Water Splitting on TiO_2-Based Electrochemical Cells, a Small Cluster Study

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In every studied reaction mechanism the energy values and the entropic contribution to the free energy of H_2, H_2O and O_2 are needed. The cartesian coordinates in (Å) and molecular energies (in eV) of H_2 and H_2O at 0K, employed in every considered path, are the followings:

H_2 $E_{0K} = -31.83295$ $ZPEC = 0.272$

H	0.000	0.000	-0.371
H	0.000	0.000	0.371

H_2O $E_{0K} = -2079.193$ $ZPEC = 0.575$

O	0.000	1.990	5.881
H	0.000	0.775	-0.516
H	0.000	-0.775	-0.516

The gas phase entropic contribution to the free energies at standard thermodynamic conditions, for the H_2 and H_2O molecules, computed by the vibrational analysis and within the same level of theory are:

$$TS(\mathrm{H_2}) = 0.402 \text{ eV} \tag{1}$$

$$TS(\mathrm{H_2O}) = 0.601 \text{ eV} \tag{2}$$

The contribution of the O_2 molecule is taken from experimental values in Ref.[1]

$$TS(\mathrm{O_2}) = 0.633 \text{ eV} \tag{3}$$

The O_2 molecular energy is computed indirectly by fixing the experimental free energy change of the water decomposition reaction: $H_2O \rightarrow \frac{1}{2}O_2 + H_2$ ($\Delta G = 2.46$ eV) and using the previous results (Eqs. 1, 2, 3). The zero point correction to the O_2 molecular energy is included in this value:

$$E(\mathrm{O_2}) = -4088.953 \text{ eV} \tag{4}$$

The cartesian coordinates, the molecular and zero point energies of every structure considered in the proposed reaction mechanisms are shown below (all the energies are given in eV while the cartesian coordinates are in Å)

Water splitting on TiO_2: $TiO_2 + 2H_2O \rightarrow TiO_2 + 2H_2 + O_2$.

TiO_2 $E_{0K} = -2720.767 \times 10$ $ZPEC = 0.145$

O	1.392	0.509	0.000
TI	0.000	-0.326	0.000
O	-1.392	0.509	0.000

$Ti(OH)_4$ $E_{0K} = -3137.118 \times 10$ $ZPEC = 1.37$

TI	-0.000	0.000	0.000
O	0.227	-1.454	-1.066
O	-0.226	1.454	-1.066
O	1.454	0.227	1.066

O	-1.454	-0.226	1.066
H	2.354	-0.116	1.068
H	-2.354	0.116	1.068
H	0.116	2.354	-1.069
H	-0.116	-2.354	-1.068

$Ti(OH)_3O$ $E_{0K} = -3135.248 \times 10$ $ZPEC = 1.08$

O	1.403	1.084	-0.399
TI	0.009	-0.035	-0.085
O	0.305	-1.764	-0.526
O	-1.493	0.591	-0.875
O	-0.169	-0.019	1.758
H	-0.093	-2.449	-1.073
H	-2.321	1.024	-0.646
H	2.359	1.011	-0.494

$Ti(OH)_2O_2$ $E_{0K} = -3133.491 \times 10$ $ZPEC = 0.848$

O	1.169	-1.552	-0.017
TI	0.206	-0.013	0.082
O	-1.412	-0.031	0.913
O	-1.491	0.052	-0.569
O	1.215	1.499	0.118
H	1.081	2.450	0.195
H	1.007	-2.500	-0.059

TiOHO $E_{0K} = -2722.424 \times 10$ $ZPEC = 0.419$

O	-1.213	0.770	-0.021
TI	-0.149	-0.467	0.025
O	1.622	0.020	0.003
H	2.116	0.844	-0.032

Water splitting on Ti_2O_4: $Ti_2O_4 + 2H_2O \rightarrow Ti_2O_4 + 2H_2 + O_2$.

Ti_2O_4 $E_{0K} = -5441.985 \times 10$ $ZPEC = 0.389$

TI	1.335	-0.000	-0.562
O	0.055	1.251	-0.081
O	0.056	-1.254	-0.085
TI	-1.224	-0.002	0.397
O	-2.546	-0.001	-0.561
O	2.657	-0.001	0.395

$Ti_2O_6H_4$ $E_{0K} = -5858.352 \times 10$ $ZPEC = 1.60$

O	0.163	-1.233	0.000
Ti	-1.767	-0.670	0.000
O	-0.626	1.006	0.000
Ti	1.304	0.442	0.000
O	2.885	-0.443	0.000
O	1.783	2.227	0.000

O	-2.246	-2.454	0.000
O	-3.349	0.216	0.000
H	2.636	2.672	0.000
H	2.898	-1.401	0.000
H	-3.099	-2.899	0.000
H	-3.361	1.174	0.000

$Ti_2O_4H_3{\cdot}O_2$ $E_{0K} = -5856.222 \times 10$ $ZPEC = 1.27$

O	-2.777	1.800	-0.315
TI	-1.916	0.240	0.028
O	-0.060	0.248	-0.040
TI	1.727	0.003	-0.173
O	2.789	1.476	-0.123
O	-2.812	-1.278	0.412
O	2.306	-1.469	-1.085
O	2.408	-1.598	0.385
H	-3.539	2.369	-0.438
H	-3.089	-2.175	0.605
H	2.864	2.431	-0.053

$Ti_2O_4H_2$ $E_{0K} = -5445.167 \times 10$ $ZPEC = 0.915$

O	0.159	1.654	0.471
TI	-1.197	0.162	0.519
O	-2.332	-0.255	-0.845
TI	1.261	-0.086	0.278
O	1.874	-0.711	-1.108
O	-0.097	-0.953	1.366
H	-2.537	-0.908	-1.519
H	0.150	2.493	-0.002

Ti_2O_4H $E_{0K} = -5443.644 \times 10$ $ZPEC = 0.631$

O	0.196	1.228	-0.229
TI	-1.109	-0.075	-0.056
O	-2.910	-0.237	-0.350
TI	1.604	0.014	-0.279
O	2.646	0.119	0.973
O	0.284	-1.284	-0.109
H	-3.801	-0.407	-0.657

Water splitting on Ti(OH)$_4$: $Ti(OH)_4 + 2H_2O \rightarrow Ti(OH)_4 + 2H_2 + O_2$.
$Ti(OH)_4$ $E_{0K} = -3137.118 \times 10$ $ZPEC = 1.37$

TI	-0.000	0.000	0.000
O	0.227	-1.454	-1.066
O	-0.226	1.454	-1.066
O	1.454	0.227	1.066
O	-1.454	-0.226	1.066
H	2.354	-0.116	1.068
H	-2.354	0.116	1.068
H	0.116	2.354	-1.069
H	-0.116	-2.354	-1.068

$Ti(OH)_4$-H_2O $E_{0K} = -3345.066 \times 10$ $ZPEC = 2.06$

O	0.603	-0.915	1.138
TI	-0.496	0.019	0.012
O	-1.567	-1.118	-0.899
O	0.603	0.947	-1.118
O	-1.556	1.163	0.929
H	-1.565	1.557	1.807
H	-1.577	-1.512	-1.778
H	0.534	1.838	-1.478
H	0.522	-1.803	1.504
O	3.269	-0.064	-0.059
H	2.671	0.365	-0.688
H	2.675	-0.443	0.606

$Ti(OH)_5$ $E_{0K} = -3343.203 \times 10$ $ZPEC = 1.72$

O	0.136	1.975	0.020
TI	0.194	0.154	0.054
O	1.907	-0.189	-0.430
O	-0.610	-0.963	-1.355
O	0.081	-0.581	1.730
H	2.417	-0.697	-1.068
H	-0.656	2.501	0.185
H	0.832	-0.873	2.261
H	-0.995	-1.848	-1.290
O	-1.911	0.144	-0.001
H	-2.283	-0.577	0.537

$Ti(OH)_3$-OOH $E_{0K} = -3341.536 \times 10$ $ZPEC = 1.51$

O	0.156	-0.204	1.506
TI	-0.163	-0.286	-0.298
O	0.678	1.806	-0.427
O	-0.685	1.446	-0.832
O	-1.601	-1.342	-0.572
O	1.205	-0.972	-1.276
H	2.044	-0.622	-1.591
H	0.545	2.247	0.431
H	-0.191	-0.744	2.224
H	-1.890	-2.048	-1.159

$Ti(OH)_3OO$ $E_{0K} = -3339.837 \times 10$ $ZPEC = 1.19$

O	1.633	-0.074	-1.044
TI	0.252	-0.086	0.131
O	-1.192	0.007	-1.278
O	-1.774	-0.061	-0.093
O	0.400	-1.637	1.060
O	0.402	1.401	1.148
H	0.101	-1.936	1.925
H	1.057	2.102	1.232
H	1.771	0.029	-1.991

$Ti(OH)_3OO\text{-}H_2O$ $E_{0K} = -3547.810 \times 10$ $ZPEC = 1.94$

O	-0.527	-1.555	-0.874
TI	0.004	-0.002	0.033
O	-0.148	0.029	1.835
O	1.920	-0.663	-0.083
O	1.920	0.653	-0.113
O	-0.528	1.519	-0.926
H	0.081	2.186	-1.264
H	-0.925	0.060	2.405
H	0.080	-2.236	-1.186
O	-2.280	-0.001	0.110
H	-2.476	-0.802	-0.400
H	-2.473	0.772	-0.445

Water splitting on $Ti(OH)_4^-$: $Ti(OH)_4^- + 2H_2O \rightarrow Ti(OH)_4^- + 2H_2 + O_2$.
$Ti(OH)_4^-$ $E_{0K} = -3137.148 \times 10$ $ZPEC = 1.36$

TI	-0.000	0.021	-0.000
O	-1.014	1.153	-1.207
O	1.014	1.154	1.206
O	1.207	-1.111	-1.014
O	-1.206	-1.111	1.014
H	0.933	-1.537	-1.836
H	-0.932	-1.536	1.837
H	1.836	1.580	0.933
H	-1.837	1.578	-0.933

$Ti(OH)_4\text{-}H_2O^-$ $E_{0K} = -3345.150 \times 10$ $ZPEC = 2.06$

O	0.746	-1.340	-0.708
TI	-0.487	-0.000	0.000
O	-1.671	0.774	-1.312
O	0.746	1.340	0.708
O	-1.670	-0.774	1.312
H	-2.387	-1.369	1.052
H	-2.387	1.369	-1.052
H	0.667	1.617	1.628
H	0.667	-1.617	-1.628
O	3.198	0.000	-0.000
H	2.573	0.694	0.288
H	2.573	-0.694	-0.288

$Ti(OH)_5^-$ $E_{0K} = -3343.615 \times 10$ $ZPEC = 1.80$

O	-1.855	0.120	0.425
TI	0.036	0.013	-0.052
O	-0.073	-1.720	0.784
O	0.242	1.744	0.746
O	-0.271	0.031	-1.909
H	-1.210	0.018	-2.137
H	0.825	-2.058	0.900
H	-0.620	2.010	1.091
H	-2.157	-0.679	0.874

O	1.952	-0.155	0.017
H	2.372	0.611	0.427

$Ti(OH)_4O^-$ $E_{0K} = -3341.766 \times 10$ $ZPEC = 1.45$

O	0.464	0.955	1.626
TI	-0.027	0.090	0.016
O	-1.892	-0.271	0.361
O	-0.023	-1.789	-0.169
O	1.861	-0.200	-0.330
O	-0.475	1.220	-1.428
H	-1.386	1.094	-1.713
H	-2.114	-1.108	0.778
H	1.413	0.814	1.732
H	2.124	-0.953	-0.864

$Ti(OH)_3{\cdot}O_2^-$ $E_{0K} = -3340.112 \times 10$ $ZPEC = 1.17$

O	0.578	-1.187	-1.361
TI	0.136	-0.002	0.058
O	-1.327	1.194	0.188
O	-1.721	-0.170	-0.259
O	1.399	1.404	-0.080
O	0.487	-0.864	1.694
H	1.103	2.311	-0.208
H	-0.151	-1.525	1.991
H	-0.125	-1.397	-1.988

$Ti(OH)_3{\cdot}O_2$-H_2O^- $E_{0K} = -3548.107 \times 10$ $ZPEC = 1.88$

O	-0.900	0.004	1.460
TI	0.340	0.148	0.008
O	-0.798	-0.269	-1.468
O	1.815	-0.836	-0.626
O	1.587	-0.991	0.837
O	0.895	1.934	-0.048
H	1.792	2.143	-0.334
H	-0.535	-0.957	-2.089
H	-0.723	-0.645	2.150
O	-3.345	-0.222	-0.053
H	-2.709	-0.269	-0.790
H	-2.743	-0.110	0.706

Water splitting on $Ti(OH)_2$-O_2-$Ti(OH)_2$: $Ti(OH)_2$-O_2-$Ti(OH)_2$+$2H_2O \rightarrow Ti(OH)_2$-$O_2$-$Ti(OH)_2$+ $2H_2 + O_2$.
$Ti(OH)_2$-O_2-$Ti(OH)_2$ $E_{0K} = -5857.972 \times 10$ $ZPEC = 1.64$

O	0.163	-1.233	0.000
Ti	-1.767	-0.670	0.000
O	-0.626	1.006	0.000
Ti	1.304	0.442	0.000
O	2.885	-0.443	0.000
O	1.783	2.227	0.000
O	-2.246	-2.454	0.000

O	-3.349	0.216	0.000
H	2.636	2.672	0.000
H	2.898	-1.401	0.000
H	-3.099	-2.899	0.000
H	-3.361	1.174	0.000

$Ti(OH)_2$-O_2-$Ti(OH)_2$-H_2O $E_{0K} = -6065.922 \times 10$ $ZPEC = 2.28$

O	-0.372	-1.513	0.000
TI	1.365	-0.433	0.000
O	2.937	0.514	0.000
TI	-1.636	-0.274	0.000
O	-2.429	1.409	0.000
O	0.132	0.842	0.000
O	-3.196	-1.212	0.000
O	2.168	-2.117	0.000
H	3.835	0.156	0.000
H	1.707	-2.965	0.000
H	-4.093	-0.851	0.000
H	-1.993	2.270	0.000
O	1.561	3.384	0.000
H	0.931	2.644	0.000
H	2.428	2.957	0.000

$Ti(OH)_3$-O-$Ti(OH)_2O$ $E_{0K} = -6064.100 \times 10$ $ZPEC = 1.99$

O	-0.044	-0.540	0.000
TI	-1.899	-0.178	0.000
O	-3.675	0.360	0.000
TI	1.758	-0.269	0.000
O	3.487	0.514	0.000
O	1.362	1.551	0.000
O	2.490	-1.956	0.000
O	-1.558	1.674	0.000
O	-2.439	-1.939	0.000
H	3.375	-2.337	0.000
H	3.704	1.456	0.000
H	-3.311	-2.351	0.000
H	-3.876	1.307	0.000
H	-0.656	2.034	0.000

$Ti(OH)_3$-O-$Ti(OH)\cdot O_2$ $E_{0K} = -6062.291 \times 10$ $ZPEC = 1.70$

O	0.192	-0.313	0.000
TI	-1.610	-0.563	0.000
O	-2.323	-2.250	0.000
TI	2.010	0.210	0.000
O	3.844	0.481	0.000
O	1.716	2.016	0.000
O	2.498	-1.620	0.000
O	-2.748	0.739	0.000
O	-3.259	1.950	0.000
H	1.839	-2.324	0.000
H	4.401	-0.311	0.000
H	2.231	2.830	0.000
H	-3.194	-2.661	0.000

$Ti(OH)_3$-O-$Ti(OH)\cdot O_2$-H_2O $E_{0K} = -6270.254 \times 10$ $ZPEC = 2.38$

O	-0.378	0.372	0.000
TI	-2.122	-0.239	0.000
O	-2.829	1.533	0.000
TI	1.513	0.324	0.000
O	2.104	-1.309	0.000
O	3.277	-1.933	0.000
O	3.273	0.957	0.000
O	-3.938	-0.706	0.000
O	-1.721	-2.038	0.000
H	-2.229	2.288	0.000
H	-4.598	0.001	0.000
H	-2.342	-2.778	0.000
H	3.943	0.245	0.000
O	1.393	2.549	0.000
H	0.702	3.219	0.000
H	2.279	2.941	0.000

$Ti(OH)_3$-OH-$Ti(OH)_2\cdot O_2$ $E_{0K} = -6270.261 \times 10$ $ZPEC = 2.41$

O	-0.357	-0.516	0.000
TI	-2.239	-0.116	0.000
O	-4.021	0.425	0.000
TI	1.745	0.215	0.000
O	1.041	1.921	0.000
O	3.495	0.275	0.000
O	4.474	-0.639	0.000
O	1.831	-1.676	0.000
O	-2.662	-1.891	0.000
O	-1.814	1.686	0.000
H	-2.483	2.383	0.000
H	-4.812	-0.129	0.000
H	-3.126	-2.733	0.000
H	-0.082	-1.455	0.000
H	2.758	-1.991	0.000
H	0.106	2.183	0.000

$Ti_2O_6H_5$ $E_{0K} = -5859.877 \times 10$ $ZPEC = 1.85$

O	0.022	0.477	1.070
TI	1.433	0.057	-0.215
O	2.366	-1.449	0.217
TI	-1.492	0.222	-0.342
O	-2.264	1.804	-0.820
O	-2.496	-1.266	-0.034
O	0.197	-0.197	-1.397
O	2.522	1.477	-0.590
H	-0.010	0.754	1.989
H	-3.000	2.344	-1.112
H	-2.671	-2.202	0.077
H	2.320	-2.379	-0.027
H	3.458	1.684	-0.517

Water splitting on Ti(OH)$_3$-O-Ti(OH)$_3$: Ti(OH)$_3$-O-Ti(OH)$_3$ + 2H$_2$O → Ti(OH)$_3$-O-Ti(OH)$_3$ + 2H$_2$ + O$_2$.
Ti(OH)$_3$-O-Ti(OH)$_3$ $E_{0\mathrm{K}} = -6065.916 \times 10$ $ZPEC = 2.29$

O	0.007	0.209	0.000
TI	-1.837	-0.041	0.000
O	-2.159	1.835	0.000
O	-1.846	-1.880	0.000
O	-3.707	-0.100	0.000
TI	1.857	-0.004	0.000
O	2.129	1.882	0.000
O	1.923	-1.839	0.000
O	3.728	-0.009	0.000
H	-2.617	-2.461	0.000
H	-4.190	0.739	0.000
H	-1.420	2.455	0.000
H	2.699	-2.413	0.000
H	4.168	0.854	0.000
H	1.373	2.483	0.000

Ti(OH)$_3$-O-Ti(OH)$_3$-H$_2$O $E_{0\mathrm{K}} = -6273 \times 10$ $ZPEC = 2.93$

O	0.030	0.333	0.000
TI	-1.819	0.106	0.000
O	-1.829	-1.753	0.000
TI	1.889	0.456	0.000
O	2.252	-1.367	0.000
O	3.734	0.725	0.000
O	1.861	2.351	0.000
O	-2.147	1.972	0.000
O	-3.681	0.019	0.000
O	0.408	-3.635	0.000
H	-1.458	2.646	0.000
H	1.051	2.875	0.000
H	-4.202	0.834	0.000
H	4.085	1.626	0.000
H	3.163	-1.693	0.000
H	-2.660	-2.247	0.000
H	-0.411	-3.115	0.000
H	1.116	-2.971	0.000

Ti(OH)$_3$-O-Ti(OH)$_4$ $E_{0\mathrm{K}} = -6272.439 \times 10$ $ZPEC = 2.55$

O	1.830	-0.085	2.129
TI	1.461	-0.121	0.350
O	3.547	0.213	-0.037
O	-0.299	-0.717	0.279
O	2.299	-1.461	-0.772
O	1.164	1.462	-0.481
H	2.619	0.221	2.590
H	0.257	1.753	-0.718
H	2.376	-1.446	-1.735
H	3.663	0.722	-0.860
TI	-1.949	-0.178	-0.157
O	-2.712	-1.281	-1.377
O	-1.612	1.508	-0.876

O	-3.041	-0.015	1.282
H	-2.490	-2.066	-1.887
H	-3.863	-0.411	1.588
H	-2.213	2.251	-0.993

$Ti(OH)_3$-O-$Ti(OH)_2$-OOH $E_{0\mathrm{K}} = -6270.347 \times 10$ $ZPEC = 2.38$

O	0.385	0.587	0.000
TI	2.096	-0.042	0.000
O	3.828	-0.772	0.000
O	-3.373	0.060	0.000
O	-1.254	-1.479	0.000
O	-4.022	-1.207	0.000
TI	-1.492	0.329	0.000
O	-1.906	2.144	0.000
O	2.901	1.646	0.000
O	1.463	-1.836	0.000
H	2.073	-2.584	0.000
H	4.613	-0.208	0.000
H	2.388	2.465	0.000
H	-2.685	2.710	0.000
H	-0.354	-1.882	0.000
H	-4.952	-0.927	0.000

$Ti(OH)_3$-O-$Ti(OH)_2$-OO $E_{0\mathrm{K}} = -6268 \times 10$ $ZPEC = 2.04$

O	-0.223	0.480	0.000
TI	-1.996	-0.098	0.000
O	-3.811	-0.530	0.000
TI	1.645	0.543	0.000
O	3.481	0.683	0.000
O	1.772	-1.348	0.000
O	2.046	-2.587	0.000
O	1.614	2.415	0.000
O	-1.609	-1.898	0.000
O	-2.652	1.684	0.000
H	-2.213	-2.650	0.000
H	-4.463	0.185	0.000
H	-2.063	2.448	0.000
H	4.010	1.491	0.000
H	0.758	2.862	0.000

Vibrational density of states (VDOS) and partial vibrational density of states (PVDOS)
The VDOS in each panel of the Fig. 8 in the body of the article is computed by:

$$\rho(\omega) = \sum_{i=1}^{3N-6} \frac{1}{\sqrt{2\pi}\sigma} \exp(-\frac{(\omega-\omega_i)^2}{2\sigma^2}) \tag{5}$$

where N is the number of atoms contained in each structure, $\sigma = 30$ cm^{-1} and ω_i are the vibrational frequencies of the normal modes after the exclusion of pure translational and rotational frequencies.

The corresponding vibrational frequencies of the structures considered in the Fig. 8 are shown in the fallowing tables:

ω_i[**Ti(OH)**$_4$] (**cm**$^{-1}$)	ω_i[**Ti(OH)**$_4$**-H**$_2$**O**] (**cm**$^{-1}$)	ω_i[**Ti(OH)**$_5$] (**cm**$^{-1}$)
108.348	16.834	62.687
133.748	87.718	72.646
157.688	138.865	144.652
157.721	159.145	163.024
200.932	167.004	200.026
215.901	176.069	213.767
235.592	194.305	235.262
235.599	216.661	269.875
309.120	233.063	288.093
437.743	260.783	305.228
452.165	289.179	331.114
452.186	311.751	378.485
457.941	345.541	446.124
760.558	383.268	484.596
802.786	459.750	499.442
811.637	483.841	557.691
811.640	520.104	591.005
4230.053	594.157	608.627
4230.284	613.714	694.332
4230.295	687.660	706.946
4238.039	752.887	745.300
-	764.304	765.854
-	789.449	3707.189
-	1735.806	3794.498
-	3713.506	3810.466
-	3789.660	3818.852
-	3832.199	3869.141
-	3835.130	-
-	3849.801	-
-	3853.709	-

ω_i[**Ti(OH)$_3$OOH**] (**cm^{-1}**)	ω_i[**Ti(OH)$_3$O$_2$**] (**cm^{-1}**)	ω_i[**Ti(OH)$_3$O$_2$-H$_2$O**] (**cm^{-1}**)
126.356	49.414	60.305
131.780	139.796	131.028
152.435	167.590	134.725
172.953	186.925	180.072
180.886	202.556	202.324
195.792	223.400	211.489
212.071	243.867	219.382
228.390	286.413	254.287
299.190	328.840	256.336
345.767	393.820	300.355
392.415	443.332	366.757
500.682	490.011	387.039
540.106	506.881	411.047
583.286	552.085	412.986
642.238	719.135	475.231
712.940	767.374	583.700
759.162	778.083	628.286
773.134	1197.445	648.087
894.399	3842.218	659.916
1337.386	3846.541	666.545
3667.607	3851.075	716.568
3834.226	-	767.096
3846.587	-	781.014
3864.476	-	1212.637
-	-	1693.140
-	-	3685.210
-	-	3781.141
-	-	3819.086
-	-	3821.130
-	-	3842.582

The PVDOS gives the contribution of each atom in the structure of the VDOS. As it is highlighted in the article, the PVDOS shows that the O-O peak in Fig. 8 e) is composed by contributions coming from the oxygen atoms in the preformed O_2 molecule. The eigenvectors of the normal modes are expressed by the relative displacements of the atoms in the structure:

$$\vec{u}^i = \{x^i_\alpha, y^i_\alpha, z^i_\alpha\} \tag{6}$$

where $\vec{u}^i$ is a $3N$ dimensional vector, α runs from 1 to the number of atoms in the structure (N) while i denote the corresponding normal mode. The set of $\vec{u}^i$ computed as it is implemented in GAMESS are orthonormalized according to:

$$\sum_\alpha m_\alpha \{x^i_\alpha x^j_\alpha + y^i_\alpha y^j_\alpha + z^i_\alpha z^j_\alpha\} = \delta_{i,j} \tag{7}$$

where m_α is the mass of the atom α. Considering the ortonormalization rule of the $\vec{u}^i$ vectors, the

VDOS can be written as:

$$\rho(\omega) = \sum_{i=1}^{3N-6} \frac{\sum_{\alpha} m_{\alpha}\{{x_{\alpha}^{i}}^{2} + {y_{\alpha}^{i}}^{2} + {z_{\alpha}^{i}}^{2}\}}{\sqrt{2\pi}\sigma} \exp(-\frac{(\omega-\omega_i)^2}{2\sigma^2}) \tag{8}$$

from Eq. 8 it can be set:

$$\rho(\omega) = \sum_{\alpha} \rho_{\alpha}(\omega) \tag{9}$$

where:

$$\rho_{\alpha}(\omega) = \sum_{i=1}^{3N-6} \frac{m_{\alpha}\{{x_{\alpha}^{i}}^{2} + {y_{\alpha}^{i}}^{2} + {z_{\alpha}^{i}}^{2}\}}{\sqrt{2\pi}\sigma} \exp(-\frac{(\omega-\omega_i)^2}{2\sigma^2}) \tag{10}$$

is the PVDOS (i.e. the contribution of the atom α to the total VDOS) corresponding to the atom α.

In the Fig. 1 it is shown the VDOS of the structure $Ti(OH)_3O_2$ as it is in the panel e) of the Fig. 8 in the article. In different colors are shown the PVDOS of every atom of the structure. The O-O peak in the VDOS is composed by the contributions of the oxygen atoms: O2 and O3 (blue and yellow lines). It can be seen (looking at the cartesian coordinates of the $Ti(OH)_3O_2$) that the O2 and O3 oxygen atoms correspond to the preformed O_2 molecule in the $Ti(OH)_3O_2$ structure.

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[1] Atkins, P. W. *Physical Chemistry*, 6th ed. Oxford University Press: Oxford, U. K., 1998; pp 485, 925-927, and 942.

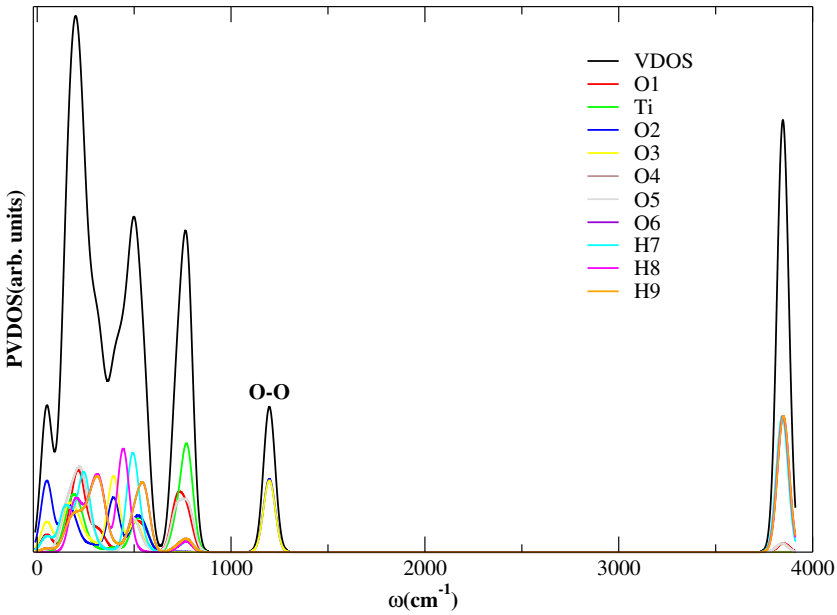
VDOS
O1
Ti
O2
O3
O4
O5
O6
H7
H8
H9
O-O
PVDOS(arb. units)
0
1000
2000
3000
4000
ω(cm-1)

FIG. 1.