

MODELING OF SYNGAS REACTIONS AND HYDROGEN GENERATION OVER SULFIDES

University Coal Research Contractors Review Meeting
June 4, 2003

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Overall Scheme

Modeling Methods

MoS₂ – Reactive Edges and Sites

Reactions with Hydrogen

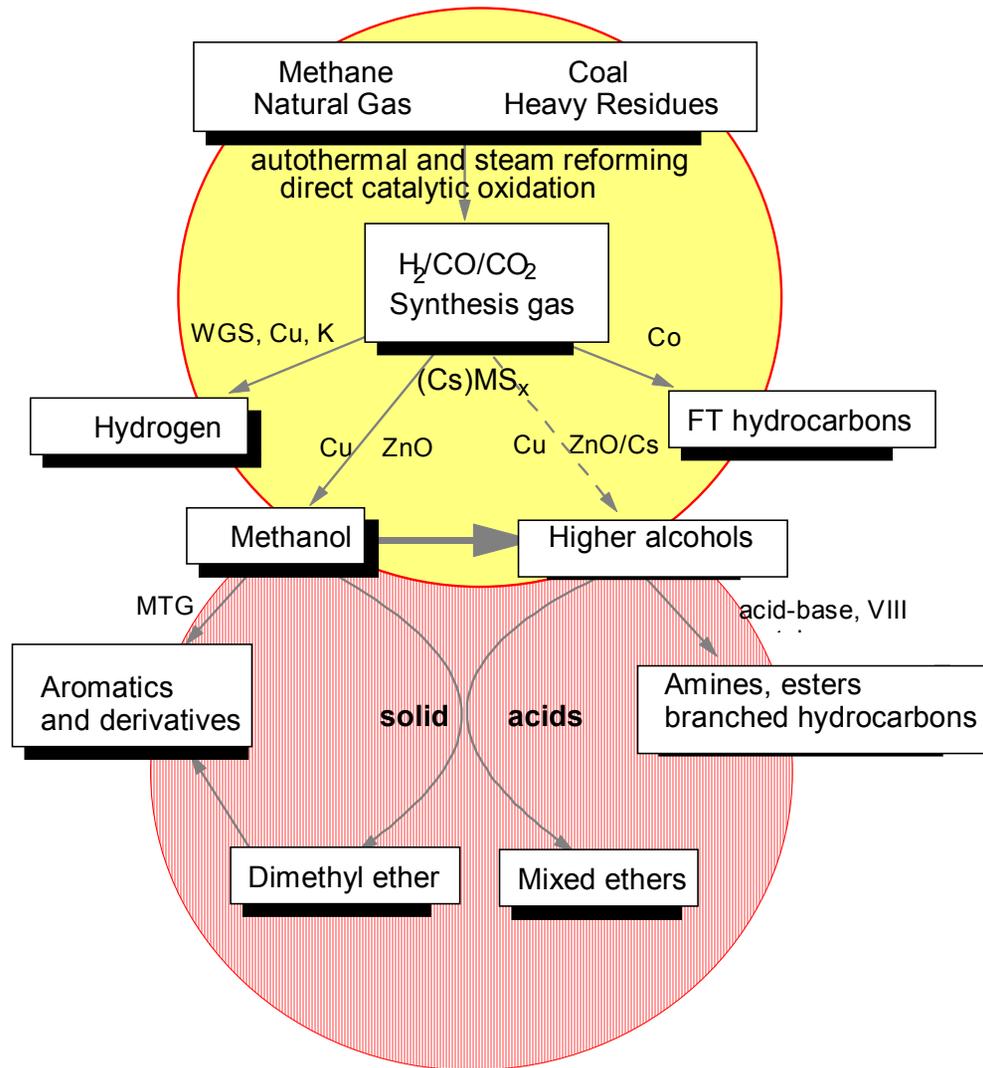
The Adsorption Entropy Penalty

The Sites and Effects of Alkali

The Transition State

Reactions with Hydrogen and Carbon Monoxide

Contributions of Modeling



An overall scheme for conversion of sources of carbon to alcohols, ethers, olefins, aromatics and amines. All these processes are catalyzed.

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Contributions of Modeling

Modeling: Theoretical Background and Platforms I

A. Empirical methods:

MMFF – Merck Molecular Force Field “standard” molecular dynamics

GULP – General Utility Lattice Properties (j.gale@ic.ac.uk)

B. Semiempirical methods:

Pm3(tm) – Semi-empirical molecular orbital method [*J. J. P. Stewart, J. Comp. Chem.* **10** (1989) 209]

Ligand-Field Theory Codes – calculation of correlation term diagrams and optical transitions in low-symmetry systems (*P.J. Hutta & K. Klier, QCPE*)

DMol³ - DFT-LCAO with the double-numerical basis set [*B. Delley, J. Chem. Phys.* **92** (1990) 508] and effective core potential (ECP) for core electrons

VASP - Vienna Ab Initio Simulation Package with plane-wave basis and ultra-soft pseudopotentials: [*G. Kresse, J. Furthmüller, Comput. Mat. Sci.* **6** (1996) 15; *Phys. Rev.* **B54** (1996) 11169; G. Kresse, J. Hafner, *J. Phys.: Condens. Matter* **6** (1994) 8245; D. Vanderbilt, *Phys. Rev.* **B41** (1990) 7892

Modeling: Theoretical Background and Platforms II

C. All-electron methods:

WIEN2k - Full Potential Augmented Plane-Waves plus local orbitals (APW+LO) and linearized augmented plane-waves (LAPW). [*P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, J. Luitz*, <http://www.wien2k.at>.] Spin-orbit coupling is implemented in P. Novak, "Calculation of spin-orbit coupling", http://www.wien2k.at/reg_user/textbooks/novak_lecture_on_spinorbit.ps

DMol³ w/DNP basis set

Spartan w/DN** basis set

QChem w/6-31G** basis set

The last three methods give comparable results for cluster calculations

Modeling: Theoretical Background and Platforms III

D. Optimizations:

Force Driven damped Newton method: New coordinates $\mathbf{R}_m^{\tau+1}$ of atom m after optimization step τ are set as $\mathbf{R}_m^{\tau+1} = \mathbf{R}_m^{\tau} + \eta_m(\mathbf{R}_m^{\tau} - \mathbf{R}_m^{\tau-1}) + \delta_m \mathbf{F}_m$, where the “friction” parameter η and the “step-size” parameter δ are selected to best fit the optimization task and \mathbf{F}_m are forces on each atom m .

BFGS - Broyden-Fletcher-Goldfarb-Shanno scheme, in: *R. Fletcher, Practical Methods of Optimization, Wiley, New York, 1987, p. 55 ff.*

RFO - Rational Function Optimization: *A. Banerjee, N. Adams, J. Simons, R. Shepard, J. Phys. Chem. 89 (1985) 52.*

E. Transition States:

Searches for saddle points on potential energy surfaces (PES), modified for tunneling for surface reactions involving hydrogen. Examples in: *K. Klier, “The Transition State in Heterogeneous Catalysis”, Topics in Catalysis 18 (2002) 141*

In DFT, the (valence and core) orbital energies ε_i are obtained as solutions of the set of the Kohn-Sham equations

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \psi_{i,\text{K-S}} = \varepsilon_i \psi_{i,\text{K-S}}$$

where the effective potential

$$v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r})}$$

and the total energy

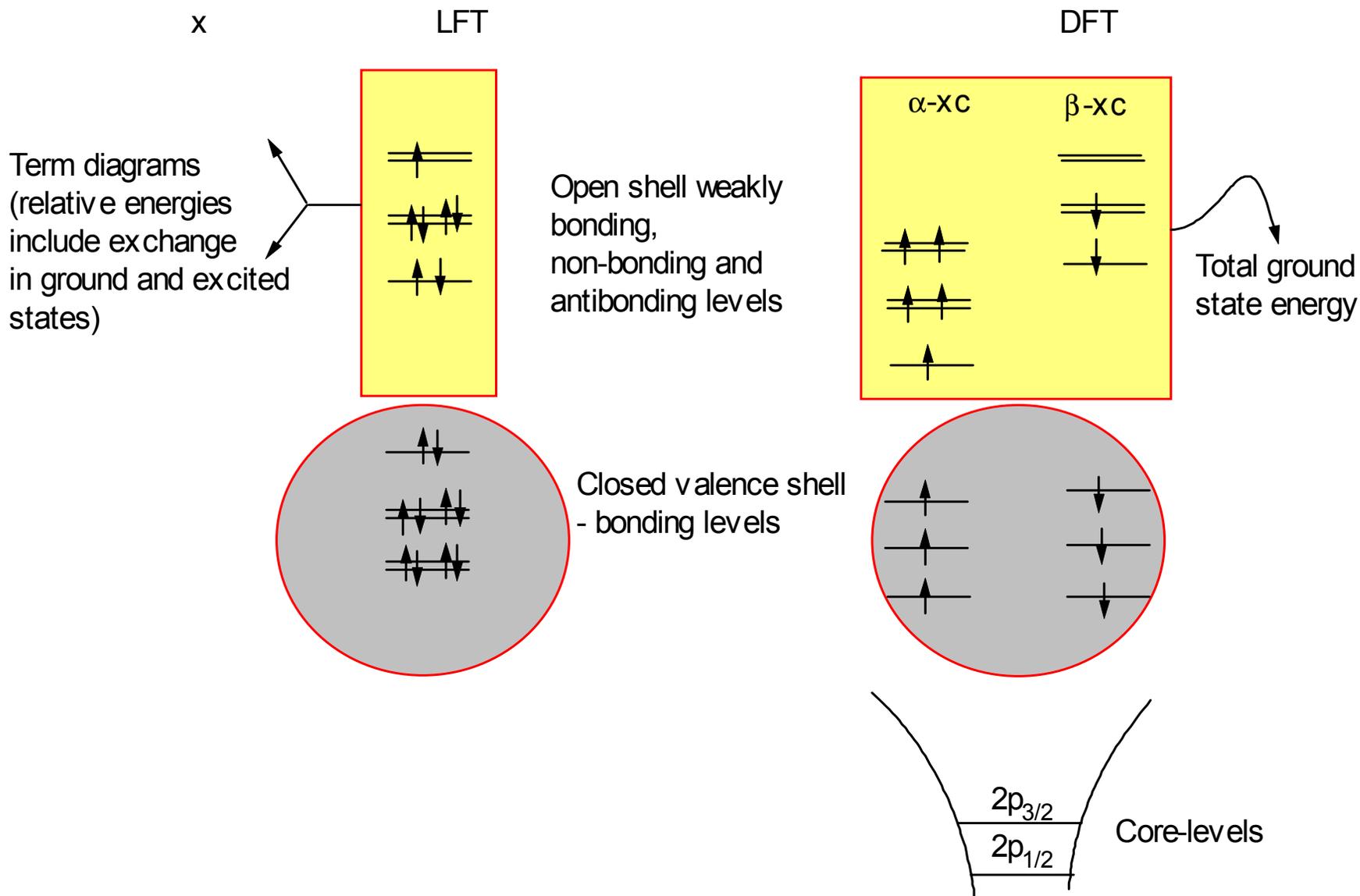
$$E = \sum_i \varepsilon_i - J[\rho] + E_{\text{xc}}[\rho] - \int v_{\text{xc}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}$$

with a universal density functional (e.g. Perdew-Burke-Ernzerhof)

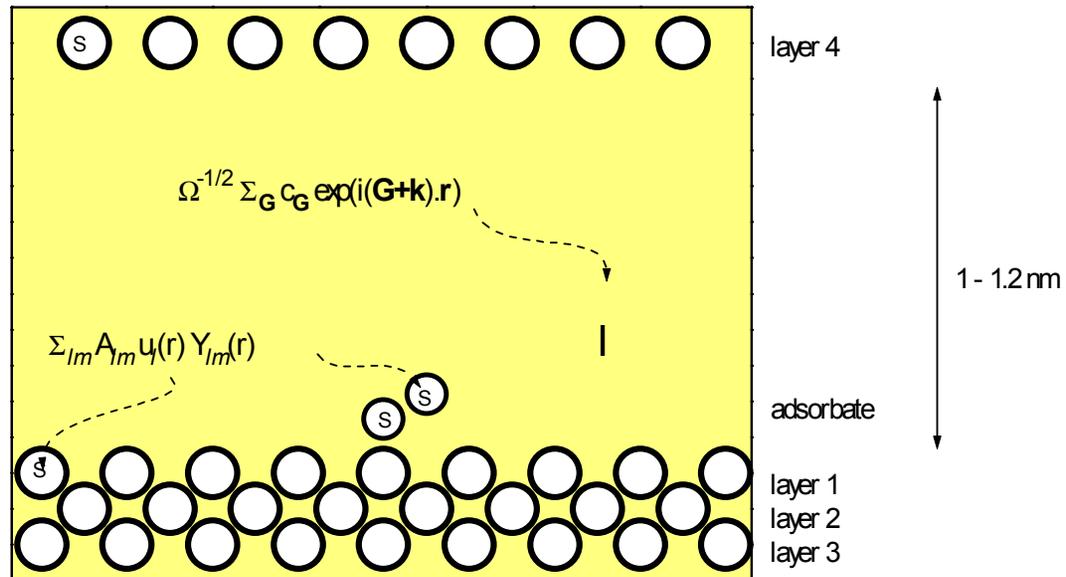
$$F[\rho] = T_s[\rho] - J[\rho] + E_{\text{xc}}[\rho],$$

and T_s is the kinetic energy of a reference system with electron density ρ free of the 'external potential' of atomic nuclei $v(\mathbf{r})$.

In open-shell systems, unbalanced electron spin gives rise to differences in chemical behavior between molecules, clusters, surfaces and solids



Surface is a complex defect to model; edge – even more complex
 Edges with adsorbates – a challenge
 Reactions of adsorbates with transition states – a future



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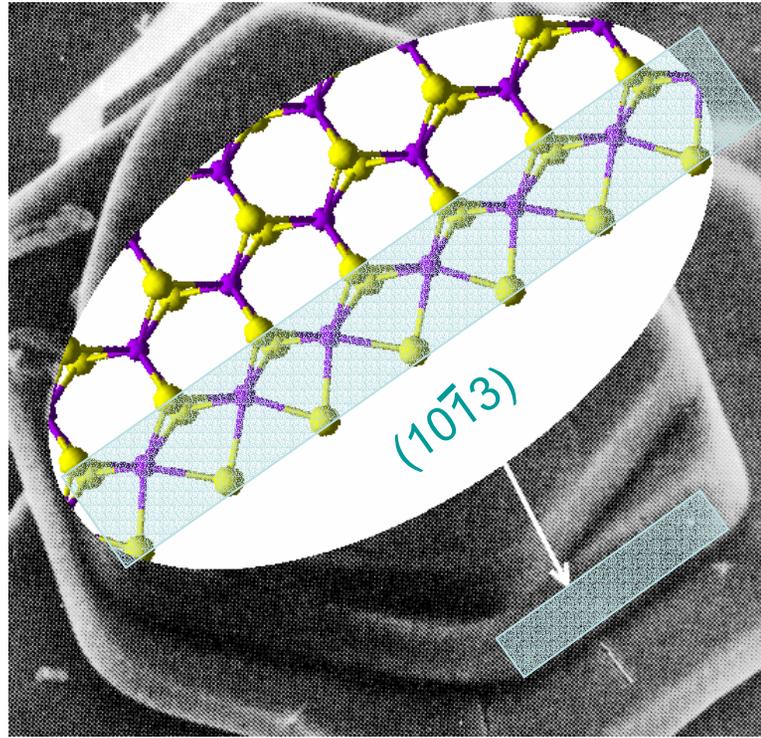
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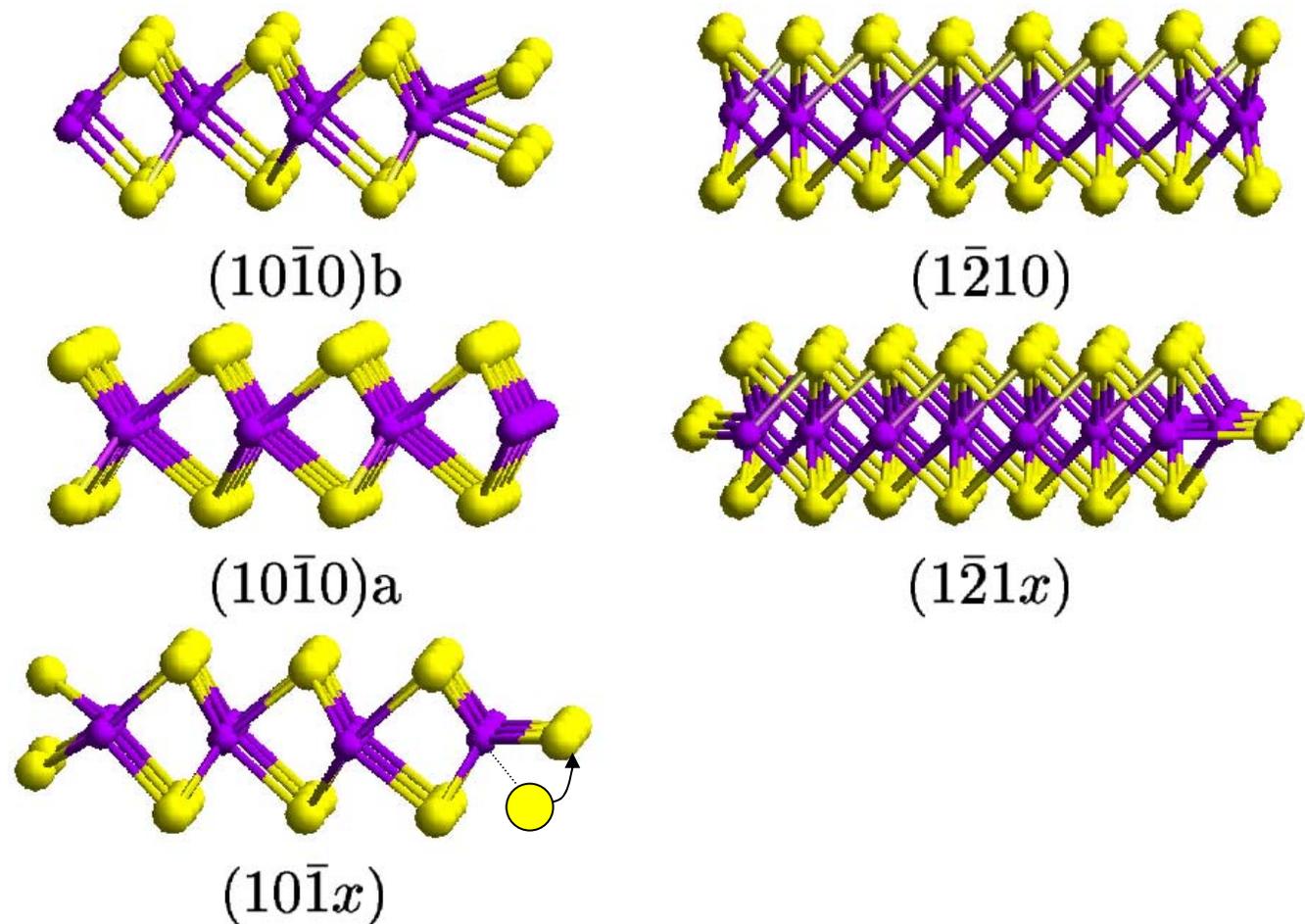
Reactions with Hydrogen and Carbon Monoxide

Contributions of Modeling

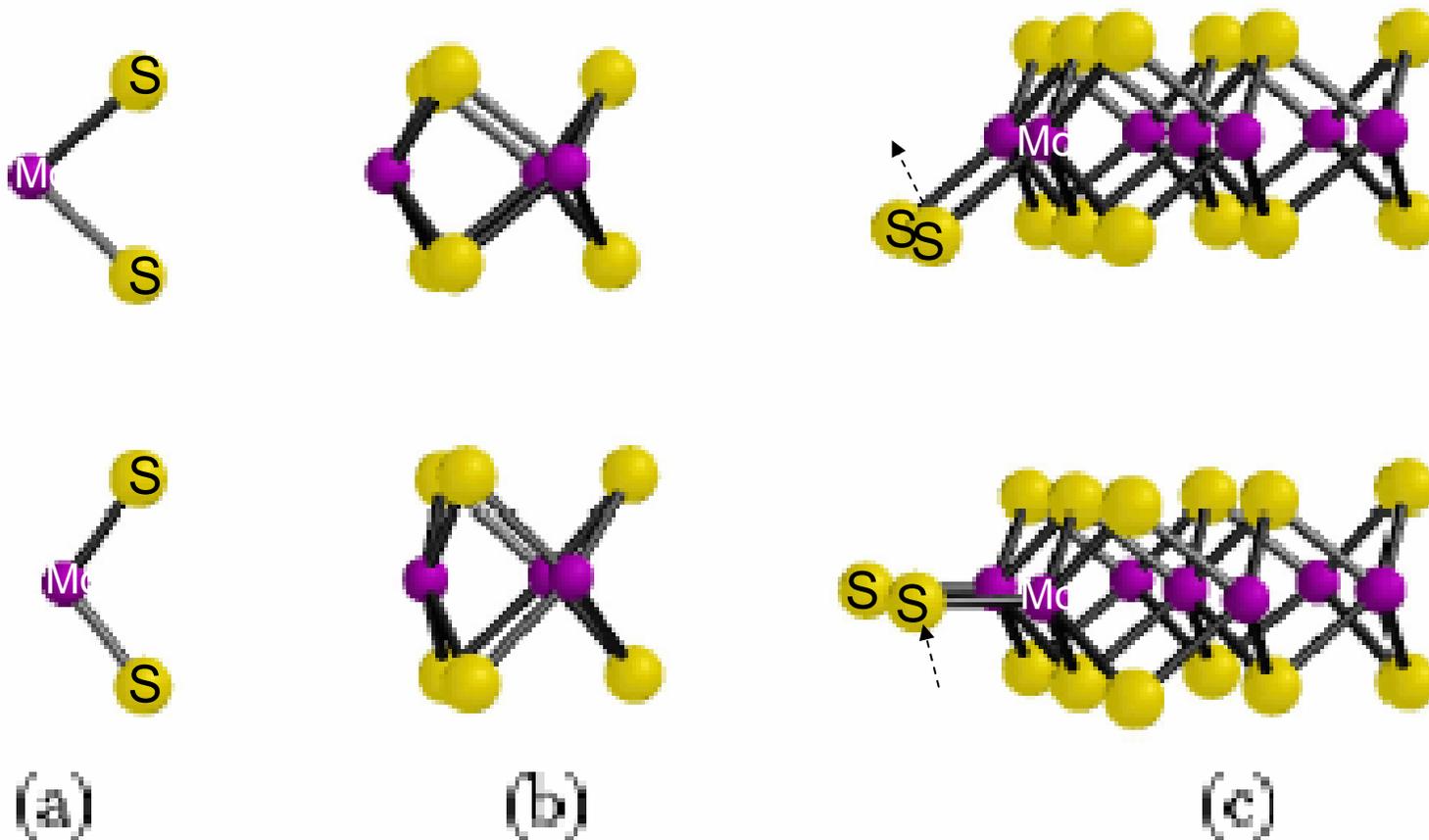


The atomic structure of the edges of the single-crystal MoS₂ in this electron micrograph by Chianelli et al. [J. Catal. 92 (1985), 56] has been determined [Spirko et al., Surf. Sci., submitted] to be the $(10\bar{1}3)$ edge pictured in the inset.

MoS₂ edges are sites of reactivity toward H₂, O₂, CO, metals, organic compounds. 'Stable' edges are relaxed (10-1x) where Mo coordination increases due to movement of S up and sideways (J.A. Spirko, M.L. Neiman, A.M. Oelker, K. Klier, Surf. Sci., submitted). DFT/GGA/DNP.



Clusters Mo_xS_{2x} (unrelaxed, top; relaxed, bottom) begin to reconstruct like edges when $x \geq 7$ (right). Smaller sizes are high spin (triplets) all the way down to a single molecule (left), whose calculated properties are in excellent agreement with experiment [Liang and Andrews, JPC A106 (2002) 6945, Spirko et al., present study]



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Hydrogen - the “Big Picture”:

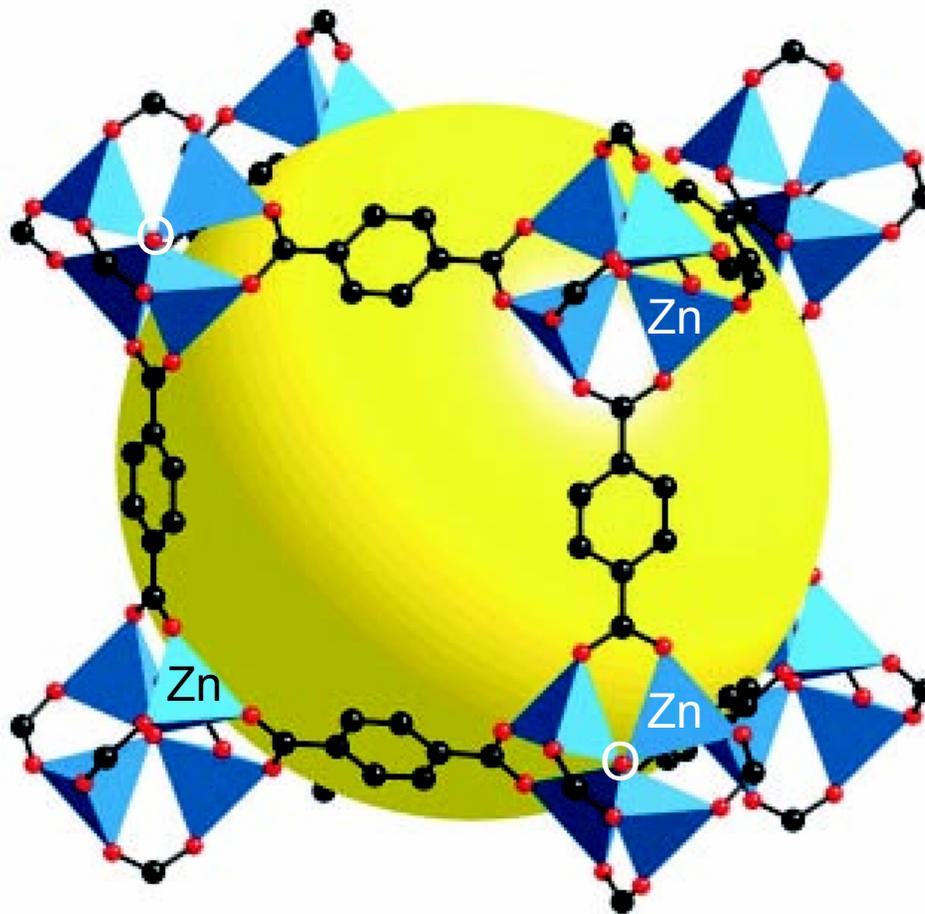
From Tom Mebrahtu: “**Advanced Materials for Hydrogen Storage Applications**”
APCI, February 16, 2003)

<http://www.airproducts.com/corp/rel/03025.asp>

President Bush, State of the Union Address – January 28, 2003

“Tonight I am proposing \$1.2 billion in research funding so that America can lead the world in developing clean, hydrogen-powered automobiles ... A simple chemical reaction between hydrogen and oxygen generates energy, which can be used to power a car producing only water, not exhaust fumes. With a new national commitment, our scientists and engineers will overcome obstacles to taking these cars from laboratory to showrooms so that the first car driven by a child born today could be powered by hydrogen, and pollution-free. Join me in this important innovation to make our air significantly cleaner, and our country much less dependent on foreign sources of energy.”

Rosi et al., *Science* **300** (2003) 1127, *C&E News* 5/19/03, p. 11, *New York Times* 5/16/03. report molecular H₂ storage 4 wt. % at 78 K and 1 wt.% at 298 K, 20 bar. Material: Zn₄O(BDC)₃
BDC = 1,4-benzenedicarboxylate



Hydrogen in Heterogeneous Systems - General Issues and Activation on Sulfides

Tasks:

- Comprehensive critical review “Hydrogen Activation, Generation and Storage” (Abby Oelker and KK)
- “Relative Stabilities of Clusters and Edges, and Electronic Surface States in MoS₂” (Jeff Spirko, Mike Neiman and KK)
- “Activation of Hydrogen on Unpromoted and Alkali-Promoted TS₂ Chalcogenides” (Jeff and KK)

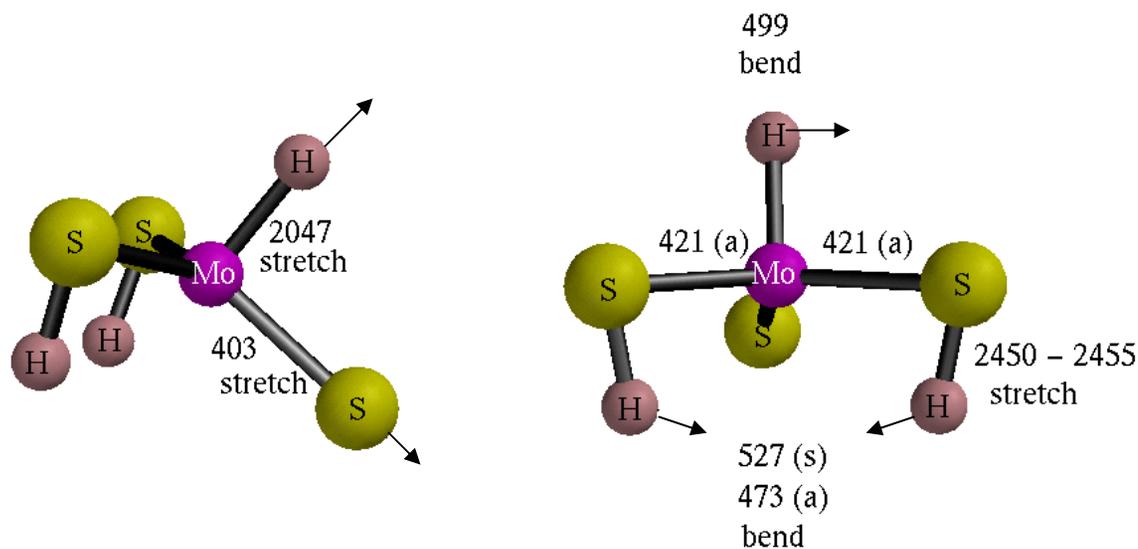
Hydrogen Activation, Generation and Storage

A.M. Oelker and K. Klier

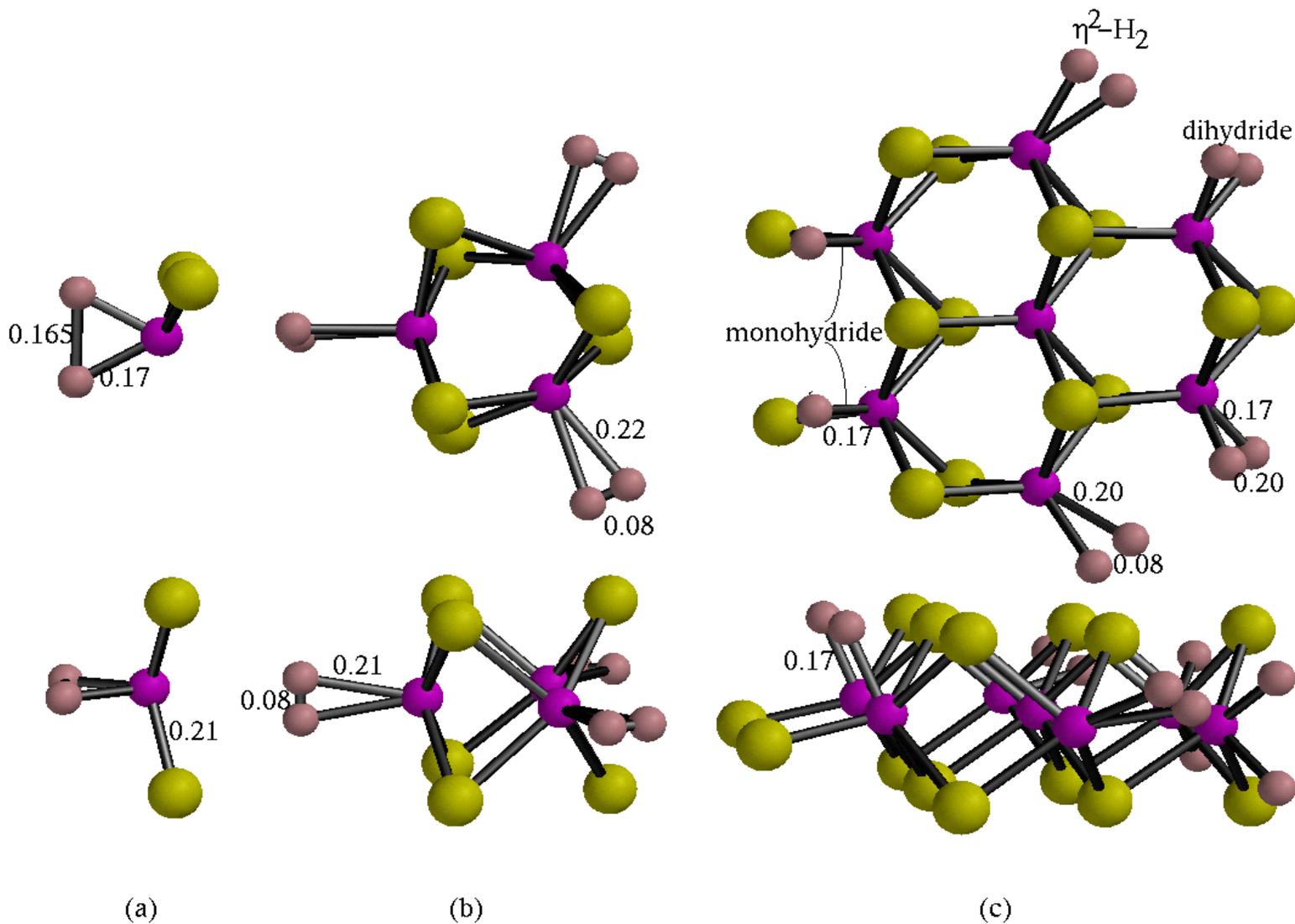
Contents:

- I. Hydrogen as Panacea
- II. Production of Hydrogen
 - A. Steam Reforming
 - B. Partial Oxidation
 - C. Autothermal Reforming
 - D. Electrolysis, Thermolysis, Photolysis of Water
 - E. Biomass Gasification, Biohydrogen
- III. Storage of Hydrogen
 - A. Dilemmas Regarding Conventional Storage
 - B. Carbon Nanotubes
 - C. Hydrogenated Organic Compounds
 - D. Glass Spheres & Zeolites
 - E. Liquid Hydrogen
 - F. Metal Hydrides (Reversible)
- IV. Summary, Conclusion

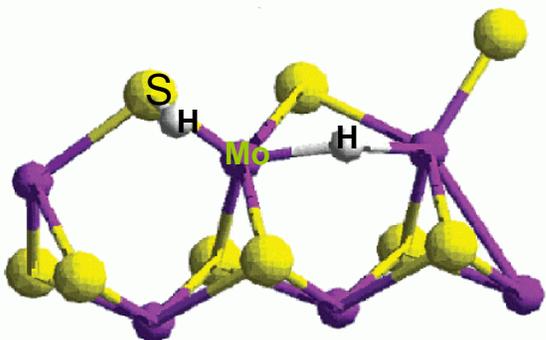
MoS₂ relaxed edges (10-1x) adsorb H₂ dissociatively and heteropolarly into MoH and SH species [S. Cristol et al., JPC **B106** (2002) 5659; **B104** (2000) 11220, DFT/GGA/VASP]. **The challenge:** No experiment has found Mo-H, and S-H has been argued indirectly based on low-frequency modes observed by neutron scattering [P.N. Jones et al., Surf. Sci. **207** (1988) 105 to 660 cm⁻¹; C.J. Wright et al., J.C.S. Faraday I, **76** (1980) 640, 662, 847, 1348, 1977 (v.w.) cm⁻¹, reinterpreted by C.M. Sayers, J. Phys. **C14** (1981) 4969 as bending Mo-S-H mode with overtones]. Our calculations (DFT/GGA/DN^{**}):



MoS₂ clusters bind H₂ to form monohydrides, dihydrides and η^2 -H₂ complexes, all on exposed Mo atoms [J.A. Spirko, M.L. Neiman, A.M. Oelker, K. Klier]. DFT/GGA/DN**. Interatomic distances are in nm. Energies of formation: -40 kcal/mol H₂ (a) to +2.8 kcal/mol H₂ (c).



MoS₂ does not bind H₂ on the most stable (10 $\bar{1}$ x) edges [Cristol et al., VASP[#], Neiman et al., DMol^{3*}]. H₂ dissociates on the less stable (1010) and (1 $\bar{2}$ 11) edges. Adsorption energies are in kcal/mol H₂.



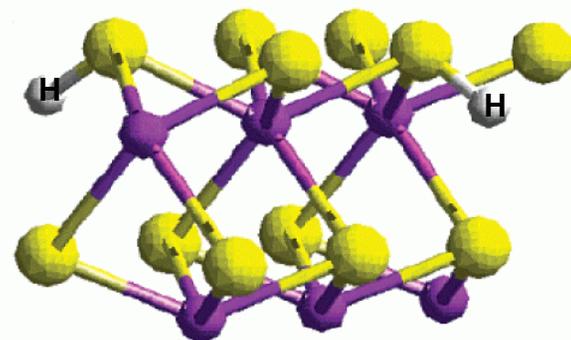
(10 $\bar{1}$ x) *Left*

$$\Delta E = 0.2 \text{ kcal/mol}^\#$$



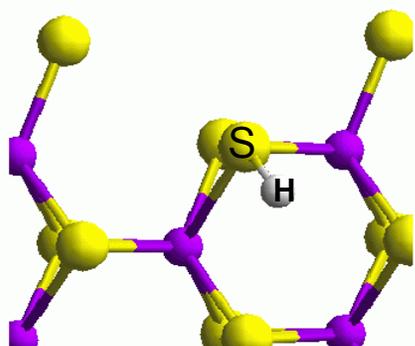
(10 $\bar{1}$ x) *Right*

$$\Delta E = 6.2 \text{ kcal/mol}^\#$$



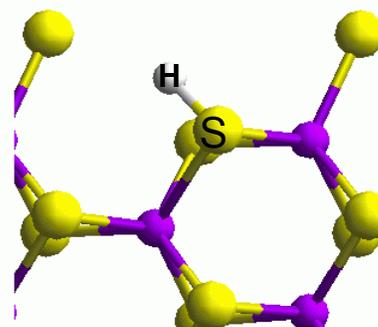
(10 $\bar{1}$ 0)*a Left*

$$\Delta E = -31.8 \text{ kcal/mol}^\#$$



(1 $\bar{2}$ 11) *Left*

$$\Delta E = -24.4 \text{ kcal/mol}^*$$



(1 $\bar{2}$ 11) *Left*

$$\Delta E = -21.7 \text{ kcal/mol}^*$$

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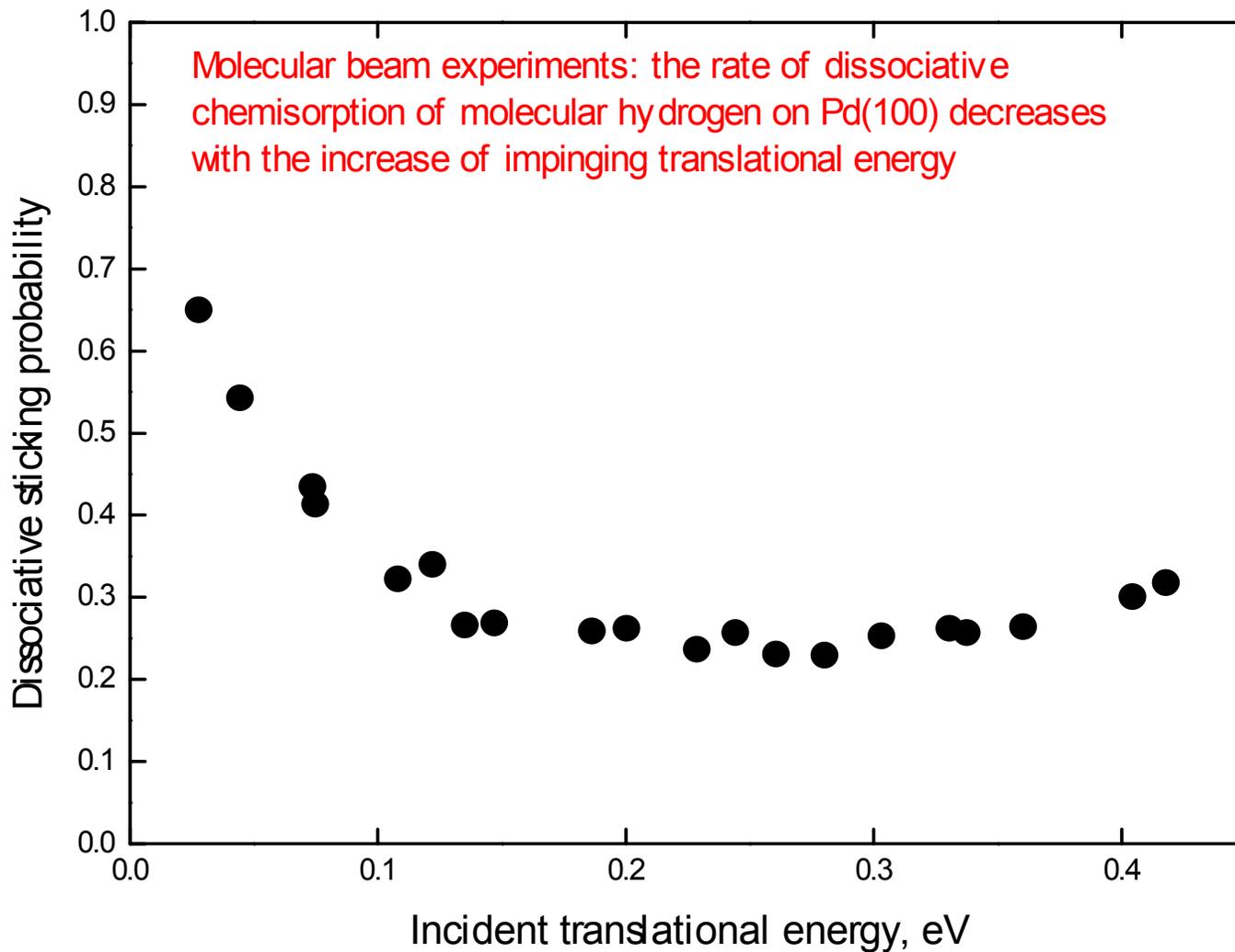
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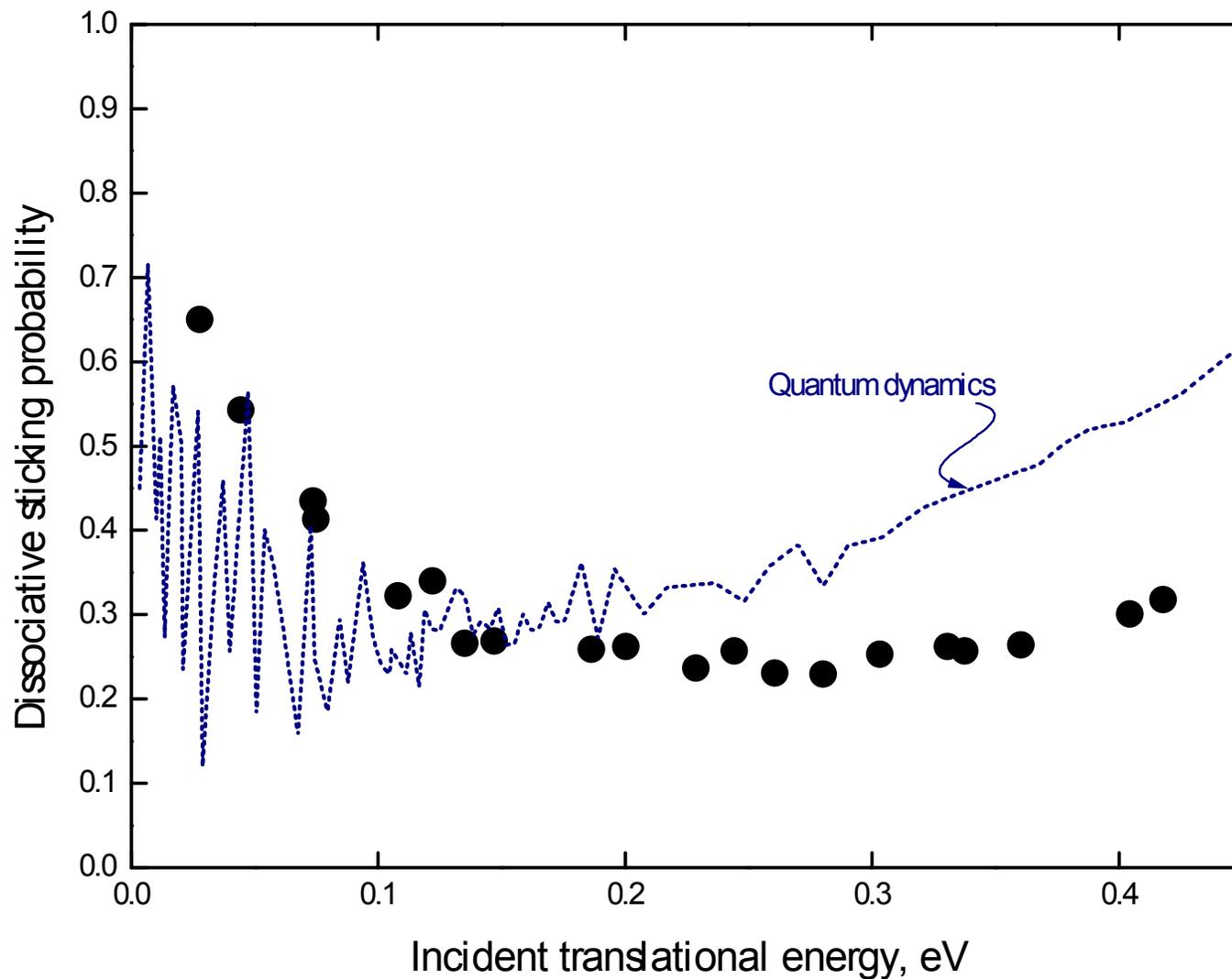
Reactions with Hydrogen and Carbon Monoxide

Contributions of Modeling



[● Rendulic, Anger, Winkler, Surf. Sci. **208** ('89) 404
..... Gross, Wilke, Scheffler, PRB Lett. **75**('95) 2718;
based on PES of Wilke&Scheffler, PRB **53**('96)4926]

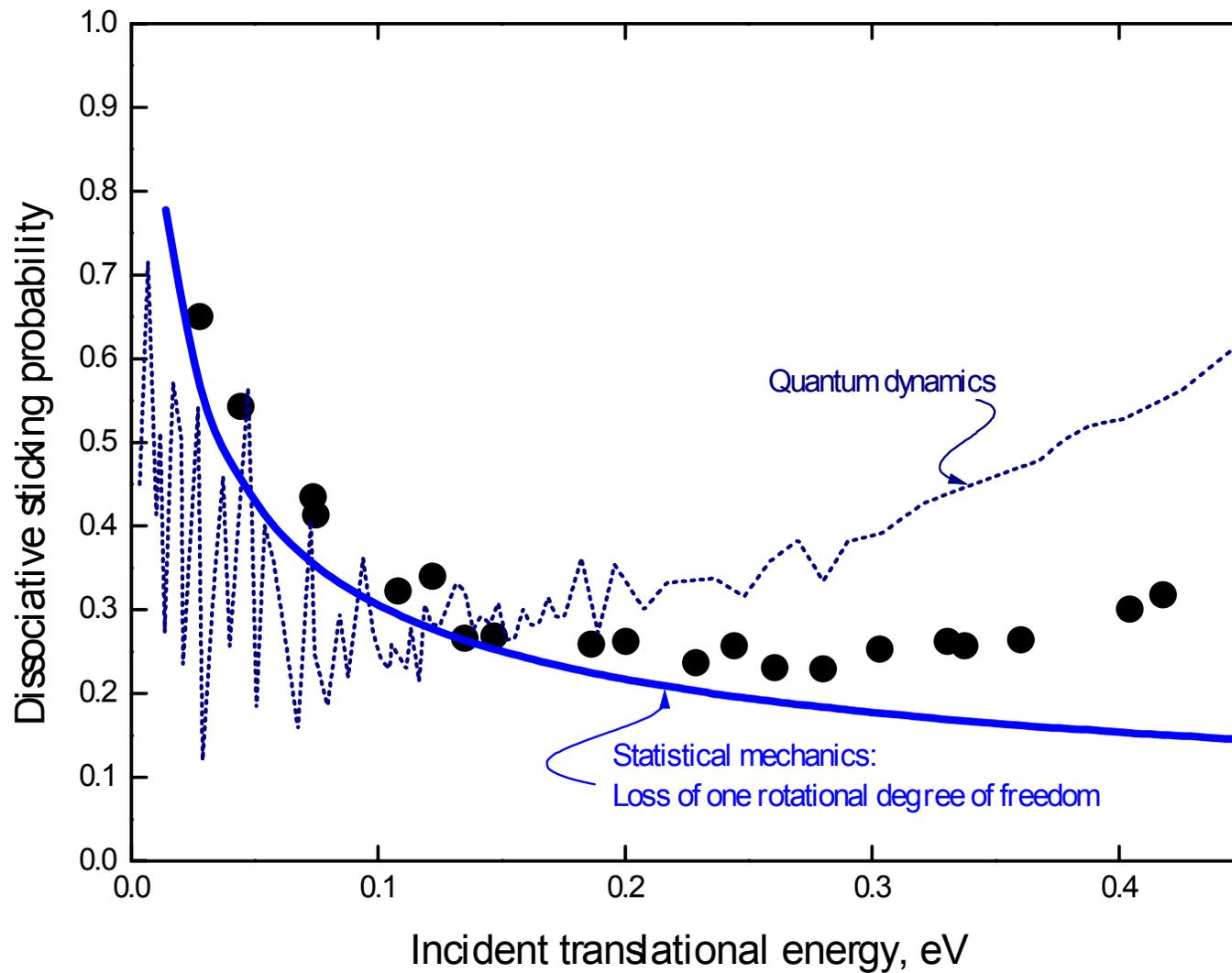
H₂ on Pd(100)



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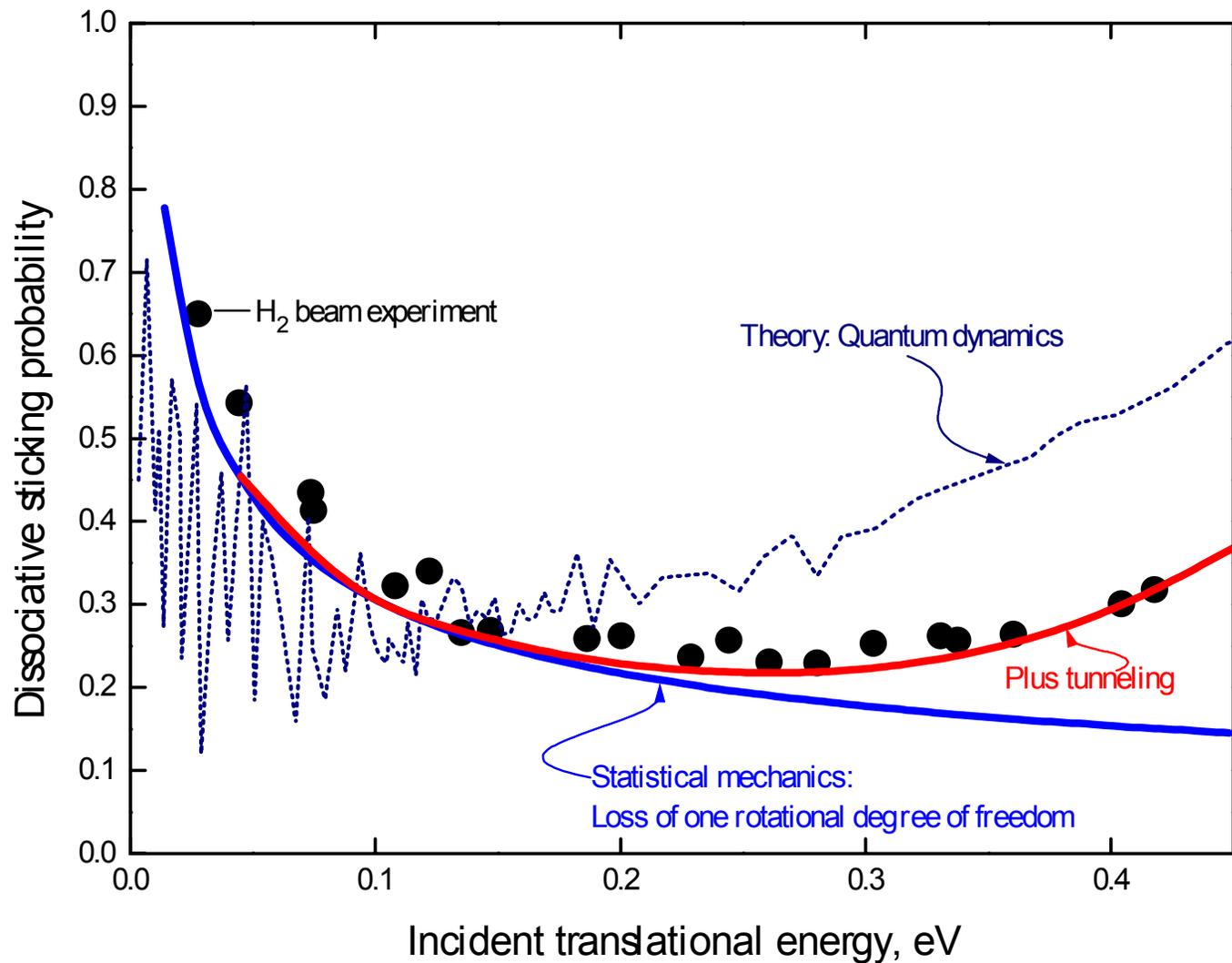
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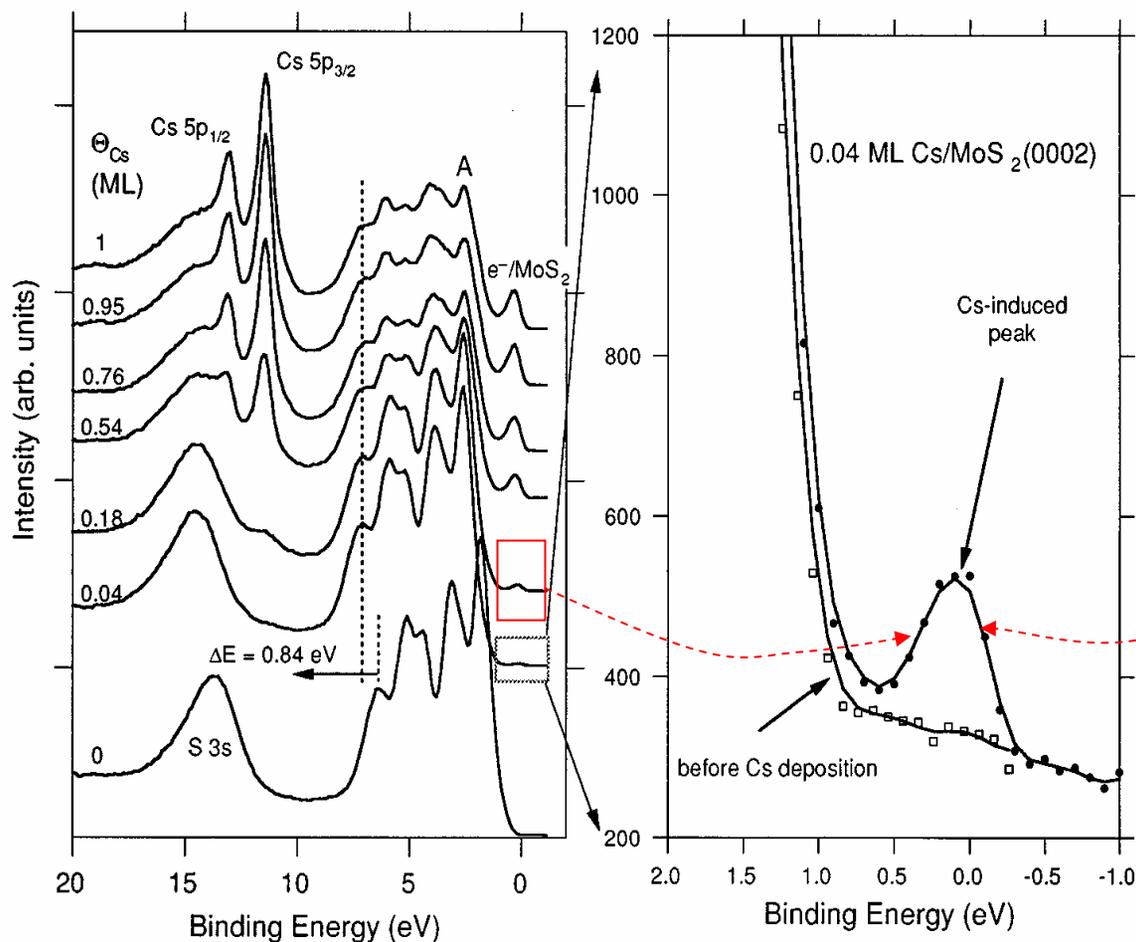
Reactions with Hydrogen and Carbon Monoxide

Contributions of Modeling

Alkali doping of sulfides gives rise to profound changes in their surface activity: K^+ , Cs^+ promote alcohol synthesis from $CO+H_2$ over MoS_2 , alkali intercalate to form electron donor-acceptor (EDA) complexes, Cs^0 chemisorbs and Li^0 reacts with a complete 'supra-valence electron' transfer to MoS_2 conduction band [cf. Park et al. JPC **100** (1996) 10739; JPC **B104** (2000) 3145]

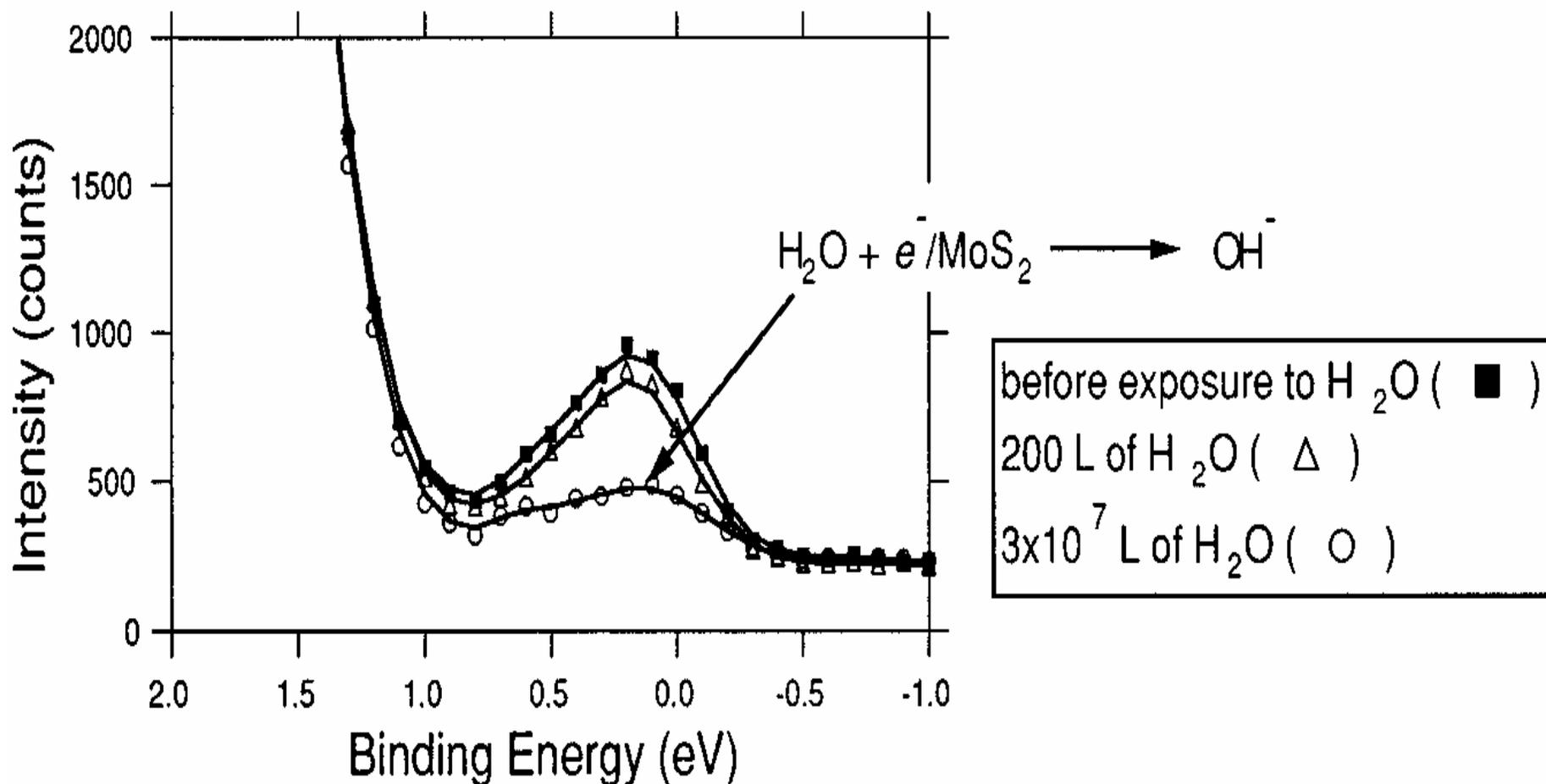
(a) Valence Band of Cs/MoS₂(0002)

(b) Above the VB Maximum

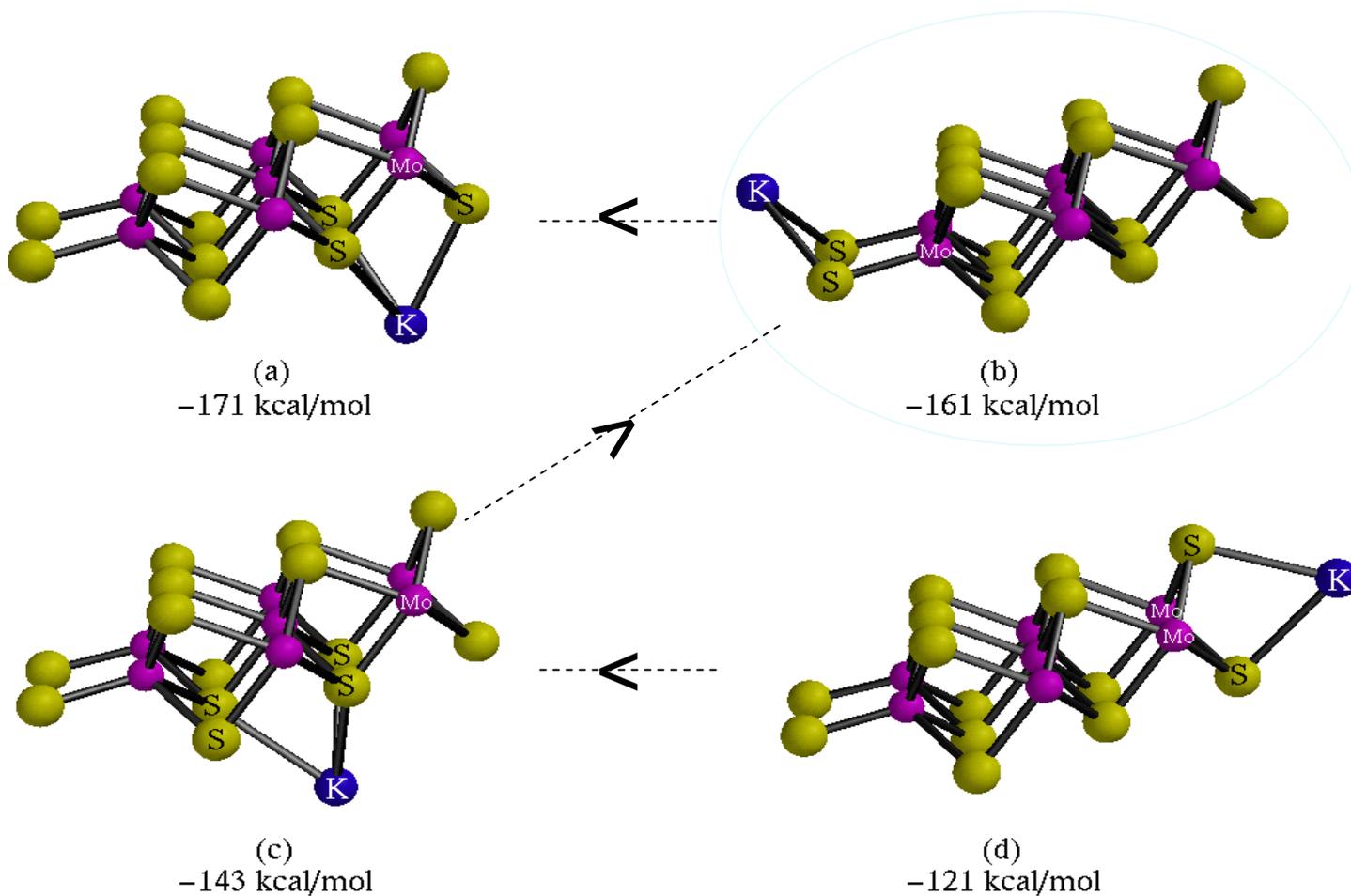


which reacts with electron acceptors [*cf.* Park et al. JCP **111** (1999) 1636, a combined HR-XPS and theoretical study] to form monodispersed $\text{Cs}^+_{(s)}\text{-MoS}_2\text{-OH}^-_{(s)}$ catalytic system

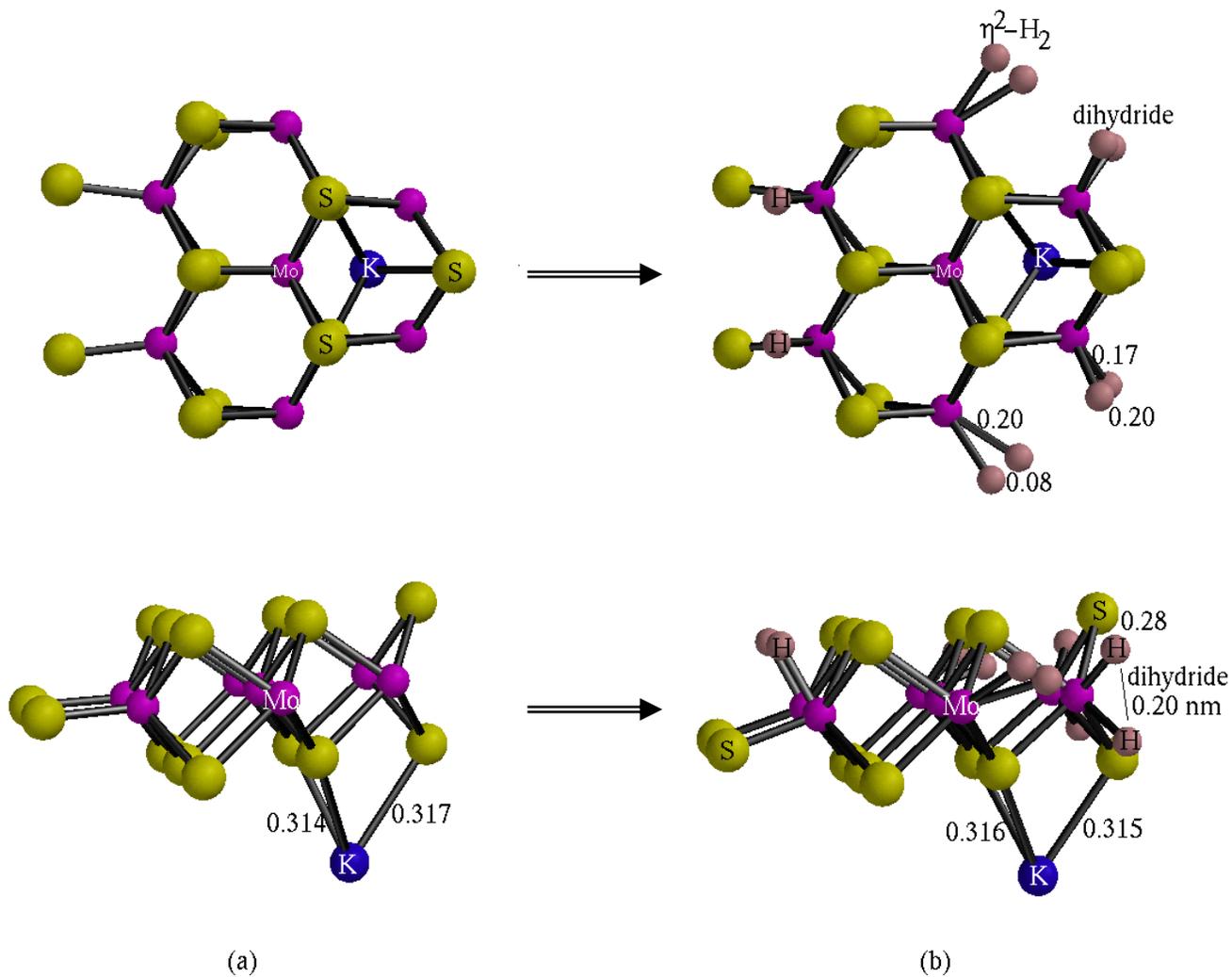
(c) Above Valence Band Maximum



Potassium site preference (\rightarrow) for sites on the Mo_7S_{14} cluster:
(a) trigonal hollowsite-edge, (b) on $(10\bar{1}3)$ edge, (c) on (0001) basal plane, (d) on $(\bar{1}210)$ edge. Energies of $\text{K}^\circ + \text{Mo}_7\text{S}_{14}$ are in kcal/mol K°

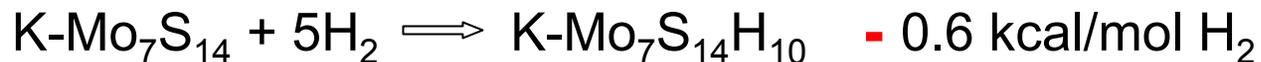


Potassium doping of MoS₂ clusters favors dissociative chemisorption of H₂. Interatomic distances are in nm. Energy of formation (DFT/GGA/DN**) of (b) K-Mo₇S₁₄H₁₀ from (a) K-Mo₇S₁₄ and molecular hydrogen is -3.0 kcal/mol, in contrast to K-free system, +14.0 kcal/mol. **K-Mo(4d²)S₂ is Mo_xTc(4d³)_{1-x}S₂ !!!**



Potassium promotes hydrogen activation on Mo₇S₁₄

K-MoS₂ is Mo_xTc_{1-x}S₂ !!!



Compare with potassium-free reaction:



Potassium promotes hydrogen activation on both MoS₂ and NbS₂

T_xS_{2x} clusters adsorb molecular hydrogen dissociatively into Mo-bonded $\eta^2\text{-H}_2$ [$d(\text{H-H}) < 0.1\text{nm}$, $\nu \sim 3000\text{ cm}^{-1}$], also discovered in Si, *cf.* M.Stavola et al., PR Lett. **88**, 105507, 245503 (2002); PRB **65**, 245208; PRB **66**, 075216 (2002), and dihydride [$d(\text{H-H}) > 0.16\text{nm}$], *cf.* G.J. Kubas, J. Organomet. Chem. **635** (2001) 37. Mo-H vib. frequencies in dihydride are 1800 – 2000 cm⁻¹. On MoS₂ monomer, dihydride is formed without a barrier, on NbS₂ with a barrier ~ 15 kcal/mol, on K-doped NbS₂ with a small barrier of < 5.5 kcal/mol:

K-NbS₂ is MoS₂!!!



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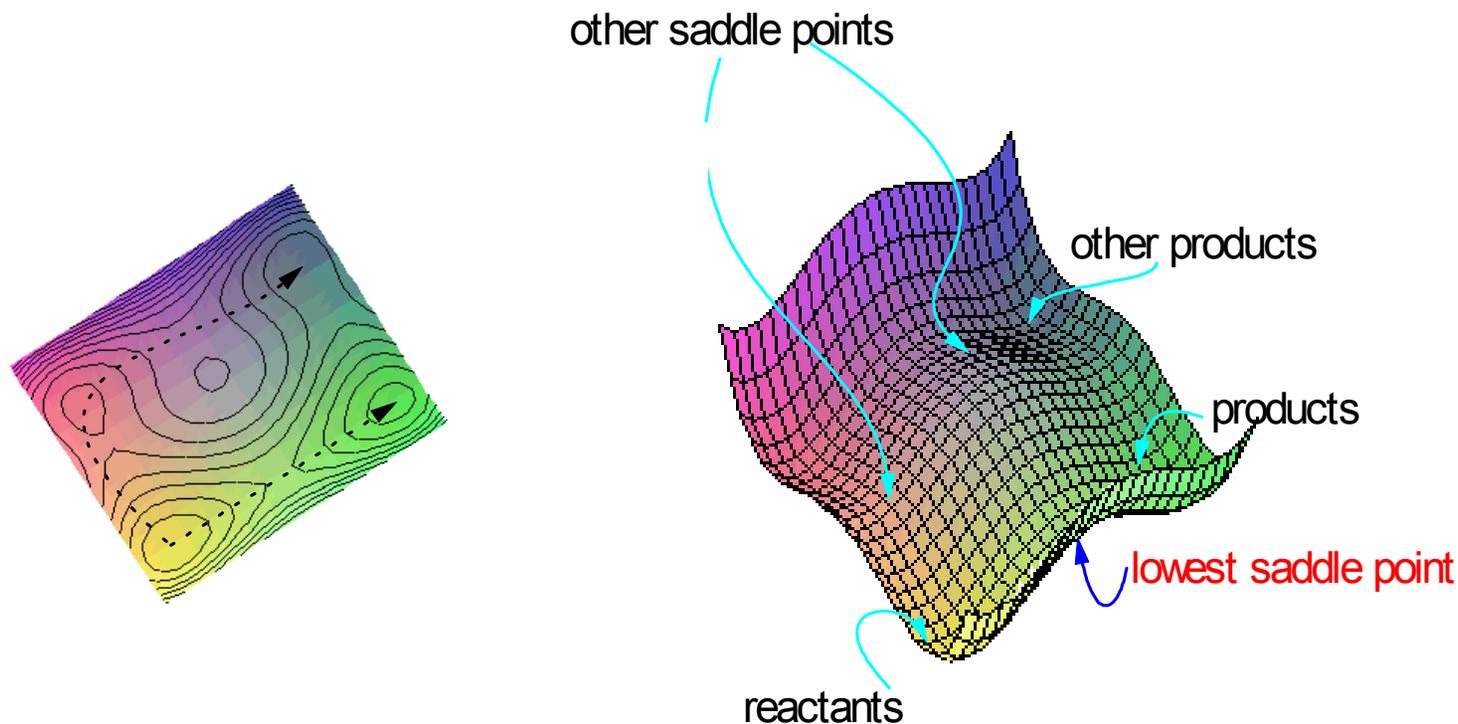
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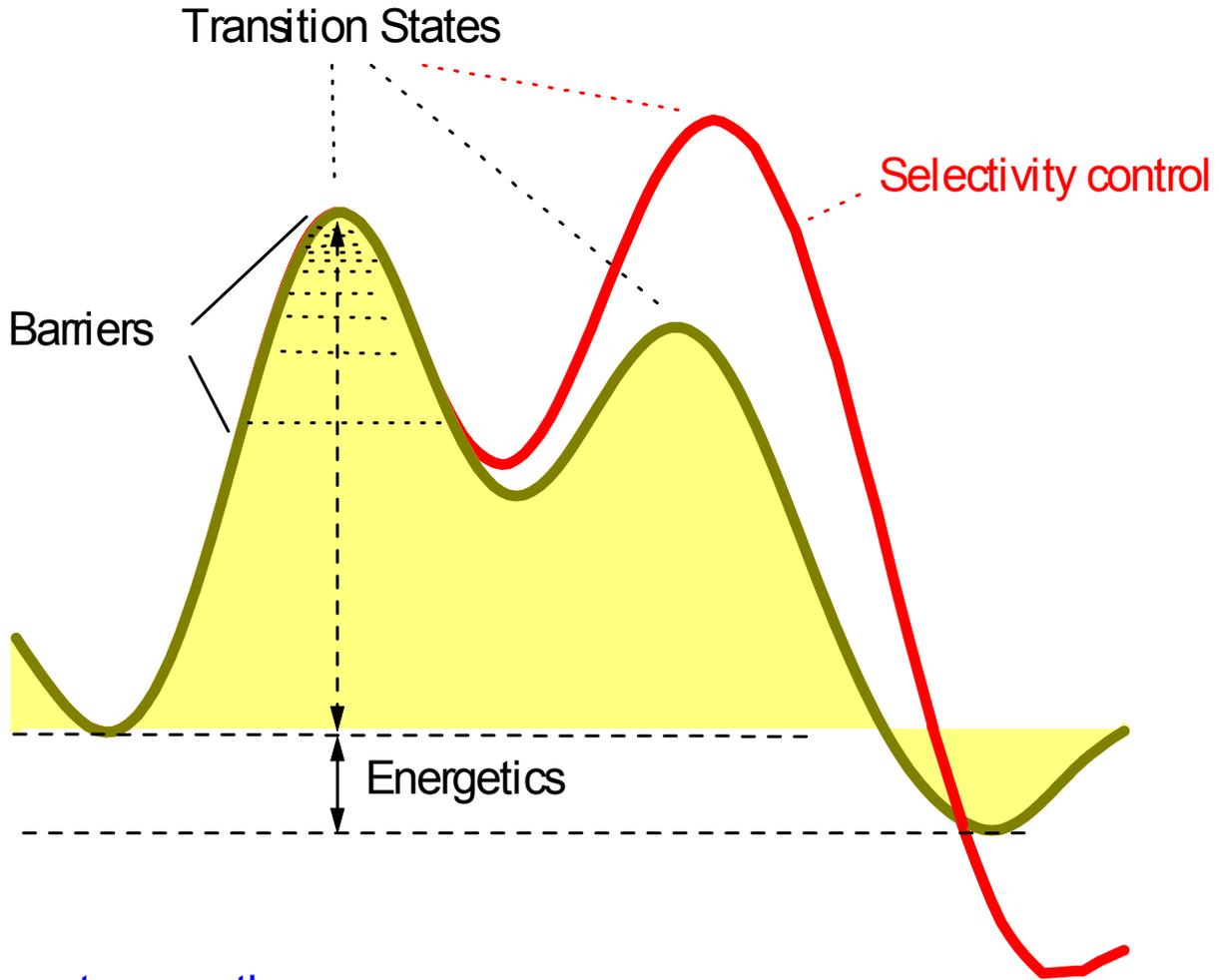
Contributions of Modeling

The search for transition state (TS) involves the location of saddle points in a reaction landscape with many stationary points

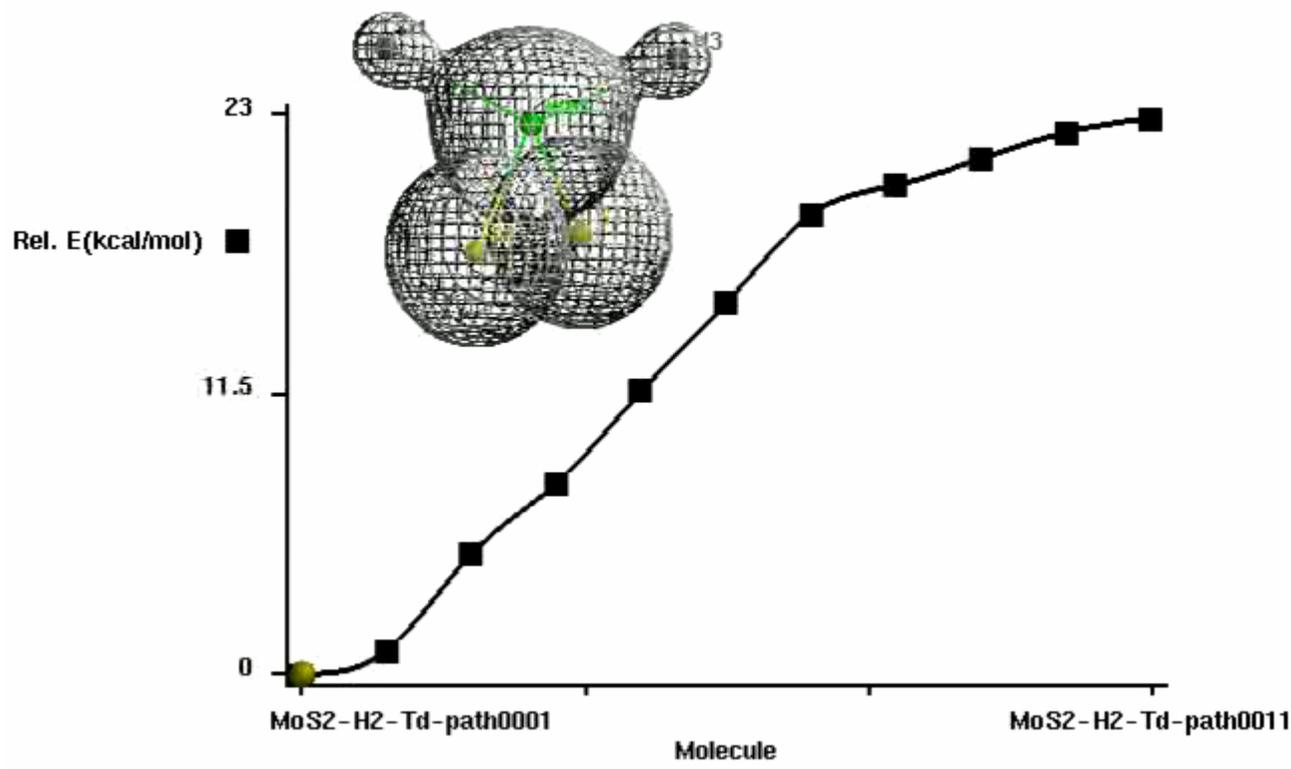


A qualifying TS has zero energy derivatives and a negative curvature along the reaction coordinate. There is a lowest TS.

Catalytic issues

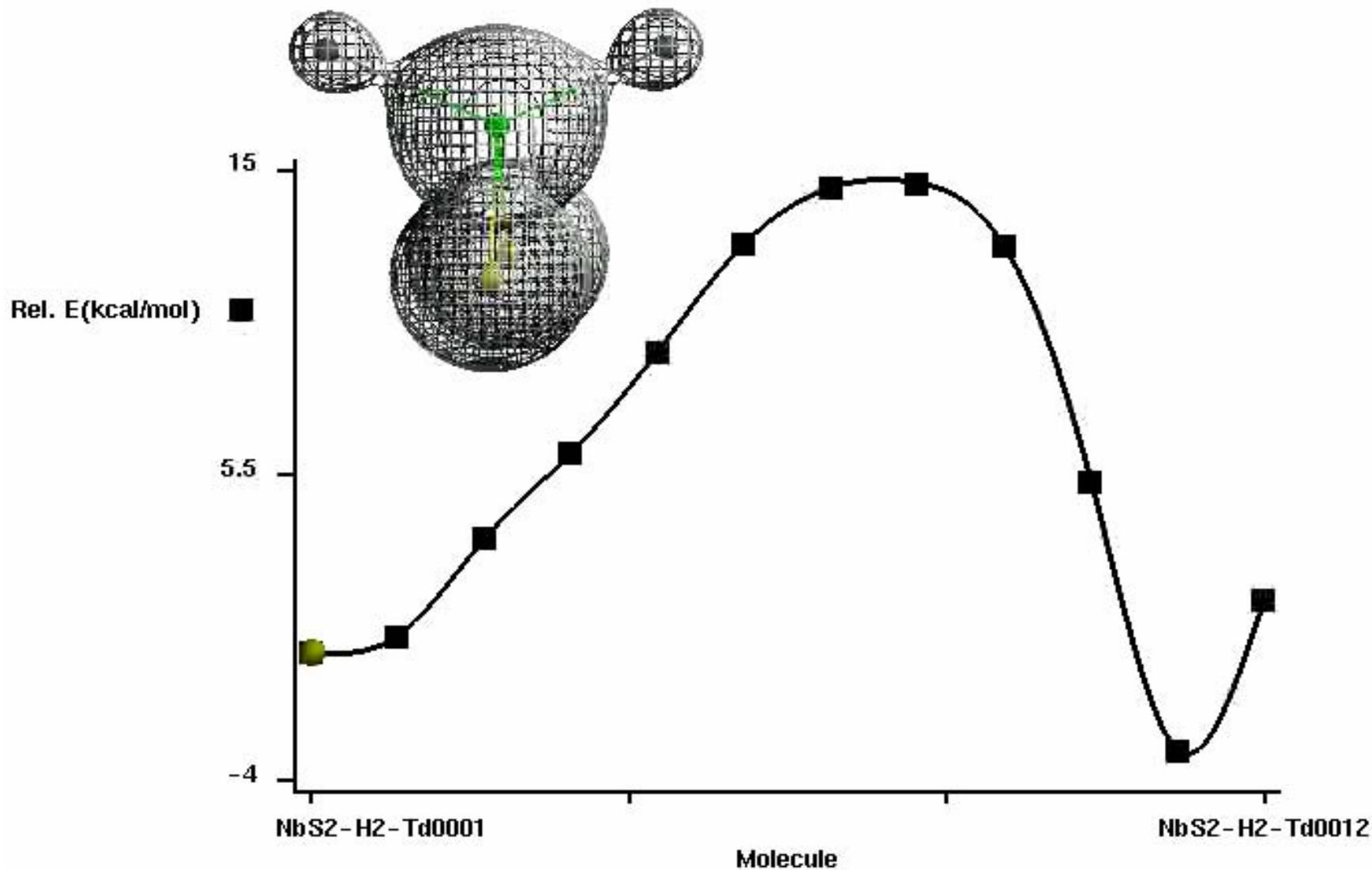


Molybdenum Disulfide Dissociates Hydrogen Molecule
into a
Dihydride Without Activation Barrier
DFT/GGA/DN** Coordinate Driving

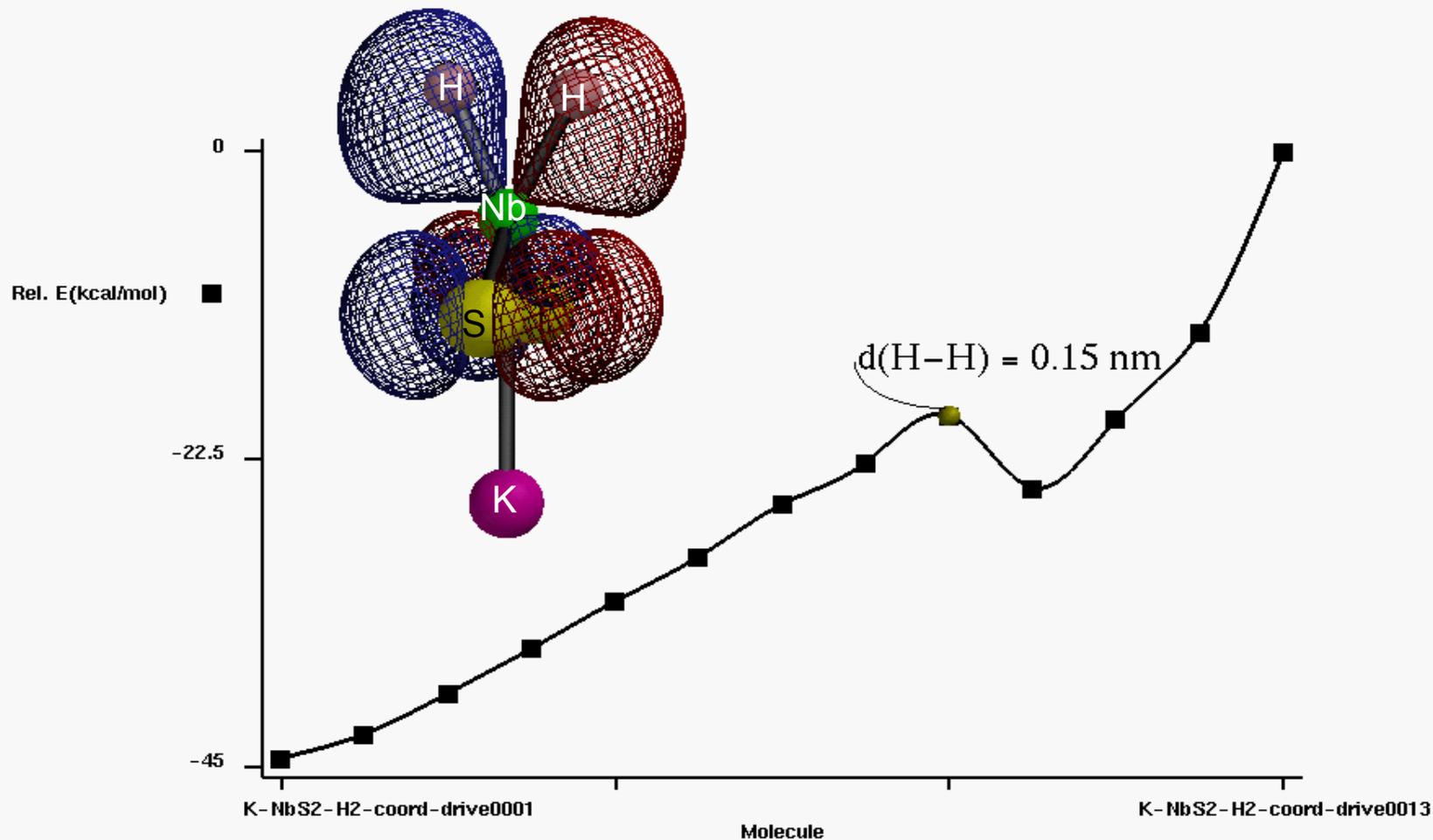


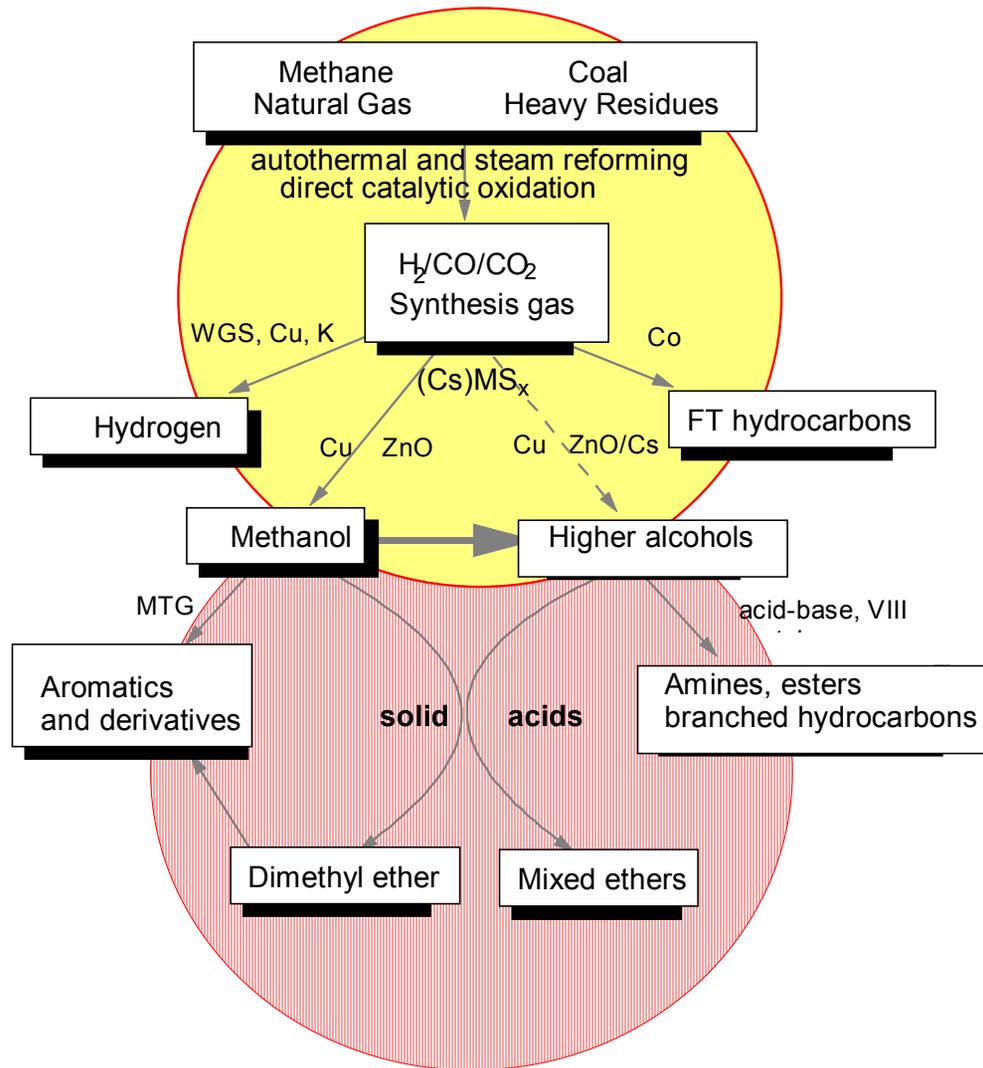
Niobium Disulfide Dissociates Molecular Hydrogen into a Dihydride With a Barrier of < 15 kcal/mol

DFT/GGA/DN** Coordinate Driving



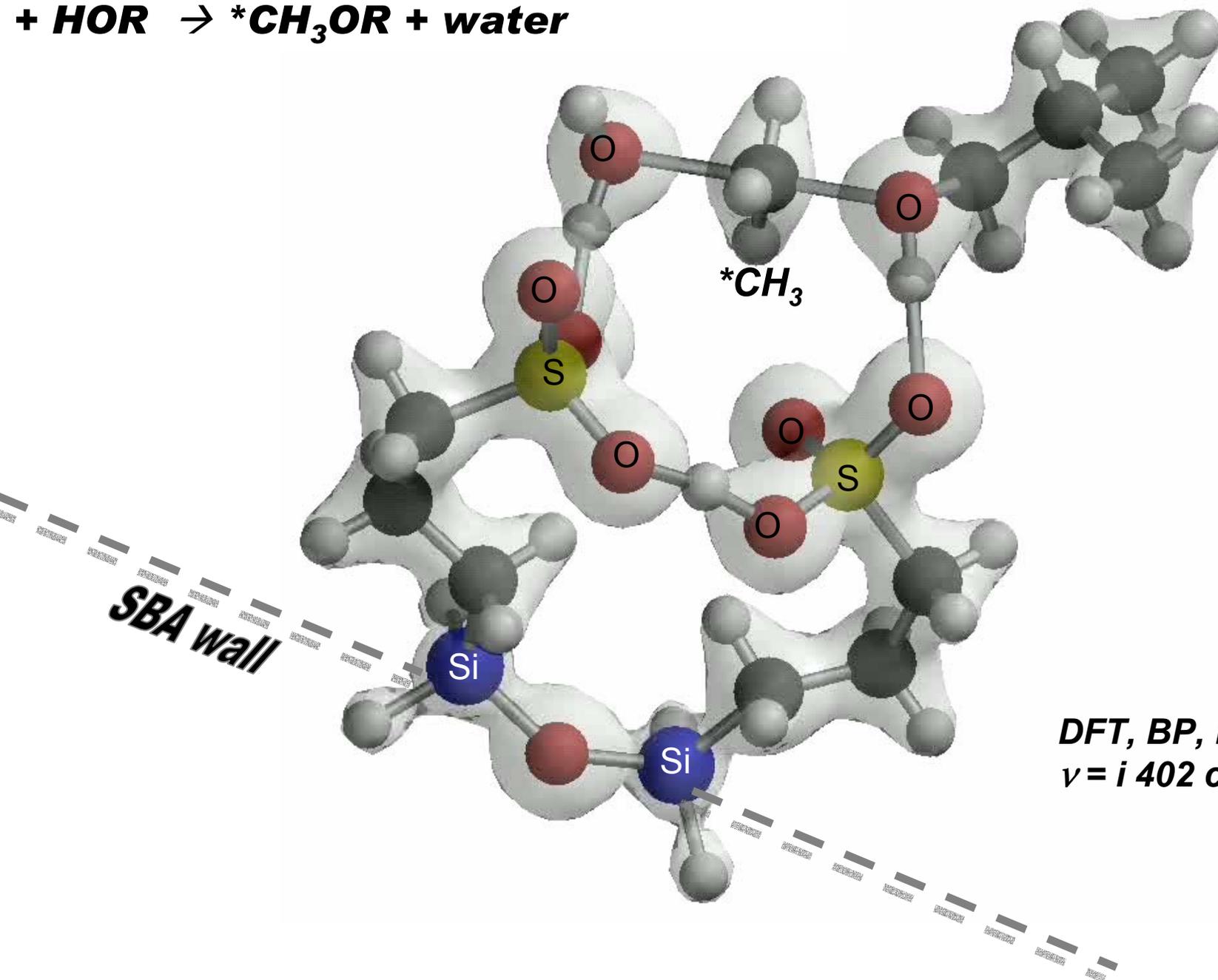
K-doped NbS₂ Dissociates Molecular Hydrogen into a Dihydride
With a Barrier of < 5.5 kcal/mol. Antisymmetric HOMO is Shown at the
Barrier. DFT/GGA/DN** Coordinate Driving





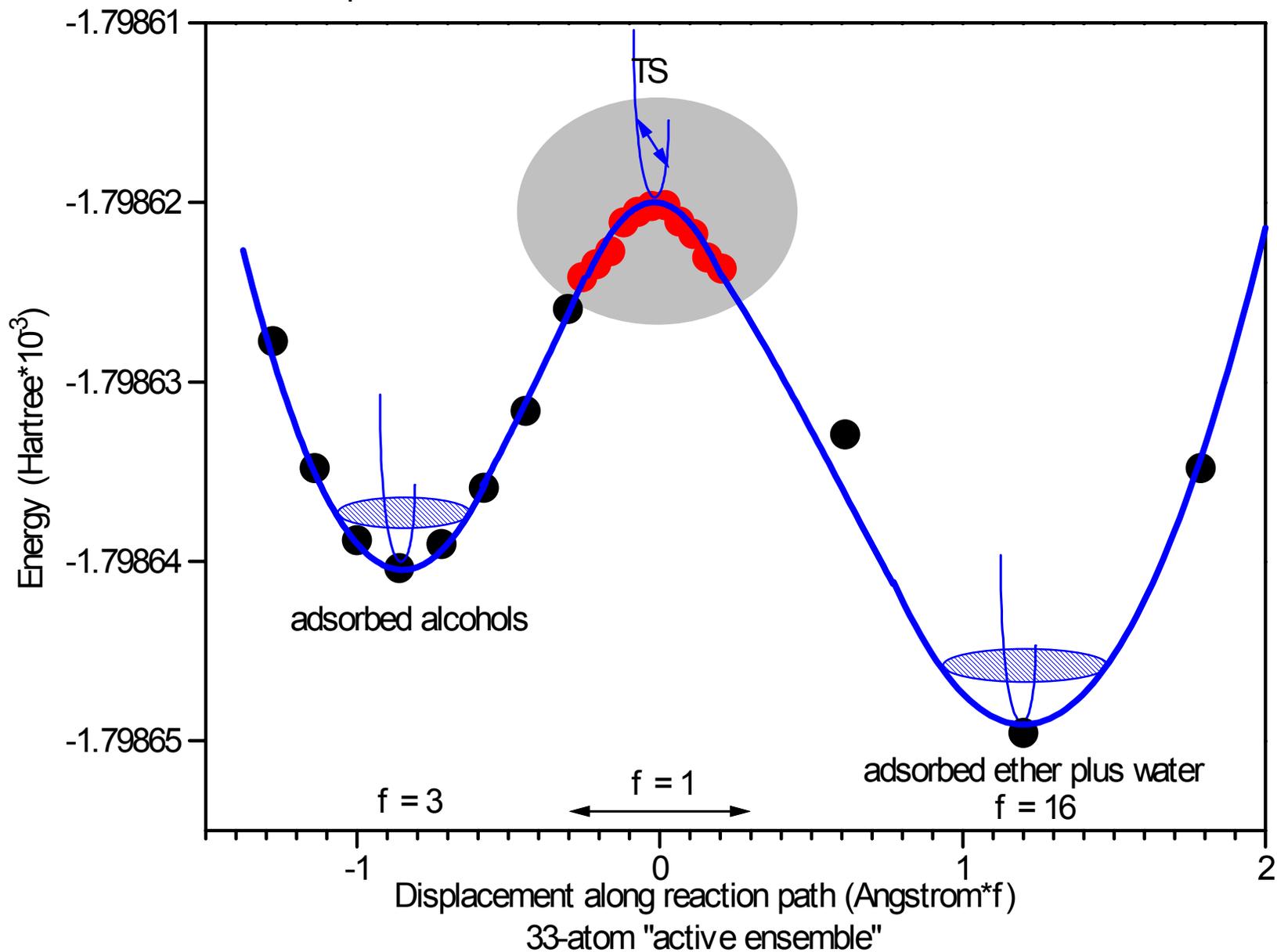
An overall scheme for conversion of sources of carbon to alcohols, ethers, olefins, aromatics and amines. All these processes are catalyzed.

**TS for inverting S_N2 pathway HO^*CH_3
+ HOR \rightarrow *CH_3OR + water**



Reaction path for the reaction $\text{MeOH} + i\text{-BuOH} \rightarrow \text{MIBE} + \text{water}$

Stationary points optimized by DFT/BP/DN** and neighborhood mapped at discrete points of intrinsic reaction coordinate



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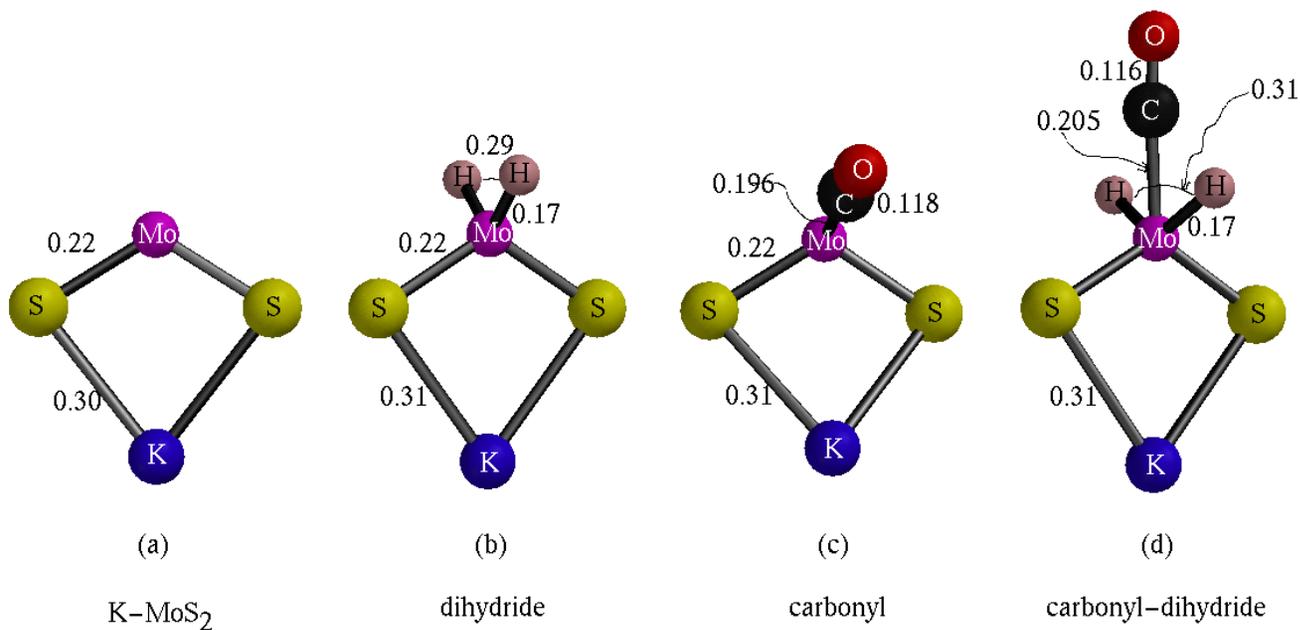
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Contributions of Modeling

CO activation for oxygenate synthesis:

- CO makes readily (inert) carbonyls and hydrido-carbonyls, but does not insert into the Mo-H bond



E_f (kcal/mol)

- 45.7

-64.4

-77.8

\angle (S-Mo-S): 116°

114°

115°

116°

\angle (H-Mo-H):

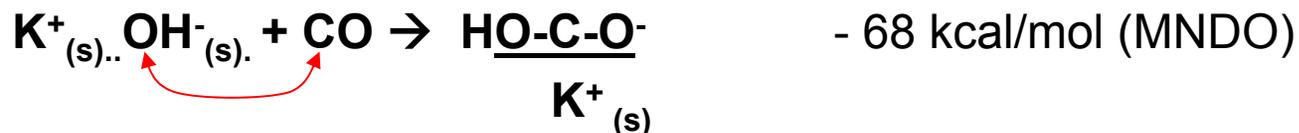
117°

128°

CO activation for oxygenate synthesis:

- CO inserts into the $\text{HO}^-_{(s)}$ counterion of the alkali

– Associative mechanism involves a facile nucleophilic attack of CO coordinated to the alkali cation by the $\text{HO}^-_{(s)}$ counterion,



followed by 1,2 antarafacial sigmatropic transfer of hydrogen to form surface formate



[K. Klier et al., in “Methane Conversion”, Elsevier (ed. D.M. Bibby et al.)
1988, 109-125]

Higher level calculations are desirable, incl. those of the TS energies

Mechanism of Methanol Synthesis

- **Activate H_2 on the defect sites of the sulfide**
- **Activate CO in the coordination sphere of an alkali promoter (Cs > Rb > K > Na ~ Li)**
- **Hydrogenate formate to methoxide**
- **Hydrolyze surface methoxide to methanol**

Contributions of modeling

- Understanding and selection of viable mechanisms – H₂ activation via homopolar antisymmetric ‘driving down’ of the $\sigma^*(\text{H-H})$ orbital, CO activation by base attack
- Predictions of :

Energy barriers as a function of catalyst composition and structure – finding the lowest pass

Vibrational frequencies of adsorbed reactants and incentives for search of new species (dihydrides) by spectroscopy

Significance of entropy penalties in hydrogen activation

Effects of alkali on activation of reaction components

Kinetics and thermodynamics



