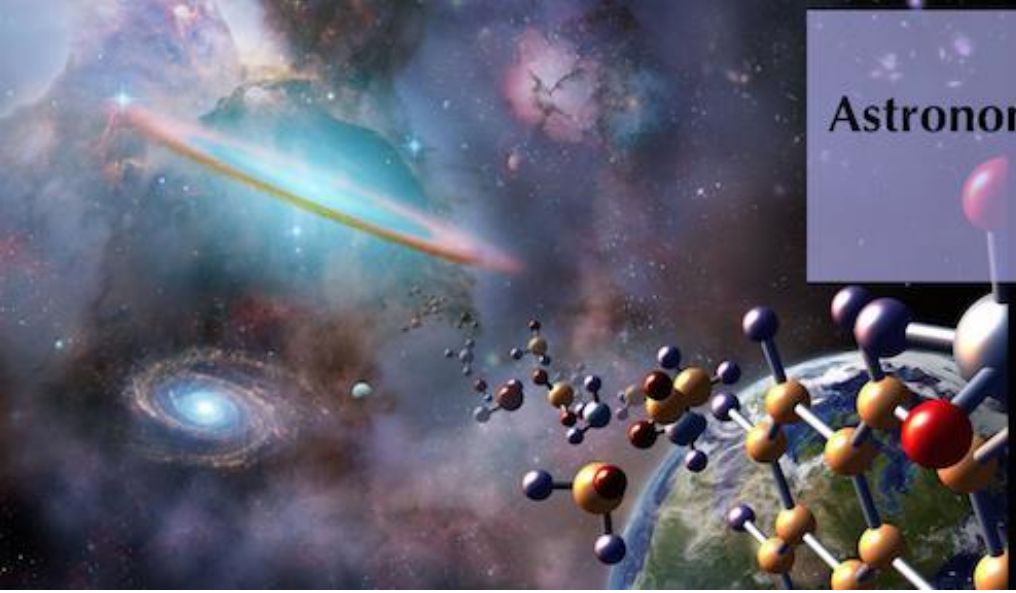


Astronomical Complex Organic Molecules in different environments

1st Italian Workshop on Astrochemistry
March 10-11 2016
Palazzo Strozzi, Florence, Italy

The rôle of surfaces in prebiotic chemistry

Piero Ugliengo

University of Torino Dip. Chimica

Via P. Giuria, 7 - Torino

Università degli Studi di Torino
nis CENTRE FOR NANOSTRUCTURED INTERFACES AND SURFACES

A collaborative work

Dip. Chimica - NIS Centre – Torino University

Dep. Quimica UAB Barcelona

J. Navarro

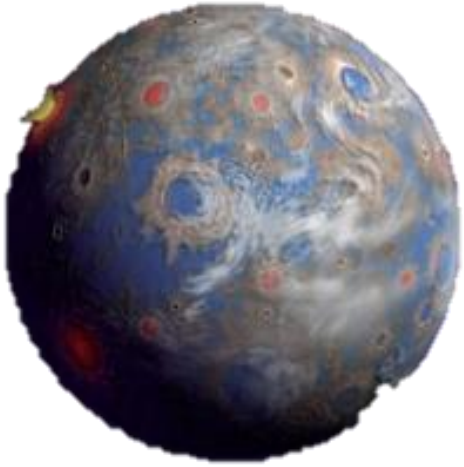
M. Sodupe

A. Rimola

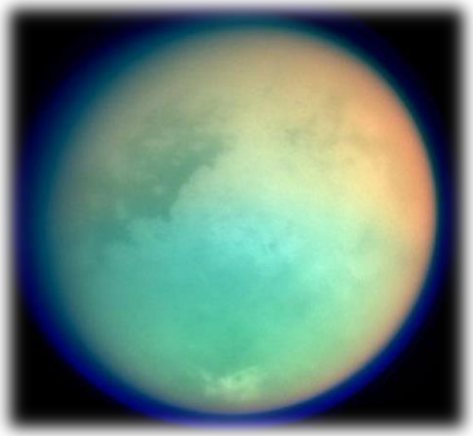
Chemical processes of prebiotic relevance

Chemistry in ISM (gas, dust)

Chemistry in Comets



Chemical evolution on primordial Earth



Chemistry on primordial atmosphers (Titan)

Chemical scenarios

Omogeneous chemistry

Gas-phase reactions

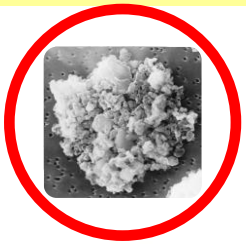
$H_2 + h\nu \rightarrow H_2^+$

$H_2^+ + H_2 \rightarrow H_3^+ + H$

Models of primordial atmospheres

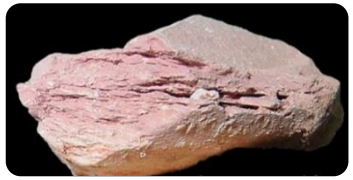
Titan atmosphere

Heterogeneous chemistry



Reactions at the grain surfaces (ice, olivine, silica, PAH, IDP)

Reactions at the mineral surfaces (feldspar, clays, FeS_2, etc.)



Can computer simulation contribute?

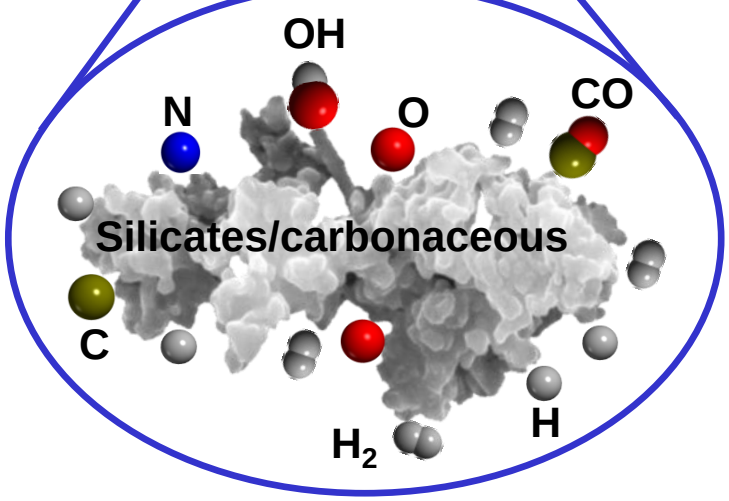
Grains in molecular clouds

Celestial Valentine
W5 star-forming region
Portrait from NASA's
Spitzer Space Telescope

Diffuse Clouds

Dust Particles + Gaseous Atoms and Molecules

$n_{at} \approx 10^2$ cm^{-3}
T ≈ 80 – 100 K

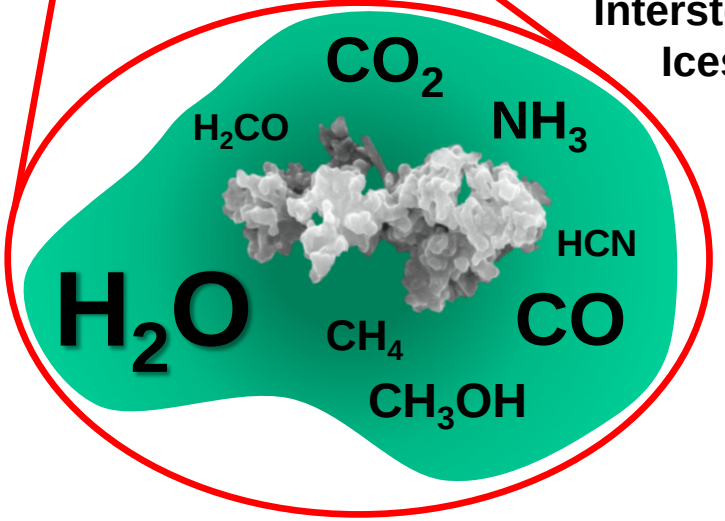


CORE

Dense Clouds

Dust Particles + Interstellar Ices

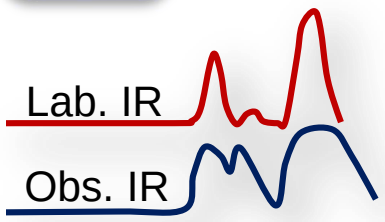
$n_{at} \approx 10^4$ cm^{-3}
T ≈ 10 – 30 K



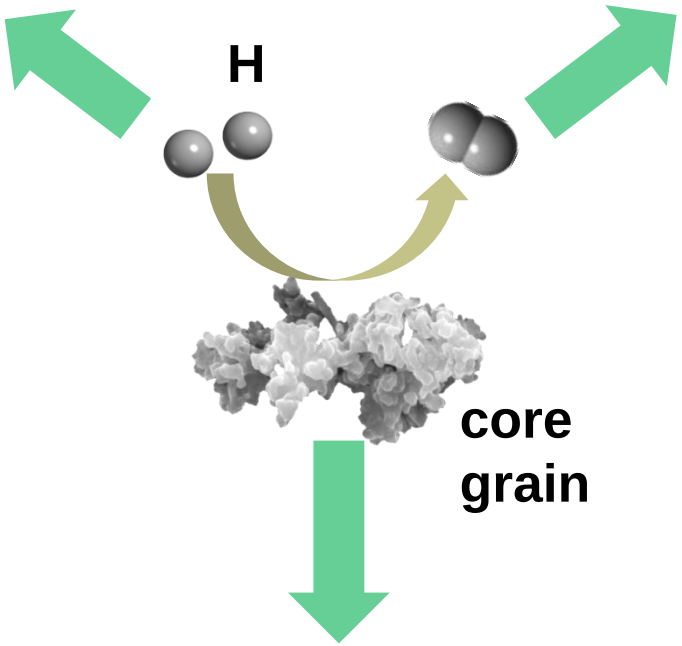
CORE+MANTLE

Current approaches to H_2 on interstellar dust

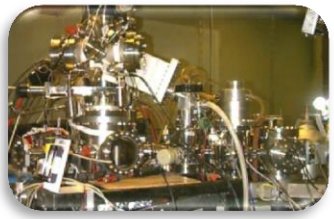
Spectroscopic Measurements

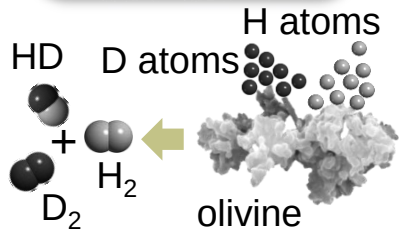


Molster, F. et al., *Space Sci. Rev.* **2005**, 119, 3-28



Chemical Reactivity





Perets, H. B. et al., *Astrophys. J. Lett.* **2007,** *661,* L163-L166

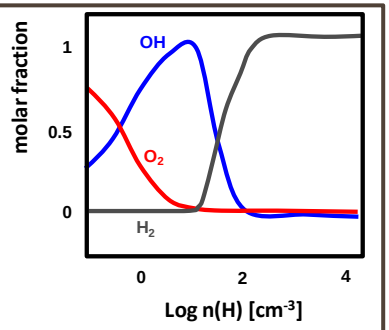
Numerical Astrochemical Models

Rate Equation Models

$H + H \rightarrow H_2$

$O + O \rightarrow O_2$

$H + O \rightarrow OH$



Caselli, P. et al., *Astrophys. J.* **1998,** 495, 309-316

Relevance of chemical modeling

Spectroscopic Measurements

Chemical Reactivity Experiments

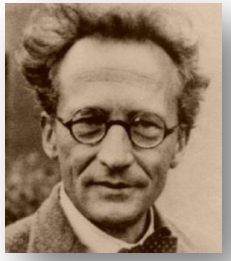
Numerical Astrochemical Models

Average Data

Lack of Atomic-Scale Information

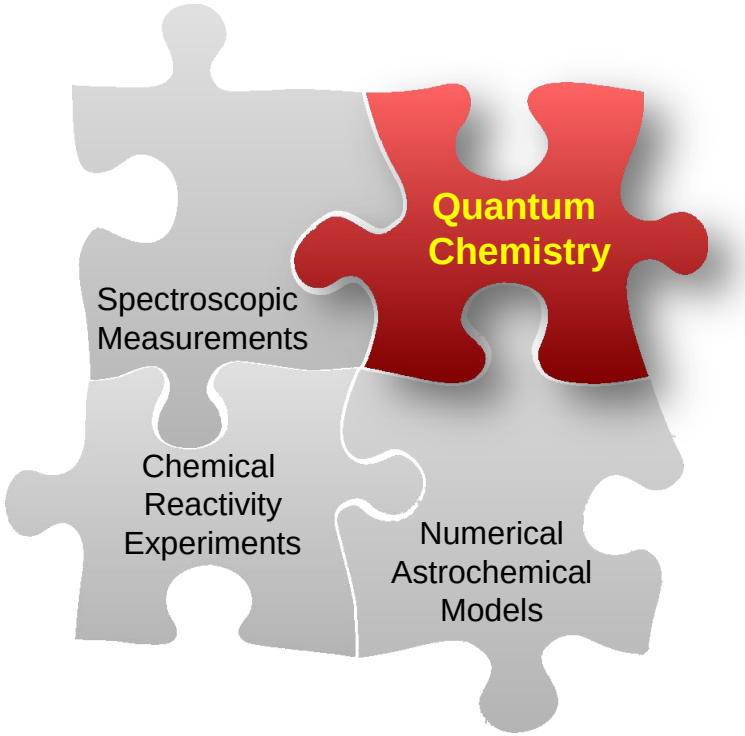
Molecular Simulations Based on QUANTUM MECHANICAL METHODS

The Schrödinger Equation



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

"If we can solve this equation we know everything about the systems"



The ab-initio simulation: attacking the SE

Schrödinger equation

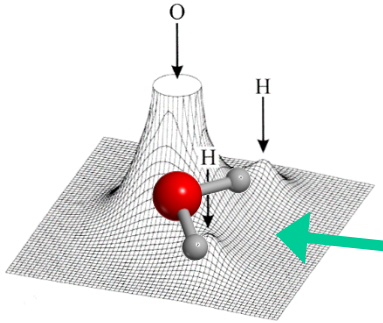
$$\hat{H}\Psi_i\left(\vec{x}_1,\vec{x}_2,\ldots,\vec{x}_N,\vec{R}_1,\vec{R}_2,\ldots,\vec{R}_M\right)=E_i\Psi_i\left(\vec{x}_1,\vec{x}_2,\ldots,\vec{x}_N,\vec{R}_1,\vec{R}_2,\ldots,\vec{R}_M\right)$$

$$\hat{H} = T_e + T_n + V_{en} + V_{ee} + V_{nn}$$

Hartree-Fock (thousands atoms) → Møller-Plesset: (MP2 ~ 60-200 atoms) → CI-SD, CCSD, CCSD(T) (CCSD(T) ~ 10-90 atoms)

Density Functional Methods

HK1964



H_2O: 10 e^- and 3 nuclei

$$\Psi_{H_2O}(\mathbf{r}_1,\ldots,\mathbf{r}_{10};\mathbf{R}_1,\ldots,\mathbf{R}_3)$$

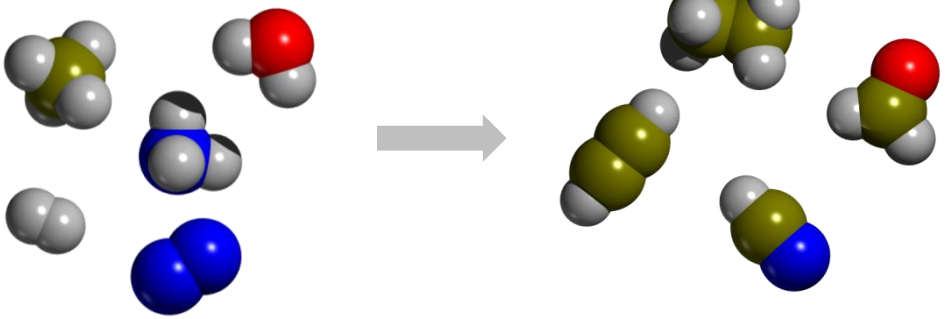
$$\rho(x,y,z) \Leftrightarrow E = F\,[\rho\,(x,y,z)]$$

$\rho\,(x,y,z)$ is a function of **three spatial variables** irrespective of the system complexity and contains all relevant ingredients of a given physical system. F is unfortunately unknown.

$$F\,[\rho] = \quad \textbf{B-LYP} \quad \textbf{B3-LYP} \quad \textbf{PW91} \quad \textbf{PBE} \quad \ldots$$

From molecules to crystals and surfaces

Gas-phase processes

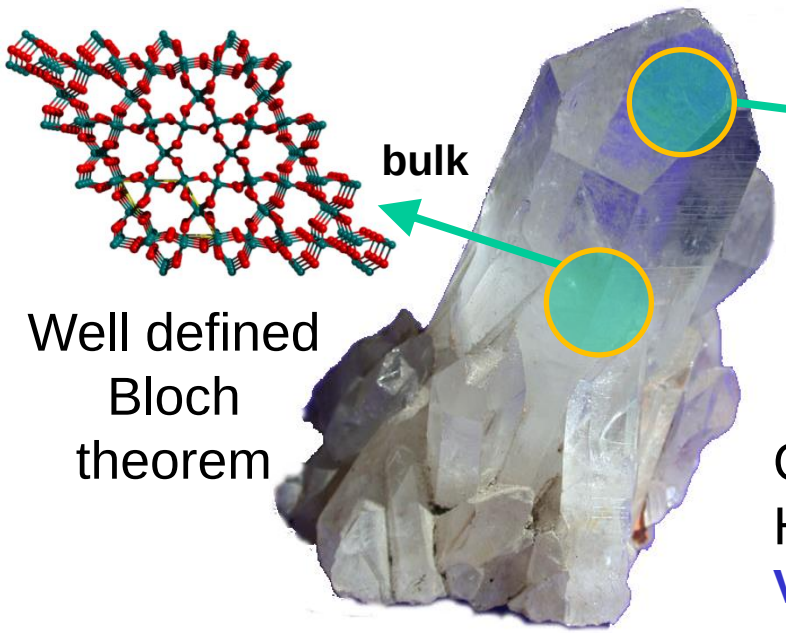


DFT
MP2
CCSDT(T)
Locate TS

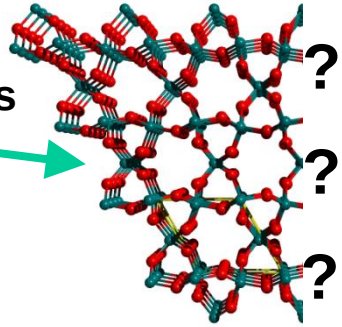
accuracy

Gaussian09, ORCA, Gamess…

Crystals and surfaces



Well defined Bloch theorem



? Bonds cuts. How?

? How to terminate?

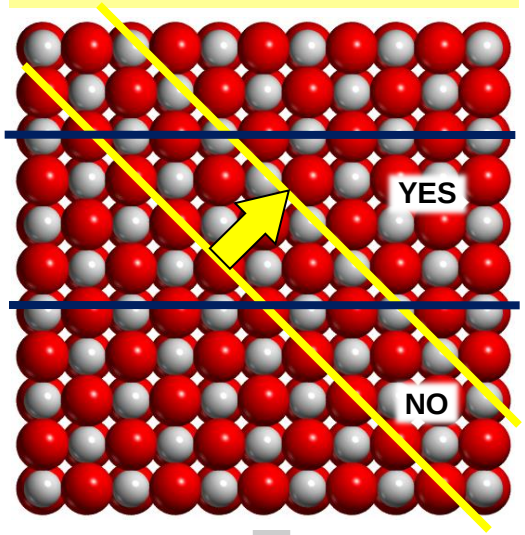
? Reconstruction?

Only **DFT** (B3LYP with CRYSTAL09)
Harder to locate TS

VASP, CPMD, QMespresso, CRYSTAL09, CP2K

Termination at surfaces: ionic, covalent, molecular crystals

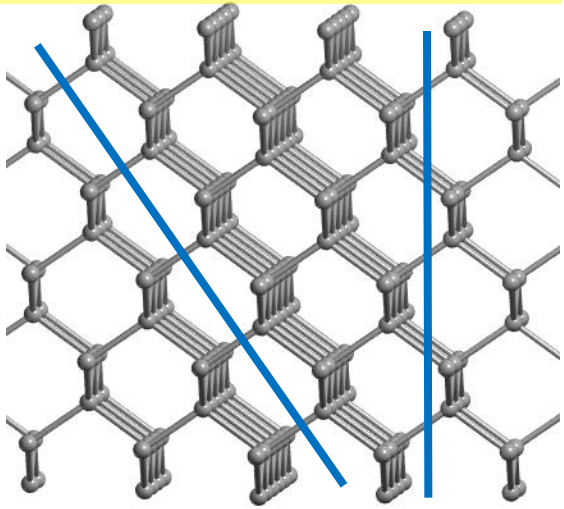
IONIC



Surfaces exhibiting net dipole across the surface are **unstable** (yellow lines)

Cations at the surface tend to move inwards. The reverse for anions. (surface relaxation)

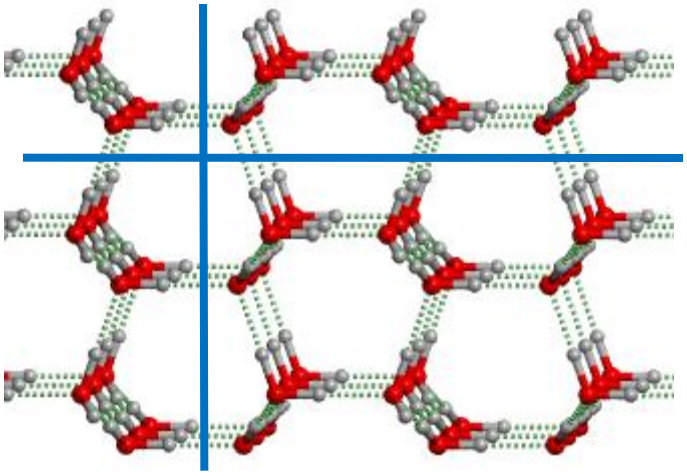
COVALENT



Cutting bonds leave unsatisfied dangling bonds which are **very reactive**

Dangling bonds tend to self-heal by surface reconstruction

MOLECULAR



Only inter-molecular bonds are cut. **No dangling bonds** left.

Large molecular displacements may stabilize polar surfaces

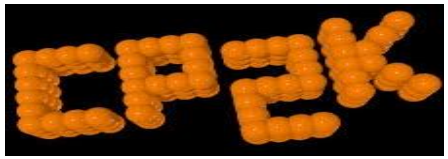
Quantum mechanical codes for periodic systems

Treatment of 0D, 1D,
2D and 3D structures

HF, LDA, GGA, HYBRID

Gaussian Basis Set

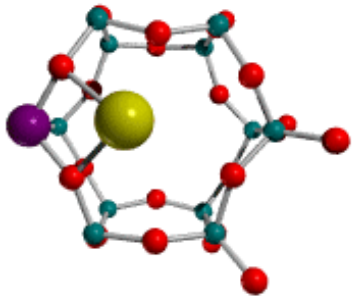
www.crystal.unito.it



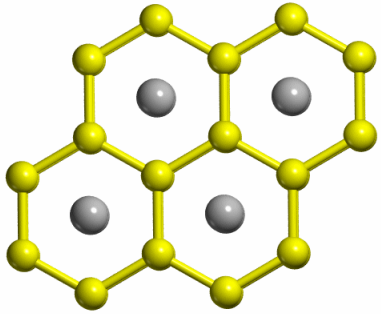
Treatment of 3D structures
Gaussian and
Plane Waves
approaches

HF, LDA, GGA,
HYBRID, MP2,
RPA…

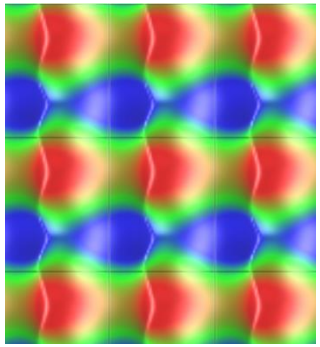
www.cp2k.org



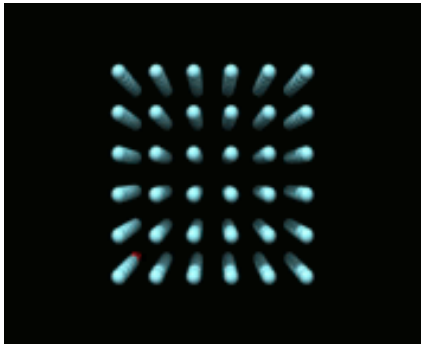
Geometry
Optimizations



Frequency
Calculations



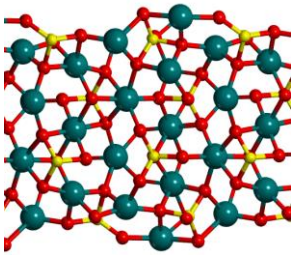
Electrostatic
Potential Maps



Molecular
Dynamics

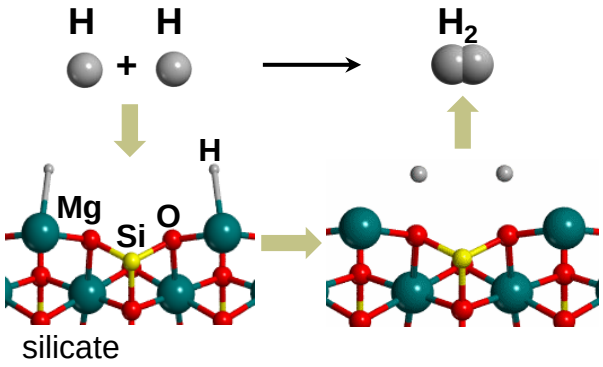
Questions to be addressed by QM methods

Physicochemical properties of the silicates

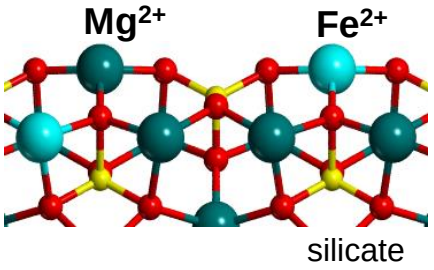


- Structural
- Vibrational
- Electronic
- Dielectric

Which are the actual mechanistic steps?



What is the effect of metal ions?

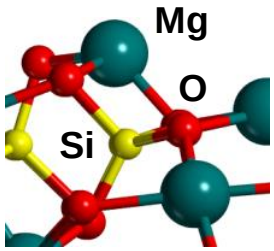


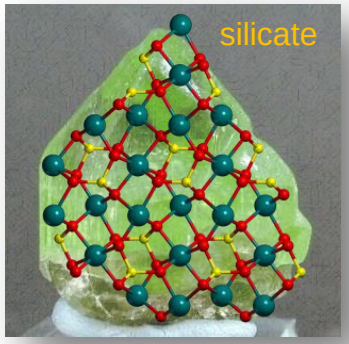
Mg^{2+}: [Ne]

Fe^{2+}: [Ar] $3d^6$

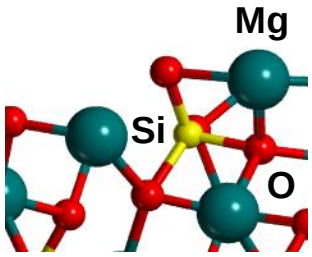
How important is the role of surface morphology?

(110) surface



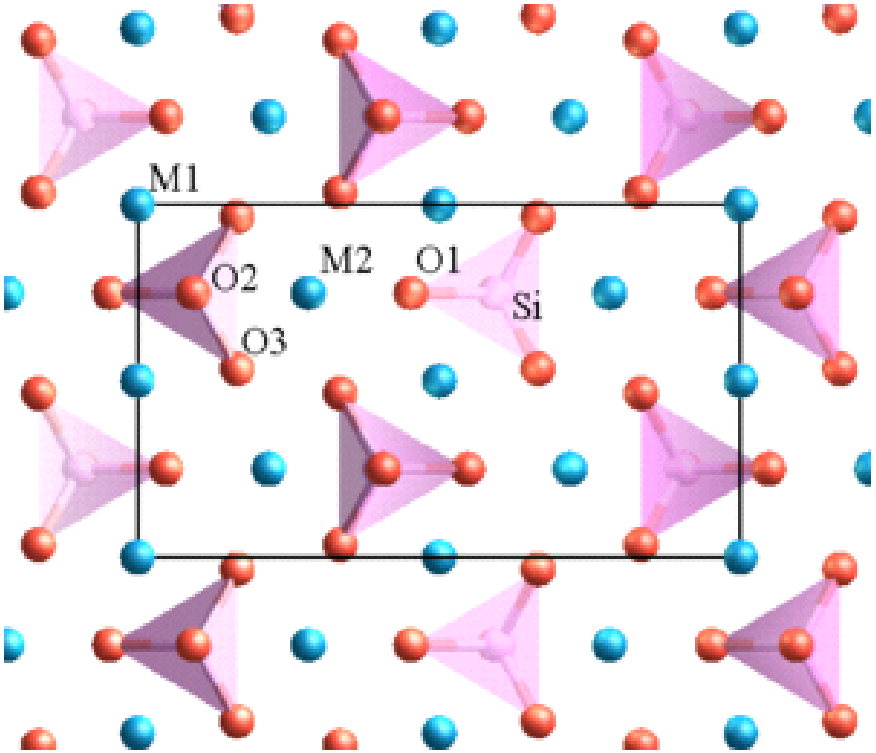


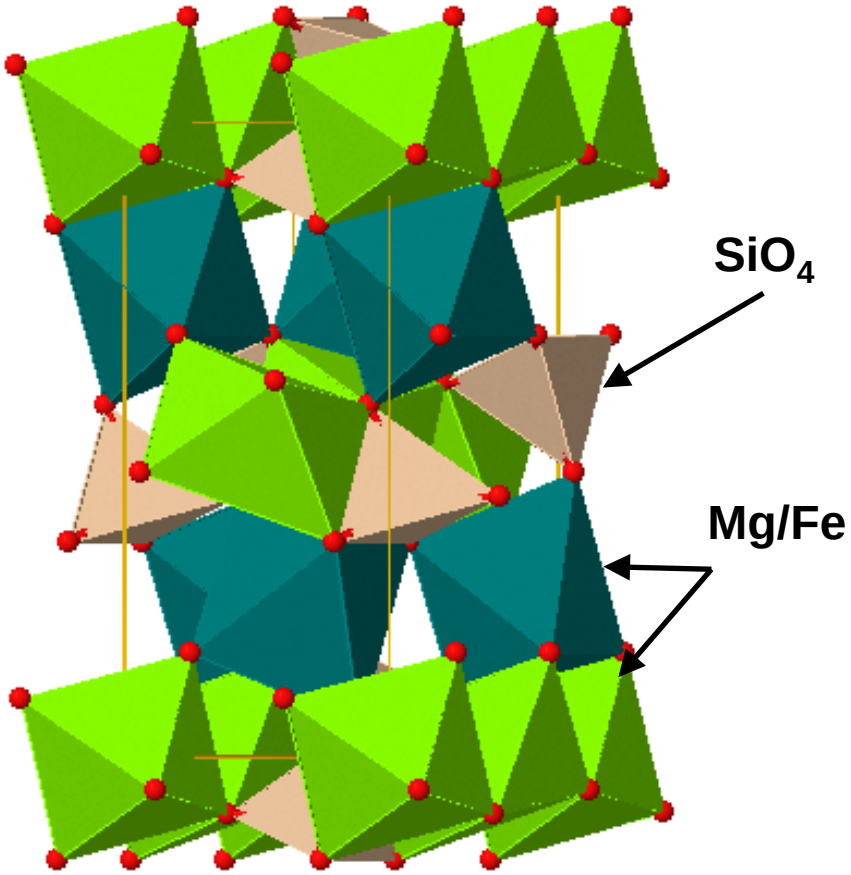
(001) surface



Periodic approach to core grain simulation

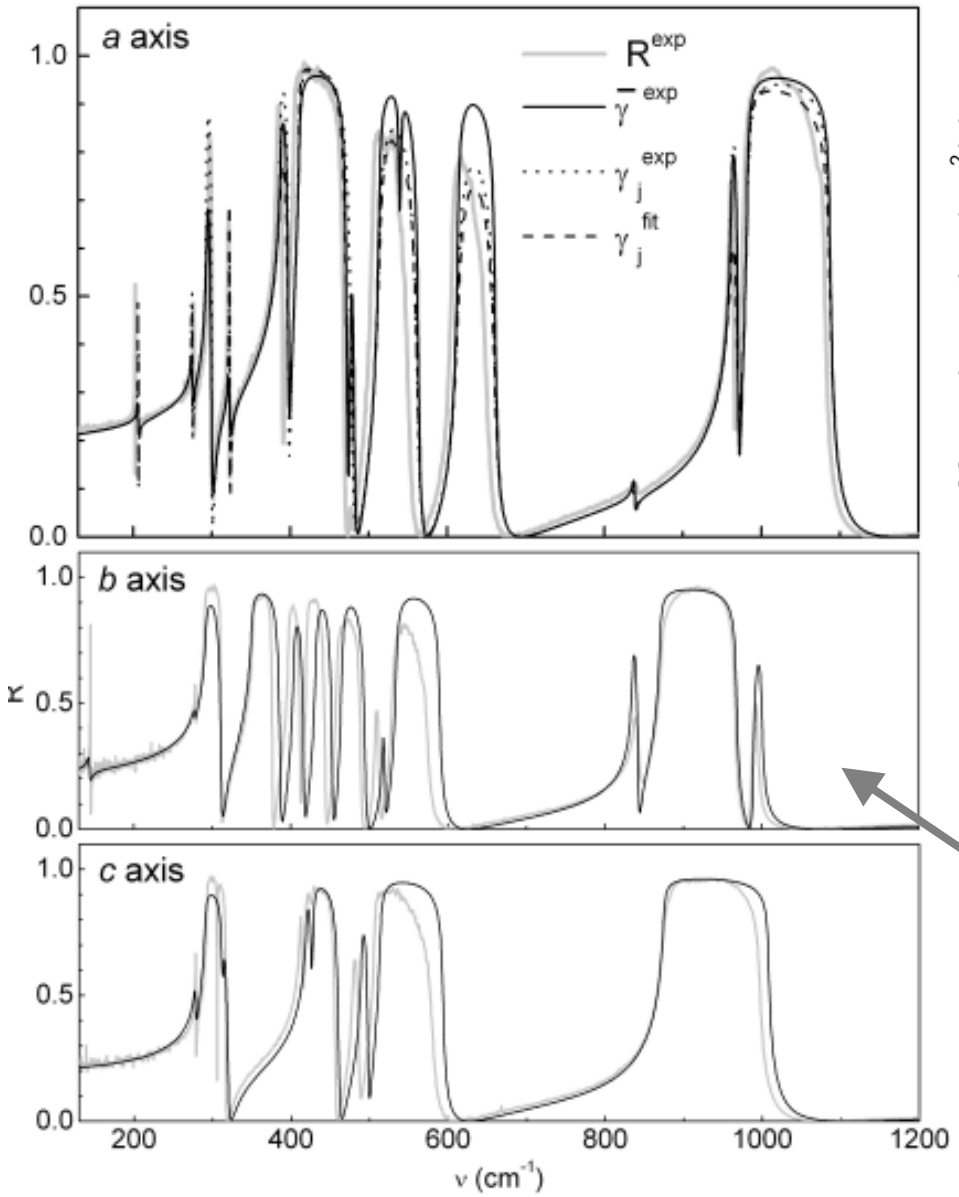
M1, M2 = Mg, Fe

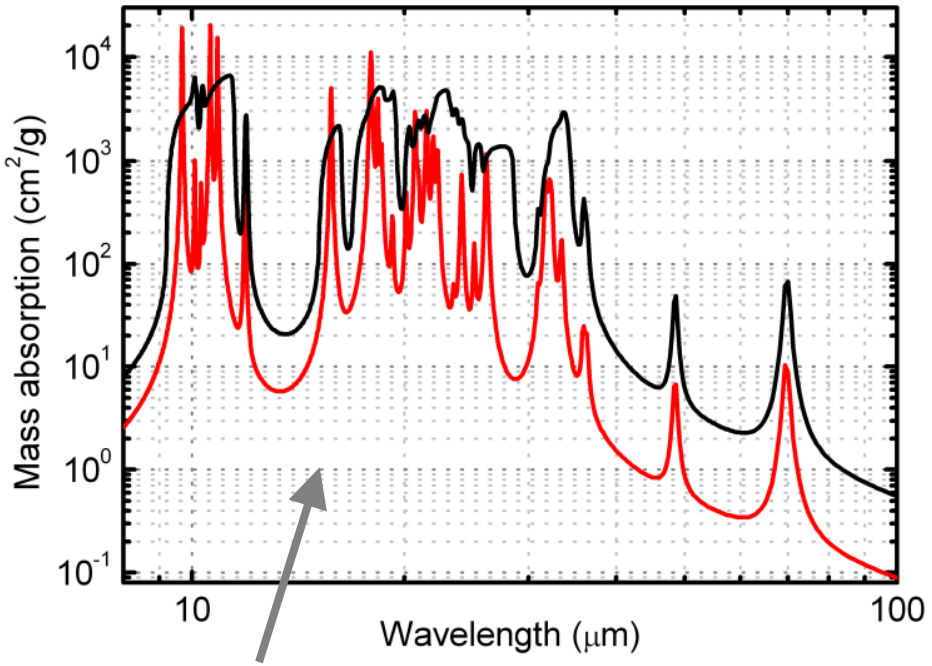




Forsterite($x=0$)/Fayalite($x=2$) $Mg_{2-x}Fe_xSiO_4$

Reflectance spectrum of crystalline forsterite Mg_2SiO_4





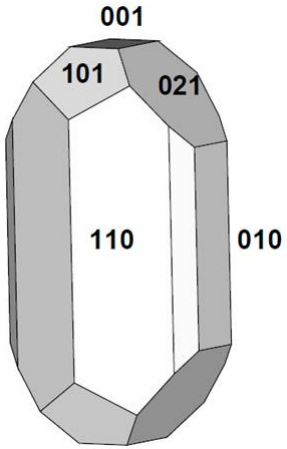
B3LYP mass adsorption spectrum (**red**: spherical; **black**: continuous distribution of ellipsoids)

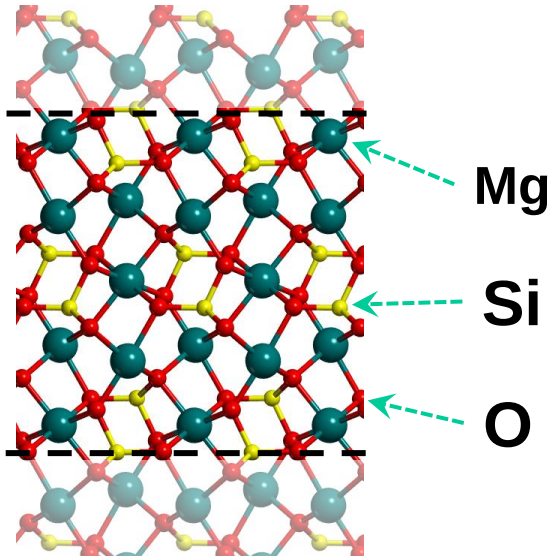
B3LYP reflectance spectra with different damping factors γ

M. De La Pierre *et al, J. Comp. Chem*., (2011) , *32*, 1775.

Crystalline surfaces of forsterite Mg_2SiO_4

Crystal morphology of Forsterite



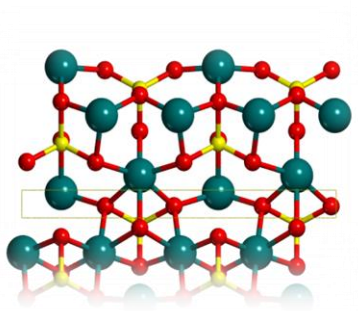


Mg_2SiO_4 bulk

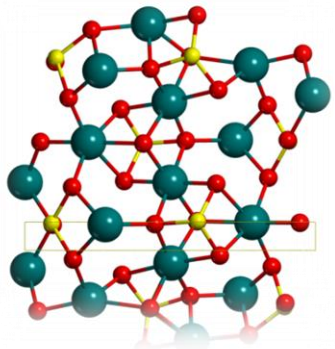
Surface energies of Mg_2SiO_4 surfaces

Surface	γ (J m^{-2})
(010)	1.22
(101)	1.78
(001)	1.78
(021)	1.90
(110)	2.18

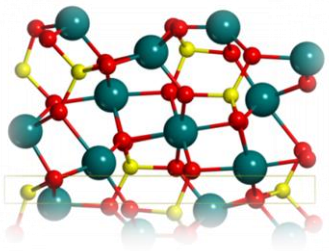
Bruno, M. et al., *J. Phys. Chem. C* **2014,** *118,* 2498-2506



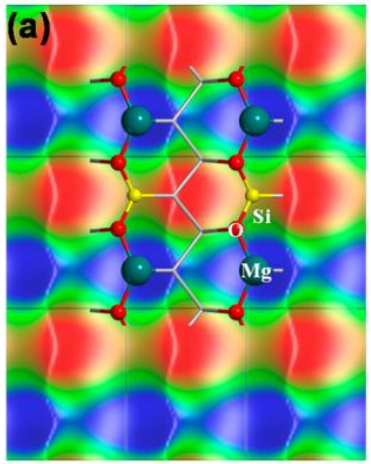
(010)



(001)

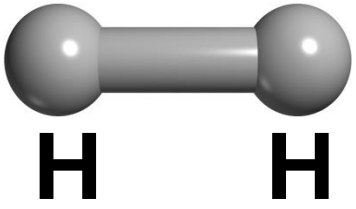


(110)



Relevance of the interstellar H2

ASTROPHYSICAL



- The most abundant molecules in ISM
- An effective coolant for gases and m. clouds
- Does not form from gas-phase reaction
- **Does form on grains in m. clouds**

ASTROCHEMISTRY

$$\mathbf{H_2 + c.r. \rightarrow H_2^+ + e^- + c.r.} \qquad \mathbf{H_2^+ + H_2 \rightarrow H_3^+ + H}$$

Chemistry of oxygen

$$H_3^+ + O \rightarrow OH^+ + H_2$$

$$OH^+ + H_2 \rightarrow H_2O^+ + H$$

$$H_2O^+ + H_2 \rightarrow H_3O^+ + H$$

$$H_3O^+ + e^- \rightarrow H_2O + H$$

Most abundant molecule in the SOLID-phase

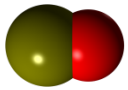
Chemistry of carbon

$$H_3^+ + C \rightarrow CH^+ + H_2$$

$$CH^+ + H_2 \rightarrow CH_3^+ + h\nu$$

$$CH_3^+ + O \rightarrow HCO^+ + H_2$$

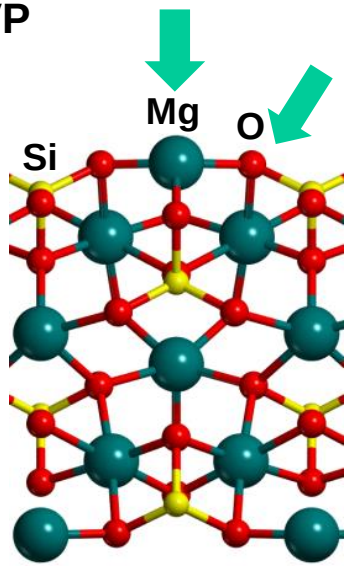
$$HCO^+ + e^- \rightarrow CO + H$$



2nd most abundant molecule in the GAS-phase

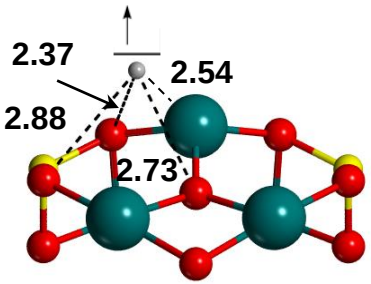
Adsorption of H at the (010) Mg_2SiO_4 forsterite

Geometry optimization: **B3LYP-D2*/DZVP**
Energy refinement: **TZVP//DZVP**
ZPE-corrected energies in **kcal/mol**
BSSE corrected values



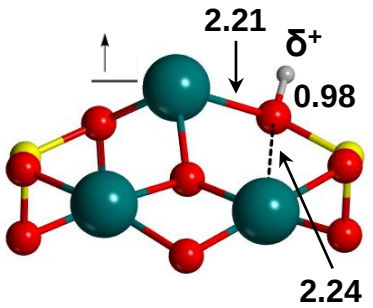
Navarro-Ruiz, J. et al.,
Phys. Chem. Chem. Phys.
2014, *16,* 17447-17457

Phys-010-Mg1



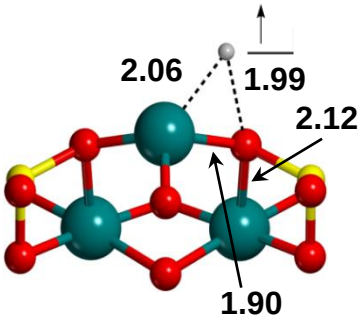
$\Delta_{ads}U_0$ **-1.6**

Chem-010-O1



$\Delta_{ads}U_0$ **-9.0**

Phys-010-Mg2

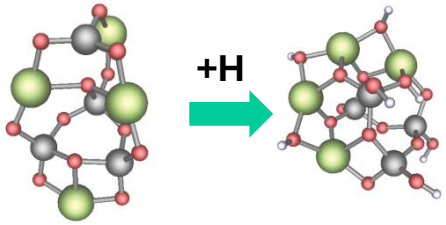


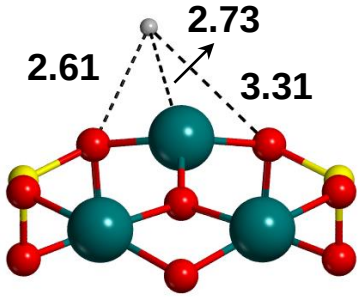
$\Delta_{ads}U_0$ **-2.1**

Electr. energy	Mg1	Mg2	O1
B3LYP-D2*	-3.3	-4.3	-16.7
BLYP-D2*	-3.0	-5.0	-15.8
BHLYP-D2*	-2.5	-1.9	-15.2
PBE-D2*	-4.3	-5.0	-18.7

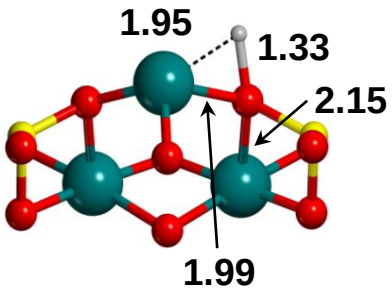
Diffusion of H at the (010) Mg_2SiO_4 forsterite

ZPE-corrected **B3LYP-D2*/TZVP//B3LYP-D2*-DZVP** in **kcal/mol**

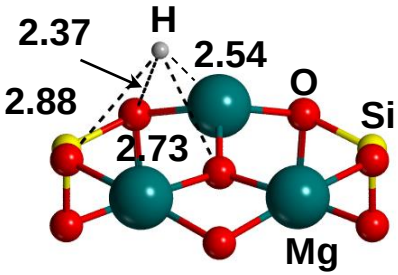




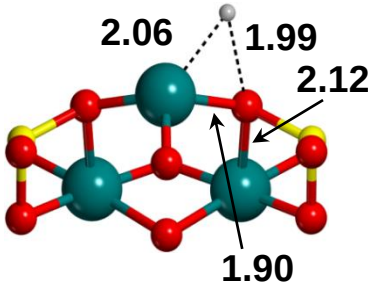
010–$TS_{Mg1→Mg2}$



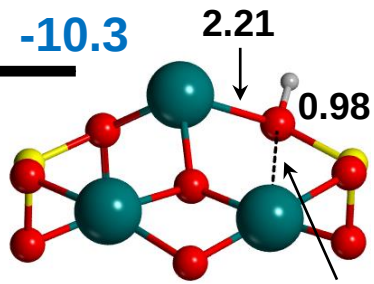
010–$TS_{Mg2→O1}$



010–Mg1



010–Mg2



010–O1

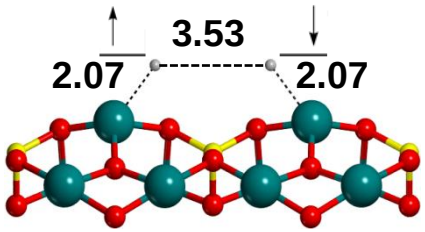
Method	$\Delta E(H_{jump})$
B3LYP-D2*	**4.1**
Kerkeni	0.14-4.8
Goumans	1.6
Exp.	0.57

Method	$\Delta E(H_{phys})$
B3LYP-D2*	**-2.7**
Kerkeni	-1.4/-5.8
Goumans	-2.5
Sidis	-3.2
Exp.	-1.0

Adsorption of a second H at the (010) Mg_2SiO_4 forsterite

ZPE-corrected **B3LYP-D2*/TZVP//B3LYP-D2*-DZVP** in **kcal/mol**

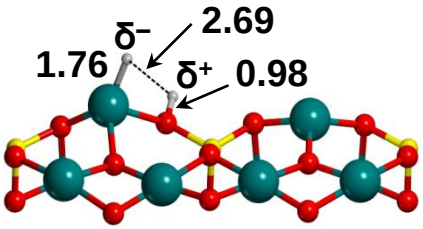
Phys-Mg–Mg



$\Delta_{ads}U_0$ **-5.0**

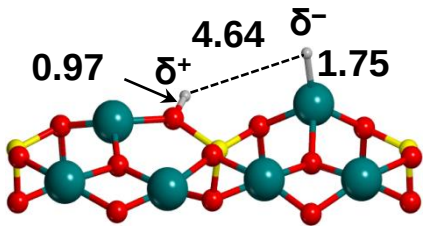
- 2H physisorbed states
- Spin densities on the H atoms

Chem-Mg–O



$\Delta_{ads}U_0$ **-89.3**

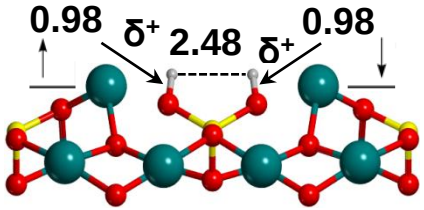
- $O^{-}\cdots H^{+}$ proton and $Mg^{+}\cdots H^{-}$ hydride character
- H bond between H^{-} and H^{+}



$\Delta_{ads}U_0$ **-71.3**

- $O^{-}\cdots H^{+}$ proton and $Mg^{+}\cdots H^{-}$ hydride character

Chem-O–O

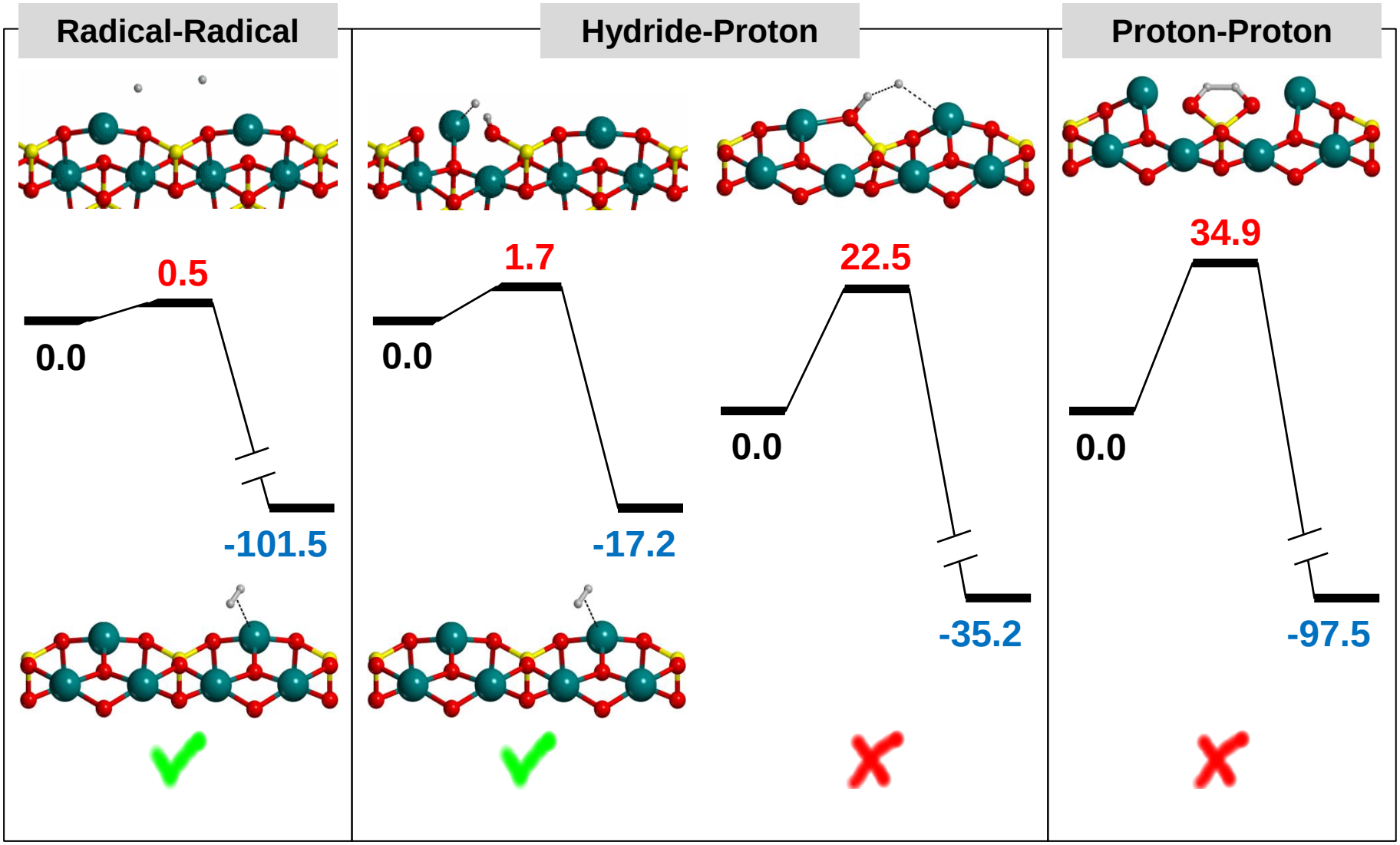


$\Delta_{ads}U_0$ **-9.0**

- 2H chemisorbed states
- Formation of a surface geminal Si–$(OH)_2$ groups
- Spin densities on the bare Mg atoms

L-H formation of H_2 at the (010) Mg_2SiO_4 forsterite

ZPE-corrected **B3LYP-D2*/TZVP//B3LYP-D2*-DZVP** in **kcal/mol**



Tunnel for H_2 formation at the (010) Mg_2SiO_4 forsterite

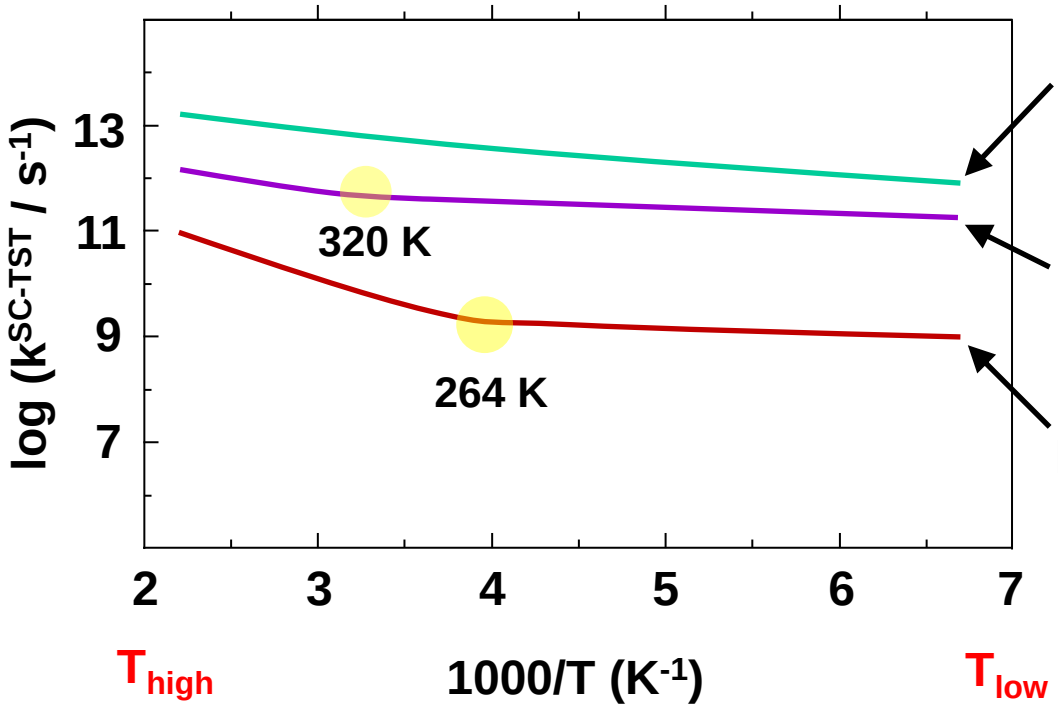
Rate Constants via classical Eyring Equation	Tunneling Coefficients via Fermann & Auerbach Correction	Final Semi-classical Rate Constant

$$k^{TST} = \frac{k_B T}{h} \frac{q^{\neq}}{q_{REACT}} \exp\left(-\frac{\Delta U_0^{\neq}}{RT}\right)$$

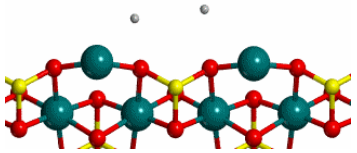
$$\Gamma(T) = \exp\left(\frac{\Delta U_0^{\neq}}{k_B T}\right) \exp\left(\frac{2\pi \Delta U_0^{\neq}}{h\nu^{\neq}}\right)\left(1 + \frac{2\pi k_B T}{h\nu^{\neq}}\right)$$

$$k^{SC-TST} = \Gamma(T) \times k^{TST}$$

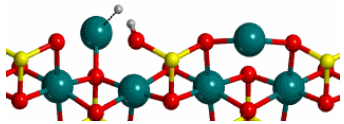
J. Phys. Chem, 2000, 112, 6787



H• •H coupling



$H^+ \cdots H^-$ coupling



H jump