adsorption
Desorption
Transport

Rare or infrequent event processes.

Crystal Growth, Coarsening, Corrosion, Surface Reactivity, Catalysis

Modeling Kinetics

Deterministic Kinetics

Averaging over components/sites.

Solution of sets of coupled differential equations.

Stochastic Kinetics

Kinetics governed by transition probability.

Lattice-based methods to follow spatial behavior

Mean Field
Quasi Chemical
Dynamic or Kinetic Monte Carlo
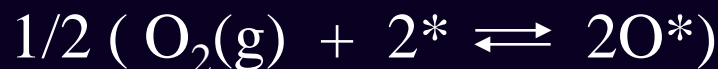
Deterministic Kinetics

Early spatial averaging

Loss of structure and spatial composition.

Kinetics based on concentrations or coverage

(moles/area or moles/volume)

Example: CO Oxidation

$$CO(g) + * \rightleftharpoons CO*$$
$$1/2 (O_2(g) + 2* \rightleftharpoons 2O*)$$
$$CO* + O* \rightleftharpoons CO_2(g) + 2*$$

$$R_{srxn} = [CO*] \, [O*]$$

$$[CO*] = K_{CO}P_{CO}[*]$$

$$[O*] = K_{O_2}^{1/2} P_{O_2}^{1/2}[*]$$

$$\theta^* = C^* / C_T = [1 + K_{CO}P_{CO} + K_{O_2}^{1/2} P^{1/2}]$$

$$r_{srxn} = \frac{k_{srxn}K_{CO}K_{O_2}^{1/2}P_{CO}P_{O_2}^{1/2}}{[1 + K_{CO}P_{CO} + K_{O_2}^{1/2} P^{1/2}]}$$

Average surface coverage and heat of adsorption

Solutions for Deterministic Kinetics

Analytical Rate Expression.

$$r_{srxn} = \frac{k_{srxn} K_{CO} K_{O_2}^{1/2} P_{CO} P_{O_2}^{1/2}}{[1 + K_{CO} P_{CO} + K_{O_2}^{1/2} P^{1/2}]}$$

Sets of differential equations.

$$\frac{d\theta_{CO}}{dt} = k_{A_{CO}} P_{CO} [\theta^*] - k_{D_{CO}} P_{CO} [\theta_{CO}^*] - k_{srxn} [\theta_{CO}^*][\theta_O^*]$$

$$\frac{d\theta_{CO}}{dt} = \ldots\ldots$$

For Surfaces: Coverage Effects

Reactivity = f (Coverage)

1) Ideal

Langmuir Kinetics – No Interactions

$$r_{srxn} = \frac{k_{srxn}K_{CO}K_{O_2}^{1/2}P_{CO}P_{O_2}^{1/2}}{[1 + K_{CO}P_{CO} + K_{O_2}^{1/2}P^{1/2}]}$$

Site competition

2) Non-Ideal

Temkin Isotherm

Two parameter model to treat site distributions.
Still avoids lateral interactions.

Freundlich Isotherm

Treats adsorbates in a general analytical model.
No spatial discrimination.

Lattice Based Methods

1) Ideal Lattice Gas

No Lateral Interactions

Langmuirian isotherm

$r = k\theta_A$ $A \longrightarrow B$

$r = k\theta_A\theta_B$ $A + B \longrightarrow C$

Power Law Kinetics

2) Mean Field Approximation

Simplest Statistical Approximation

Random distribution of molecules

No explicit lateral interactions

Average interaction energy

3) Quasi Chemical Approximation

Simplest statistical approach that considers explicit
    particle configurations.

Simple Grand Canonical distribution of 2-site clusters.

Replace the interactions between molecules with average self
    consistent interaction energy by solving:

$$\frac{P_{AA} P_{OO}}{P_{AO}^2} = 0.25 \exp(-\varepsilon_{AA} / T)$$

P_{AA}, P_{AO}, P_{OO} = Probabilities for 2-adsorbed, 1-adsorbed,
                and 0-adsorbed sites being occupied.

$P_{AA} + P_{AO} + P_{OO} = 1$ $2P_{AA} + P_{AO} = 2\theta_A$

QSA can calculate probabilities for arrangements of other
    adsorbed molecules (A, B)

4) Bethe – Peirerls Approximation

Expansion to other more detailed interactions of central sites and adjacent sites.

5) Kinetic or Dynamic Monte Carlo Simulation

Used to treat non-ideal and more complex systems.

Stochastic Methods

System dynamics governed by the Master Equation.

> *System = an infinite number of species/sites.*
> *State = particular configuration of the system.*

$$X_1 \rightarrow X_2 \rightarrow X_3 \rightarrow X_4 \rightarrow X_5 \rightarrow X_6 \rightarrow X_7 \rightarrow X_8 \quad \ldots\ldots X_n \rightarrow X_{n+1}$$

Master Equation

$$\frac{\partial P(\bar{x}_i, t)}{\partial t} = \sum_{\{\bar{x}_j\}} \left\{ P(\bar{x}_j, t) T(\bar{x}_j -> \bar{x}_i) - P(\bar{x}_i, t) T(\bar{x}_i -> \bar{x}_j) \right\}$$

Balance on the forces that drive the system from one state to another.

Master Equation

$$\frac{dP_i}{dt} = \sum_j \left[w_{ji} P_j - w_{ij} P_i \right]$$

P_i = Probability that the system is in state i at time t.

*W_{ij} and W_{ji} are the transition probabilities
(Rates of at which one state converts to the other)*

Detailed Balance Must Hold

$$w_{ji} P_j = w_{ij} P_i$$

Master Equation (contd.)

Equilibrium probability distribution of configurations must obey a Boltzmann distribution.

$$P_i = Z^{-1} \exp(-H(i) / k_B T)$$

Partition Function   Hamiltonian

Analytical Solution

    Only possible for a few simple systems.

Numerical Solution

    Dynamic or Kinetic Monte Carlo Simulation

Kinetic Monte Carlo Simulation

Extension of the equilibrium methods such as the Metropolis method (1953) for sampling geometries for desired physical ensembles by very simple rules involving movement of atoms one at time.

First methods developed in the 1960's in order to move systems dynamically from state to state. (Beeler – 1966 Radiation Damage)

Algorithm development:

      1975 Bortz, Kalos and Lebowitz (BKL) - Surfaces (physics)

      1976 Gillespie - Well Mixed Systems (Chemistry)

Dynamic (Kinetic) Monte Carlo Simulation

Fixed Time Step – Time Space

Δt	Δt	Δt	Δt	Δt	Δt	Δt	Δt	Δt	Δt	Δt	Δt	Δt	Δt	Δt

t_1 t_2 t_3 t_4 t_5 t_6 ... t_{n-1} t_n t_{n+1}
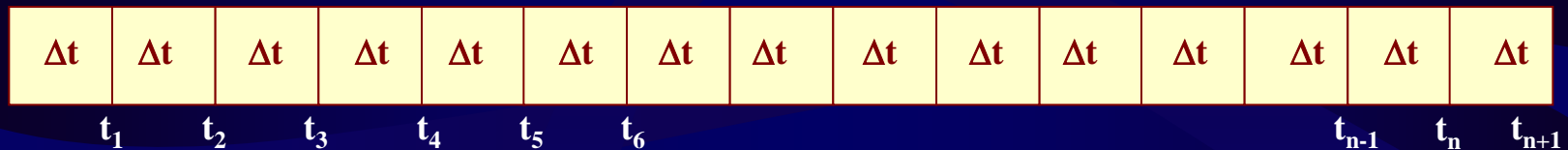
$\Delta t =$ fixed time increment

Move in time – monitor events.

Variable Time Step – Event Space

t_1 t_2 t_3 t_4 t_5 t_6 t_7 t_8 t_9 t_{10} t_{11} t_{12} ... t_{n-1} t_n t_{n+1}
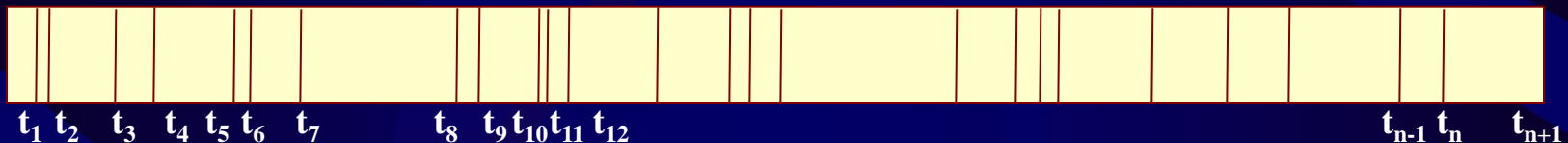
$\Delta t =$ variable time step

Move in event space – update time.

Kinetic (Dynamic) Monte Carlo Simulation
Fixed Time Step Approach

$$A \longrightarrow B$$
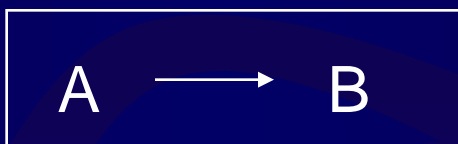
Probability that A reacts to B.

$$P_{AB} = 1 - \exp\left(-k_{AB}\Delta t\right)$$

$k_{apparent}$

Δt_{fixed}

A

B

Assume for example that P_{AB} works out to be a value of 0.1

Fixed Time Step Progression

t=0	A	A	A	A	A	A	A	A	A	A	A	A

0.4 | 0.01 | 0.7 | 0.11 | 0.9 | 0.3 | 0.6 | 0.03 | 0.4 | 0.8 | 0.09 | 0.2 |

$X_A = 1.00$

t=Δt	A	B	A	A	A	A	A	B	A	A	B	A

0.08 | 0.02 |

$X_A = 0.75$

t=2Δt	B	B	A	A	B	A	A	B	B	A	B	A

0.03 | 0.09 |

$X_A = 0.50$

t=3Δt	B	B	A	B	B	A	A	B	B	A	B	B

$X_A = 0.33$

.

.

.

t = nΔ t= final time

Draw Backs for Fixed-Time Step

$$A \xrightarrow{k_{AB}} B \xrightarrow{k_{BC}} C$$

Δt_{fixed}

A

↓

B

B ⟶ C

B
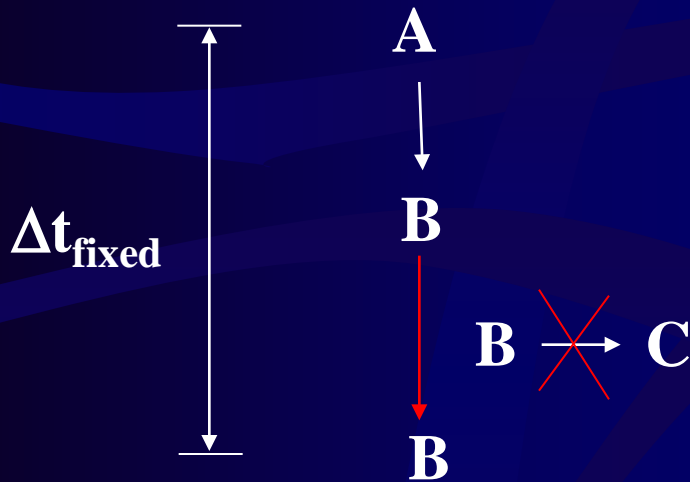
Multistep processes are not allowed to continue to react within the time step.

Drawbacks of Fixed Time Step Approach

Need to know all of the time steps and pathways before reaction.

Example: $\quad A \longrightarrow B \longrightarrow C$

$$P_{AB} = 1 - \exp(-k_{AB}\Delta t)$$

$$P_{BC} = 1 - \exp(-k_{BC}\Delta t)$$

$$P_{AC} = -\frac{k_{BC}}{k_{AB} - k_{BC}} P_{AB} + \frac{k_{AB}}{k_{AB} - k_{BC}} P_{BC}$$

Mathematically it is not an exact approach.

$$\lim_{\Delta t -> 0} = \Delta t_i \, (variable)$$

(becomes exact)

Variable Time Step Approach

$$P_i = RN = 1 - \exp\left(-\sum_{i=1}^{N_{events}} k_i \Delta t_i\right)$$

Time

$$\Delta t_i(\text{variable}) = \frac{-\ln(RN)}{\sum_{i=1}^{N} k_i}$$

Time at which the next event (regardless of type) occurs.

Event

$$S_i = \frac{\sum_{j>i}^{N} k_j}{\sum_{i=1}^{N} k_i}$$

If $S_{i-1} <$ RN $< S_i$ then event $= i$

Transition Probabilities

Elementary Processes

$$w_{ij} \ = \ k_{ij}$$

k_{ij} are derived from Transition State Theory

$$k_i = A_i \exp(-E_i / kT)$$

Apparent Kinetic Parameters

$$r_{srxn} = \frac{k_{srxn} K_{CO} K_{O_2}^{1/2} P_{CO} P_{O_2}^{1/2}}{[1 + K_{CO} P_{CO} + K_{O_2}^{1/2} P^{1/2}]}$$

$$k_{app\_CO\_Oxid} = r_{srxn} / P_{CO} P_{O2}^{1/2} = \left[\frac{k_{srxn} K_{CO} K_{O_2}^{1/2} P_{CO} P_{O_2}^{1/2}}{[1 + K_{CO} P_{CO} + K_{O_2}^{1/2} P^{1/2}]} \middle/ P_{CO} P_{O2}^{1/2} \right]$$

Stochastic Monte Carlo Algorithm Structure
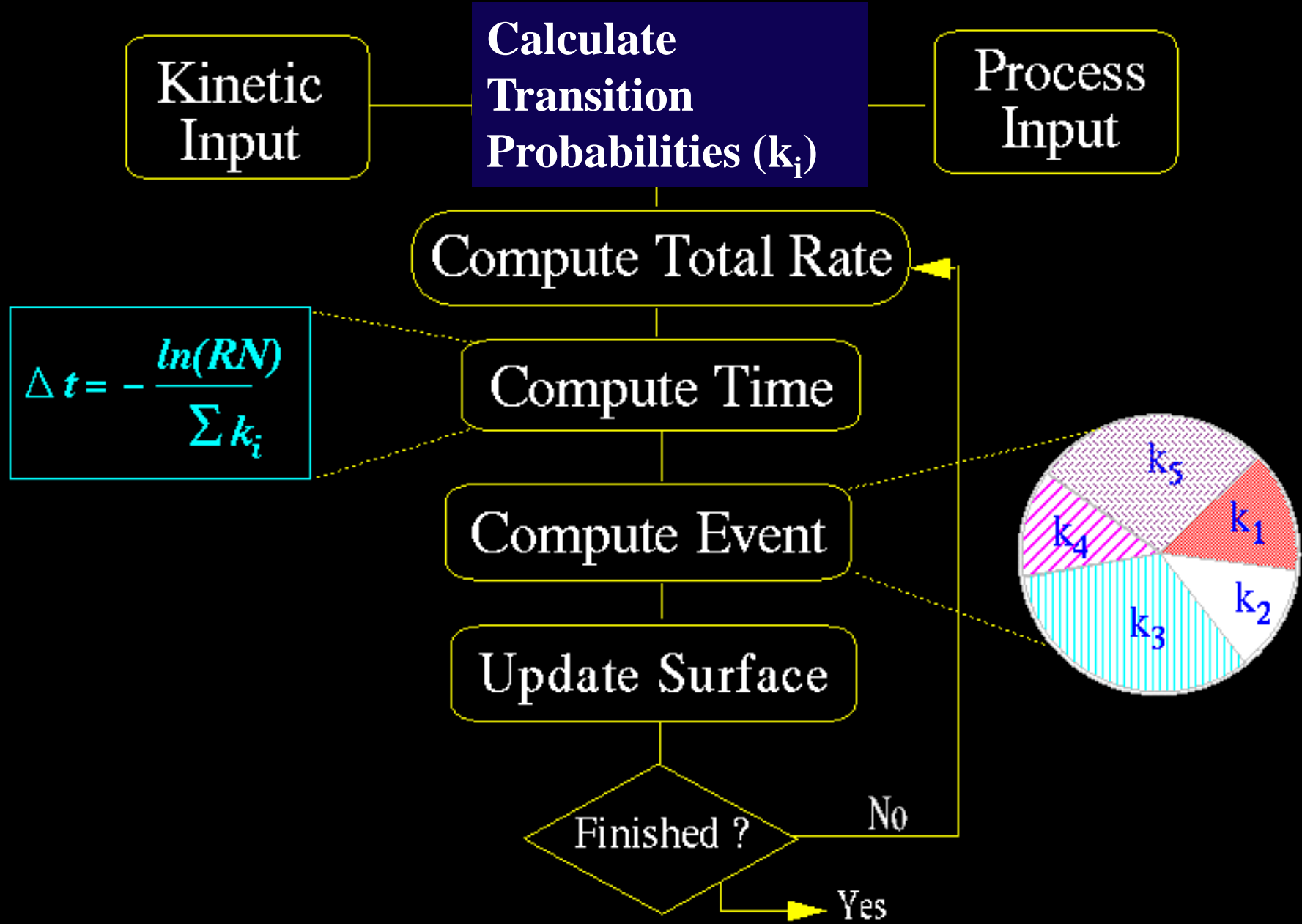
Variable Time Step Approach

Simulations proceed in event space (event-by-event)

Time is updated at each event.

Exact mathematical approach.

Drawbacks

Disparate processes are difficult to simulate.

On average the system moves at the fastest time step scales.

Fast diffusion can swamp out slower reaction steps.

Variable Time Step Approaches

Two Major Variants

Rejection Free Algorithms

Method that was just presented

Null –Event Algorithms

Easier to implement and faster

Null Event KMC Algorithm

Randomly pick ith Event

Calculate the Rate of i.

Normalize the rates

Select a process or null event.

Execute the event

Update time

No

Yes

$t = t_{final}$?
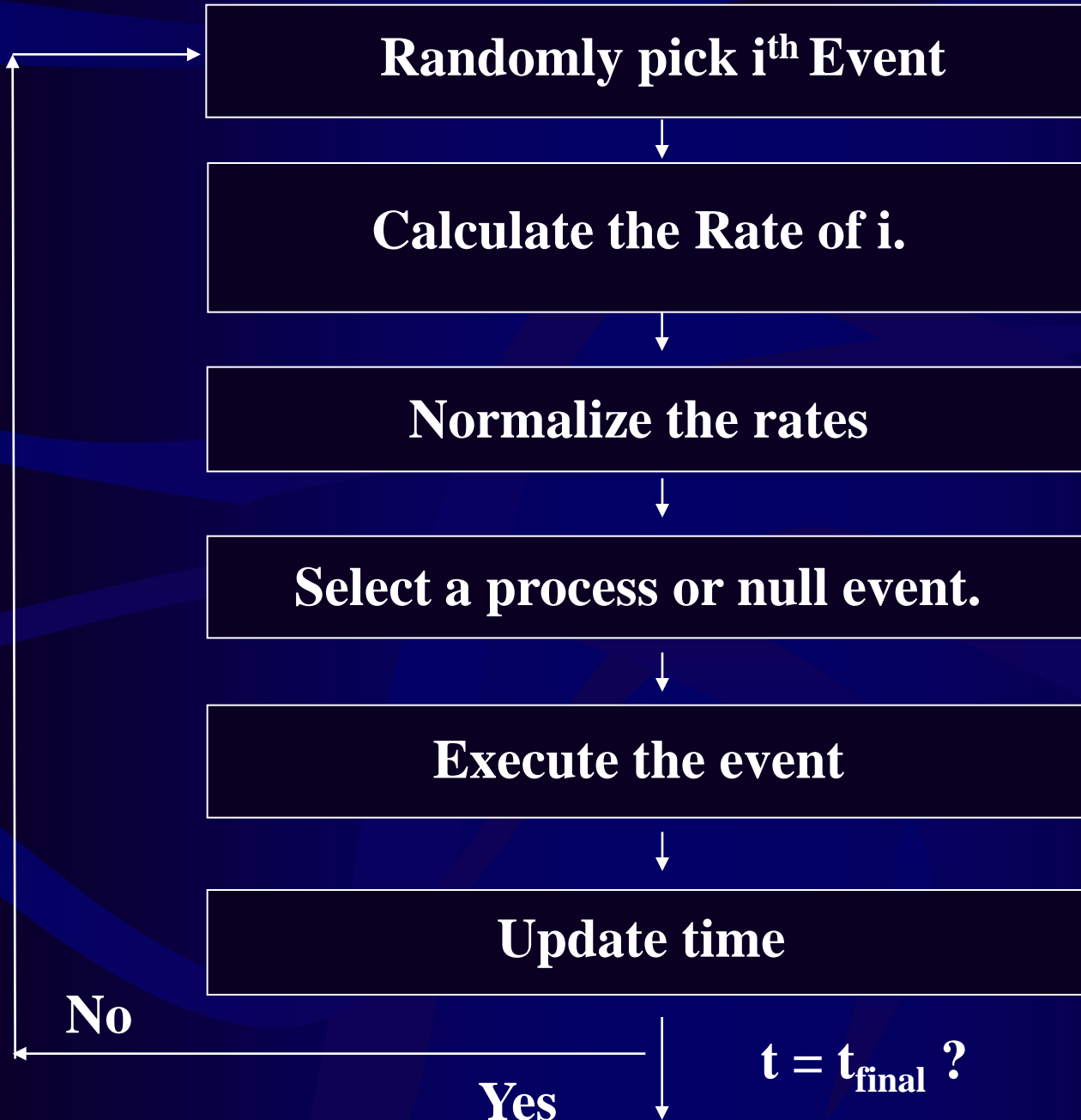
Simulating Surface Kinetics

Simple Models

Non-interacting surface species and sites
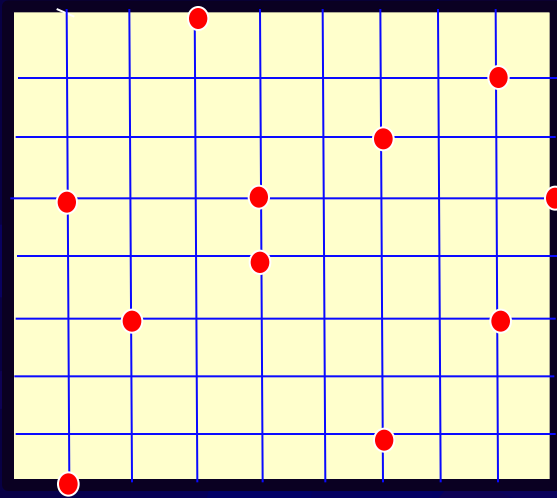
Pairwise Interactions and External Fields

$$H = -\sum_{i}\sum_{i'} J\left(\left\|i - i'\right\|\right)\sigma_i\sigma_{i'} + \sum_{i} h\sigma_i$$

$\sigma_i = 1$ or $\sigma_i{}' = 1$ Occupied

$\sigma_i = 0$ or $\sigma_i{}' = 1$ Empty
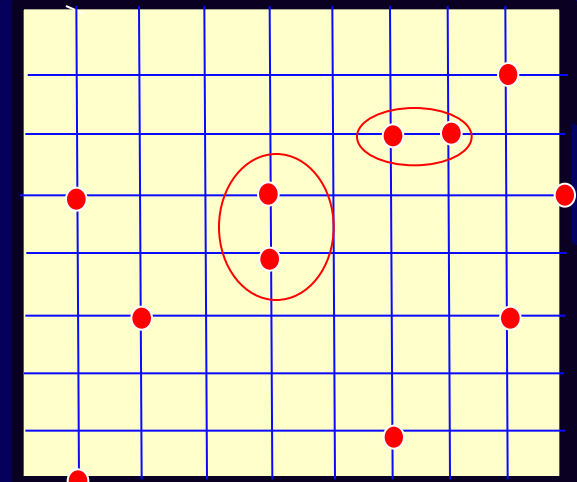
Modeling Surface Kinetic Processes
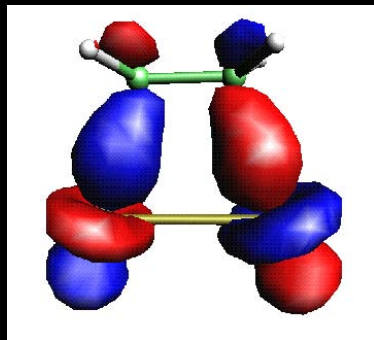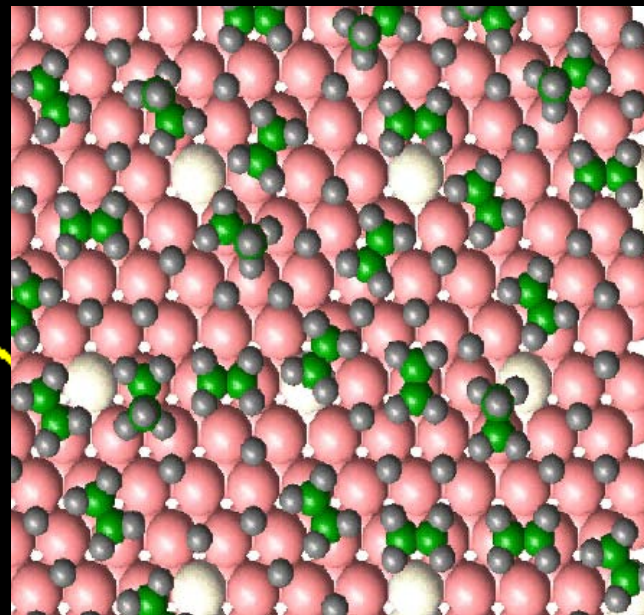
Kinetics Depend on Local Surface Structure
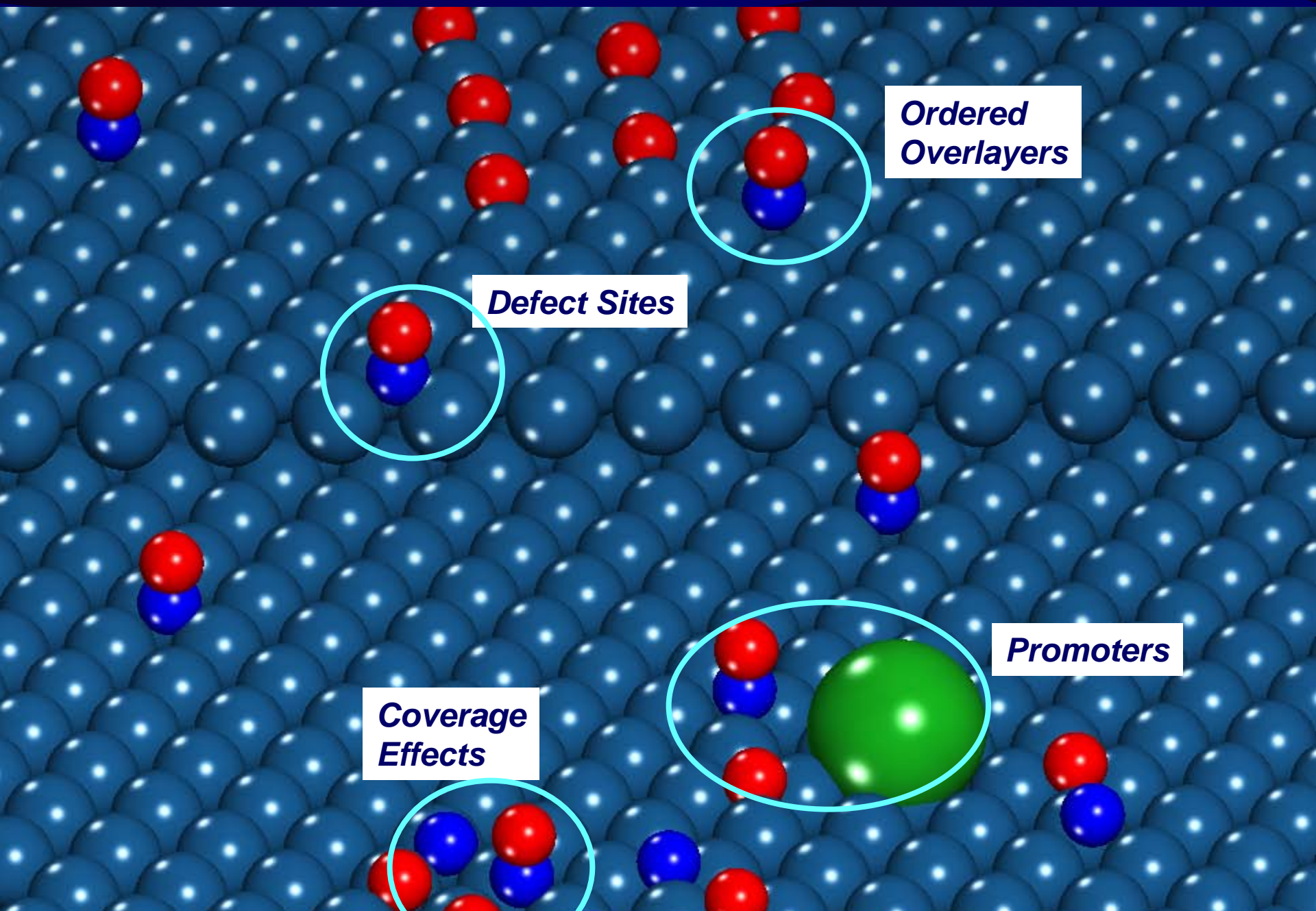
Ordered Overlayers

Defect Sites

Promoters

Coverage Effects
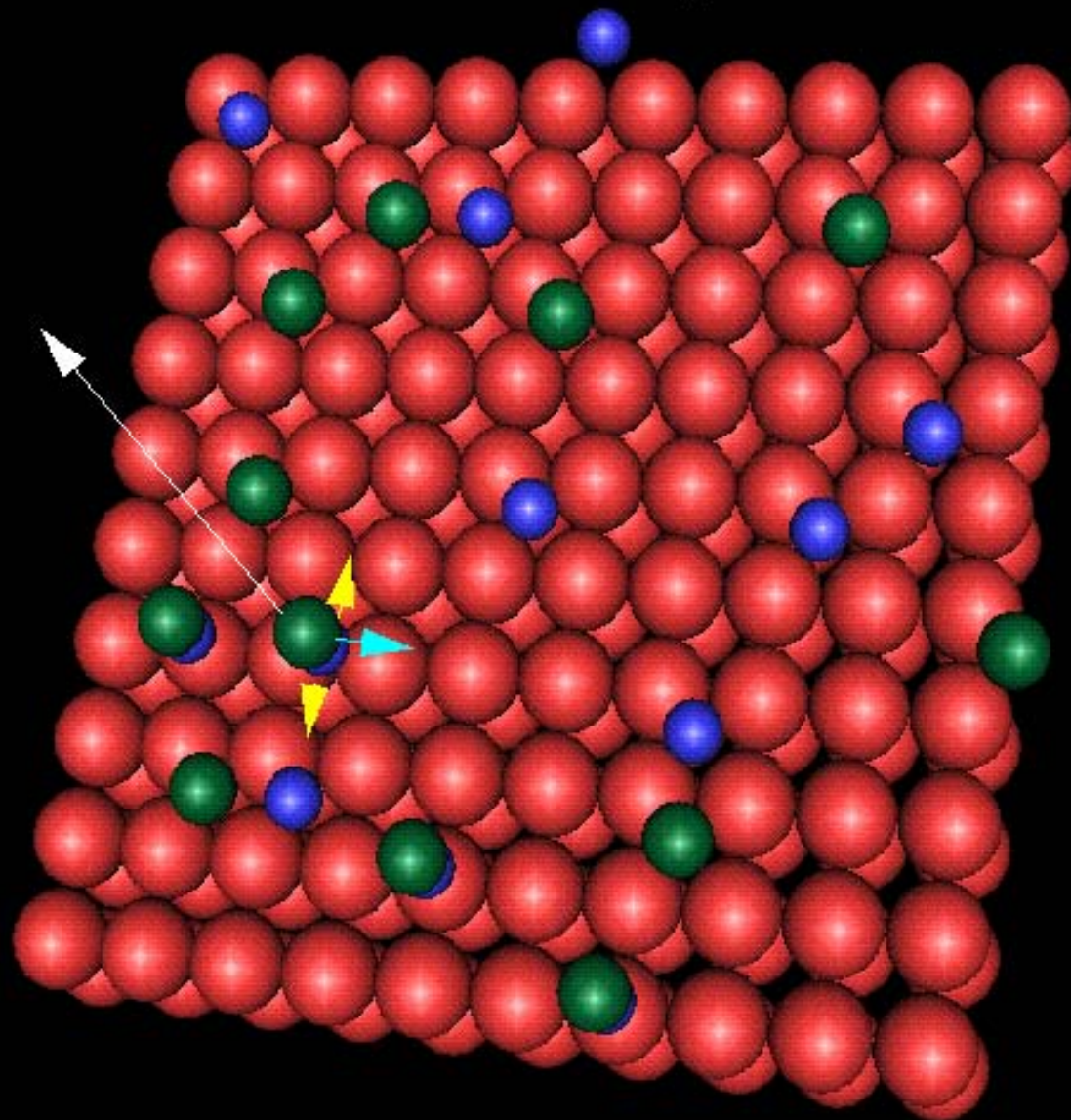
Surface Kinetic Processes

Catalysis
Corrosion
Thin Film Growth
Lubrication
Membranes for Separation

Opportunities - Ab Initio-Based KMC

Natural framework for integrating in QM results.

Begins to connect disparate time and length scales.

Directly incorporate atomic structure.

Allows for structure -reactivity

Enables materials design

Allows for spatiotemporal behavior.

Oscillations, Waves, Etc.

Direct accounting of the local and extended structure and their influence on kinetics.

Challenges - Ab Initio-Based KMC

Shear Number of Rate Constants for KMC

Accuracy of DFT Methods

Applicability of TST

Treatment of Disparate Time/Length Scales

Simulating Dynamics

(Quantum dynamical effects, transition state dynamics, Particle dynamics)

Simulating Disparate Time Scales

Brute Force Simulation of Both Fast and Slow Processes.

Ignore Fast Processes (diffusion) ($r_d = 0$).

Treat as Fast Processes as Fully Equilibrated (r_d = infinity)

Hybrid Fixed/Variable Time Step Algorithm (Used Here).

Variable time steps
Slow Processes (RXN)

Fixed Δt
Fast Processes

Fixed t Diffusion

Fixed t Diffusion
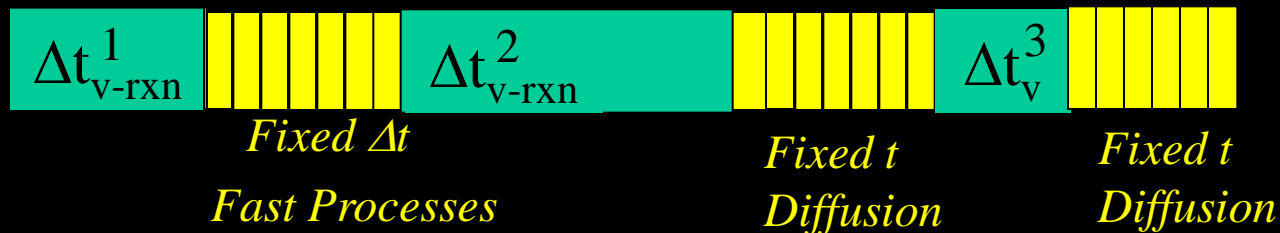
Leap Frog Approach (Gillespie)

Hybrid Variable/Fixed Time Method

Average Δt_v **(From previous n variable time steps)**

Divide Δt_v into fixed time steps

m is set by user
$$\Delta t_f = \Delta t_{v\,avg}/m$$
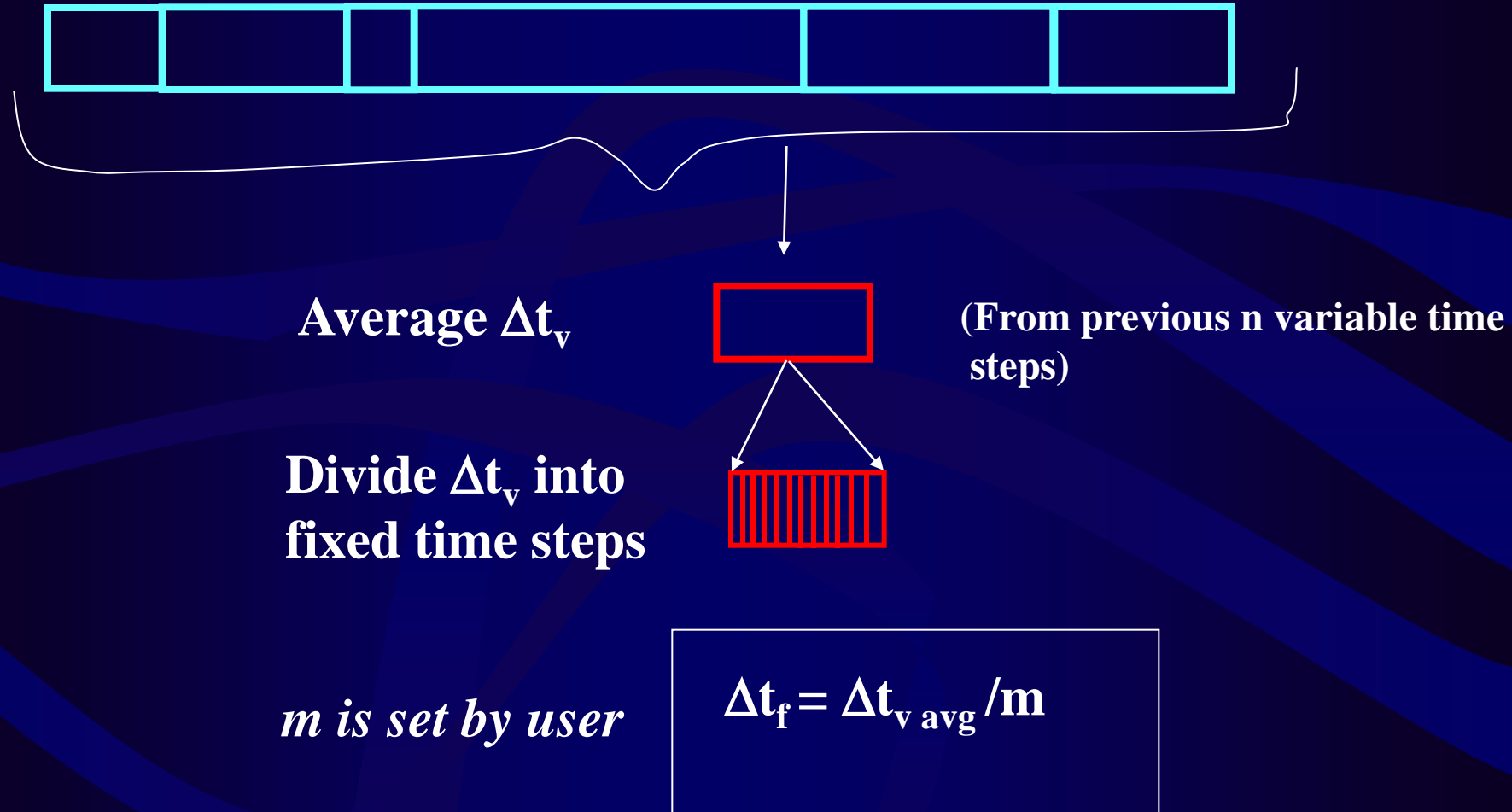
m balances accuracy and CPU effort.

Algorithm Specifics
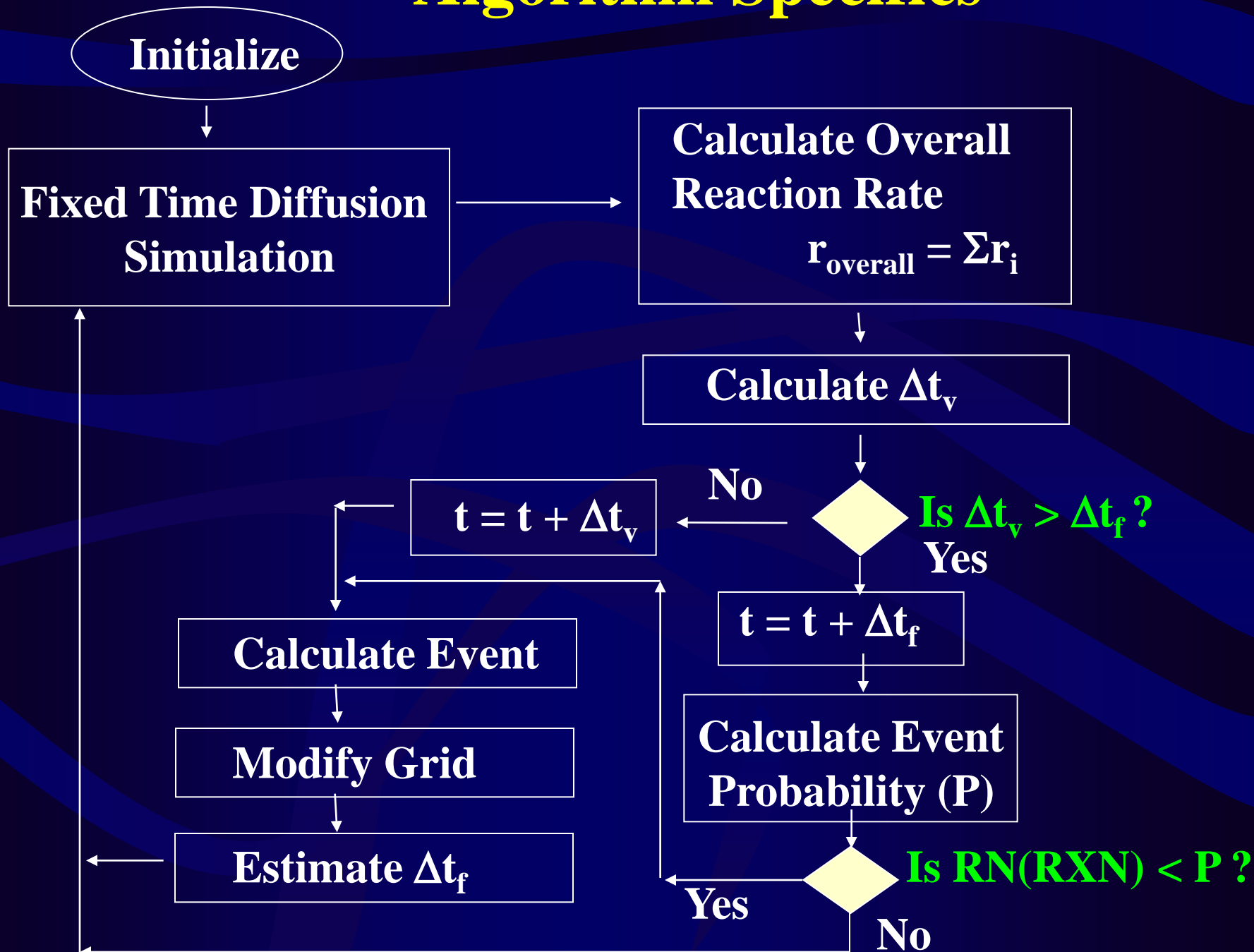
Lateral Interactions

Important in Determining Kinetics

Historical Note

Discovered by J.K. Roberts in 1939

Desorption rate was a function of fractional coverage.

$$r_D = 2\, k_d\, P_{AA} \qquad \text{where} \qquad E_D = f(\theta_A)$$

Approximate lateral interactions of the entire system as a collection of clusters or sites.

J.K. Roberts, Some Problems in Adsorption, Cambridge Univ. Press, Cambridge, 1939.

Lateral Interactions

Can be attractive of repulsive

Charge transfer, Coulombic or steric interactions

Can be treated as "Through Surface" or "Through Space"

Responsible for non-ideality in the kinetics,
island and pattern formation, kinetic oscillations.

Described experimentally as nearest-neighbor and
next-nearest-neighbor interactoins.

$$Q_A = Q_0 - \Sigma \omega_{Ai} - \Sigma \omega_{Ai'}$$

Methods for Calculating Interactions
On-the-Fly or Pre-determined database

Tight-Binding or Semiempirical QM

Pairwise Interactions

Three Body Interactions   *Kreuzer, Scheffler, others*

Ab initio based Lattice Gas Hamiltonian

$$H = E_s^{hcp}\sum_i n_i + E_s^{fcc} + \sum_i n_i + 1/2\left(V_{1n}^{hcp}\sum n_i n_{i+a} + V_{1n}^{fcc}\sum n_i n_{i+a} + V_{1n}^{hcp-fcc}\sum_i n_i n_{i+a'} + V_{2n}^{hcp}\sum_i n_i n_{i+b} + V_{2n}^{fcc}\sum_i n_i n_{i+b} + ... + V_{trio}^{hcp}\sum_{i,a,a"} n_i n_{i+a} n_{i,a,a"}\right)$$

Bond Order Conservation

Force Fields

Modified Bond Order Conservation

Adsorbate Interactions

Through Surface Lateral Interactions

Modified Bond Order Conservation

Through Space Interactions

Orientation–Dependent
Merck Molecular Force Field Model
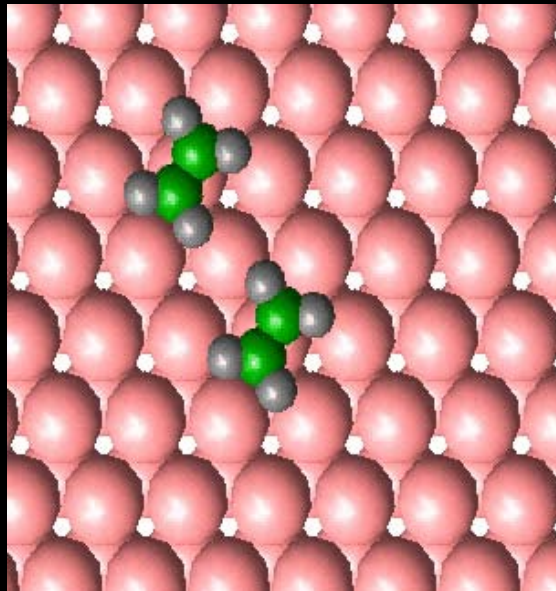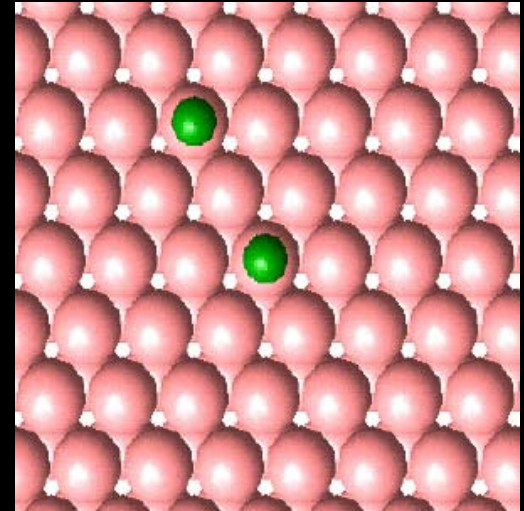
Bond Order Conservation

Shustorovich and Sellers

Bond Order Potential

$$x = \exp\left[-\frac{(r - r_o)}{a}\right]$$

2-Center Bond Energy

$$E(x) = -Q_o\left(2x - x^2\right)$$

Bond Order Conservation

$$\sum_{i=1}^{n} x_{A,i} = 1$$

Influence on Adsorption Energy

$$Q_{A,new} = Q_A \sum_{i=1}^{n}\left[2x_{A,i} - x_{A,i}^2\right] = Q_o\left[2 - \frac{1}{n}\right]$$

BOC Estimates of Activation Barriers

Gas Phase Adsorption and Recombination

$$A\text{-}B + * \xrightarrow{E_{for}} A* + B*$$

$$A* + B* \xrightarrow{E_{rev}} A\text{-}B$$

$$\Delta H = D_{AB} - Q_A - Q_B$$

$$E_{for} = 0.5 \cdot \left(\Delta H + \frac{Q_A \cdot Q_B}{Q_A + Q_B}\right) + \gamma$$

$$E_{rev} = E_{for} - \Delta H$$

if $E_{for} < 0$ if $E_{rev} < 0$,

$$E_{for} = 0 \qquad E_{rev} = 0$$
$$E_{rev} = \Delta H \qquad E_{for} = \Delta H$$
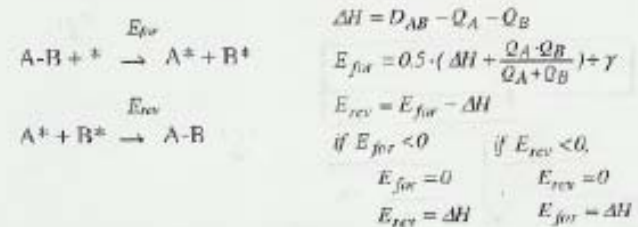
Surface Dissociation and Recombination

$$A\text{-}B* + * \xrightarrow{E_{for}} A* + B*$$

$$A* + B* \xrightarrow{E_{rev}} A\text{-}B*$$

$$\Delta H = Q_{AB} + D_{AB} - Q_A - Q_B$$

$$E = 0.5 \cdot \left(\Delta H + \frac{Q_A \cdot Q_B}{Q_A + Q_B}\right) + \gamma$$

if $E_{for} < 0$ if $E_{rev} < 0$,

$$E_{for} = 0 \qquad E_{rev} = 0$$
$$E_{rev} = \Delta H \qquad E_{for} = \Delta H$$
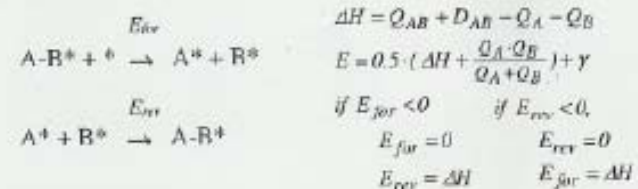
Surface Disproportionation

$$A* + B\text{-}C* \xrightarrow{E_{for}} A\text{-}B* + C*$$

$$A\text{-}B* + C* \xrightarrow{E_{rev}} A* + B\text{-}C*$$

$$\Delta H = Q_A + Q_{BC} + D_{BC} - Q_{AB} - Q_C - D_{AB}$$

if $D_{BC} > D_{AB}$

$$E_{for} = 0.5 \cdot \left(\Delta H + \frac{Q_C \cdot Q_{AB}}{Q_C + Q_{AB}}\right) + \gamma$$

else

$$E_{for} = 0.5 \cdot \left(\Delta H + \frac{Q_A \cdot Q_{BC}}{Q_A + Q_{BC}}\right) + \gamma$$

$$E_{rev} = E - \Delta H$$

if $E_{for} < 0$ if $E_{rev} < 0$,

$$E_{for} = 0 \qquad E_{rev} = 0$$
$$E_{rev} = \Delta H \qquad E_{for} = \Delta H$$
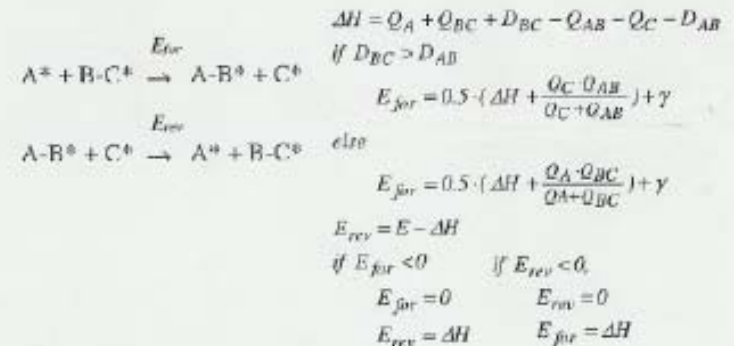
Eley-Rideal Disproportionation

$$A* + B\text{-}C \xrightarrow{E_{for}} A\text{-}B* + C*$$

$$A\text{-}B* + C* \xrightarrow{E_{rev}} A* + B\text{-}C$$

$$\Delta H = Q_A + Q_{BC} + D_{BC} - Q_{AB} - Q_C - D_{AB}$$

if $D_{BC} > D_{AB}$

$$E_{for} = 0.5 \cdot \left(\Delta H + \frac{Q_C \cdot Q_{AB}}{Q_C + Q_{AB}} - Q_{BC}\right) + \gamma$$

else

$$E_{for} = 0.5 \cdot \left(\Delta H + \frac{Q_A \cdot Q_{BC}}{Q_A + Q_{BC}} - Q_{BC}\right) + \gamma$$

$$E_{rev} = E - \Delta H$$

if $E_{for} < 0$ if $E_{rev} < 0$,

$$E_{for} = 0 \qquad E_{rev} = 0$$
$$E_{rev} = \Delta H \qquad E_{for} = \Delta H$$
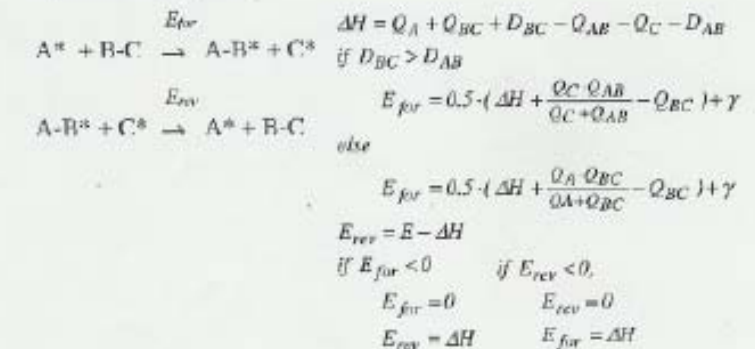
Lateral Interaction Example

Coverage Effects on Oxygen Binding Energies

Plaisance and Neurock, 2007.
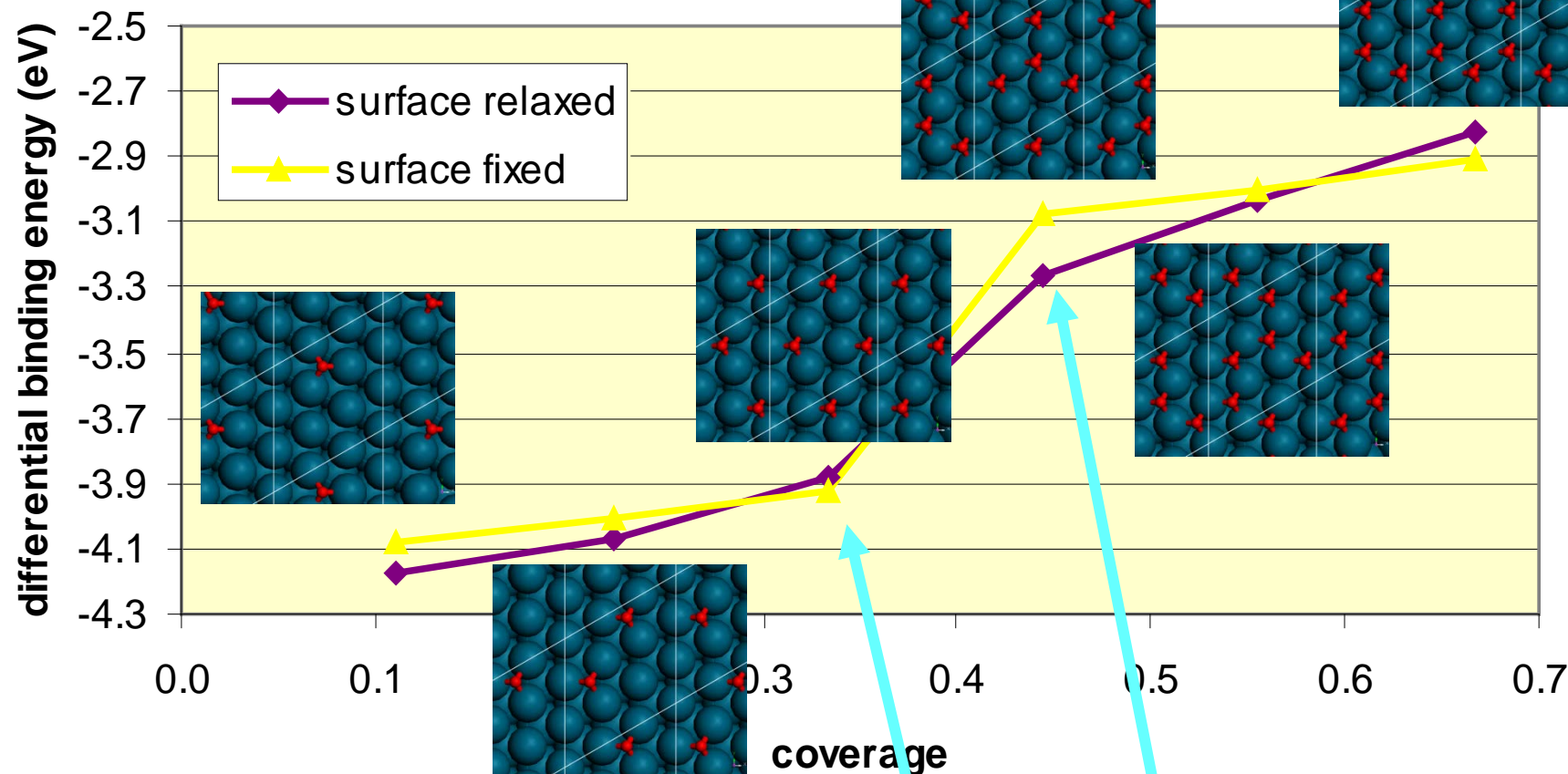
No Metal Atom Sharing   1 Metal Atom Sharing

Coverage Effects on Ethylidyne Binding Energies

Plaisance and Neurock, 2007.

Steric Interactions

1 Metal Atom Sharing

No Metal Atom Sharing

Legend:
- CH3C (fcc)
- CH3C (hcp)

Y-axis: differential binding energy (-1.00, -1.60, -2.20, -2.80, -3.40, -4.00, -4.60, -5.20, -5.80)

X-axis: 0.00, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70
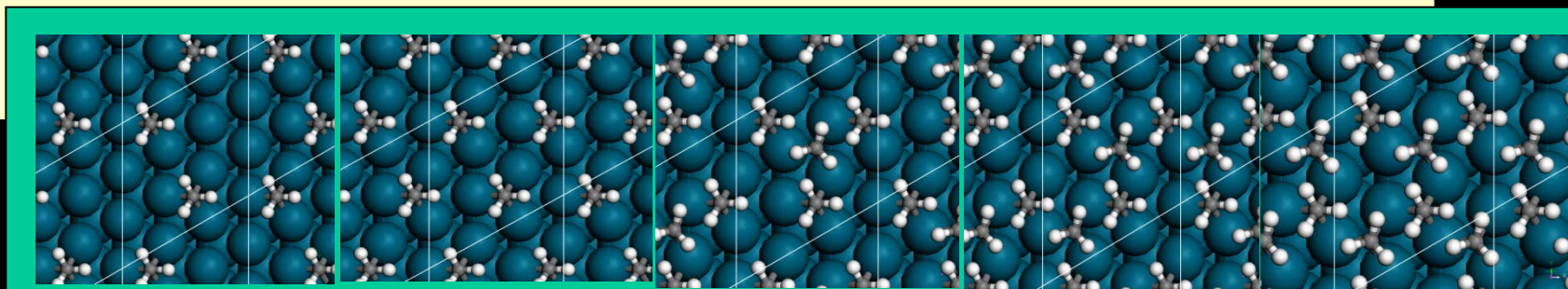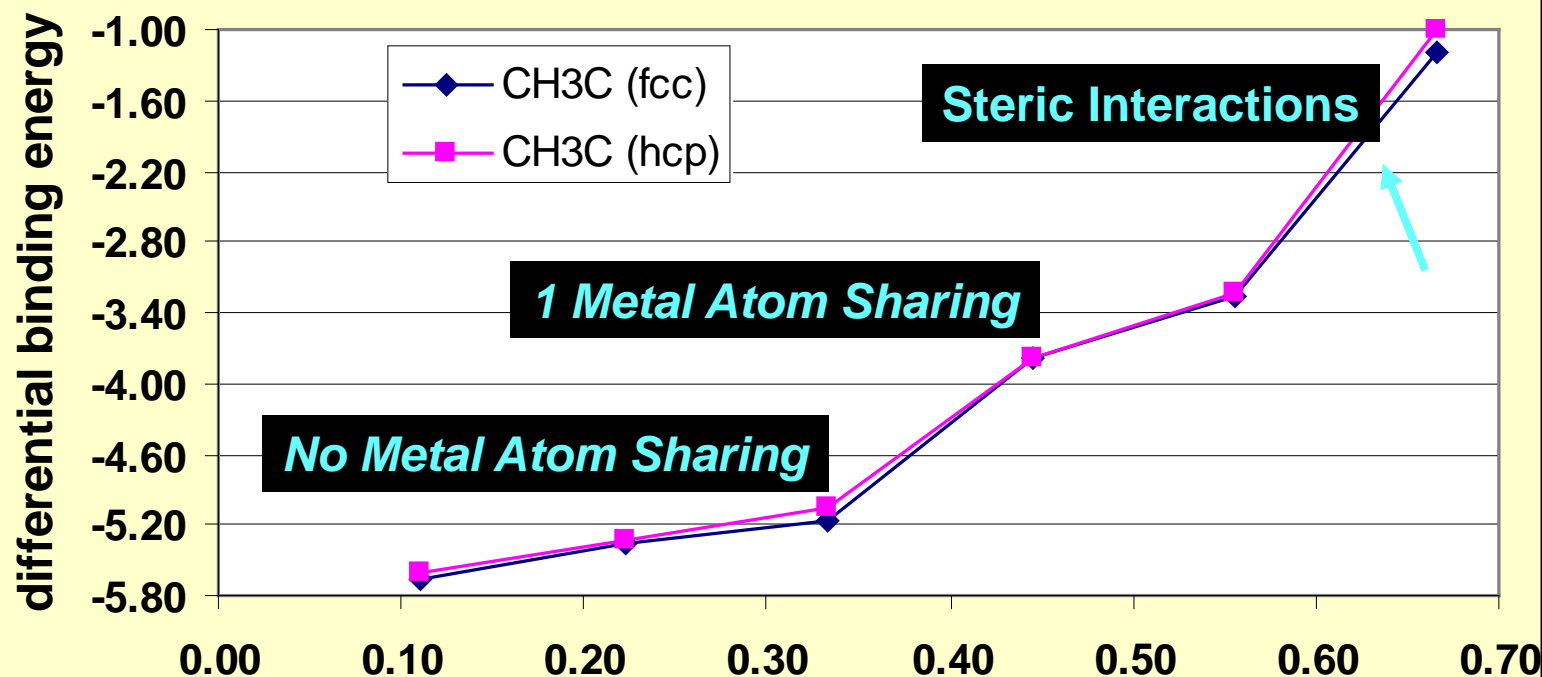
Significant changes in BE (1-4 eV) for strongly bound Interm.

Influence of Lateral Interactions on the Transition State Energy
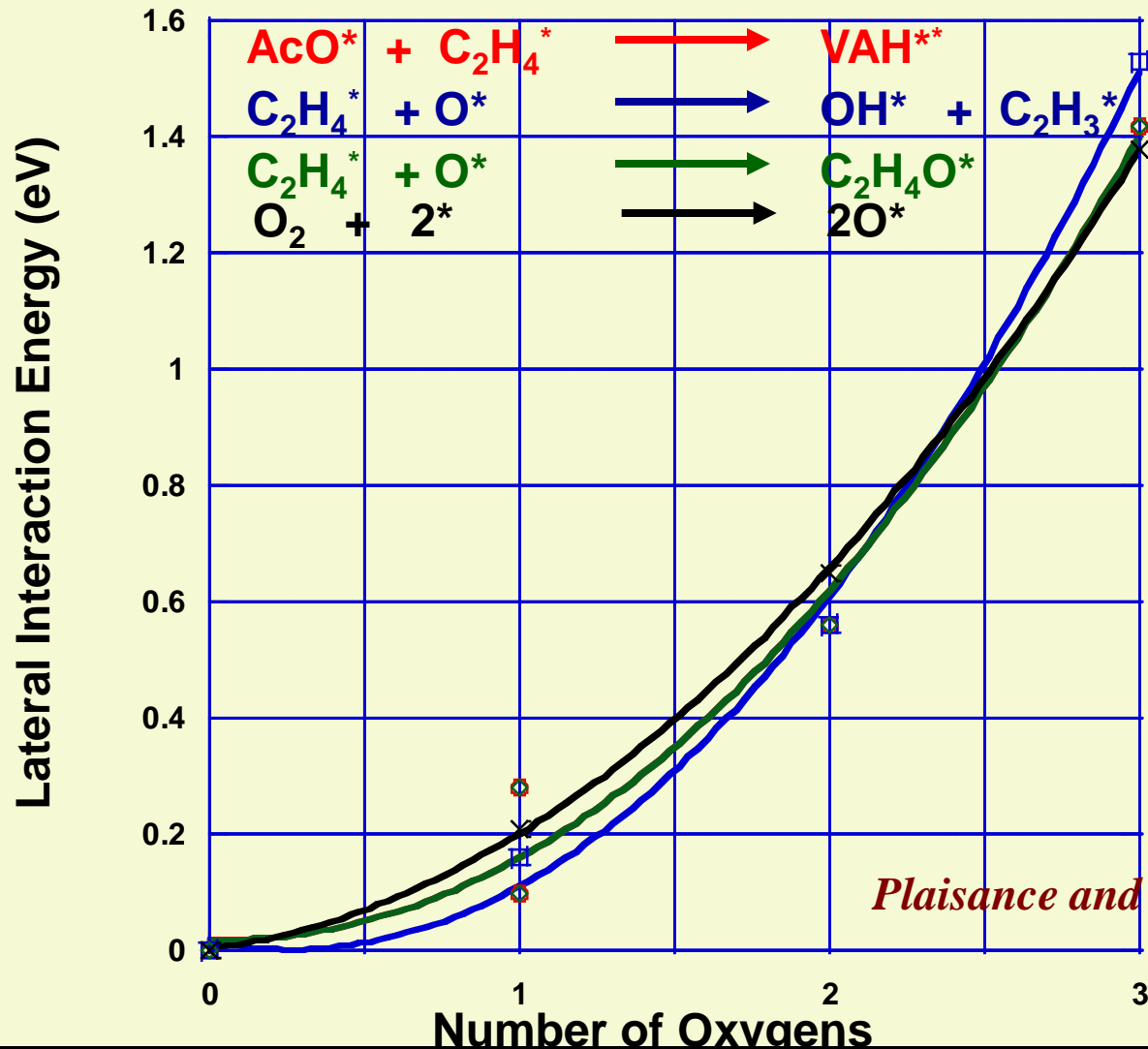
Plaisance and Neurock, 2007.

Influence of Coverage on Activation Barriers

Evans – Polanyi Relationships
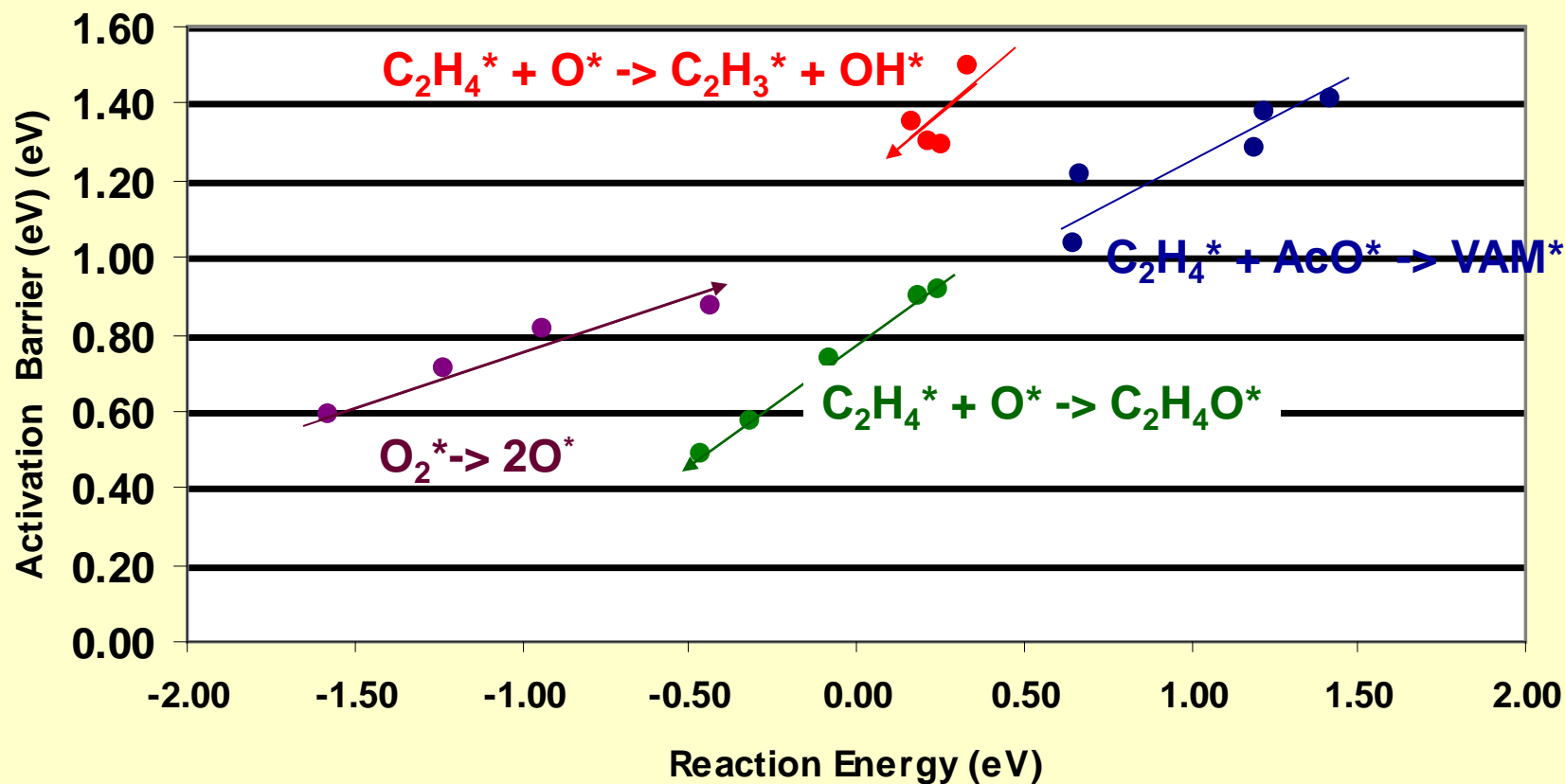
Plaisance and Neurock, 2007.

Lateral Interactions

Bond Order Conservation – Through Surface

Merck Force Field – Through Space
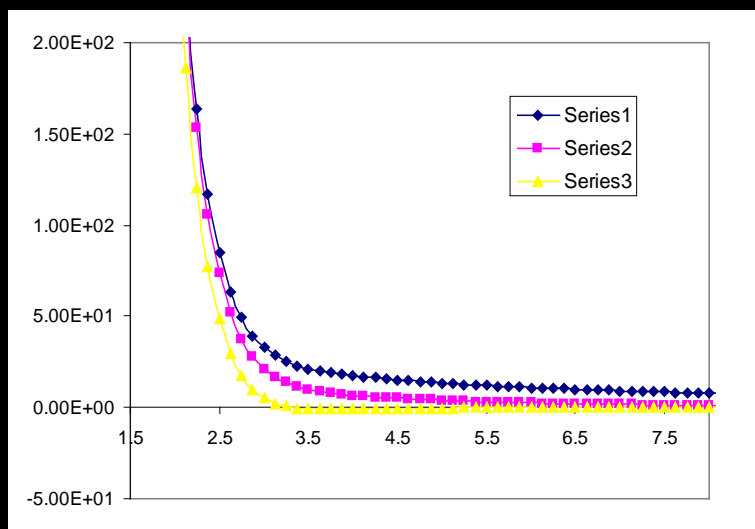
MMFF/BOC Effectively Capture Lateral Interactions

Applications

Applications

NO$_x$ Abatement

Toward computational design

VAM Synthesis

Designing ensembles

Acetylene Hydrogenation

Multiscale methods

Catalyst Development Engine™ Tools
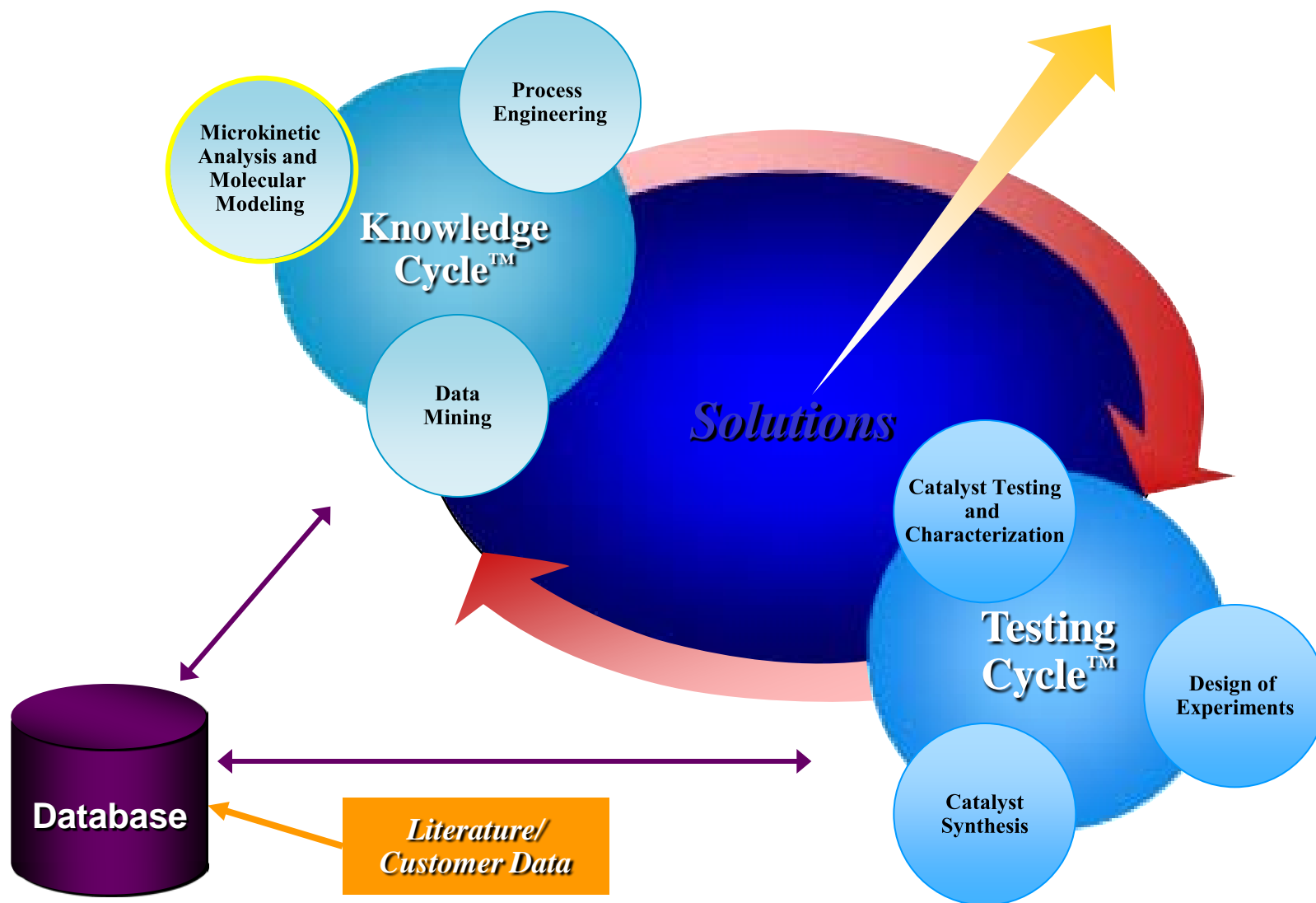
Decomposition of Nitric Oxide on Platinum

First order in NO
Inhibited by oxygen

$$r = \frac{k[\text{NO}]}{1 + \alpha K[\text{O}_2]}$$

E_a 18.4 kcal/mol

NO Dissociation barrier

Activation Energies (kcal/mol)

Pt--foil	*13.3*
Pt-wire	*14.3*
PtRh Wire	*24.6-26.9*
Pt-Wire	*22.0-25.0*
Pt/Al2O3	*3.1*

Amirnazmi and Boudart, J. Catal. 39, 383 (1975).

Screening for Catalyst Ranking

Parallel HTE Experiments

Conditions

[NO]= 1.34 torr
[O$_2$]= 60 torr
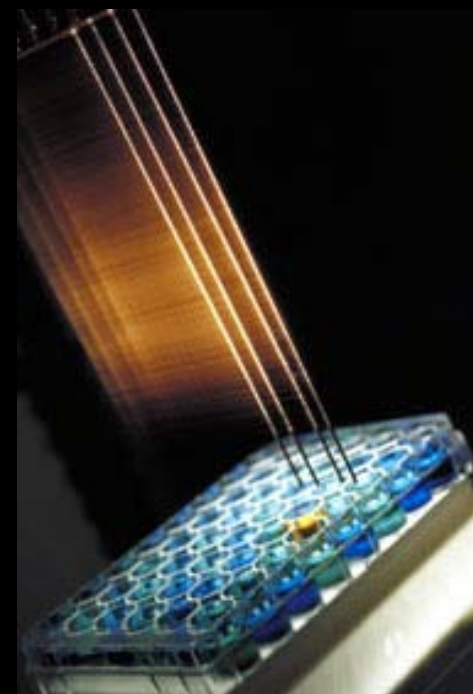
Selective Data

Catalyst	Metal (weight %)	Dispersion (%)	N$_2$ formation, TOF x 10^{-4} (s^{-1})	
			773 K	873 K
Pt/Al$_2$O$_3$	4.8	29.0	4	15
Rh/Al$_2$O$_3$	0.9	85.9	0	0
⋮			⋮	⋮

Working Reaction Mechanism

$$5NO(g) + * \rightleftharpoons 5NO*$$

$$NO* + * \rightleftharpoons N* + O*$$

$$NO* + O* \rightleftharpoons NO_2* + *$$

$$NO* + N* \rightleftharpoons N_2O* + *$$

$$NO* + NO* \rightleftharpoons N_2O* + O*$$

$$N_2O* \rightarrow N_2(g) + O*$$

$$N* + N* \rightarrow N_2(g) + 2*$$

$$O* + O* \rightleftharpoons O_2(g) + 2*$$

$$N_2O* \rightleftharpoons N_2O(g) + *$$

$$NO_2* \rightleftharpoons NO_2(g) + *$$

Pt Surfaces Examined

Corrugation

{111}

{100}

{211}

{410}
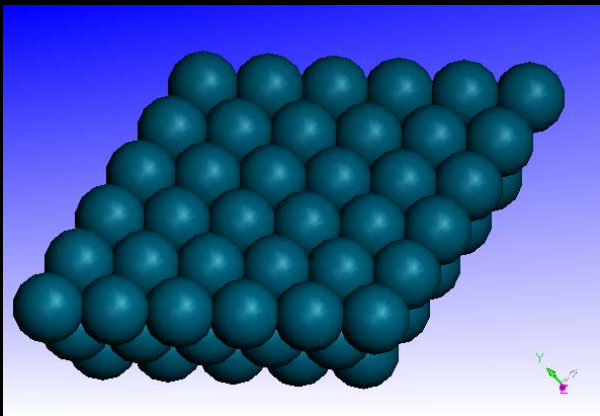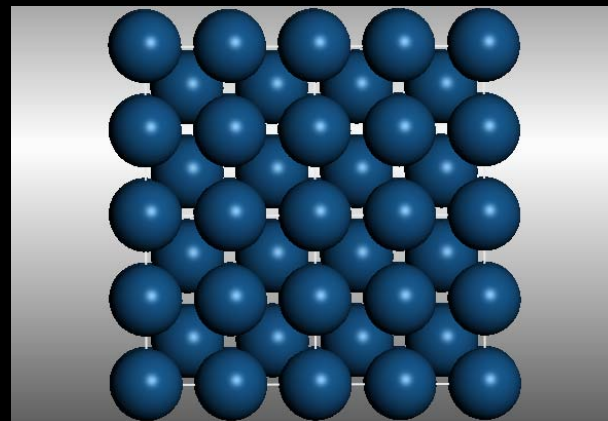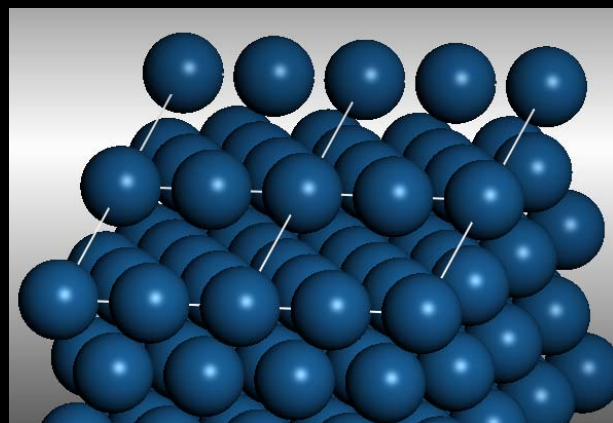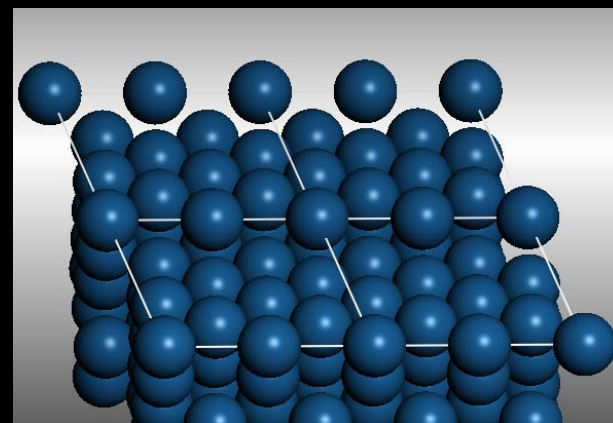
Openness
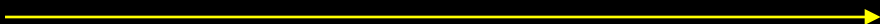
NO Dissociation over Pt{111}

NO chemisorbed at fcc sites
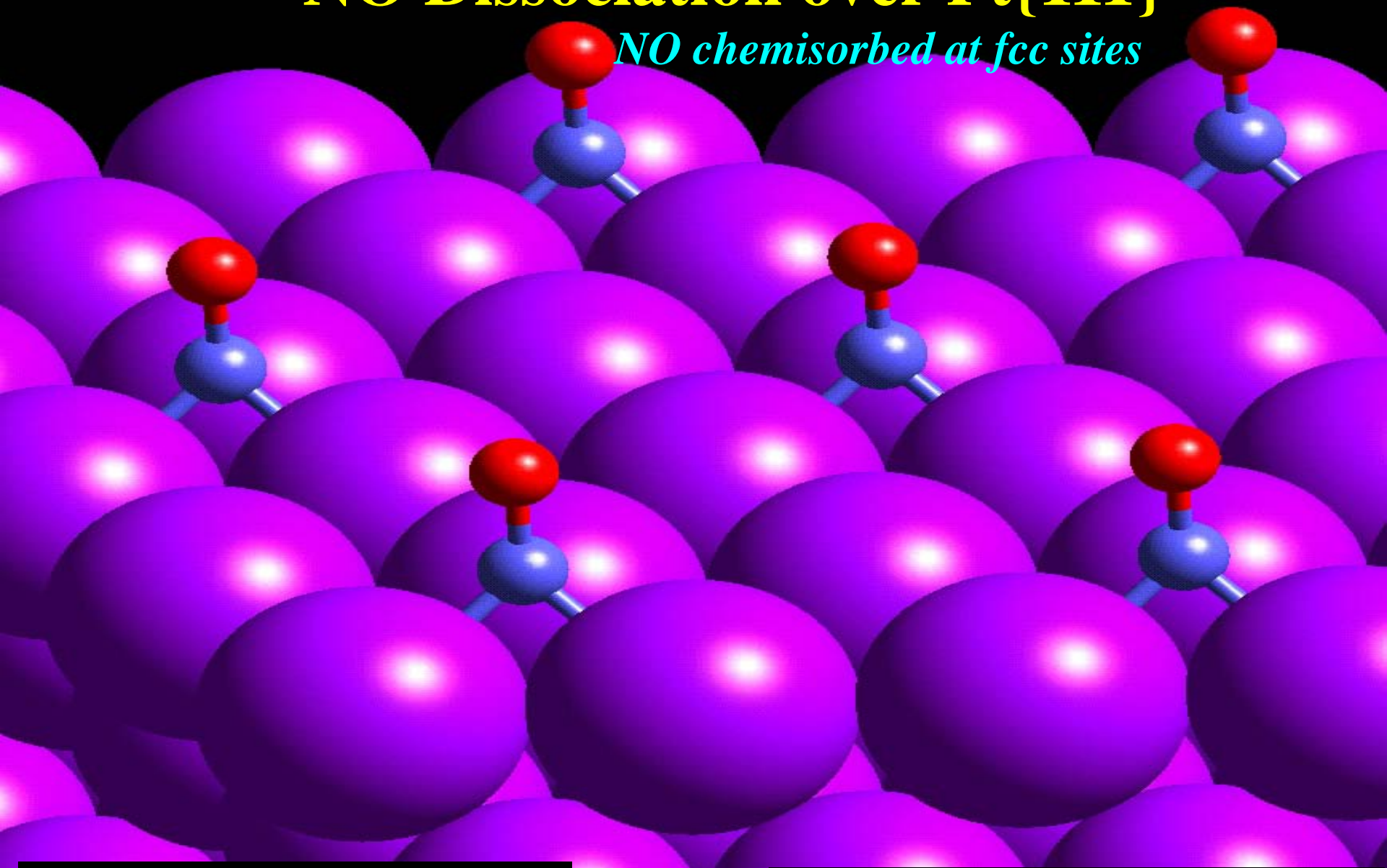
$E_{ads} = -183 \ kJ/mol$

Ge, Q., and M. Neurock, J. Am. Chem. Soc., 126 (5), 1551-1559, 2004.

Transition State

1.89
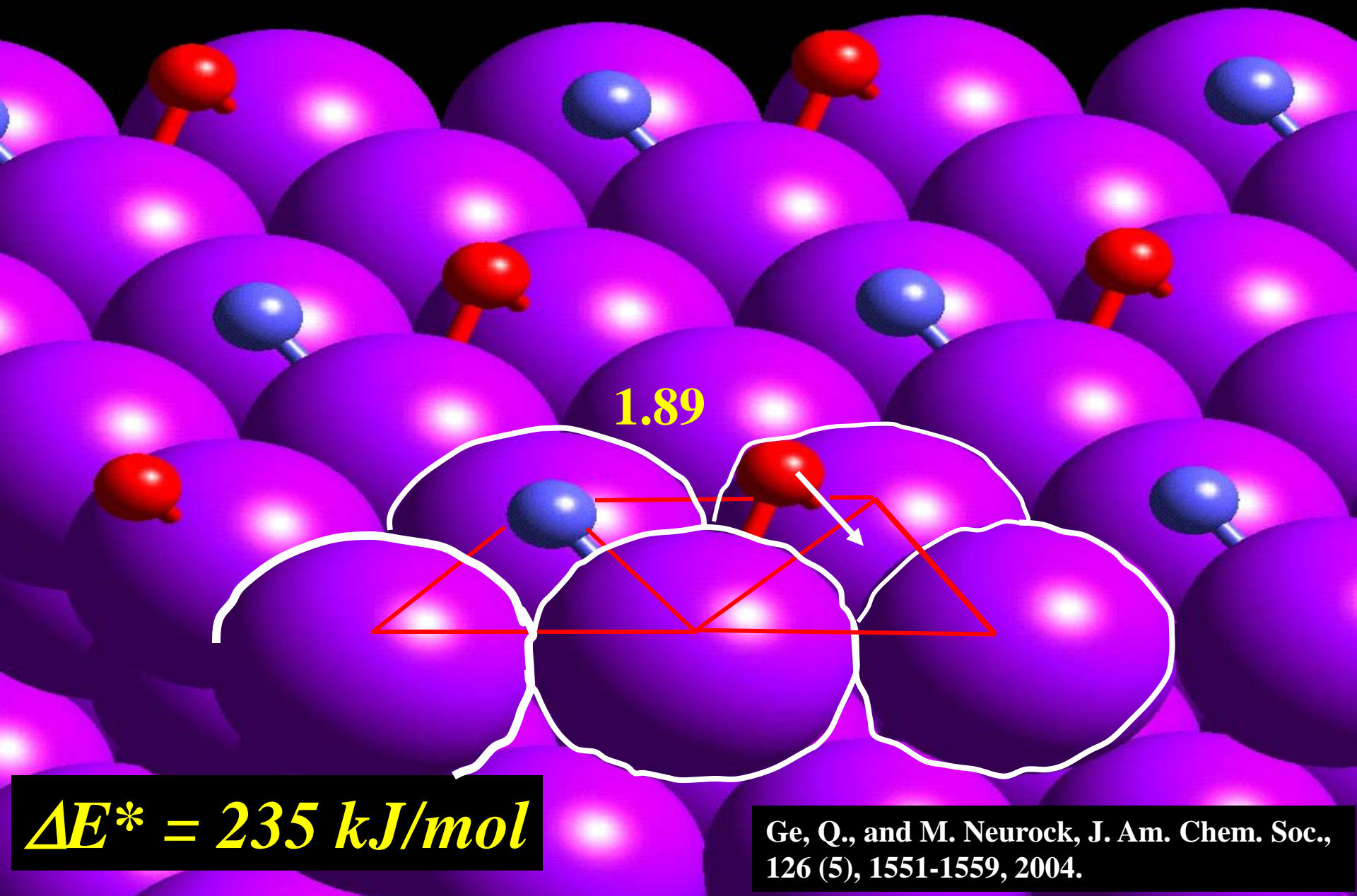
$\Delta E^* = 235 \, kJ/mol$

Final State
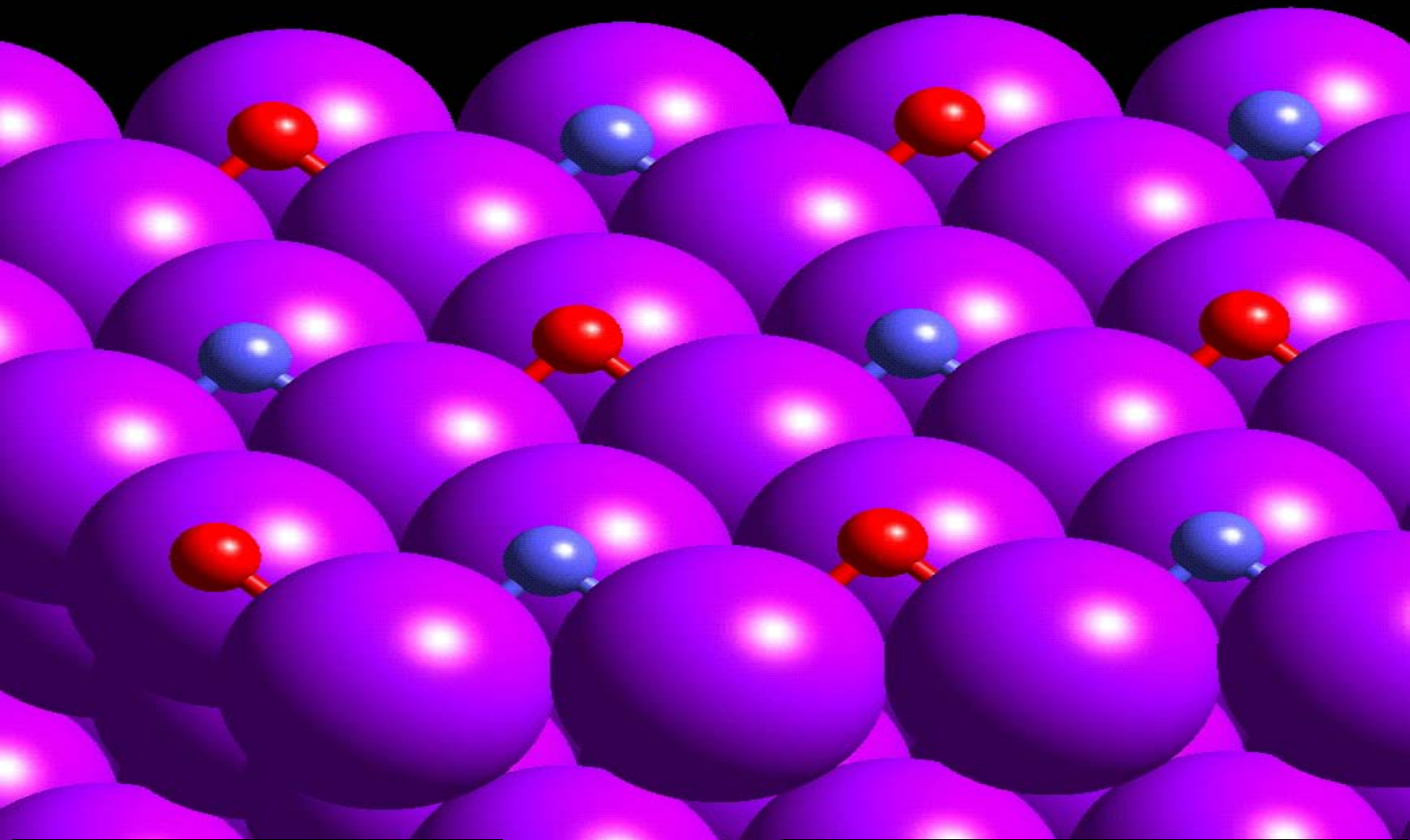
$\Delta E_{rxn} = 78\ kJ/mol$

Ge, Q., and M. Neurock, J. Am. Chem. Soc., 126 (5), 1551-1559, 2004.

NO Dissociation over Pt(100)

Reactant
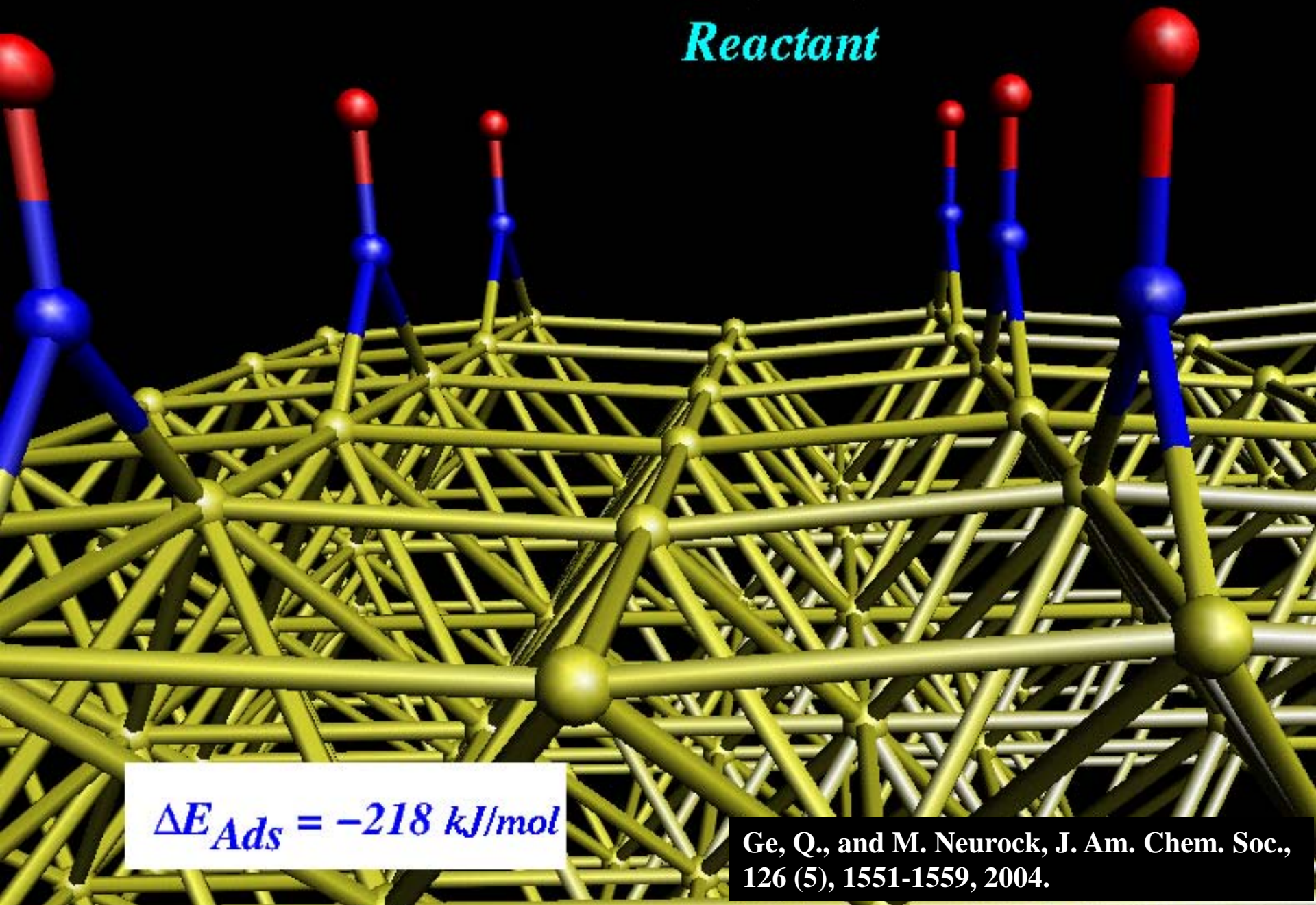
$\Delta E_{Ads} = -218 \ kJ/mol$

Ge, Q., and M. Neurock, J. Am. Chem. Soc., 126 (5), 1551-1559, 2004.
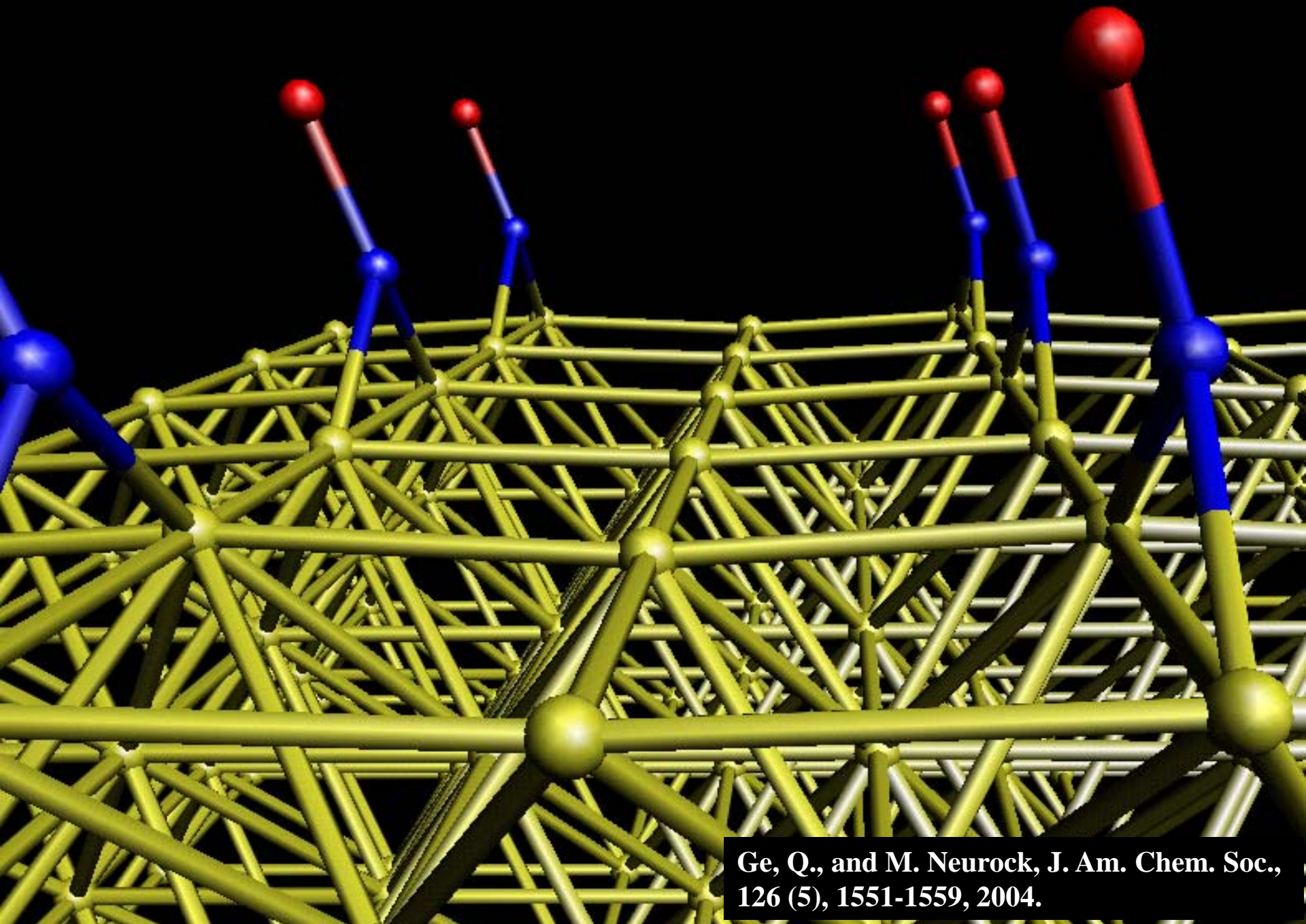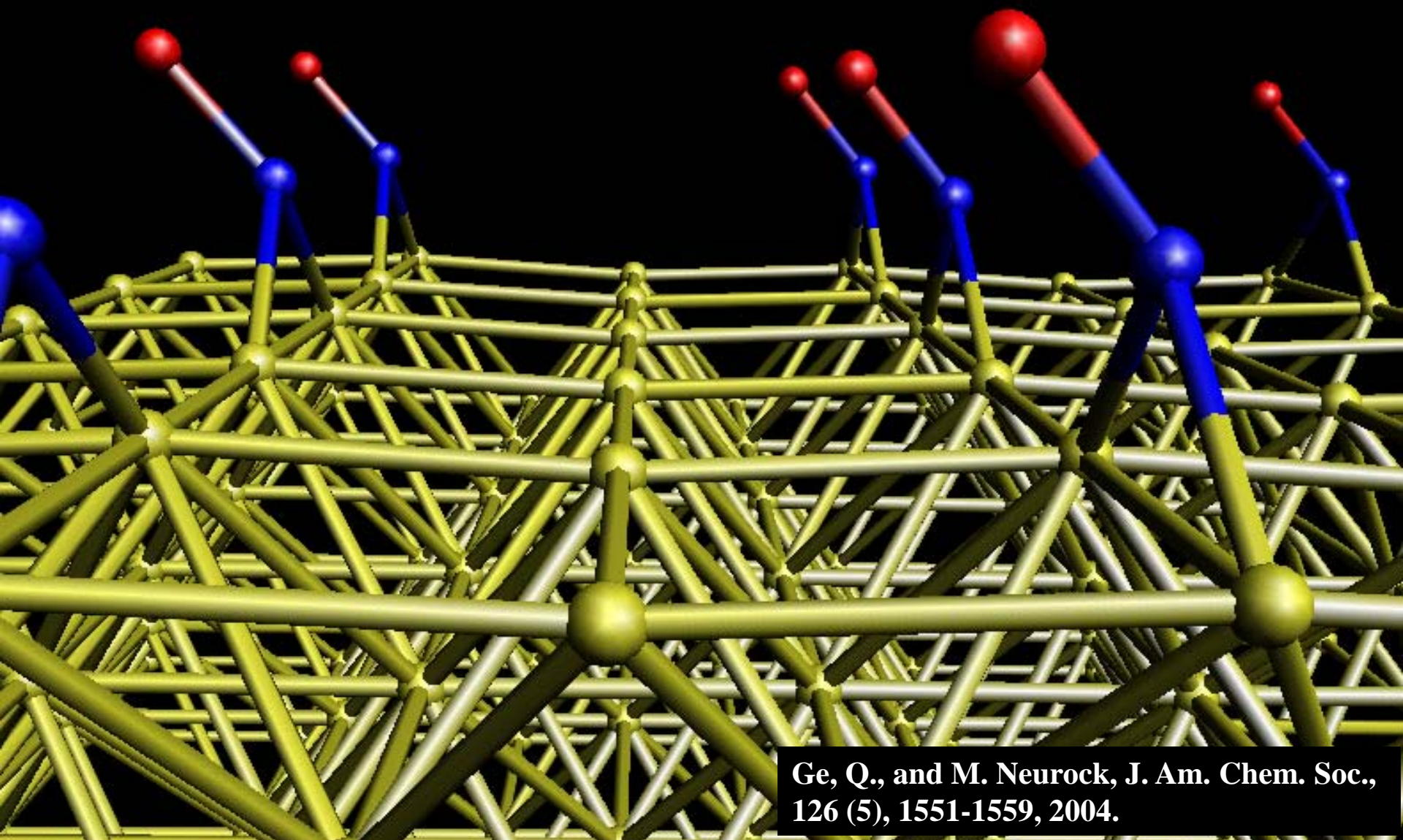
Ge, Q., and M. Neurock, J. Am. Chem. Soc., 126 (5), 1551-1559, 2004.
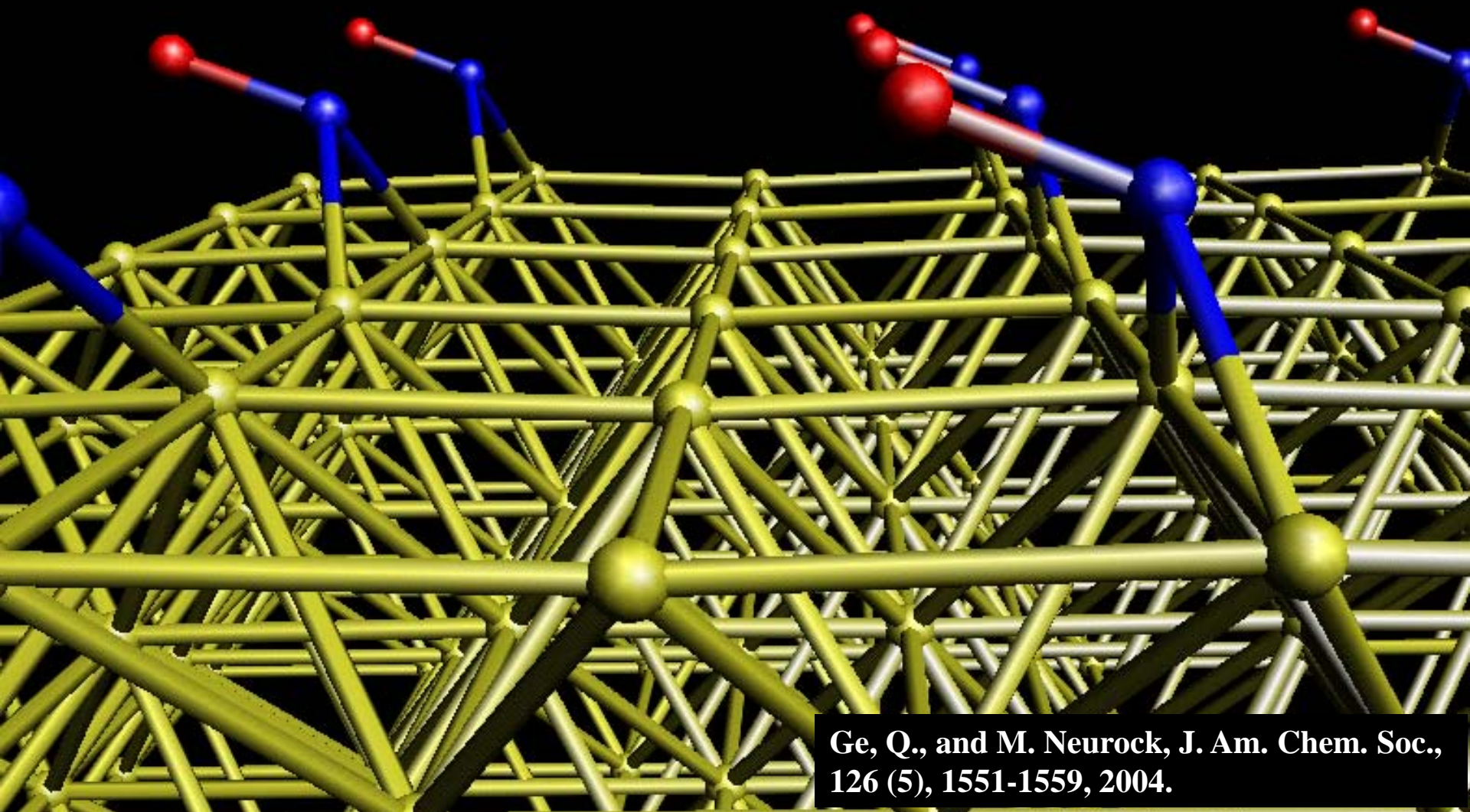
Ge, Q., and M. Neurock, J. Am. Chem. Soc., 126 (5), 1551-1559, 2004.

Transition State
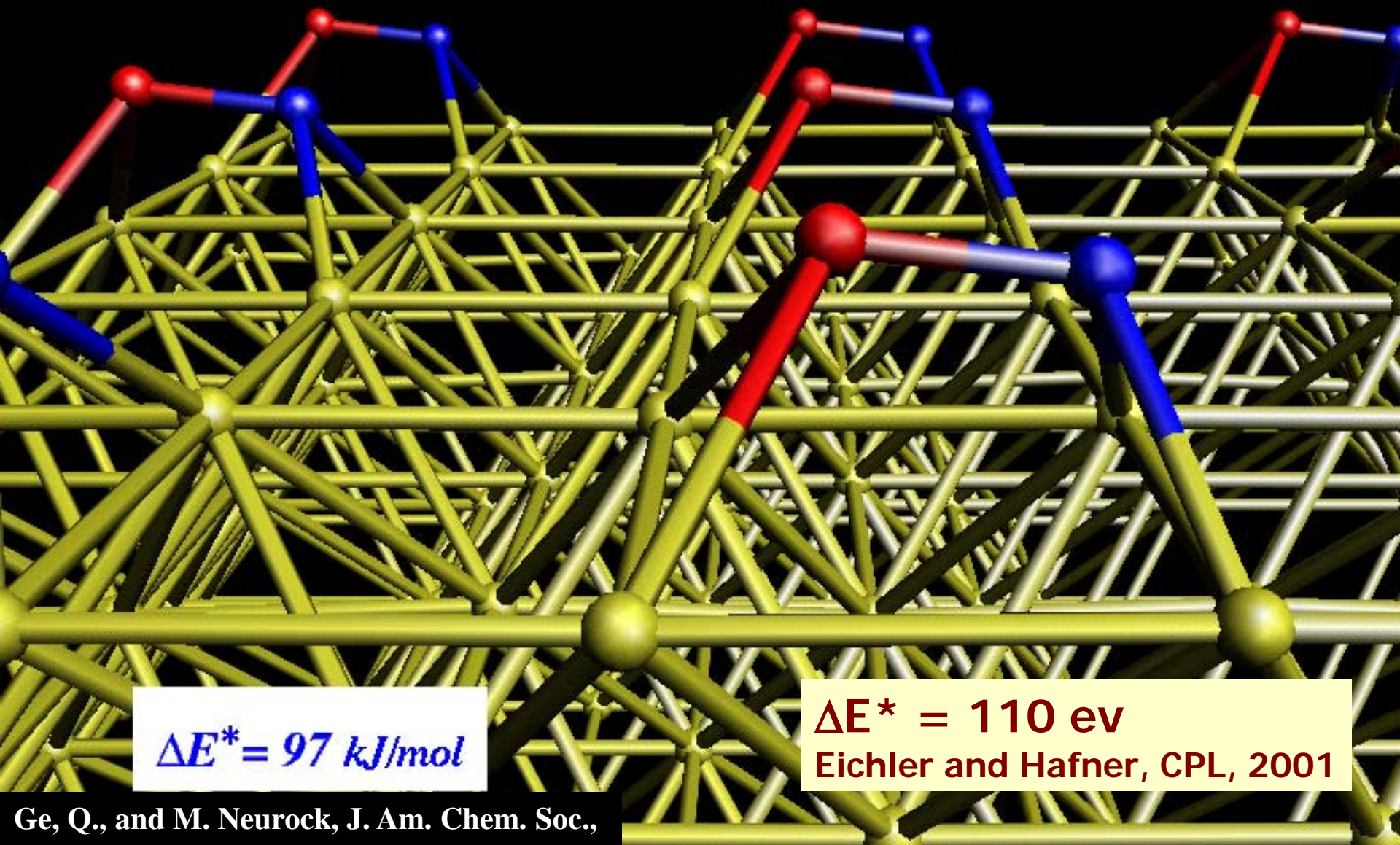
$\Delta E^* = 97\ kJ/mol$

$\Delta E^* = 110\ ev$
Eichler and Hafner, CPL, 2001

Ge, Q., and M. Neurock, J. Am. Chem. Soc.,

Structure Sensitivity for NO Decomposition
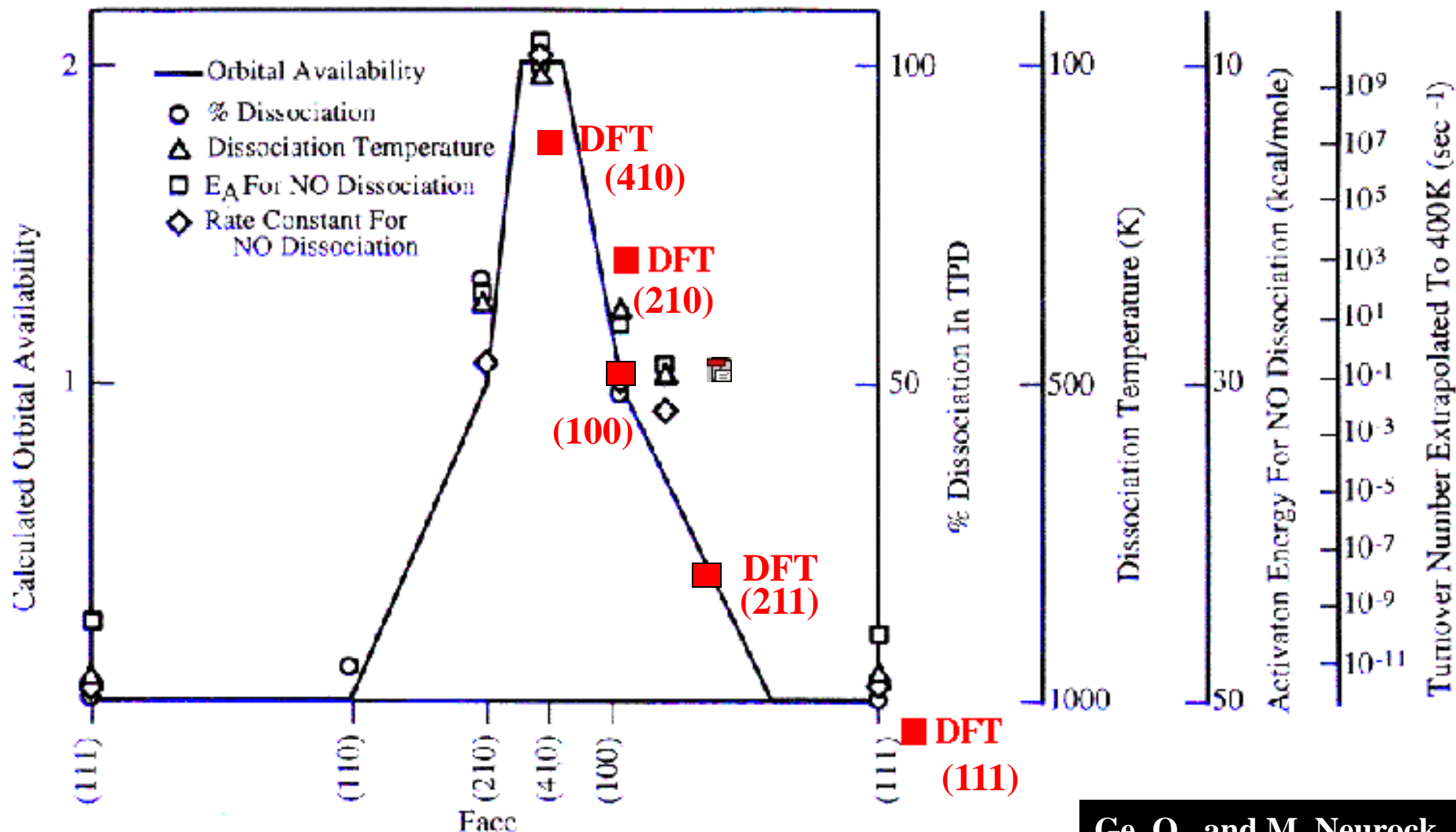
Figure 6.14 The rate on nitric oxide dissociation on several of the faces of platinum zone axes of the stereographic triangle. (Adapted from Masel [1983].)

NO Coupling

$$NO* \;+\; NO* \longrightarrow NNO* \;+\; O*$$

Initial state: Dimer-like adsorbed NO
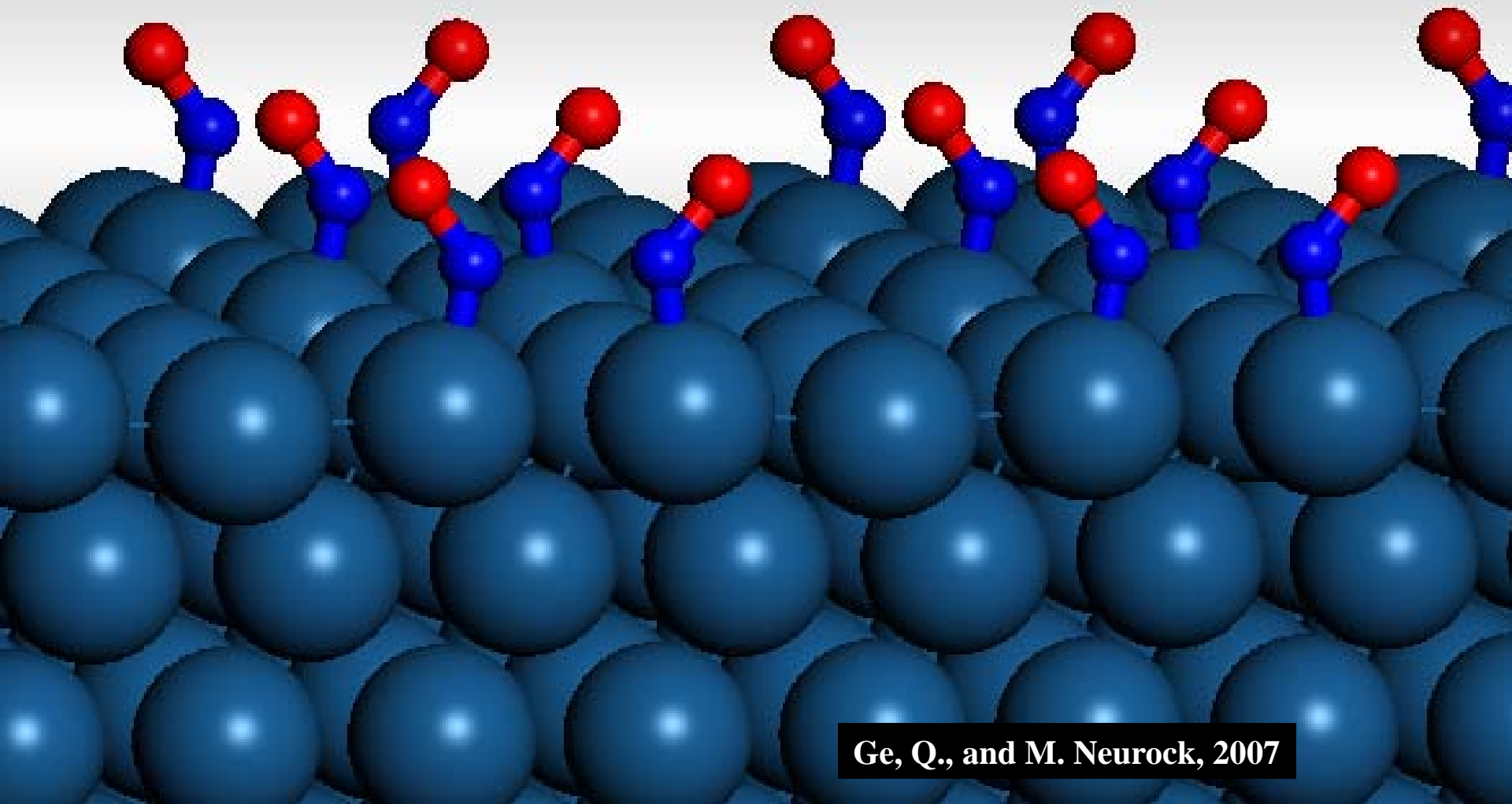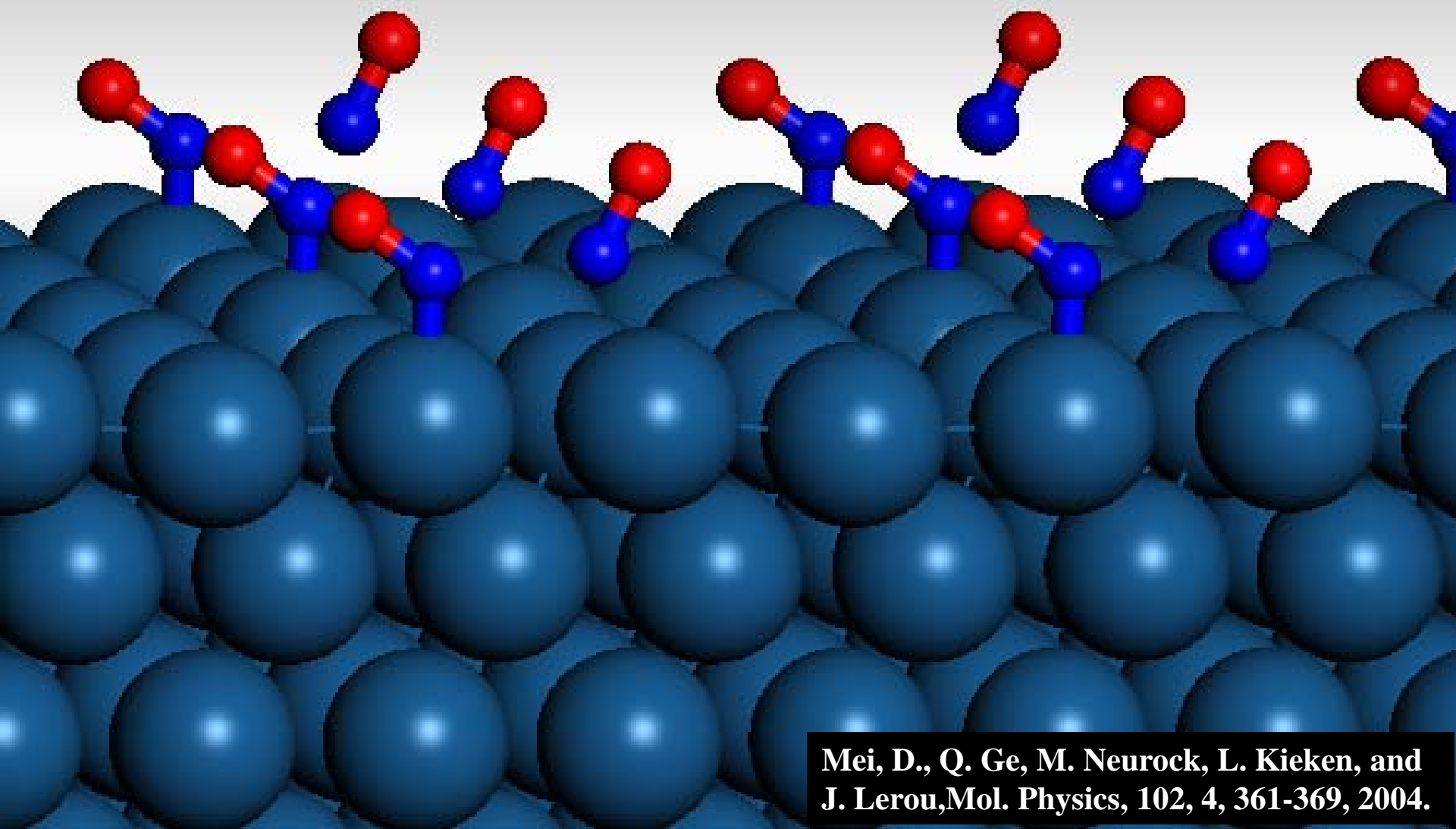
Transition State
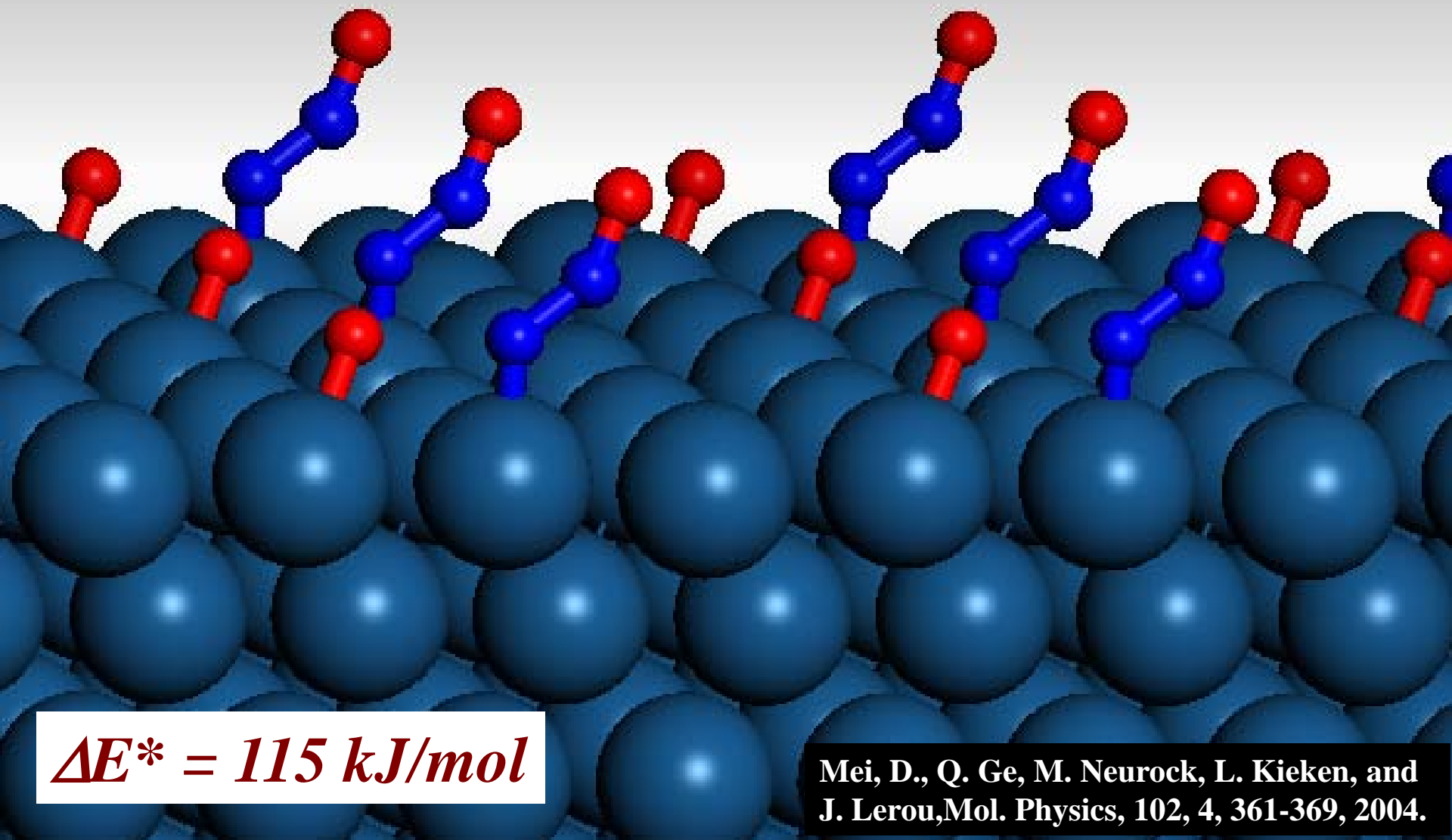
$\Delta E^* = 115 \ kJ/mol$
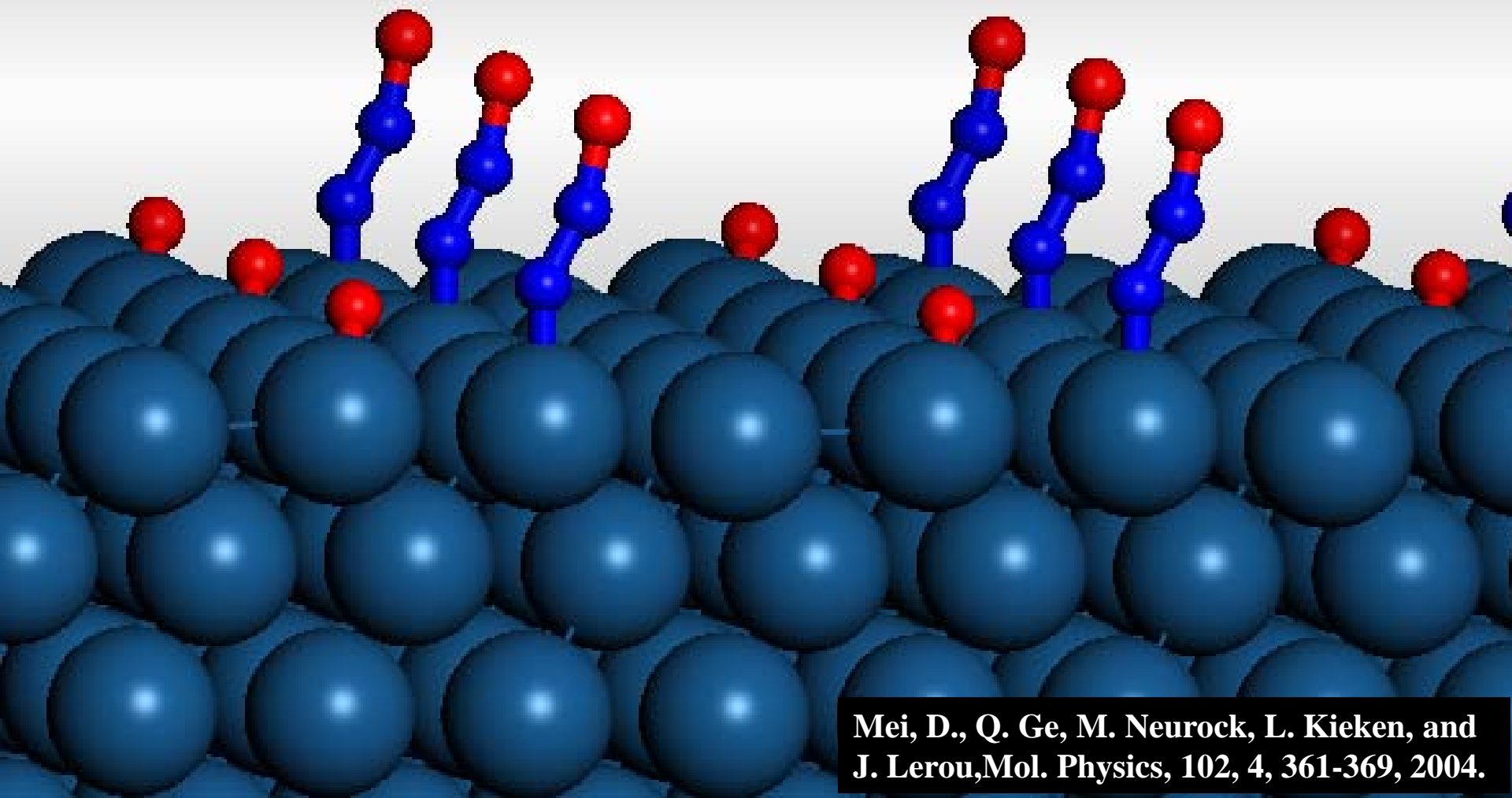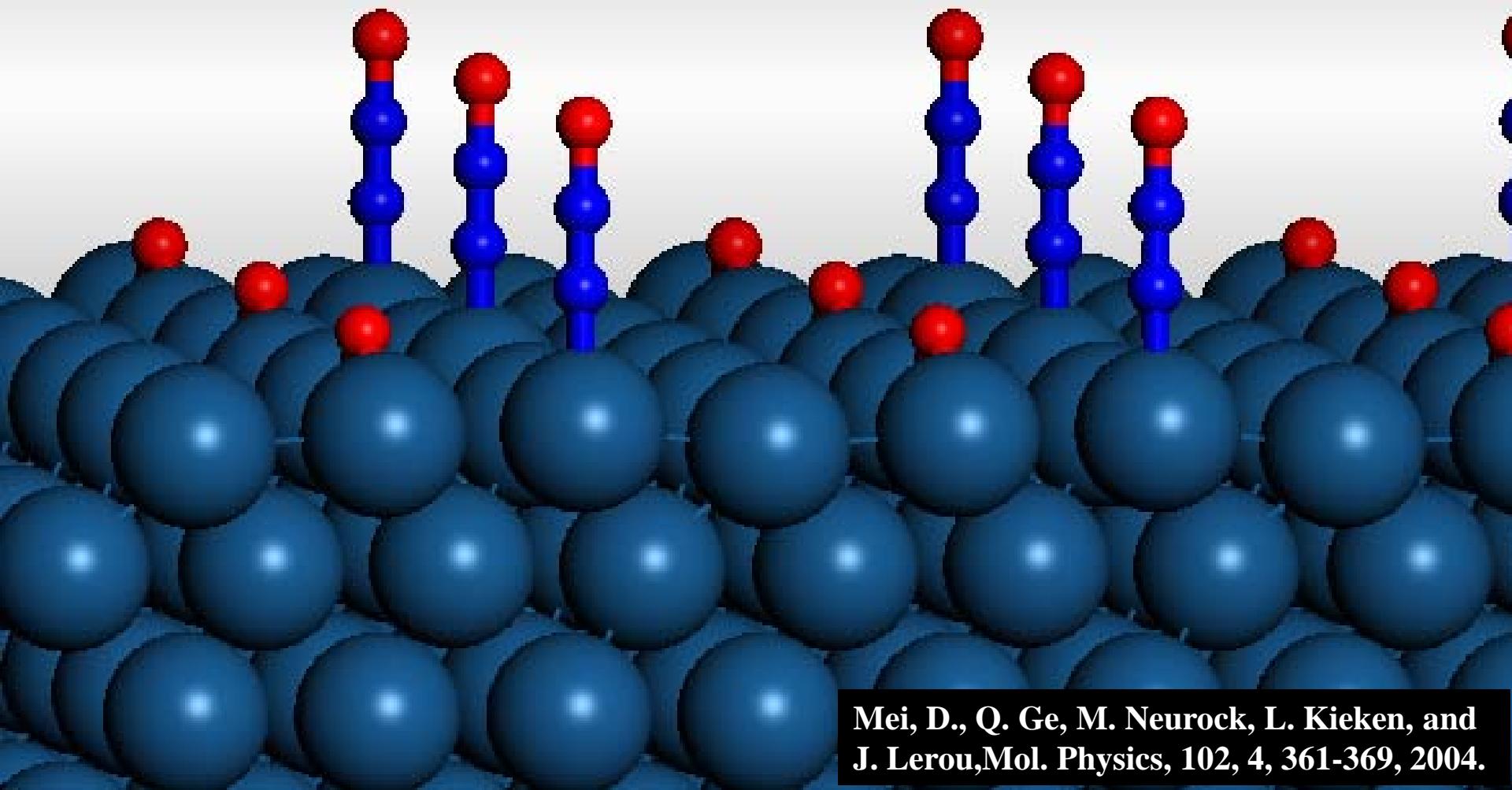
Mei, D., Q. Ge, M. Neurock, L. Kieken, and J. Lerou,Mol. Physics, 102, 4, 361-369, 2004.

Mei, D., Q. Ge, M. Neurock, L. Kieken, and J. Lerou,Mol. Physics, 102, 4, 361-369, 2004.

Ab Initio Derived Kinetics

Reaction	E_{for} (kJ/mol)	E_{rev} (kJ/mol)	E_{for} (kJ/mol)	E_{rev} (kJ/mol)	ν_{for} (s$_0$) (s^{-1})	ν_{rev} (s$_0$) (s^{-1})
	Pt(100)		Rh(100)			
$NO\,(g) + * \leftrightarrow NO*$	0.0	214.3	0.0	263.8	0.7	1×10^{13}
$NO* + * \rightarrow N* + O*$	97.1	21.0	76.1	184.4	1×10^{13}	1×10^{13}
$NO* + O* \rightarrow NO_2* + *$	133.0	49.1	182.0	0.0	1×10^{13}	1×10^{13}
$NO* + N* \rightarrow N_2O* + *$	141.9	92.7	204.7	0.0	1×10^{13}	1×10^{13}
$NO* + NO* \rightarrow N_2O* + O*$	115.2	0.0	96.4	0.0	1×10^{13}	1×10^{13}
$N_2O* \rightarrow N_2(g) + O*$	0.0	102.9	0.0	178.1	1×10^{13}	1×10^{13}
$N* + N* \rightarrow N_2(g) + 2*$	9.0	140.8	204.4	69.5	1×10^{13}	1×10^{13}
$O* + O* \leftrightarrow O_2(g) + 2*$	0.0	218.6	0.0	458.6	1×10^{15}	0.1
$NO_2* \rightarrow NO_2(g) + *$	118.7	0.0	177.4	0.0	1×10^{13}	1×10^{13}
$N_2O* \rightarrow N_2O(g) + *$	26.5	0.0	54.0	0.0	1×10^{13}	1×10^{13}

Modeling Surface Kinetics and Dynamics

Quantum Chemistry

Adsorption Energies
Activation Barriers
Rate Constants
Equilibrium Constants

Reactivity

Monte Carlo Simulation

Nitric Oxide Decomposition over Pt(100)

TPD
Catalytic Reaction Analyses

Simulating Temperature Programmed Desorption

Equilibrate the surface via adsorption, desorption and surface diffusion at low temperature to simulate experimental protocol.

Turn off all adsorption steps and consider only desorption, surface diffusion and possibly surface reaction steps.

Ramp the temperature through the simulations by:

$$T = T_o + \beta\, t$$
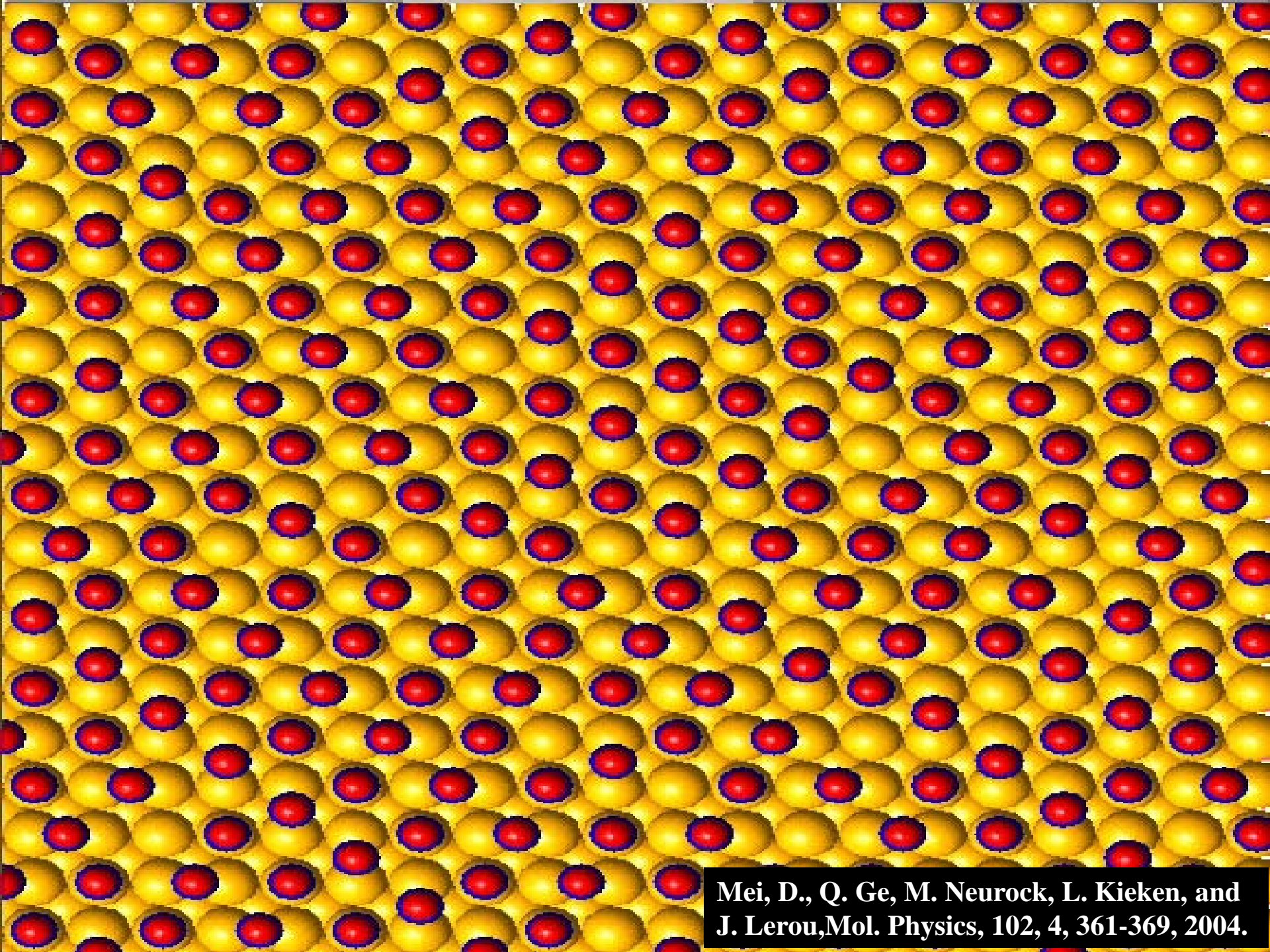
Nitric Oxide TPD on Pt(100)

Simulation

- $\theta \leq 0.40$ ML, all NO dissociated

- $\theta \geq 0.40$ ML, NO desorbs before dissociation

- θsat = 0.54 ML

- Dissociation ratio at saturation is 62%

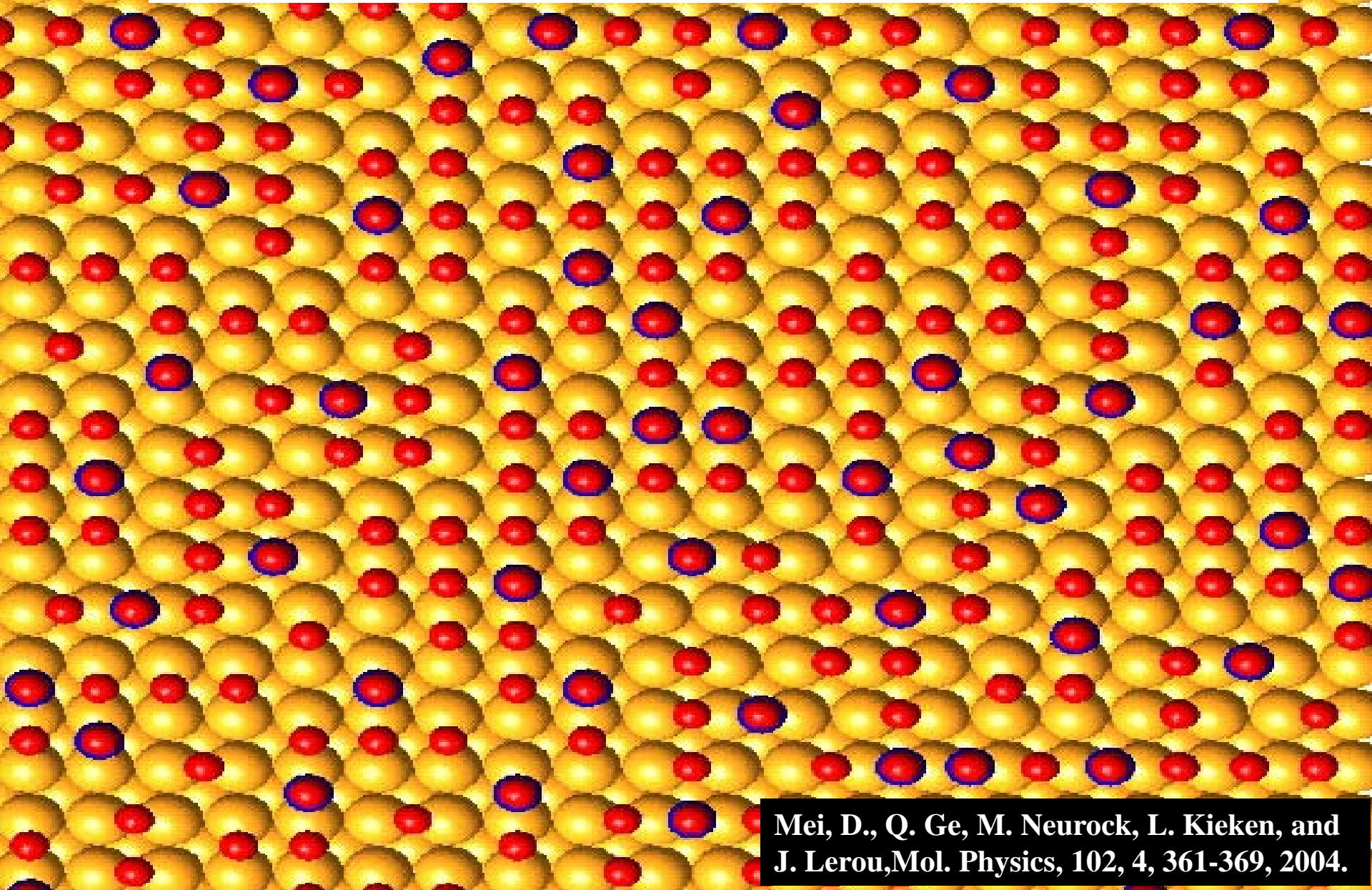- N_2 desorption peaks (400 - 450 K)

- O_2 desorption peaks (600 - 800 K)

- Small amounts of N2O are formed at lower temperatures.

Experiment

- θsat = 0.50 ML

- Dissociation ratio at saturation is 25-66%

- N_2 desorption peaks (400 - 500 K)

- O_2 desorption peaks (600 - 800 K)

Catalytic Decomposition of Nitric Oxide over Pt(100)

Nitric Oxide Catalytic Decomposition Mechanism

$$NO(g) + * \longleftrightarrow NO*$$

$$O_2(g) + 2* \longleftrightarrow O* + O*$$

$$NO* + * \longleftrightarrow N* + O*$$

$$NO* + O* \longleftrightarrow NO_2* + *$$

$$NO* + N* \longleftrightarrow N_2O* + *$$

$$NO* + NO* \longleftrightarrow N_2O* + O*$$

$$N_2O* \longrightarrow N_2(g) + O*$$

$$N* + N* \longrightarrow N_2(g) + 2*$$

$$N_2O* \longrightarrow N_2O(g) + *$$

$$NO_2* \longrightarrow NO_2(g) + *$$

Nitric Oxide Decomposition in Excess of Oxygen over Pt(100)

Nitric Oxide Decomposition in Excess of Oxygen over Pt(100)

1000K   800K   700K   600K   575K

N₂ Formation

NO + O₂ over Pt(100)
P_{NO} = 0.468 torr
P_{O_2} = 60.8 torr

■ N_2 Ea = 28.3 kJ/mol
● NO_2

NO₂ Formation

y-axis: ln(TOF) ($Pt^{-1} s^{-1}$)

x-axis: 1/T (K^{-1})

Mei, D., Q. Ge, M. Neurock, L. Kieken, and J. Lerou, Mol. Physics, 102, 4, 361-369, 2004.
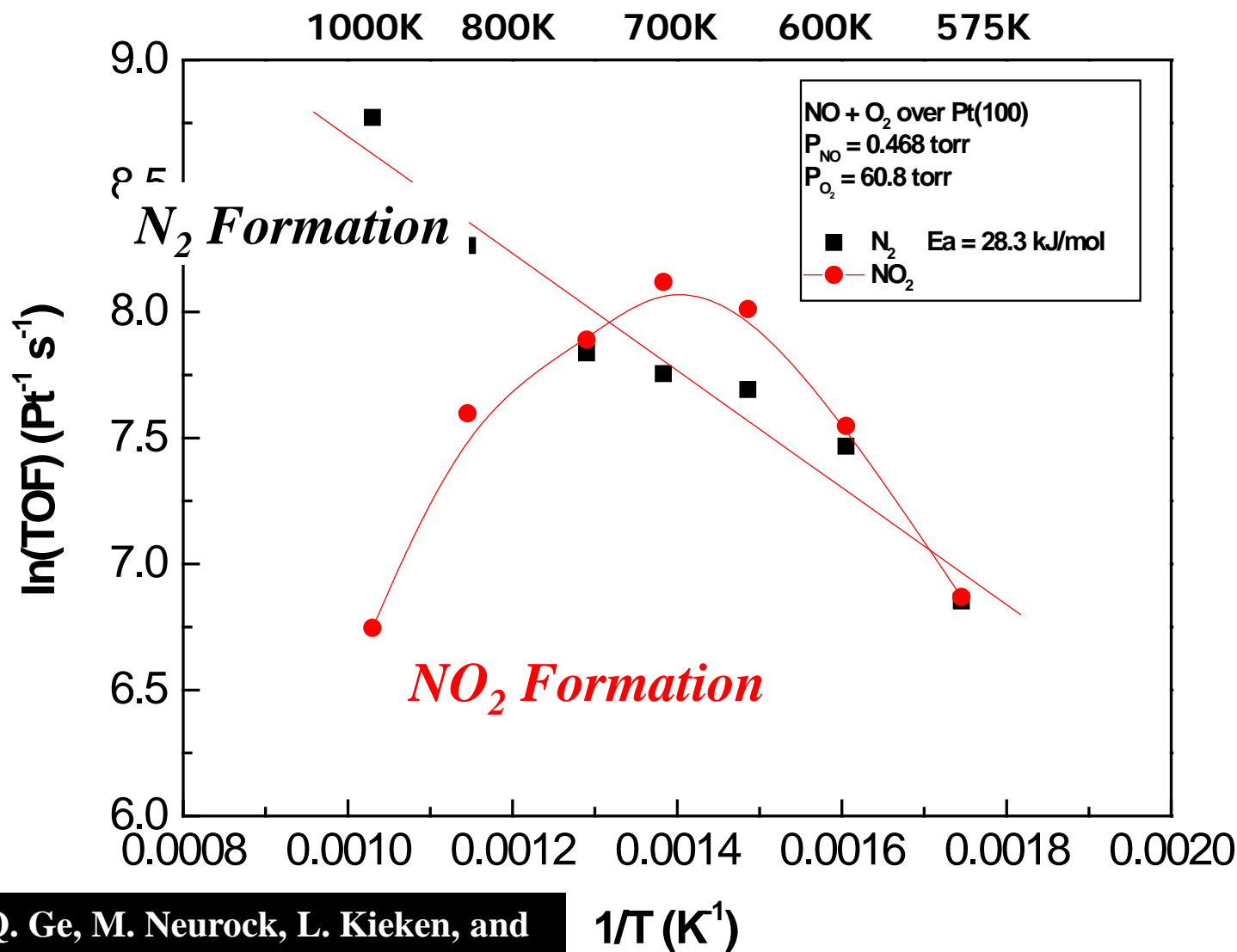
Nitric Oxide Decomposition in Excess of Oxygen over Pt(100)

Global Reaction Orders

Legend in figure:

NO+O$_2$ over Pt(100)

T = 723 K

— ● — NO order = 0.9

— ■ — O$_2$ order = -0.4

$$r_{N2} = k' \, P_{NO}^{\alpha} P_{O2}^{\beta}$$

Axes: $\ln r_{N_2}$ (vertical); $\ln p_{NO}$ or $\ln p_{O_2}$ (horizontal)

Mei, D., Q. Ge, M. Neurock, L. Kieken, and J. Lerou, Mol. Physics, 102, 4, 361-369, 2004.
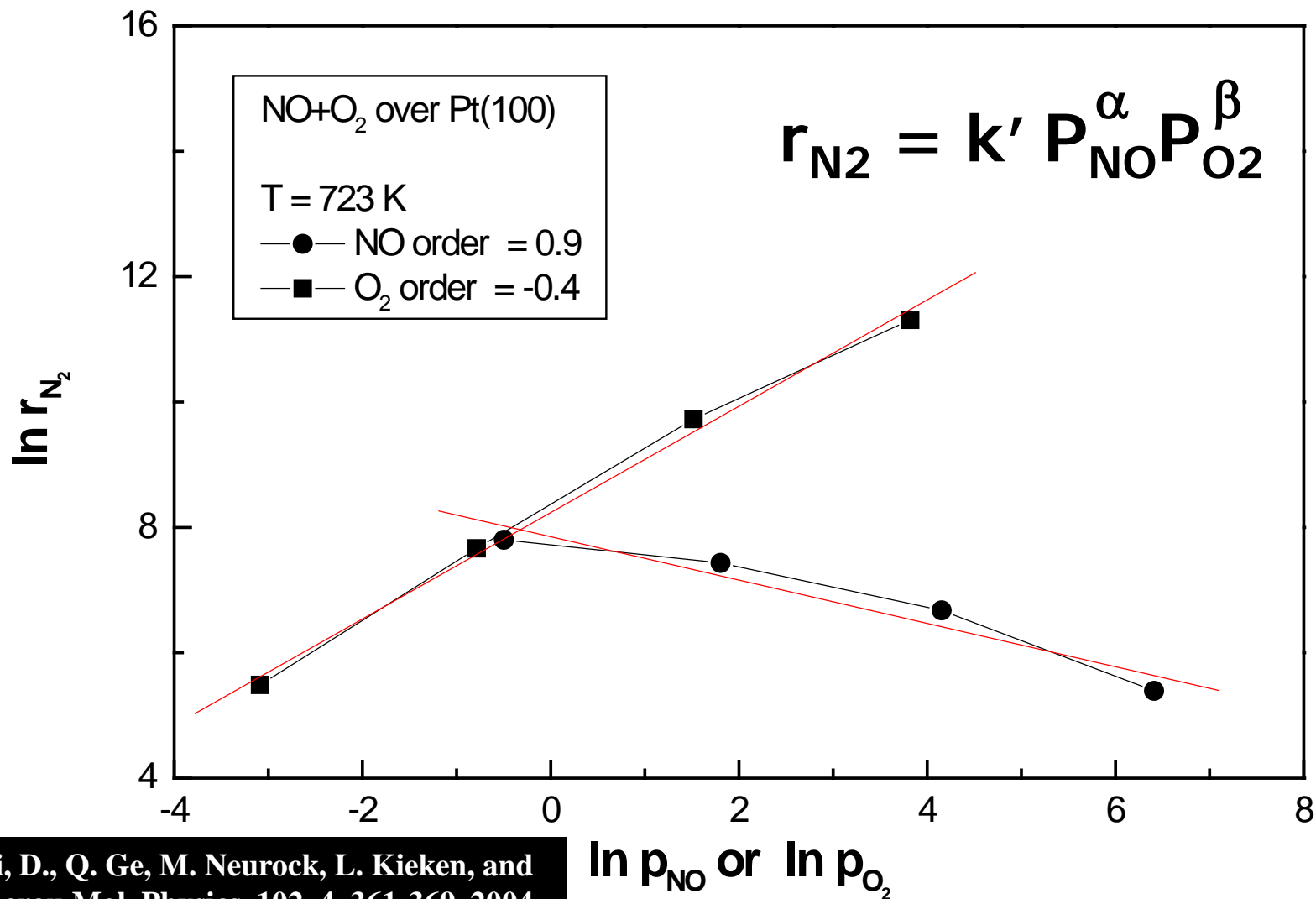
Nitric Oxide Decomposition in Excess of Oxygen over Pt(100)
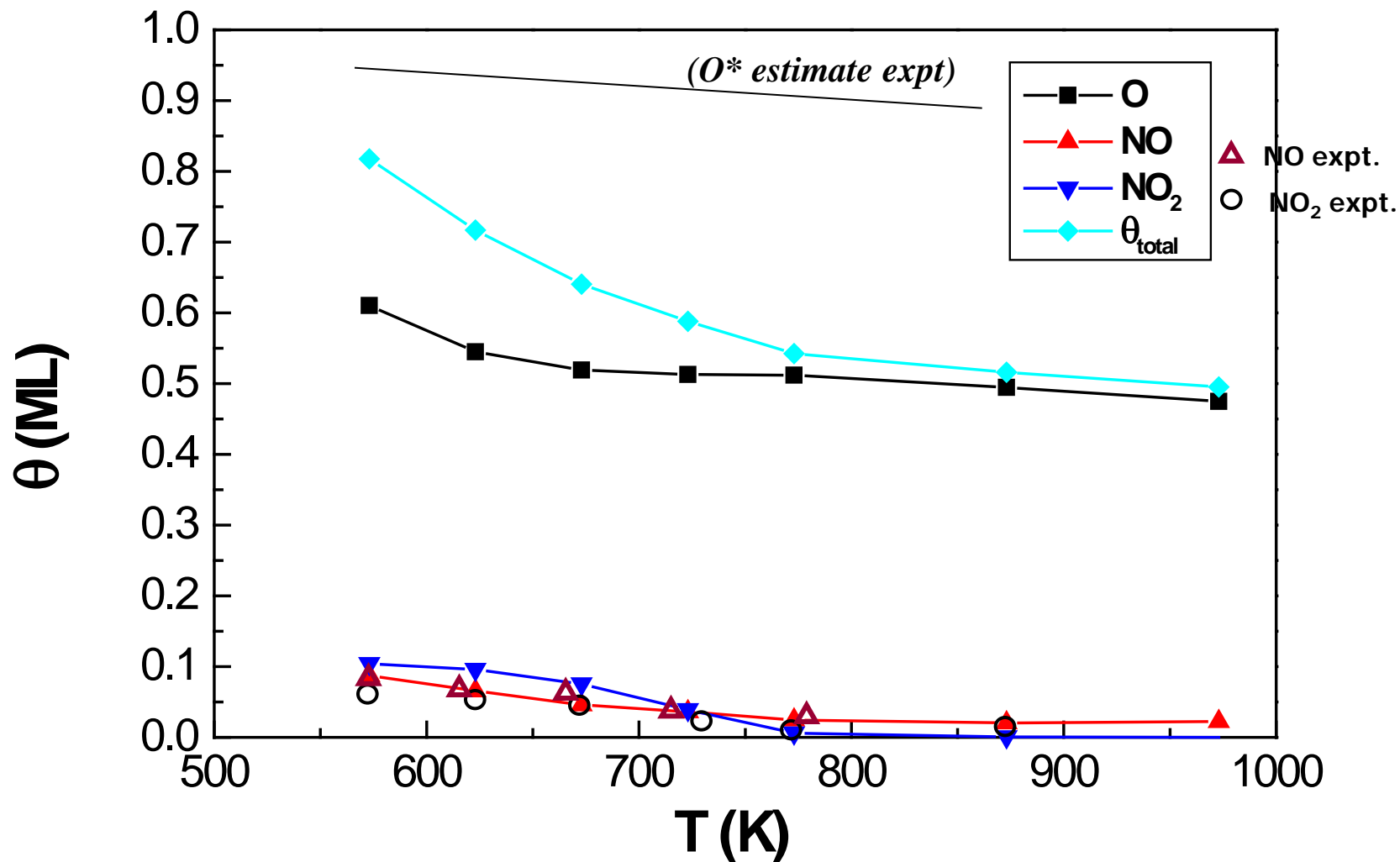
Experimental Data from L. Olsson et al. , *J. Phys.Chem. B*, 103, 10433-10439 (1999); 105, 6895-6906 (2001)

Nitric Oxide Decomposition over Rh(100) surface

TPD
Catalytic Reaction Chemistry

Nitric Oxide TPD on Rh(100)

Simulation

- $\theta \leq 0.30$ ML, all NO dissociated

- $\theta \geq 0.30$ ML, NO desorbs before dissociation

- $\theta sat = 0.62$ ML

- Dissociation ratio at saturation is 53%

- N_2 desorption peaks (600 – 750 K)

- O_2 desorption peaks (1300-1500 K)

Experiment

- $\theta \leq 0.28$ ML, all NO dissociated

- $\theta \geq 0.28$ ML, NO desorbs before dissociation

- $\theta sat = 0.65$ ML

- Dissociation ratio at saturation is 52%

- N_2 desorption peaks (650 – 850 K)

- O_2 desorption peaks (1200-1400 K)

Nitric Oxide Decompostion over Rh(100)

Nitric Oxide Decomposition in Excess of Oxygen over Rh(100)
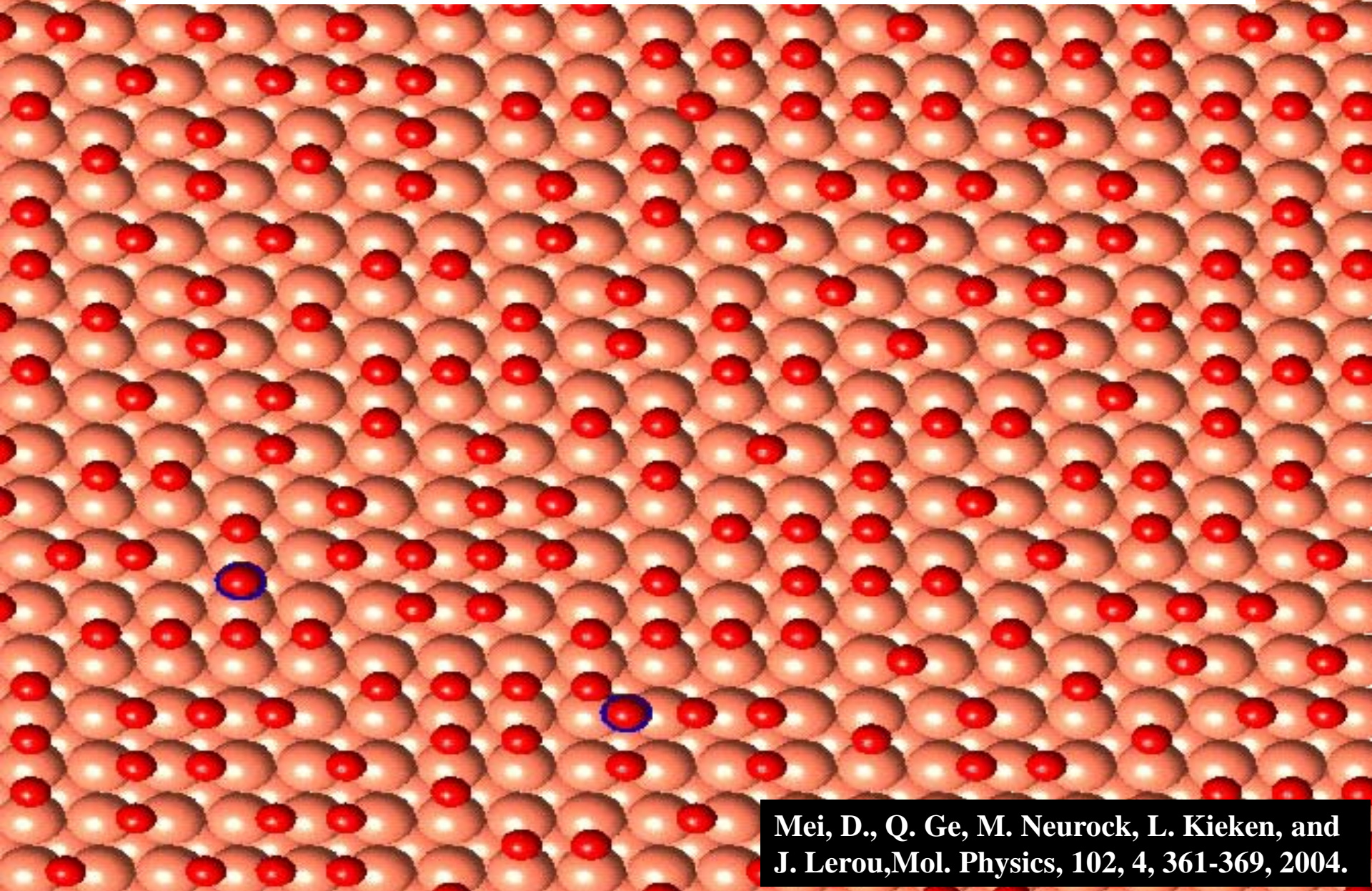
Nitric Oxide Decomposition in Excess of Oxygen over Rh(100)

Turnover Frequency vs Temperature

NO Oxidation on Rh(100)
P_{NO} = 0.468 torr
P_{O_2} = 60.8 torr

● N$_2$
■ NO$_2$
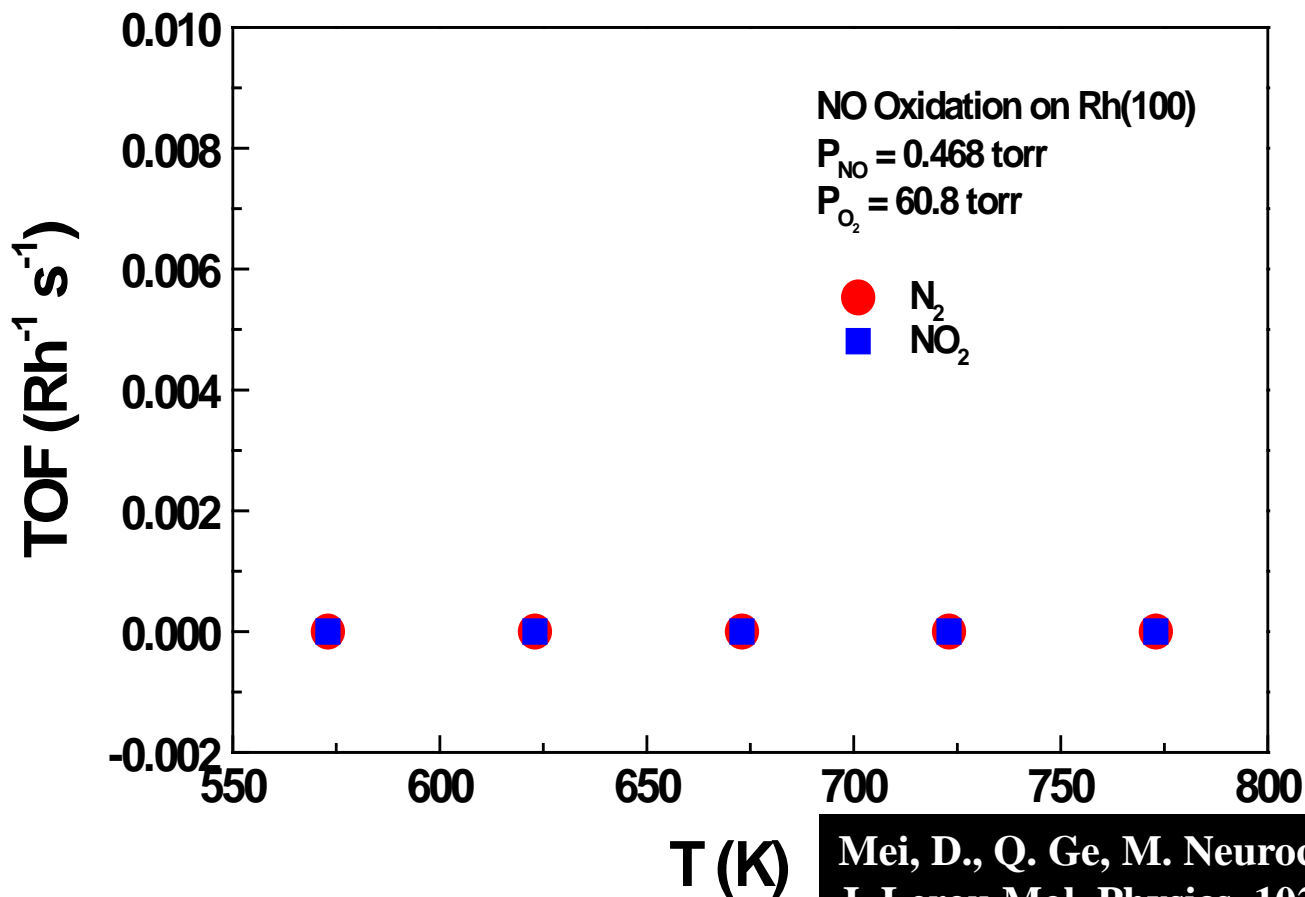
Periodic Trends

Sabatier's Principle
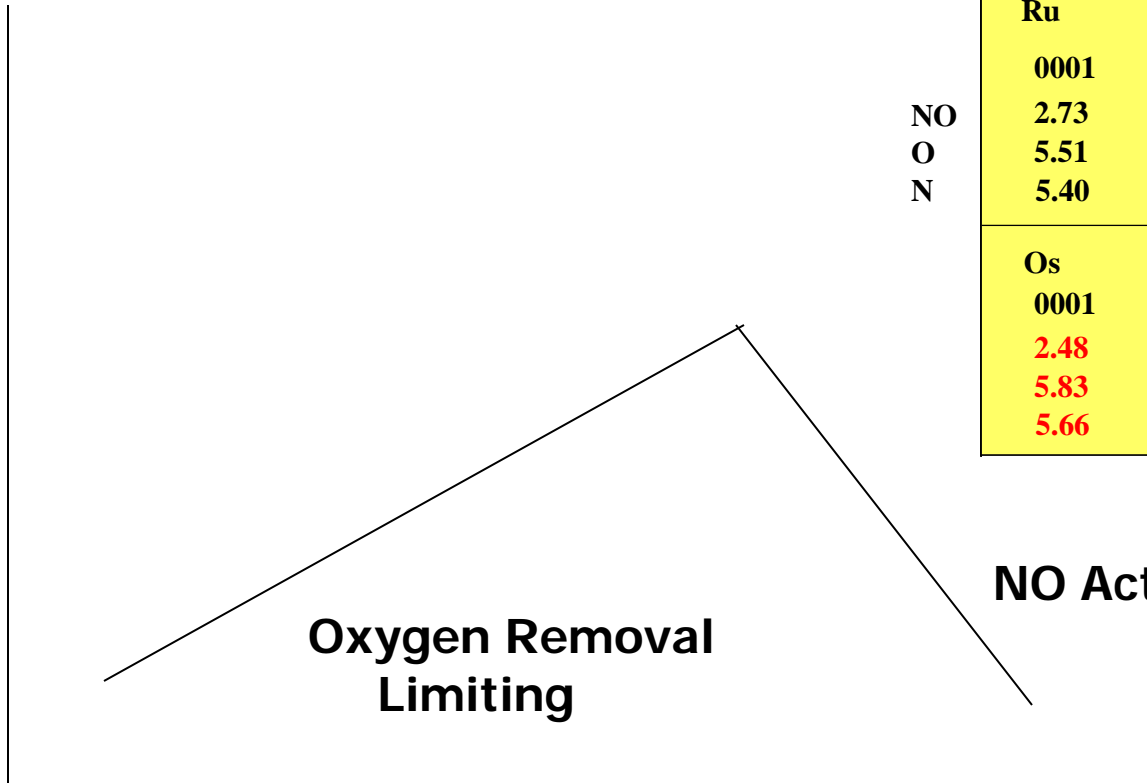
	Fe	Co		Ni		Cu	
		0001		**111**	**100**	**111**	**100**
NO		2.55			4.52	1.35	??
O		5.40				3.85	??
N		5.62		5.38	5.66	5.03	??
	Ru	**Rh**		**Pd**		**Ag**	
	0001	**111**	**100**	**111**	**100**	**111**	**100**
NO	2.73	2.50	2.68	2.24	2.15	0.52	??
O	5.51	4.45	4.81	4.45	3.63	2.20	??
N	5.40	5.38	4.62	4.10	3.79	3.57	??
	Os	**Ir**		**Pt**		**Au**	
	0001	**111**	**100**	**111**	**100**	**111**	**100**
	2.48	1.88	2.66	1.90	2.22	0.53	??
	5.83	4.91	5.30	4.62	4.29	2.72	??
	5.66	4.68	5.00	4.09	4.08	3.30	??

NO Activation Limiting

Oxygen Removal Limiting

Position in the Periodic Table

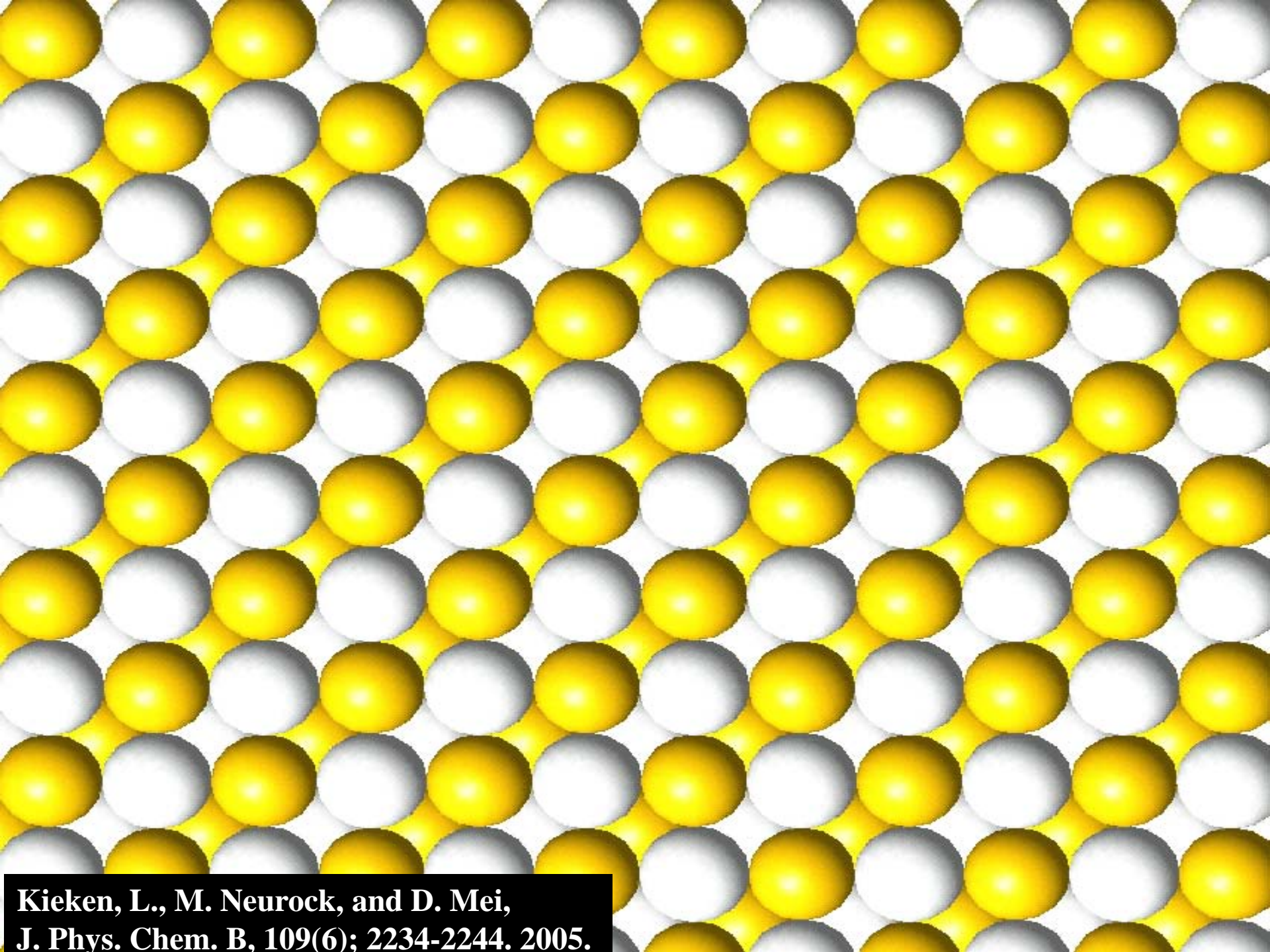# Cycle 2

Manipulating Surface Chemistry

Bimetallics

PtAu
PtSn

Scouting Compositional Effects PtAu Alloys
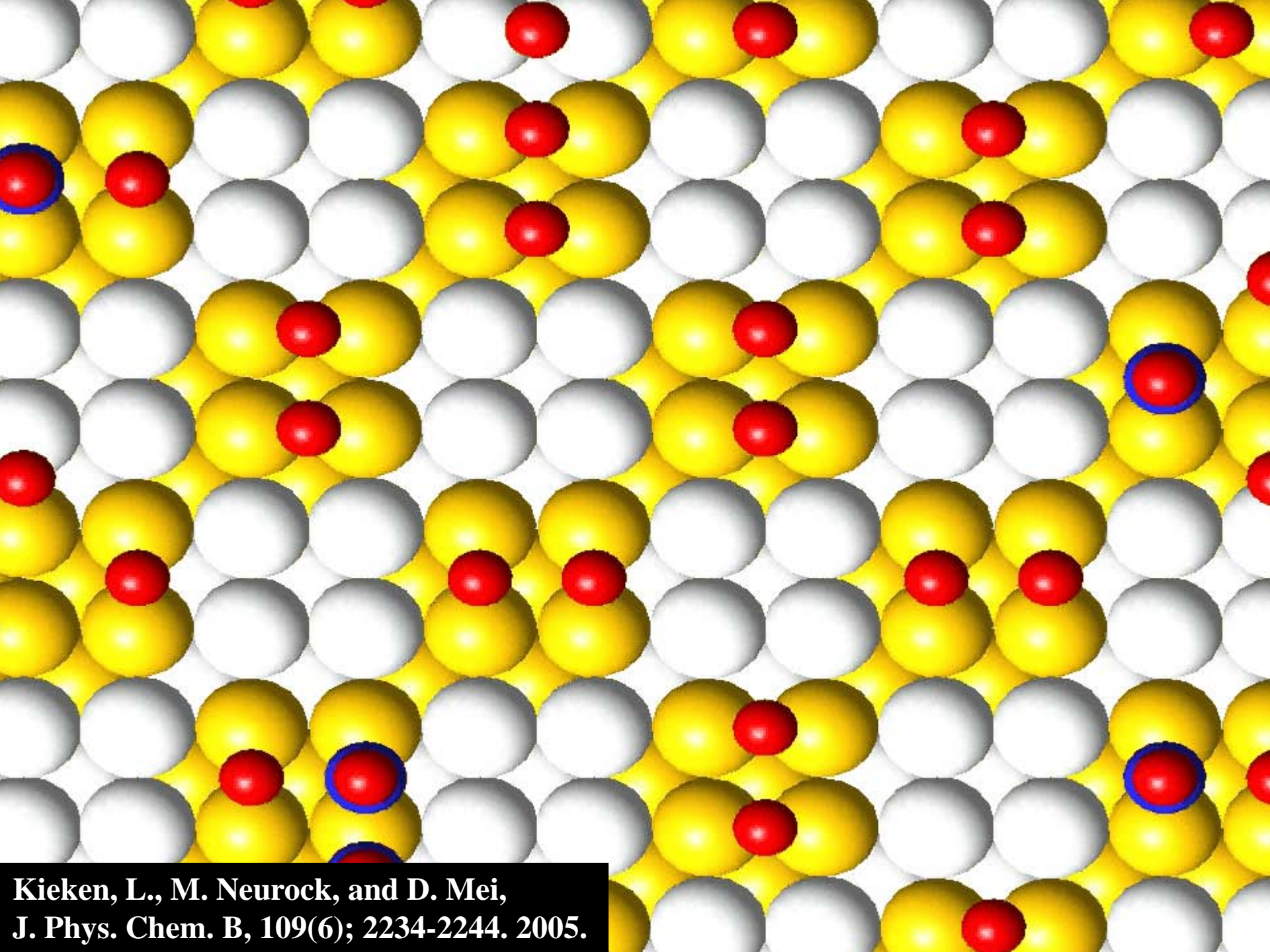
Kieken, L., M. Neurock, and D. Mei,
J. Phys. Chem. B, 109(6); 2234-2244. 2005.

Effect of Ensemble on NO Decomposition
Over 100 Different PtAu Arrangements Analyzed
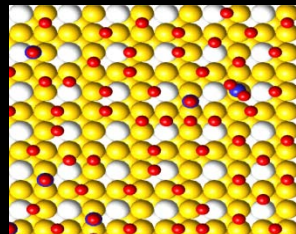
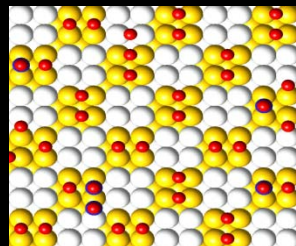|	TOF (N2)	TOF (NO2)	S (N_2/N_2+NO_2)	θ_O
	8.35	8.27	52.0%	0.431
	8.36	8.89	36.7%	0.222
	8.94	8.54	60.2%	0.194
	9.4 (7.66)	9.63	44.6%	0.132
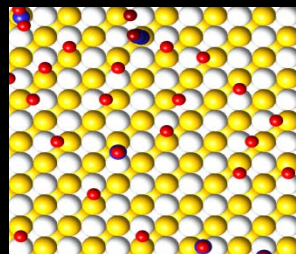
Catalyst Development Engine™ Tools
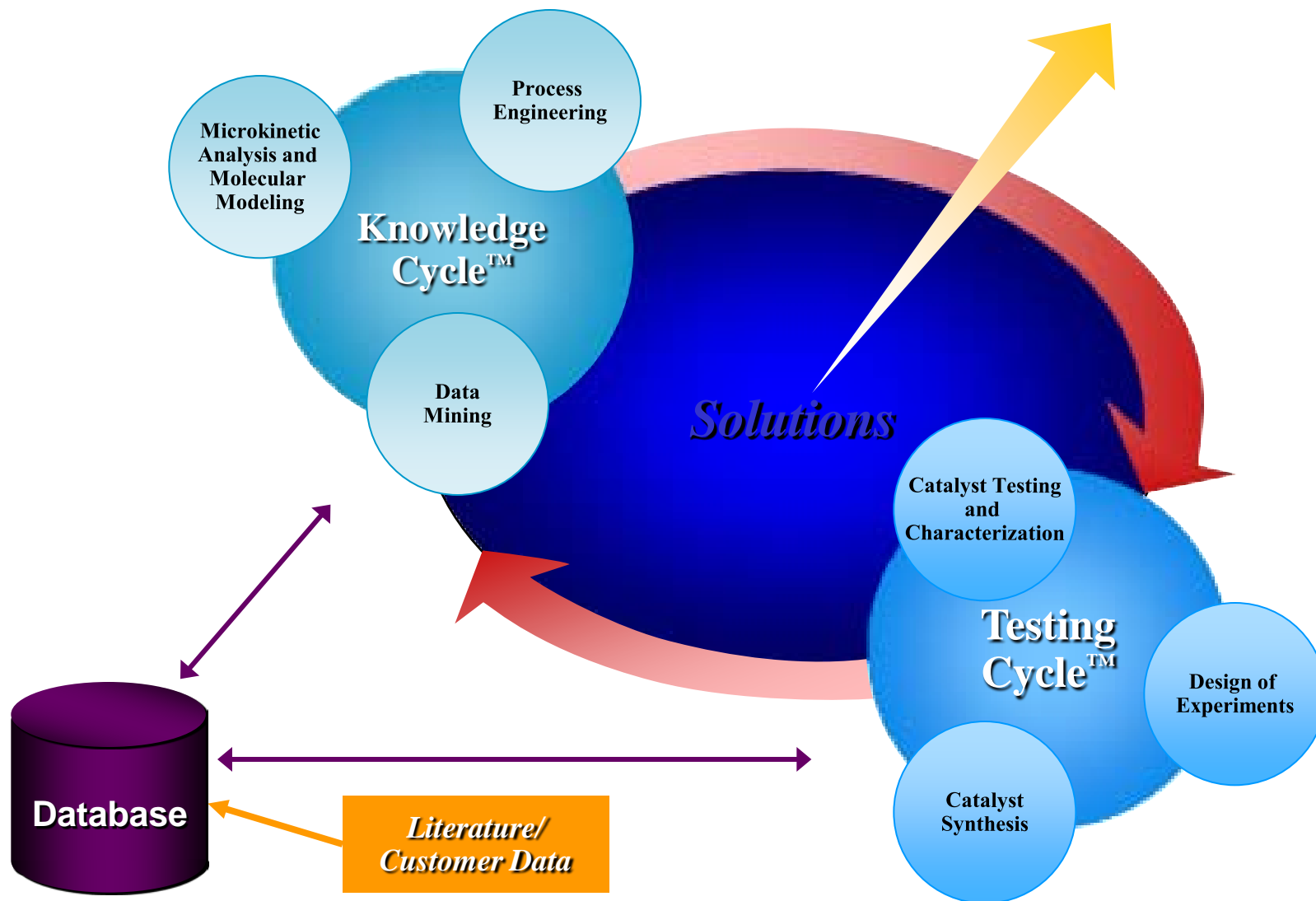
Cycle 3 - Suggestions

Beyond the Limitations of Sabatier and Evans Polanyi

Bifunctional Materials (Metal w/ Oxide Functionality)
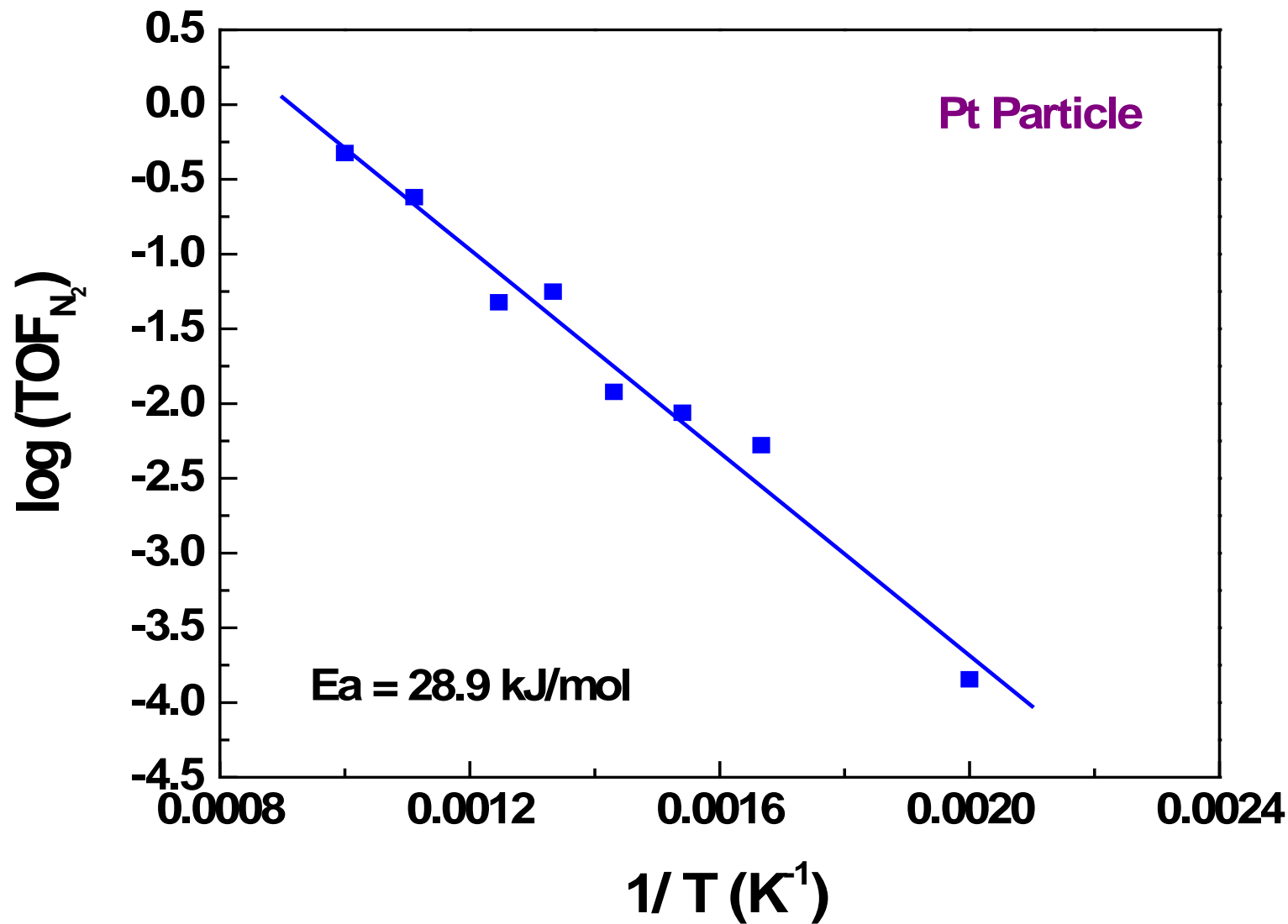
Pt-Ceria (Rapid Oxygen Shuttler)

Pt-YSZ (Anionic oxygen promoters)

Pt - Co_xO_y (Pt w/ Magnetic Promotion)

PtAg-Co_xO_y (Isolated Pt w/ Magnetic Promotion)

3D Particle Simulations

N$_2$ Formation over Entire Particle

Pt Particle

Ea = 28.9 kJ/mol