Development of a general MLIP workflow for reactive, “green” designer solvents

CECAM workshop: MLIPs and Accessible Databases, Day 2

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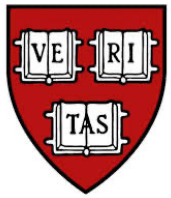
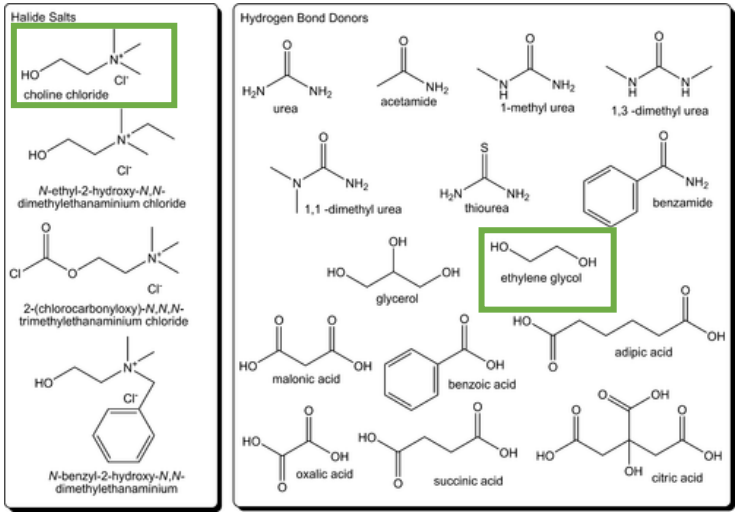
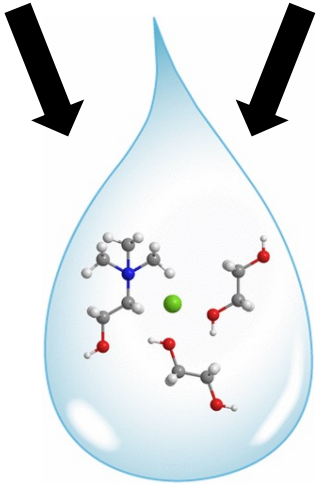
Georgia Institute of Technology

School of Chemical and Biomolecular Engineering



Promising “green” designer solvents are not simple mixtures





Smith, E.L., Abbott, A.P., and Ryder, K.S., *Chemical Reviews* **114**(21), 11060-11082 (2014).

PAPER

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Cite this: *Green Chem.*, 2022, **24**, 6685

Choline chloride–ethylene glycol based deep-eutectic solvents as lixiviants for cobalt recovery from lithium-ion battery cathode materials: are these solvents really green in high-temperature processes?†

Nand Peeters, [a] Kwinten Janssens, [b] Dirk de Vos, [b] Koen Binnemans [a] and Sofía Riaño [*a]

Thermal Instability of Choline Chloride-Based Deep Eutectic Solvents and Its Influence on Their Toxicity—Important Limitations of DESs as Sustainable Materials

Mateusz Marchel, Hubert Cieśliński, and Grzegorz Boczkaj*

Cite This: *Ind. Eng. Chem. Res.* 2022, 61, 11288–11300

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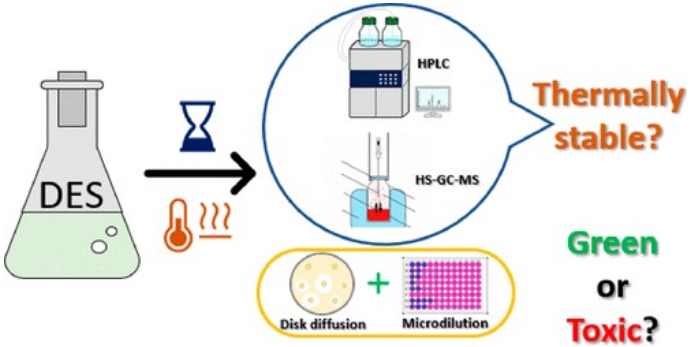
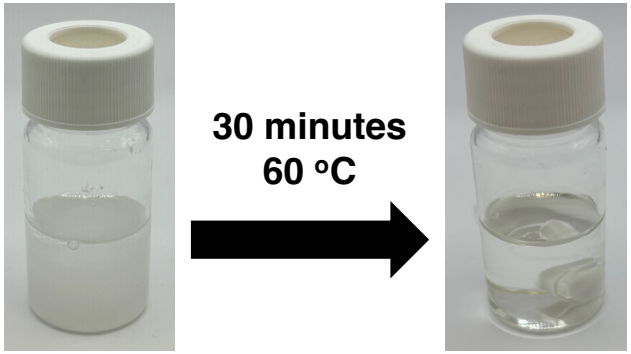


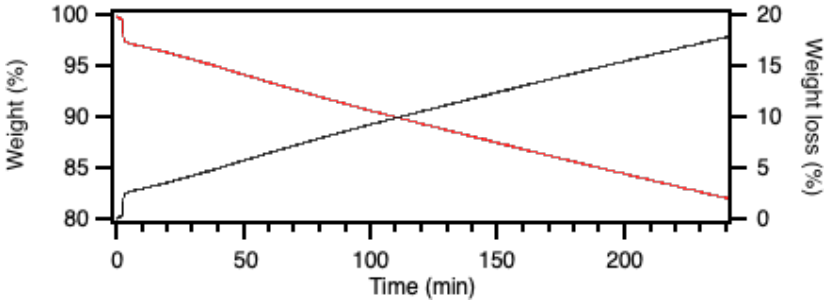
What is the long-term thermal stability of ethaline?

Ethaline undergoes decomposition already at room temperature

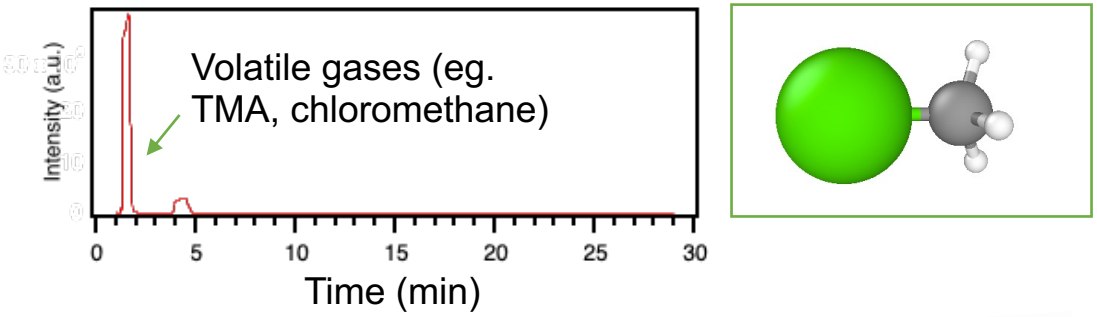
(a) Synthesis of ethaline (60 °C, 4 hour)

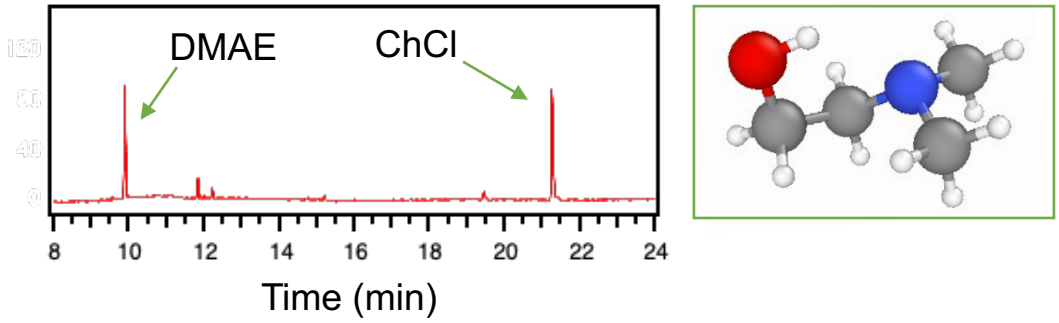


(b) Isothermal TGA of ethaline (60 °C, 4 hour)



(c) Tentatively identified compounds (TIC) of ethaline

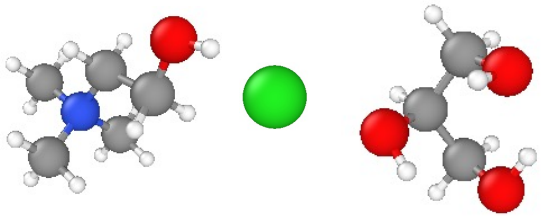


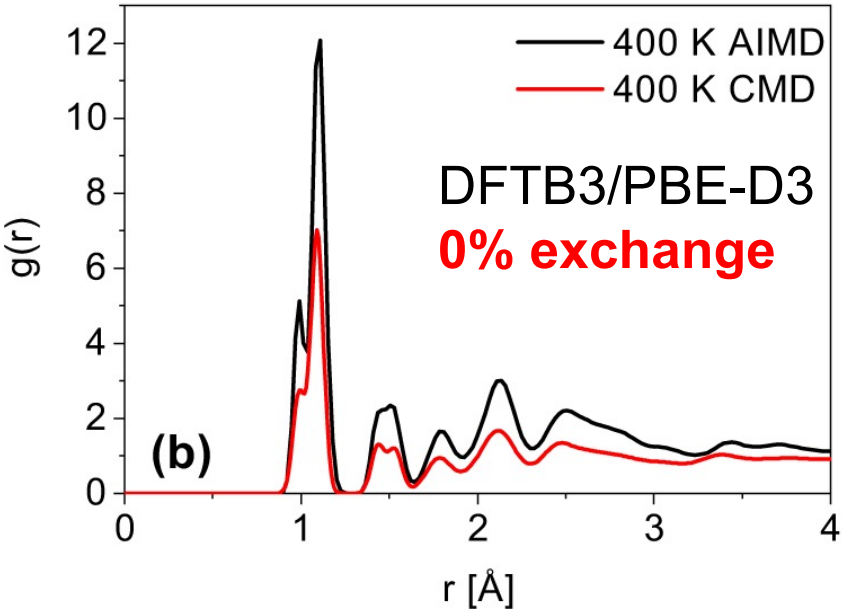


What controls decomposition in ethaline and what are design principles for thermodynamically stable solvents?

Need: **Reactive force field for organic liquids**

In modeling ethaline: Benchmarked *ab initio* studies are missing

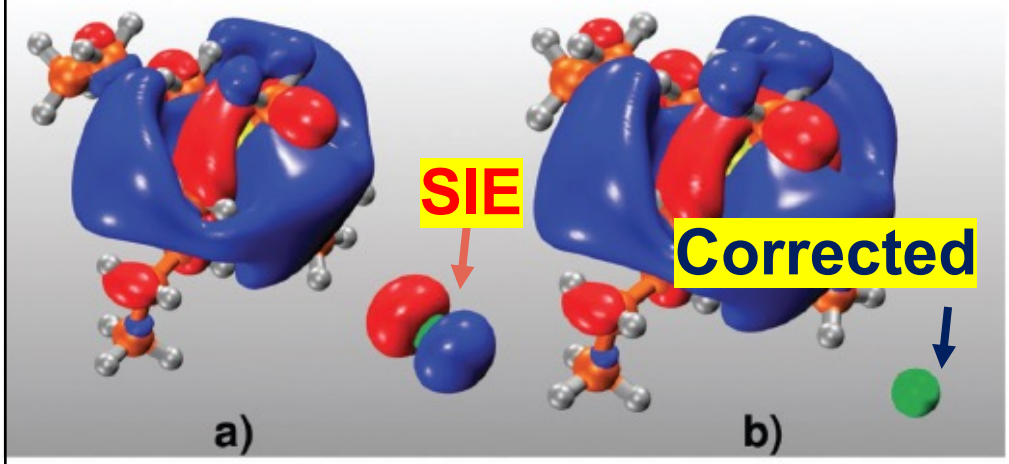




Spittle, S., Poe, D., Doherty, B. *et al*. *Nat. Commun.* **13**, 219 (2022).

$$E_{XC} = E_C + (1-\alpha)E_{X,local} + \alpha E_X^{HF}$$

At least 30% exchange

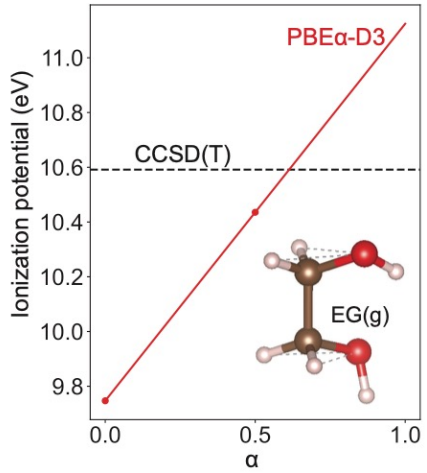


Grimme, S., Hujo, W., Kirchner, B., *Phys. Chem. Chem. Phys.* **14**, 4875–4883 (2012).

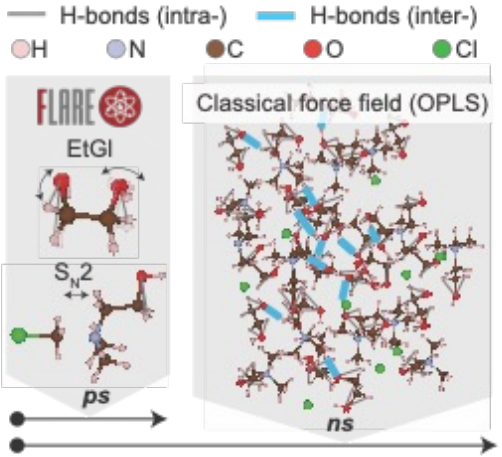
What is correction, α, need in ethaline to remove artificial charge transfer?

From DFT to MLIP: The developed workflow

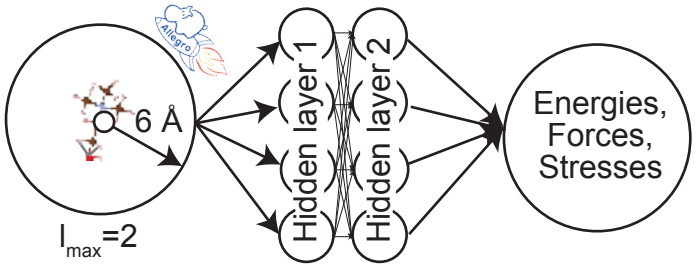
DFT approach



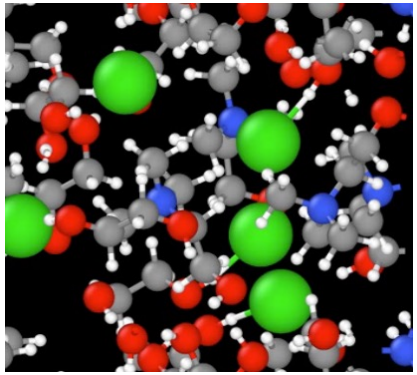
Intra- and inter-molecular sampling

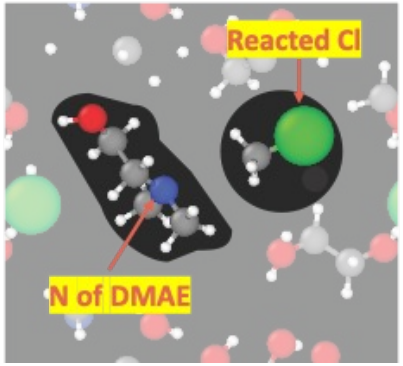


MLIP



MD simulations

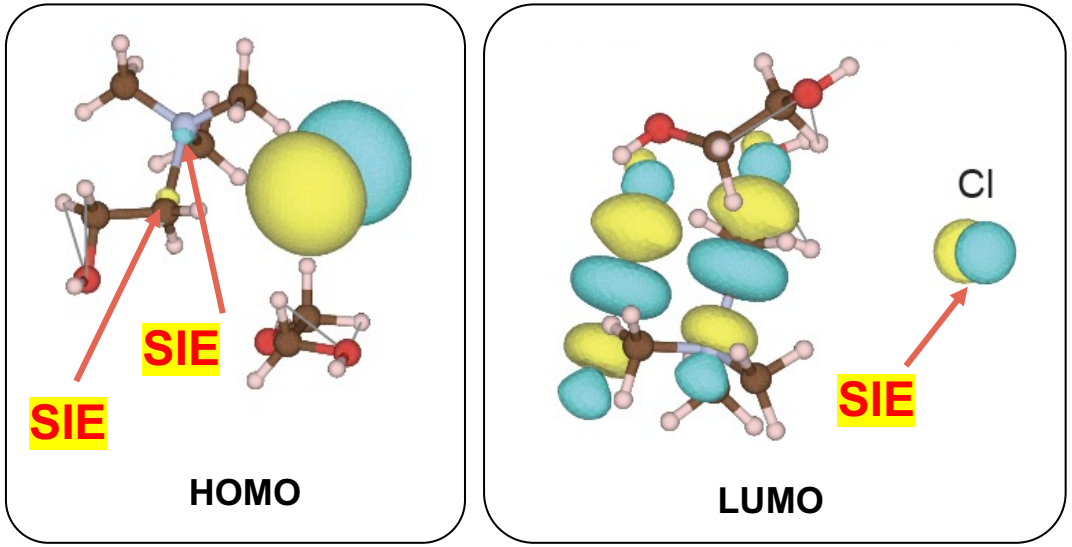


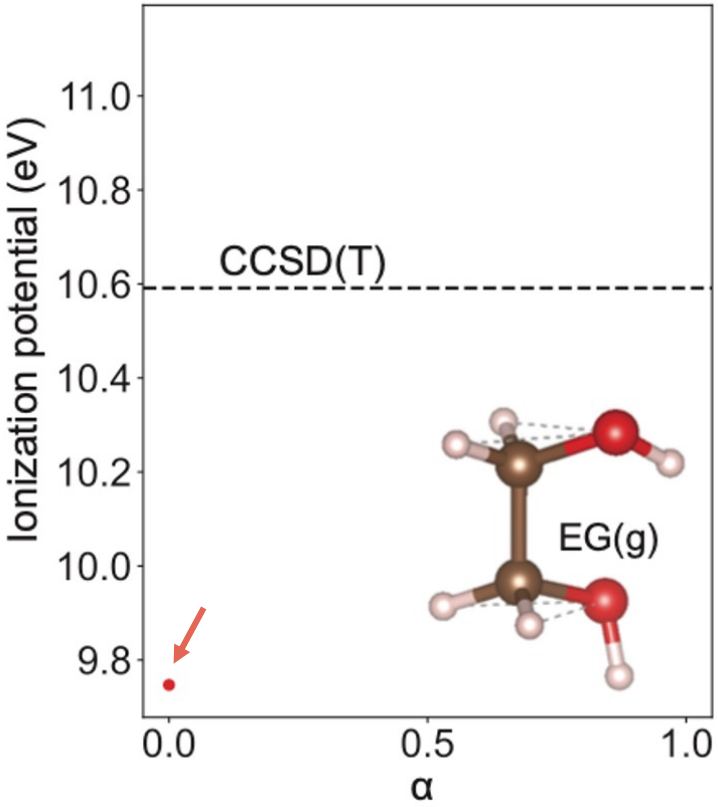


Benchmarking exact exchange correction

Ethylene glycol molecule	Ionization potential (eV)
CCSD(T) IP, NIST structure	**10.59 (plotted)** (experiments: 10.21-10.55)

PBE-D3 ($\alpha = 0.0$)

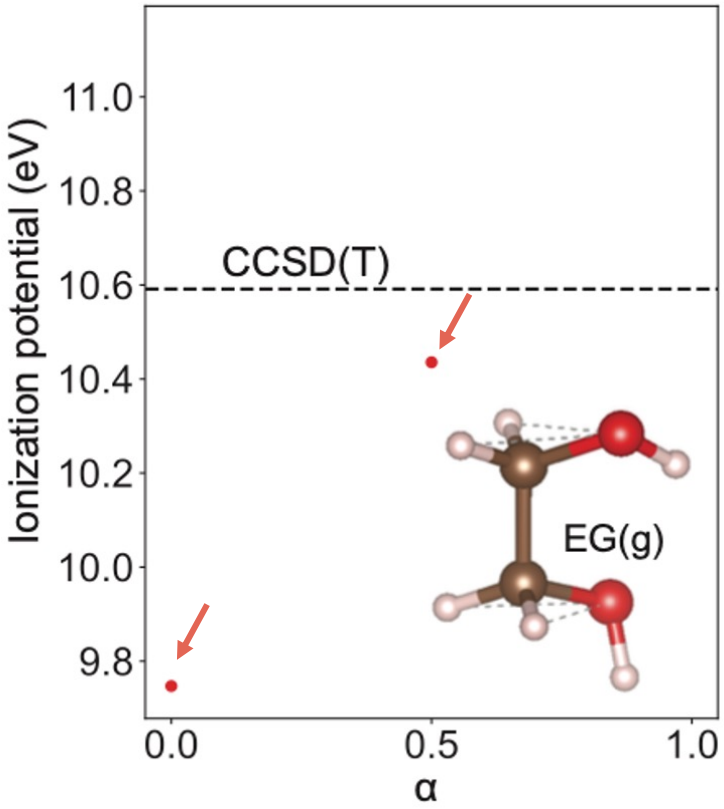




Benchmarking exact exchange correction

Ethylene glycol molecule	Ionization potential (eV)
CCSD(T) IP, NIST structure	**10.59 (plotted)** (experiments: 10.21-10.55)

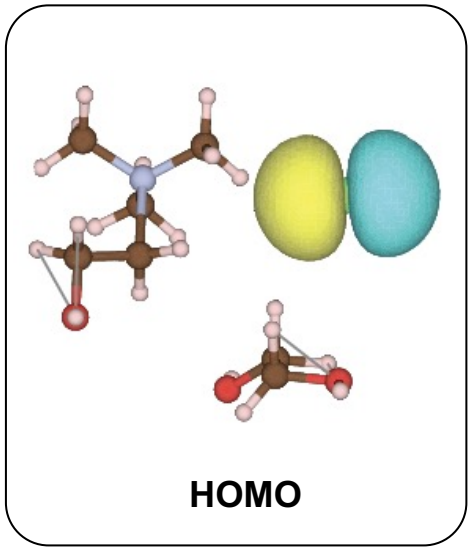
PBE-D3 ($\alpha = 0.5$)

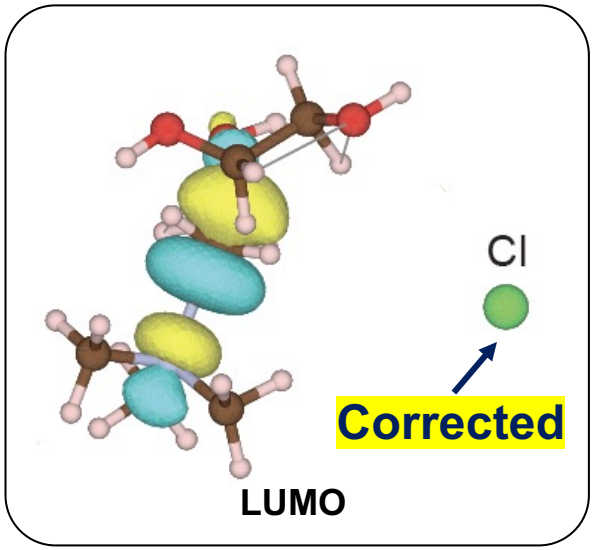


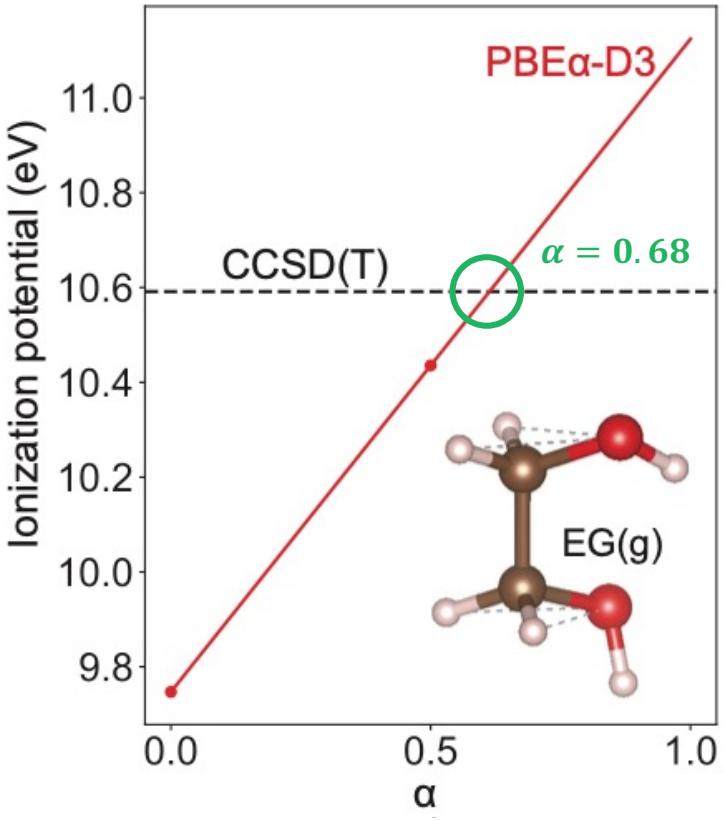
Benchmarking exact exchange correction

Ethylene glycol molecule	Ionization potential (eV)
CCSD(T) IP, NIST structure	**10.59 (plotted)** (experiments: 10.21-10.55)

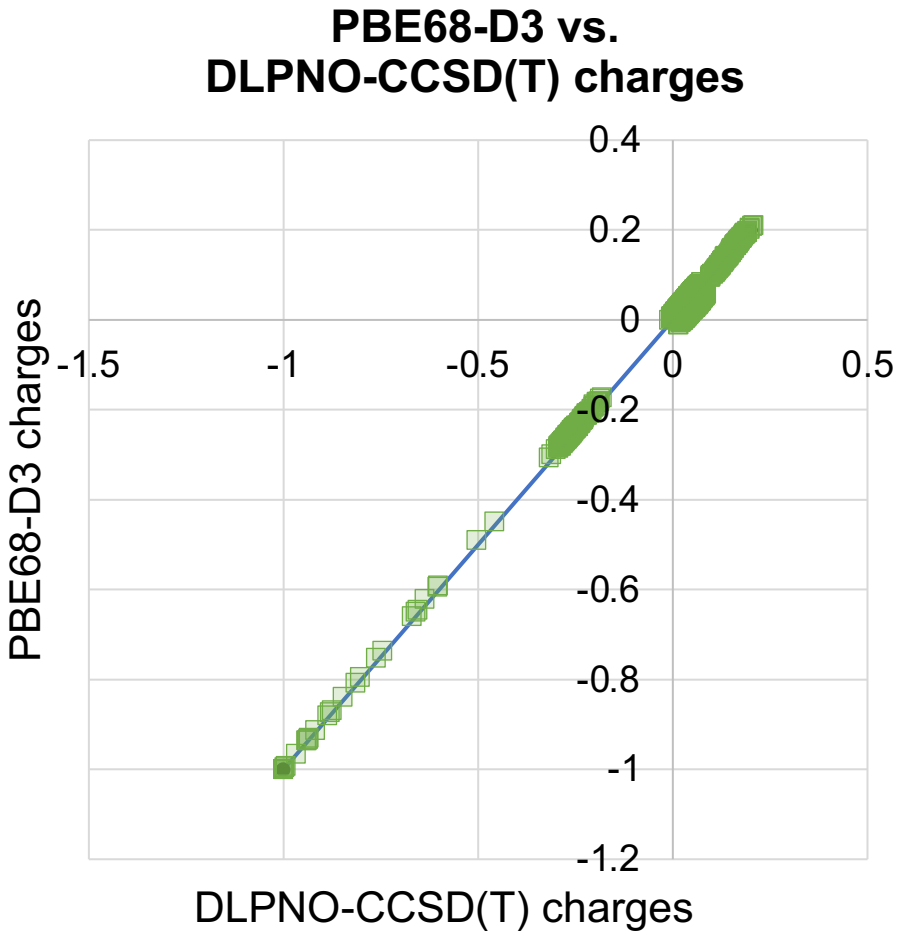
PBE-D3 ($\alpha = 0.68$)

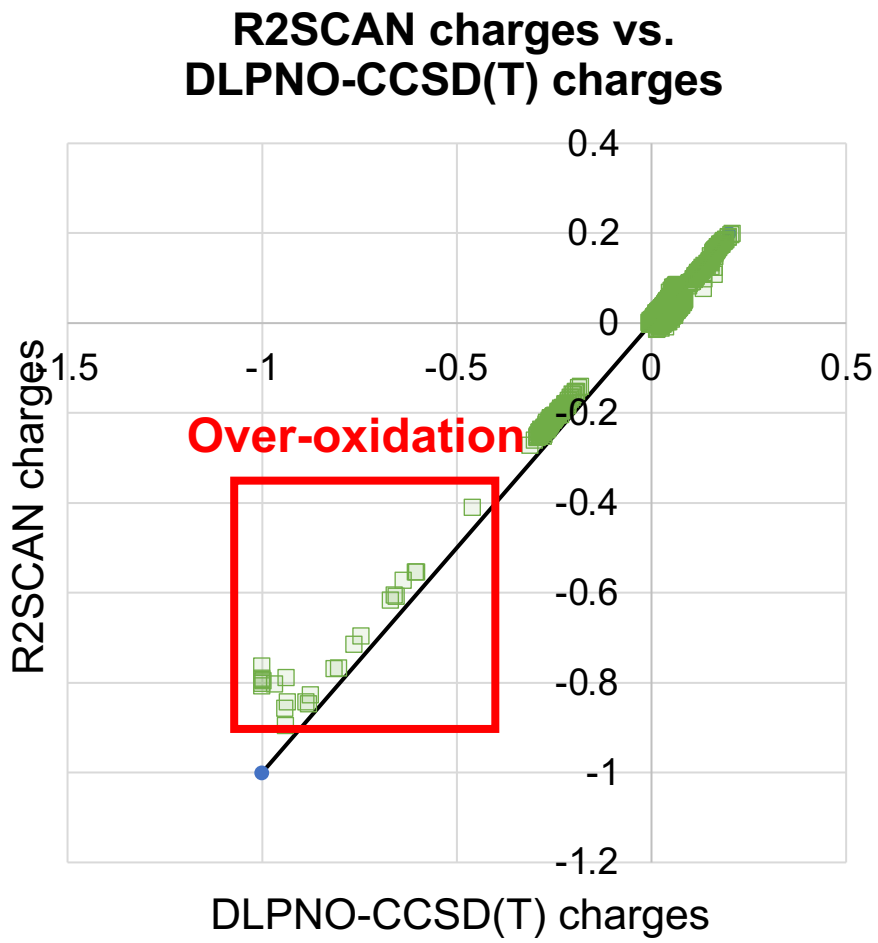






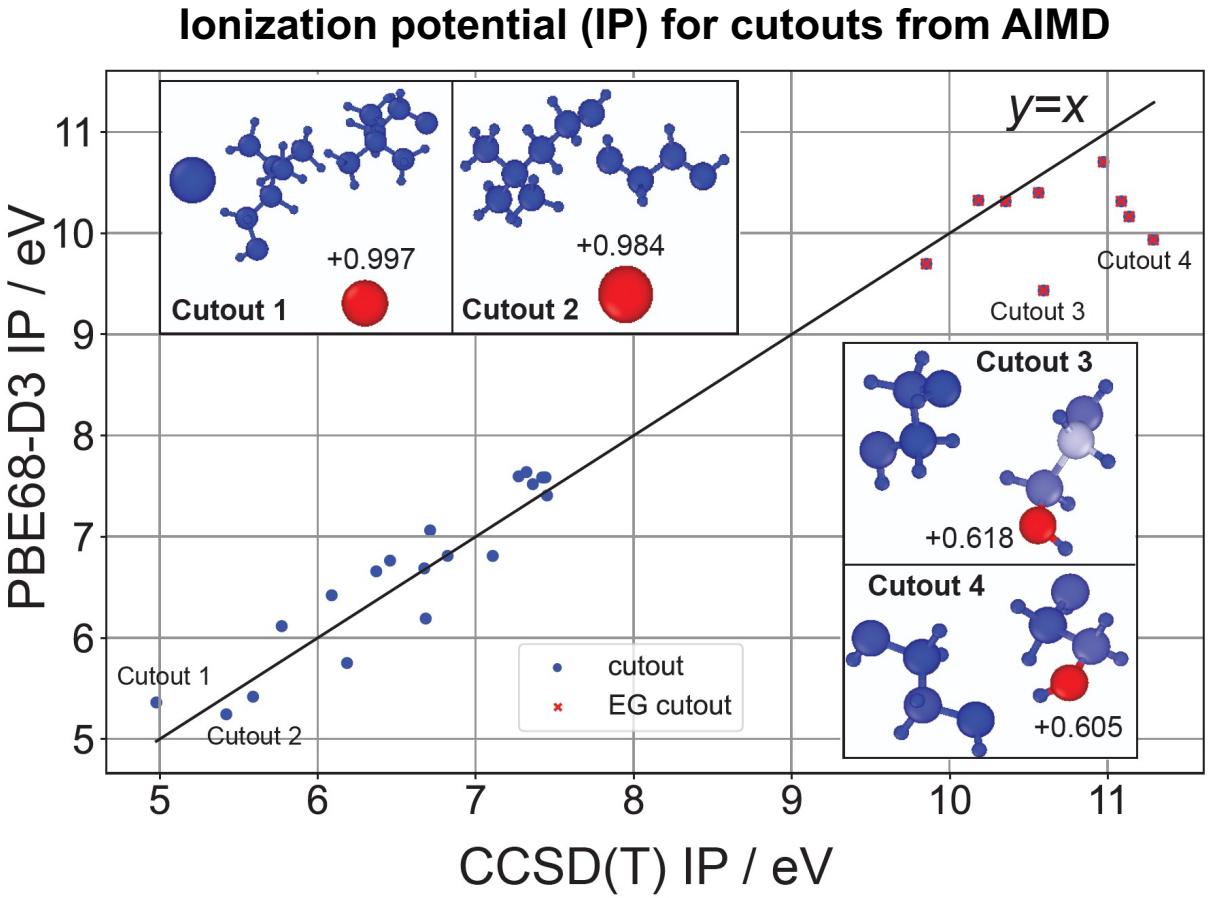
Does the correction work for charge transfer in ethaline?





Clear reproduction of charge transfer in PBE68-D3 compared to CCSD(T).

Does the correction work for IPs in ethaline?



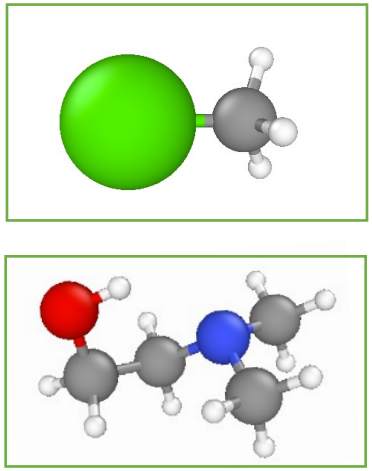
Yes:

- ✓ Oxidation is localized
- ✓ Cl is oxidized first, contrary to what others have assumed [1]
- ✓ IP is configuration dependent [2]

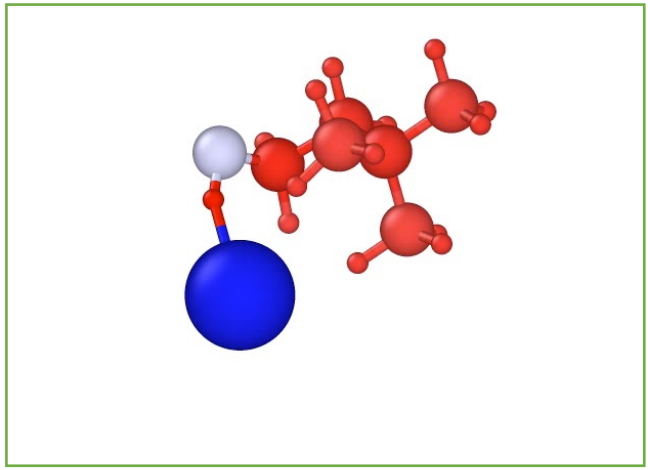
[1] Wang, S., Zhang, Z., Lu, Z., and Xu, Z. *Green Chem.* **22**, 4473-4482, (2020)
[2] Fadel, E.R., Faglioni, F., Samsonidze, G. *et al.*, *Nat Commun.* **10**, 3360, (2019).

Does the correction work for the S_N2 reaction barrier?

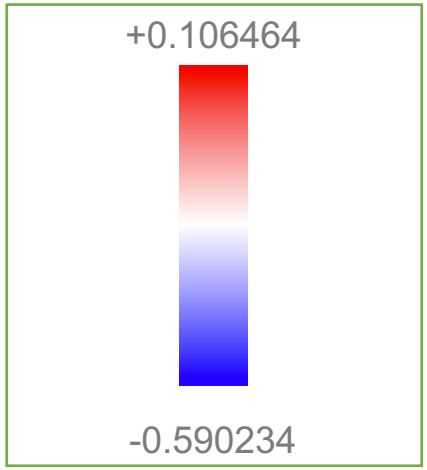
Decomposition products



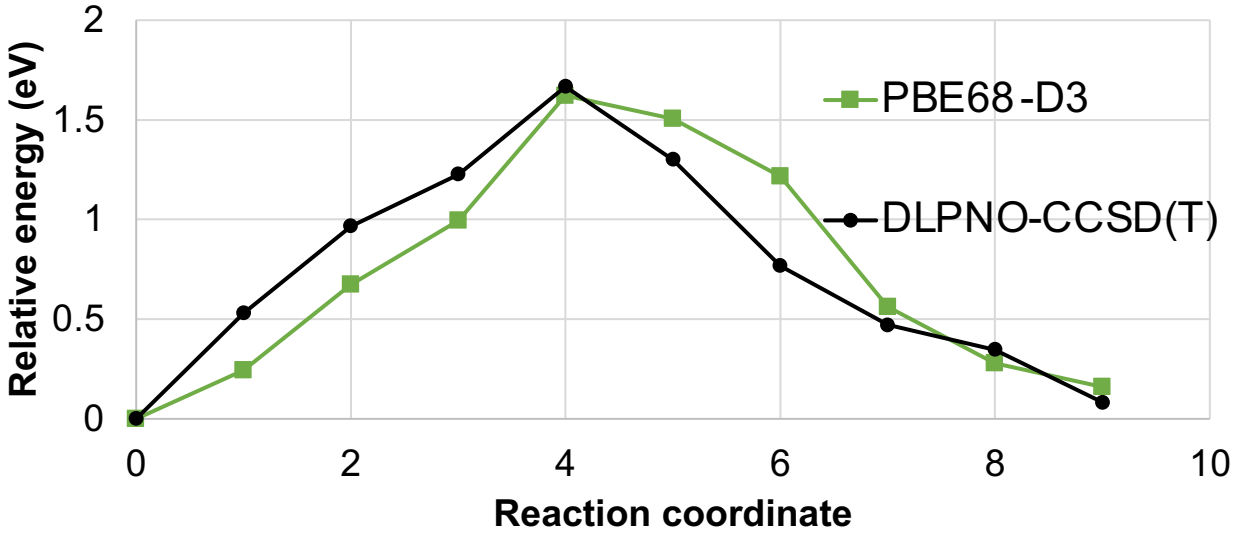
Climbing-Image NEB in vacuum



Hirshfeld charges



Gas-phase S_N2 reaction predicts > 1.5 eV barrier

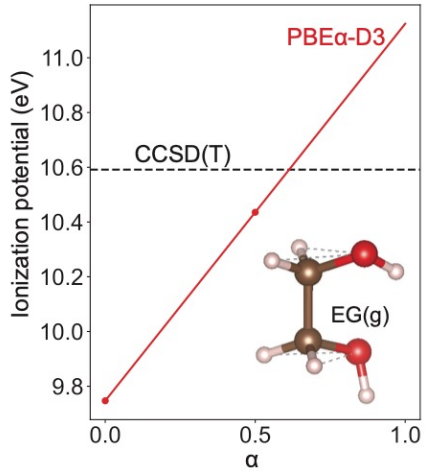


Missing considerations:

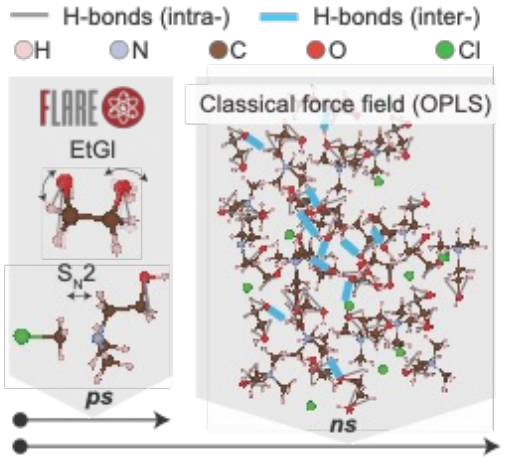
- Solvation shell
- Hydrogen bonding

From DFT to MLIP: The developed workflow

DFT approach

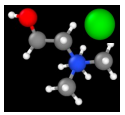


Intra- and inter-molecular sampling

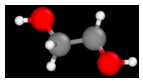


Active learning using FLARE

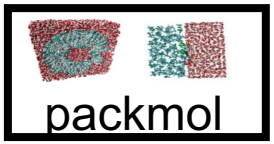
Initialize configurations



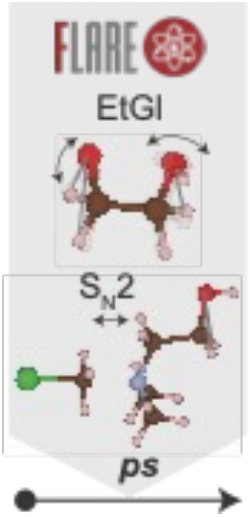
$\times n$



$\times 2n$

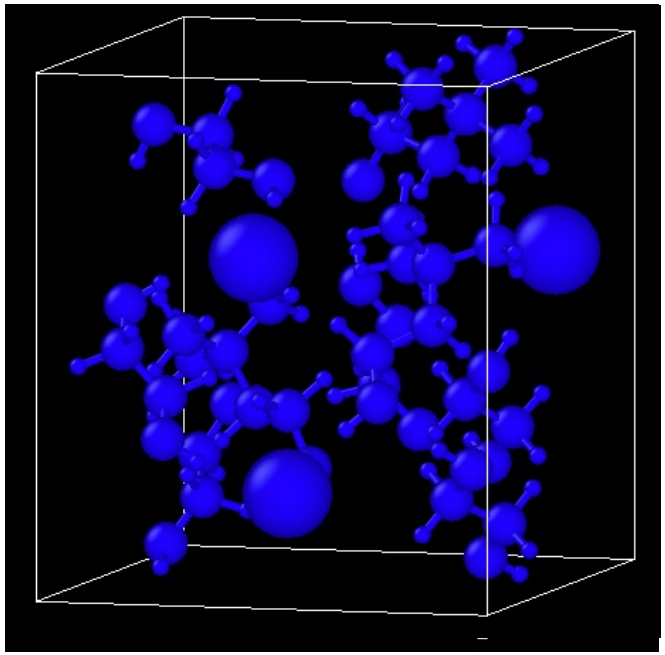


PBE68-D3

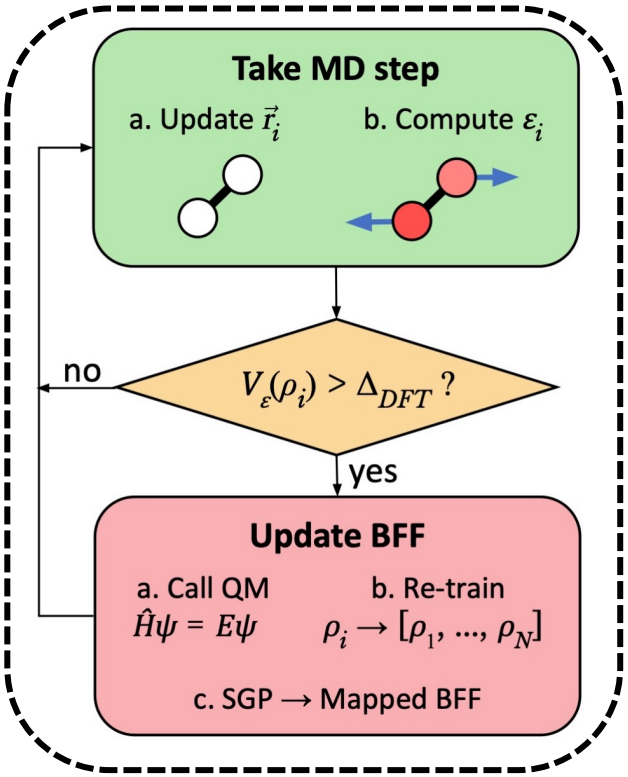


⏰ **AIMD with hybrid DFT**

✅ **Active learning with hybrid DFT**



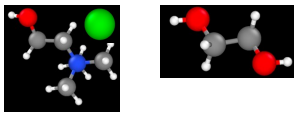
Low unc. **High unc.**



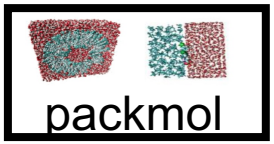
Vandermause, J., Xie, Y., Lim, J.S. *et al*. *Nat Commun* **13**, 5183 (2022).

Active learning using FLARE

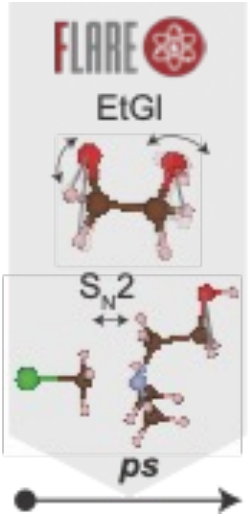
Initialize configurations



$\times n$ $\times 2n$

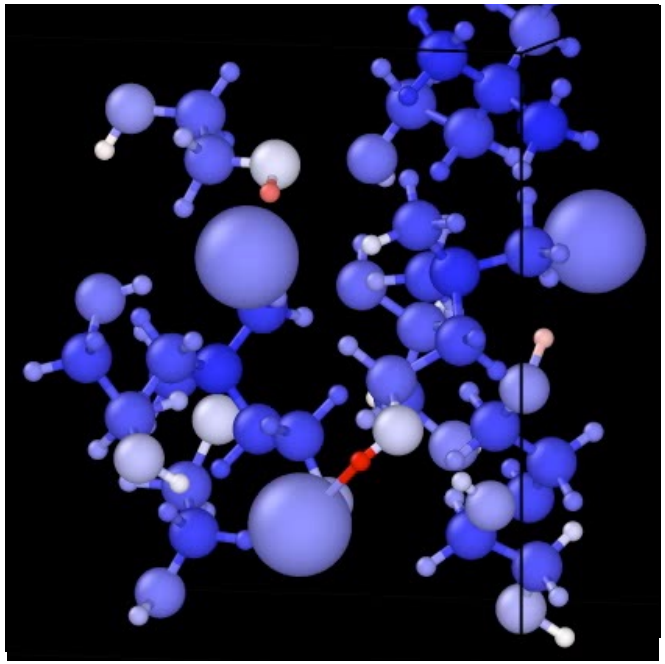


PBE68-D3

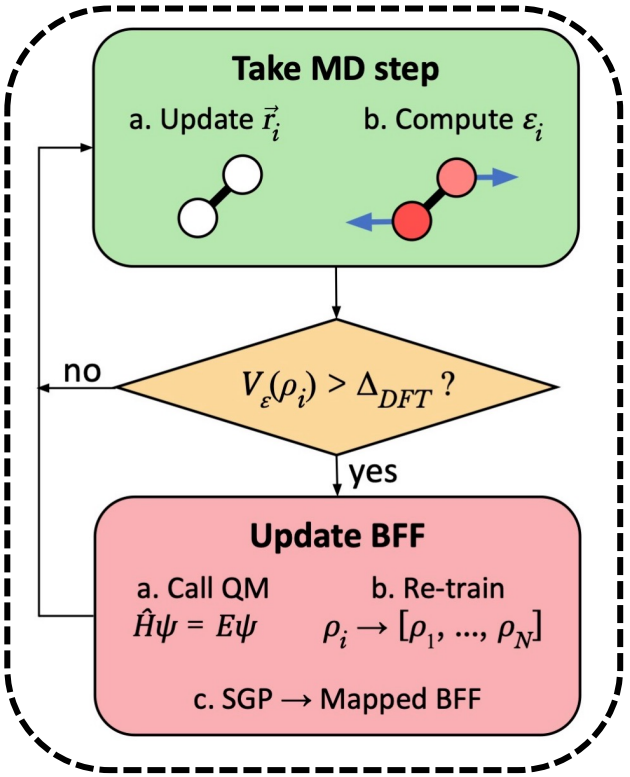


⏰ **AIMD with hybrid DFT**

✅ **Active learning with hybrid DFT**



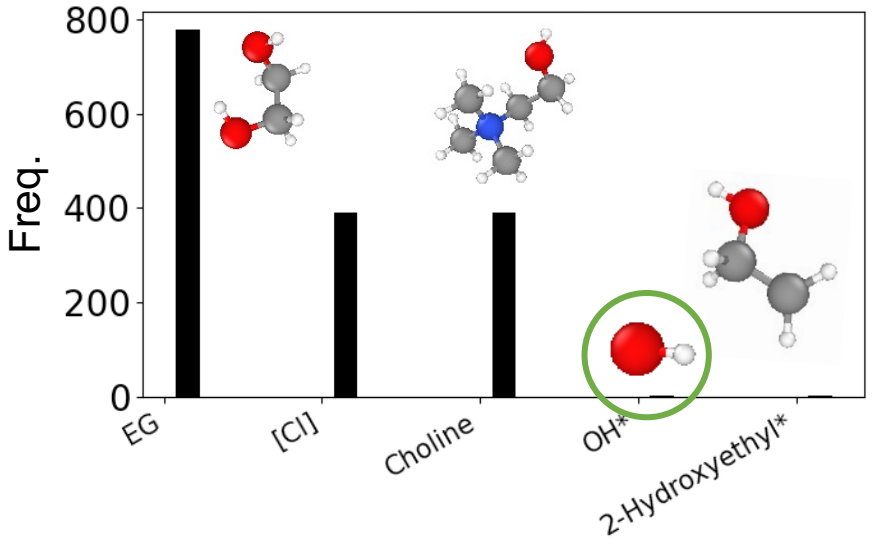
Low unc. **High unc.**



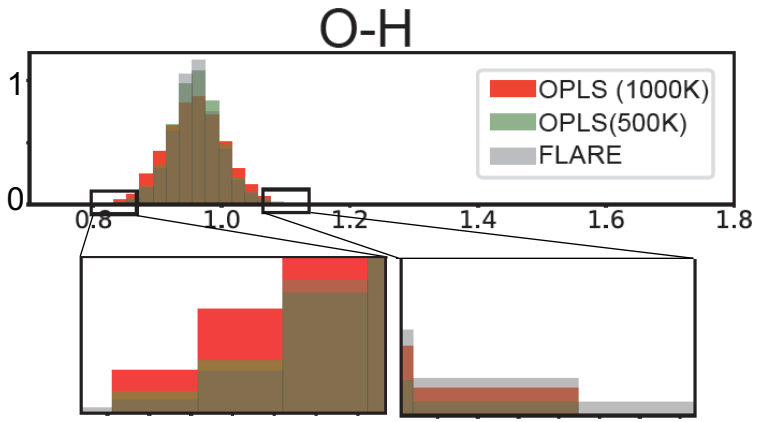
Vandermause, J., Xie, Y., Lim, J.S. *et al*. *Nat Commun* **13**, 5183 (2022).

Active learning for intramolecular diversity

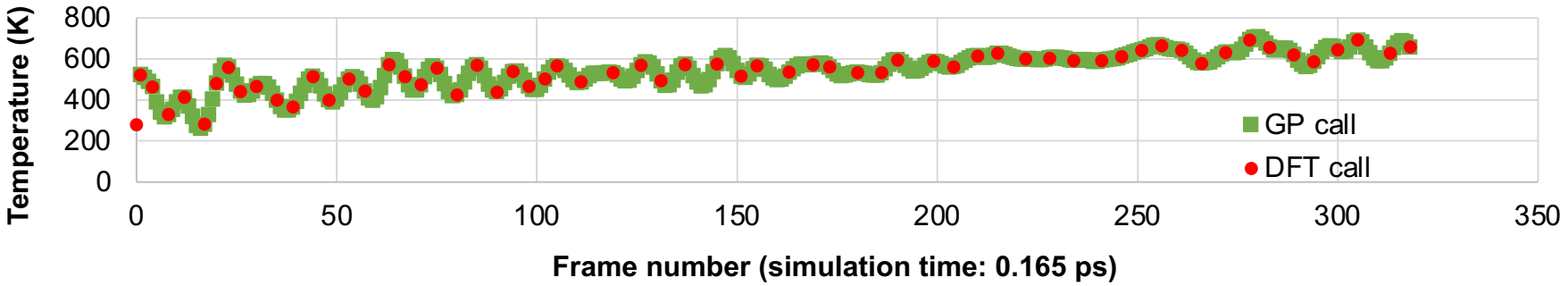
Molecules are mostly connected according to SMILES



Connected molecules have a wide range of bond lengths (example: **OH**)

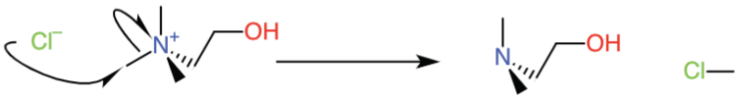


Temperature increases during “NVE” active learning



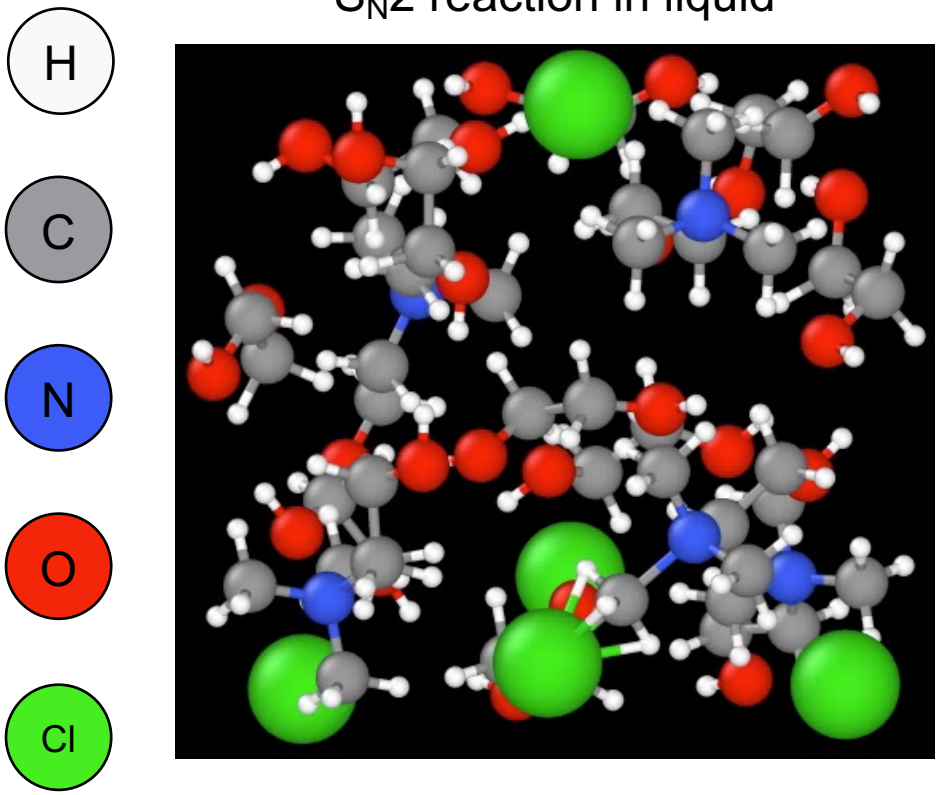
Advantage #1: Active learning continuously explores TD landscape, sampling bond lengths representative of those of classical FF at higher temperatures.

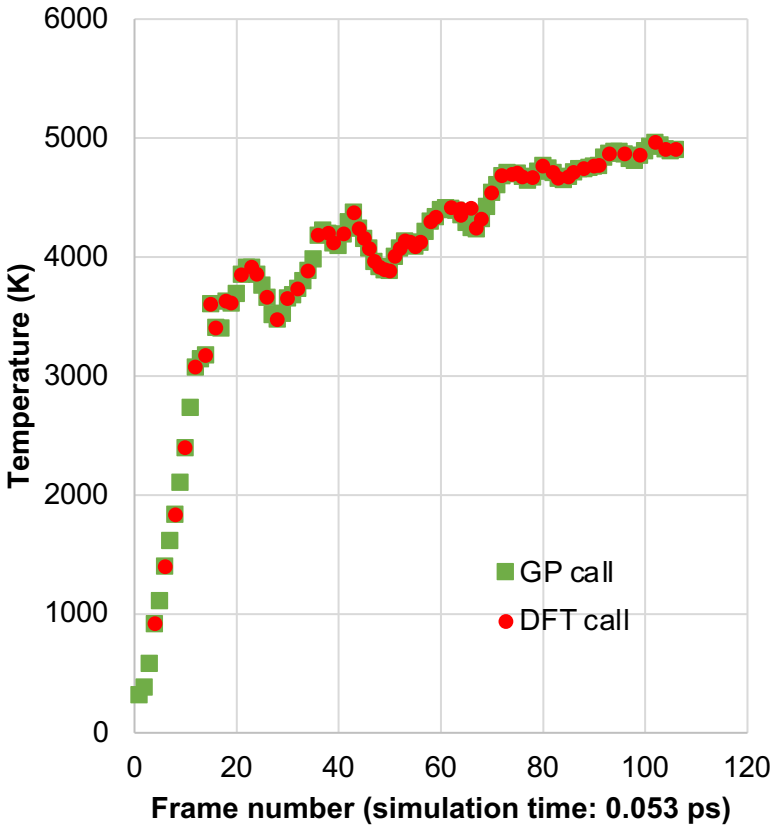
Active learning for intramolecular diversity



Learning around the transition state results in much higher temperatures

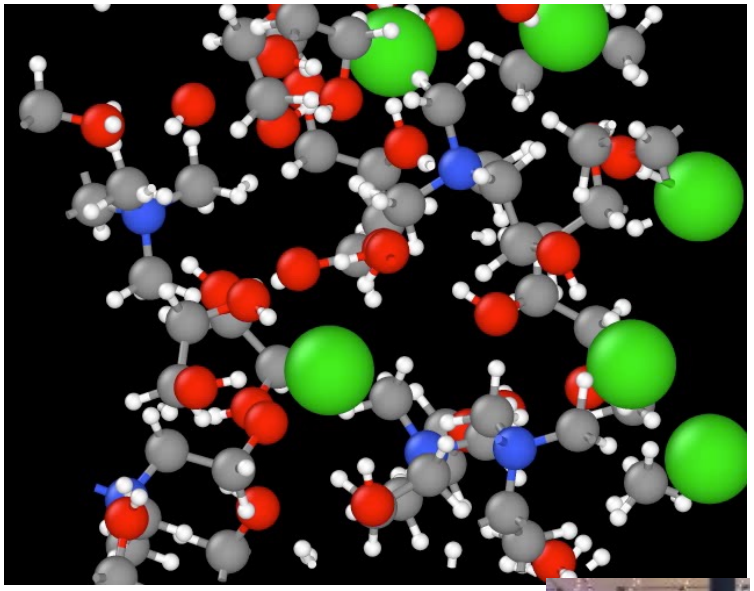
S_N2 reaction in liquid



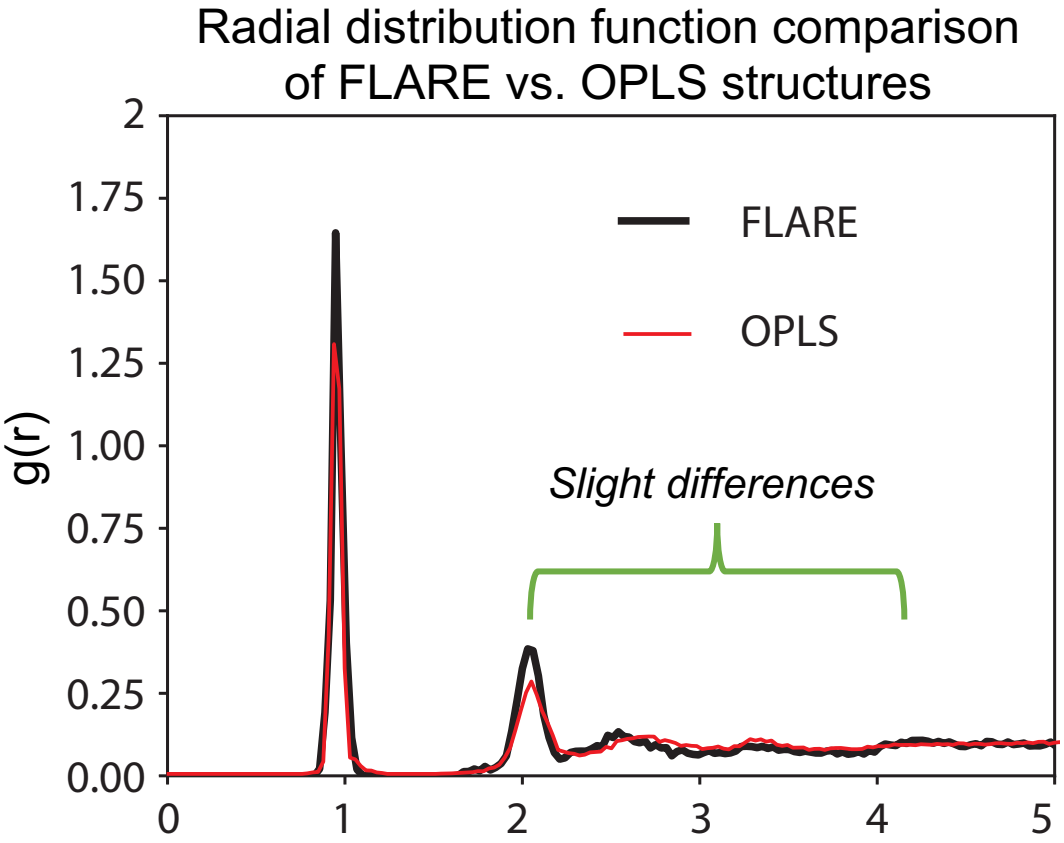


Advantage #2: Workflow can also sample around transition states.

What about intermolecular diversity?



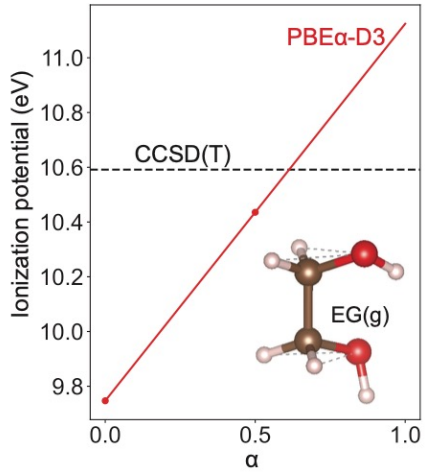
OPLS-AA @ 300 K
1 ns, every 10 ps



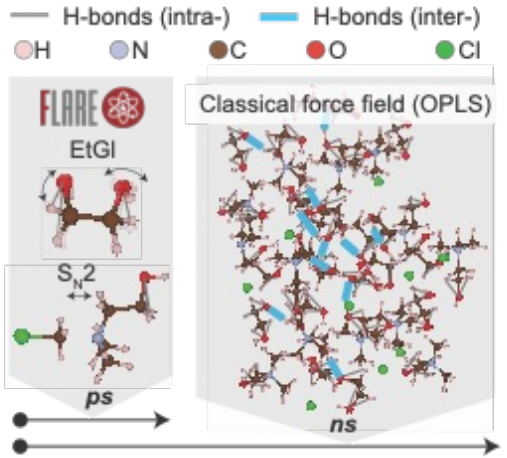
Solution: Circumvent time-scale limitations of FLARE with classical force fields

From DFT to MLIP: The developed workflow

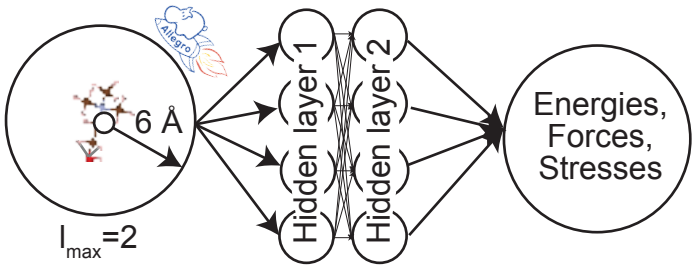
DFT approach



Active learning for sampling



MLIP



MLIP parameters, iteration 0 (MLIP-0)

- 5 FLARE runs
- S_N2 reaction

593 frames

- OPLS @ 300 K

100 frames

rmax=6.0
l_max=2
num_layers=2
Force-Energy-Stress: 1-100-1000
ZBL, no single atom energies

num_tensor_features = 32
latent_mlp_latent_dimensions: [128,128]
edge_eng_mlp_nolinearity: [128]
learning_rate: 0.002
batch_size: 2

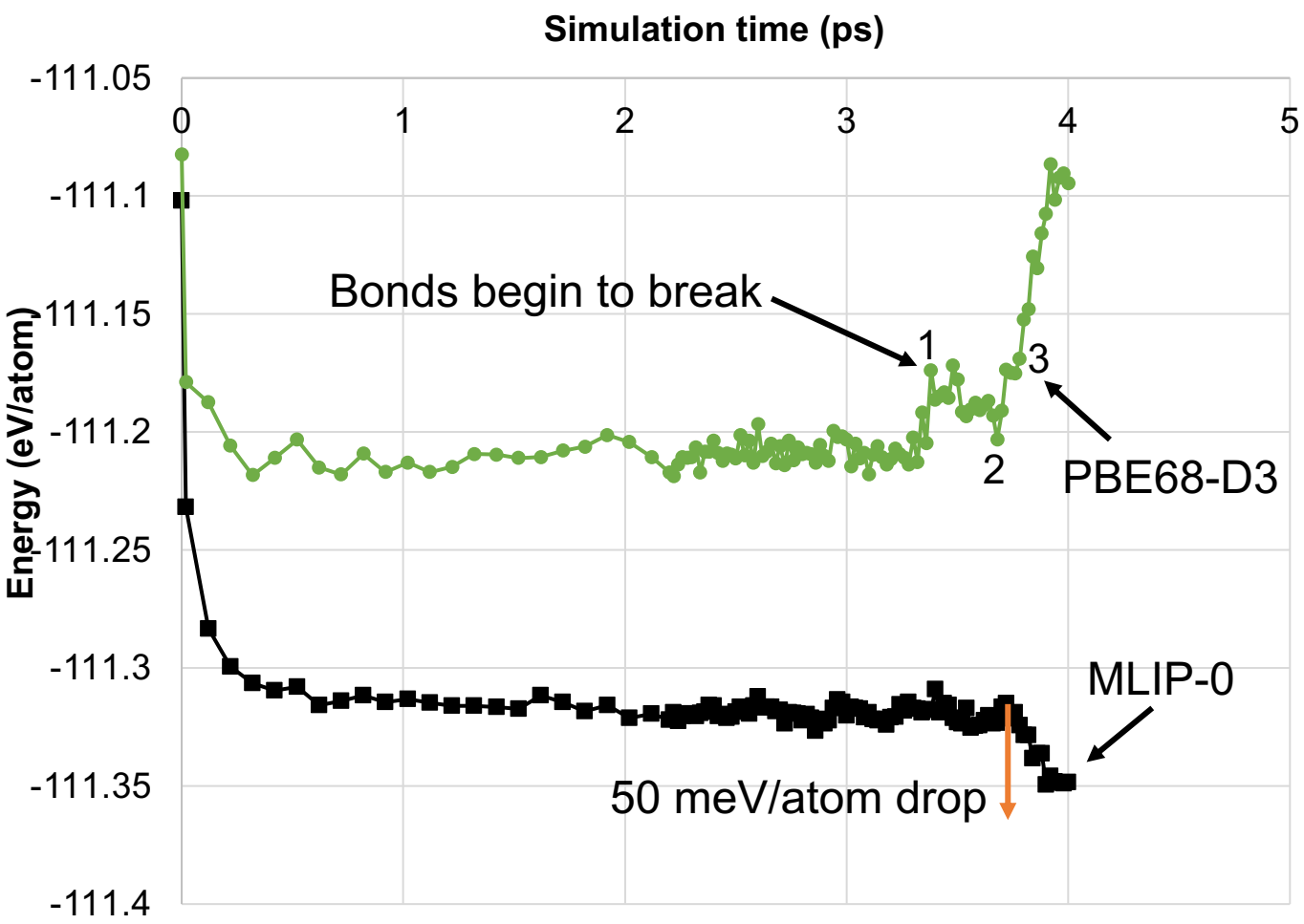
70%/15%/15% train-validation-test split

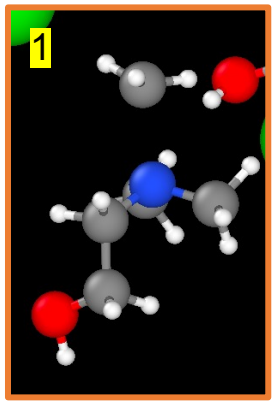
MLIP-0 test errors

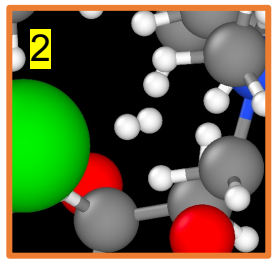
Force MAE per specie (eV/Å)	
C	0.044
Cl	0.033
H	0.025
N	0.049
O	0.051
Stress RMSE	
8.41E-4	
Entire system	
f_mae (eV/Å)	0.033
f_rmse (eV/Å)	0.074
e/N_{mae} (meV/atom)	0.38

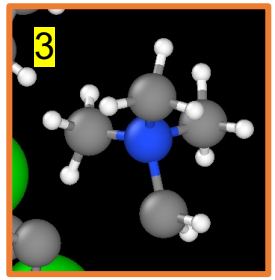
[1] Musaelian, A., Batzner, S., Johansson, A. *et al. Nat Commun* **14**, 579 (2023).
[2] Goodwin, Z. A. H. *et al,* J. Phys. Chem. Lett. **15**, 7539-7547 (2024).

MLIP-0 almost immediately begins to react



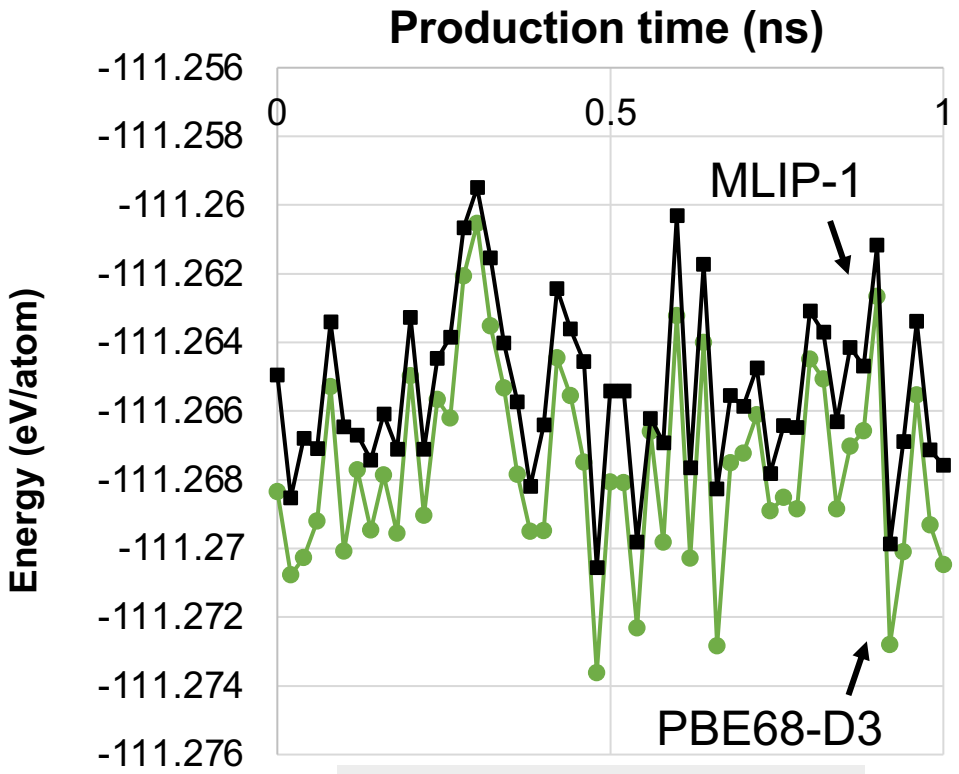




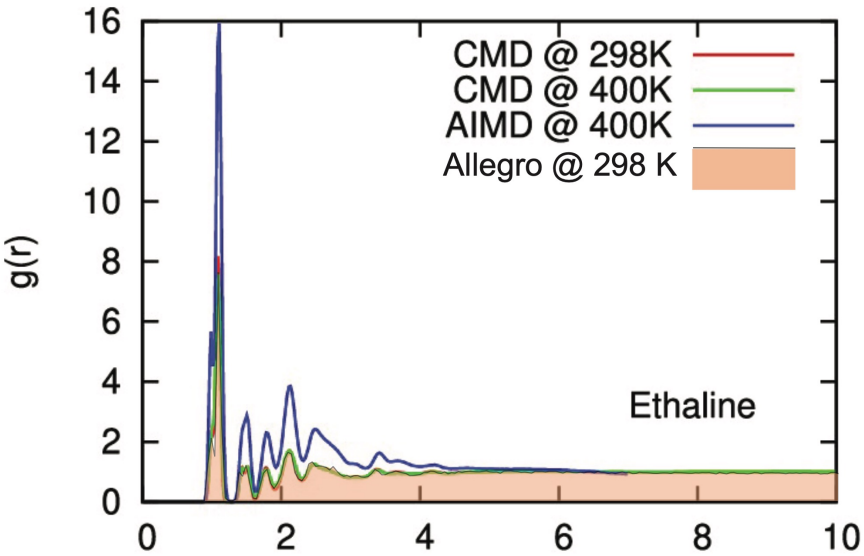


Unphysical reactions predicted after a few picoseconds. Retrain potential using frames prior to and during the unphysical reactions (generating MLIP-1).

MLIP-1 no longer predicts unphysical reactions



Max error: 4.5 meV/atom
RMSE: 2.3 meV/atom

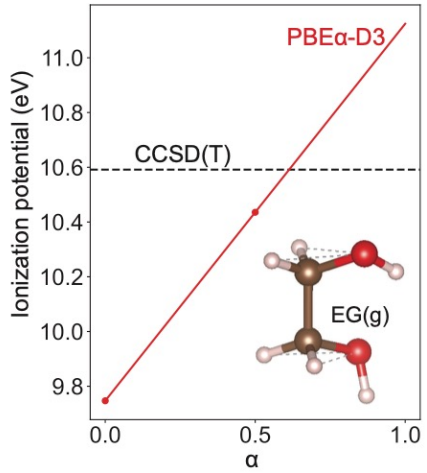


Zhang, Y. *et al*, J. Phys. Chem. B **124**, 25, (2020).

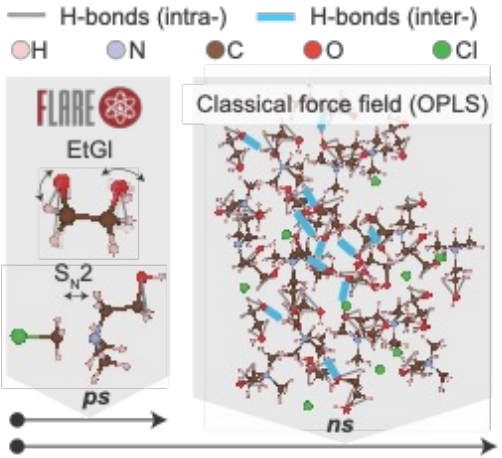
System energies agree with DFT < 5 meV/atom and no characteristic drops of 50 meV/atom are observed during equilibration and production.

From DFT to MLIP: The developed workflow

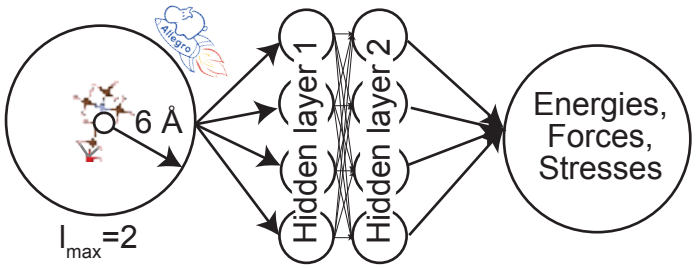
DFT approach



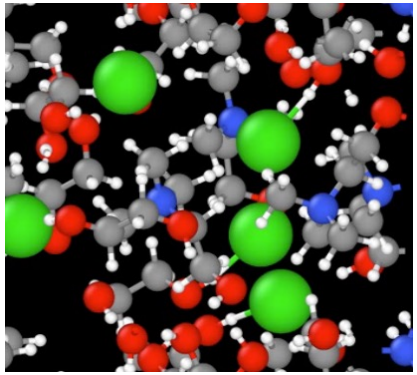
Active learning for sampling

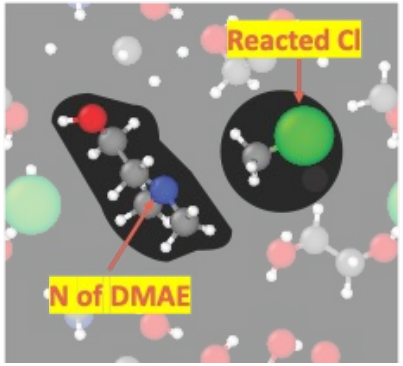


MLIP

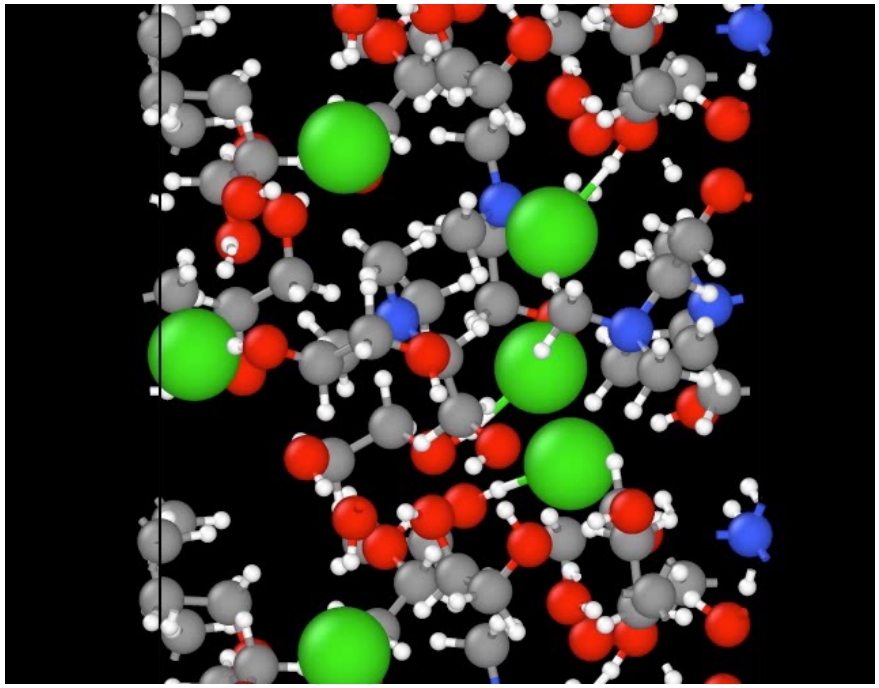


MD simulations

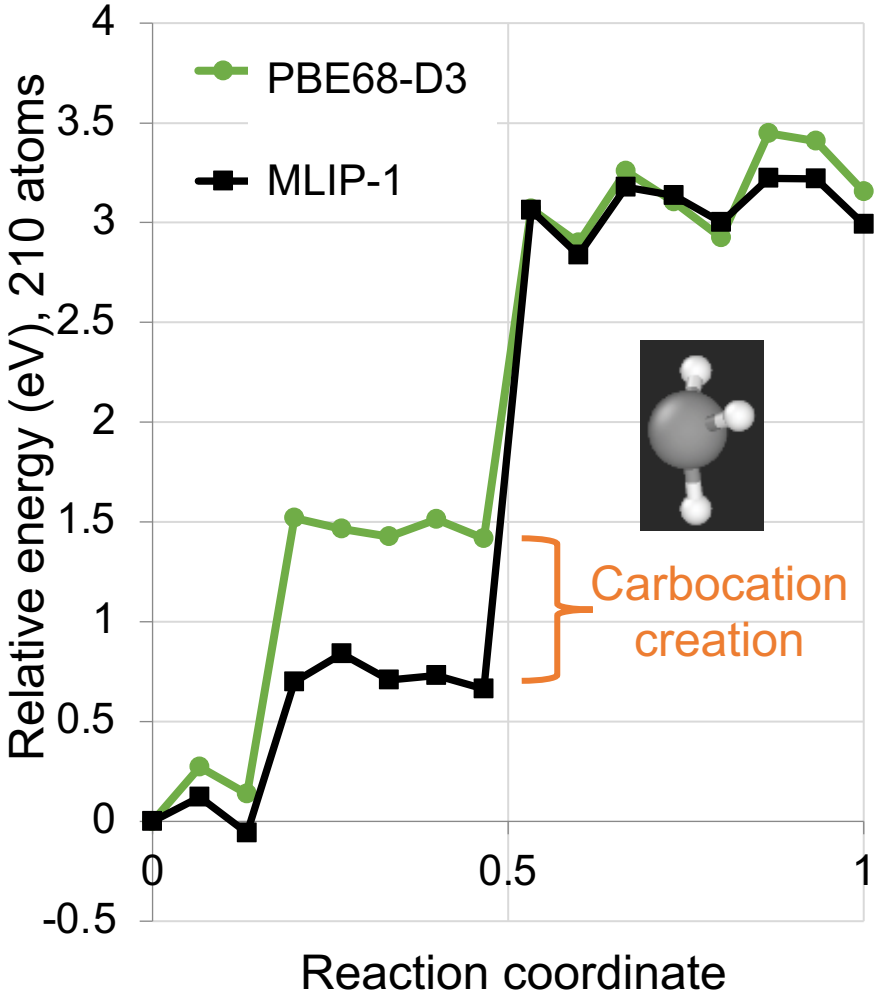




MLIP-1 Minimum Energy Pathway deviates from DFT



Minimum Energy Pathway (MEP)
for a candidate reaction, 200 ps



Deviation in the MEP is due to the generation of a new intermediate species.

Retraining with explicit reaction pathways

- 5 FLARE runs
- S_N2 reaction

593 frames

- OPLS @ 300 K, 400 K

100 frames

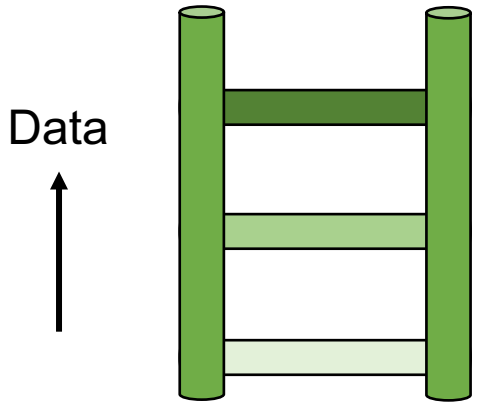
- MLIP Trajectory

58 frames, 4 ps

- Reaction pathways (4)

64 frames

MLIP-0 MLIP-1 MLIP-2



Kinetics

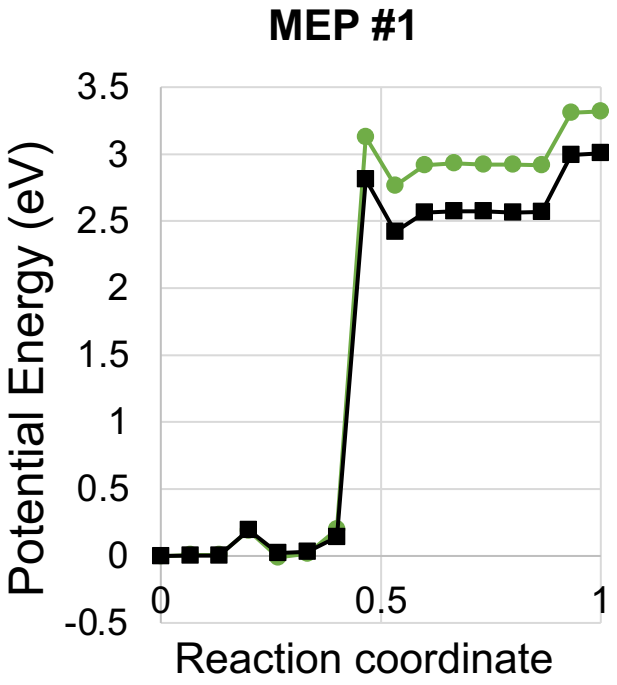
Thermodynamics

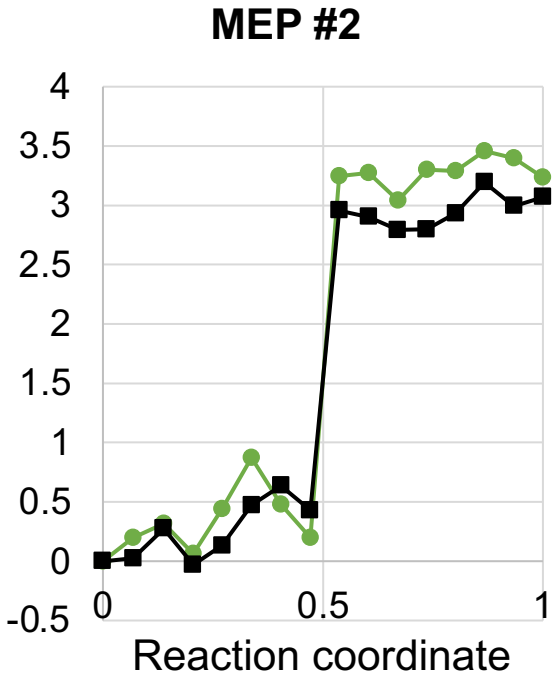
Stable potential

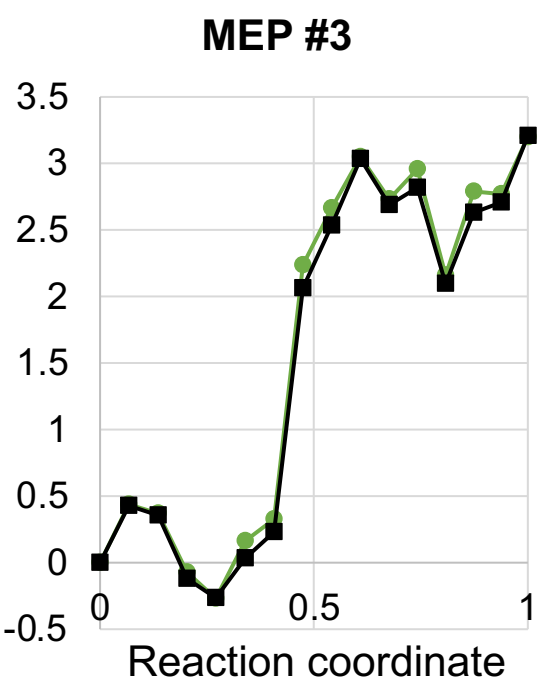
MLIP-2 test errors

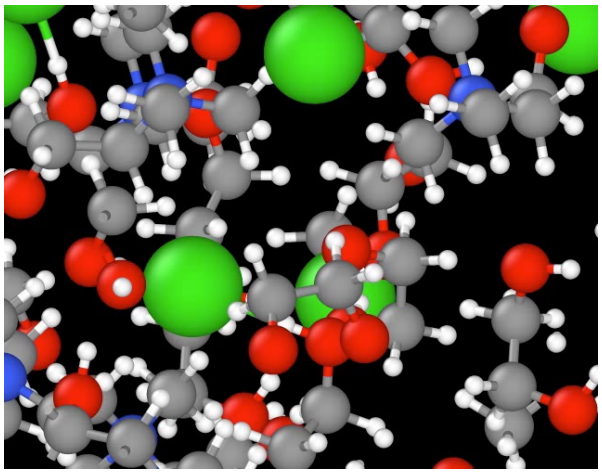
Force MAE per specie (eV/Å)	
C	0.037
Cl	0.032
H	0.022
N	0.04
O	0.046
Stress RMSE	
4.46E-4	
Entire system	
f_mae (eV/Å)	0.028
f_rmse (eV/Å)	0.077
e/N_{mae} (meV/atom)	0.54

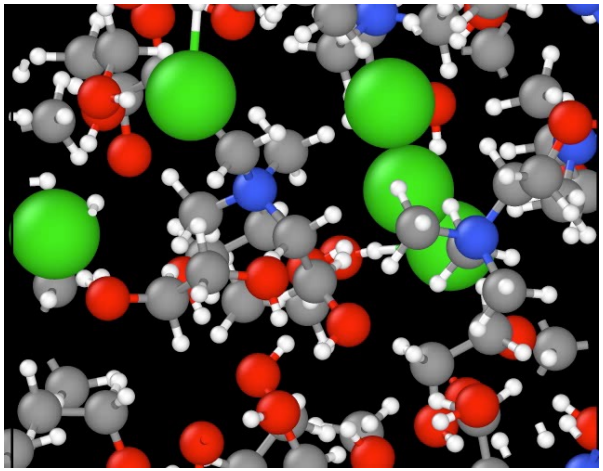
MLIP-2 exhibits improved reaction barriers

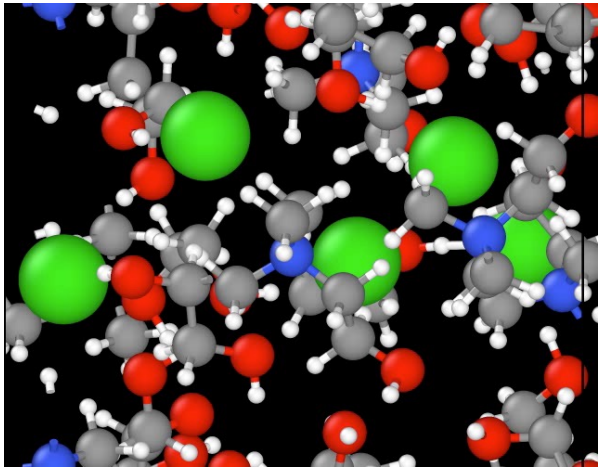




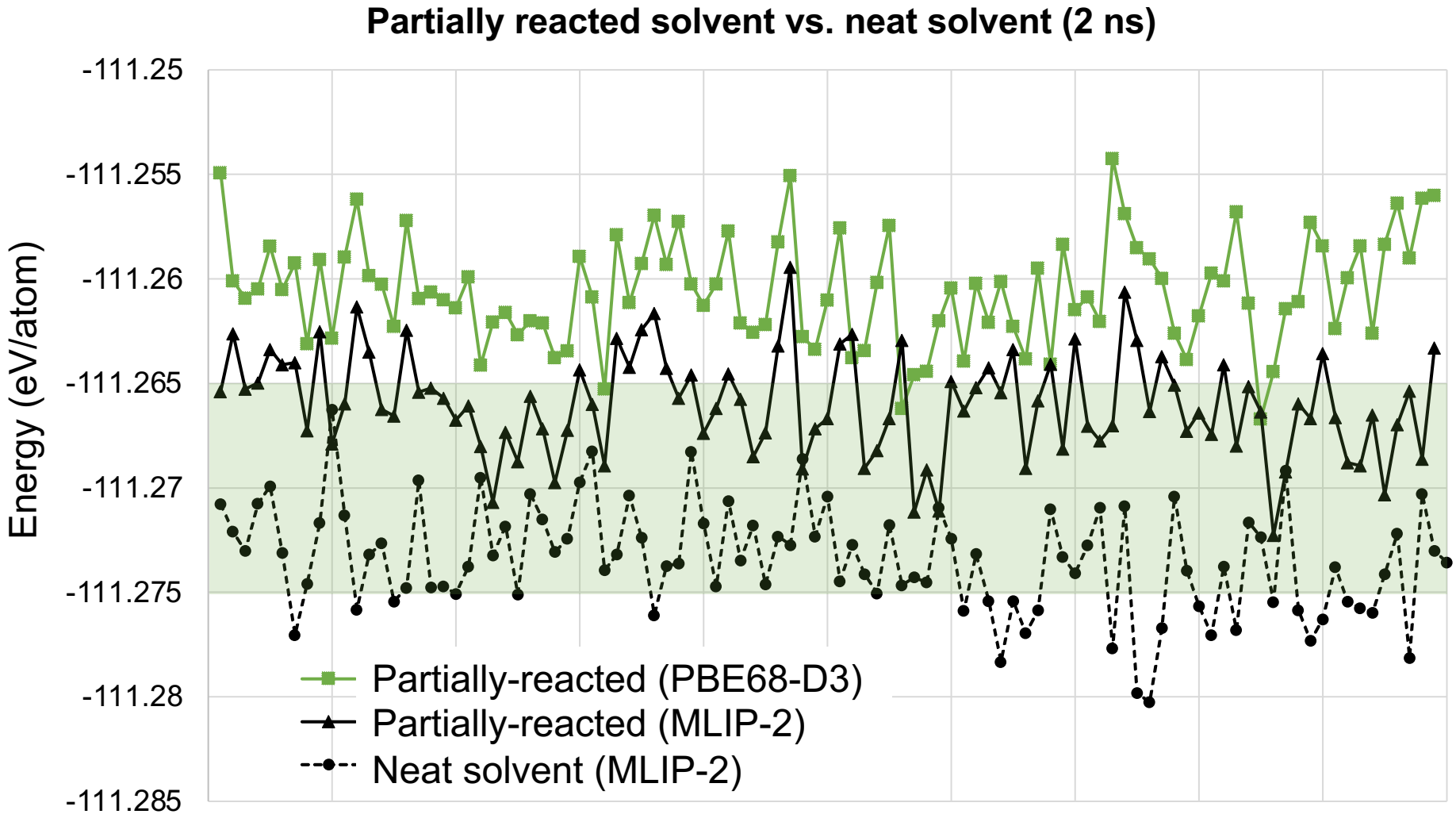






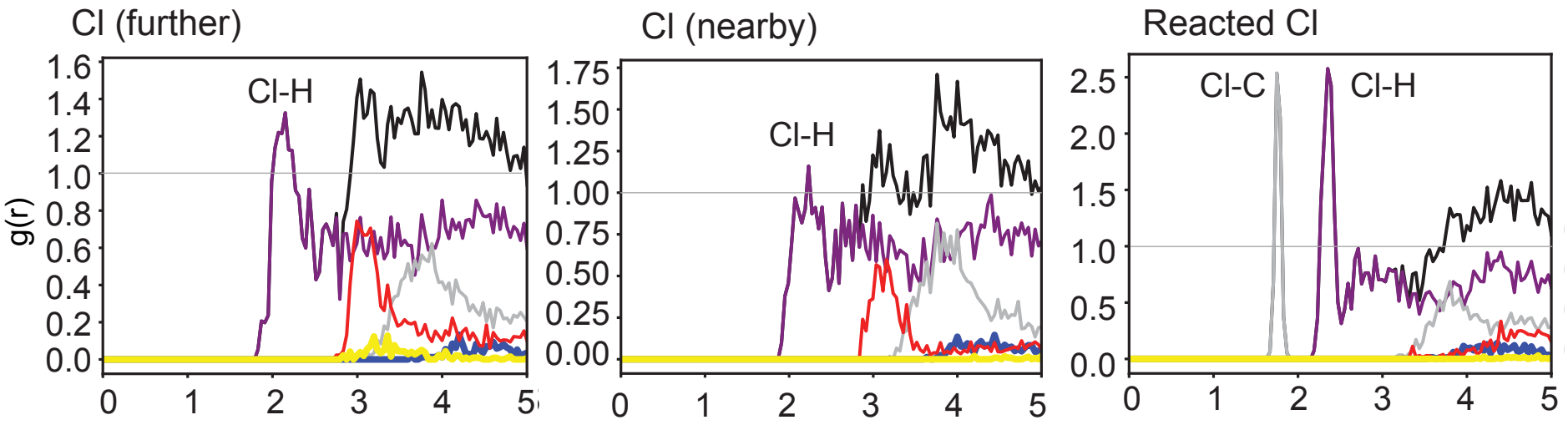


Decomposition products are further stabilized by solvent

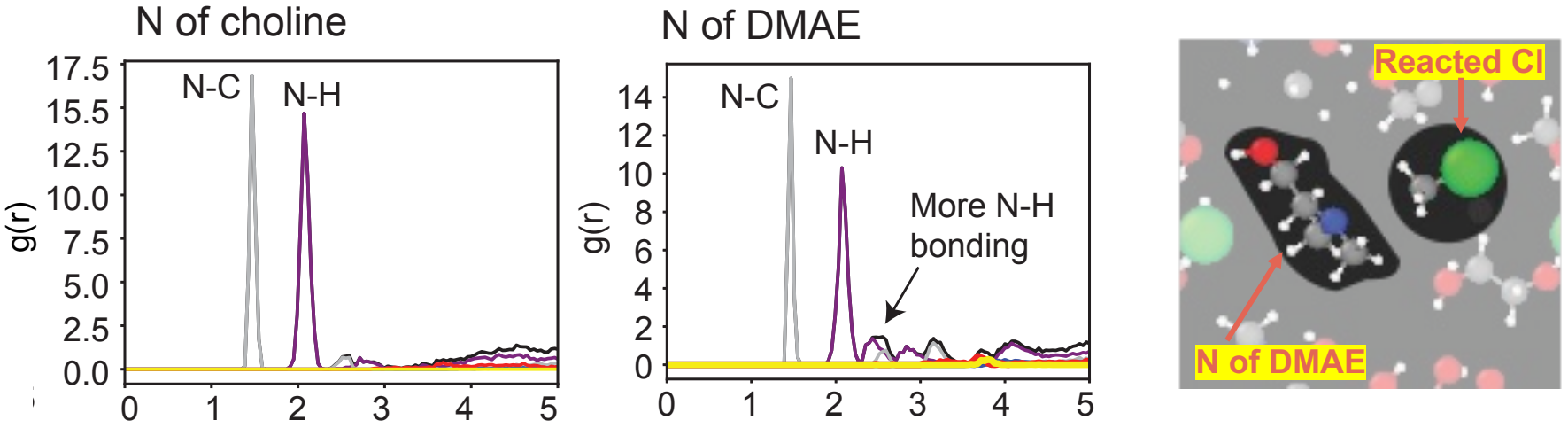


Nonpolar products rearrange and form new solvation environments, **~1 eV lower** in energy than MEP end states.

Reason for stabilization: Solvation environments change

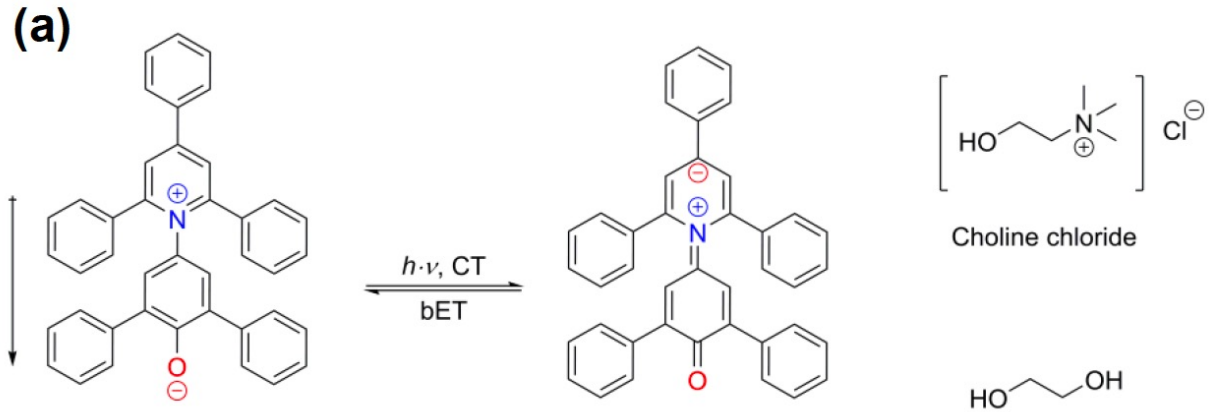


CH_3Cl generates **local "void"** and has a different interaction with surrounding solvent. DMAE straightens and has preferential "self-interaction".

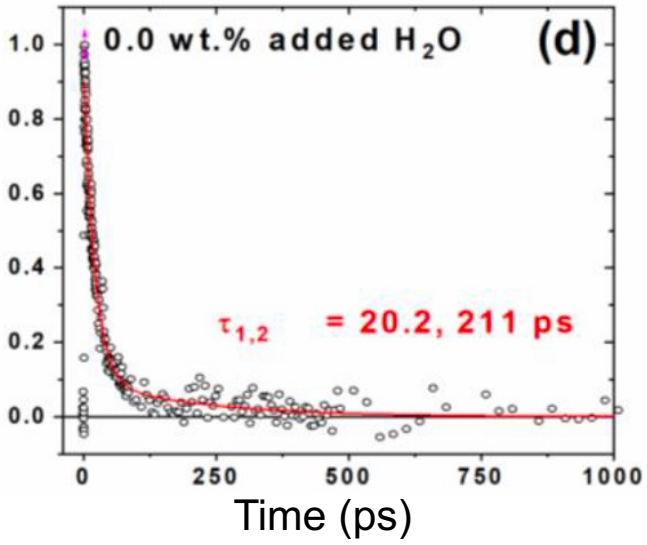


Solvation rearrangements during charge transfer should be considered.

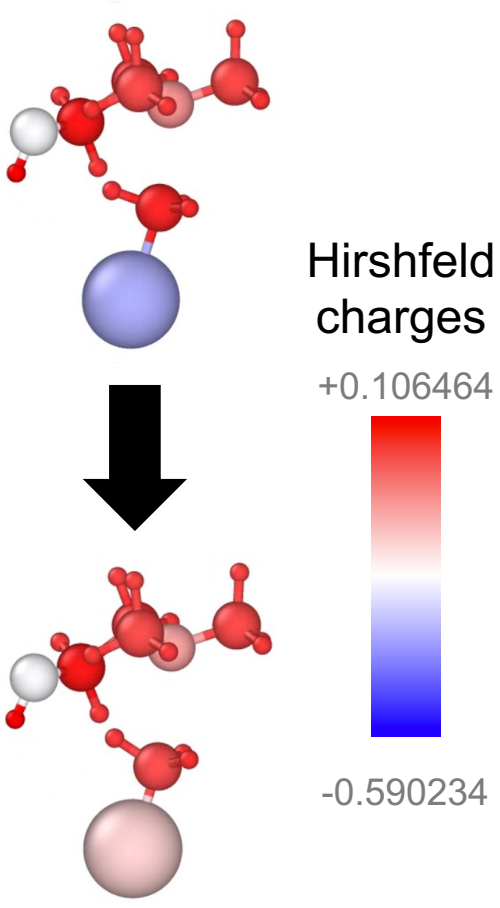
Another perspective: Solvent relaxation in ethaline **drives intramolecular charge transfer**



Femtosecond transient absorption spectra on B30 molecule probes fast (EG) and slow (choline) solvent dynamics in ethaline

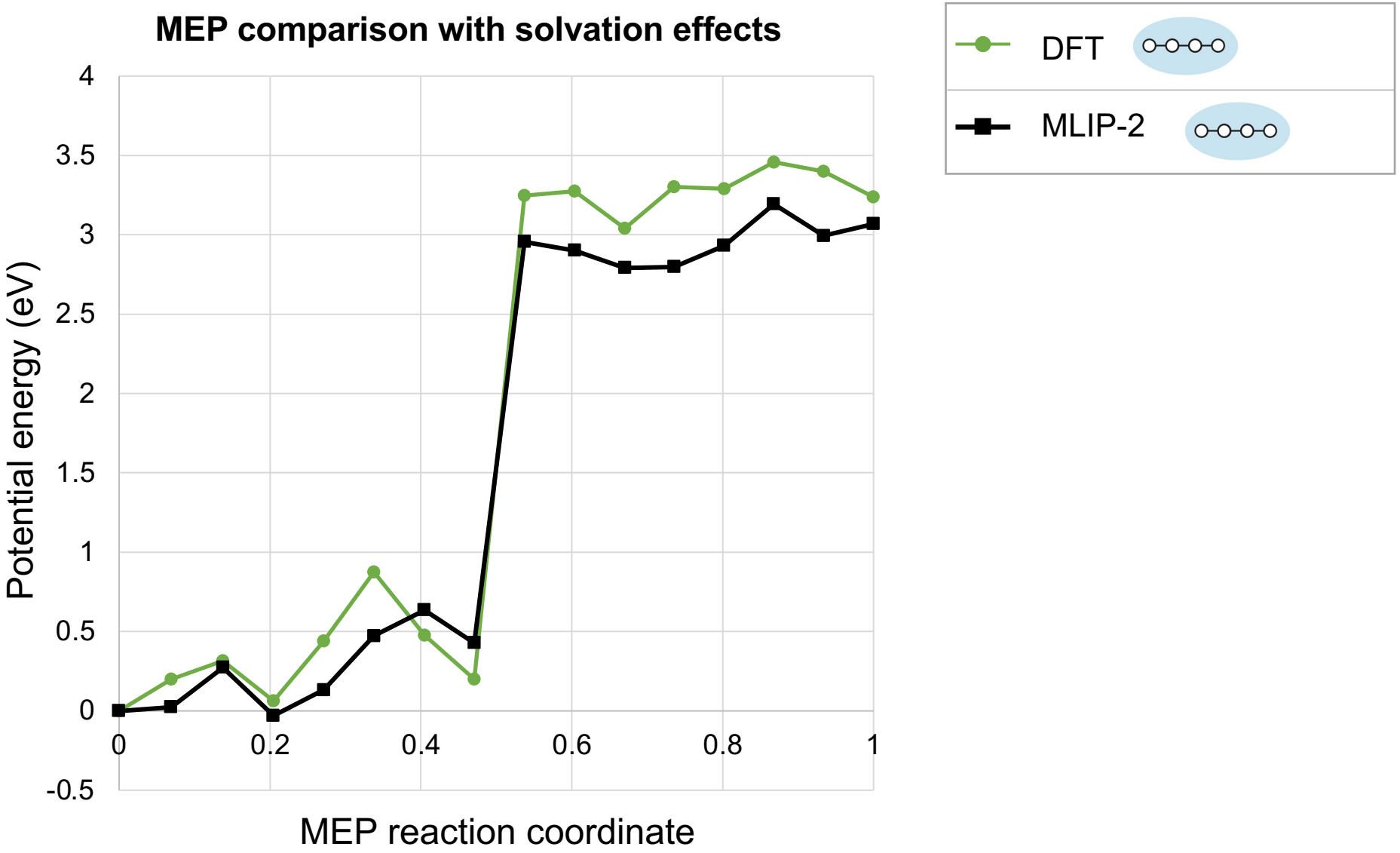


Intramolecular charge transfer in CH_3Cl:

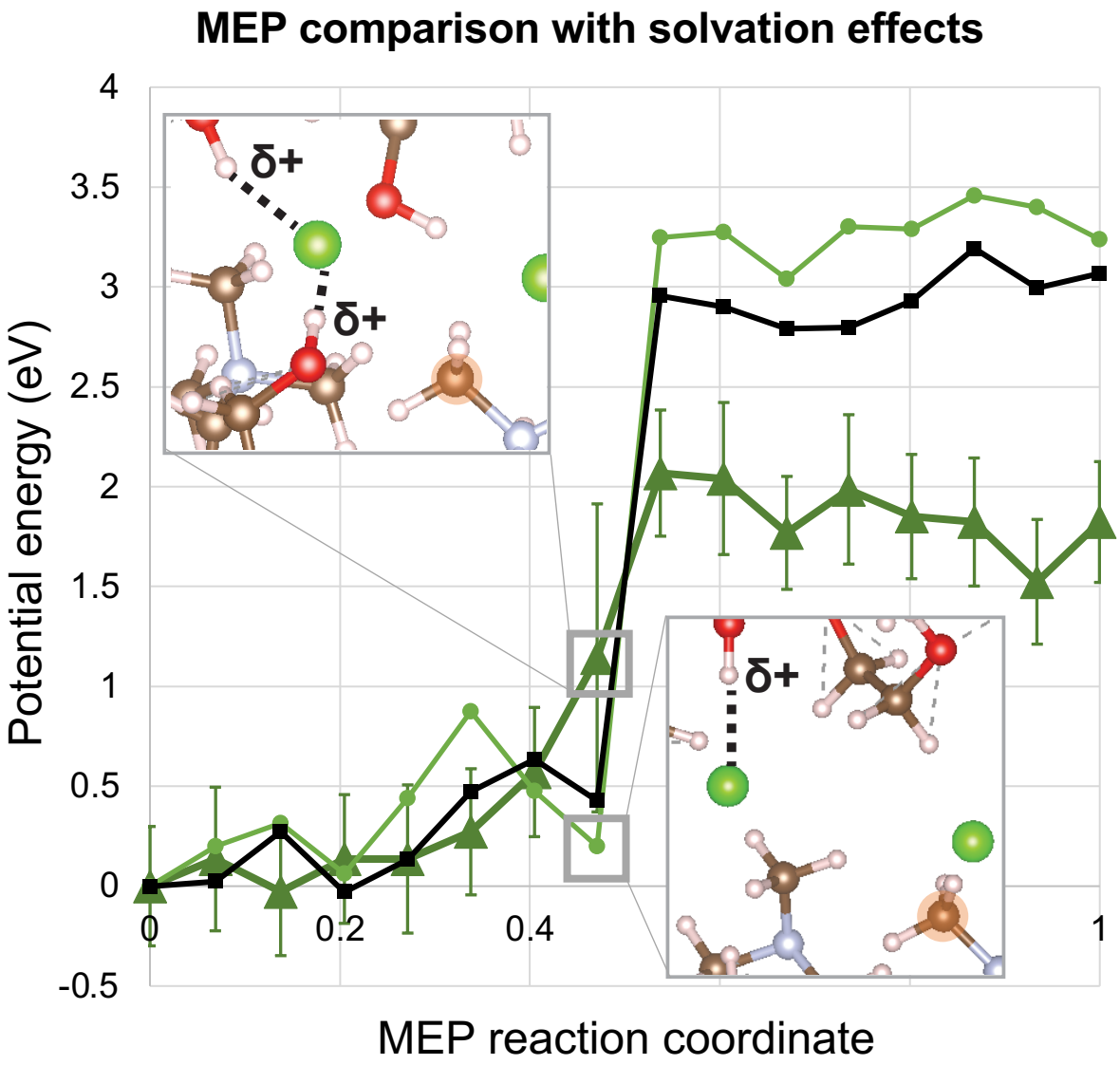


Alfurayj, I., Fraenza, C. C., Zhang, Y., Pandian, R. *et al, J. Phys Chem B*, **125**, 8888–8901, (2021).

H-bonding and solvation rearrangement lower reaction barrier



H-bonding and solvation rearrangement lower reaction barrier



DFT

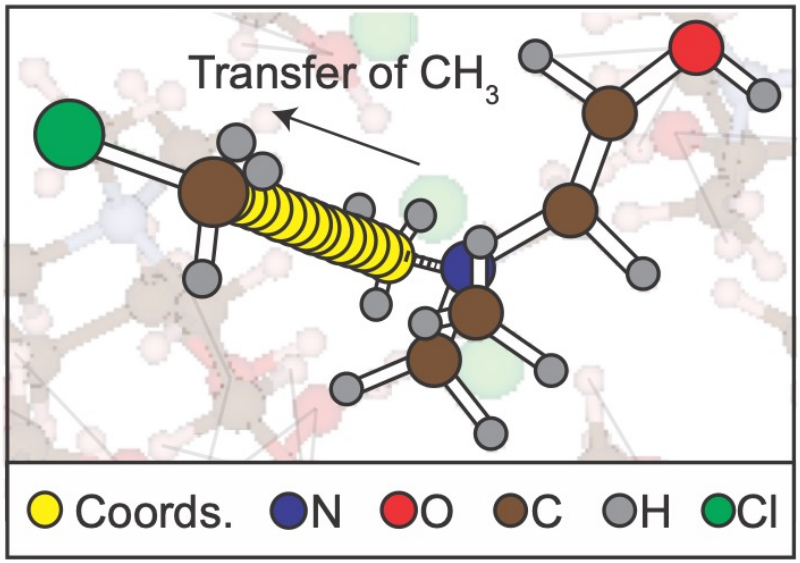
MLIP-2

NVE-DFT on structures from MLIP-2 **with 200 ps solvent relaxation**

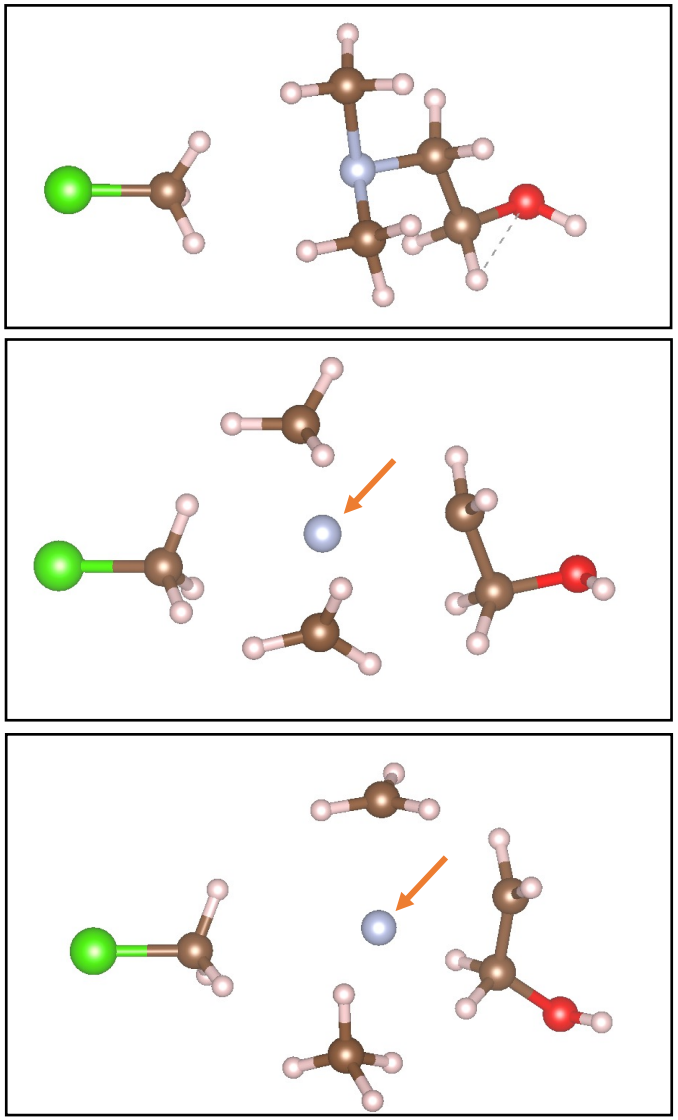
➡ Missing effects:

- Solvation shell dynamics (**~1 eV stabilization of products**)
- Hydrogen bonding dynamics (**±200-600 meV fluctuations**)

What about Umbrella Sampling-MLIP?



MLIP-2 is stable but predicts **isolated N formation** instead of transferring the methyl group



Explicit solvent not shown

Conclusions & Acknowledgements

- Chemical decomposition in organic solvents can be studied using the general workflow developed here.
    1. Hybrid DFT with a sufficiently-large (>0.3) exact exchange enables the study of charge transfer to CCSD(T) accuracy.
    2. Iterative training is essential for reproducing thermodynamically and kinetically consistent results with DFT.
    3. Some characteristic failures of MLIP:
        a. Artificially decreasing energy during equilibration (A drop of ~50 meV/atom indicates broken bonds)
        b. Under-prediction of reaction barriers.
- When reactions change polarity, solvation equilibration may be important.
- Simulations reveal dynamic H-bonding in green solvents “flattens” the PES, in this case by holding Cl near reaction sites, initiating the reaction.

Dr. Whai Shin Amanda Ooi, Columbia

Dr. Zachary A. H. Goodwin, Harvard

Dean Ah-Hyung Alissa Park, Columbia/UCLA

Prof. Boris Kozinsky, Harvard

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