Reactive Scattering of N_2 on Ru(0001): High Incidence and Vibrational Energies

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Overview

Vibrational pre-excitation has recently been discussed as a way to activate N_2 molecules on ruthenium surfaces via plasma-enabled catalysis, which allows to overcome scaling relations for ammonia synthesis.[1,2] In this context, the enhancement of the dissociative sticking (=dissociative chemisorption) probability plays a key role. However, well-defined experimental data from **molecular beam experiments** is limited to N_2 incidence energies of $\leq 3.2\,\mathrm{eV}$[3–5], and microkinetic models have only estimated the promotion of N_2 dissociation due to vibrational pre-excitation based on simple models.[1]

In this work, we use the **high dimensional neural network potential (HDNNP)** energy surface constructed in earlier work from the Leiden group[6] to calculate **dissociative chemisorption (DC)** probabilities ($\to$ ③) as a function of incidence energy and initial vibrational state of the incoming N_2 molecules ($\to$ ①). We use the so-called quasi-classical trajectory (QCT) method as implemented in the LAMMPS code.[7] The HDNNP is based on density functional theory calculations using the RPBE functional[8], originally targeting the energy regime relevant for the aforementioned molecular beam experiments in which the N_2 vibrational ground state dominates ($\to$ ②). Consequently, care must be taken when extrapolating to the higher energy regime that is of interest here ($\to$ ④).
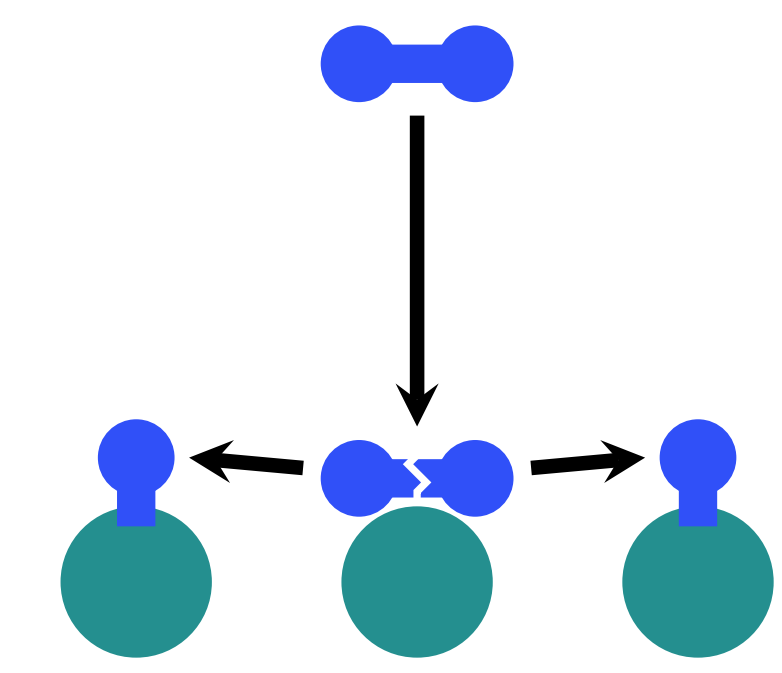
Types of Surface Interactions
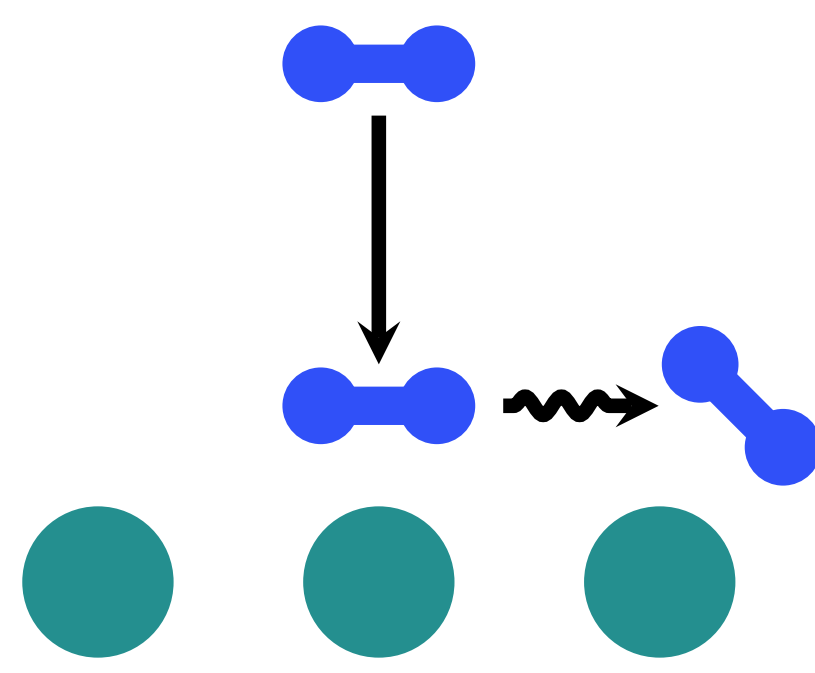
**Trapping**: The molecule is captured by the surface potentials and hovers above it for several picoseconds.
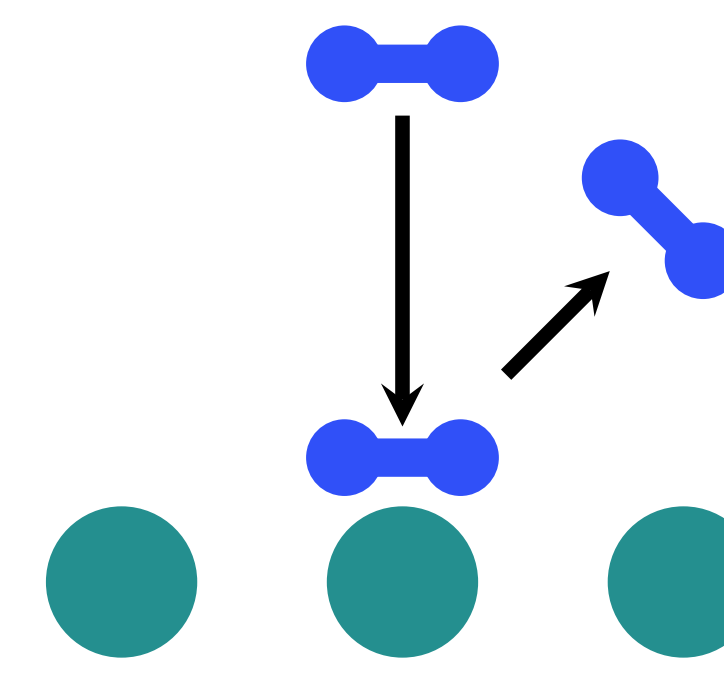
Scattering: The molecule bounces off the surface and returns back to the gas phase.

Dissociative Chemisorption: The molecules bond breaks and the halves bond to the surface.

① N_2 Vibrational States

- Using Fourier Grid Hamiltionian[9] with the HDNNP to compute vibrational states.

- In agreement with established Morse potential and spectrum with $\omega_0 = 2358.57\,\mathrm{cm}^{-1}$ and $\omega_0 x_0 = 14.324\,\mathrm{cm}^{-1}$ [10].

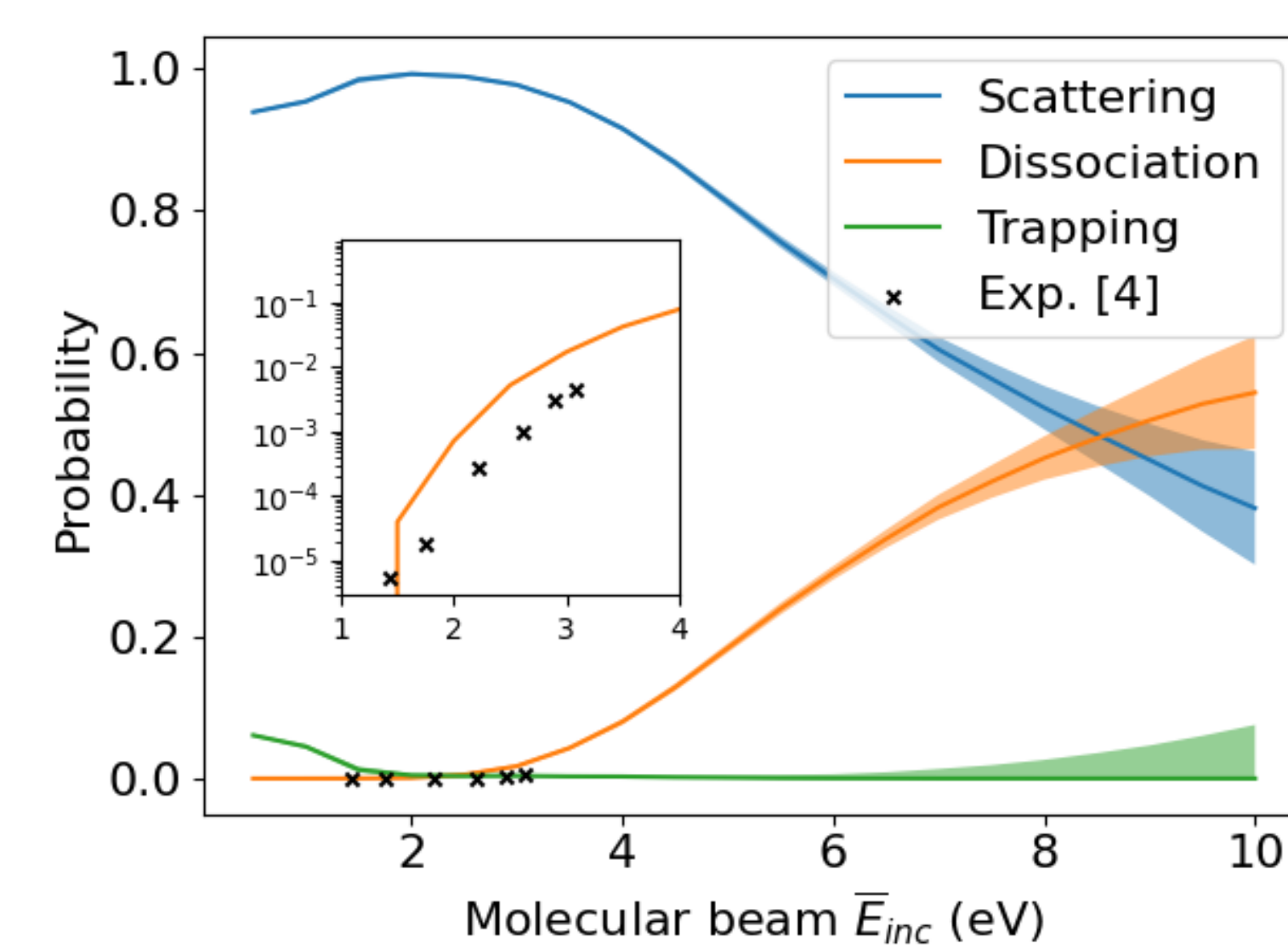- We consider the 10 lowest energy vibrational states.
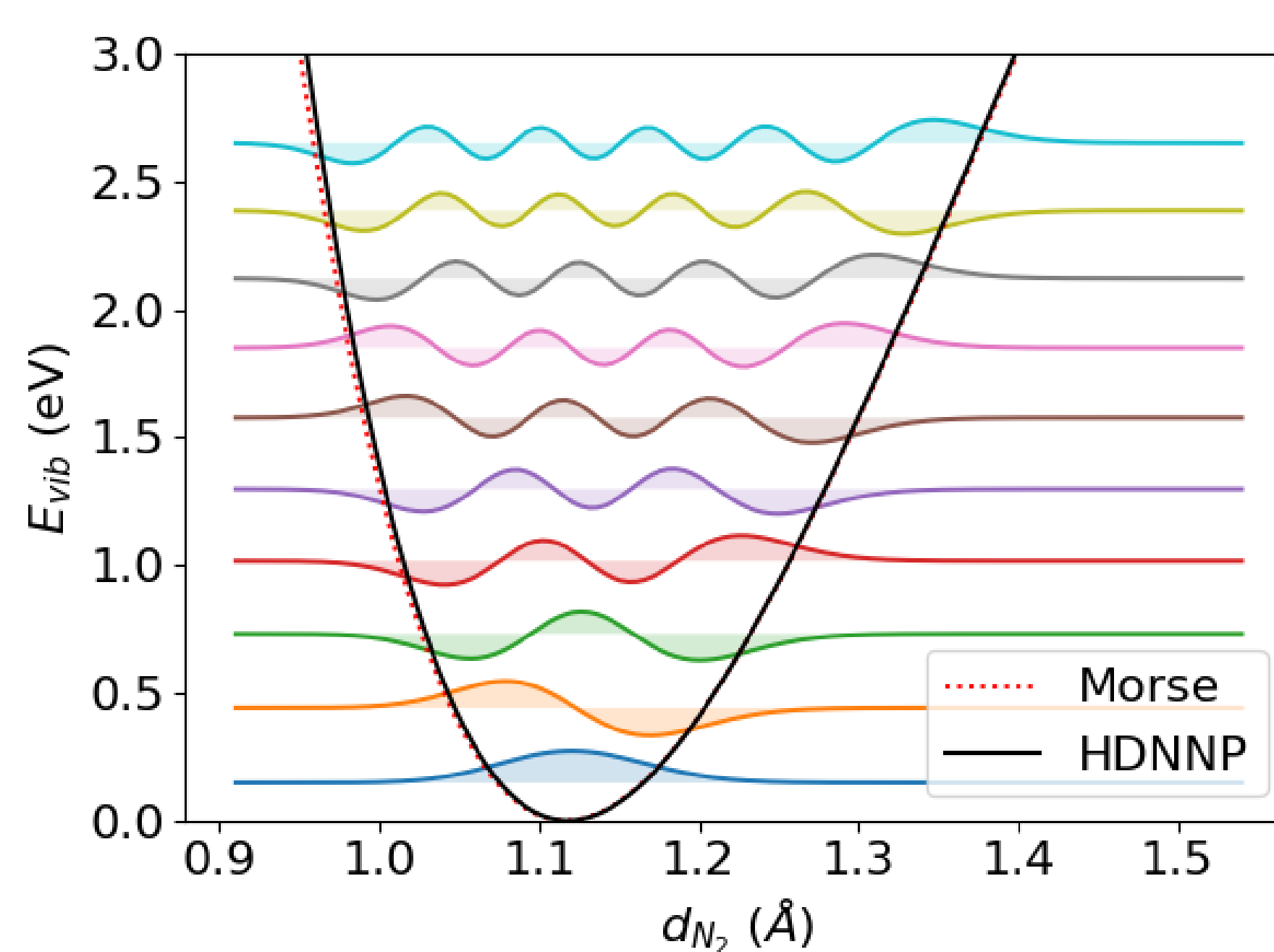
② Simulating Molecular Beams

- Incidence velocity v is distributed around v_s with spread α like a **molecular beam**.

$$f(v) \propto v^3 \exp((v - v_s)^2/\alpha^2)$$

- Rovibrational states (ν, j) are **Boltzmann distributed** with $T_{vib} = 1100\,\mathrm{K}$ and $T_{rot} = 110\,\mathrm{K}$[4].

$$P(\nu, j) \propto \exp\left(-\frac{E_{rot}(j)}{k_B T_{rot}}\right) \exp\left(-\frac{E_{vib}(\nu)}{k_B T_{vib}}\right)$$


③ Vibrational Efficacy

- We compute dissociation probabilities for **monochromatic beams**: No spread in incidence velocity.

- We observe an increase in **probability uncertainty** with incidence and vibrational energy.

- Vibrational excitation roughly corresponds to a **shift in incidence energy**.
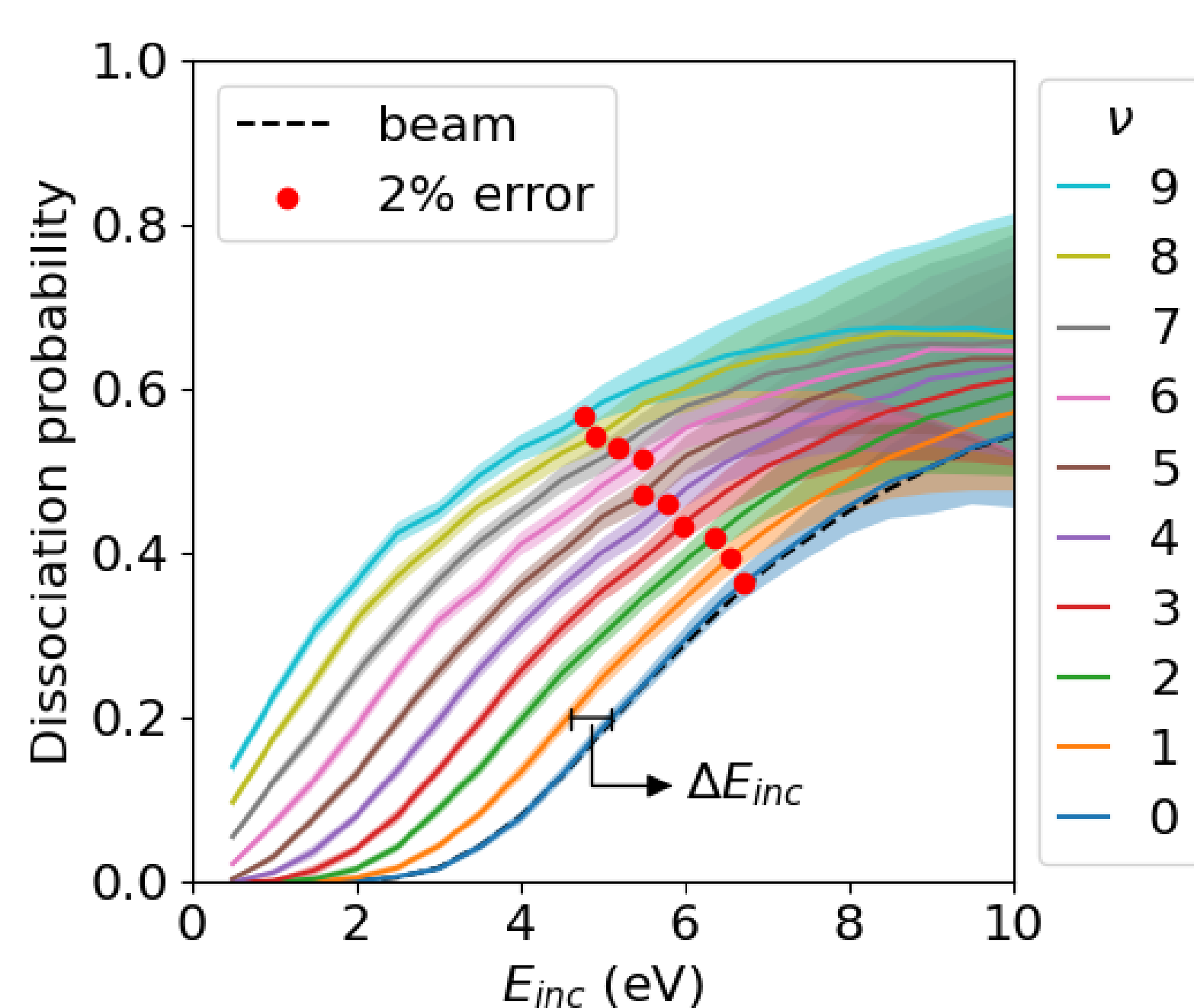
- Vibrational efficacy is a measure of the **efficiency of the use of vibrational energy** w.r.t. kinetic energy for dissociation.

- We compute **effective shifts** induced by vibrational shifts w.r.t. the ground state.

- We find that vibrational excitation is roughly $1.8\times$ **more efficient** at promoting DC than incidence energy.
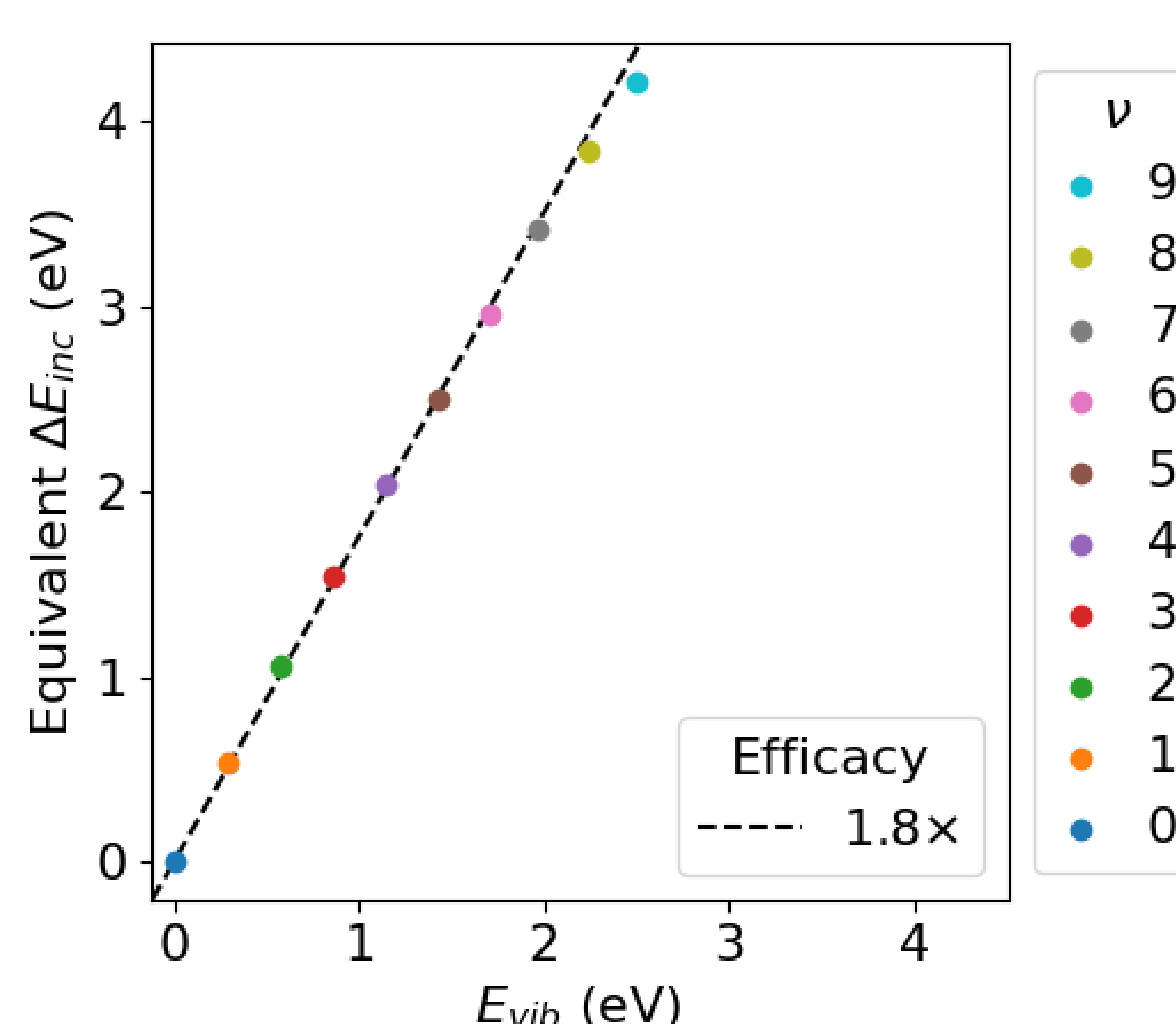
④ Extrapolation Analysis

- The HDNNP sets outer limits for structural descriptor values of atomic environments (symmetry functions). Beyond these limits we expect **unreliable extrapolation**[11].

- Exceeding these limits during a QCT **halts the trajectory** and marks it as extrapolation geometry.

- Comparing the energies of extrapolation geometries and final geometries from regular runs, we see that extrapolation geometries tend to be **higher in potential energy**.
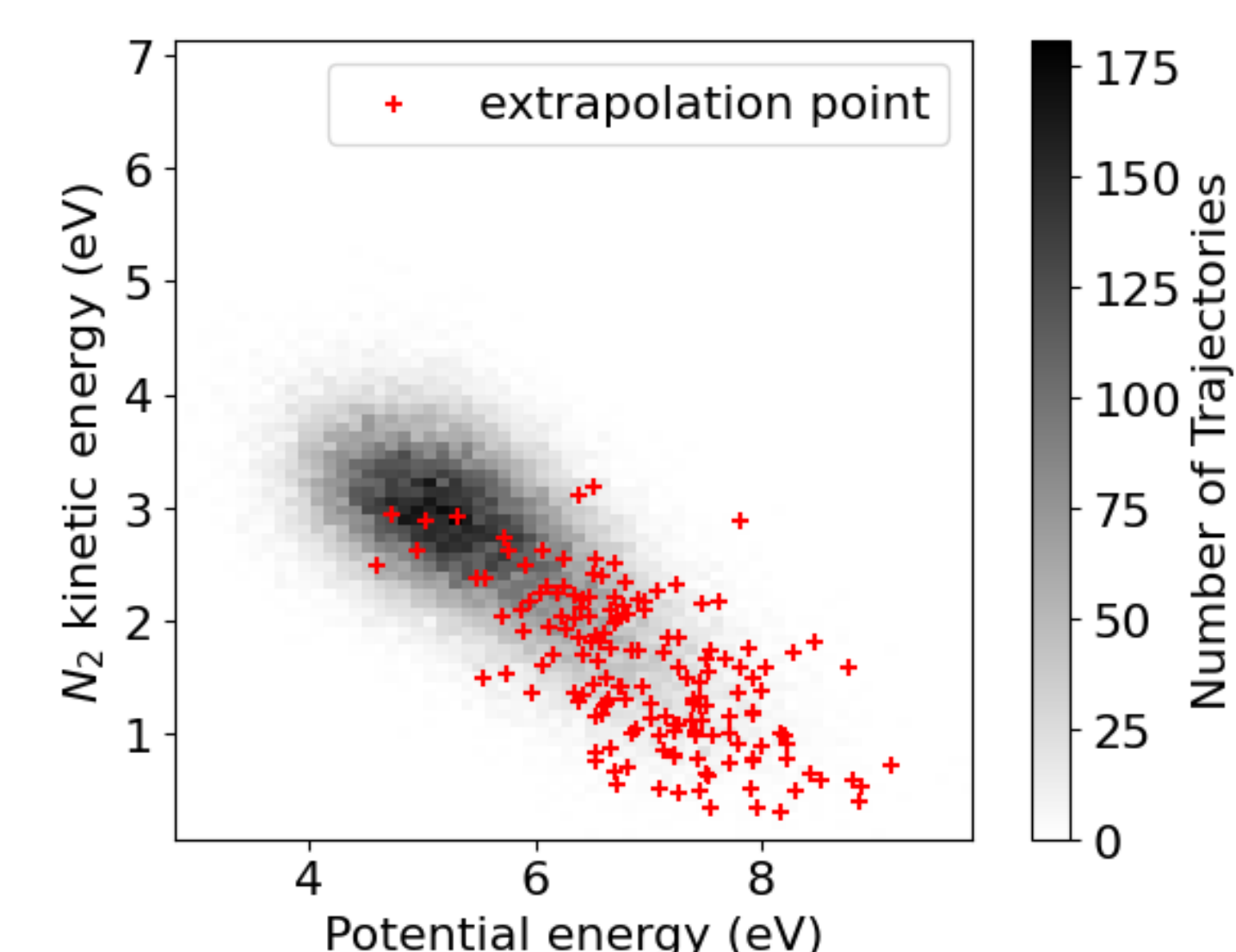
Conclusions and Outlook

- Up to $\leq 6\,\mathrm{eV}$ for $\nu = 0$ ($\leq 5\,\mathrm{eV}$ for $\nu = 9$), our simulations show an increase of the dissociation probability increases by more than one order of magnitude compared to the energy regime considered in molecular beam experiments before.

- In this incidence energy regime and up to $\nu = 9$, it is 1.8 times more efficient to supply vibrational instead of incidence energy to increase the dissociation probability.

- The previously constructed HDNNP needs to be superseeded by a new machine-learning potential to reliably describe larger both incidence and vibrational energies.

References

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