



Surface Adsorption on Interstellar Water Ice I_h

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- The Surface Model
- Benchmarking
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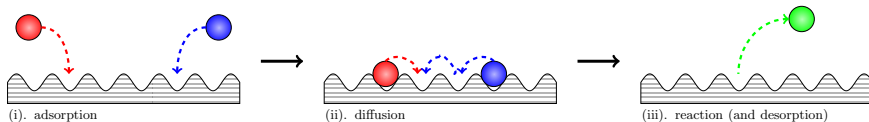
Introduction: Interstellar Dust

- The existence of interstellar dust was first inferred by Trumpler in 1930.^[1]
- Observed molecular abundances in the interstellar medium (ISM) can not be explained by gas-phase chemistry alone.
- Surface processes on interstellar dust may play an important role.
- In the cold ISM, dust particles are often covered in ices, mostly H_2O , CO_2 and CO .
- Surfaces can have a strong effect on reaction barriers.



Introduction: Surface Reaction Mechanisms

Langmuir–Hinshelwood (LH) mechanism



Eley–Rideal (ER) mechanism

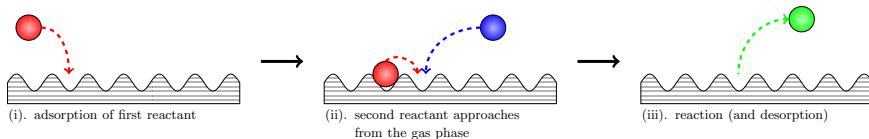


Figure: Schematic representation of the LH and the ER mechanism.



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The Surface Model: The Fletcher Surface

- Water ice I_h consists of layers of hexagonally ordered oxygen atoms and disordered hydrogen atoms.
 - ▶ When optimizing on the PES, some sensible initial geometry has to be given.
 - ▶ Fletcher surface uses a specific ordering of hydrogen atoms to minimize free energy.^[2]
 - ▶ Rows of identical H_2O orientation.

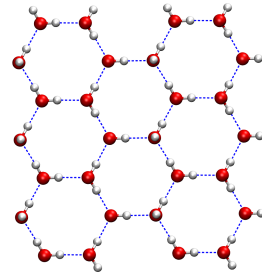


Figure: Fletcher surface (0001) basal layer



The Surface Model: QM/MM

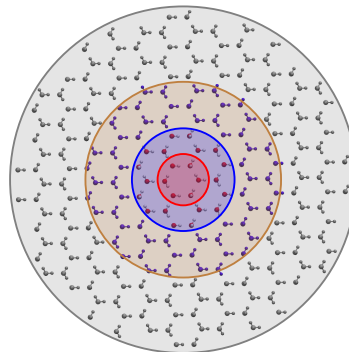
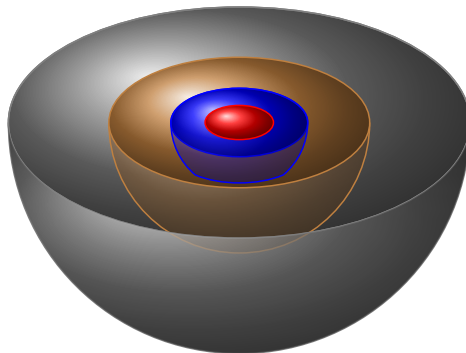


Figure: QM/MM decomposition: QM domain with **def2-TZVPD** and **def2-TZVP** basis set. MM region with **active** and **frozen** TIP3P QM atoms.



The Surface Model: ZPE correction

- The Hessian for the ZPE has to be approximated by finite differences.
 - ▶ For the 108 atoms of the QM region, that means 649 energy and gradient calculations.
- Assumption: atoms far from the center will not contribute much to the ZPE correction.
 - ▶ Only the 18 atoms of the central ring are displaced.
 - ▶ 109 energy and gradient calculations.



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Benchmarking: Definitions

- Studied interactions: $\text{H}_2\text{O} \cdots \text{H}$, $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$ and $\text{H}_2\text{O} \cdots {}^3\text{O}$.
- Calculate optimum geometries for various functional + basis set combinations and evaluate them by reference data in terms of energy and geometry.
- Reference calculations with CCSD(T)-F12a/VTZ-F12.
- Comparing interaction energies by

$$\Delta E^{\text{int}} = E_{\text{DFT}}^{\text{int}} - E_{\text{CC}}^{\text{int}}.$$

- Geometries can be compared by

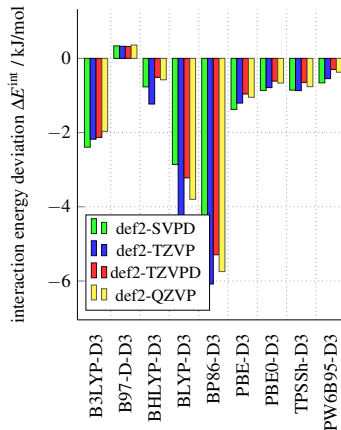
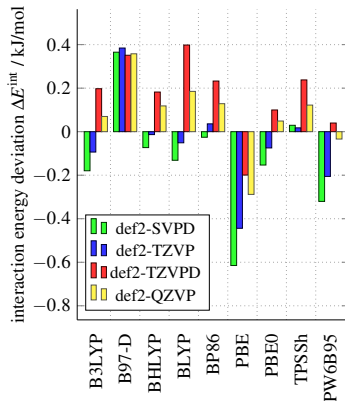
$$\text{RMSD}(\mathbf{R}_{\text{DFT}}^M; \mathbf{R}_{\text{CC}}^M) = \sqrt{\frac{1}{M} \sum_{k=1}^M |\mathbf{r}_{\text{DFT}}^k - \mathbf{r}_{\text{CC}}^k|^2}.$$





Benchmarking: $\text{H}_2\text{O} \cdots \text{H}$

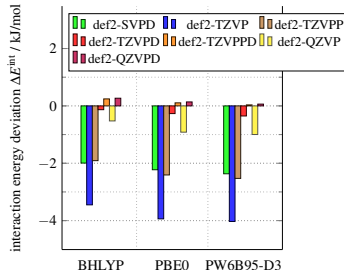
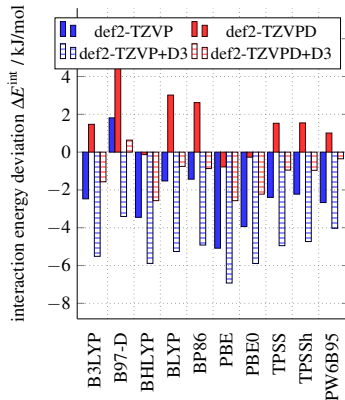
- Reference energy of $E_{\text{CC}}^{\text{int}} = -0.40 \text{ kJ/mol}$.





Benchmarking: $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$

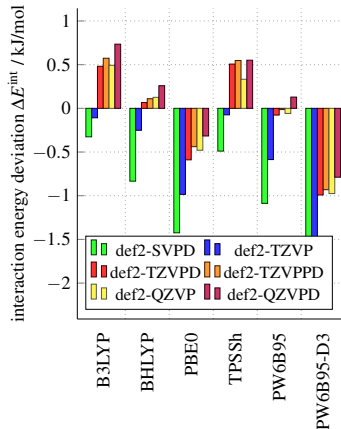
- Reference energy of $E_{\text{CC}}^{\text{int}} = -20.80$ kJ/mol.





Benchmarking: $\text{H}_2\text{O} \cdots {}^3\text{O}$

- Reference energy of $E_{\text{CC}}^{\text{int}} = -6.72 \text{ kJ/mol}$.





Benchmarking: Summary

- Dispersion correction for $\text{H}_2\text{O} \cdots \text{H}$ problematic.
- Energies calculated with def2-TZVP and def2-TZVPD are usually among the most accurate. For $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$, def2-TZVPD performs better than def2-TZVP.
 - ▶ Hybrid basis set with def2-TZVPD on central ring and def2-TZVP for the rest.
- The best functionals for interaction energy calculations are B3LYP, BHLYP, PBE0, TPSSh and PW6B95 and PW6B95-D3.
- Optimum geometries with the above functionals and basis sets are also good, RMSDs of always less than 0.1 Å, typically around 0.02 Å.





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Gas Phase: Energies of Formation

- Energy of formation: $E^0(X) = E(X) - M_H \frac{E(H_2)}{2} - M_O \frac{E(^3O_2)}{2}$.

Table: Energies of formation (in kJ/mol) for DFT functionals and CCSD(T)-F12a.

	B3LYP	BHLYP	PBE0	TPSSh	PW6B95	CCSD(T)-F12a
H	217.04	213.17	204.96	222.13	212.72	216.45
H ₂ O	-215.65	-224.54	-222.74	-197.51	-220.11	-238.28
H ₂ O ₂	-98.26	-97.16	-104.82	-85.65	-101.84	-129.08
OH	42.89	16.85	43.01	51.30	46.06	36.49
HO ₂	21.75	19.85	19.16	25.28	21.96	14.75
¹ O	519.48	482.52	543.69	538.46	521.61	451.63
³ O	252.00	204.88	254.89	246.85	253.28	245.13
¹ O ₂	162.16	177.97	171.07	163.27	160.38	120.91
MAD	22.92	25.24	26.77	30.77	22.94	
MAX	67.86	57.05	92.06	86.84	69.98	
MIN	0.60	-40.26	-11.49	1.72	-3.73	
MEAN	22.92	9.44	23.90	30.77	22.01	



Gas Phase: Reaction Energies

Table: Reaction energies (in kJ/mol) for DFT functionals and CCSD(T)-F12a.

		B3LYP	BHLYP	PBE0	TPSSh	PW6B95	CCSD(T)-F12a
OH + H → H ₂ O	E^{ZPE}	-475.58	-454.56	-470.70	-470.94	-478.89	-491.23
	ΔE^{ZPE}	33.58	34.87	34.05	33.59	34.09	34.06
H ₂ O + ¹ O → H ₂ O ₂	E^{ZPE}	-402.09	-355.15	-425.77	-426.60	-403.33	-342.42
	ΔE^{ZPE}	13.66	15.44	14.41	13.31	14.23	13.38
OH + OH → H ₂ O ₂	E^{ZPE}	-184.03	-130.86	-190.84	-188.24	-193.96	-202.06
	ΔE^{ZPE}	25.19	27.21	25.99	24.94	25.90	25.07
HO ₂ + H → H ₂ O ₂	E^{ZPE}	-337.05	-330.18	-328.94	-333.06	-336.51	-360.28
	ΔE^{ZPE}	32.40	34.02	33.11	32.22	33.01	32.44
OH + ³ O → HO ₂	E^{ZPE}	-273.14	-201.88	-278.73	-272.87	-277.38	-266.88
	ΔE^{ZPE}	14.84	16.29	15.36	14.69	15.31	15.00
³ O ₂ + H → HO ₂	E^{ZPE}	-195.30	-193.32	-185.80	-196.85	-190.76	-201.70
	ΔE^{ZPE}	27.07	28.57	27.54	26.95	27.51	27.78
$E_{\text{DFT}}^{\text{ZPE}} - E_{\text{CCSD(T)-F12a}}^{\text{ZPE}}$	MAD	19.36	41.30	26.58	23.19	19.58	
	MIN	-59.67	-12.72	-83.35	-84.18	-60.91	
	MAX	23.22	71.20	31.34	27.22	23.76	
	MEAN	-1.27	37.66	-4.01	-4.28	-3.83	



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Adsorption Energies: Comparing ZPE Corrections

Table: Adsorption energies (in kJ/mol) for the B3LYP functional with different ZPE corrections.

	E_{B3LYP}	$\Delta E_{\text{B3LYP}}^{\text{all}}$	$\Delta E_{\text{B3LYP}}^{\text{ring}}$	$\Delta E_{\text{PBE0}}^{\text{ring}}$
s-H	-1.71	5.03	3.28	2.84
s-H ₂	-2.65	8.42	6.80	6.81
s-H ₂ O	-48.01	15.98	14.84	14.45
s-H ₂ O ₂	-41.76	9.28	10.09	9.51
s-OH	-44.99	13.60	12.11	12.05
s-HO ₂	-65.48	13.17	11.66	11.59
s- ³ O	-16.17	2.69	3.35	3.04
s- ¹ O ₂	-8.41	2.46	3.86	4.96
s- ³ O ₂	-2.62	3.06	3.90	3.86



Adsorption Energies

Table: Adsorption energies (in kJ/mol) for different DFT functionals. Including an average energy $E_{\text{avg}}^{\text{ads}}$.

	B3LYP	BHLYP	PBE0	TPSSH	PW	PW-D3	$E_{\text{avg}}^{\text{ads}}$	experimental, E_{ads}
s-H	3.32	3.77	3.37	-5.05	3.29	1.27	1.66	
s-H ₂	5.77	5.11	3.57	4.55	4.65	2.47	4.35	
s-H ₂ O	-32.03	-35.07	-36.90	-30.92	-33.51	-41.17	-34.9	-48.00±0.50 ^a
s-H ₂ O ₂	-32.47	-35.99	-37.64	-31.04	-34.85	-44.33	-36.05	
s-OH	-31.39	-32.88	-35.69	-31.10	-32.78	-39.66	-33.92	-13.77 to -39.58 ^b
s-HO ₂	-52.30	-49.10	-56.97	-54.10	-51.08	-57.80	-53.56	
s- ³ O	-13.48	-5.16	-11.25	-13.22	-12.85	-18.13	-12.35	-13.80±0.50 or -15.38± 0.75 ^c
s- ¹ O ₂	-5.95	-7.51	-11.44	-9.44	-7.44	-12.53	-9.05	
s- ³ O ₂	0.45	-0.65	-1.52	-0.52	26.68	7.04	-0.56 [†]	-7.52 ^d
MAD	2.06	1.93	1.74	2.29	4.17	4.85		
MIN	-1.13	-0.14	-3.42	-6.72	-0.50	-8.28		
MAX	3.58	7.19	1.71	5.02	27.23	7.60		
MEAN	1.81	1.88	-1.12	0.40	4.06	-3.16		

^a Adsorption on Au grain covered in crystalline water. For other grain materials between 42.15 and 49.79 kJ/mol. Fraser *et al.* 2001.^[3]

^b Adsorption on an amorphous silicate. He, Vidali 2014.^[4]

^c Adsorption on porous amorphous water ice and amorphous silicate, respectively. He *et al.* 2015.^[5]

^d Adsorption on an amorphous silicate. He, Jing, Vidali 2014.^[6]

[†] Average excluding both PW and PW-D3.



Reaction Energies

Table: Surface reaction energies (in kJ/mol) with Eley-Rideal type reactions. All energies are ZPE corrected with $\Delta E_{\text{B3LYP}}^{\text{ZPE/all}}$. PW is short for PW6B95. The last column contains average values. The deviations of these are listed in the last four rows for each functional.

		B3LYP	BHLYP	PBE0	TPSSh	PW	PW-D3	$E_{\text{hybrid}}^{\text{react}}$
s-OH	+H _(g) → s-H ₂ O	-476.22	-458.03	-472.39	-470.76	-480.13	-480.92	-492.71
s-H ₂ O	+ ¹ O _(g) → s-H ₂ O ₂	-402.54	-357.85	-427.27	-426.38	-405.24	-407.50	-344.17
s-OH	+OH _(g) → s-H ₂ O ₂	-185.12	-137.04	-194.02	-187.84	-197.12	-200.16	-205.33
s-HO ₂	+H _(g) → s-H ₂ O ₂	-317.22	-318.69	-310.31	-309.82	-320.89	-323.99	-343.39
s-OH	+ ³ O _(g) → s-HO ₂	-294.05	-219.54	-300.54	-295.71	-296.15	-296.10	-287.00
s- ³ O	+OH _(g) → s-HO ₂	-311.96	-248.31	-325.41	-313.50	-316.45	-318.00	-308.95
s- ³ O ₂	+H _(g) → s-HO ₂	-248.05	-243.27	-241.72	-250.31	-268.95	-256.14	-254.74
$E_{\text{DFT}} - E_{\text{hybrid}}^{\text{react}}$	MAD	19.71	40.13	27.26	24.70	19.32	17.04	
	MIN	-58.37	-13.68	-83.10	-82.21	-61.07	-63.33	
	MAX	26.17	68.29	33.07	33.57	22.49	19.39	
	MEAN	0.16	36.22	-5.06	-2.58	-6.95	-6.65	

- Hybrid reaction energy $E_{\text{hybrid}}^{\text{react}} = \Delta E_{\text{avg}}^{\text{ads}} + E_{\text{CCSD(T)-F12a}}^{\text{react, gas}}$



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Binding Sites

- Search for different PES minima on the central ring for ^3O using the BHLYP functional.
- Optimizations started at a distribution of initial geometries according to (cylindrical coordinates)

$$y(r, \phi) = y_0 + \left(A - B \cos(3\phi) \right) \sin^2 \left(\frac{r}{r_{\max}} \frac{\pi}{2} \right).$$

- ▶ $5 \times 15 = 75$ initial geometries in r and ϕ respectively.

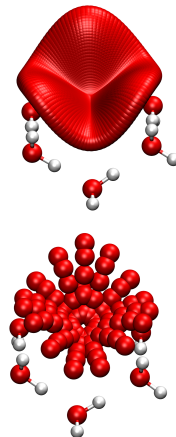


Figure: The initial guesses for binding sites.



Binding Sites

- 71 of the 75 optimum searches converged.
- Main binding sites:
 - ▶ Above the center with $E^{\text{ads}} = -7.58$ kJ/mol.
 - ▶ At left and right boundary above broken hydrogen bond with energy around $E^{\text{ads}} = -8.40$ kJ/mol.
 - ▶ Above the connecting line between two oxygen atoms with broken hydrogen bond with $E^{\text{ads}} = -8.40$ kJ/mol.

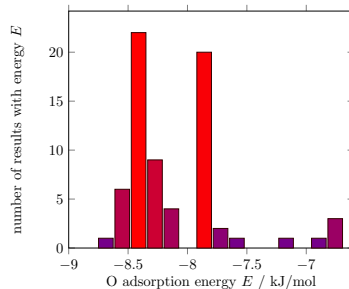


Figure: Population of optimum geometry energies (in kJ/mol). One geometry at $E = -5.01$ kJ/mol is not included.



Transition State

- We calculated the transition state of the reaction $\text{OH} + \text{H}_2 \longrightarrow \text{H}_2\text{O} + \text{H}$.
 - Compare gas-phase reaction to surface reaction.
- We used the B3LYP functional with ZPE correction. Transition state geometries (saddle points) were obtained with the dimer method.^[7]
- Orientation of the $\text{OH} + \text{H}_2$ subsystem was guessed at the beginning.
- Pre-reactive complex $\text{OH} + \text{H}_2$ and the products $\text{H}_2\text{O} + \text{H}$ were also optimized.

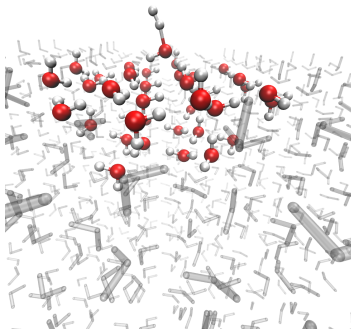


Figure: $\text{OH} + \text{H}_2$ transition state on Fletcher surface. Transparent atoms are in the MM region.



Transition State

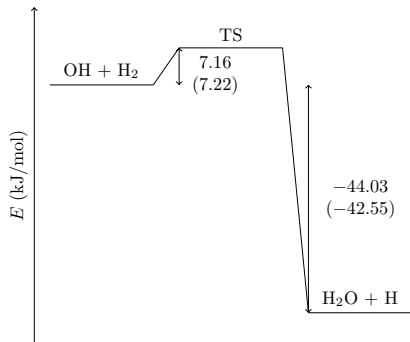


Figure: Energy diagram for the reaction $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ on the surface. Values in parentheses are for the gas phase reaction.

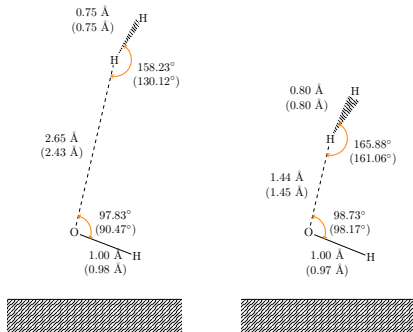


Figure: Left: Optimum geometry for $\text{OH} + \text{H}_2$. Right: Transition state for $\text{OH} + \text{H}_2$. Values are given for the adsorbate, values in parentheses are for the gas phase.



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Conclusions

- DFT methods are able to describe interaction energies with H₂O accurately.
 - ▶ Recommended functionals: B3LYP, BHLYP, PBE0, TPSSh and PW6B95 and PW6B95-D3.
 - ▶ Recommended basis set: Hybrid def2-TZVP/def2-TZVPD.
- ZPE correction does not have to consider all QM atoms. The ZPE correction changes only slightly among functionals.
- By combining coupled-cluster gas-phase reaction energies and DFT adsorption energies, ER reaction energies can be obtained.
- The orientation-dependence of binding sites could have a strong impact on the results.
- Transition states can be computed with the dimer method.





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Discussion