Bridging the Structure Gap in Heterogeneous Catalysis: The Impact of Defects

in Dissociative Chemisorption of Methane on Ir Surfaces

Xueyao Zhou^{1,2}, Yaolong Zhang¹, Hua Guo^{2,*} and Bin Jiang^{1,*}

¹Hefei National Laboratory for Physical Science at the Microscale, Department of

Chemical Physics, University of Science and Technology of China, Hefei, Anhui

230026, China

²Department of Chemistry and Chemical Biology, University of New Mexico,

Albuquerque, New Mexico 87131, USA

Supporting information

*: corresponding authors: hguo@unm.edu, bjiangch@ustc.edu.cn

Computational details

1. Density functional theory calculations and data sampling

All density functional theory (DFT) energy points used in this work to develop the high-dimensional reactive potential energy (PES) of CH₄+Ir system were calculated with the Vienna Ab initio Simulation Package (VASP)^{1, 2} using the optPBE-vdW functional.³ The interaction between the ionic core and valence electrons were described by the projector-augmented wave (PAW) method⁴ using a plane wave basis set with a kinetic energy cutoff of 400 eV. The Brillouin zone was sampled by a 3×2 × 1 k-point mesh. The Methfessel–Paxton method with a width parameter of 0.1eV was used to extrapolate the total energy to the zero temperature value. The Ir(332) surface was modeled by a 10 layer slab in a 3×1 supercell with the size of (12.918 Å \times 8.263 Å), where the top six layers were allowed to move in the geometry optimization and *ab initio* molecular dynamics (AIMD) calculations.⁵ The vacuum space between slabs is 15 Å. To keep the cell size and the number of Ir atoms in the cell similar to that of Ir(332) model, a 3×5 supercell with a 4-layer slab having the size of 13.771 Å \times 8.263 Å was used for Ir(111) with the top two layers moveable. Saddle points for the methane dissociative chemisorption on Ir surfaces were determined by dimer method⁶ in DFT calculations. Calculated relative energies and structural parameters were shown in Table S1-4.

We have previously calculated 450 AIMD trajectories for the dissociative chemisorption of methane in laser-off conditions on Ir(332) at several incident energies $(E_i = 0.1, 0.75, 1.11 \text{ and } 1.28 \text{ eV})$ and $T_s = 1000 \text{ K}$.⁵ These calculations are extremely

time consuming and inefficient for dynamical investigations. An obvious solution is to develop high-fidelity analytical PES based on DFT energies and forces using machine learning so that no additional electronic structure calculation is needed.⁷ To this end, we have constructed such a high-dimensional PES including both the molecular and surface coordinates.⁸ About 13000 representative points were selected out of 380,000 AIMD snapshots using a force-based sampling procedure,⁹ which were then trained to yield a primitive PES. As this primitive PES covers mainly methane in the ground vibrational state, additional 924 points were sampled from much more efficient quasiclassical trajectories (QCT) simulating the dissociation of vibrationally excited methane on Ir(322) using the primitive PES. The intermediate PES relied on data points on Ir(332) was tested against the $CH_4+Ir(111)$ system, but it was found that the stationary point properties on Ir(111) were not perfectly reproduced. To better describe the stationary points on the terrace, additional 200 DFT energy points along optimized path of dissociative adsorption of CH_4 on Ir(111) were added to the training set, arriving at 14906 DFT points to generate the final PES used for dynamical calculations.

2. Neural network potential energy surface

Here, both potential energies and analytical forces of these data points were learned simultaneously with our recently developed embedded atomic neural network (EANN) method.¹⁰ Briefly, the total energy of the system is the sum of the embedded atomic energies of an *N*-atom system, $E = \sum_{i=1}^{N} E_i(\mathbf{p}^i)$, each of which is described by an elementdependent NN as a function of embedded density-like descriptor \mathbf{p}^i , formally representing the local electron density provided by neighbor atoms surrounding the embedded atom.¹⁰ Each component of ρ^i can be efficiently constructed by the square of the linear combination of "atomic orbitals" of all neighboring atoms, which mimics the computation of electron density from atomic orbitals in quantum chemistry. Following our recent work,¹¹ a set of piecewise atomic orbitals of each neighboring atom *j* are used,

$$\varphi_{l_x l_y l_z}^{\alpha, r_{in}, r_{out}}(\hat{\mathbf{r}}_{ij}) = x^{l_x} y^{l_y} z^{l_z} f_{r_{in}, r_{out}}^{\alpha}(r_{ij}), \qquad (S1)$$

where $\hat{\mathbf{r}}_{ij}$ is the Cartesian coordinates of the embedded atom *i* relative to atom *j*, r_{ij} is the distance between them, l_x , l_y , and l_z are equivalent of the projections of the orbital angular momentum and their sum is the total orbital angular momentum (*L*), and $f_{r_{in},r_{out}}^{\alpha}(r_{ij})$ is a piecewise switching function in the radial degree of freedom,

$$f_{r_{\text{in}},r_{\text{out}}}^{\alpha}(r) = \begin{cases} 1 & x \le 0, \\ \frac{\exp\left[-\alpha x^{2}(2-x)^{2}\right] - \exp(-\alpha)}{1 - \exp(-\alpha)} & 0 < x < 1, \\ 0 & x \ge 1, \end{cases}$$
(S2)

where $x = (r - r_{in}) / (r_{out} - r_{in})$ and α , r_{in} , r_{out} , are parameters that determine the shape and interval of the switching function. For each set of $\varphi_{l_x l_y l_z}^{\alpha, r_{in}, r_{out}}(\hat{\mathbf{r}}_{ij})$ for neighbor atoms, the corresponding density-like descriptor is given by,

$$\rho_L^{i,\alpha,r_{\rm in},r_{\rm out}} = \sum_{l_x,l_y,l_z}^{l_x+l_y+l_z=L} \frac{L!}{l_x!l_y!l_z!} (\sum_{j=1}^{L} c_j \varphi_{l_xl_yl_z}^{\alpha,r_{\rm in},r_{\rm out}}(\hat{\mathbf{r}}_{ij}))^2,$$
(S3)

where c_j is the element-dependent linear combination coefficient of an orbital of atom j and optimized in the training process, and $\frac{L!}{l_x!l_y!l_z!}$ the prefactor allowing the transformation from the two-body summation to three-body angular basis. In other words, the density-like descriptors given in Eq. (3) scale linearly with respect to the

number of neighboring atoms and implicitly involve three-body information. The EANN model has been successfully applied to representation of PESs in various systems, including molecules,¹⁰ condensed phase systems,¹⁰ as well as gas-surface reactions,^{12, 13} and the piecewise EANN (PEANN) model used here further improves its efficiency. The well converged PEANN PES has a $60 \times 30 \times 60 \times 1$ neural network structure for each atom with *L* up to 2. r_{in} and r_{out} are evenly space grids of [0.6, 6.3] and [1.5, 7.2] Å with an interval of 0.3 Å. α in eq. (S2) is determined by $\alpha = 10 \times (r_{in} - r_{out})/3.5^{r_{in}}$. An important character of the PEANN PES is that it describes methane interacting with both the (111) and (332) facets of Ir at high temperatures.

3. Dynamical calculations

QCT calculations were performed using a modified version of the VENUS code.¹⁴ Like in our earlier AIMD simulations,⁸ surface configurations were selected randomly from an NVT run of the surface equilibrated to the target temperature of 1000 K. CH₄ was initially set at 8.0 Å above the surface and the molecular center was chosen randomly within the surface unit cell. The molecule was allowed to collide with the surface along the surface normal with the incidence energy ranging from 0.03 to 0.5 eV. To mimic the experimental laser-off conditions,¹⁵ the initial vibrational state energies were sampled from a Boltzmann distribution with the vibrational temperature taken as the nozzle temperature ($T_N = 300$ K) and the rotational temperature was set as zero, assuming very efficient cooling in the supersonic beam experiment. For describing state-resolved experiments,¹⁵ the antisymmetric stretching mode (1 ν_3) of CH₄ was excited via the standard normal mode sampling procedure, and the rotational

state was selected by a symmetric top with J = 2, K = 0. The initial orientation of the impinging molecule was chosen randomly. The trajectory was propagated with a time step of 0.1 fs. A trajectory was considered as "reactive" if one of the C-H bonds stretched to 2.2 Å, "scattered" when the molecule was reflected back to 8.1 Å above the surface, and "trapped" if the molecule remained stuck on the surface after the maximum propagation time of 10 ps (30 ps in some cases). Note that these trajectories might eventually react or desorb if propagated for longer time. A few thousand trajectories at high incidence energies and up to 10^5 trajectories at each low incident energy were computed to achieve reasonable statistics, which is currently unattainable with AIMD.

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Table S1. Adsorption energies (E_{ad}) and structural parameters (see Figure S1 to find the illustration) of CH₄ on Ir(111) predicted by the PEANN PES, compared with DFT results using the optPBE-vdW functional. The nomenclature of stationary points follows our previous work.⁵ E_{ad} is relative to the asymptotic energy of the free CH₄ molecule above the surface by 7.0 Å. Available reference data of E_{ad} are listed for comparison.

name	$E_{\rm ad}({\rm eV})$	$E_{\rm ad}({\rm eV})$ $r_{\rm C-H}({\rm \AA})$		$\theta_{\rm HCH}(^{\circ})$				
PEANN PES								
H1-top	0.151	1.10	3.81	109.5				
H2-top	0.160	1.10	3.82	109.5				
H3-top	0.168	1.10	3.80 109.5					
		DFT						
H1-top	0.152	1.10	3.78	109.5				
H2-top	0.161	1.10	3.76	109.5				
H3-top	0.169	1.10	3.74	109.5				
Reference data (E_{ad})								
0.18ª, 0.22 ^b								
D D 0 1 (

^afrom Ref. 16.

^bfrom Ref. 17.

Name	$E_{\rm ad}(eV)$	$r_{\rm C-H}$ (Å)	$Z_{\rm C}(\rm \AA)$	$\theta_{\rm HCH}(^{\circ})$			
PEANN PES							
H3-step top	0.253	1.10	2.07	109.5			
H2-step top	0.252	1.10	2.65	109.5			
H2-1 st top	0.173	1.10	3.73	109.5			
H2-1 st bridge	0.154	1.10	3.81	109.5			
H2-1 st hcp	0.155	1.10	3.46	109.5			
DFT							
H3-step top	0.247	1.10	2.26	109.5			
H2-step top	0.240	1.10	2.46	109.5			
H2-1 st top	0.174	1.10	3.75	109.5			
H2-1 st bridge	0.168	1.10	3.81	109.5			
H2-1 st hcp	0.167	1.10	3.57	109.5			

Table S2. Same as Table S1, but for CH₄+Ir(332) system.

available reference data of <i>L</i> _b are also listed for comparison.								
	PEANN PES				DFT			
Name	$E_{b}(eV)$	$d_{ ext{C-H}}(ext{Å})$	Z _C (Å)	$ heta(\circ)$	E _b (eV)	$d_{ ext{C-H}}(ext{\AA})$	Z _C (Å)	$ heta(\circ)$
Rigid surface								
tbe	0.877	1.60	2.31	129.8	0.866	1.58	2.32	131.0
tba	0.838	1.60	2.32	128.8	0.865	1.55	2.33	131.9
Ref. data (E_b)			0	.83ª, 0.85	5 ^b , 0.836 ^c	;		
Relaxed surface								
tbe	0.684	1.54	2.27	127.7	0.696	1.55	2.28	129.9
tba	0.703	1.52	2.28	128.9	0.698	1.53	2.28	129.4
Ref. data (E_b)			0	.66ª, 0.62	2 ^b , 0.642 ^c	;		

Table S3. The same as Table S1 but for dissociation barriers (E_b) and transition states. Available reference data of E_b are also listed for comparison.

^athe lowest barrier of DFT-PBE calculations from Ref. 18.

^bthe lowest barrier of RFF from Ref. 16.

^cfrom SRP32-vdW calculations from Ref. 17.

	PEANN PES				DFT			
Name	$E_{\rm b}({\rm eV})$	$d_{\text{C-H}}(\text{\AA})$	$Z_{\rm C}({\rm \AA})$	$ heta(\circ)$	$E_{\rm b}({\rm eV})$	$d_{\text{C-H}}(\text{\AA})$	$Z_{\rm C}({\rm \AA})$	$ heta(\circ)$
			Rig	id surfa	ce			
bta-s	0.310	1.54	1.81	96.5	0.297	1.53	1.80	96.1
bte-s	0.326	1.57	1.78	95.7	0.304	1.56	1.77	95.1
bbe-s	0.360	1.56	1.99	119.8	0.345	1.56	1.95	118.1
tbe-t	0.863	1.60	2.26	127.3	0.846	1.58	2.29	130.0
tba-t	0.848	1.57	2.30	129.6	0.845	1.56	2.30	130.6
			Rela	xed surf	ace			
bta-s	0.241	1.52	1.85	98.6	0.216	1.51	1.81	96.5
bte-s	0.243	1.54	1.82	97.5	0.220	1.54	1.74	94.0
bbe-s	0.276	1.53	2.02	121.5	0.252	1.54	1.91	116.1
tbe-t	0.691	1.55	2.24	127.2	0.673	1.56	2.24	127.0
tba-t	0.698	1.53	2.26	131.8	0.672	1.52	2.25	127.2

Table S4. Same as Table S3, but for CH_4 +Ir(332) system.

Table S5. Comparison of electronic coupling .parameters ($\Delta E_b/\Delta Z_{Ir}$) on PEANN PES and available reference data on Ir(111) and Ir(332).

	$\Delta E_{\rm b}/\Delta Z_{\rm Ir} ({\rm eV/\AA})$			
	Ir(111)			
PEANN PES	-1.38			
Reference data	-1.41 ^a , -1.50 ^b , ~1.70 ^c , 1.56 ^d			
	Ir(332)			
PEANN-PES	-0.96			
Reference data	-0.94ª			

^afrom DFT calculations via optPBE-vdW functional of Ref. 5.

^bfrom DFT calculations via PBE functional of Ref. 18.

^cfrom RFF data of Ref. 16.

^dfrom DFT calculations via SRP32-vdW functional of Ref. 17.

E_i (eV)	$P_{\rm trap}$	v (Å/ps)	$\tau(\mathrm{ps})$	$P_{\rm diss}$	$S_{0, ext{defect}}^{ ext{direct}}$	$S_{0,\mathrm{terrace}}$	
Laser-off							
0.03	5.6×10 ⁻¹	5.7		9.5×10-3	1.0×10 ⁻²	4.0×10-5	
0.04	5.0×10 ⁻¹	5.7		9.5×10 ⁻³	9.6×10 ⁻³	2.0×10 ⁻⁵	
0.07	3.8×10 ⁻¹	5.8		9.6×10-3	8.8×10 ⁻³	6.0×10 ⁻⁵	
0.09	2.8×10 ⁻¹	5.8		9.6×10 ⁻³	1.3×10 ⁻²	1.0×10 ⁻⁴	
0.13	1.6×10 ⁻¹	6.1	19	9.7×10 ⁻³	1.9×10 ⁻²	1.8×10 ⁻⁴	
0.17	8.2×10 ⁻²	6.1		9.7×10-3	2.7×10 ⁻²	2.6×10-4	
0.25	2.1×10 ⁻²	6.0		9.7×10 ⁻³	5.7×10 ⁻²	1.1×10 ⁻³	
0.34	3.3×10 ⁻³	6.9		1.0×10 ⁻²	7.7×10 ⁻²	3.0×10 ⁻³	
0.50	3.0×10 ⁻⁴	9.2		1.3×10 ⁻²	1.5×10 ⁻¹	1.3×10 ⁻²	
			CH ₄ (1)	V ₃)			
0.03	5.3×10 ⁻¹	6.0		3.6×10 ⁻²	3.3×10 ⁻²	2.6×10 ⁻⁴	
0.04	4.6×10 ⁻¹	6.0		3.6×10 ⁻²	3.8×10 ⁻²	3.6×10 ⁻⁴	
0.07	3.4×10 ⁻¹	6.1		3.6×10 ⁻²	4.4×10 ⁻²	3.2×10 ⁻⁴	
0.09	2.6×10 ⁻¹	6.1		3.6×10 ⁻²	3.9×10 ⁻²	6.4×10 ⁻⁴	
0.13	1.5×10 ⁻¹	6.3	19	3.7×10 ⁻²	7.0×10 ⁻²	1.2×10 ⁻³	
0.17	8.1×10 ⁻²	6.3		3.7×10 ⁻²	6.2×10 ⁻²	1.8×10 ⁻³	
0.25	2.1×10 ⁻²	6.6		3.7×10 ⁻²	1.1×10 ⁻¹	4.3×10 ⁻³	
0.34	4.4×10-3	8.1		4.0×10 ⁻²	1.4×10 ⁻¹	1.0×10 ⁻²	
0.50	6.0×10 ⁻¹	5.4		3.5×10 ⁻²	2.5×10 ⁻¹	3.8×10 ⁻²	

Table S6. Parameters in the model to predict S_0 of CH₄ on defected Ir surfaces.



Figure S1. Structures of adsorption (a, b) and transition states for dissociative adsorption (c, d) of CH₄ on Ir(111) (a, c) and Ir(332) (b, d) to define the structural parameters: $Z_{\rm C}$ is the height of C atom above its nearest Ir atom. For adsorption geometries, $r_{\rm C-H}$ is the length of one of four equivalent C-H bonds of CH₄ and $\theta_{\rm HCH}$ is the angle between two C-H bonds. For transition states, $d_{\rm C-H}$ is the length of the dissociating C-H bond and θ is the polar angle between the breaking C-H bond and the Z axis.



Figure S2. Comparison of one-dimensional potential energy curves of CH₄ approaching the rigid Ir(332) (black) and Ir(111) (red) surfaces by the PEANN PES (solid lines) and DFT calculations (circles), as a function of Z_C by moving the "H3-step-top" and "H2-top" adsorption structures up and down on the Ir(332) and Ir(111) surfaces, respectively.



Figure S3. Harmonic vibrational energies of $CH_4(1\nu_3)$ as a function of free propagation time over 1000 QCT trajectories at $E_i = 0.03$ eV. Note that the time scale is ~500 fs for CH₄ to reach the interaction region from 8.0 Å above the surface.



Figure S4. Vertical displacement distributions (ΔZ_{Ir}) of topmost Ir atoms relative to their equilibrium positions for Ir(111) (a) and Ir(332) (b) systems, obtained from the AIMD calculations and the MD calculations on PEANN PES at $T_s = 1000$ K.



Figure S5. Comparison of $\Delta Z_{\rm Ir}$ distributions from the MD calculations on PEANN PES and RFF of Ref. ¹⁶ for Ir(111) at $T_{\rm s} = 1000$ K, where $\Delta Z_{\rm Ir}$ is the vertical displacement of topmost Ir atoms with respect to the average height of six nearest surface atoms.



Figure S6. Comparison of indirect contribution of defect sites ($S_{0,defect}^{indirect}$) between our and Jackson's models with a step density of 0.5%.