Supporting Information

Long-Lived Hot Electron in a Metallic Particle for Plasmonics and Catalysis: *Ab Initio* Nonadiabatic Molecular Dynamics with Machine Learning

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Machine learning molecular dynamics

The deep-learning neural network potential (DP) training database includes a wide variety of Pt metal clusters that are either free or supported on a pristine MoS_2 monolayer slab, see Table S1. The total number of configurations in the database amounts to ~60k, a relatively larger number that is required to ensure that the intrinsically nonphysical form of the machine learning (ML) model has "learned" the relevant physics of the system. The database was mainly populated from *ab initio* molecular dynamics (AIMD) trajectories within an NVT ensemble at temperatures that range between 100 and 1600 K. We employed a relatively large 2-4 femtosecond (fs) timestep in the AIMD simulations, which is advantageous to decrease correlations between configurations along the AIMD trajectory. However, the larger timestep incurred additional computational cost due to the increase in the number of steps to converge the Kohn-Sham wavefunction between consecutive timesteps. The DP model was developed using the DeepPOT-SE approach[1] as implemented in DeePMD-Kit[2]. A cutoff radius of 7 Å was used for neighbor searching with 2 Å as the smooth cutoff. The maximum number of neighbors within the cutoff radius was set at 200. The dimensions of the embedding and fitting nets were set at 25x50x100 and 240x240x240, respectively. The neural net was trained using the Adam stochastic gradient descent method with a learning rate that decreased exponentially from the starting value of 0.001. The input data were split into training and testing sets. The testing data were not used for optimizing the weights of the network but rather were employed as an independent test for cross-validation. The training dataset was comprised of the energies and forces from the DFT database, *i.e.* for each configuration with N atoms, we had $3N+1$ reference values.

Table S1. Chemical composition of the configurations included in the databased along with the number of structures. A total of 59585 configurations are included in the database.

Training sets	Counts	Training sets	Counts
Pt_{20}	323	$Mo_{36}S_{72}Pt_{30}$	14262
Pt_{80}	2468	$Mo_{36}S_{72}Pt_{20}$	8429
Pt_{208}	40	$Mo_{81}S_{162}Pt_{185}$	94
Pt_{38}	107	$Mo_{36}S_{72}Pt_{16}$	1392
Pt_{12}	325	$Mo_{36}S_{72}Pt_{9}$	1740
Pt_{40}	148	$Mo_{36}S_{72}Pt_{15}$	1854
Pt_{34}	228	$Mo_{36}S_{72}Pt_{55}$	605
Pt_{256}	1717	$Mo_{36}S_{72}Pt_{10}$	1874
Pt_{192}	86	$Mo_{81}S_{162}Pt_{106}$	198
Pt_{55}	72	$Mo_{36}S_{72}Pt_{7}$	524
Pt_{13}	230	$Mo_{36}S_{72}Pt_{6}$	304
Pt_{15}	927	$Mo_{81}S_{162}Pt_{155}$	152
$Mo_{36}S_{72}$	1034	$Mo_{81}S_{162}Pt_{82}$	1471
$Mo_{81}S_{162}$	333	$Mo_{36}S_{72}Pt_{8}$	3630
		$Mo_{81}S_{162}Pt_{311}$	11
		$Mo_{36}S_{72}Pt_{14}$	1968
		$Mo_{81}S_{162}Pt_{92}$	331
		$Mo_{36}S_{72}Pt_{18}$	95
		$Mo_{36}S_{72}Pt_{38}$	6139
		$Mo_{36}S_{72}Pt_{19}$	18
		$Mo_{144}S_{288}Pt_{145}$	7
		$Mo_{36}S_{72}Pt_{17}$	1410
		$Mo_{81}S_{162}Pt_{134}$	197
		$Mo_{36}S_{72}Pt_{13}$	92
		$Mo_{36}S_{72}Pt_{11}$	4750

To check the validity of the ML method used, we compared the total energies of the system predicted by ML with the corresponding *ab initio* energies calculated for the same geometries. We chose 1 ps trajectories after the switching behavior, *i.e.*, the top Pt atom shifted from the center. This situation provides the more challenging example for the ML force field than the fully bonded structure. Because the ML force field was trained with CP2K, while the *ab initio* calculations were done with VASP, we could not compare the absolute total energies. Instead, we examined the relative total energies as shown in Figure S1. The figure shows fluctuation of the total energy away from the canonically averaged values for each method. The data demonstrate that the behavior of the total energy obtained from the ML calculation is very similar to that in the *ab initio* calculation. The root-mean-square deviation is only 1.1 meV/atom. This test indicates that the switching behavior predicted by the ML method is reliable.

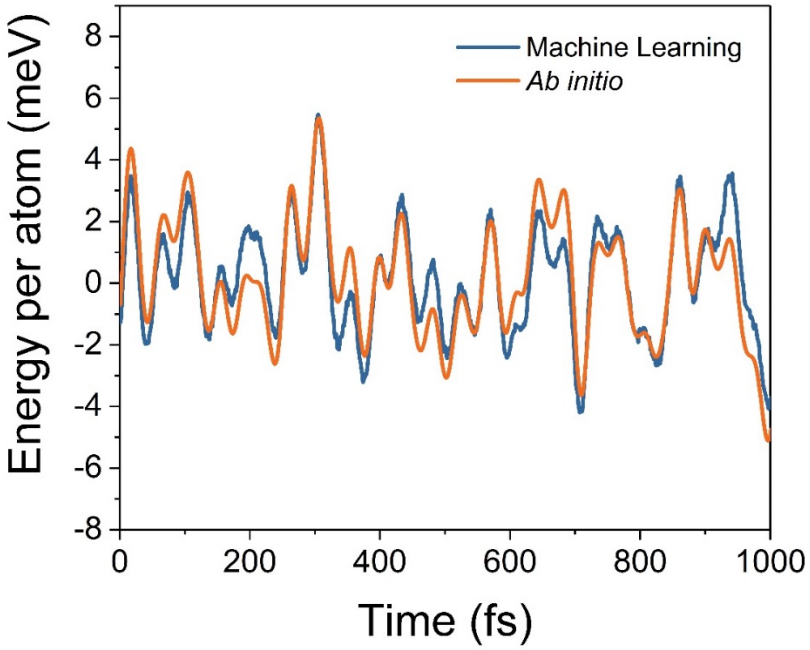

Figure S1. Evolution of the total energies of the Shifted system calculated with the machine learning and *ab initio* methods. The zero of energy is set to the average total energy obtained separately for each method.

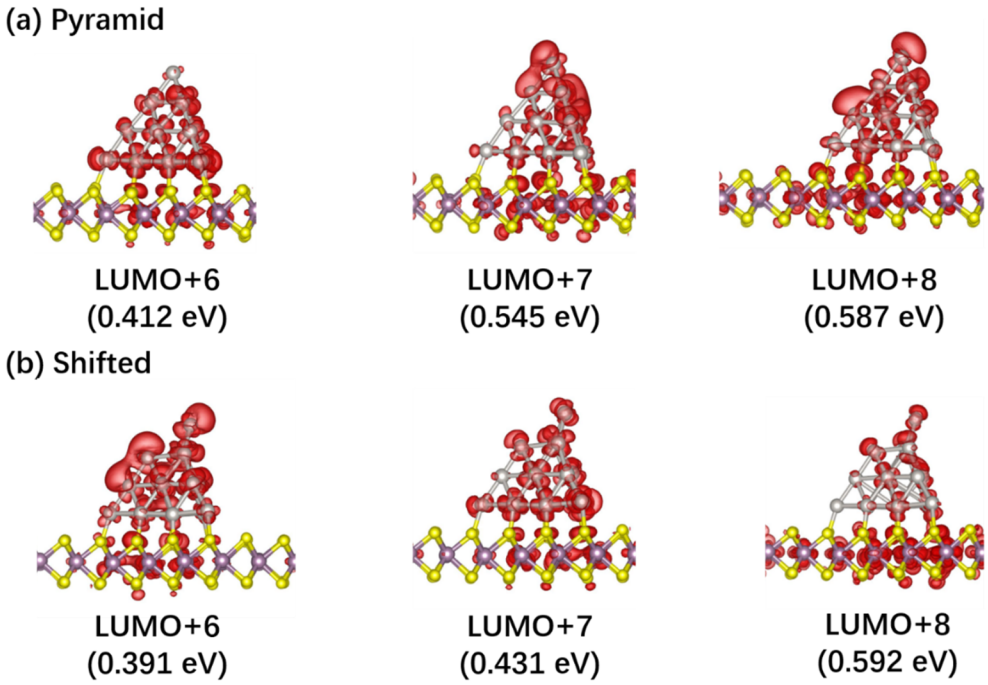

Figure S2. Charge densities of LUMO+6, LUMO+7 and LUMO+8 in the Pyramid and Shifted structures. The energy reference is set at the average energy of LUMO.

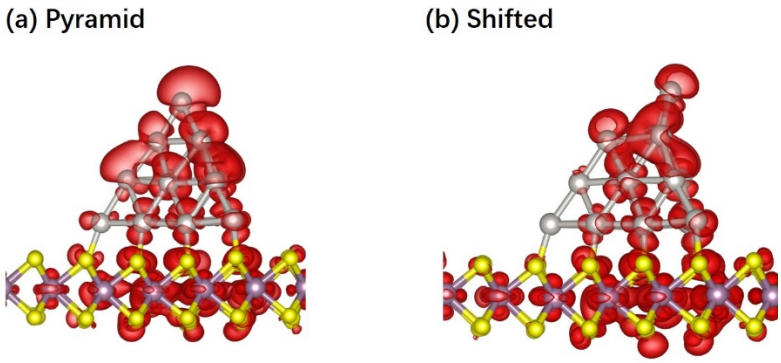

Figure S3. Canonically averaged electron density of the trap state in the two systems.

1. Zhang, L. F.; Han, J. Q.; Wang, H.; Saidi, W. A.; Car, R.; E, W. N., End-To-End Symmetry Preserving Inter-Atomic Potential Energy Model for Finite and Extended Systems. *Adv. Neural. Inf. Process. Syst.* **2018,** *31*, 4436-4446.
2. DeePMD-Kit. https://github.com/deepmodeling/deepmd-kit (accessed July 28, 2020).