Methane dissociation on Ni(111) and Pt(111):
The effects of lattice motion and relaxation on reactivity

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University of Massachusetts, Amherst

Motivations
● Motivations
Theory
Electronic structure calculations and potential energy surface
Temperature dependence
Dynamics
Comparison with the experiments
Conclusion

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- Study and understand the methane dissociation on metals

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- Study and understand the methane dissociation on metals
- Understand the influence of the surface temperature on the reactivity

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- Study and understand the methane dissociation on metals
- Understand the influence of the surface temperature on the reactivity

$\Rightarrow$ We wish to elucidate some unexplained variations in reactivity and temperature dependence from one metal to another

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Theory
- Approximations
- Coordinate system

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Approximations

- Born-Oppenheimer approximation

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Approximations

- Born-Oppenheimer approximation
- Adiabatic approximation

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- Born-Oppenheimer approximation
- Adiabatic approximation
- This splits the problem in 2 parts

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$\Rightarrow$ Electronic structure calculations (15 DOFs for methane)

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$\Rightarrow$ Electronic structure calculations (15 DOFs for methane)

$\Rightarrow$ Dynamics

DFT results are fit with a LEPS form, which depends on only 3 DOFs: Z, r, and θ, and we set $V = V_0(Z, r, \theta)$

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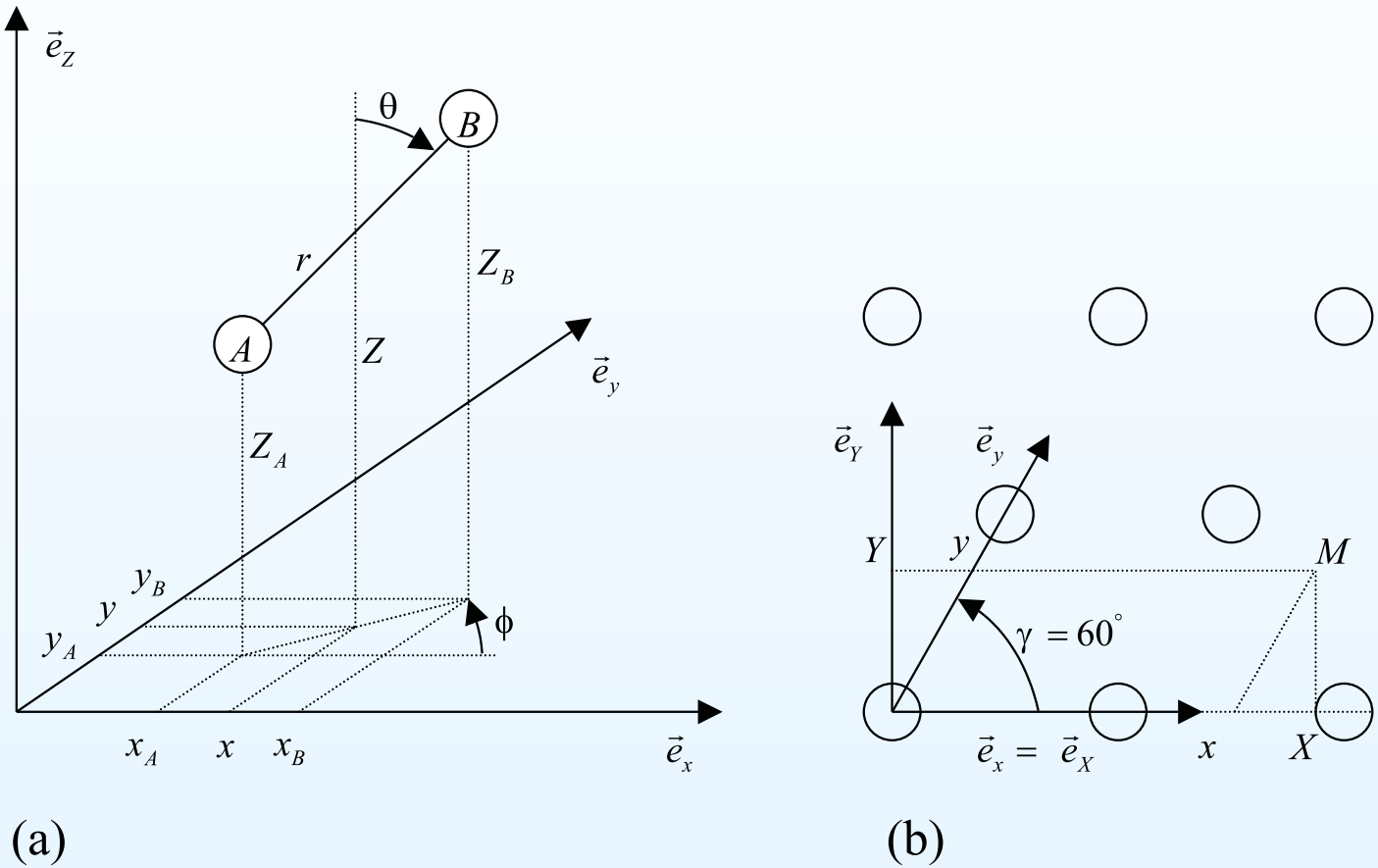

A=CH_3, B=H, only 3 DOFs (Z, r, and θ)

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To compute the total electronic energies, we use the Vienna *Ab initio* Simulation Package (VASP)

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- Density Functional Theory (DFT)

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- Density Functional Theory (DFT)
- Fully non-local optimized ultrasoft pseudopotential (USPP), or projected augmented wave potential (PAWP)

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- Asymmetric slab supercell with periodic boundary conditions for the metal surface
- Plane wave basis set

Electronic structure calculations

(Ni111PSh1b)

$\Rightarrow E_p = 0.361$ eV

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- The PES is based onto a LEPS form (London-Eyring-Polanyi-Sato)
  $\Rightarrow$ Interpolation of DFT results

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$\Rightarrow$ a total of 12 parameters for the 3D (Z, r, θ) LEPS

How to find the MEP?

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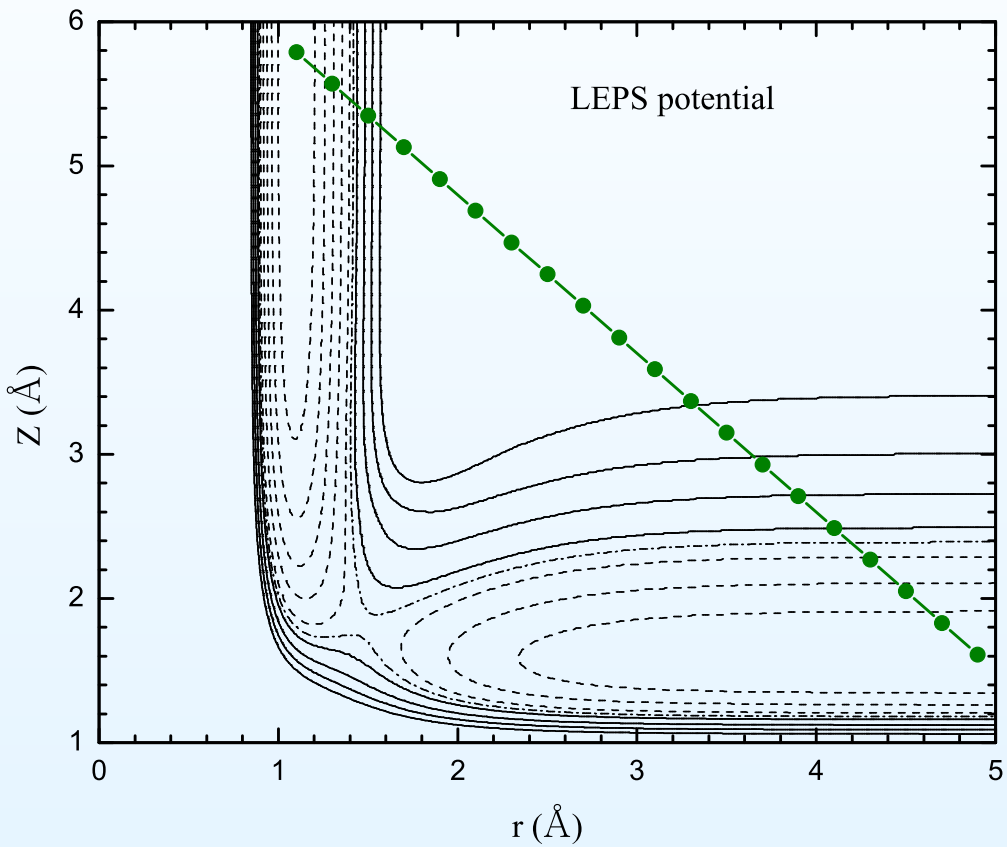
Climbing Image - NEB method (Henkelman *et al.*)



Start from a linear path of initial «images»

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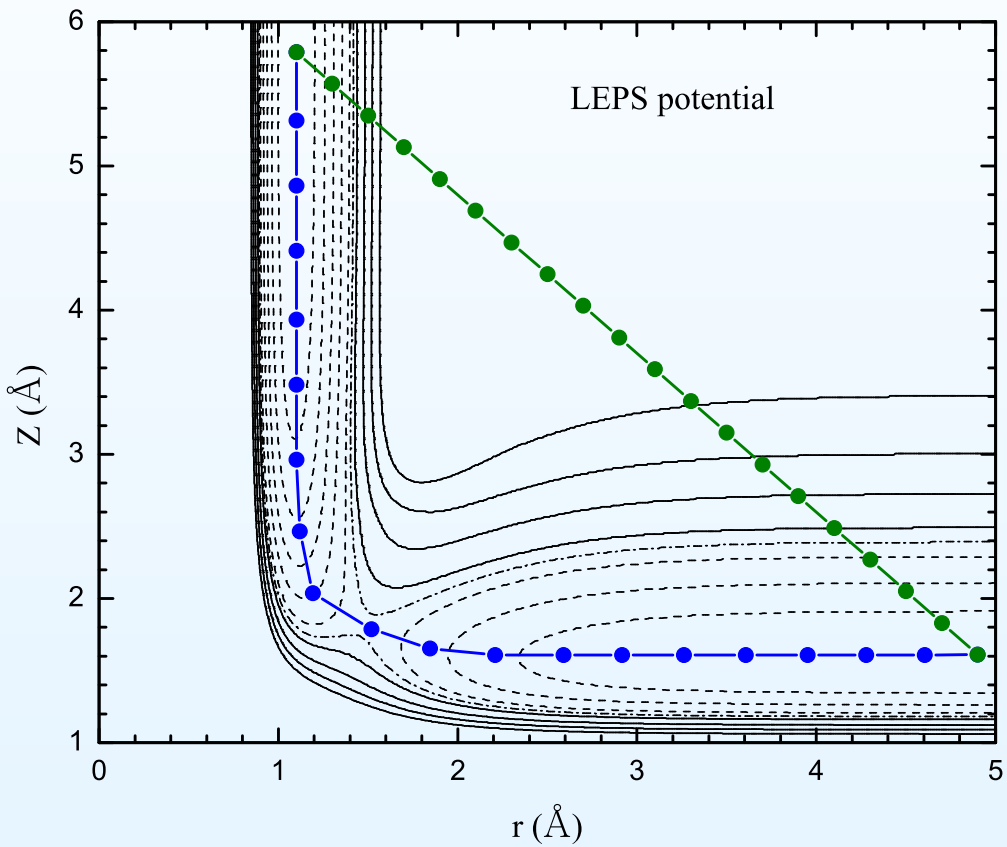

⇒ The transition state is found, and the images are evenly spaced on each side of the TS

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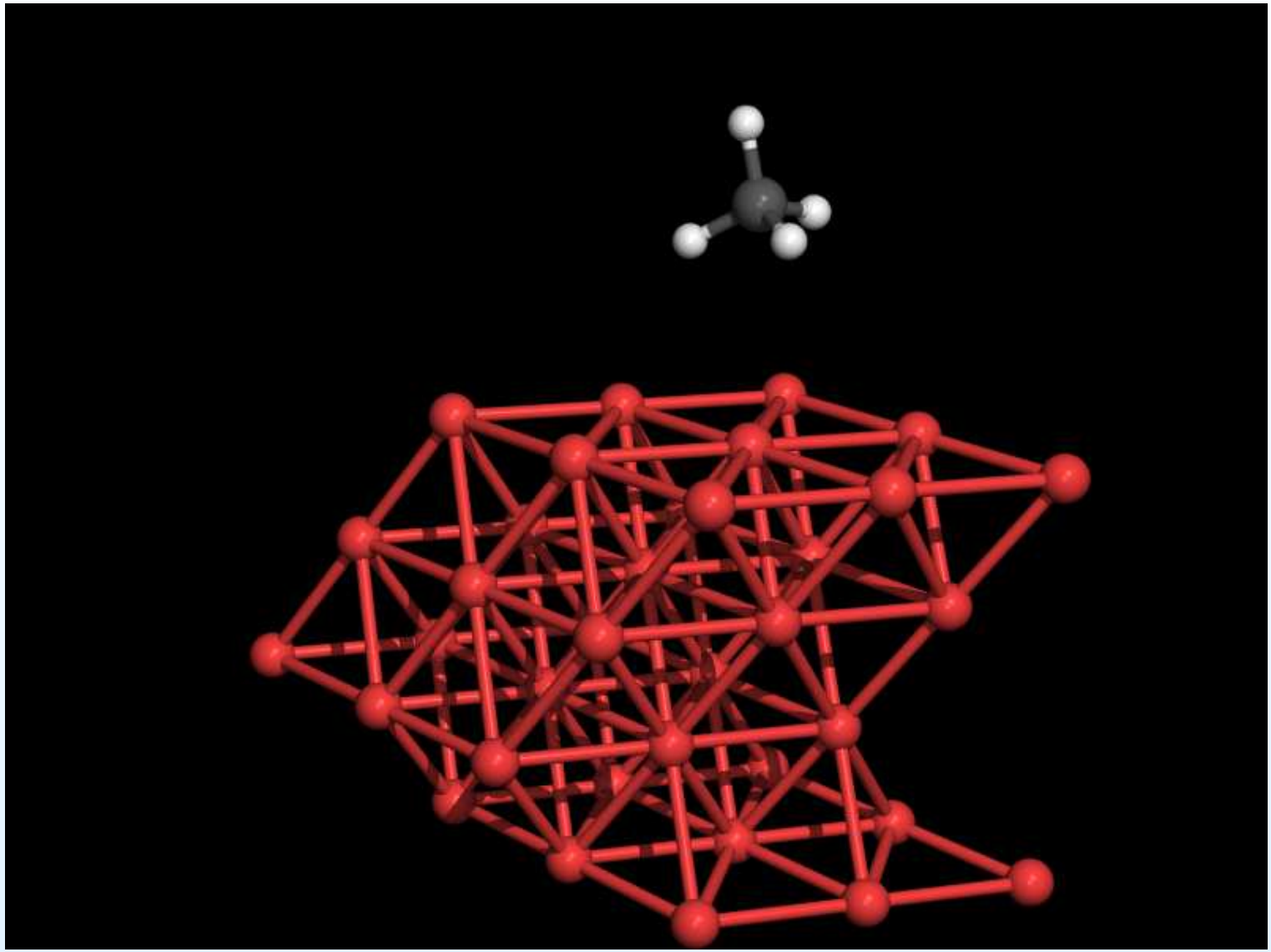

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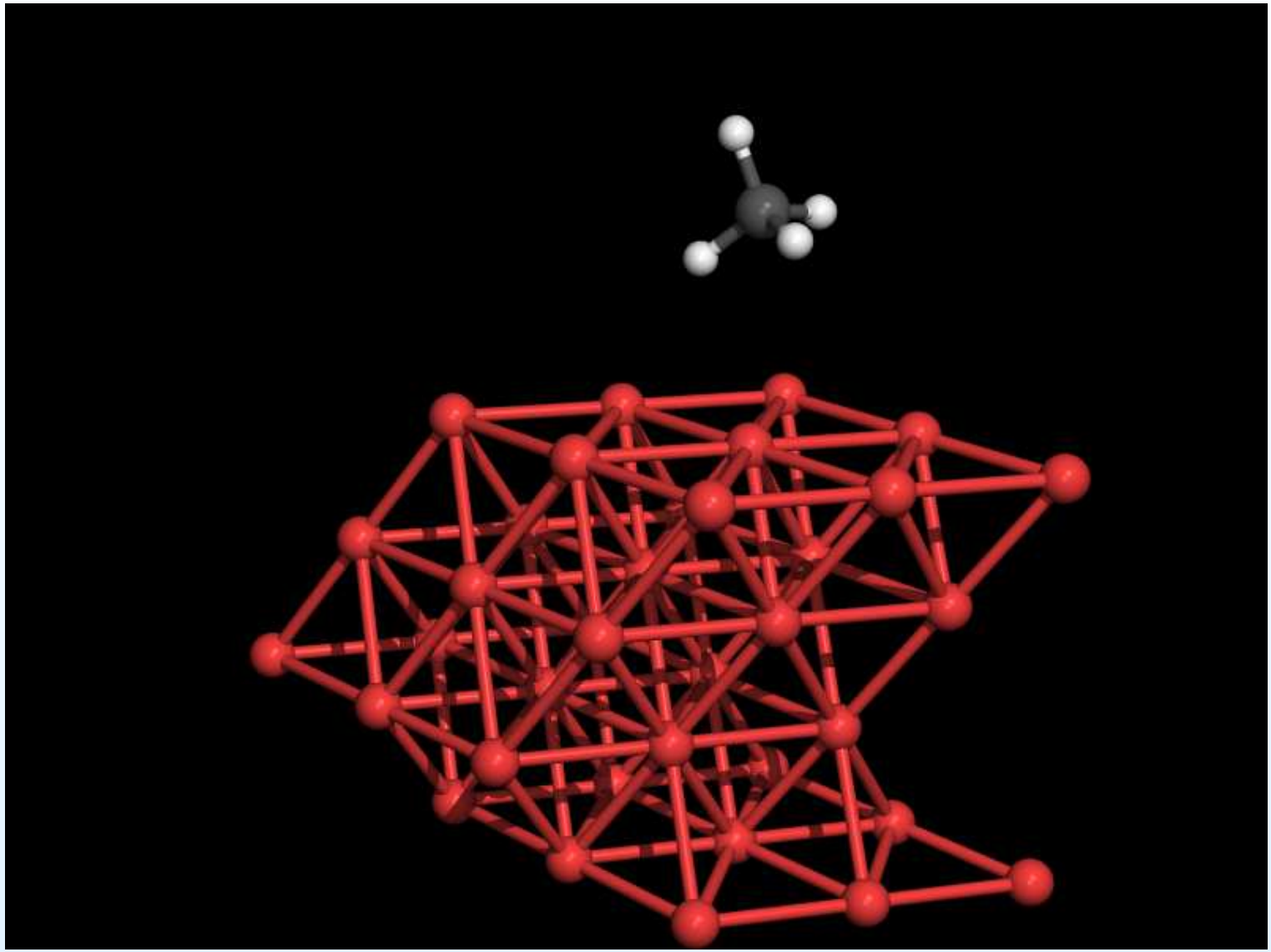

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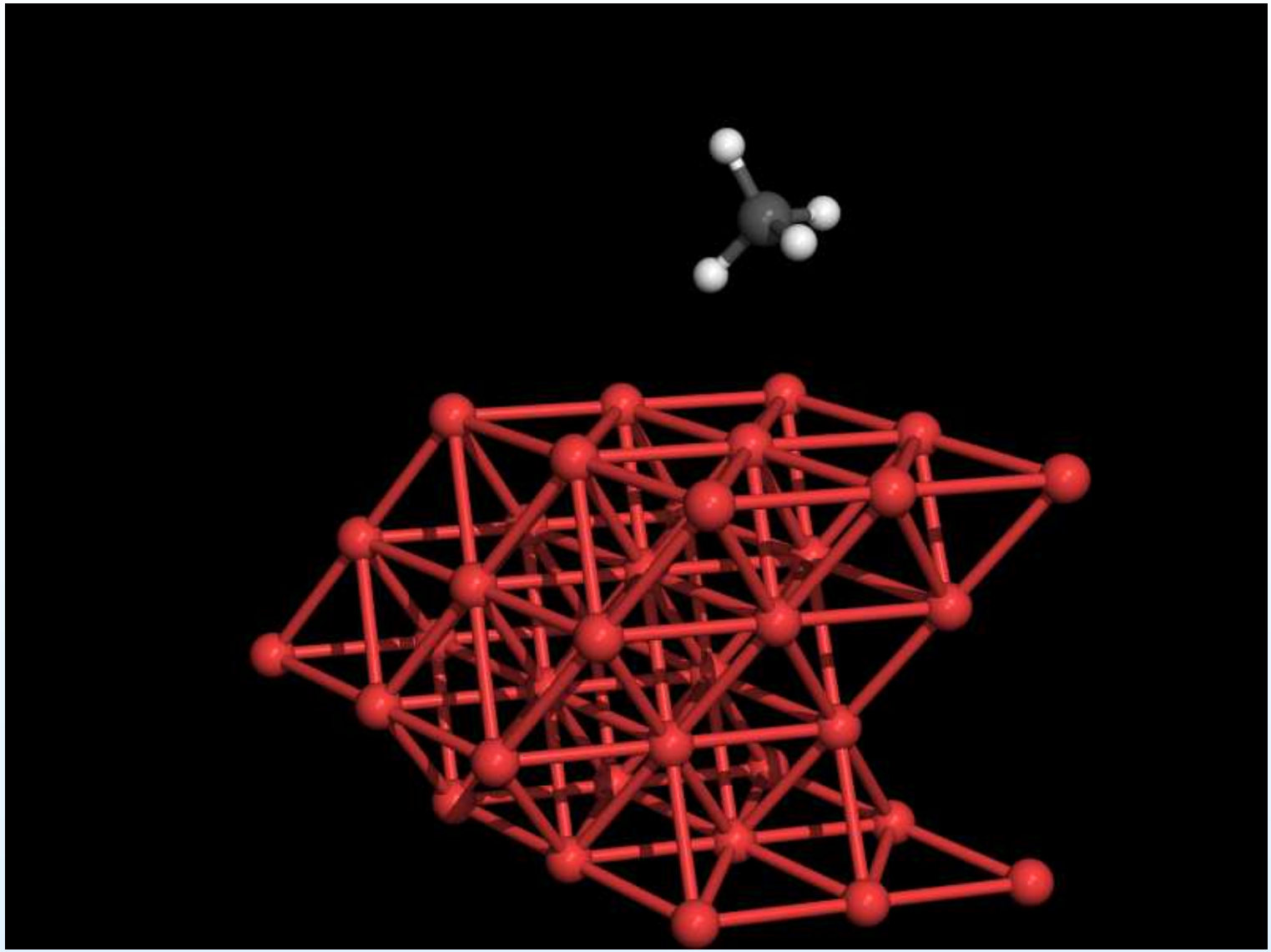

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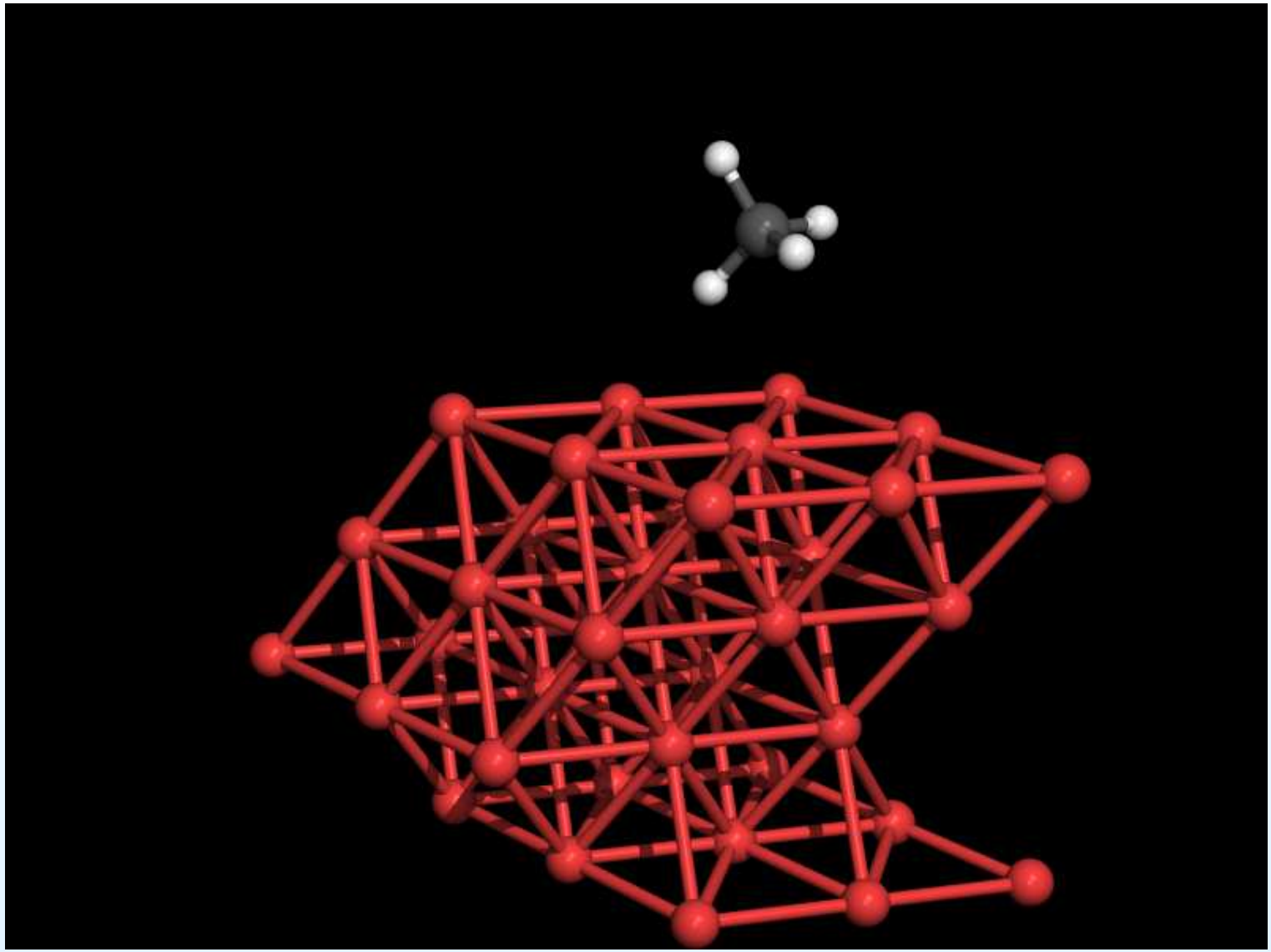

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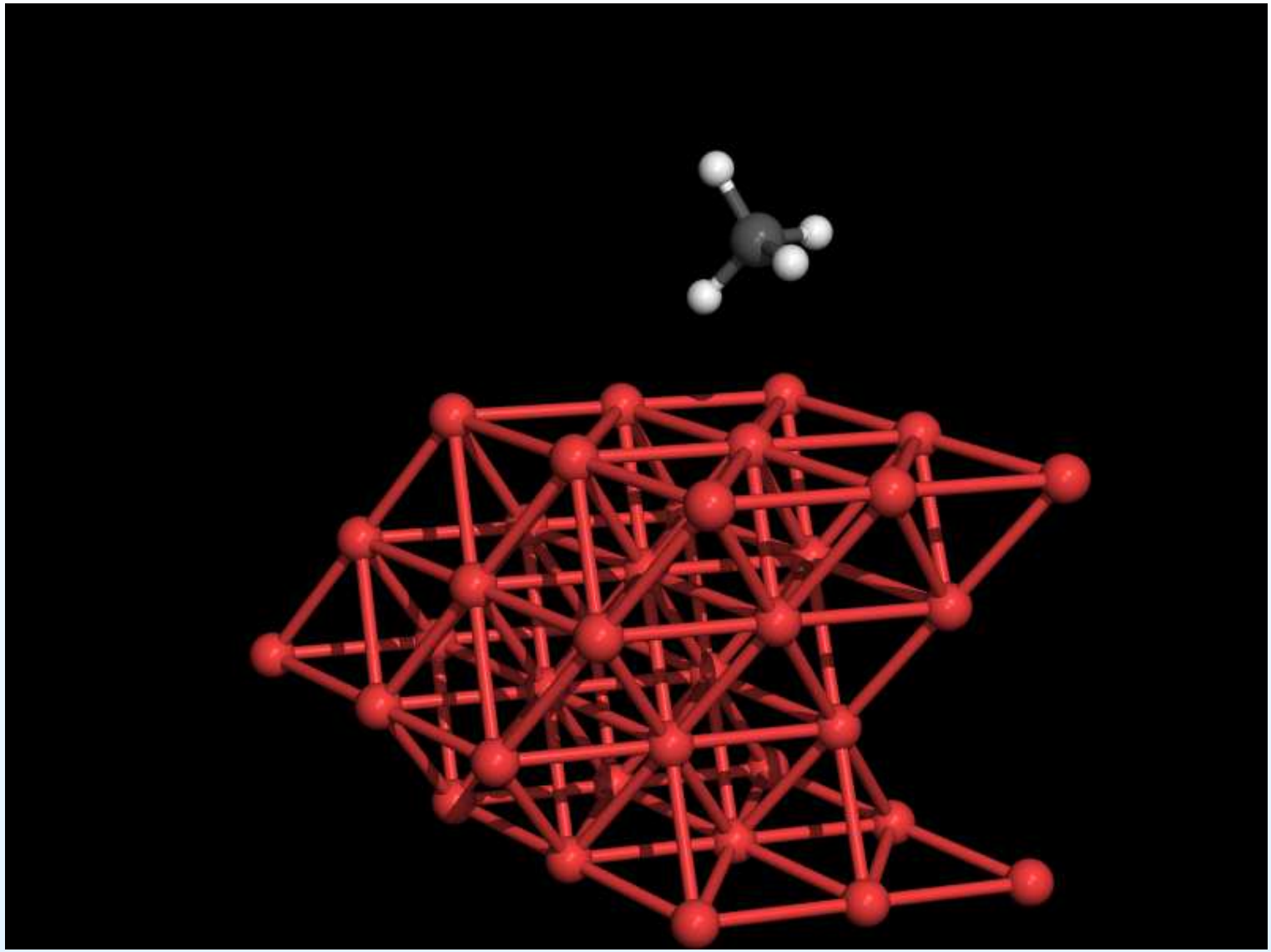

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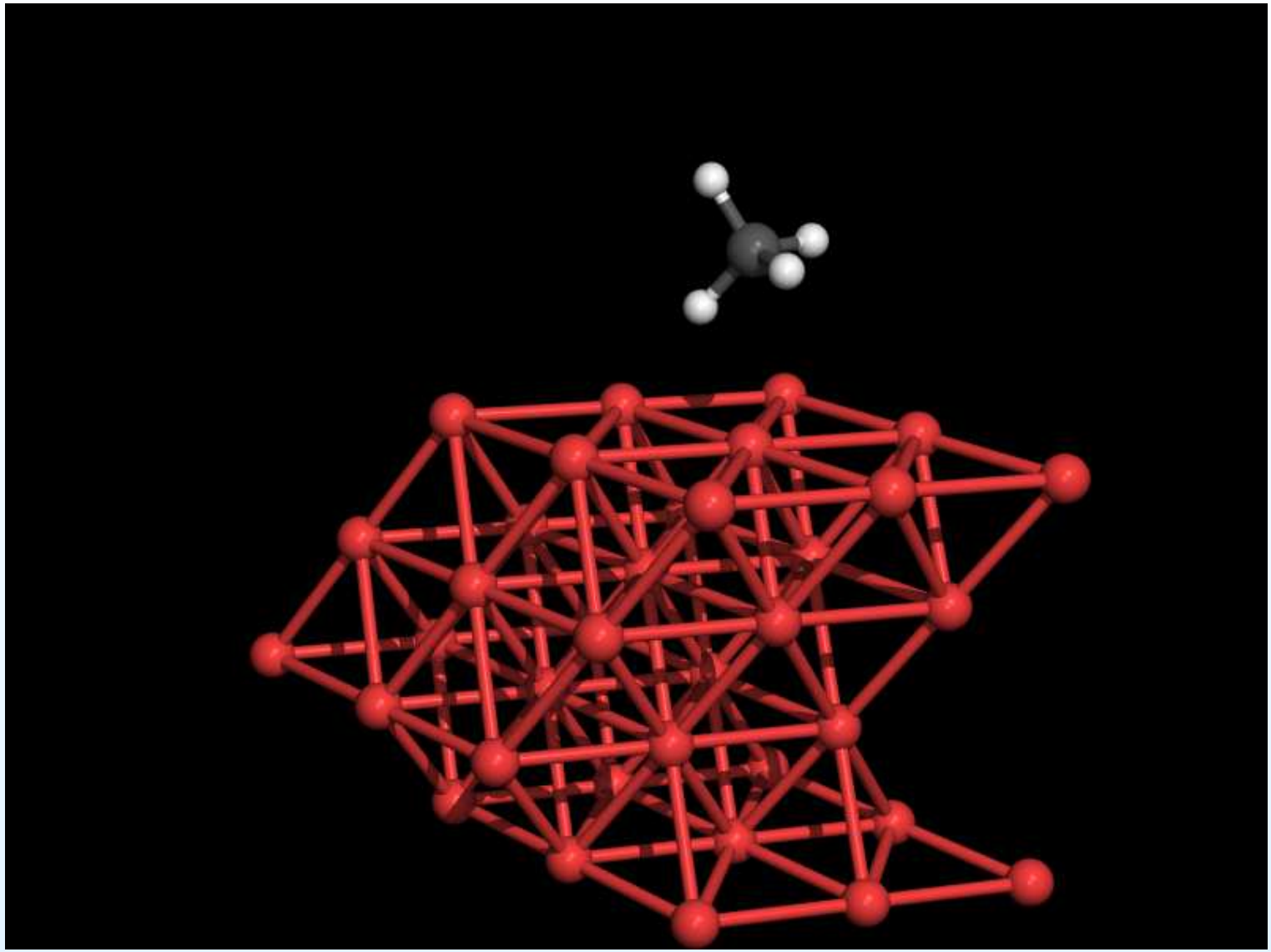

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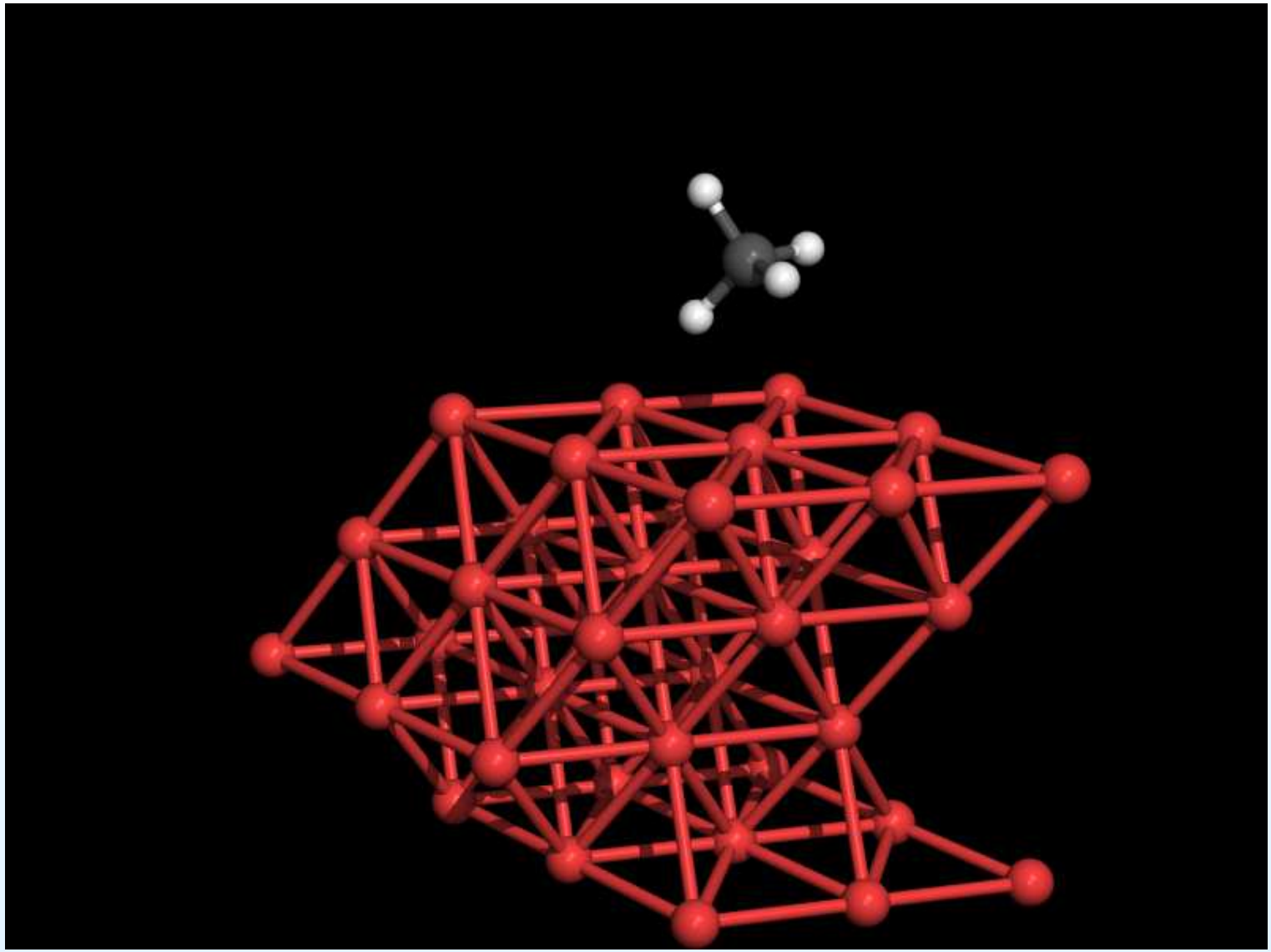

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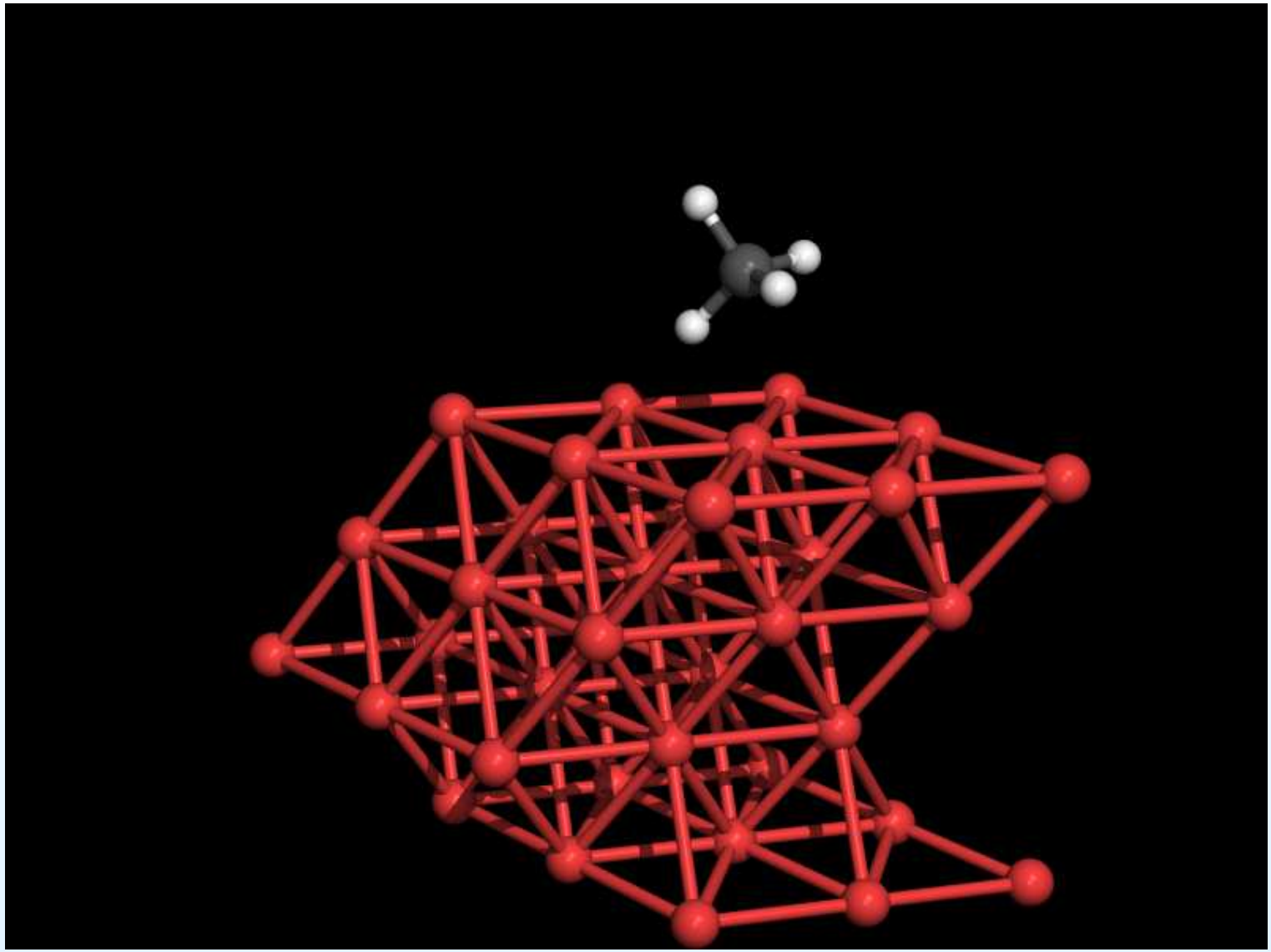

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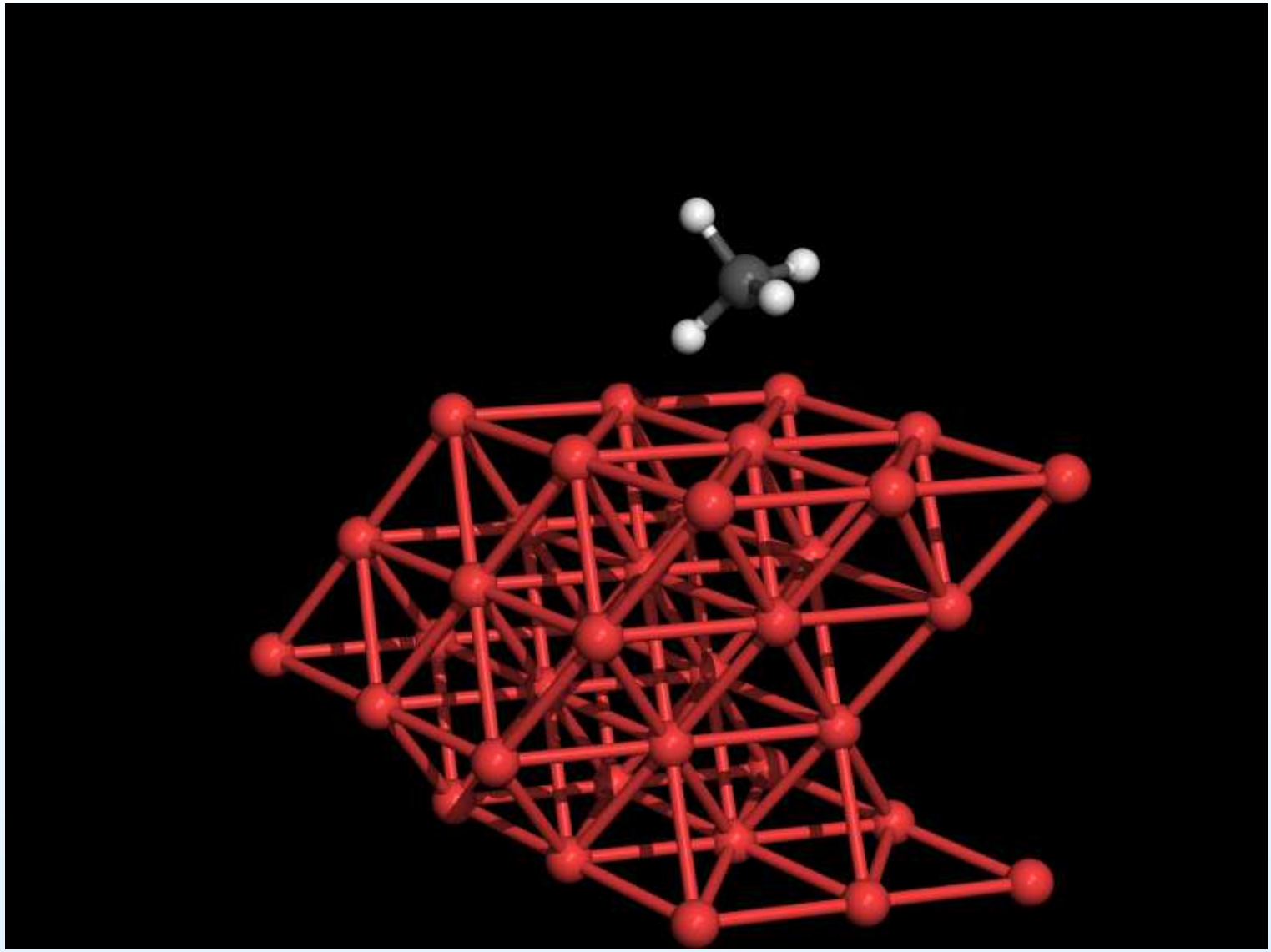

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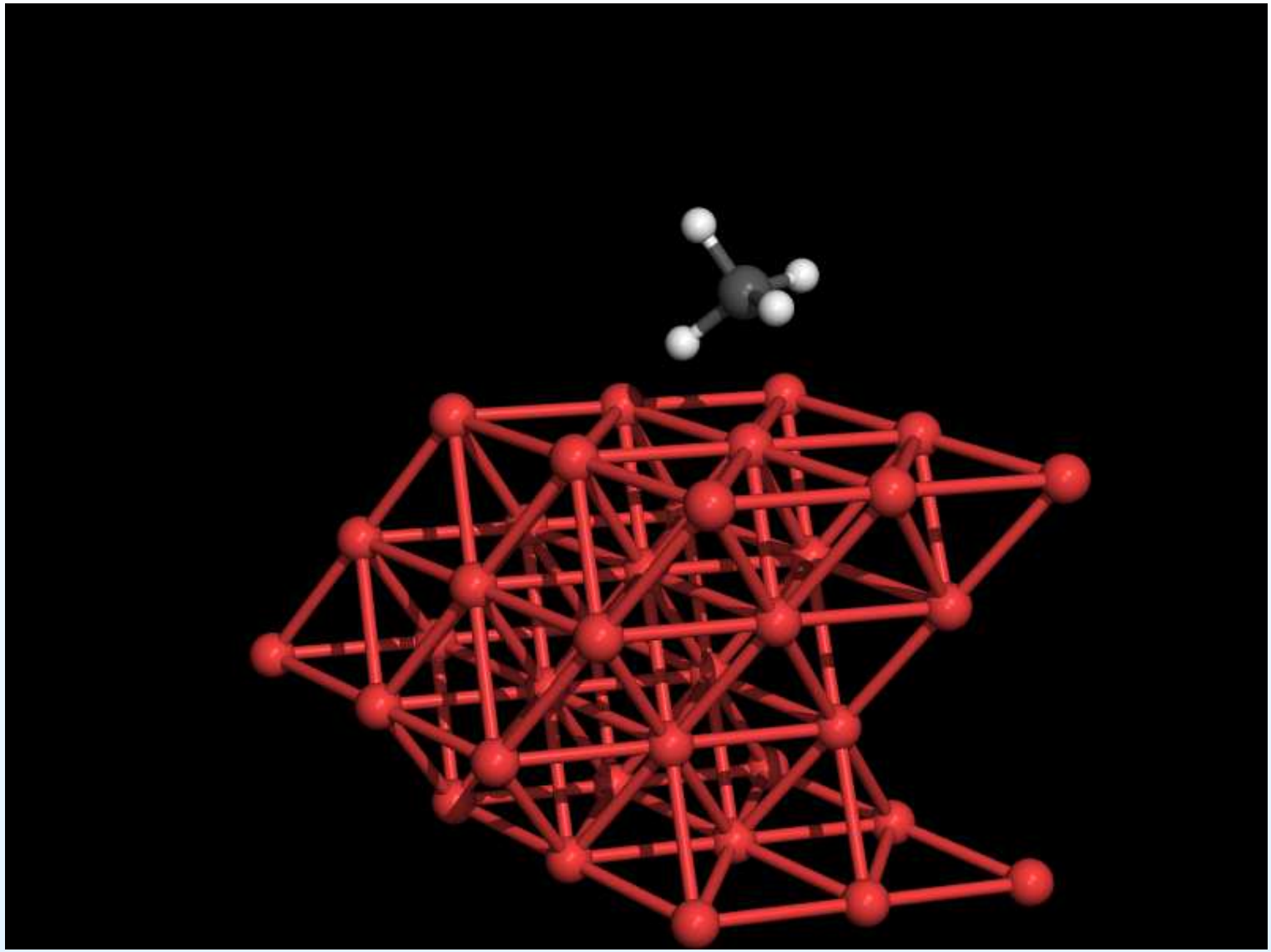

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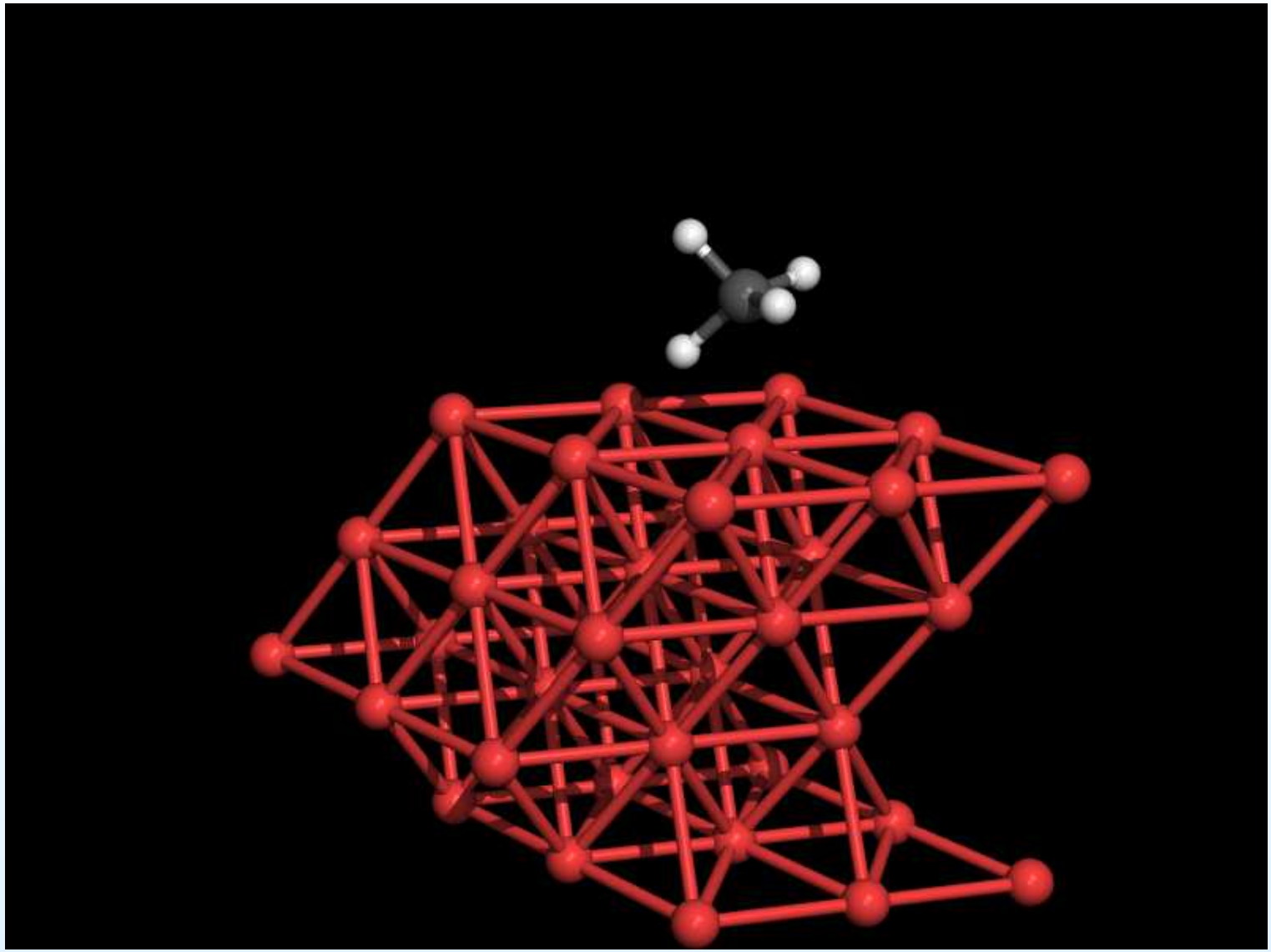

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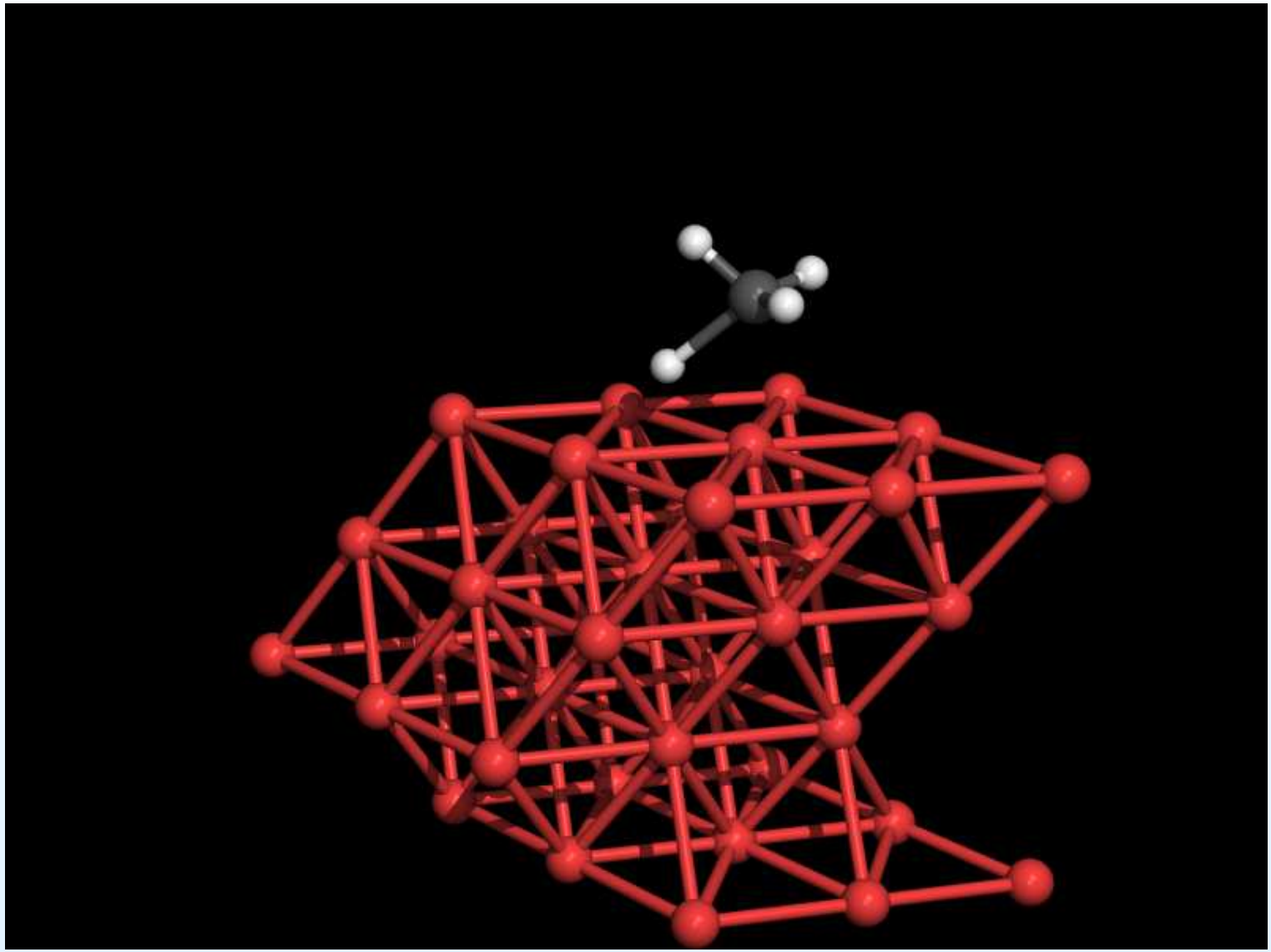

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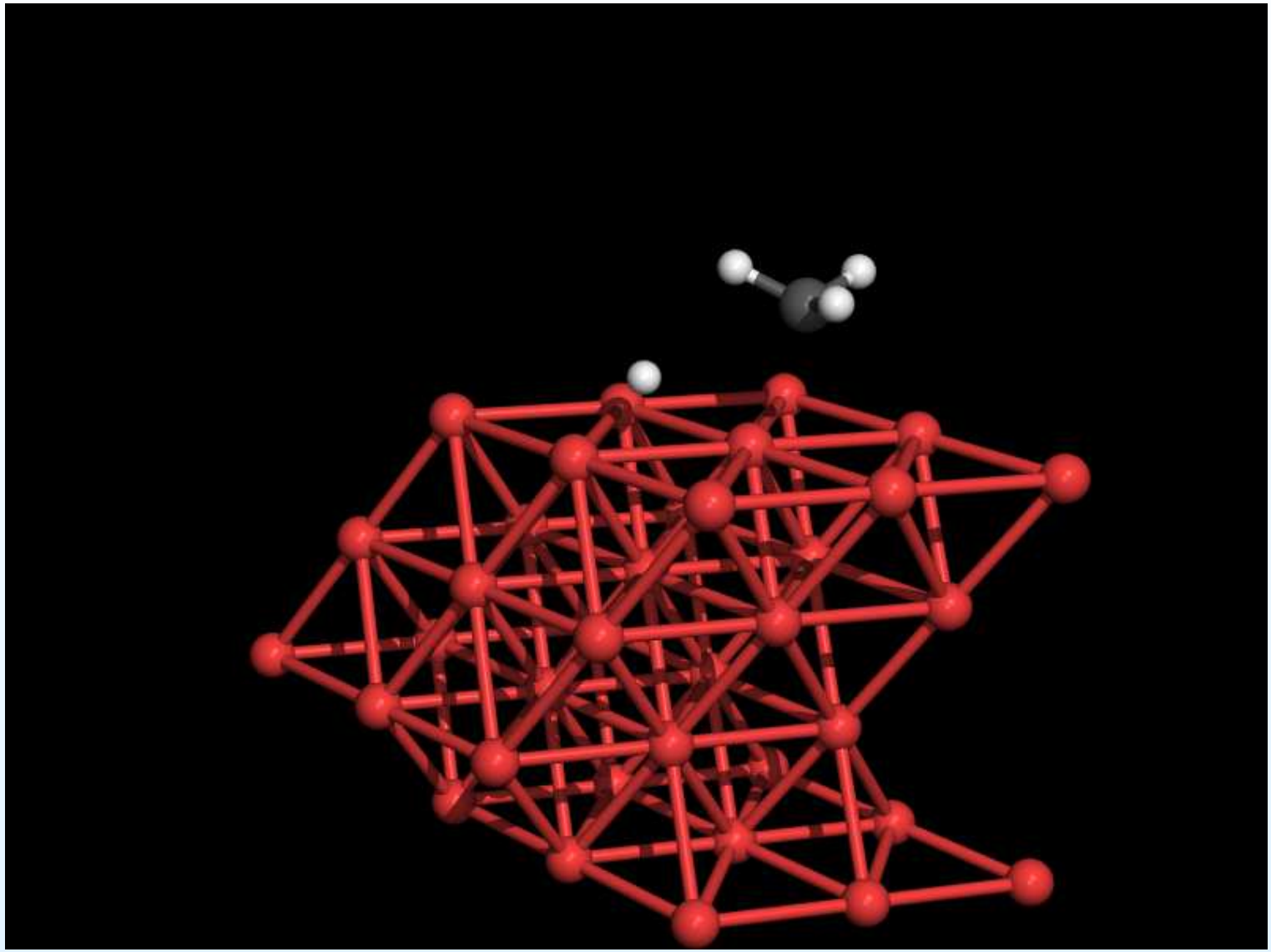

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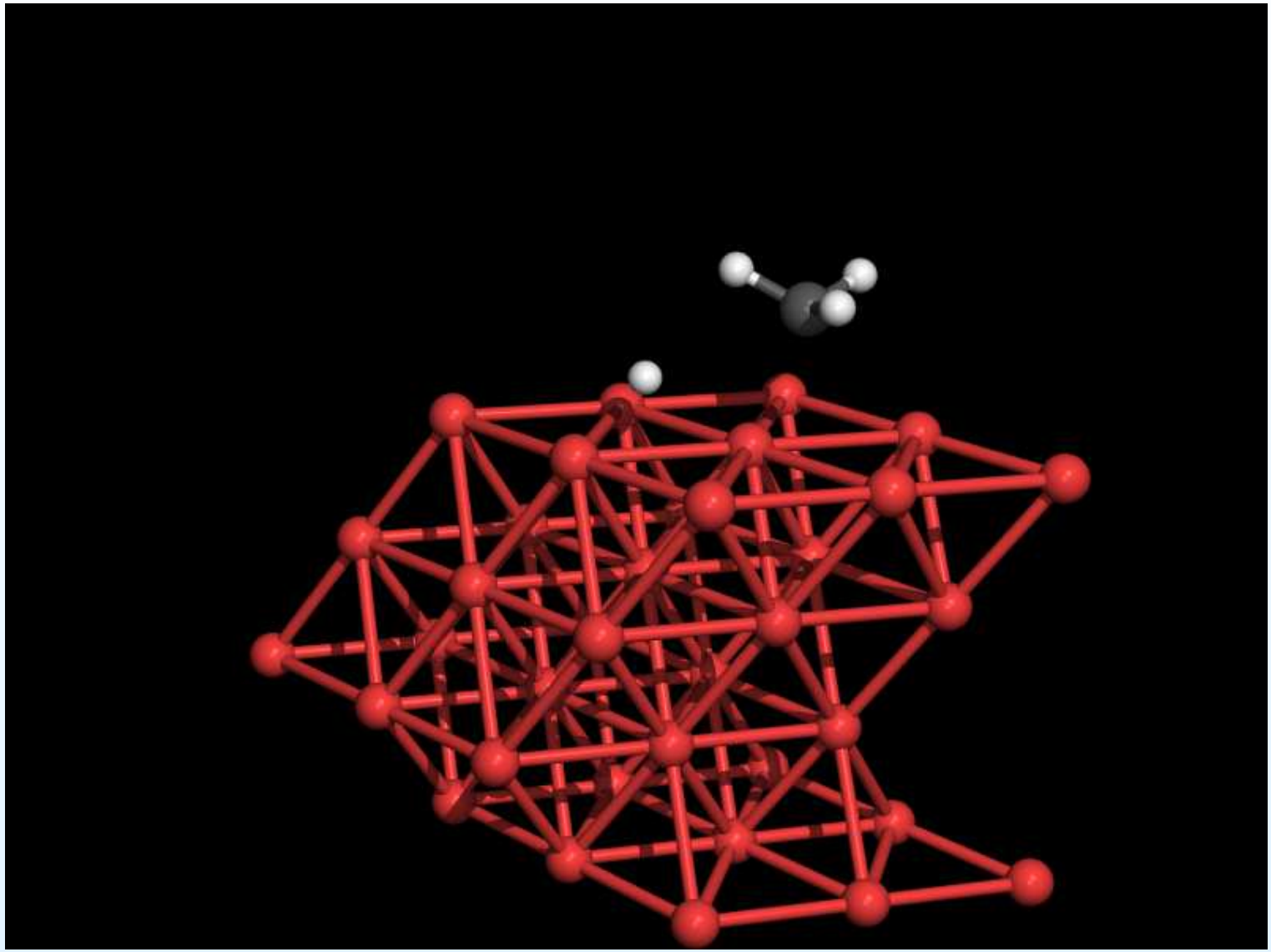

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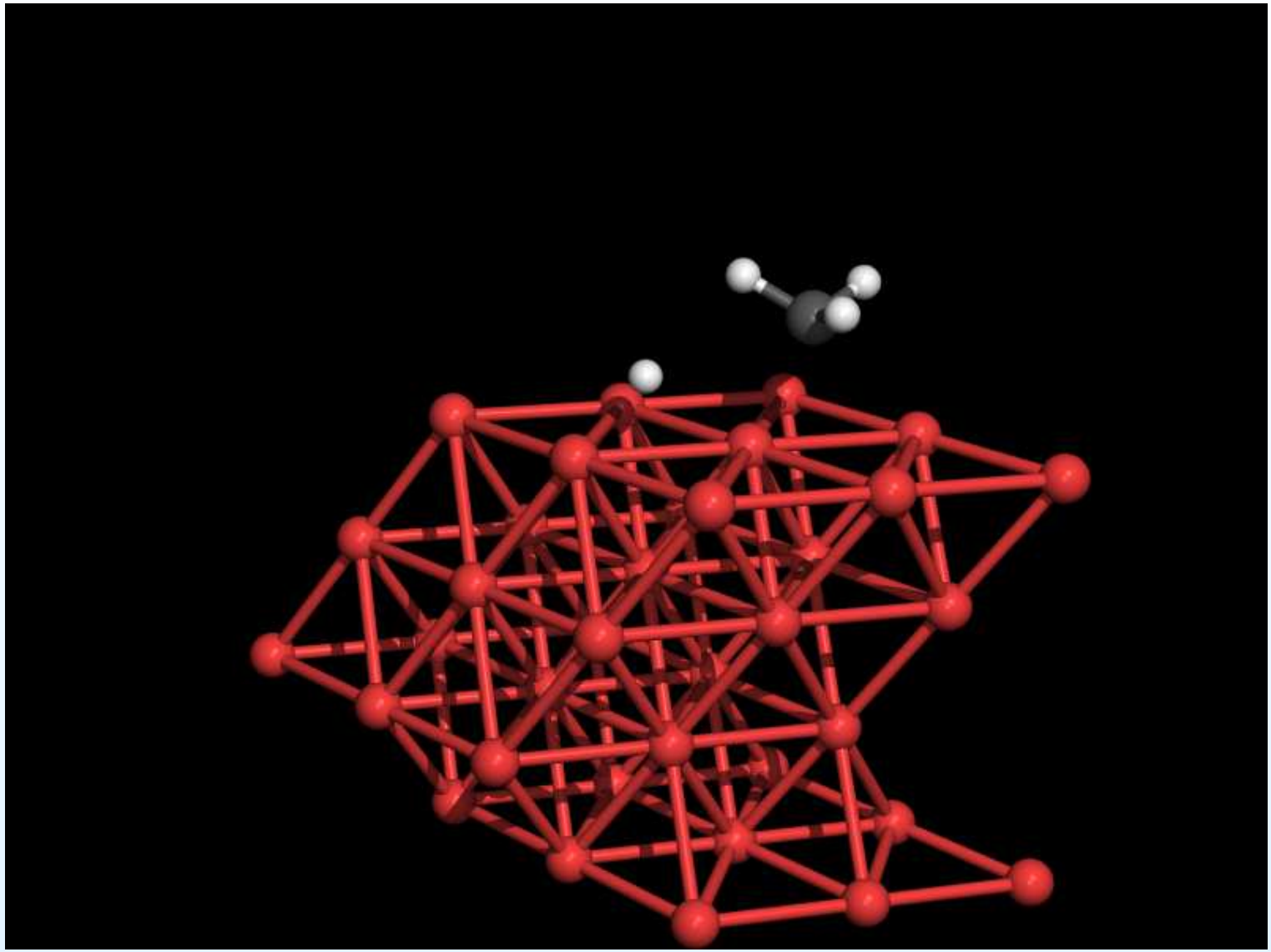

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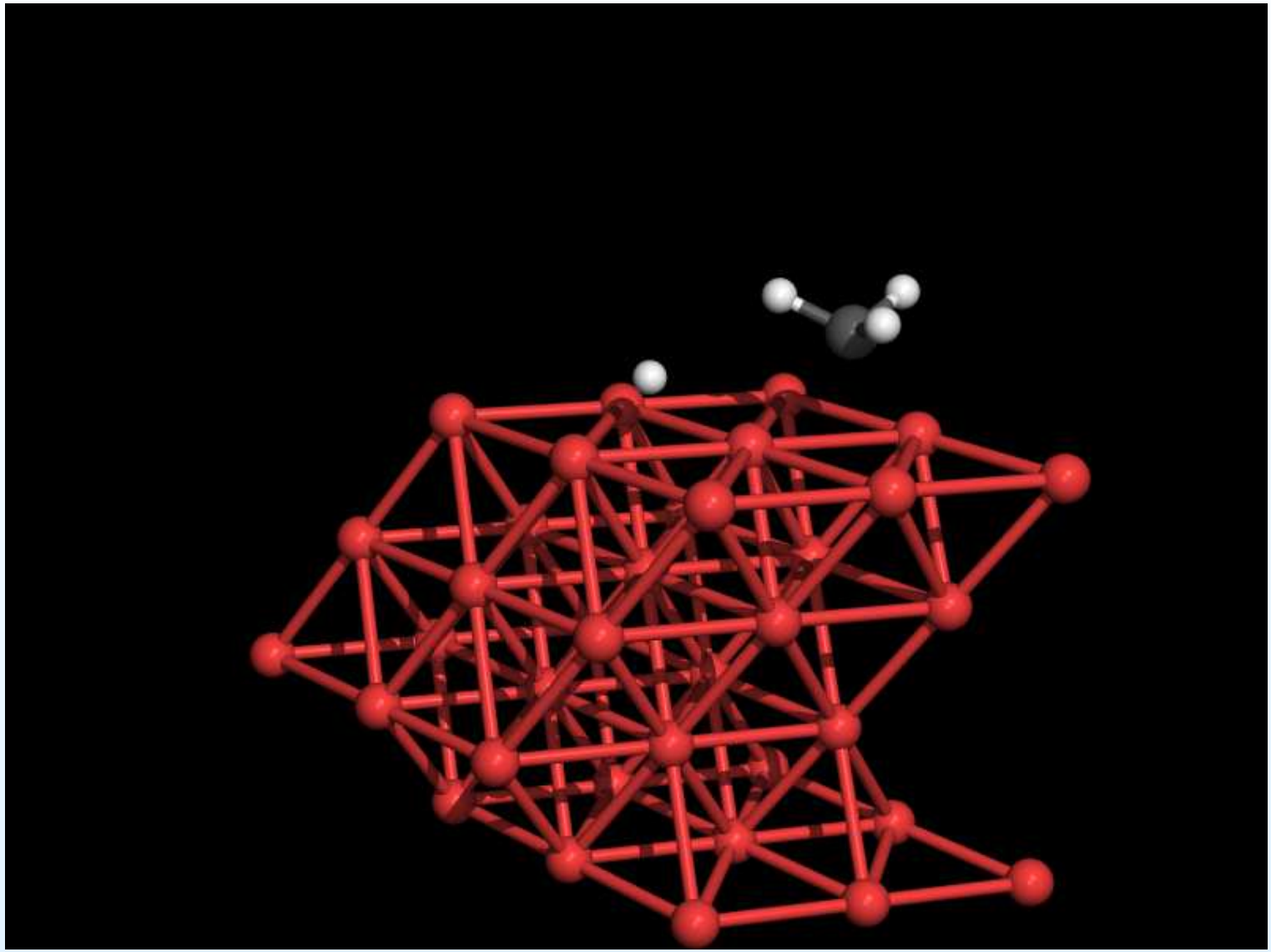

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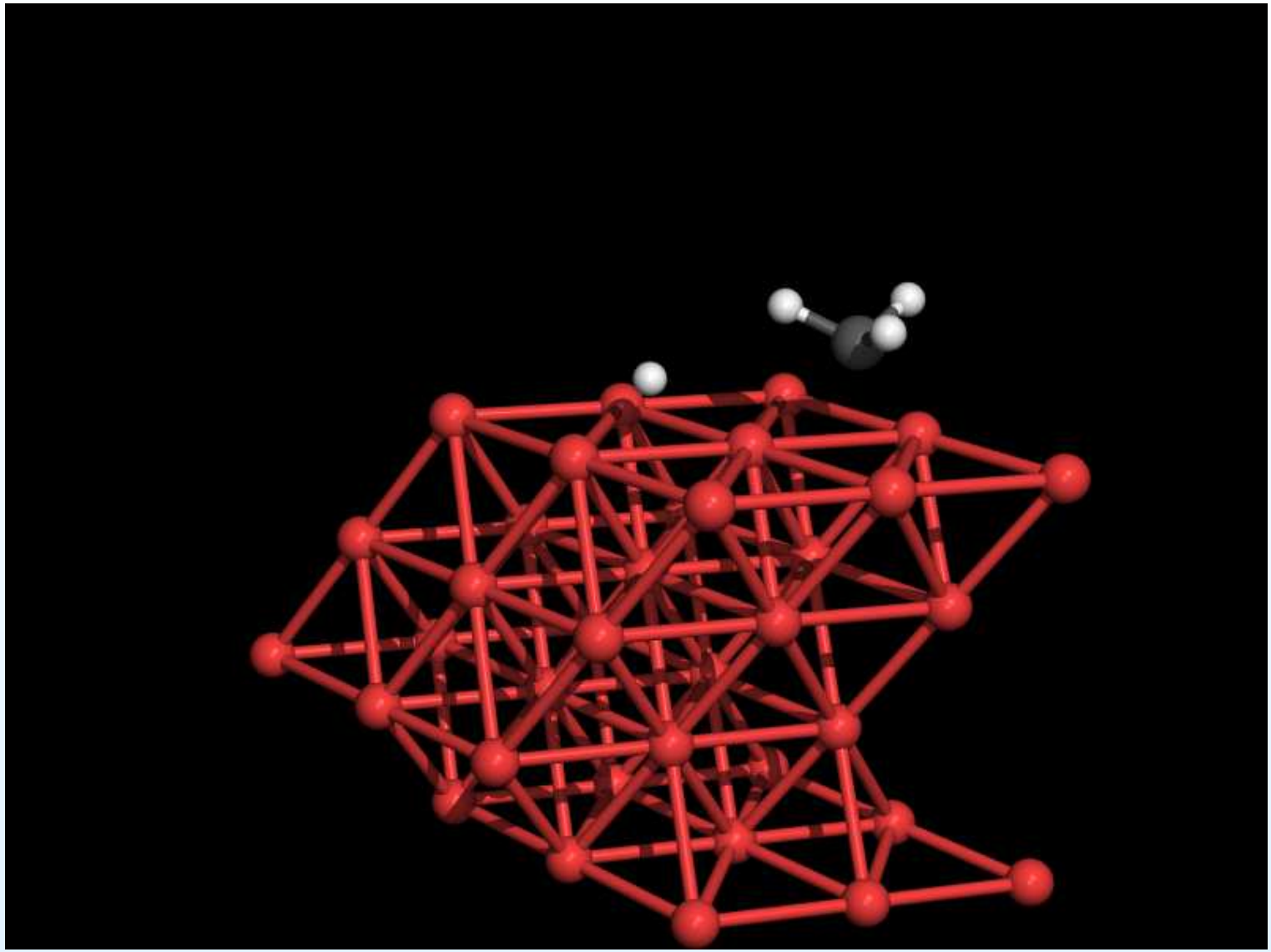

Minimum Energy Path (MEP)

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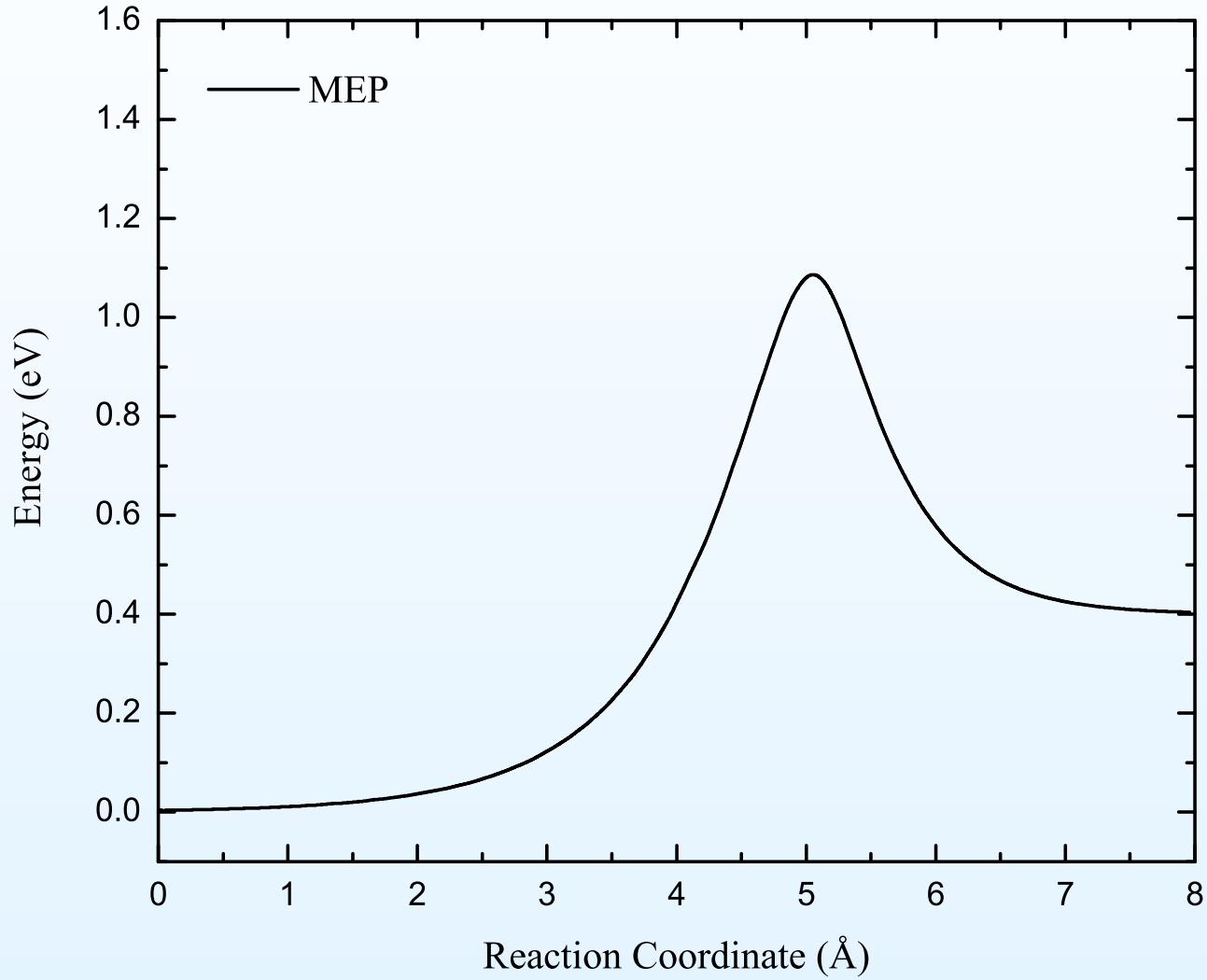
Electronic structure calculations and potential energy surface
- Electronic structure calculations
- Potential energy surface
- How to find the MEP?
- Minimum Energy Path (MEP)
- Product states for Ni(111)
- Transition states for Ni(111)
- Product states for Pt(111)
- Transition states for Pt(111)

Temperature dependence
Dynamics
Comparison with the experiments
Conclusion



$\Rightarrow E_b = 1.075$ eV and $E_p = 0.361$ eV

Product states for Ni(111)

(Ni111PSb2)

$E_p = 0.735$ eV

(Ni111PSh1b)

$E_p = 0.361$ eV

(Ni111PSh3a)

$E_p = 0.387$ eV

(Ni111PSb2n)

$E_p = 0.736$ eV

(Ni111PSh1bn)

$E_p = 0.537$ eV

(Ni111PSh3an)

$E_p = 0.553$ eV

Product states for Ni(111)

- Does the lowest product state always lead to the lowest transition state?

Product states for Ni(111)

- Does the lowest product state always lead to the lowest transition state?
- Are all transition states first order saddle points?

Transition states for Ni(111)

(Ni111TSb2)

$E_b = 1.116$ eV

(Ni111TSh1b)

$E_b = 1.075$ eV

(Ni111TSh3a)

$E_b = 1.072$ eV

(Ni111TSb2n)

$E_b = 1.101$ eV

(Ni111TSh1bn)

$E_b = 1.068$ eV

(Ni111TSh3an)

$E_b = 1.065$ eV

Product states for Pt(111)

(Pt111PSt2) (Pt111PSh1a) (Pt111PSh3b)

$E_p = 0.308$ eV $E_p = 0.182$ eV $E_p = 0.251$ eV

(Pt111PSt2n) (Pt111PSh1an) (Pt111PSh3bn)

$E_p = 0.308$ eV $E_p = 0.169$ eV $E_p = 0.225$ eV

Transition states for Pt(111)

(Pt111TSt2)

$E_b = 0.928$ eV

(Pt111TSh1a)

$E_b = 0.962$ eV

(Pt111TSh3b)

$E_b = 0.949$ eV

(Pt111TSt2n)

$E_b = 0.934$ eV

(Pt111TSh1an)

$E_b = 0.978$ eV

(Pt111TSh3bn)

$E_b = 0.955$ eV

Motivations

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Electronic structure calculations and potential energy surface

Temperature dependence

- Temperature dependence
- Electronic and mechanical effects - Ni(111)
- Mechanical effect - Ni(111)
- Electronic and mechanical effects - Pt(111)
- Mechanical effect - Pt(111)
- Electronic and mechanical effects

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Temperature dependence

Temperature dependence

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The lattice motion is modeled by allowing the Ni atom over which the reaction occurs to move normal to the surface, corresponding to the DOF Q

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● Mechanical effect - Ni(111)
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Temperature dependence

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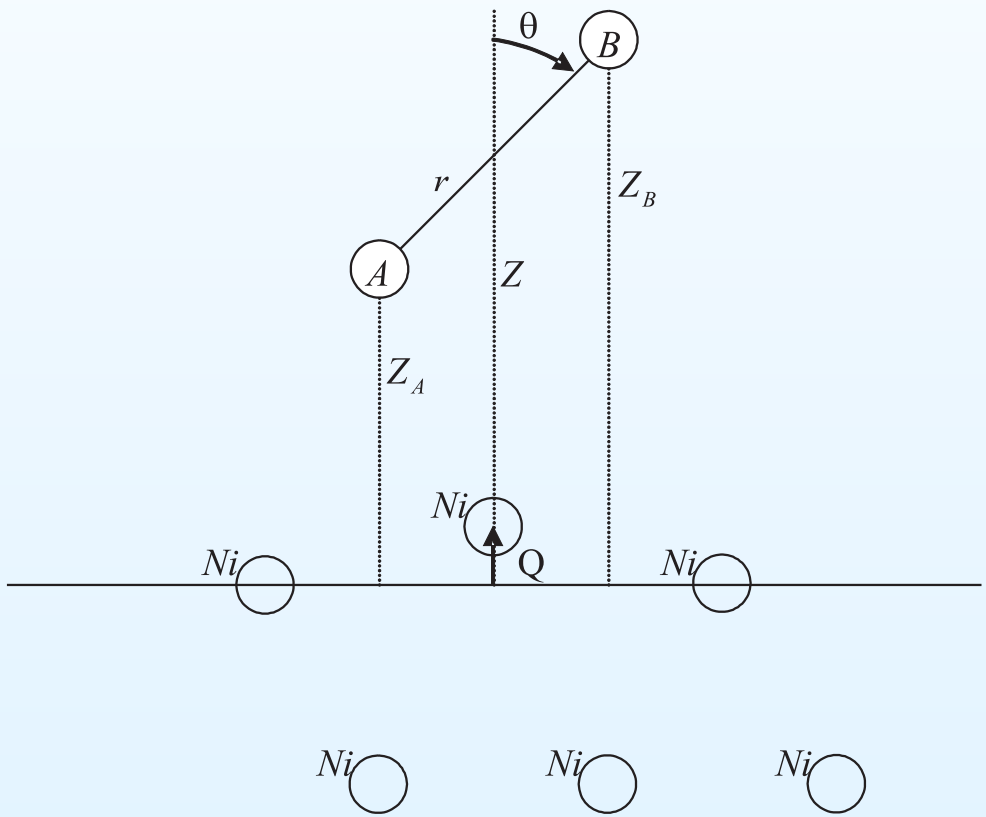

$\Rightarrow$ lattice=single oscillator (A=CH_3 and B=H)

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● Mechanical effect - Ni(111)
● Electronic and mechanical effects - Pt(111)
● Mechanical effect - Pt(111)
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Temperature dependence

- We consider two forms of the surface oscillator (SO) model:

- A Morse oscillator form (SO-M model), for which

$$V = V_0(Z - Q, r, \theta) + V_l(Q)$$

- A harmonic form (SO-H model), for which

$$V = V_0(Z - Q, r, \theta) + \frac{1}{2}\kappa Q^2$$

[Luntz and Harris, Surf. Sci. **258**, 397 (1991)]

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Temperature dependence

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$V = V_0(Z - Q, r, \theta) + \frac{1}{2}\kappa Q^2$
[Luntz and Harris, Surf. Sci. **258**, 397 (1991)]

- In our lattice reconstruction (LR) model, we allow the lattice to fully respond to the presence of the methane. For five values of Q, the MEP is computed using the CI-NEB method

Temperature dependence

Motivations

Theory

Electronic structure calculations and potential energy surface

Temperature dependence

- Temperature dependence
- Electronic and mechanical effects - Ni(111)
- Mechanical effect - Ni(111)
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- Electronic and mechanical effects

Dynamics

Comparison with the experiments

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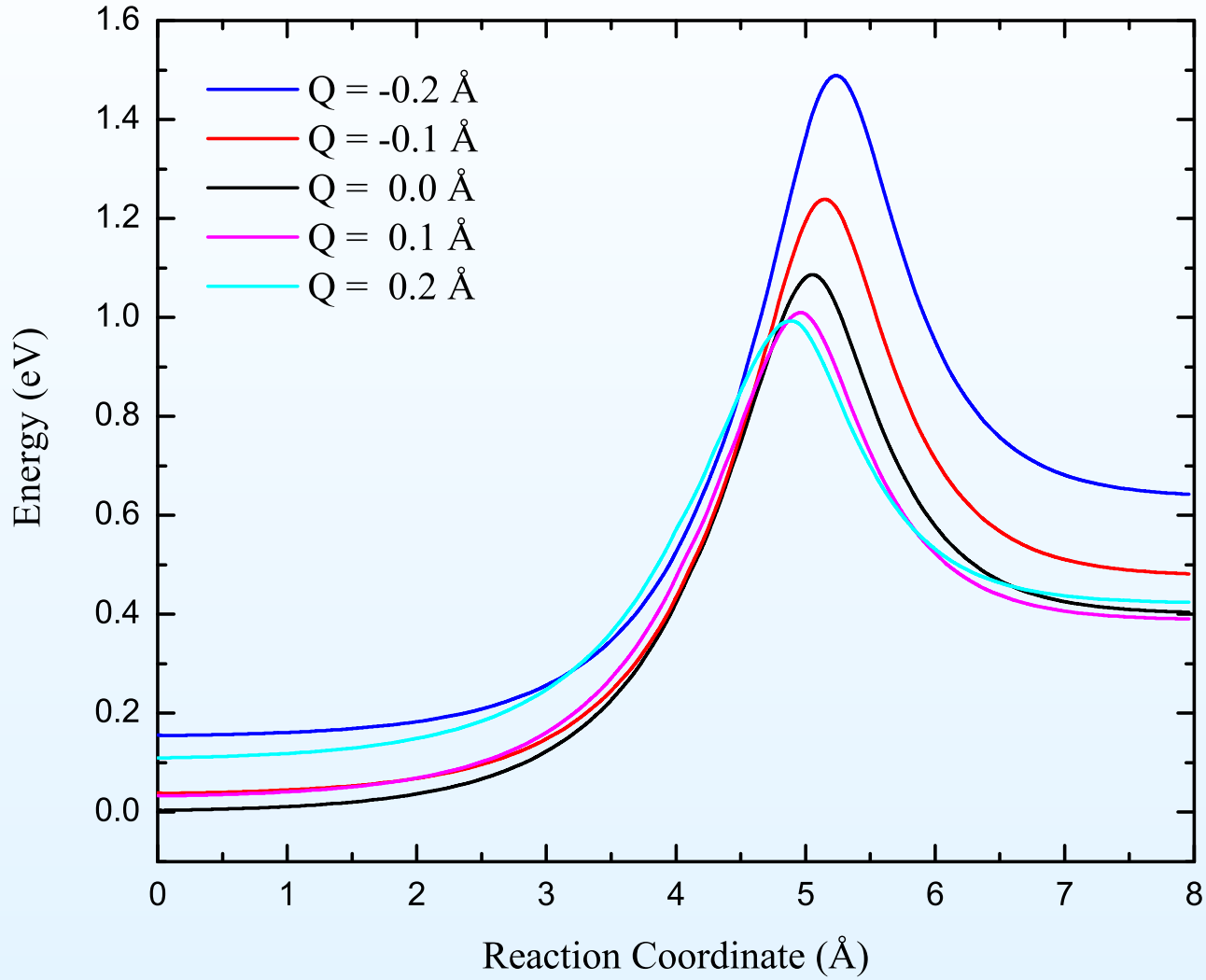

$\Rightarrow$ When Q varies, two important properties can be seen: The electronic effect, and the mechanical effect

Electronic and mechanical effects - Ni(111)

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- Mechanical effect - Pt(111)
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Ni(111)	E_b (eV)	ΔE_b (eV)	Z_b (Å)	ΔZ_b (Å)
$Q = -0.2$ Å	1.325	0.250	1.923	-0.133
$Q = -0.1$ Å	1.196	0.121	1.994	-0.063
$Q = 0.0$ Å	1.075	0.000	2.057	0.000
$Q = 0.1$ Å	0.963	-0.112	2.133	0.076
$Q = 0.2$ Å	0.862	-0.213	2.202	0.145

To fit the barrier height $E_b(Q)$, 3 LEPS parameters are made Q-dependent (D_1, D_2, and Δ_3)

Mechanical effect - Ni(111)

Motivations

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Electronic structure calculations and potential energy surface

Temperature dependence

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- Mechanical effect - Ni(111)
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- Mechanical effect - Pt(111)
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Dynamics

Comparison with the experiments

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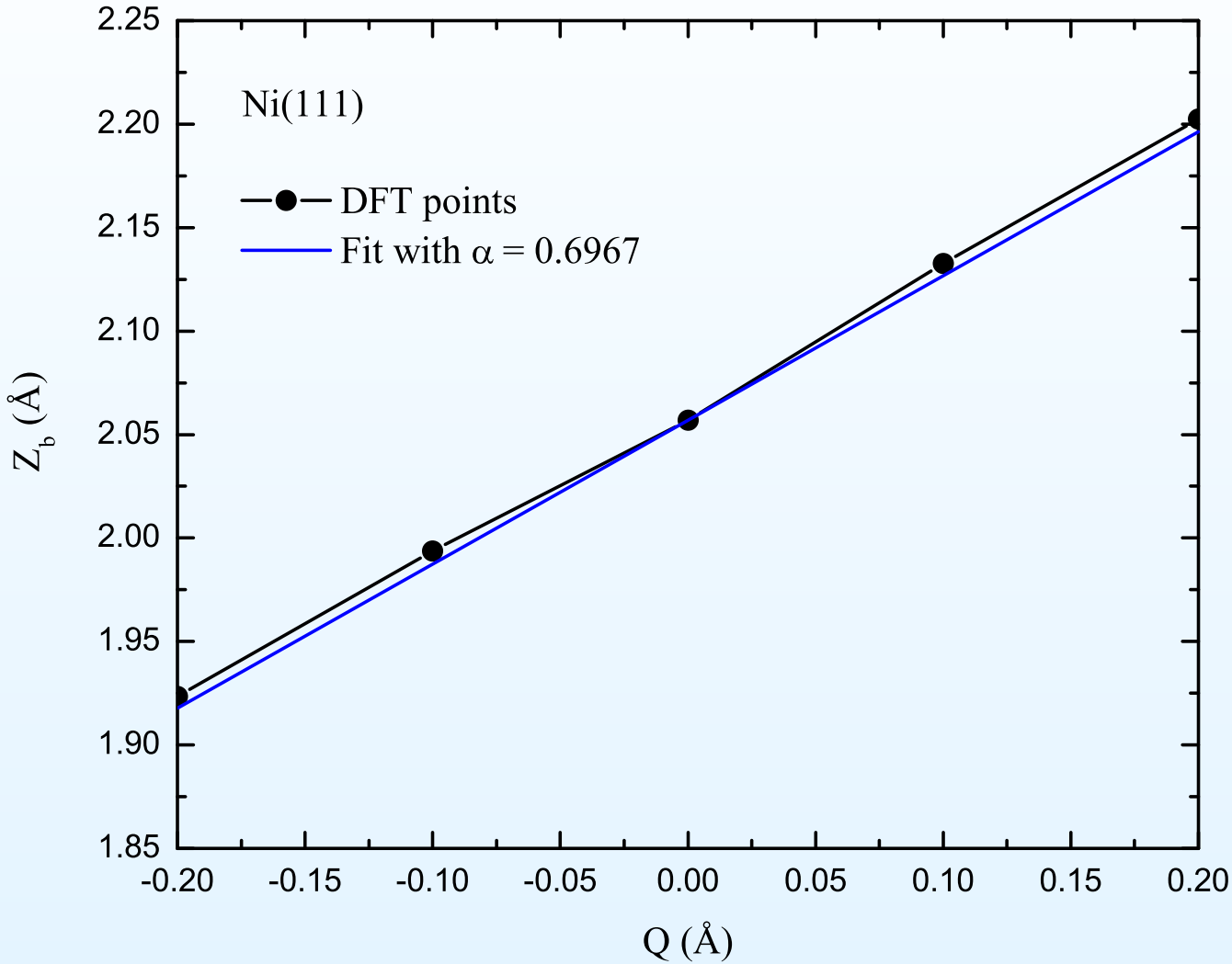

The barrier location $Z_b(Q)$ can be approximated with a linear fit, $\Rightarrow \alpha = 0.697$

Electronic and mechanical effects - Pt(111)

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Pt(111)	E_b (eV)	ΔE_b (eV)	Z_b (Å)	ΔZ_b (Å)
$Q = -0.2$ Å	1.171	0.237	2.048	-0.156
$Q = -0.1$ Å	1.041	0.107	2.123	-0.081
$Q = 0.0$ Å	0.934	0.000	2.204	0.000
$Q = 0.1$ Å	0.851	-0.083	2.289	0.085
$Q = 0.2$ Å	0.787	-0.147	2.377	0.173

To fit the barrier height $E_b(Q)$, 3 LEPS parameters are made Q-dependent (D_1, D_2, and Δ_3)

Mechanical effect - Pt(111)

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- Mechanical effect - Ni(111)
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- Mechanical effect - Pt(111)
- Electronic and mechanical effects

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Comparison with the experiments

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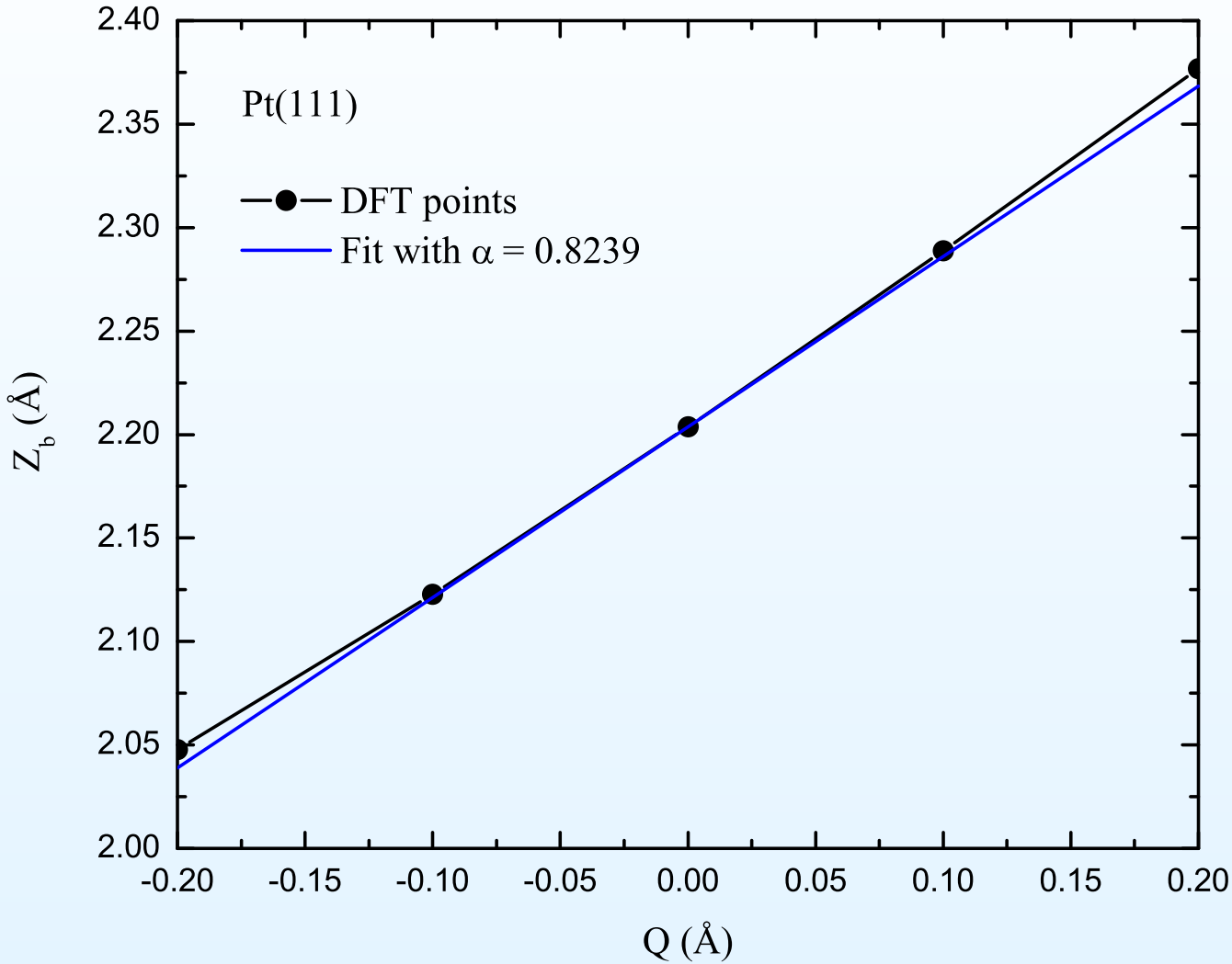

The barrier location $Z_b(Q)$ can be approximated with a linear fit, $\Rightarrow \alpha = 0.824$

Electronic and mechanical effects

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Temperature dependence
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- Mechanical effect - Pt(111)
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Conclusion

- Electronic effect: The lattice puckers during the reaction (puckering effect). The barrier becomes lower when Q increases, enhancing the reactivity

Electronic and mechanical effects

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Dynamics
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Conclusion

- Electronic effect: The lattice puckers during the reaction (puckering effect). The barrier becomes lower when Q increases, enhancing the reactivity
- Mechanical effect: The lattice atom recoils into the bulk during the reaction (recoil effect). This takes energy away from the reaction coordinate, increasing the apparent activation barrier and lowering the reactivity

Electronic and mechanical effects

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- PES: $V_0(Z, r, \theta) \Rightarrow V_{new}(Q, Z - \alpha Q, r, \theta) + V_l(Q)$

Electronic and mechanical effects

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Dynamics
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- Mechanical effect: The lattice atom recoils into the bulk during the reaction (recoil effect). This takes energy away from the reaction coordinate, increasing the apparent activation barrier and lowering the reactivity
- PES: $V_0(Z, r, \theta) \Rightarrow V_{new}(Q, Z - \alpha Q, r, \theta) + V_l(Q)$
- There is a competition between the puckering effect and the recoil effect

Motivations

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- Lattice response - CH_4 on Ni(111) and Pt(111)
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- Dynamics - CH_4 on Ni(111) and Pt(111)

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Comparison with the experiments
Conclusion

Dynamics

To compute the reaction probabilities, we use a time-dependent method involving a small time step propagator

- Hamiltonian,
$$\hat{H} = \hat{H}_0 + \hat{V} = -\frac{\hbar^2 \nabla_Q^2}{2M_s} - \frac{\hbar^2 \nabla_Z^2}{2M} - \frac{\hbar^2 \nabla_{\vec{r}}^2}{2\mu} + V(Q, Z, r, \theta),$$
where $M_s =$ Ni mass, $M = CH_4$ mass, and $\mu = CH_3$-H reduced mass

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where $M_s =$ Ni mass, $M = CH_4$ mass, and $\mu = CH_3$-H reduced mass

- Time-dependent Schrödinger equation,
$$i\hbar \frac{\partial \Psi(t)}{\partial t} = \hat{H}\Psi(t) \Rightarrow \Psi(t) = e^{-i\frac{\hat{H}}{\hbar}\Delta t}\Psi(0)$$

Dynamics

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Comparison with the experiments
Conclusion

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- Hamiltonian,
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where $M_s =$ Ni mass, $M = CH_4$ mass, and $\mu = CH_3$-H reduced mass

- Time-dependent Schrödinger equation,
$$i\hbar \frac{\partial \Psi(t)}{\partial t} = \hat{H}\Psi(t) \Rightarrow \Psi(t) = e^{-i\frac{\hat{H}}{\hbar}\Delta t}\Psi(0)$$

- Second-order Split Operator Propagator (SOP),
$$\hat{U}(\Delta t) = e^{-i\frac{\hat{H}_0}{2\hbar}\Delta t} e^{-i\frac{\hat{V}}{\hbar}\Delta t} e^{-i\frac{\hat{H}_0}{2\hbar}\Delta t} + \hat{O}(\Delta t^3)$$

Dynamics

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- Dynamics - CH_4 on Pt(111)
- Dynamics - CH_4 on Ni(111) and Pt(111)

Comparison with the experiments
Conclusion

- Initial wave function,
  $\Psi(0) = \frac{1}{r\sqrt{2\pi}}\zeta_{n_0}(Q)G(Z)\xi_{v_0}^{j_0}(r)\Theta_{j_0}^{m_0}(\theta)e^{im_0\phi}$

Dynamics

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- FBR-DVR Formalism $\Rightarrow$ Discrete transforms (Fourier, Bessel, Gauss-Legendre)

Dynamics

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Comparison with the experiments
Conclusion

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- FBR-DVR Formalism $\Rightarrow$ Discrete transforms (Fourier, Bessel, Gauss-Legendre)
- Flux-analysis to extract the reaction probabilities

Wavepacket evolution

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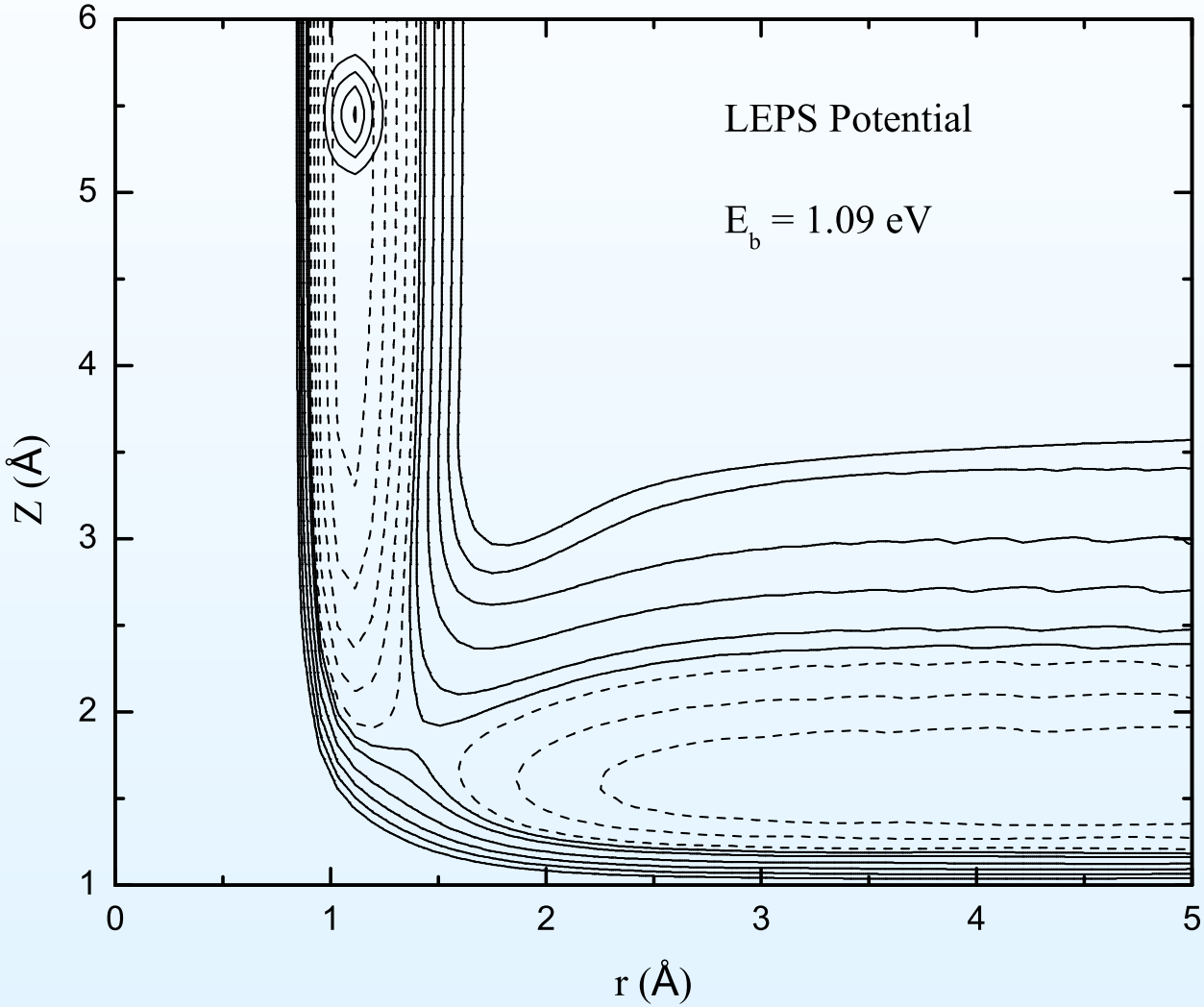
Comparison with the experiments
Conclusion

Probability density into the plane $(r0Z)$, at $t = 0$



$\Rightarrow$ the wavepacket is localized along r and Z

Wavepacket evolution

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- Wavepacket evolution
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- Dynamics - CH_4 on Ni(111) and Pt(111)

Comparison with the experiments

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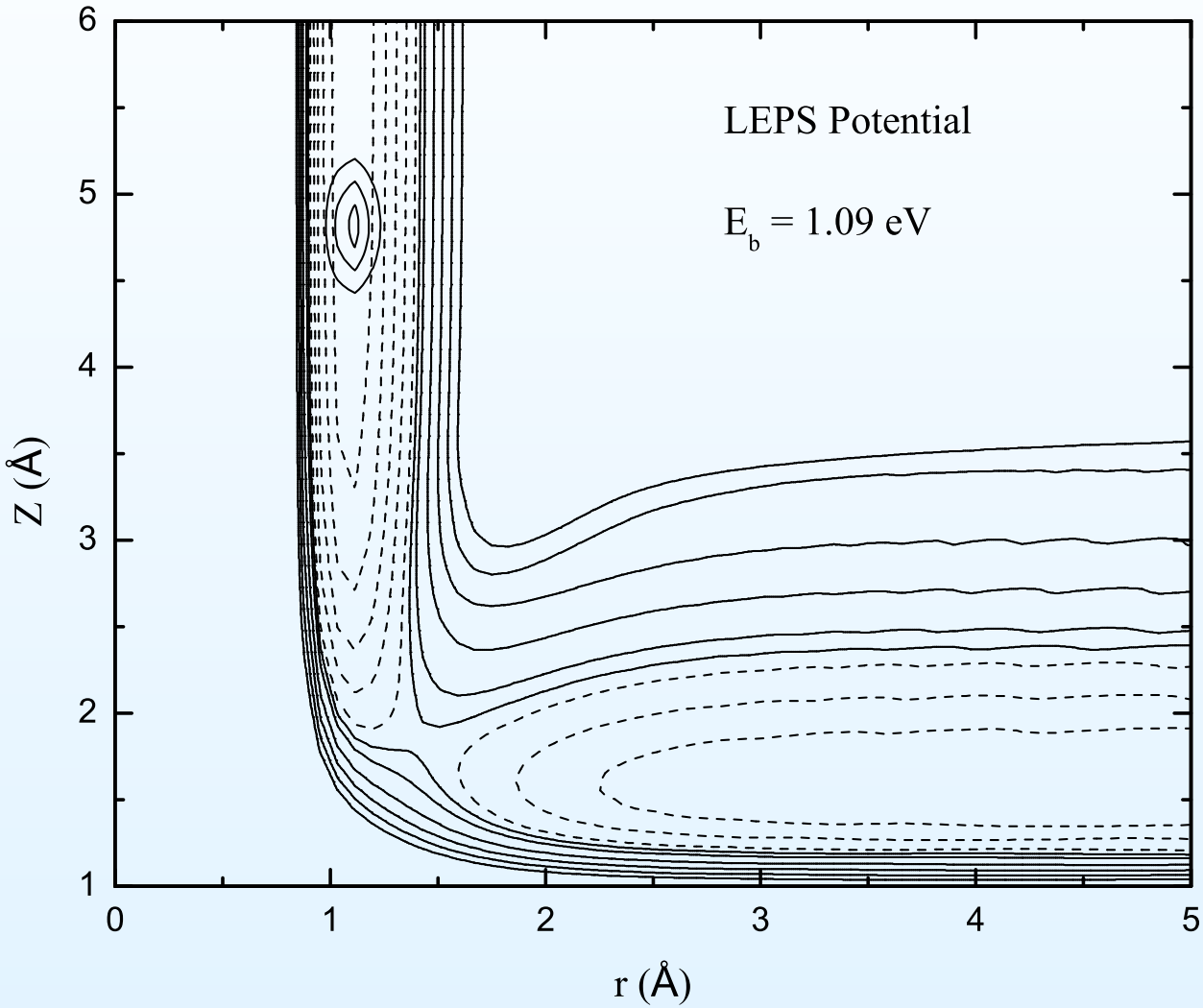
Probability density into the plane $(r0Z)$, at $t = 50\Delta t$



Wavepacket evolution

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Comparison with the experiments

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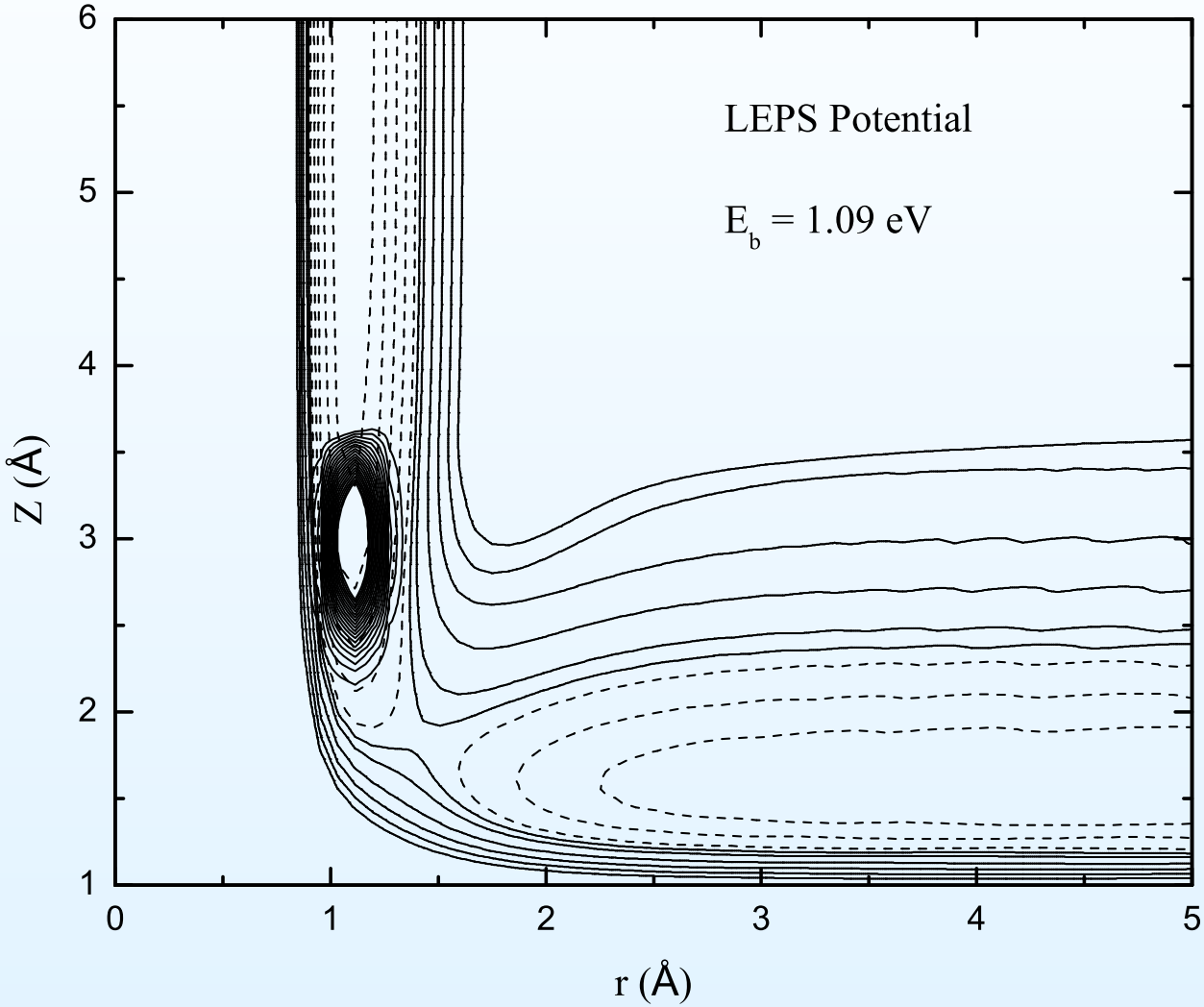
Probability density into the plane $(r0Z)$, at $t = 200\Delta t$



Wavepacket evolution

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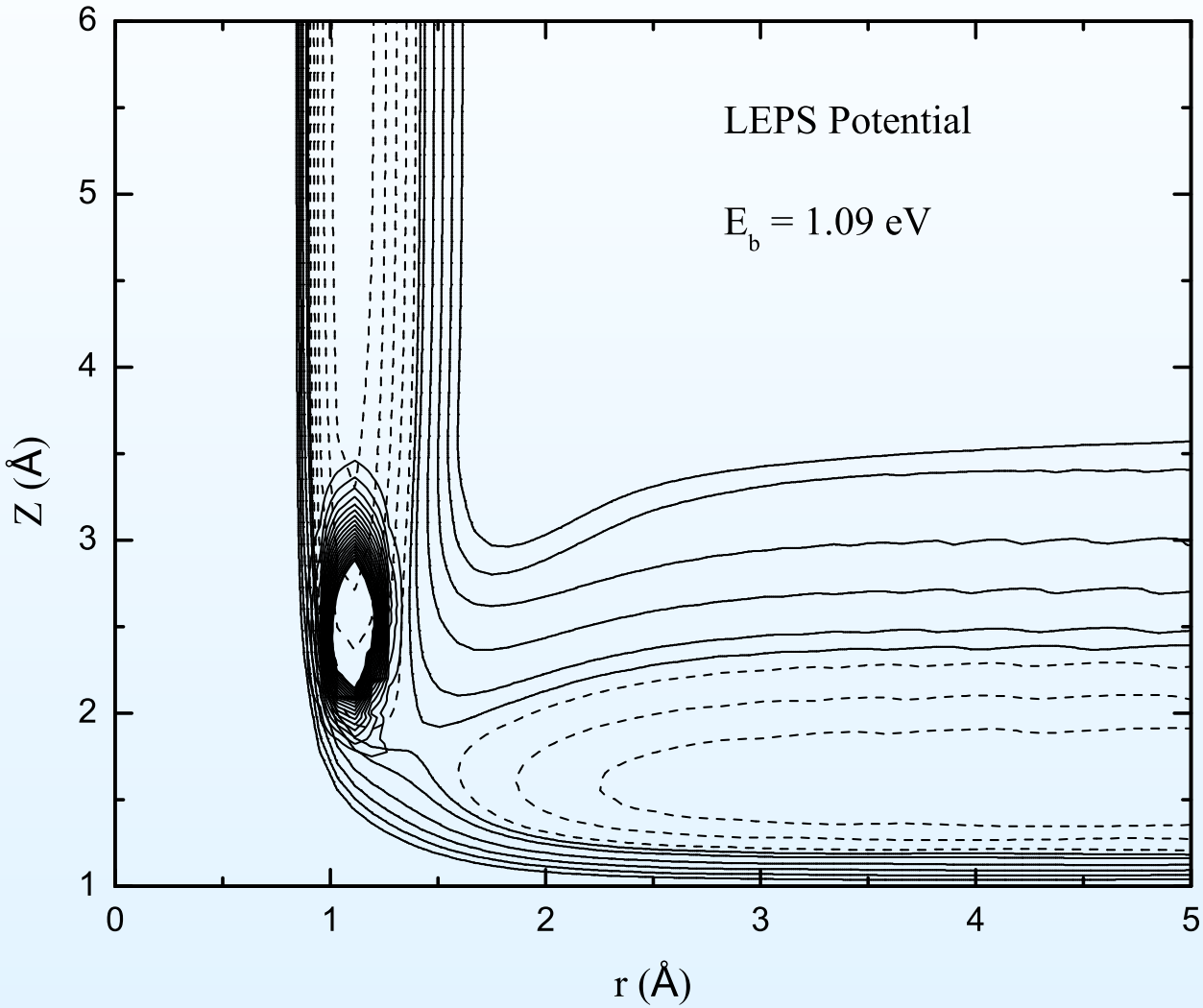
- Dynamics - CH_4 on Ni(111) and Pt(111)

Comparison with the experiments

Conclusion

Probability density into the plane $(r0Z)$, at $t = 250\Delta t$



Wavepacket evolution

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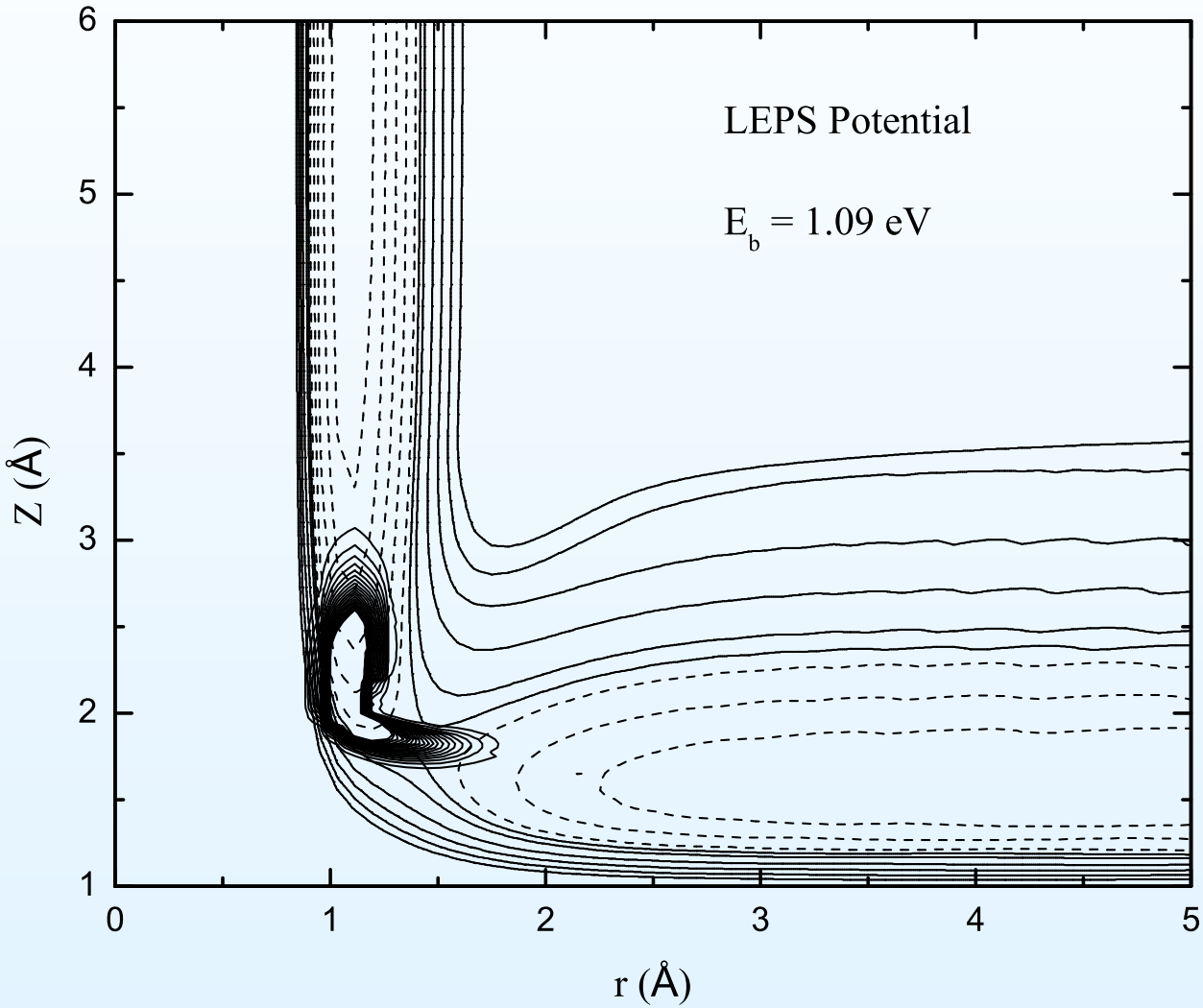
Comparison with the experiments
Conclusion

Probability density into the plane $(r0Z)$, at $t = 300\Delta t$



$\Rightarrow \langle Z \rangle$ is minimum, the flux analysis can start

Wavepacket evolution

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- Dynamics - CH_4 on Pt(111)
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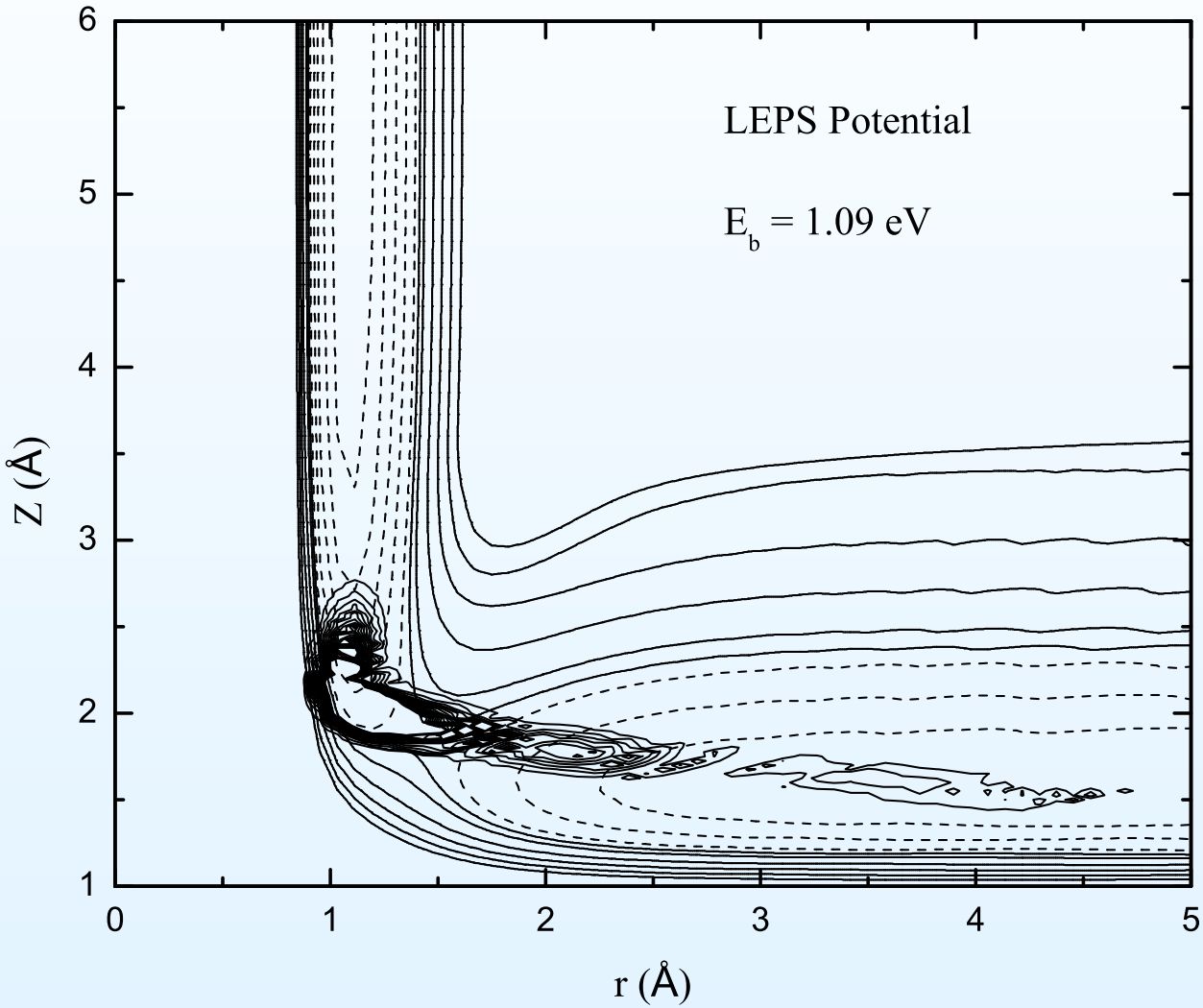
Comparison with the experiments

Conclusion

Probability density into the plane $(r0Z)$, at $t = 350\Delta t$



Wavepacket evolution

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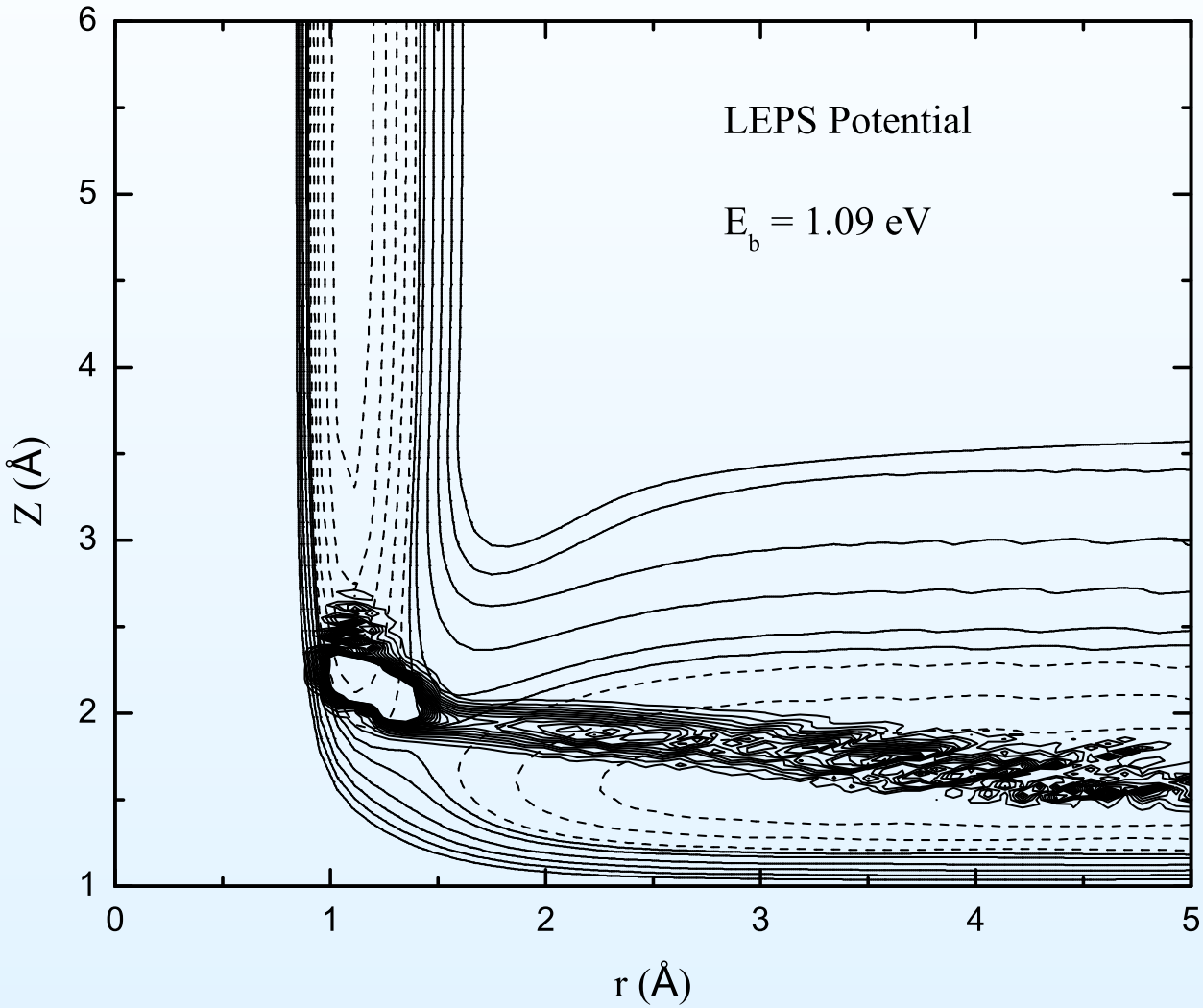
- Lattice response - CH_4 on Ni(111) and Pt(111)
- Dynamics - CH_4 on Ni(111)
- Dynamics - CH_4 on Pt(111)
- Dynamics - CH_4 on Ni(111) and Pt(111)

Comparison with the experiments
Conclusion

Probability density into the plane $(r0Z)$, at $t = 400\Delta t$



Wavepacket evolution

Motivations

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Electronic structure calculations and potential energy surface

Temperature dependence

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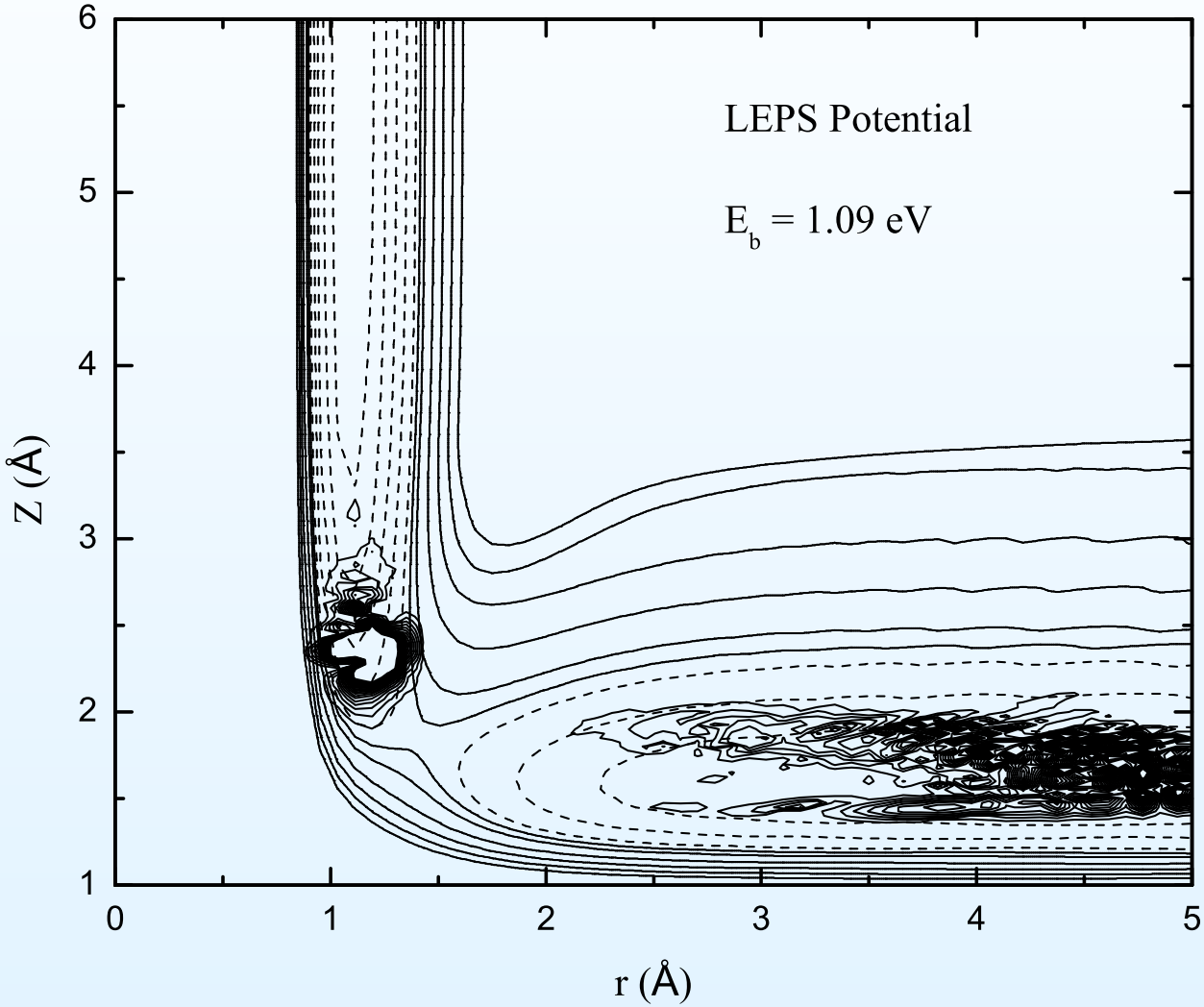
- Wavepacket evolution
- Lattice response - CH_4 on Ni(111) and Pt(111)
- Dynamics - CH_4 on Ni(111)
- Dynamics - CH_4 on Pt(111)
- Dynamics - CH_4 on Ni(111) and Pt(111)

Comparison with the experiments

Conclusion

Probability density into the plane $(r0Z)$, at $t = 450\Delta t$



Lattice response - CH_4 on Ni(111) and Pt(111)

Motivations

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Electronic structure calculations and potential energy surface

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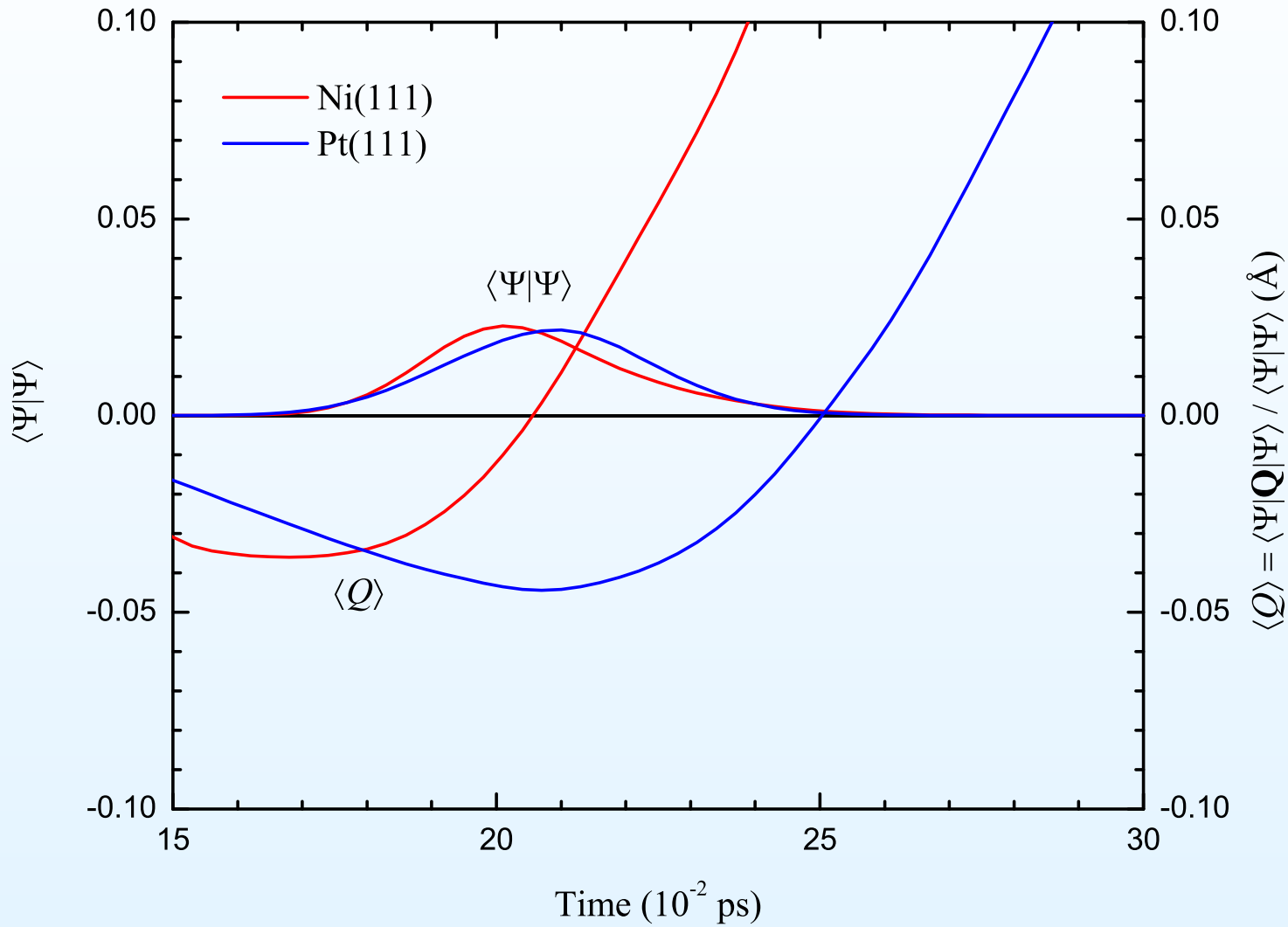
- Lattice response - CH_4 on Ni(111) and Pt(111)
- Dynamics - CH_4 on Ni(111)
- Dynamics - CH_4 on Pt(111)
- Dynamics - CH_4 on Ni(111) and Pt(111)

Comparison with the experiments

Conclusion



Dynamics - CH_4 on Ni(111)

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Temperature dependence

Dynamics

- Dynamics
- Wavepacket evolution
- Lattice response - CH_4 on Ni(111) and Pt(111)
- Dynamics - CH_4 on Ni(111)
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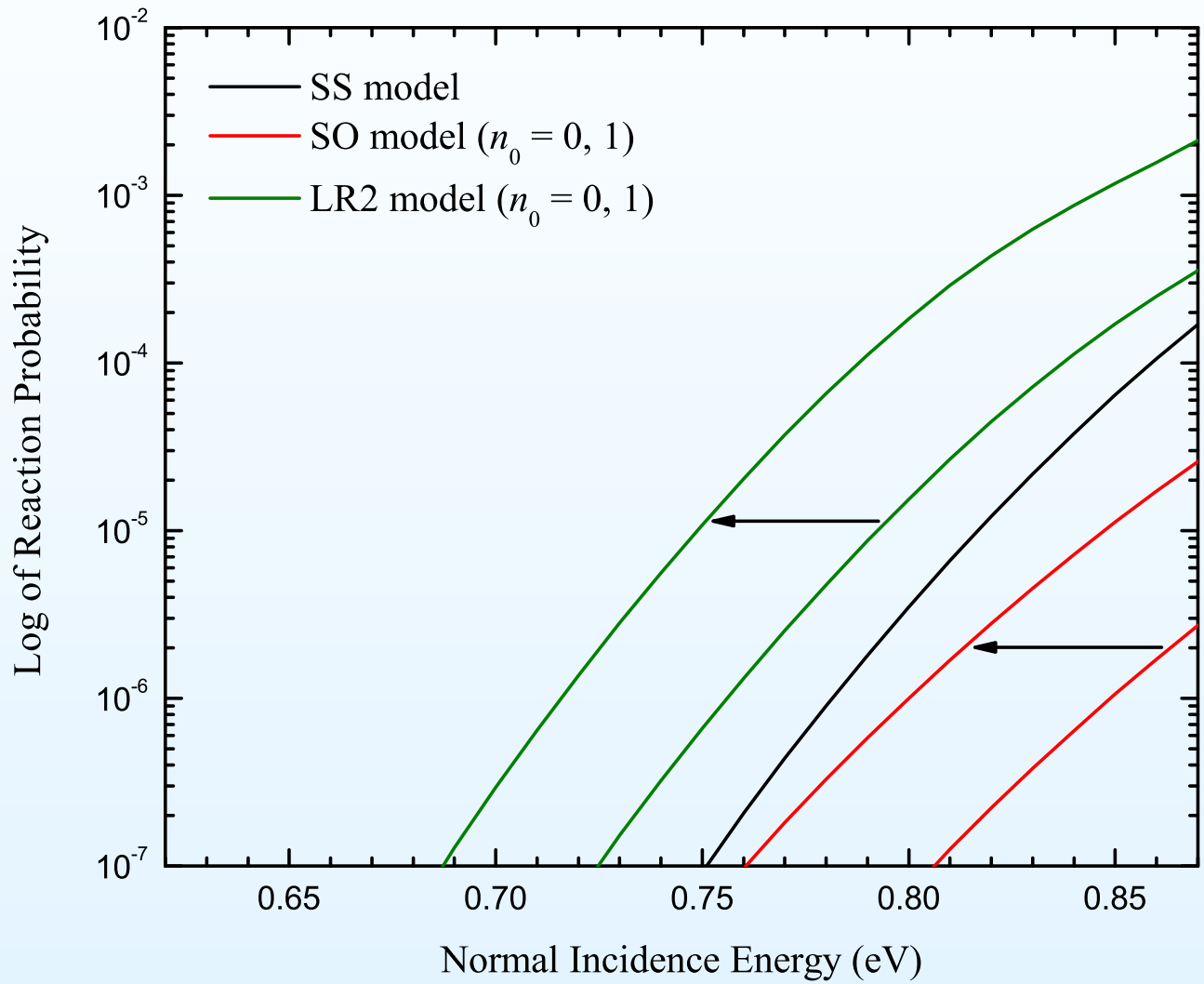
- Dynamics - CH_4 on Ni(111) and Pt(111)

Comparison with the experiments

Conclusion



Dynamics - CH_4 on Pt(111)

Motivations

Theory

Electronic structure calculations and potential energy surface

Temperature dependence

Dynamics

- Dynamics
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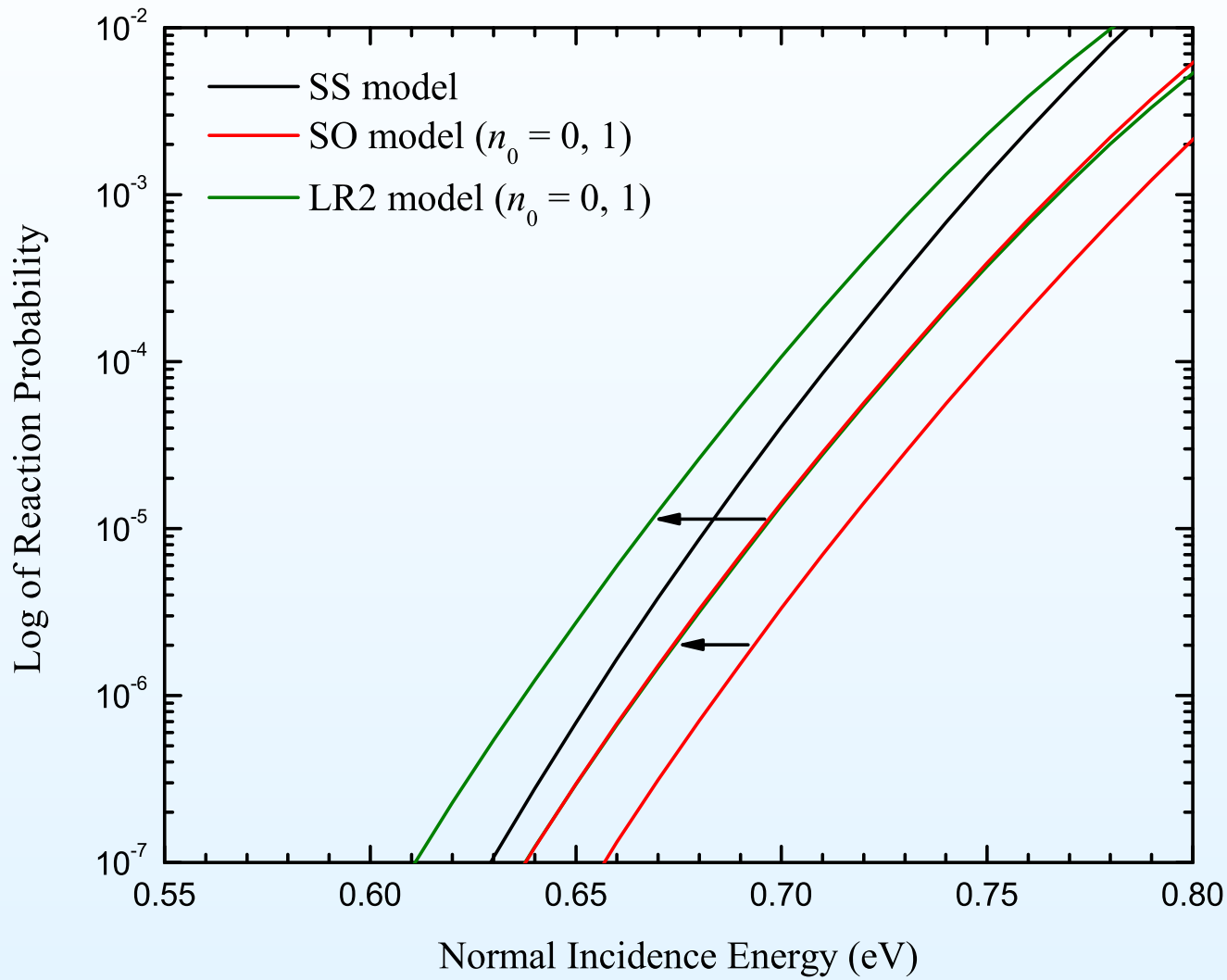
- Dynamics - CH_4 on Ni(111)
- Dynamics - CH_4 on Pt(111)
- Dynamics - CH_4 on Ni(111) and Pt(111)

Comparison with the experiments

Conclusion



Dynamics - CH_4 on Ni(111) and Pt(111)

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Comparison with the experiments
Conclusion

- Reaction probabilities for a given n_0 are computed with a 4D (Q, Z, r, θ) time-dependent wavepacket method (n_0 is the initial lattice quantum number)

Dynamics - CH_4 on Ni(111) and Pt(111)

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Comparison with the experiments
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- Reaction probabilities for a given n_0 are computed with a 4D (Q, Z, r, θ) time-dependent wavepacket method (n_0 is the initial lattice quantum number)
- Reaction probabilities for a given surface temperature (T_s) are computed by Boltzmann averaging the previous results over n_0

Dynamics - CH_4 on Ni(111) and Pt(111)

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- Reaction probabilities for a given n_0 are computed with a 4D (Q, Z, r, θ) time-dependent wavepacket method (n_0 is the initial lattice quantum number)
- Reaction probabilities for a given surface temperature (T_s) are computed by Boltzmann averaging the previous results over n_0
- However, energy levels spacings are very small for both Ni(111) and Pt(111) (≈ 21 meV for Ni(111) and ≈ 11 meV for Pt(111))

Dynamics - CH_4 on Ni(111) and Pt(111)

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- Reaction probabilities for a given n_0 are computed with a 4D (Q, Z, r, θ) time-dependent wavepacket method (n_0 is the initial lattice quantum number)
- Reaction probabilities for a given surface temperature (T_s) are computed by Boltzmann averaging the previous results over n_0
- However, energy levels spacings are very small for both Ni(111) and Pt(111) (≈ 21 meV for Ni(111) and ≈ 11 meV for Pt(111))

$\Rightarrow$ Many n_0 states are required to converge the Boltzmann distribution (≈ 20 states for Ni(111) and ≈ 50 states for Pt(111))

Dynamics - CH_4 on Ni(111) and Pt(111)

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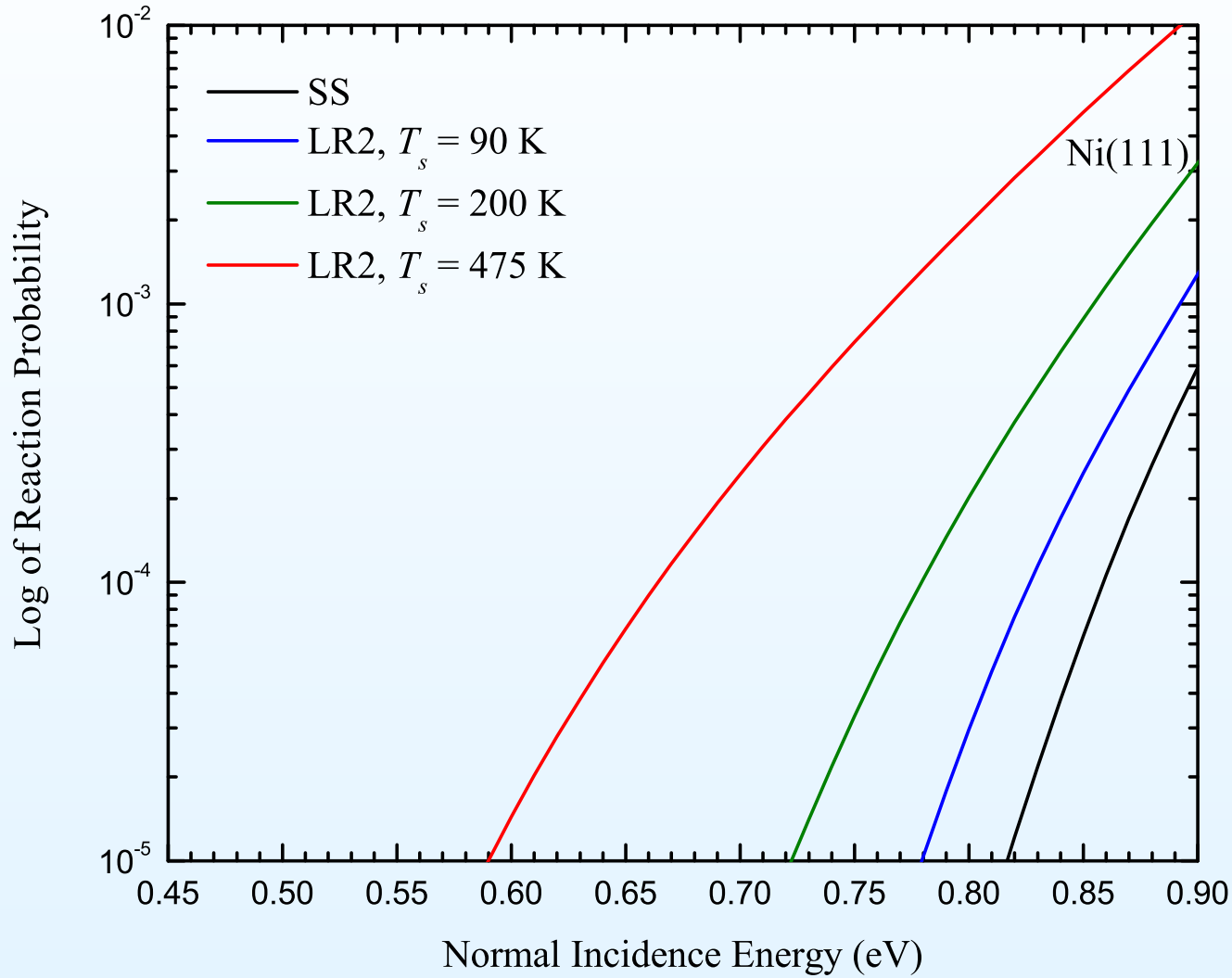

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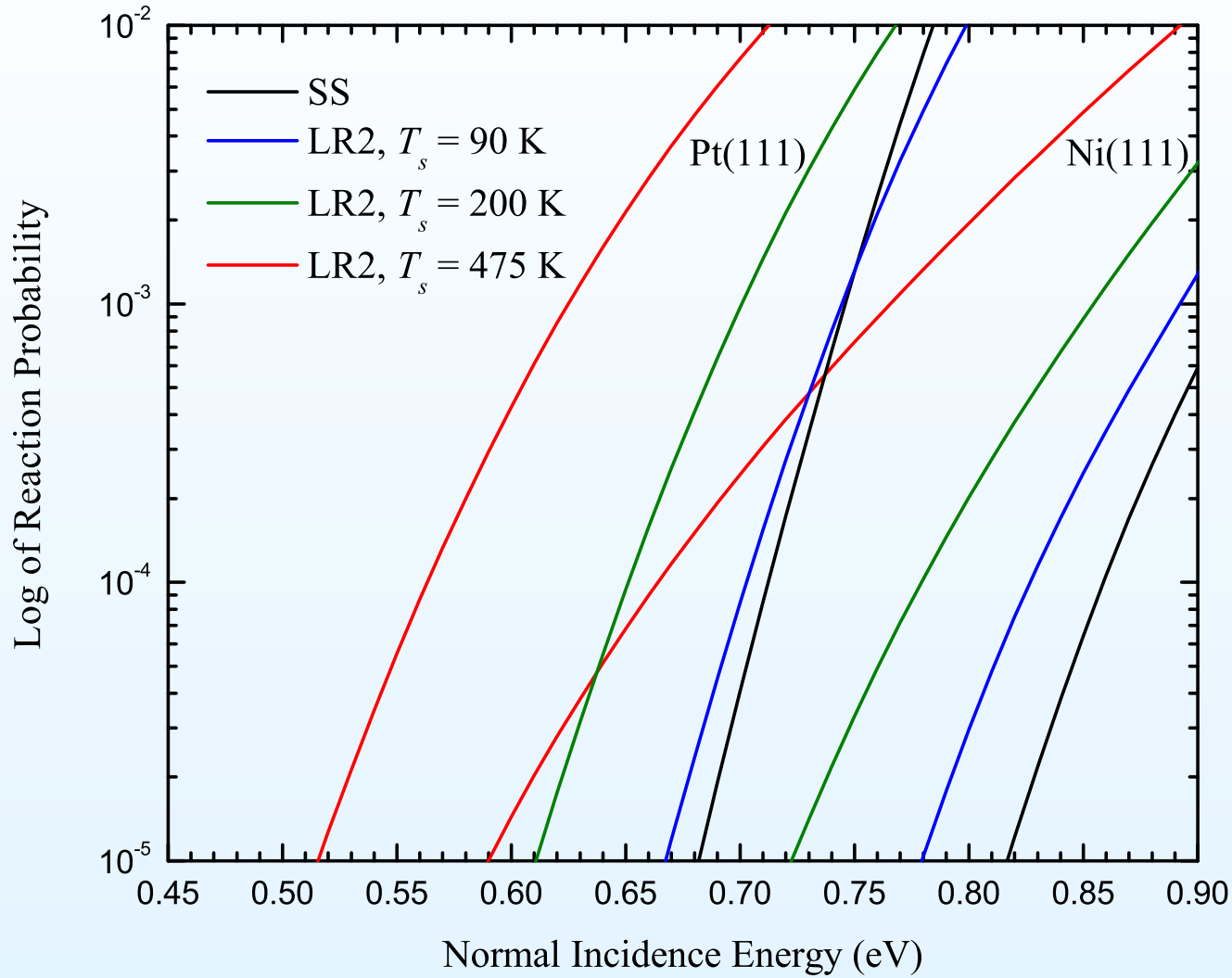

Motivations

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Comparison with the experiments

- Experiments from Killelea and Utz - CD_3H on Ni(111)
- Experiments from Campbell and Utz - CH_4 on Ni(111)
- Experiments from Bisson *et al.* - CH_4 on Ni(111) and Pt(111)

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Experiments from Killelea and Utz - CD_3H on Ni(111)

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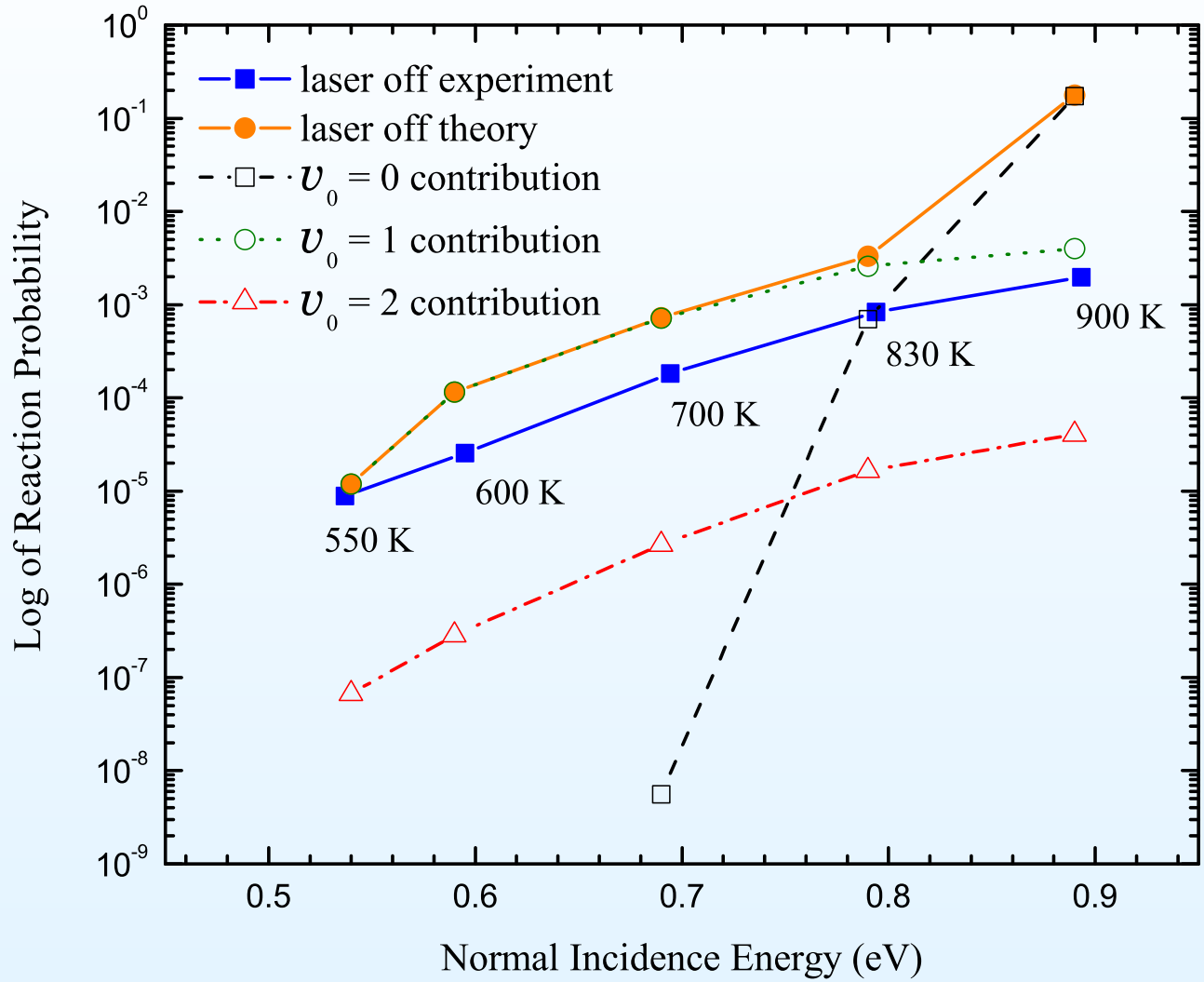

Surface temperature, $T_s = 90$ K

Experiments from Campbell and Utz - CH_4 on Ni(111)

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Comparison with the experiments

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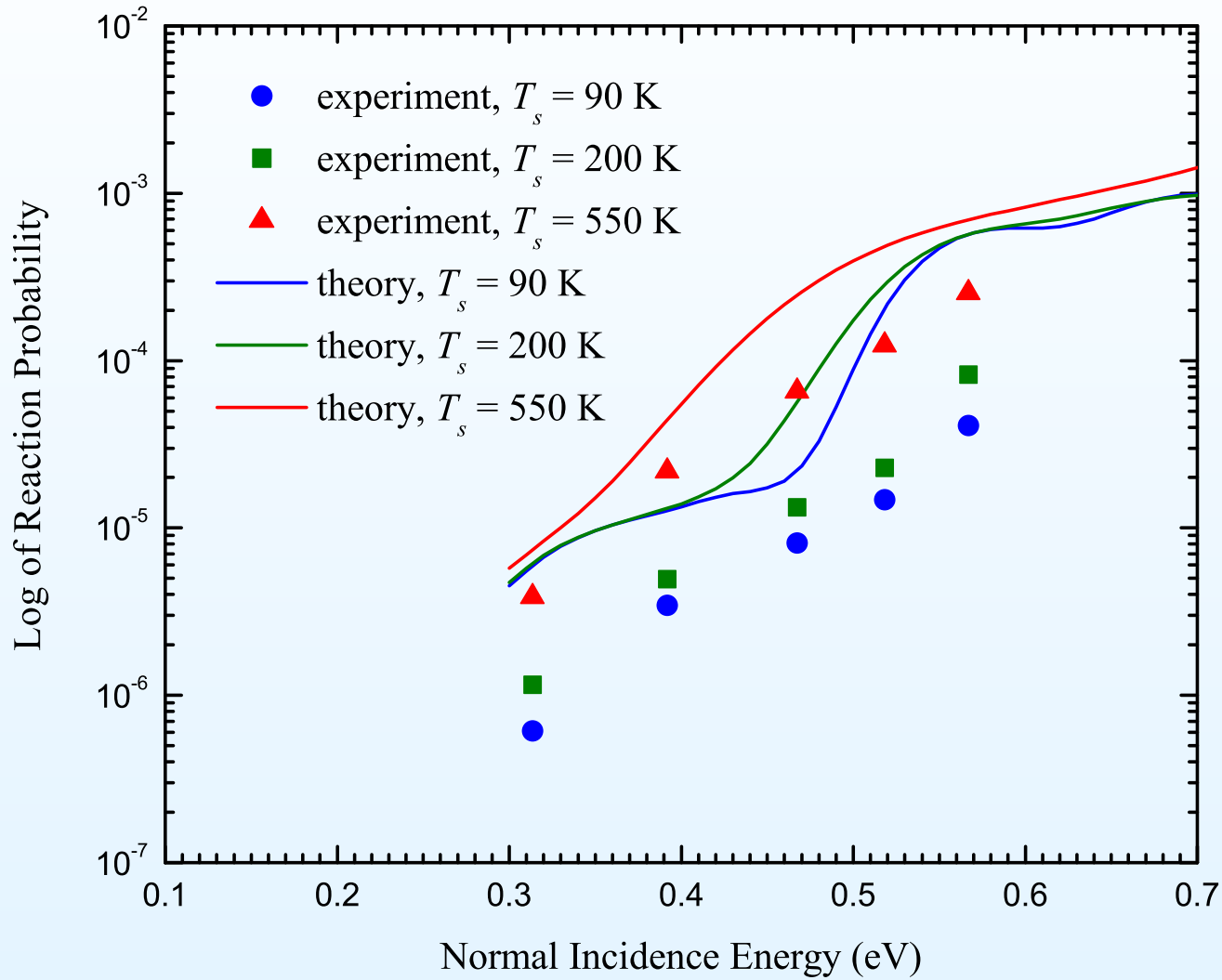

Experiments from Campbell and Utz - CH_4 on Ni(111)

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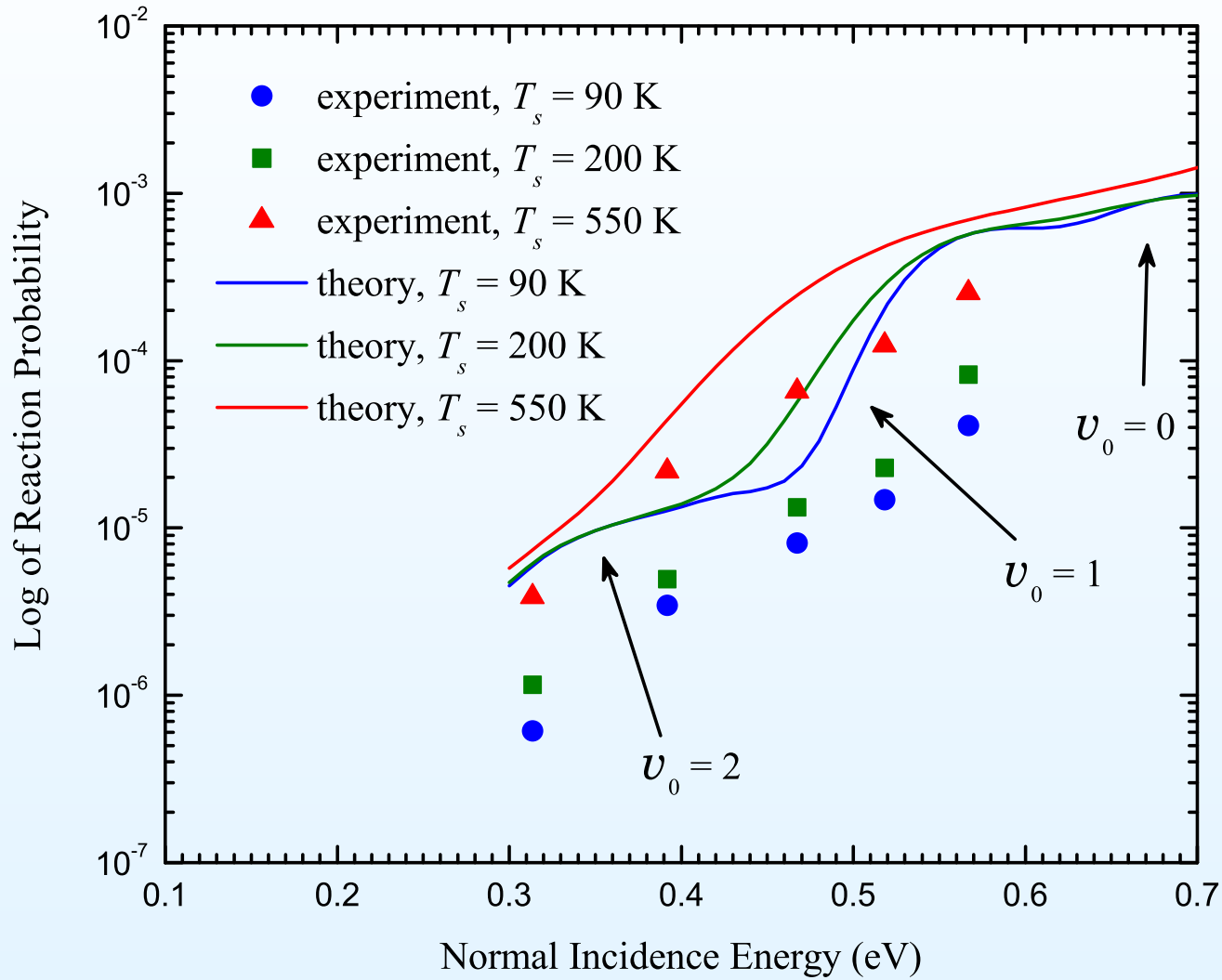

Nozzle temperature, $T_n = 700$ K

Experiments from Bisson *et al.* - CH_4 on Ni(111) and Pt(111)

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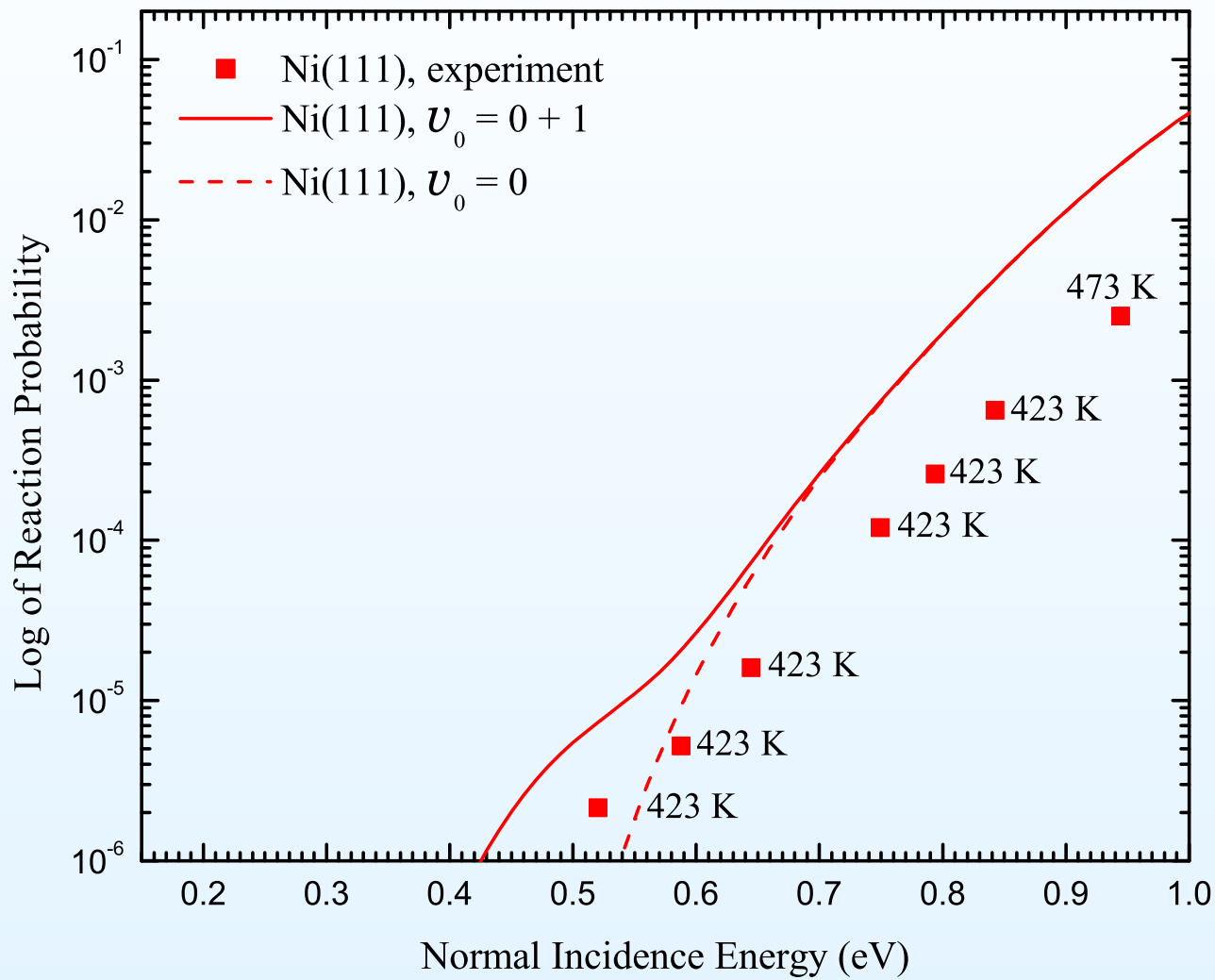

$T_s = 475$ K for Ni(111)

Experiments from Bisson *et al.* - CH_4 on Ni(111) and Pt(111)

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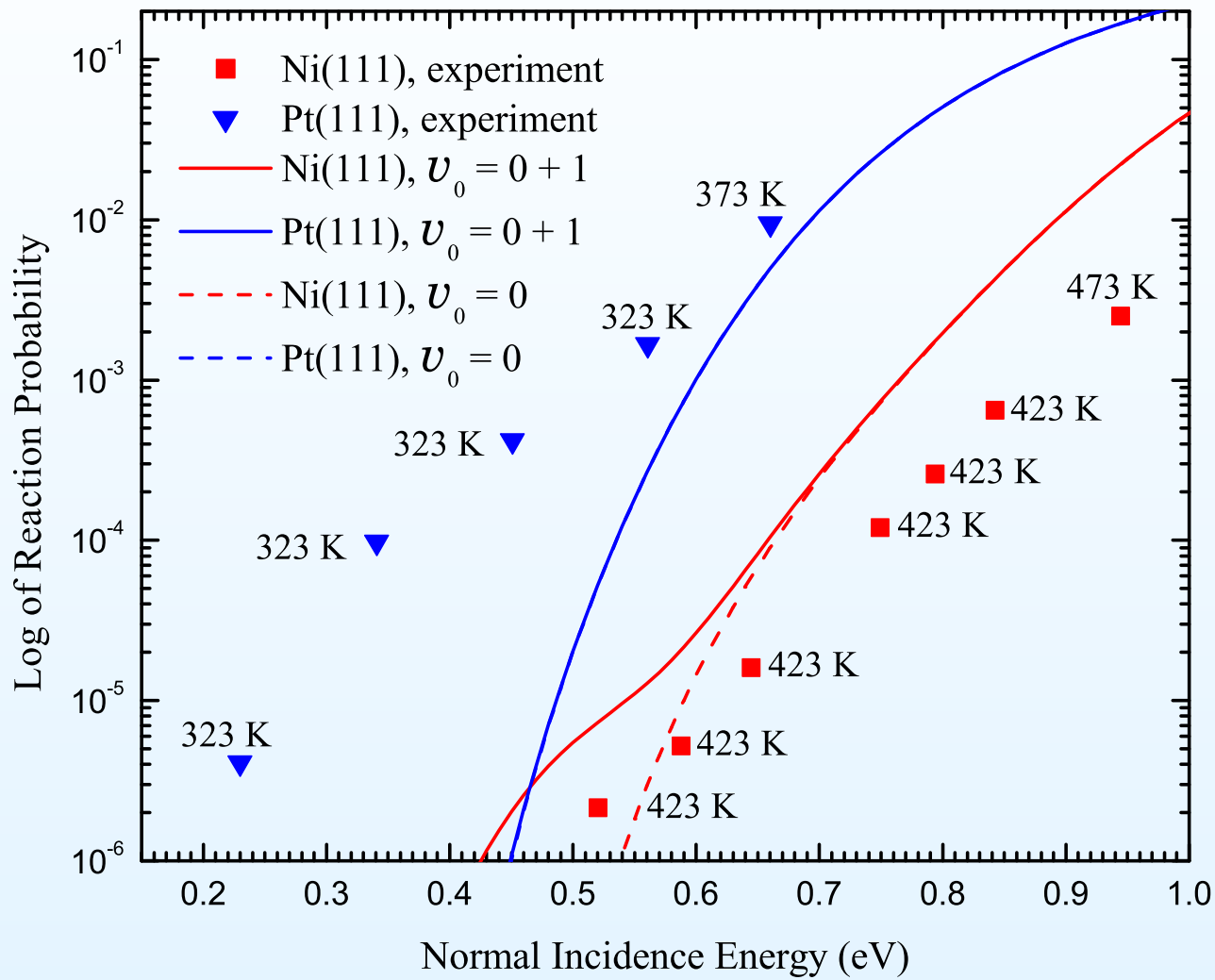

$T_s = 475$ K for Ni(111), and 600 K for Pt(111)

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Conclusion

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- Results for Ni(111) and Pt(111) published in:

- S. Nave and B. Jackson, Phys. Rev. Lett. **98**, 173003 (2007)
- S. Nave and B. Jackson, J. Chem. Phys. **127**, 224702 (2007)
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- Lack of reactivity for CH_4 on Pt(111)

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- Lack of reactivity for CH_4 on Pt(111)
- Extend this method to the Ni(100), Pt(100), and Pt(110)-(1$\times$2) surfaces

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- Lack of reactivity for CH_4 on Pt(111)
- Extend this method to the Ni(100), Pt(100), and Pt(110)-(1$\times$2) surfaces
- Treat Z and Q classically to save some computing time

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Conclusion and perspectives

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- Lack of reactivity for CH_4 on Pt(111)
- Extend this method to the Ni(100), Pt(100), and Pt(110)-(1$\times$2) surfaces
- Treat Z and Q classically to save some computing time
- Additional DFT calculations might be needed, in particular to characterize the Q-dependence