Supporting Information

A Computational Study of H_2 Dissociation on Silver Surfaces: The Effect of Oxygen in the Added Row Structure of Ag(110)

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Table 1S. Unit cell parameters of Ag(110)

	Ag(110)		Ag(111)	Ag(221)
	2x2	3x2		
a, Å	5.855	8.782	5.855	8.782
b, Å	8.280	8.280	5.855	5.855
c, Å	17.565	17.565	16.732	20.700
	$\alpha = \beta = \gamma = 90°$		$\alpha = \gamma = 90°, \beta = 60°$	$\alpha = \beta = \gamma = 90°$

Table 2S. Total energy E_{tot} of atoms in the gas phase

Species	O	H
E_{tot}, eV	-1.810	-1.119

Table 3S. Cartesian coordinates (Å) of substrate atoms (clean 5-layer Ag (110) with top 2 layers relaxed) and the total energy E_{tot} (eV)

	2x2			3x2		
	x	y	z	x	y	z
Ag	0.000	0.000	8.830	0.000	0.000	8.830
Ag	2.927	0.000	8.830	2.927	0.000	8.830
Ag	0.000	4.140	8.830	5.855	0..000	8.830
Ag	2.927	4.140	8.830	0.000	4.140	8.830
Ag	1.464	2.070	10.178	2.927	4.140	8.830
Ag	4.391	2.070	10.178	5.855	4.140	8.830
Ag	1.464	6.210	10.178	1.464	2.070	10.178
Ag	4.391	6.210	10.178	4.391	2.070	10.178
Ag	0.000	0.000	11.710	7.319	2.070	10.178
Ag	2.927	0.000	11.710	1.464	6.210	10.178
Ag	0.000	4.140	11.710	4.391	6.210	10.178
Ag	2.927	4.140	11.710	7.319	6.210	10.178
Ag	1.464	2.070	13.173	0.000	0.000	11.710
Ag	4.391	2.070	13.173	2.927	0.000	11.710
Ag	1.464	6.210	13.173	5.855	0..000	11.710
Ag	4.391	6.210	13.173	0.000	4.140	11.710
Ag	0.000	0.000	14.637	2.927	4.140	11.710
Ag	2.927	0.000	14.637	5.855	4.140	11.710
Ag	0.000	4.140	14.637	1.464	2.070	13.173
Ag	2.927	4.140	14.637	4.391	2.070	13.173
Ag				7.319	2.070	13.173
Ag				1.464	6.210	13.173
Ag				4.391	6.210	13.173
Ag				7.319	6.210	13.173
Ag				0.000	0.000	14.637
Ag				2.927	0.000	14.637
Ag				5.855	0.000	14.637
Ag				0.000	4.140	14.637
Ag				2.927	4.140	14.637
Ag				5.855	4.140	14.637
E_{tot}			-49.100			-73.875

Table 4S. Cartesian coordinates (Å) of substrate atoms (clean 5-layer Ag(111) and Ag(221) with top 2-layer relaxed) and the resulting total energies E_{tot}(eV)

	Ag(111)			Ag(221)		
	x	y	z	x	y	z
Ag	0.000	0.000	4.770	0.000	0.000	8.280
Ag	2.927	0.000	4.770	0.000	2.927	8.280
Ag	4.391	2.535	4.770	2.439	1.464	8.970
Ag	1.464	2.535	4.770	2.439	4.391	8.970
Ag	1.464	0.845	7.181	4.879	0.000	9.660
Ag	4.391	0.845	7.181	4.879	2.927	9.660
Ag	5.855	3.380	7.181	7.318	1.464	10.350
Ag	2.927	3.380	7.181	7.318	4.391	10.350
Ag	2.927	1.690	9.561	0.976	0.000	11.040
Ag	5.855	1.690	9.561	0.976	2.927	11.040
Ag	7.318	4.225	9.561	3.415	1.464	11.730
Ag	4.391	4.225	9.561	3.415	4.391	11.730
Ag	4.391	2.535	11.951	5.855	0.000	12.420
Ag	1.464	2.535	11.951	5.855	2.927	12.420
Ag	0.000	0.000	11.951	8.294	1.464	13.110
Ag	2.927	0.000	11.951	8.294	4.391	13.110
Ag	5.855	3.380	14.341	1.952	0.000	13.800
Ag	2.927	3.380	14.341	1.952	2.927	13.800
Ag	1.464	0.845	14.341	4.391	1.464	14.490
Ag	4.391	0.845	14.341	4.391	4.391	14.490
Ag				6.831	0.000	15.180
Ag				6.831	2.927	15.180
Ag				0.488	1.464	15.870
Ag				0.488	4.391	15.870
Ag				2.927	0.000	16.560
Ag				2.927	2.927	16.560
Ag				5.367	1.464	17.250
Ag				5.367	4.391	17.250
Ag				7.806	0.000	17.940
Ag				7.806	2.927	17.940
Ag				1.464	1.464	18.630
Ag				1.464	4.391	18.630
Ag				3.903	0.000	19.320
Ag				3.903	2.927	19.320
Ag				6.343	1.464	20.010
Ag				6.343	4.391	20.010
Ag				8.782	0.000	0.000
Ag				8.782	2.927	0.000
Ag				2.683	1.464	0.690
Ag				2.683	4.391	0.690
E_{tot}			-51.7411			-103.2905

Table 5S. The Cartesian coordinates (Å) of various adsorbed species on Ag(110), Ag(111) and Ag(221) slabs and the corresponding total energies E_{tot} (eV).

		x	y	z	E_{tot}
Ag(110)	top	0.000	0.000	7.1734	-51.738
	short bridge	1.4637	0.000	7.7687	-52.252
	long bridge	0.000	2.070	8.8139	-52.222
	4-fold hollow	1.4637	2.07	8.4299	-51.968
Ag(111)	top	0.000	0.000	3.108	-54.416
	bridge	1.464	0.000	3.676	-54.803
	fcc	2.927	1.690	3.860	-54.917
	hcp	1.464	0.845	3.866	-54.908
Ag(221)	edge bridge	0.044	1.464	7.267	-106.538
	3-fold terrace	5.845	1.464	8.912	-106.478
	3-fold edge hollow-2	1.899	2.927	7.797	-106.582
	3-fold edge hollow-1	0.990	1.464	7.580	-106.530

Table 6S. Structure (Å) and total energy E_{tot} (eV) of complexes relevant to hydrogen dissociation on Ag(110) surface

		x	y	z			
IS [a]	H	2.5614	0.0000	5.8303			
	H	3.3042	0.0000	5.8303			
	E_{tot}			-55.901			
		FS			TS		
		x	y	z	x	y	z
SB/SB	H	1.4637	0.0000	7.7570	2.1588	0.0000	7.3400
	H	4.3911	0.0000	7.7570	3.7094	0.0000	7.3400
	E_{tot}			-55.308			-54.529
3f/3f	H	1.4637	1.0607	8.4544	0.8089	8.1484	7.3706
	H	4.3911	7.2193	8.4544	5.0458	0.1316	7.3706
	E_{tot}			-55.556			-54.521
LB/LB [b]	H	0.0000	2.0700	8.8015	0.6125	1.4000	7.8305
	H	2.9274	2.0700	8.8015	2.3244	1.4000	7.8305
	E_{tot}			-55.201			-54.223
SB/LB	H	0.0000	2.0700	8.8139	0.4976	1.6916	8.3263
	H	1.4637	0.0000	7.7687	1.2430	0.7038	7.7614
	E_{tot}			-55.336			-54.636
SB/3-f	H	1.4637	4.1111	7.7799	0.3610	7.8460	7.2509
	H	4.3911	5.2595	8.4563	4.7322	7.8572	7.6228
	E_{tot}			-55.449			-54.561
LB/3-f	H	2.9355	2.1015	8.8122	0.8565	0.7547	7.5741
	H	1.4787	5.2188	8.4005	5.1476	0.9244	7.6142
	E_{tot}			-55.359			-54.471

[v] H_2 at 300 pm height.
[b] Complex oriented along the troughs.

Table 7S. Vibrational frequencies (cm^{-1}) of transition state (TS) and final state (FS) complexes for H-H bond breaking on Ag(110) surface

		ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
SB/SB	TS	1608	1538	481	263	138	1113 *i*
	FS	1149	1132	1111	1061	449	389
3f/3f	TS	1264	963	565	469	376	1228 *i*
	FS	1012	1002	930	919	687	582
LB/LB[a]	TS	1094	1004	352	323	38	889 *i*
	FS	861	746	722	653	547	382
SB/LB	TS	1623	1584	548	398	157	996 *i*
	FS	1146	1027	725	595	455	246
SB/3-f	TS	1583	1453	424	174	157	1123 *i*
	FS	1168	1027	1022	904	571	223
LB/3-f	TS	1585	1522	533	440	238	1058 *i*
	FS	990	930	712	588	541	443

[a] Complex oriented along the troughs.

Table 8S: Comparison of nearest-neighbor distance r_u between hydrogen atoms in neighboring unit cells and the distance r(H-H) between hydrogen atoms within a unit cell. Distances in Å.

Sites[a]	r(H-H)	θ =1/2		θ =1/3	
		r_u, pm	E_r, kJ/mol	r_u, pm	E_r, kJ/mol
5 / 5	293	293	57	585	61
6 / 6	361	361	33	623	49
7 / **7** [e]	293	293	68	585	67
5 / **7**	277	496	54	768	63
5 / 6	318	318	44	599	55
7 / 6	347	540	52	878	58

[a] Short bridge – **5**, 3-fold – **6**, long bridge – **7**.
[e] Complex oriented along the troughs.

Table 9S. Cartesian coordinates (Å) of added row atoms on Ag (110) and the resulting total energy E_{tot} (eV)

		x	y	z	E_{tot}
clean					-65.991
	O	1.4637	0.0000	7.0744	
	O	1.4637	4.1400	7.0744	
	Ag	1.4637	2.0700	7.1650	
	Ag	1.4637	6.2100	7.1650	
TS					-72.049
	H	1.4637	0.4309	5.8769	
	H	1.4637	1.4865	5.2675	
	O	1.4637	8.2489	6.8624	
	O	1.4637	4.2023	7.1131	
	Ag	1.4637	2.1639	7.0268	
	Ag	1.4637	6.2251	7.1972	
Inter					-72.466
	H	1.4637	-0.090	5.4548	
	H	1.4637	2.2042	5.1795	
	O	1.4637	-0.037	6.4275	
	O	1.4637	4.0549	7.1168	
	Ag	1.4637	2.0374	6.8199	
	Ag	1.4637	6.2327	7.3527	
DS					-72.335
	H	1.4637	8.4002	5.2362	
	H	1.4637	3.3737	5.2999	
	O	1.4637	0.2577	6.2013	
	O	1.4637	4.3454	7.0913	
	Ag	1.4637	2.3358	6.5971	
	Ag	1.4637	6.5126	7.2047	
FS					-75.115
	H	1.4637	0.0364	5.4328	
	H	1.4637	4.1036	5.4328	
	O	1.4637	0.0103	6.4088	
	O	1.4637	4.12972	6.4088	
	Ag	1.4637	2.0700	7.3389	
	Ag	1.4637	6.2100	7.3389	

Table 10S. Vibrational frequencies (cm^{-1}) of transition state (TS), intermediate stable state(Inter), diffusion transition state of the diffusion step (DS), and final state (FS) for H-H bond breaking on Ag(110) surface

	TS	Inter	DS	FS
ν_1	1914	3608	3603	3576
ν_2	1192	1586	1526	3573
ν_3	855	824	830	690
ν_4	843	481	243	683
ν_5	213	240	205	191
ν_6	654*i*	135	380*i*	170