Critical assessment of the performance of mBEEF and RPBE XC functionals for C_2H_2 and C_2H_4 adsorption on transition metal surfaces

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NOMAD

NOVEL MATERIALS DISCOVERY

MAX-PLANCK-GESELLSCHAFT

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Outline

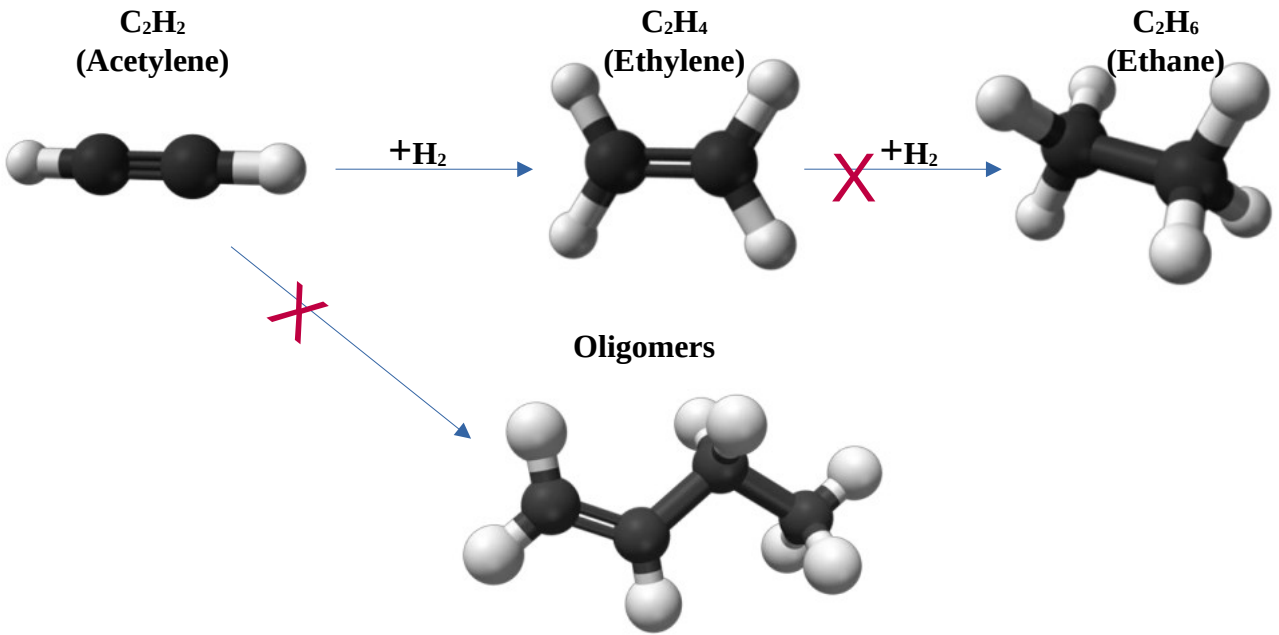
- The importance of the adsorption of C_2H_2 and C_2H_4 molecules on TMSs

- Why focusing on mBEEF and RPBE XC functionals

- Investigated properties to evaluate the selected XC functionals
  - Vibrational frequencies
  - Adsorption energy

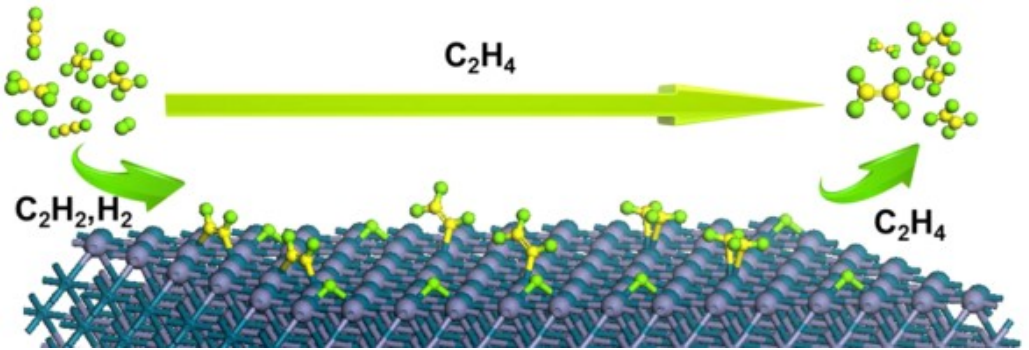
The importance of C_2H_2 and C_2H_4 adsorption on TMSs

- C_2H_4 is one of the largest chemical building blocks for polymers production
- C_2H_2 presents in many C_2H_4's synthesis ways which deactivates the catalyst that is used for the polymerization of C_2H_4
- Using TM-based heterogeneous catalysts for selective hydrogenation:
  - A highly selective catalyst to convert all of the C_2H_2 to C_2H_4
  - Prevent over-hydrogenation and oligomerization of C_2H_2 to form higher molecular weight compounds



Why focusing on mBEEF and RPBE XC functionals

- Computational study is one of the powerful tools to investigate such processes



[1] Photo is taken from: H. Zhou, X. Yang, L. Li, X. Liu, Y. Huang, X. Pan, A.Wang, J. Li, and T. Zhang, ACS Catal. 6, 1054−1061 (2016).

Why focusing on mBEEF and RPBE XC functionals

- Computational study is one of the powerful tools to investigate processes
  - Among them, DFT is a useful theoretical approach in condensed matter physics for the catalytic systems
  - The reliability of DFT results strongly depends on the choice of XC functional
    - **RPBE** GGA-XC functional which is specifically developed to treat **adsorption properties** can accurately predict chemisorption energies[1-4]
    - A recently work on TM surfaces shows **mBEEF** metaGGA-XC functional provides good agreement of **surface energies** and **work functions** with related experimental data[5]
    - Previous benchmark studies show that the challenge of finding an optimal functional that could simultaneously capture both covalent and non-covalent interactions persists

[1] B.-T. Teng, X.-D. Wen, M. Fan, F.-M. Wu, and Y. Zhang, Physical Chemistry Chemical Physics 16, 18563 (2014).
[2] J. Wellendorff, T. L. Silbaugh, D. Garcia-Pintos, J. K. Nørskov, T. Bligaard, F. Studt, and C. T. Campbell, Surface Science 640, 36 (2015).
[3] J. Wellendorff, K. T. Lundgaard, A. Møgelhøj, V. Petzold, D. D. Landis, J. K. Nørskov, T. Bligaard, and K. W. Jacobsen, Phys. Rev. B 85, 235149 (2012).
[4] S. M. Sharada, R. K. Karlsson, Y. Maimaiti, J. Voss, and T. Bligaard, Physical Review B 100, 035439 (2019).
[5] L. Kabalan, I. Kowalec, R. Catlow, and A. Logsdail, (2021).

Vibrational Mode Analysis for C_2H_2 and C_2H_4 on molecules

Problem:

Limitation/Lack of enough experimental results for simple properties of C_2H_2 and C_2H_4 on the pure and alloy TM surfaces (e.g., adsorption energy)

Question:

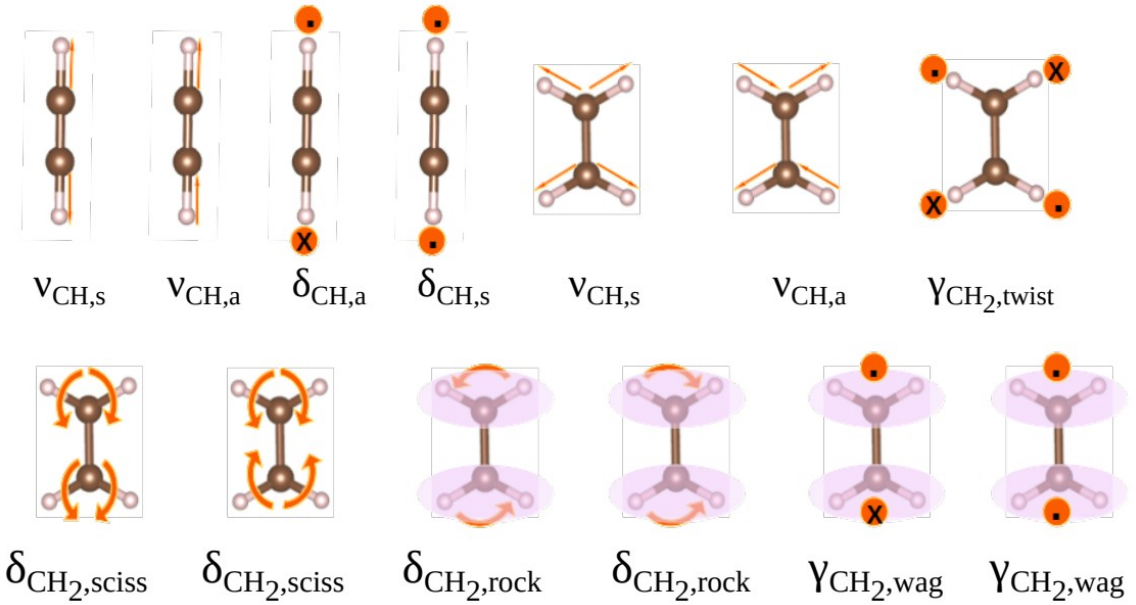
What other properties can also be compared with the experimental results?

Idea:

The vibrational modes of C_2H_2 and C_2H_4 molecules on the mono-metal surface had been measured mainly by EELS (electron energy loss spectroscopy) and actively reported in 1980~90s.

The XC functional that can describe the vibrational modes of C_2H_2 and C_2H_4 on the mono-metal surfaces can also describe those on the corresponding alloy surface.

Vibrational Modes of C_2H_2 and C_2H_4



ν : stretching modes δ : in-plane bending modes γ : out-of-plane bending modes
s : symmetry modes a : asymmetry modes

Computational details

- DFT calculations:

FHI-aims, tight setting, applying dipole correction, scalar-relativistic (atomic ZORA)

- Seven-layer (111) slabs of Pd, Pt, Cu, and Rh: four bottom-layer fixed

- Vacuum: at least 15 Å

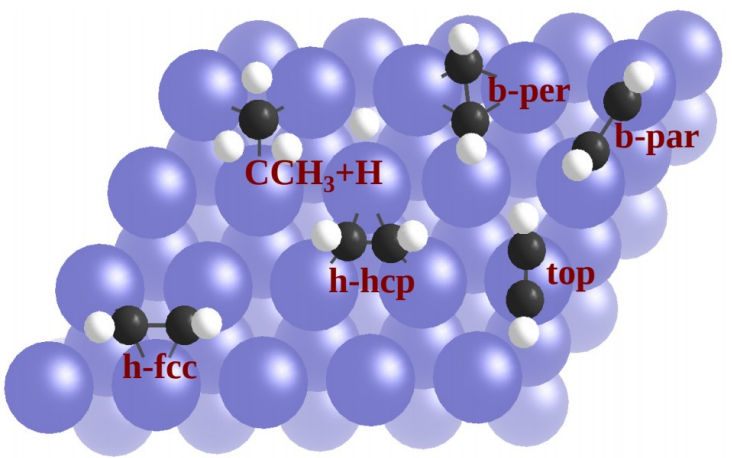
- Employing Phonopy

- Adsorption energy:

$$E_{ads} = E_{mol+slab} - E_{slab} - E_{mol}$$

- C_2H_4 dissociation on Pt(111) under the reaction:

$$C_2H_4 + Pt(111) \longrightarrow (CCH_3 + H)/Pt(111)$$



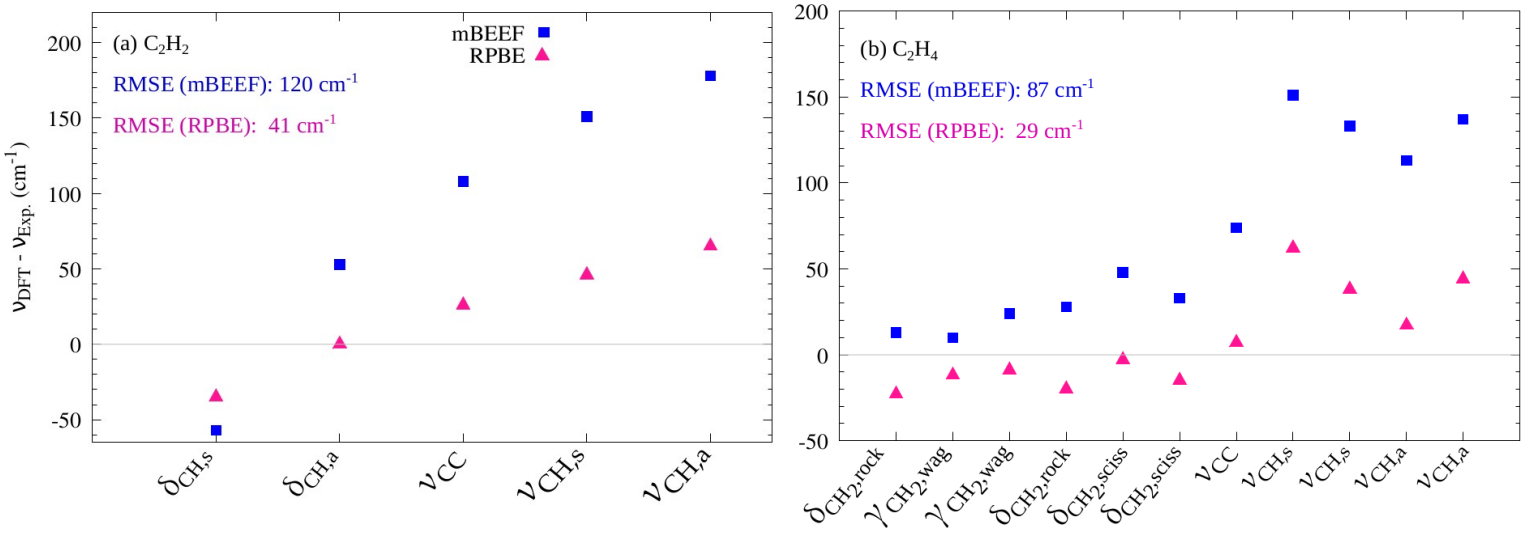
Vibrational Frequencies of gas-phase C_2H_2 and C_2H_4 molecules

The vibrational frequencies (in cm^{-1}) of the C_2H_2 and C_2H_4 molecules obtained by mBEEF and RPBE XC functionals along with the experimental data.

C_2H_2	mBEEF	RPBE	Exp.[a]
$\delta_{CH,s}$	555	578	612
$\delta_{CH,a}$	782	730	729
ν_{CC}	2082	2001	1974
$\nu_{CH,s}$	3446	3342	3295
$\nu_{CH,a}$	3551	3439	3373
RMSE (cm^{-1})	120	41	
C_2H_4			Exp.[b]
$\delta_{CH_2,rocking}$	839	804	826
$\gamma_{CH_2,wagging}$	950	929	940
$\gamma_{CH_2,wagging}$	973	941	949
$\gamma_{CH_2,twisting}$	1080	1032	—
$\delta_{CH_2,rocking}$	1250	1203	1222
$\delta_{CH_2,scissoring}$	1390	1340	1342
$\delta_{CH_2,scissoring}$	1477	1430	1444
ν_{C-C}	1697	1631	1623
ν_{CH},s	3140	3052	2989
ν_{CH},s	3159	3065	3026
ν_{CH},a	3216	3121	3103
ν_{CH},a	3242	3150	3105
RMSE (cm^{-1})	87	29	

[a] G. Herzberg, Electronic spectra and electronic structure of polyatomic molecules, Vol. 3 (van Nostrand, 1966).
[b] D. Van Lerberghe, I. Wright, and J. Duncan, Journal of Molecular Spectroscopy 42, 251 (1972).

Vibrational Frequencies of gas-phase C_2H_2 and C_2H_4 molecules



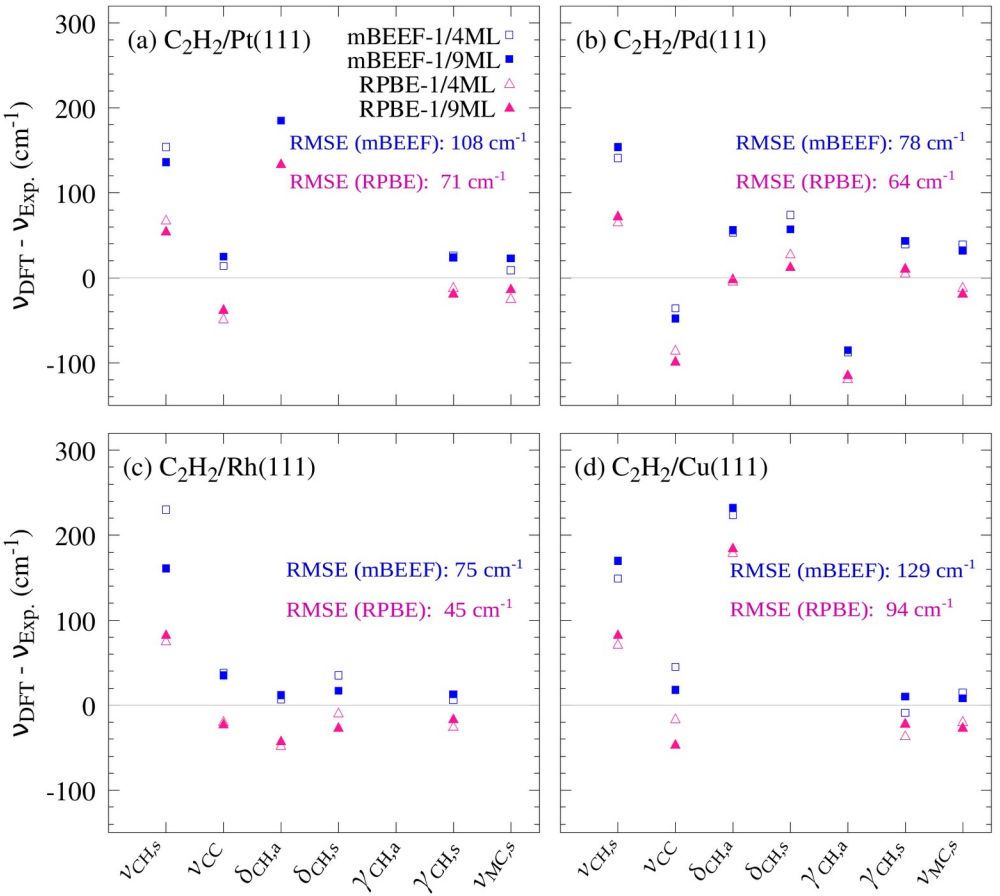
Frequency differences of different vibrational modes of gas-phase C_2H_2 and C_2H_4 molecules with the related experimental values.

Stretching force constants of the gas-phase C_2H_2 and C_2H_4 molecules

The stretching C-C and C-H force constants k (in N/m) obtained by mBEEF and RPBE. The related experimental values are obtained from the experimental vibrational frequencies.

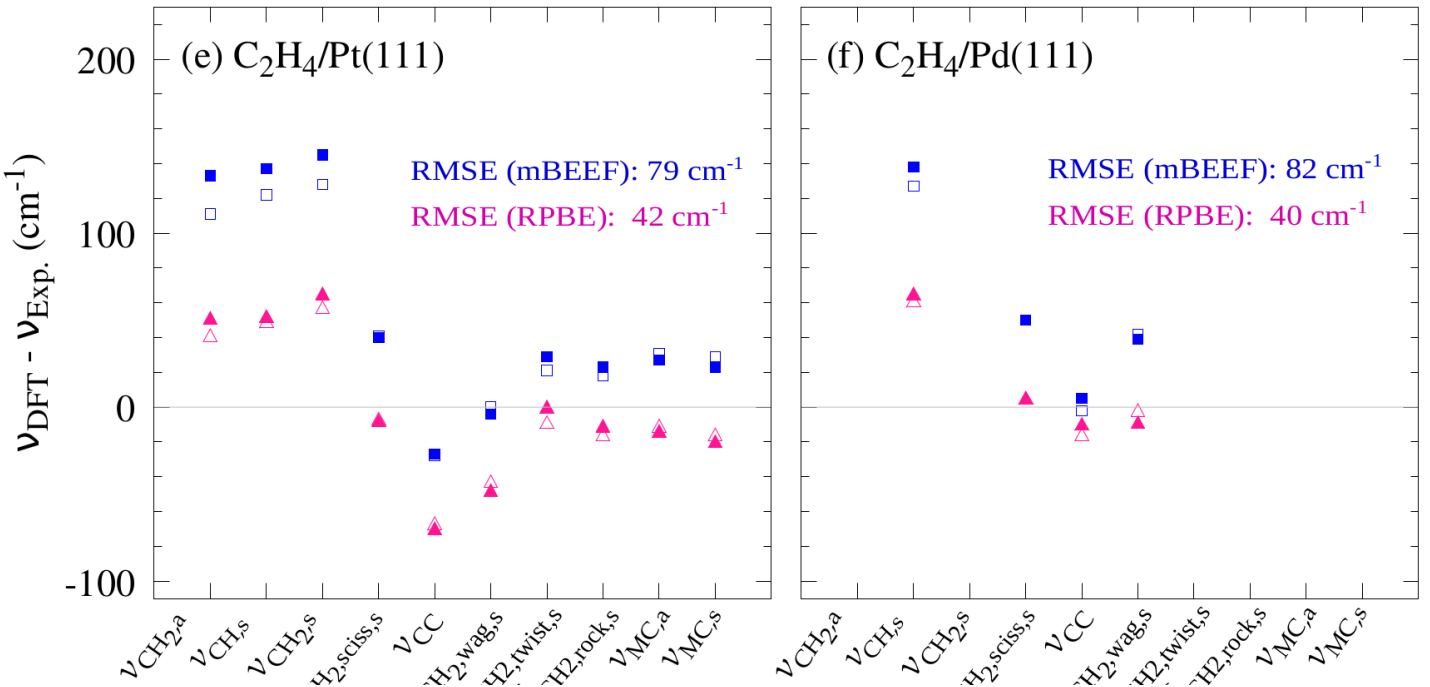
C_2H_2	mBEEF	RPBE	Exp.
k_{C-C}	1533	1416	1378
k_{C-H} (s)	691	648	623
k_{C-H} (a)	650	612	595
C_2H_4			
k_{C-C}	1019	941	932
k_{C-H} (s)	540	510	489
k_{C-H} (s)	547	514	502
k_{C-H} (a)	566	534	527
k_{C-H} (a)	576	544	528

Vibrational Frequencies of adsorbed C_2H_2 molecule



Frequency differences of different vibrational modes of adsorbed C_2H_2 molecule with the related experimental values.

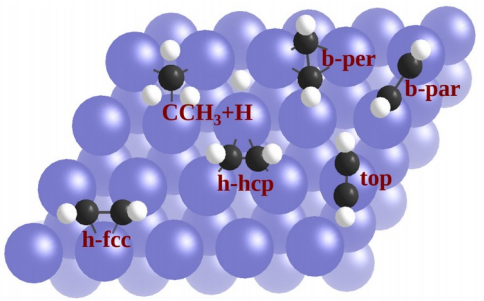
Vibrational Frequencies of adsorbed C_2H_4 molecule



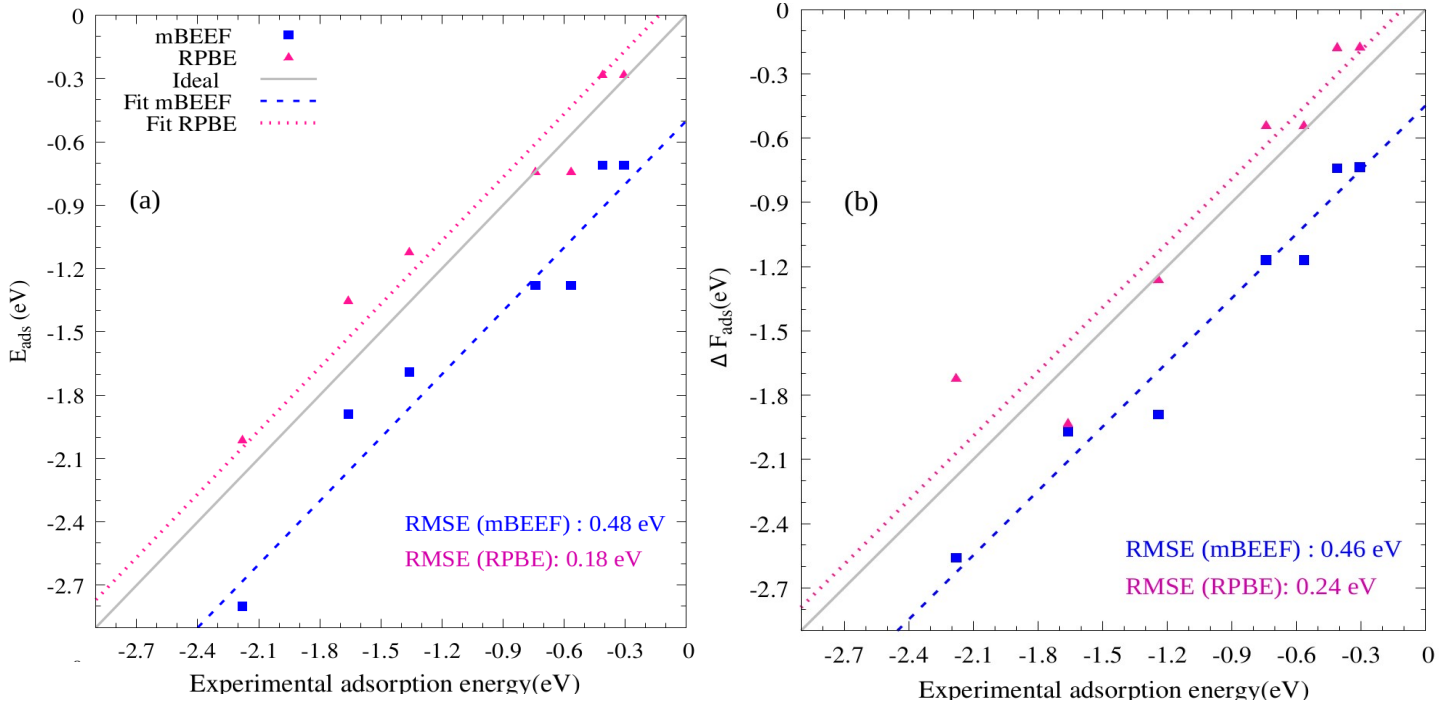
Frequency differences of different vibrational modes of adsorbed C_2H_4 molecule with the related experimental values. The blue and pink colors indicate the differences obtained from mBEEF and RPBE functionals, respectively.

Adsorption energy and geometry to evaluate the mBEEF and RPBE XC functionals

system	site	θ (ML)	mBEEF	RPBE	Exp.	Others.
C_2H_2/Pt(111)	h-fcc	1/4	-2.58	-1.80		-2.37[32](PW91), -2.26[37] (PW91)
		1/9	-2.60	-1.90		-2.11[51](BEEF-vdW)
		1/16	-2.80	-2.01	-2.18(initial,173K)[50]	
		cluster				-2.17[52](B3LYP)
	b-par	1/4	changed	-1.39		-1.99[32](PW91)
	top	1/4	-0.69	-0.23		-0.73[32](PW91)
C_2H_4/Pt(111)	top	1/4	-0.71	-0.28	-0.41±0.1(112K)[48]	-0.76[53](PW91)
		1/4			-0.22−-0.39(110K)[54]	-0.55[55](PW)
		1/4				-0.40[56](Tight-Binding)
		1/9	-0.93	-0.36		-0.87[57](PW91)
		cluster				-1.07[52](B3LYP)
	b-par	1/4	-1.28	-0.74	-0.39−-0.74(110K)[54]	-1.21[53](PW91)
		1/4			-0.74(100K)[36]	-1.26[55](PW)
		1/4				-0.58[56] (Tight-Binding)
		1/9			-1.24(initial)[50]	-1.25[57](PW91)
		cluster				-1.77[52](B3LYP)
		0.6< θ <1.2			-1.41[58]	
	CCH3+H	1/9	-1.69	-1.12	-1.36(300K)[49]	-1.65[12],-1.74[49] (PBE)
		1/9			-1.24(300K)[59] [a]	-1.20[12] (RPBE)
		1/9				-1.75[49] (optPBE)
		1/9				-1.83[12] (optPBE-vdW)
		1/9				-1.34[12] (BEEF-vdW)
		1/9				-1.43[49] (BEEF)
		1/9				-1.68[12] (MS2)
		1/9				-2.21[12] (SCAN)
		1/9				-2.33[12] (SCAN+rVV10)
		1/9				-2.21[12] (HSE06)
		1/9				-1.44[53] (PW91)
		1/16	-1.89	-1.35	-1.66(initial, T=303K)[50]	
		θ =0.05			-1.43[59] [a]	
		θ <0.10			-1.80±0.04[60]	
		θ =0.17			-1.29±0.03[60]	
		cluster				-1.32[52](B3LYP)



Adsorption energy and geometry to evaluate the mBEEF and RPBE XC functionals



(a) Calculated adsorption energies (E_{ads}) and (b) adsorption free energies ($\Delta F_{ads} = E_{ads} + F_{vib}$) of C_2H_2 and C_2H_4 on the Pt(111) surface versus corresponding experimental values. Data points of each functional fitted to y=x+a are also shown by dashed lines and dotted lines for mBEEEF and RPBE functionals, respectively. Th gray line shows the ideal y=x.

Conclusion

- mBEEF results in higher RMSE of vibrational modes:
  - gas-phase:
    C_2H_2: RMSE(mBEEF): 120 cm^{-1} RMSE(RPBE): 41 cm^{-1}
    C_2H_4: RMSE(mBEEF): 87 cm^{-1} RMSE(RPBE): 29 cm^{-1}
  - adsorbed:
    RMSE(mBEEF): 118 cm^{-1} RMSE(RPBE): 61 cm^{-1}
- The local minima are so sensitive to the initial starting geometry
  - b-par bridge site for C_2H_2 adsorption cannot be captured via mBEEF
- RPBE results in lower RMSE in adsorption energy
  - RMSE of adsorption energy: mBEEF: 0.48 eV RPBE: 18 eV
  - RMSE of adsorption free energy: mBEEF: 0.46 eV RPBE: 24 eV

Thank you…

Questions?