

Supporting information

for

**An ab initio based full-dimensional potential energy surface for $\text{OH} + \text{O}_2 \rightleftharpoons \text{HO}_3$
and low-lying vibrational levels of HO_3**

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Table S-I. Geometries and energies of *trans*-HO₃, *cis*-HO₃ and i-TS calculated from the PESs based on both M06 and MRCI-F12 method with a comparison with MRCI+Q/CBS results and experimental results.

Parameter	<i>trans</i> -HO ₃				<i>cis</i> -HO ₃			i-TS	
	PES (M06-L)	PES (MRCI-F12)	MRCI+Q/CBS	Expt. ¹	PES (M06-L)	PES (MRCI-F12)	MRCI+Q/CBS	PES (M06-L)	PES (MRCI-F12)
$R_{O''H}/\text{\AA}$	0.968	0.971	0.977	0.972	0.971	0.975	0.980	0.967	0.971
$R_{O'O''}/\text{\AA}$	1.625	1.658	1.700	1.688	1.568	1.573	1.607	1.648	1.667
$R_{OO'}/\text{\AA}$	1.216	1.224	1.221	1.225	1.233	1.244	1.242	1.219	1.228
$\theta_{O'O''H}/^\circ$	96.55	96.33	94.88	90.0	98.45	96.76	95.36	97.09	97.09
$\theta_{OO'O''}/^\circ$	110.96	110.04	110.35	111.0	113.46	111.97	111.94	112.60	112.34
$\varphi_{OO'O''H}/^\circ$	180	180	180	180	0	0	0	75.65	81.40
$\Delta E/\text{cm}^{-1}$	0	0	0	0	202.85	32.98	26.93	654.03	365.22

Table S-II. Comparison of calculated harmonic frequencies (in cm^{-1}) of the stationary points for HO_3 with other *ab initio* results for HO_3 .²

<i>trans</i>			<i>cis</i>			i-TS		
MRCI+Q/ VTZ ²	PES (MRCI- F12)	PES (M06-L)	MRCI+Q /VTZ ²	PES (MRCI- F12)	PES (M06-L)	MRCI+Q/ VTZ ²	PES (MRCI- F12)	PES (M06-L)
147.6	160.9	200.3	238.5	221.7	256.5	160.2i	158.2i	212.3i
222.0	300.4	338.7	282.2	314.1	352.2	167.5	254.3	270.3
501.4	507.0	584.2	595.7	612.3	654.8	503.1	541.2	574.6
1094.3	1114.4	1165.9	1221.6	1244.5	1247.8	1052.2	1107.5	1107.4
1421.4	1429.7	1461.4	1356.0	1385.4	1420.8	1391.8	1390.3	1427.1
3761.9	3780.0	3799.0	3721.7	3717.7	3729.7	3758.1	3768.6	3794.8

Table S-III. Calculated vibrational levels (in cm^{-1}) of HO_3 and their assignment in terms of the six normal mode quantum numbers ($n_1n_2n_3n_4n_5n_6$).

par.	E_{abs}	$E\text{-ZPE}_{\text{trans}}$	$E\text{-ZPE}_{\text{cis}}$	<i>trans</i>	<i>cis</i>
+1	3582.463	0.000		(000000)	
+1	3582.467	0.004		(000000)	
+1	3693.809		0.000		(000000)
+1	3693.827		0.017		(000000)
-1	3709.394	126.931		(000001)	
-1	3709.398	126.934		(000001)	
+1	3806.817	224.354		(000002)	
+1	3806.819	224.355		(000002)	
-1	3823.173		129.363		(000001)
-1	3823.183		129.373		(000001)
+1	3844.434	261.970		(000010)	
+1	3844.438	261.974		(000010)	
+1	3901.562		207.752		(000002)
-1	3901.563	319.099		(000003)	
+1	3901.569		207.760		(000002)
-1	3901.570	319.106		(000003)	
-1	3956.749	374.285		(000011)	
-1	3956.753	374.290		(000011)	
+1	3958.218		264.409		(000010)
+1	3958.227		264.417		(000010)
+1	4020.228	437.765	326.419		
+1	4020.231	437.768	326.422		
-1	4024.997	442.534	331.188		
-1	4025.003	442.539	331.193		
+1	4053.862	471.399		(000012)	
+1	4053.866	471.403		(000012)	
+1	4065.401	482.937		(000100)	
+1	4065.425	482.961		(000100)	
+1	4071.952	489.488		(000020)	
+1	4071.958	489.495		(000020)	
-1	4078.436		384.626		(000011)
-1	4078.441		384.632		(000011)
+1	4113.917	531.454	420.108		
+1	4113.927	531.464	420.118		
-1	4114.613	532.149	420.803		
-1	4114.617	532.154	420.808		
+1	4122.169	539.705	428.359		
+1	4122.223	539.759	428.413		
-1	4144.094	561.631	450.285		
-1	4144.122	561.658	450.312		

+1	4151.912	569.448	458.102		
+1	4152.217	569.753	458.407		
-1	4158.313	575.850	464.504		
-1	4158.409	575.945	464.599		
+1	4173.799	591.335	479.990		
+1	4173.802	591.339	479.993		
+1	4177.434	594.971	483.625		
+1	4177.443	594.980	483.634		
+1	4182.305		488.495		(000020)
+1	4182.332		488.523		(000020)
-1	4186.527	604.063	492.717		
-1	4186.914	604.451	493.105		
+1	4188.287	605.823	494.477		
+1	4189.275	606.811	495.465		
+1	4193.677	611.213	499.867		
+1	4195.052	612.589	501.243		
-1	4195.556	613.093	501.747		
-1	4195.570	613.107	501.761		
+1	4196.743	614.280	502.934		
+1	4209.492	627.029	515.683		
+1	4209.929	627.465	516.119		
-1	4210.154	627.691	516.345		
-1	4210.242	627.778	516.432		
+1	4215.554	633.091	521.745		
+1	4215.622	633.159	521.813		
+1	4224.958	642.495	531.149		
+1	4226.308	643.845	532.499		
+1	4226.478	644.015	532.669		
+1	4229.150	646.687	535.341		
+1	4231.064	648.601	537.255		
+1	4239.206		545.397		(000100)
+1	4239.286		545.476		(000100)
...	...				
+1	4625.742	1043.279		(001000)	
+1	4858.066		1164.257		(001000)
+1	4966.914	1384.451		(010000)	
+1	5002.035		1308.226		(010000)
+1	7184.929	3602.466		(100000)	
+1	7252.715		3558.906		(100000)
-1	7309.340	3726.876		(100001)	
+1	7795.690		4101.881		(100100)
+1	8197.352	4614.889		(101000)	
+1	10643.622	7061.158		(200000)	

Table S-IV. Calculated vibrational levels (in cm^{-1}) of DO_3 and their assignment in terms of the six normal mode quantum numbers ($n_1n_2n_3n_4n_5n_6$).

par.	E_{abs}	$E\text{-ZPE}_{\text{trans}}$	$E\text{-ZPE}_{\text{cis}}$	<i>trans</i>	<i>cis</i>
+1	2926.125	0.000		(000000)	
+1	2926.129	0.004		(000000)	
+1	3025.368	99.243	0.000		(000000)
+1	3025.385	99.260	0.017		(000000)
-1	3026.585	100.460		(000001)	
-1	3026.588	100.463		(000001)	
+1	3113.395	187.270		(000002)	
+1	3113.397	187.273		(000002)	
-1	3141.447		116.078		(000001)
-1	3141.454		116.086		(000001)
-1	3184.540	258.415		(000003)	
-1	3184.546	258.421		(000003)	
+1	3193.269	267.144		(000010)	
+1	3193.276	267.151		(000010)	
+1	3204.816		179.448		(000002)
+1	3204.824		179.456		(000002)
+1	3260.731	334.606	235.363		
+1	3260.742	334.617	235.374		
-1	3269.744		244.375		(000003)
-1	3269.750		244.382		(000003)
-1	3284.267	358.142		(000011)	
-1	3284.273	358.148		(000011)	
+1	3297.806		272.437		(000010)
+1	3297.830		272.462		(000010)
+1	3357.510	431.385		(000012)	
+1	3357.514	431.389		(000012)	
-1	3362.346	436.221	336.977		
-1	3362.357	436.232	336.989		
+1	3369.532	443.407	344.164		
+1	3369.540	443.415	344.172		
+1	3390.343	464.218		(000100)	
+1	3390.363	464.239		(000100)	
-1	3394.741		369.373		(000011)
-1	3394.748		369.380		(000011)
+1	3424.896	498.771		(000020)	
+1	3424.904	498.779		(000020)	
-1	3427.314	501.189		(000013)	
-1	3427.323	501.198		(000013)	
+1	3440.248	514.123	414.880		
+1	3440.260	514.135	414.892		

+1	3475.104		449.736		(000012)
+1	3475.120		449.751		(000012)
-1	3477.612	551.487	452.244		
-1	3477.623	551.498	452.255		
-1	3496.409	570.284		(000101)	
-1	3496.420	570.295		(000101)	
-1	3502.184	576.059		(000021)	
-1	3502.193	576.068		(000021)	
+1	3517.614		492.245		(000020)
+1	3517.650		492.282		(000020)
-1	3528.140	602.015	502.772		
-1	3528.144	602.019	502.776		
+1	3535.324	609.199	509.956		
+1	3535.360	609.235	509.992		
+1	3550.398	624.273		(000022)	
+1	3550.448	624.323		(000022)	
+1	3559.102		533.734		(000100)
+1	3559.281		533.913		(000100)
+1	3571.296	645.171	545.928		
+1	3571.301	645.177	545.933		
-1	3574.293	648.168	548.925	(000023)	
-1	3574.299	648.174	548.931	(000023)	
+1	3583.230	657.105	557.862		
+1	3583.241	657.116	557.873		
-1	3583.562	657.437	558.193		
-1	3583.578	657.453	558.210		
+1	3592.618	666.493		(000102)	
+1	3592.629	666.504		(000102)	
+1	3597.932	671.807	572.564		
+1	3597.952	671.827	572.583		
-1	3599.190	673.065	573.822		
-1	3599.194	673.070	573.826		
...	...				
+1	3737.112	810.987		(001000)	
+1	3937.176		911.808		(001000)
+1	4304.521	1378.396		(010000)	
+1	4338.032		1312.663		(010000)
+1	5582.904	2656.779		(100000)	
+1	5650.290		2624.922		(100000)
-1	5682.513	2756.388		(100001)	
+1	6379.978	3453.853		(101000)	
+1	8161.448	5235.323		(200000)	

References:

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