SUPPORTING INFORMATION FOR

How Useful Are Vibrational Frequencies of Isotopomeric O_2 Fragments for Assessing Local Symmetry? Some Simple Systems and the Vexing Case of a Galactose Oxidase Model

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Contents:

Table S1. ν(O–O) and geometries for HOOX type molecules. Frequencies are in cm^{-1}. Bond lengths are in Å

		Geometry				
		O–O	X–O	X–O–O	**ν(^{16}O–^{16}O)**	**ν(^{18}O–^{18}O)**
HOOF	DFT	1.364	1.509	106.8°	992.3	939.2
	MP2	1.368	1.444	105.4°	1008.0	956.1
	CCSD	1.371	1.428	105.2°	1021.3	967.6
HOOCl	DFT	1.399	1.801	110.9°	888.6	839.0
	MP2	1.417	1.720	108.3°	889.3	838.9
	CCSD	1.408	1.716	108.7°	934.0	880.8
HOOBr	DFT	1.375	2.037	112.2°	942.9	889.4
	MP2	1.414	1.900	109.4°	896.9	845.9
	CCSD	1.404	1.899	109.8°	940.4	886.8
HOOI	DFT	1.387	2.196	113.3°	921.3	869.0
	MP2	1.429	2.055	109.6°	888.2	837.8
	CCSD	1.416	2.049	110.4°	934.0	880.8

Table S2. ν(O–O) and geometries for OOX type molecules. Frequencies are in cm^{-1}. Bond lengths are in Å

		Geometry				
		O–O	X–O	X–O–O	**ν(^{16}O–^{16}O)**	**ν(^{18}O–^{18}O)**
OOF	DFT	1.204	1.628	112.0°	1499.1	1413.4
	MP2	1.222	1.377	110.0°	1328.3	1254.5
	CCSD	1.204	1.530	110.0°	1439.4	1358.0
	exp[1,2]				1490, 1494	1407, 1411
OOCl	DFT	1.216	2.028	116.4°	1437.8	1355.5
	MP2	1.263	1.717	112.9°	1120.8	1063.9
	CCSD	1.226	1.897	114.0°	1330.5	1254.9
	exp[3]				1440.8	1360.9
OOBr	DFT	1.216	2.224	117.9°	1451.0	1367.9
	MP2	1.278	1.823	114.0°	1046.7	991.7
	CCSD	1.215	2.148	116.4°	1421.4	1340.1
	exp[4]				1487.0	1403.0
OOI	DFT	1.223	2.419	119.2°	1430.0	1348.0
	MP2	1.182	2.489	120.8°	1746.9	1646.8

(1) E. Y. Misochko, A. V. Akimov and C. A. Wight, *J. Phys. Chem. A,* 1999, **103**, 7972.

(2) M. E. Jacox, *J. Mol. Spectrosc.,* 1980, **84**, 74.

(3) A. Arkell and I. Schwager, *J. Am. Chem. Soc.,* 1967, **89**, 5999.

(4) D. E. Tevault and R. R. Smardzewski, *J. Am. Chem. Soc.,* 1978, **100**, 3955.

Table S3 Selected bond lengths (Å) and CuOO valence bond angles (deg) for B3LYP optimized structures of **6**

Geometry	$^1\mathbf{6}_r(\eta^2)$	$^1\mathbf{6}_u(\eta^2)$	$^1\mathbf{6}_u(\eta^1)$	$^3\mathbf{6}(\eta^1)$
Bond lengths				
O^1O^2	1.347	1.328	1.311	1.294
CuO^1	1.884	1.940	1.945	2.012
CuO^2	1.889	1.938	2.600	2.770
CuO^3	2.163	1.909	1.981	1.947
CuN^4	2.000	2.083	2.074	2.226
CuN^5	2.765	3.407	2.400	2.180
CuN^6	2.073	2.345	2.312	2.274
Bond angle				
CuO^1O^2	69.3	70.0	104.2	112.0

Table S4 Computed isotopomeric O–O vibrational frequencies (cm^{-1}, scaled by 0.975) for B3LYP optimized structures of **6**

Isotopomer[a]	$^{1}\mathbf{6}_{r}(\eta^{2})$	$^{1}\mathbf{6}_{u}(\eta^{2})$	$^{1}\mathbf{6}_{u}(\eta^{1})$	$^{3}\mathbf{6}(\eta^{1})$[b]	Expt
$^{16}O^{16}O$	1067	1105, 1100[e]	1147		1120
$^{16}O^{18}O$	1034	1071	1106		1093
$^{18}O^{16}O$	1035	1071	1106		1093
$^{18}O^{18}O$	1006	1038	1074		1059
$\Delta\nu_{mix}$[c]	1	0	0		0
$\Delta\nu_{homo}$[c]	61	64	73		61

[a] In each case the oxygen atoms are listed as $O^{1}O^{2}$ as defined in Figure 1. [b] Frequencies for the triplet were not computed. [c] Frequency difference between the mixed isotopomers. [d] Isotope shift between $^{16}O^{16}O$ and $^{18}O^{18}O$. [e] The O–O stretching mode in this case couples strongly with an aromatic ring deformation so that two bands having roughly equal contributions from both modes are predicted.

Table S5 CASPT2 relative energies (kcal mol^{-1}) for **9** with various basis sets and choices of active space

Basis set	Active space	$^1\mathbf{9}_r(\eta^2)$	$^1\mathbf{9}_u(\eta^2)^a$	$^1\mathbf{9}_u(\eta^1)$	$^3\mathbf{9}(\eta^1)$
BS1	(6,6)	14.8	0.0	17.9	21.5
	(10,10)	11.6	0.0	16.0	7.1
	(12,12)	10.4	0.0	14.9	14.7
BS2	(6,6)	11.4	0.0	23.0	22.3
	(10,10)	12.8	0.0	16.1	12.5
	(12,12)	12.4	0.0	19.4	20.4
BS3	(6,6)	22.9	0.0	10.8	*a*
	(10,10)	16.6	0.0	8.1	*a*
	(12,12)	20.4	0.0	14.2	*a*

a Not reported.

Cartesian Coordinates for 6 (*m*PWPW91 optimized structures)

$^1\mathbf{6}_r(\eta^2)$

C	0.673819	-1.916465	0.924833
C	3.299582	-2.455608	-0.440268
C	1.936972	-2.439655	-1.173158
N	3.743831	-1.124393	0.039708
C	3.691738	-0.958410	1.511092
C	2.888165	0.273885	1.992873
N	1.515386	0.447066	1.418549
C	0.548468	-0.649452	1.790878
N	0.899252	-1.570666	-0.522825
C	0.908269	1.796012	1.828008
C	5.023238	-0.675233	-0.612136
C	-0.393609	-1.666814	-1.347807
C	-1.598789	-0.987367	-0.764689
C	-2.721859	-1.739517	-0.383226
C	-3.925686	-1.115706	0.006256
C	-3.968068	0.298090	-0.077325
C	-2.878620	1.102317	-0.460534
C	-1.606825	0.456551	-0.731614
O	-0.493558	1.119740	-0.969514
C	-3.039752	2.627283	-0.671769
C	-5.139524	-1.971977	0.440129
C	-4.737850	-2.879331	1.643877
C	-6.351347	-1.105811	0.877394
C	-5.594032	-2.876898	-0.746794
C	-2.104546	3.430917	0.280039
C	-2.663143	2.967661	-2.147557
C	-4.496048	3.110867	-0.424284
C	1.761995	2.987261	1.359203
C	0.603997	1.898106	3.342045
C	6.251262	-1.547215	-0.229892
C	5.300986	0.815518	-0.347067
u	1.552932	0.308723	-0.651330
H	-0.263543	-2.497464	1.023634
H	1.499298	-2.556504	1.268073
H	4.035420	-2.858480	-1.162828
H	3.274554	-3.183088	0.395290
H	1.556930	-3.480459	-1.257891
H	2.065129	-2.034648	-2.194965
H	4.711905	-0.841717	1.932091
H	3.283140	-1.874094	1.974021
H	2.827964	0.232243	3.100917
H	3.445335	1.182552	1.714501
H	0.654400	-0.920352	2.860841
H	-0.462168	-0.228902	1.637215
H	-0.035943	1.814700	1.251865
H	4.823820	-0.781794	-1.696329
H	-0.606176	-2.744364	-1.501564
H	-0.126394	-1.206417	-2.321770
H	-2.660213	-2.834417	-0.426560
H	-4.910316	0.796024	0.155472
H	-5.593661	-3.502225	1.963187
H	-4.414876	-2.264730	2.503422
H	-3.906497	-3.554785	1.376697

H	-7.177861	-1.761787	1.203968
H	-6.726056	-0.481618	0.046272
H	-6.091278	-0.441327	1.721268
H	-6.455176	-3.504249	-0.450992
H	-4.779803	-3.545846	-1.076460
H	-5.893382	-2.258437	-1.612058
H	-2.261205	4.515926	0.139125
H	-1.053167	3.193167	0.043878
H	-2.308877	3.183948	1.337810
H	-2.749210	4.055322	-2.322769
H	-3.333434	2.443465	-2.851901
H	-1.622278	2.654329	-2.350527
H	-4.554984	4.195719	-0.624290
H	-4.815987	2.944756	0.620685
H	-5.214583	2.607524	-1.096256
H	1.151869	3.905097	1.437228
H	2.050769	2.876469	0.298127
H	2.667887	3.136414	1.972609
H	0.099997	2.862418	3.535908
H	1.523971	1.879972	3.953767
H	-0.073793	1.101836	3.696344
H	7.134645	-1.229435	-0.813438
H	6.083064	-2.619178	-0.438118
H	6.507301	-1.440790	0.839913
H	6.160048	1.144256	-0.958719
H	5.554052	1.009426	0.710962
H	4.418091	1.415208	-0.642583
O	2.342880	0.613830	-2.374547
O	2.451203	1.717089	-1.556633

$^1\mathbf{6}_u(\eta^2)$

C	.716297	-1.822024	.824485
C	3.308096	-2.417922	-.534902
C	1.987528	-2.215831	-1.317116
N	3.928047	-1.199681	.008665
C	3.734956	-.970587	1.453616
C	3.003987	.338270	1.834532
N	1.593353	.520199	1.375197
C	.673530	-.586316	1.762707
N	.882948	-1.457291	-.621284
C	1.035357	1.845808	1.875257
C	5.309557	-.953129	-.506018
C	-.406670	-1.688199	-1.399095
C	-1.629217	-1.032518	-.810867
C	-2.720481	-1.828535	-.408174
C	-1.699002	.394184	-.757685
O	-.631881	1.143977	-1.069635
C	1.826416	3.042832	1.312310
C	.899444	1.947537	3.417124
C	5.769337	.492856	-.231580
C	6.361508	-1.977876	.008717
Cu	1.199723	.571176	-.898711
C	-2.960086	1.007069	-.410602
H	-.236684	-2.369246	.953905
H	1.524605	-2.505218	1.115837
H	4.001351	-2.879301	-1.266025

H	3.166355	-3.184907	.255076
H	1.609885	-3.223501	-1.598466
H	2.200789	-1.654813	-2.247416
H	4.720464	-.913650	1.960001
H	3.224871	-1.837069	1.912553
H	3.048513	.417350	2.942917
H	3.575654	1.178408	1.408160
H	.851504	-.933687	2.803003
H	-.350093	-.168617	1.719986
H	.021695	1.877019	1.432198
H	5.219810	-1.061672	-1.604473
H	-.577546	-2.781705	-1.480060
H	-.206347	-1.292606	-2.417838
O	2.087019	1.977814	-1.944288
O	2.937831	.946511	-1.732598
C	-3.928502	-1.252482	.019813
C	-4.013558	.162036	-.020524
H	-2.613040	-2.916759	-.460688
C	-3.162168	2.536487	-.549249
C	-5.142718	-2.083070	.498654
H	-4.962134	.623964	.263343
C	-2.883962	2.949864	-2.028039
C	-5.482504	-1.701730	1.972188
C	-2.193507	3.317288	.387013
C	-4.867427	-3.609929	.446182
C	-4.612130	2.974012	-.199856
C	-6.378845	-1.783401	-.403262
H	-3.577451	2.432659	-2.715080
H	-3.016995	4.040035	-2.149728
H	-1.848050	2.686283	-2.310054
H	-1.148573	3.099553	.106810
H	-2.364692	4.404428	.286348
H	-2.353436	3.036053	1.443760
H	-4.871311	2.749272	.850914
H	-4.700973	4.065984	-.339548
H	-5.356410	2.491546	-.858957
H	-4.627438	-1.917321	2.637873
H	-5.718854	-.626986	2.063297
H	-6.356647	-2.276466	2.329582
H	-4.015132	-3.891803	1.090501
H	-5.756119	-4.159369	.804668
H	-4.655888	-3.949186	-.584119
H	-6.166257	-2.044820	-1.455491
H	-7.253383	-2.369928	-.066878
H	-6.652710	-.714310	-.370236
H	2.004480	2.922451	.225536
H	1.235998	3.965880	1.454422
H	2.797491	3.185969	1.818290
H	.306418	1.117363	3.840494
H	1.881528	1.970414	3.922212
H	.377564	2.887957	3.672084
H	5.011930	1.201266	-.613073
H	5.933290	.679856	.844774
H	6.725021	.686011	-.751051
H	6.064901	-3.017576	-.220912
H	7.342453	-1.795555	-.467201
H	6.502018	-1.894931	1.101721

$^1\mathbf{6}_u(\eta^1)$

C	.728434	-2.476308	.138988
C	3.391612	-1.926133	-1.304524
C	1.989553	-1.972321	-1.962881
N	3.553812	-.866264	-.252166
C	3.549563	-1.451998	1.129695
C	2.621279	-.730823	2.131614
N	1.256555	-.453028	1.614896
C	.424354	-1.681646	1.431932
N	.874054	-1.583735	-1.050238
C	.512313	.557752	2.473025
C	4.787213	-.017461	-.520468
C	-.414448	-1.496938	-1.842416
C	-1.549203	-.831526	-1.112787
C	-2.723866	-1.530466	-.792871
C	-3.845662	-.865992	-.253168
C	-3.750250	.538952	-.113260
C	-2.598615	1.289875	-.425718
C	-1.425337	.579613	-.874012
O	-.266587	1.195039	-1.125451
C	-2.600932	2.836056	-.366048
C	-5.112277	-1.667722	.132593
C	-4.751462	-2.704127	1.241774
C	-6.246957	-.759064	.676915
C	-5.659852	-2.428165	-1.113830
C	-1.542473	3.345337	.655627
C	-2.253918	3.397117	-1.780151
C	-3.983066	3.413702	.048012
C	1.256723	1.905082	2.542565
C	.176791	.042594	3.895531
C	6.102577	-.836881	-.620178
C	4.948096	1.100640	.525809
Cu	1.449947	.339054	-.497483
H	-.103967	-3.190722	-.024247
H	1.645751	-3.075570	.245773
H	4.110334	-1.730225	-2.120470
H	3.659222	-2.917377	-.889233
H	1.824357	-2.982343	-2.399398
H	1.957212	-1.238075	-2.791613
H	4.571861	-1.432718	1.555854
H	3.271161	-2.516235	1.067922
H	2.591038	-1.339811	3.062088
H	3.067450	.243983	2.384898
H	.516738	-2.370375	2.298970
H	-.626454	-1.342171	1.375351
H	-.431108	.724863	1.916274
H	4.571991	.461825	-1.496582
H	-.702784	-2.516668	-2.173519
H	-.160876	-.887180	-2.733407
H	-2.765504	-2.607553	-.996469
H	-4.625359	1.080965	.248115
H	-5.640955	-3.296480	1.525927
H	-4.373872	-2.190064	2.144135
H	-3.970270	-3.404096	.896841
H	-7.121521	-1.378191	.945120

H	-6.573951	-.022823	-.079385
H	-5.929965	-.210901	1.582452
H	-6.561036	-3.010351	-.847139
H	-4.910128	-3.128076	-1.522518
H	-5.928458	-1.716473	-1.915149
H	-1.526107	4.450230	.668975
H	-.541080	2.981774	.364028
H	-1.779030	2.987530	1.673864
H	-2.236905	4.501763	-1.757969
H	-3.003082	3.071664	-2.523981
H	-1.259291	3.033155	-2.097007
H	-3.926047	4.516874	.047715
H	-4.279236	3.094390	1.063859
H	-4.778702	3.119013	-.660074
H	.562485	2.682683	2.906960
H	1.603361	2.218449	1.540223
H	2.118771	1.880861	3.232630
H	-.420540	.802941	4.430837
H	1.091368	-.137986	4.489448
H	-.418268	-.887532	3.874376
H	6.934385	-.156992	-.879970
H	6.064359	-1.618847	-1.398325
H	6.358715	-1.319103	.340893
H	5.730385	1.801457	.183953
H	5.258046	.708637	1.510700
H	4.013324	1.677366	.629182
O	2.845257	2.123534	-1.926769
O	2.302783	2.093707	-.736775

^{3}6(η^1)

C	.720154	-2.393291	.643359
C	3.445047	-2.029930	-.902021
C	2.030487	-2.324570	-1.485423
N	3.532013	-.782956	-.055850
C	3.557962	-1.131270	1.407815
C	2.613315	-.284707	2.280102
N	1.258966	-.104320	1.690155
C	.417474	-1.346158	1.748967
N	.917223	-1.758950	-.685332
C	.515231	1.056018	2.339231
C	4.725581	.060788	-.477993
C	-.347303	-1.685459	-1.499256
C	-1.486457	-.921260	-.864744
C	-2.684804	-1.594178	-.569395
C	-3.845450	-.903385	-.166415
C	-3.770733	.508178	-.159660
C	-2.602683	1.239041	-.456086
C	-1.381774	.509221	-.722161
O	-.214954	1.137714	-.890806
C	-2.642938	2.782024	-.597290
C	-5.131888	-1.685422	.192127
C	-4.835945	-2.657708	1.375530
C	-6.294952	-.749470	.618398
C	-5.606758	-2.515928	-1.039854
C	-1.690042	3.464119	.425685
C	-2.188135	3.159800	-2.041570

C	-4.067709	3.364815	-.378790
C	1.259123	2.386610	2.122868
C	.199254	.831444	3.838354
C	6.094014	-.643191	-.298543
C	4.709682	1.431723	.218621
Cu	1.558893	.277891	-.436118
H	-.132913	-3.103483	.615481
H	1.617573	-2.985421	.889696
H	4.122026	-1.905744	-1.765351
H	3.819903	-2.895869	-.322726
H	1.923743	-3.421256	-1.641347
H	1.962026	-1.832465	-2.474174
H	4.583643	-1.016986	1.808641
H	3.305167	-2.197681	1.520017
H	2.557921	-.753701	3.286071
H	3.043760	.721148	2.403603
H	.501220	-1.836651	2.741443
H	-.627852	-1.013837	1.614344
H	-.432181	1.106663	1.768982
H	4.543633	.228323	-1.557946
H	-.686911	-2.712579	-1.754773
H	-.053586	-1.169613	-2.437026
H	-2.709646	-2.684330	-.690144
H	-4.676002	1.070204	.072428
H	-5.741210	-3.233621	1.642672
H	-4.505370	-2.095019	2.267200
H	-4.039152	-3.375150	1.111950
H	-7.179126	-1.354722	.887087
H	-6.589060	-.069101	-.201060
H	-6.022699	-.137511	1.497386
H	-6.524236	-3.082856	-.796443
H	-4.834535	-3.236568	-1.361416
H	-5.823485	-1.850751	-1.895003
H	-1.734256	4.562938	.316563
H	-.656669	3.128081	.236682
H	-1.974050	3.204910	1.461801
H	-2.188898	4.257507	-2.169348
H	-2.868340	2.717713	-2.791308
H	-1.166337	2.779206	-2.226019
H	-4.033264	4.459050	-.526543
H	-4.440218	3.175690	.644476
H	-4.795938	2.952140	-1.100203
H	.575992	3.225377	2.343192
H	1.567339	2.480516	1.062944
H	2.144071	2.498904	2.773729
H	-.388820	1.685743	4.220084
H	1.118837	.763942	4.447936
H	-.401265	-.080056	4.005596
H	6.882736	-.023322	-.762895
H	6.121991	-1.631830	-.790126
H	6.365012	-.775443	.764364
H	5.464350	2.089987	-.247671
H	4.943709	1.362614	1.296231
H	3.721002	1.912220	.090863
O	2.946329	.551718	-2.922963
O	2.133189	1.184355	-2.134543