I. The O-O bond length of H_2O_2: derivation from Badger's rule

The vibrational frequency can be expressed by the equation[1],

$$\nu = (1 / 2\pi)\sqrt{(k_e / \mu)} \quad (1)$$

where ν is the vibrational frequency in cm^{-1}, k_e is the force constant and μ is the reduced mass of the molecules. According to Badger's rule,[2]

$$k_e = 1.86 \times 10^5 (r_e - d_{ij}) ^{-3} \quad (2)$$

where k_e is the force constant of the bond stretch in dyne·cm^{-1}, r_e is the equilibrium bond length in Å, and d_{ij} is a constant characteristic of one element in the ith row and one in the jth row of the periodic system. In case of free H_2O_2 in solution, the ν(O-O)[3] is 871 cm^{-1} with a 1.47 Å O-O bond length[4] and 4.0 mdyne/Å force constant.[5,6] The d_{ij} is calculated to be 0.695. Thus, as the O-O stretching mode shifts from 871 cm^{-1} to 838 cm^{-1} at -0.1 V, the O-O bond length of H_2O_2 changes from 1.47 Å to 1.49 Å.

References:

(1) Skoog, D. A.; Holler, F. J.; Nieman, T. A. *Principles of Instrumental Analysis*; 5th ed.; Harcourt Brace & Company, 1998.

(2) Badger, R. M. *J. Chem. Phys.* **1934**, *2*, 128-131.

(3) Arnau, J. L.; Giguere, P. A.; Abe, M.; Taylor, R. C. *Spectrochim. Acta, Part A* **1974**, *30A*, 777-796.

(4) Giguere, P. A. *J. Chem. Educ.* **1983**, *60*, 399-401.

(5) Redington, R. L.; Olson, W. B.; Cross, P. C. *J. Chem. Phys.* **1962**, *36*, 1311-1326.

(6) Blint, R. J.; Newton, M. D. *J. Chem. Phys.* **1973**, *59*, 6220-6228.

II. The geometry for DFT calculations

Pt(110)

Element	Atom number	Fractional coordinates after optimization step u	v	w
Pt	1	0.01893	0.01517	0.89271
Pt	2	0.26971	0.26413	0.79610
Pt	3	0.02005	0.01381	0.69923
Pt	4	0.01893	0.51517	0.89272
Pt	5	0.26971	0.76413	0.79610
Pt	6	0.02005	0.51381	0.69924
Pt	7	0.51903	0.01514	0.89287
Pt	8	0.76969	0.26408	0.79601
Pt	9	0.51992	0.01379	0.69916
Pt	10	0.51903	0.51514	0.89288
Pt	11	0.76969	0.76408	0.79600
Pt	12	0.51992	0.51378	0.69917

Pt(100)

Element	Atom number	Fractional coordinates after optimization step u	v	w
Pt	1	-0.01403	0.01482	0.56387
Pt	2	-0.02517	0.00690	0.83739
Pt	3	0.23096	0.26028	0.70037
Pt	4	-0.01230	0.51472	0.56376
Pt	5	-0.02491	0.50694	0.83739
Pt	6	0.23089	0.76017	0.70033
Pt	7	0.48610	0.01215	0.56373
Pt	8	0.47477	0.00685	0.83733
Pt	9	0.73073	0.26030	0.70040
Pt	10	0.48785	0.51210	0.56367
Pt	11	0.47503	0.50688	0.83735
Pt	12	0.73068	0.76017	0.70036

Pt(111)

Element	Atom number	Fractional coordinates after optimization step u	v	w
Pt	1	-0.00880	0.00143	-0.40875
Pt	2	0.66207	0.33166	-0.24707
Pt	3	0.33423	0.66066	-0.08512
Pt	4	-0.00875	0.50140	-0.40873

Pt	5	0.66207	0.83165	-0.24706
Pt	6	0.33420	0.16070	-0.08516
Pt	7	0.49121	0.50144	-0.40875
Pt	8	0.16207	0.83166	-0.24707
Pt	9	0.83422	0.16066	-0.08512
Pt	10	0.49126	0.00140	-0.40873
Pt	11	0.16207	0.33165	-0.24706
Pt	12	0.83419	0.66070	-0.08516

Au(110)

Element	Atom number	Fractional coordinates after optimization step u	v	w
Au	1	0.00808	0.00907	0.69349
Au	2	0.00853	0.51083	0.89654
Au	3	0.25845	0.75945	0.79494
Au	4	0.25841	0.26042	0.79496
Au	5	0.00805	0.50980	0.69356
Au	6	0.00851	0.01007	0.89659
Au	7	0.50884	0.00984	0.69359
Au	8	0.50889	0.51139	0.89607
Au	9	0.75865	0.76031	0.79497
Au	10	0.75864	0.26142	0.79498
Au	11	0.50880	0.51063	0.69367
Au	12	0.50897	0.01056	0.89611

Au(100)

Element	Atom number	Fractional coordinates after optimization step u	v	w
Au	1	-0.01979	-0.01184	0.06643
Au	2	-0.01986	-0.01166	0.33578
Au	3	0.23151	0.23638	0.20082
Au	4	-0.01979	0.48824	0.06641
Au	5	-0.01986	0.48842	0.33580
Au	6	0.23135	0.73636	0.20082
Au	7	0.48019	-0.01179	0.06642
Au	8	0.48012	-0.01162	0.33580
Au	9	0.73137	0.23635	0.20082
Au	10	0.48019	0.48819	0.06643
Au	11	0.48012	0.48837	0.33578
Au	12	0.73154	0.73639	0.20082

Au(111)

Element	Atom	Fractional coordinates

	number	after optimization step u	v	w
Au	1	-0.00275	0.00292	-0.16320
Au	2	0.16500	0.33500	-0.33210
Au	3	0.33000	0.17000	-0.50371
Au	4	-0.00274	0.50291	-0.16320
Au	5	0.16500	0.83500	-0.33210
Au	6	0.33000	0.67000	-0.50371
Au	7	0.49722	0.00288	-0.16320
Au	8	0.66500	0.33500	-0.33210
Au	9	0.83000	0.17000	-0.50371
Au	10	0.49722	0.50289	-0.16320
Au	11	0.66500	0.83500	-0.33210
Au	12	0.83000	0.67000	-0.50371

H_2O_2 in (110) unit cell

Element	Atom number	Fractional coordinates after optimization step u	v	w
O	1	0.45788	0.52025	0.55496
O	2	0.60604	0.42465	0.51121
H	1	0.49486	0.69597	0.55715
H	2	0.54895	0.37076	0.45507

H_2O_2 in (100) unit cell

Element	Atom number	Fractional coordinates after optimization step u	v	w
O	1	0.41427	0.49491	0.55499
O	2	0.62594	0.41800	0.50762
H	1	0.43873	0.67169	0.55335
H	2	0.54554	0.33237	0.45806

H_2O_2 in (111) unit cell

Element	Atom number	Fractional coordinates after optimization step u	v	w
O	1	0.52307	0.46080	-0.43718
O	2	0.39799	0.52408	-0.47788
H	1	0.57598	0.43423	-0.49066
H	2	0.46222	0.65870	-0.45818

H_2O_2 on Pt(110)

Element	Atom number	Fractional coordinates after optimization step

		u	v	w
Pt	1	0.01893	0.01517	0.89271
Pt	2	0.26971	0.26413	0.79610
Pt	3	0.02109	0.01554	0.70067
Pt	4	0.01893	0.51517	0.89272
Pt	5	0.26971	0.76413	0.79610
Pt	6	0.02025	0.51974	0.68390
Pt	7	0.51903	0.01514	0.89287
Pt	8	0.76969	0.26408	0.79601
Pt	9	0.52053	0.01552	0.70066
Pt	10	0.51903	0.51514	0.89288
Pt	11	0.76969	0.76408	0.79600
Pt	12	0.52008	0.51982	0.68363
O	1	0.27014	0.50111	0.60322
O	2	0.77135	0.46661	0.60476
H	1	0.26978	0.63008	0.55997
H	2	0.77175	0.55930	0.55022

H_2O_2 on Pt(100)

Element	Atom number	Fractional coordinates after optimization step u	v	w
Pt	1	-0.01456	0.02236	0.57178
Pt	2	-0.02517	0.00690	0.83739
Pt	3	0.23096	0.26028	0.70037
Pt	4	-0.03058	0.52684	0.54711
Pt	5	-0.02491	0.50694	0.83739
Pt	6	0.23089	0.76017	0.70033
Pt	7	0.48530	-0.00861	0.54580
Pt	8	0.47477	0.00685	0.83733
Pt	9	0.73073	0.26030	0.70040
Pt	10	0.47209	0.49031	0.57084
Pt	11	0.47503	0.50688	0.83735
Pt	12	0.73068	0.76017	0.70036
O	1	0.42517	0.52825	0.40427
O	2	0.65975	0.48144	0.35787
H	1	0.42970	0.71021	0.40981
H	2	0.64704	0.30211	0.35190

H_2O_2 on Pt(111)

Element	Atom number	Fractional coordinates after optimization step u	v	w
Pt	1	-0.09888	-0.04270	-0.41411
Pt	2	0.66207	0.33166	-0.24707

Pt	3	0.33423	0.66066	-0.08512
Pt	4	-0.10121	0.45629	-0.41423
Pt	5	0.66207	0.83165	-0.24706
Pt	6	0.33420	0.16070	-0.08516
Pt	7	0.40171	0.45830	-0.41442
Pt	8	0.16207	0.83166	-0.24707
Pt	9	0.83422	0.16066	-0.08512
Pt	10	0.40404	-0.04063	-0.41409
Pt	11	0.16207	0.33165	-0.24706
Pt	12	0.83419	0.66070	-0.08516
O	1	0.06096	0.52924	0.43091
O	2	0.23180	0.82858	0.39666
H	1	0.29145	0.92452	0.45060
H	2	0.21107	0.47069	0.42029

H_2O_2 on Au(110)

Element	Atom number	Fractional coordinates after optimization step u	v	w
Au	1	0.01087	0.01997	0.68275
Au	2	0.00853	0.51083	0.89654
Au	3	0.25845	0.75945	0.79494
Au	4	0.25841	0.26042	0.79496
Au	5	-0.00936	0.51870	0.67632
Au	6	0.00851	0.01007	0.89659
Au	7	0.49530	0.00198	0.67387
Au	8	0.50889	0.51139	0.89607
Au	9	0.75865	0.76031	0.79497
Au	10	0.75864	0.26142	0.79498
Au	11	0.52762	0.53767	0.67282
Au	12	0.50897	0.01056	0.89611
O	1	0.22146	0.51980	0.57916
O	2	0.55057	0.26294	0.57556
H	1	0.21265	0.66478	0.54908
H	2	0.42436	0.29918	0.54877

H_2O_2 on Au(100)

Element	Atom number	Fractional coordinates after optimization step u	v	w
Au	1	-0.01979	-0.01184	0.06643
Au	2	-0.01844	-0.00715	0.33595
Au	3	0.23151	0.23638	0.20082
Au	4	-0.01979	0.48824	0.06641
Au	5	-0.01823	0.49282	0.33544
Au	6	0.23135	0.73636	0.20082

Au	7	0.48019	-0.01179	0.06642
Au	8	0.48143	0.00296	0.33561
Au	9	0.73137	0.23635	0.20082
Au	10	0.48019	0.48819	0.06643
Au	11	0.48125	0.50279	0.33442
Au	12	0.73154	0.73639	0.20082
O	1	0.49041	0.54182	0.51526
O	2	0.68756	0.37633	0.52446
H	1	0.36019	0.43140	0.50131
H	2	0.71692	0.39332	0.58357

H_2O_2 on Au(111)

Element	Atom number	Fractional coordinates after optimization step u	v	w
Au	1	-0.07602	-0.04677	-0.16111
Au	2	0.16500	0.33500	-0.33210
Au	3	0.33000	0.17000	-0.50371
Au	4	-0.07741	0.45217	-0.16101
Au	5	0.16500	0.83500	-0.33210
Au	6	0.33000	0.67000	-0.50371
Au	7	0.42342	-0.04711	-0.16249
Au	8	0.66500	0.33500	-0.33210
Au	9	0.83000	0.17000	-0.50371
Au	10	0.42310	0.45399	-0.16232
Au	11	0.66500	0.83500	-0.33210
Au	12	0.83000	0.67000	-0.50371
O	1	0.71745	0.39293	1.03731
O	2	0.72228	0.64048	1.06017
H	1	0.51928	0.25754	1.04680
H	2	0.75358	0.72658	1.00084