Molecular Dynamics Study of Vibrationally Excited N_2 Dissociation on a Ru(0001) Surface

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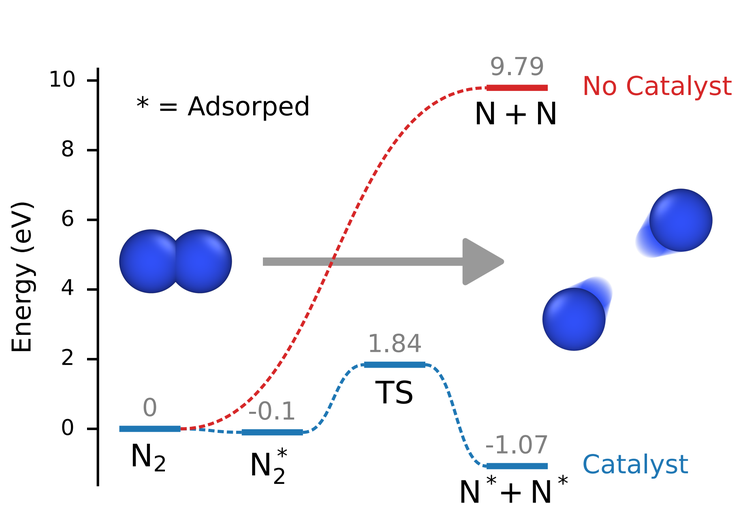
Plasma Catalysis

- Plasmas may be more efficient alternatives for ammonia production.
- Vibrational excitations play an important role in the reactivity of a plasma.
- Current models underestimate the reactivity of vibrational excitations.

Ru(0001) catalyst **lowers the energy barrier** for splitting of N_2



Transition State Theory

reaction rate:

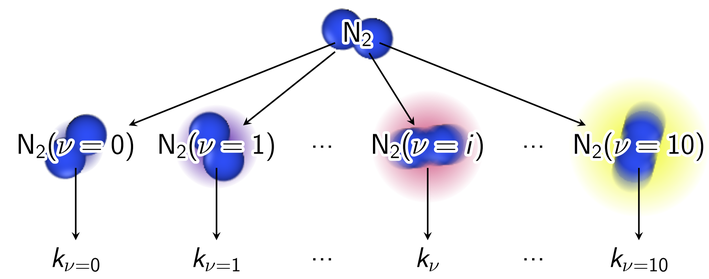
$$r = k[A][B]$$

Rate constant:

$$k = C \exp\left(\frac{-E_{\text{barrier}}}{k_B T}\right)$$

Independent of vibrational excitations

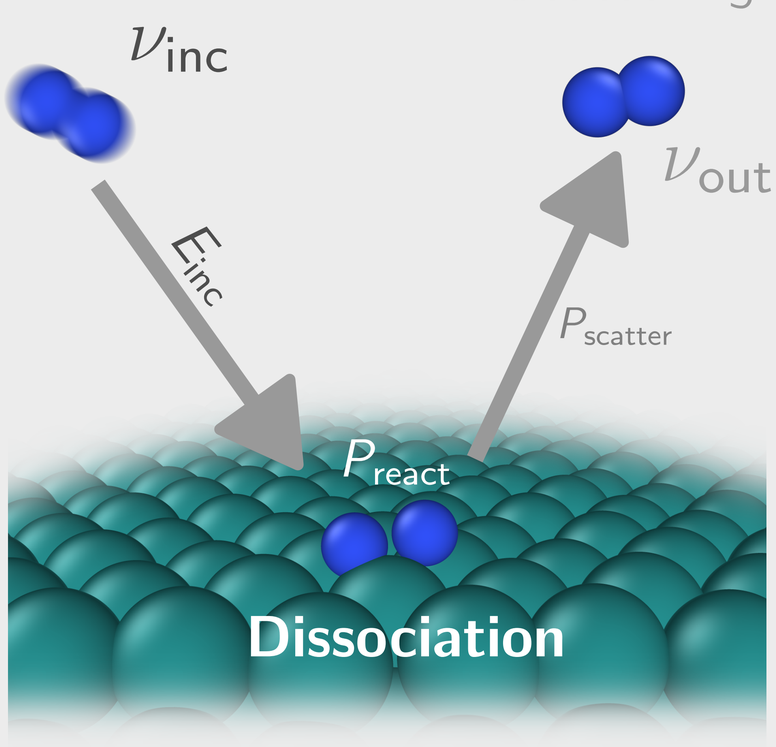
Making rates account for vibrational energy by giving **each state its own rate constant** [1]



$$k(\nu) = C \exp\left(\frac{-(E_{\text{barrier}} - \alpha E_{\text{vib}}(\nu))}{k_B T}\right)$$

Quasi-Classical Trajectories

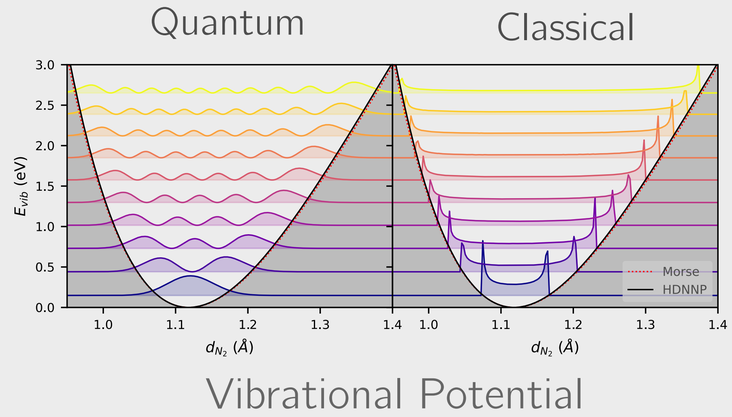
- Quasi-Classical: Initial (ro)vibrational energies are quantized according to Schrödinger equation.
- Classical molecular dynamics with LAMMPS: Quantization is not preserved!
- Machine learned potential based on RPBE density functional theory.[3]



Quantum vs Classical

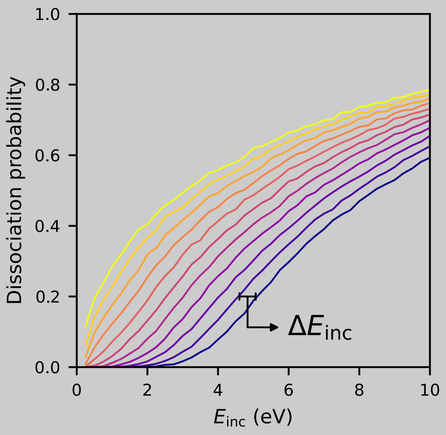
Quantum mechanics is too slow.
Classical MD lacks quantization, tunneling etc.
Middle ground: Classical energy of incoming molecule is quantized with quantum mechanical eigenenergies.

Quantum wave functions and quantized classical vibration

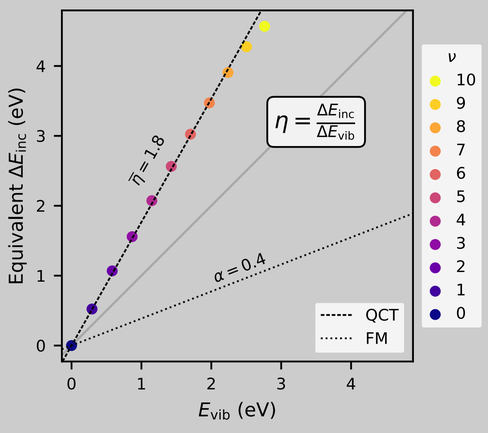


Vibrational Energy Contributions

Vibrational energy equals effective increase in Kinetic energy



The effective energy gain is more than the vibrational energy invested



Computing Reactivity

- We compute vibrational energy contributions from reaction probabilities of excited N_2 molecules.
- Using the computed reaction probabilities we see that vibrational excitations are way more reactive.
- A microkinetic model shows that the reactivity of plasmas are much higher than result from previous model.

Plasma reactivity is much higher according to dynamics

Vibrational excitations dominate N2 dissociation

Simple models do not match dynamics

Current simple approach: Fridman-Macheret model (FM) [2]

$$\alpha = \frac{E_{\text{barrier}}}{2E_{\text{barrier}} - E_{\text{reaction}}} \approx 0.4$$

Vibrational contributions from MD (Hybrid)

$$\alpha = \overline{\eta} \approx 1.8$$

MD reaction probabilities (Dynamics)

$$\langle P_\nu \rangle^{\text{QCT}} = \int_0^\infty f_{\text{MB}}(E_{\text{inc}})\, P_\nu(E_{\text{inc}})\, \mathrm{d}E_{\text{inc}}$$

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References:
[1] Mehta, P. et al. Nat. Catal. 2018, 1, 269–275
[2] Fridman, A., Plasma Chemistry; Cambridge University Press, 2008.
[3] Shakouri, K. et al. J. Phys. Chem. Lett. 2017, 8, 2131–2136.

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