Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Evaluating Chemical Bonding in Dioxides for the Development of Metal-Oxygen Batteries: Vibrational Spectroscopic Trends of Dioxygenyls, Dioxygen, Superoxides and Peroxides

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Table S1: Catalogue of Raman spectral bands reported as ν_{O-O} or related to the ν_{O-O} of [$C^+\cdots O^{\bullet}_2{}^-$] complexes with monovalent cations reported in the literature. Coordinating cation M_r and calculated i_ν and $Ж^C_{i_\nu}$ values, system information, references are shown. See references for cation structure.

M_r	ν_{O-O} (cm^{-1})	ν_{O-O} other (cm^{-1})	i_ν (Å^3)	$Ж^C_{i_\nu}$	[$C^+\cdots O^{\bullet}_2{}^-$] salt/electrolyte	Cathode	Ref.
					Cation: H^+		
1	1165*		7.2	7.2	0.1M $HClO_{4(aq.-acidic)}$	rAu†	[1]
1	1162*		7.2	7.2	0.1M $HClO_{4(aq.-acidic)}$ + 0.5 mMBi^{3+}	rAu†	[1]
1		1147	7.2	7.2	Aqueous (pH 10, NaOH)	PEI#	[2]
1	*	1150(NaO_2?)	7.2	7.2	0.1M $NaOH_{(aq.-basic)}$	rAu†	[3]
1	*	1135($Na_2O_2.H_2O$?)	7.2	7.2	0.1 M $NaOH_{(aq.-basic)}$ + 10mM H_2O_2	rAu†	[3]
1	1179		7.2	7.2	0.1 M $TBAClO_4$/DMSO	GC‡	[4]
1	1182		7.2	7.2	Pyr_{14}TFSI (leaking cell)	rAu†	ex.
					Cation: Li^+		
7	1137		5.6	39.3	0.1 M $LiClO_4$/MeCN	rAu†	[5]
7	1125	1500(ν_{C-O})	5.6	39.3	0.5 M $LiClO_4$/DMSO	GC‡	[4]
7	1128	1500	5.6	39.3	0.5 M $LiClO_4$/MeCN	GC‡	[4]
7	1134		5.6	39.3	0.1 M TBAOTf : 0.1 M LiOTf/DMSO	rAu†	[6]
7	1132		5.6	39.3	0.1 M $LiClO_4$/MeCN	rAu†	[7]
7		1110	5.6	39.3	0.1 M $LiClO_4$/DMSO	rAu†	[7,8]
7		1160 (not LiO_2)	5.6	39.3	0.1 M $LiClO_4$/DMSO/ Complexing-agent	rAu†	[8]
7	~1143		5.6	39.3	0.1 M $LiClO_4$/DMSO	Au-Ni foam†	[9]
7		1107	5.6	39.3	0.01 M LiTFSI/Pyr_{14}TFSI	NS Au†	[10]
7		1110	5.6	39.3	0.01 LiTFSI/EmimTFSI	NS Au†	[10]
7	~1175		5.6	39.3	0.5 M LiOTf/DEGME	KB/ PTFE#	[11]
7	1123		5.6	39.3	1.0 M LiOTf/TEGDME	AC/ PVDF#	[12]
7	1123	1505(ν_{C-O})	5.6	39.3	1.0 M LiOTf/TEGDME	AC/ PVDF#	[13]
7	1123	1505(ν_{C-O})	5.6	39.3	1.0 M LiOTf/TEGDME	AC/ PVDF#	[14]
7	1123	1500(ν_{C-O})	5.6	39.3	1.0 M LiOTf/TEGDME	AC/ PVDF#	[15]

M_r	ν_{O-O} (cm^{-1})	ν_{O-O} other (cm^{-1})	i_v (Å^3)	$Ж_{i_v}^{C}$	[$C^+\cdots O_2^{\bullet-}$] salt/electrolyte	Cathode	Ref.
7	1125	1500(ν_{C-O})	5.6	39.3	1.0 M LiOTf/TEGDME	Ir-rGO/ PVDF#	16
7	1125	1525(ν_{C-O})	5.6	39.3	Not specified	C/ PVDF#	17
7	1123		5.6	39.3	0.1 M $LiClO_4$/TEGDME	RuCNT/PVDF#	18
7	1130		5.6	39.3	0.5 M $LiClO_4$ / DMSO	EPPG	19
7	*****		5.6	39.3	0.5 M $LiClO_4$ / DMSO	EPPG	19
7	1130	1530	5.6	39.3	0.5 M $LiClO_4$ / DMSO	BPPG	19
7	******		5.6	39.3	0.5 M $LiClO_4$ / DMSO	BPPG	19
7	1130	1543	5.6	39.3	0.5 M $LiClO_4$ / DMSO	SuperC/PTFE	19
7	****** **		5.6	39.3	0.5 M $LiClO_4$ / DMSO	SuperC/PTFE	19
7	1130	1543(ν_{C-O})	5.6	39.3	0.5 M $LiClO_4$/DMSO	SP/PTFE (1.9 V)‡	19
7	** **	1098, 1490(ν_{C-O})	5.6	39.3	0.5 M $LiClO_4$/DMSO	SP/PTFE (3.1 V)‡	19
				Cation: Na^+			
23	1156		10.1	233	NaO_2 salt	#	20
23	1156		10.1	233	NaO_2 salt (300-200 K)	#	21
23		1164	10.1	233	NaO_2 salt (80 K)	#	21
23	1155	1152	10.1	233	NaO_2 salt (> 200 K)	#	22
23		1164, ~1145	10.1	233	NaO_2 salt (< 200 K)	#	22
23	1156	1107, 488(ν_{Au-O})	10.1	233	0.1 M NaOTf/DMSO	rAu†	23
23	1161	1119	10.1	233	0.1 M NaOTf/DMA	rAu†	23
23		1109 (sol)	10.1	233	0.1 M NaOTf/DEGDME	rAu†	23
23		1108 (sol)	10.1	233	0.1 M NaOTf/MeCN	rAu†	23
23	1156		10.1	233	0.5 M NaOTf/DEGDME	GDL#	24
23	1155		10.1	233	0.5 M NaOTf/DEGDME	CP#	25
23		1135($Na_2O_2.H_2O?$)	10.1	233	0.5 M NaOTf/DEGDME	CP#	25
23	1154		10.1	233	NaOTf/PC:Pip_{13}TFSI: TEGDME	VACNT#	26
23	1156		10.1	233	0.1 M $NaClO_4$/DME	CNT#	27
23		1136($Na_2O_2.H_2O?$)	10.1	233	0.1 M $NaClO_4$/DME +air	CNT#	27
23	1153		10.1	233	1 M $NaClO_4$/DME	P50 C#	28
23	1156		10.1	233	0.5 M NaOTf/DEGDME	KB/ PTFE#	29
23		1136($Na_2O_2.H_2O?$)	10.1	233	0.5 M NaOTf/DEGDME	KB/ PTFE#	29

M_r	ν_{O-O} (cm^{-1})	ν_{O-O} other (cm^{-1})	i_v (Å^3)	$Ж_{i_v}^{C}$	[$C^+\cdots O_2^{\bullet-}$] salt/electrolyte	Cathode	Ref.
23		1142($^{Na_2O_2.H_2O_?}$)	10.1	233	N_2O_2 salt impurity	#	30
23		1141($^{Na_2O_2.H_2O_?}$)	10.1	233	N_2O_2 salt impurity	#	31
23		1136($^{Na_2O_2.H_2O_?}$)	10.1	233	N_2O_2 salt impurity	#	32
				Cation: K^+			
39	1143		21.1	824	KO_2 salt	#	33
39		1163($^{HO_2?}$)	21.1	824	impurity in KO_2	#	33
39	1141		21.1	824	KO_2 salt (300 K)	#	21
39	~1145		21.1	824	KO_2 salt (200-80 K)	#	21
39	1146		21.1	824	KO_2 salt	#	34
39	1148		21.1	824	K_2O_2 impurity	#	32
39	1145		21.1	824	KO_2 salt	#	35
39	1145		21.1	824	KO_2 salt	#	30
39	1142		21.1	824	0.5 M KPF_6/DME	SP-Ni foam#	36
39	1144		21.1	824	KO_2 salt	#	ex.
				Cation: TMA^+			
74	1123		104.1	7700	$TMAO_2$ salt	#	35
74	1125		104.1	7700	$TMAO_2$ salt	#	37
				Cation: Rb^+			
85.5	1141		26.6	2273	Rb_2O_2 salt	#	32
85.5		1124	26.6	2273	Rb_2O_2 impurity	#	32
85.5	1,140		26.6	2273	RbO_2 salt (75-300 K)	#	21
85.5	1140		26.6	2273	RbO_2 salt	#	34
				Cation: $TMPh^+$			
91.1	1123		117.3	10,660	$TMPhO_2$ salt	#	37
				Cation: TEA^+			
130	1115		175.7	22,846	0.1M TBAOTf/MeCN	rAu†	38
				Cation: Cs^+			
133	1132		35.2	4682	CsO_2 salt	#	33
133	1134		35.2	4682	CsO_2 salt	#	39
133	1130		35.2	4682	0.1 M $CsClO_4$/DMSO	rAu†	6

M_r	ν_{O-O} (cm^{-1})	ν_{O-O} other (cm^{-1})	i_v (Å^3)	$Ж_{i_v}^{C}$	[$C^+\cdots O_2^{\bullet-}$] salt/electrolyte	Cathode	Ref.
133	1137		35.2	4682	CsO2 salt (80-300 K)	#	21
133	1134		35.2	4682	CsO_2 salt	#	40
				Cation: TMAs$^+$			
135.1	1122		168.5	22,751	$TMAsO_2$ salt	#	41
				Cation: TMAp$^+$			
136.2	1121		122.8	16,725	TMAph salt	#	41
				Cation: TPA$^+$			
186.4	1113		248.9	46,329	0.1 M TBAOTf/ MeCN	rAu†	38
				Cation: TBA$^+$			
242	1109	491(ν_{Au-O})	322.5	78,038	0.1 M $TBAClO_4$/ MeCN	rAu†	5
242	1110	486(ν_{Au-O})	322.5	78,038	0.1 M $TBAClO_4$/ DMSO	rAu†	42
242	1110		322.5	78,038	0.1 M $TBAClO_4$/ DMSO	rAu†	7
242	1110	490(ν_{Au-O})	322.5	78,038	0.1 M $TBAClO_4$/ DMSO	rAu‡	4
242	1110	490(ν_{Au-O})	322.5	78,038	0.1 M $TBAClO_4$/ DMSO	Au‡	4
242	1108	456-484(ν_{Au-O})	322.5	78,038	0.1 M $TBAClO_4$/ DMSO	Pt‡	4
242	1108	486(ν_{Au-O})	322.5	78,038	0.1 M $TBAClO_4$/ DMSO	Pd‡	4
242	~1115	~1520(ν_{C-O})	322.5	78,038	0.1 M $TBAClO_4$/ DMSO	GC‡	4
242	1106		322.5	78,038	0.1 M TBAOTf/ DMSO	rAu†	38
242	1104		322.5	78,038	0.1 M TBAOTf/ MeCN	rAu†	38
242		1131(^{NH_3} impurity)	322.5	78,038	$TBAO_2$ salt	#	41

† denotes *in situ* SERS studies at the electrode interface. ‡ denotes in situ shell isolated nanoparticle enhanced Raman spectroscopic (SHINERS) studies at the electrode interface. # denotes ex situ Raman measurements. ex. denotes unreported spectral bands we observed experimentally.

Table S2. Catalogue of estimated bond parameters for various O_2^x species calculated from the ν_{O-O} values reported in the literature as plotted in Figure 6

O_2^x complex	ν_{O-O} (cm^{-1})	Calculated K (mdyn Å^{-1})	Calculated B_L (Å)	Calculated H (kJ mol^{-1})	Calculated B_o	Closest B_o	Calculated e$^-$ covalency %	Ref.
Gaseous O_2^+	1876	16.24	1.1219	641.4	2.5	2.5	0	43,44
$O_2Sb_2F_{11}$	1864	16.04	1.1288	633.4	2.470	2.5	-12.1	45
O_2SbF_6	1862	16.01	1.1299	632.1	2.466	2.5	-13.7	43
O_2SbF_6	1861	16.00	1.1305	631.5	2.464	2.5	-14.4	45
$O_2Nb_2F_{11}$	1858	15.95	1.1322	629.5	2.458	2.5	-16.7	45
$O_2Ta_2F_{11}$	1858	15.95	1.1322	629.5	2.458	2.5	-16.7	45
O_2AsF_6	1858	15.95	1.1322	629.5	2.458	2.5	-16.7	45
O_2AsF_6	1857	15.93	1.1327	628.9	2.456	2.5	-17.4	46
O_2PF_6	1857	15.93	1.1327	628.9	2.456	2.5	-17.4	47
$O_2Bi_2F_{11}$	1853	15.87	1.1349	626.4	2.449	2.5	-20.4	45
O_2NbF_6	1853	15.87	1.1349	626.4	2.449	2.5	-20.4	45
O_2BiF_6	1847	15.77	1.1381	622.6	2.438	2.5	-24.9	45
O_2RuF_6	1838	15.62	1.1428	617.1	2.421	2.5	-31.6	45
O_2PtF_6	1838	15.61	1.1433	616.5	2.419	2.5	-32.3	45
O_2AuF_6	1835	15.58	1.1443	615.3	2.416	2.5	-33.7	45
O_2RhF_6	1825	15.41	1.1493	609.5	2.398	2.5	-41.0	45
O_2:Heme complex (asy.)	1663	12.86	1.2116	533.9	2.138	2.0	55.0	48
O_2:Heme complex	1597	11.90	1.2303	510.1	2.047	2.0	18.7	48
O_2	1556	11.33	1.2408	496.4	1.994	2.0	-2.4	49
O_2	1555	11.32	1.2410	496.1	1.993	2.0	-2.9	34
O_2	1552	11.28	1.2418	495.2	1.989	2.0	-4.4	50
O_2	1552	11.28	1.2418	495.2	1.989	2.0	-4.4	51
O_2	1549	11.24	1.2425	494.2	1.985	2.0	-5.9	52
Fe^{III}:O_2 complex	1310	8.32	1.2949	423.1	1.713	1.5	85.4	53
Fe^{III}:O_2 complex	1260	7.77	1.3054	408.3	1.660	1.5	64.1	54
$[Cr^{III}(O_2)(TMC\text{-}Im)]^{2+}$	1196	7.08	1.3195	388.5	1.592	1.5	36.8	55
HO_2	1179	6.89	1.3234	383.0	1.574	1.5	29.5	4
HO_2	1165	6.74	1.3267	378.4	1.559	1.5	23.4	1
HO_2	1162	6.71	1.3274	377.4	1.555	1.5	22.1	1
NaO_2 (in DMA)	1161	6.70	1.3276	377.0	1.554	1.5	21.7	23
NaO_2 (in DMSO)	1156	6.65	1.3288	375.4	1.549	1.5	19.5	23

O_2^x complex	ν_{O-O} (cm^{-1})	Calculated K (mdyn $Å^{-1}$)	Calculated B_L (Å)	Calculated H (kJ mol^{-1})	Calculated B_o	Closest B_o	Calculated e- covalency %	Ref.
NaO_2 (300 K)	1156	6.65	1.3288	375.4	1.549	1.5	19.5	[21]
NaO_2	1156	6.65	1.3288	375.4	1.549	1.5	19.5	[24]
NaO_2	1156	6.65	1.3288	375.4	1.549	1.5	19.5	[27]
NaO_2	1156	6.65	1.3288	375.4	1.549	1.5	19.5	[29]
NaO_2	1155	6.64	1.3290	375.0	1.548	1.5	19.1	[25]
NaO_2 (200 K)	1155	6.64	1.3290	375.0	1.548	1.5	19.1	[21]
NaO_2	1154	6.63	1.3293	374.7	1.547	1.5	18.6	[26]
NaO_2	1153	6.62	1.3295	374.3	1.545	1.5	18.2	[28]
Cu:O_2 complex - $L44^+$	1149	6.57	1.3305	373.0	1.541	1.5	16.4	[56]
KO_2	1148	6.56	1.3307	372.7	1.540	1.5	16.0	[32]
RbO_2	1148	6.56	1.3307	372.7	1.540	1.5	16.0	[57]
KO_2	1146	6.54	1.3312	372.0	1.538	1.5	15.1	[34]
KO_2	1145	6.53	1.3314	371.6	1.537	1.5	14.7	[35]
KO_2	1145	6.53	1.3314	371.6	1.537	1.5	14.7	[30]
KO_2 (200 K)	1144	6.52	1.3317	371.3	1.536	1.5	14.2	[21]
KO_2	1143	6.51	1.3319	370.9	1.535	1.5	13.8	[33]
KO_2	1142	6.50	1.3321	370.6	1.533	1.5	13.4	[36]
KO_2 (300 K)	1141	6.49	1.3324	370.3	1.532	1.5	12.9	[21]
RbO_2	1141	6.49	1.3324	370.3	1.532	1.5	12.9	[32]
RbO_2 (300 K)	1140	6.49	1.3324	370.3	1.532	1.5	12.9	[21]
RbO_2	1140	6.48	1.3326	369.9	1.531	1.5	12.5	[34]
RbO_2 (200 K)	1138	6.46	1.3331	369.2	1.529	1.5	11.6	[21]
CsO_2 (300 K)	1137	6.45	1.3334	368.9	1.528	1.5	11.2	[21]
CsO_2	1135	6.42	1.338	368.2	1.526	1.5	10.3	[57]
CsO_2	1134	6.41	1.3341	367.8	1.525	1.5	9.8	[39]
CsO_2	1134	6.41	1.3341	367.8	1.525	1.5	9.8	[40]
CsO_2	1132	6.39	1.3346	367.1	1.522	1.5	9.0	[33]
Cu:O_2 complex - $TPA^{6,N}$	1130	6.37	1.3351	366.4	1.520	1.5	8.1	[58]
$TMAO_2$	1125	6.32	1.3363	364.7	1.515	1.5	5.9	[37]
$(TP^{Me2})_2SmO_2$	1124	6.31	1.3366	364.3	1.514	1.5	5.4	[52]
$TMAO_2$	1123	6.30	1.3368	364.0	1.512	1.5	5.0	[35]
$TMPhO_2$	1123	6.30	1.3368	364.0	1.512	1.5	5.0	[37]
Co^{III}:O_2 complex 2	1123	6.30	1.3368	364.0	1.512	1.5	5.0	[59]
$TMAsO_2$	1122	6.29	1.3371	363.6	1.511	1.5	4.5	[37]
Co^{III}:O_2 complex 1	1122	6.29	1.3371	363.6	1.511	1.5	4.5	[59]
Cu:O_2 complex - L42a	1122	6.29	1.3371	363.6	1.511	1.5	4.5	[56,60]

O_2^x complex	ν_{O-O} (cm^{-1})	Calculated K (mdyn $Å^{-1}$)	Calculated B_L (Å)	Calculated H (kJ mol^{-1})	Calculated B_o	Closest B_o	Calculated e⁻ covalency %	Ref.
$TMAphO_2$	1121	6.28	1.3373	363.3	1.510	1.5	4.1	41
Cu:O_2 complex - L41b	1121	6.28	1.3373	363.3	1.510	1.5	4.1	56
Cu:O_2 complex - L41c	1121	6.28	1.3373	363.3	1.510	1.5	4.1	56
Cu:O_2 complex - L42d	1120	6.27	1.3376	362.9	1.509	1.5	3.6	56
Cu:O_2 complex - $Tren^{Me}$	1120	6.27	1.3376	362.9	1.509	1.5	3.6	58
Cu:O_2 complex - $Tren^{TMG}$	1120	6.27	1.3376	362.9	1.509	1.5	3.6	58
Cu:O_2 complex - TACN	1120	6.27	1.3376	362.9	1.509	1.5	3.6	58
Cu:O_2 complex - L44	1117	6.23	1.3383	361.8	1.506	1.5	2.3	56
Cu:O_2 complex - L68	1117	6.23	1.3383	361.8	1.506	1.5	2.3	56
$TEAO_2$ (in MeCN on Au)	1115	6.21	1.3388	361.1	1.504	1.5	1.4	38
$TPAO_2$ (inMeCN on Au)	1113	6.19	1.3393	360.4	1.501	1.5	0.5	38
Cu:O_2 complex - Tp^{tBu}	1112	6.18	1.3396	360.1	1.500	1.5	0.1	60
Cu:O_2 complex - L39a	1112	6.18	1.3396	360.1	1.500	1.5	0.1	56
Molecule 1	1112	6.18	1.3396	360.1	1.500	1.5	0.1	52
$TBAO_2$ (in DMSO on Au)	1110	6.16	1.3401	359.3	1.498	1.5	-0.8	42
$TBAO_2$ (in DMSO on Au)	1110	6.16	1.3401	359.3	1.498	1.5	-0.8	7
$TBAO_2$ (in DMSO on Au)	1110	6.16	1.3401	359.3	1.498	1.5	-0.8	4
$TBAO_2$ (in MeCN on Au)	1109	6.15	1.3403	359.0	1.497	1.5	-1.3	5
Co^{III}:O_2 complex 3	1108	6.14	1.3406	358.6	1.496	1.5	-1.7	59
$TBAO_2$ (in DMSO on Pd)	1108	6.14	1.3406	358.6	1.496	1.5	-1.7	4
$TBAO_2$ (in DMSO on GC)	1107	6.13	1.3408	358.2	1.495	1.5	-2.2	4
$TBAO_2$ (in MeCN on Au)	1104	6.10	1.3416	357.2	1.491	1.5	-3.5	38
Cu:O_2 complex - L28a	1104	6.10	1.3416	357.2	1.491	1.5	-3.5	56
Molecule 3	1104	6.10	1.3416	357.2	1.491	1.5	-3.5	52
Co^{III} complex 4	1099	6.04	1.3429	355.3	1.486	1.5	-5.3	59
Cu:O_2 complex - L42b	1096	6.01	1.3437	354.2	1.482	1.5	-7.1	56
Co^{III} complex	1078	5.79	1.3493	346.3	1.458	1.5	-16.7	59
Molecule 4	1072	5.76	1.3501	345.1	1.455	1.5	-18.1	52
Co^{III} complex B	1063	5.66	1.3525	341.6	1.44	1.5	-22.2	59
Cu:O_2 complexe – $Tp^{Ad,iPr}$	1058	5.61	1.3539	339.7	1.439	1.5	-24.6	60
$O^{\bullet-}_2$ – on Ag (UHV)	1057							61
$O^{\bullet-}_2$ – on Ag (UHV)	1053	5.56	1.3553	337.7	1.433	1.5	-26.9	62
Cu:O_2 complex – L39b	1043	5.45	1.3582	333.6	1.421	1.5	-31.6	56
Cu^{II}:O_2 complex – HB_3	1043	5.45	1.3582	333.6	1.421	1.5	-31.6	58
Cu^{II}:O_2 complex – PddcT	1033	5.35	1.3611	329.5	1.409	1.5	-36.3	58
Cu^{II}:O_2 complex – L33c	1033	5.35	1.3611	329.5	1.409	1.5	-36.3	56

O_2^x complex	ν_{O-O} (cm^{-1})	Calculated K (mdyn $Å^{-1}$)	Calculated B_L (Å)	Calculated H (kJ mol^{-1})	Calculated B_o	Closest B_o	Calculated e⁻ covalency %	Ref.
Molecule 5	1027	5.29	1.3629	326.9	1.402	1.5	-39.2	[52]
Molecule 8	983	4.83	1.3767	307.4	1.348	1.5	-60.7	[52]
Cu:O_2 complex – L2g	977	4.77	1.3787	304.5	1.341	1.5	-63.7	[56]
Cu:O_2 complex – L3b	974	4.74	1.3797	303.1	1.337	1.5	-65.2	[56]
Cu:O_2 complex – L74a	970	4.70	1.3807	301.7	1.333	1.5	-66.8	[56]
Cu:O_2 complex – L74b	970	4.69	1.3810	301.2	1.332	1.5	-67.3	[56]
Cu:O_2 complex – Dk^{iPr}	968	4.67	1.3817	300.2	1.329	1.5	-68.3	[60]
Cu:O_2 complex – L2d	968	4.67	1.3817	300.2	1.329	1.5	-68.3	[56]
Molecule 6	968	4.67	1.3817	300.2	1.329	1.5	-68.3	[52]
Cu:O_2 complex – H_3bpa	964	4.63	1.3831	298.3	1.324	1.5	-70.3	[60]
Cu:O_2 complex – L75	964	4.63	1.3831	298.3	1.324	1.5	-70.3	[56]
Multiple organo:O_2 complexes	1000-800							[63]
Cu:O_2 complex – Dk^{iPr}	961	4.60	1.3841	296.8	1.320	1.5	-71.9	[60]
Cu:O_2 complex – L2e	961	4.60	1.3841	296.8	1.320	1.5	-71.9	[56]
ZnO_2	944	4.43	1.3902	288.2	1.298	1.5	-80.7	[32]
MgO_2	934	4.33	1.3939	283	1.285	1.5	-85.9	[32]
CdO_2	932	4.30	1.3946	282.0	1.283	1.5	-86.8	[32]
Organic:O_2	910 895 848	4.08	1.4031	269.9	1.253	1.5	-98.8	[64]
Organic:O_2	910 892 844	4.08	1.4031	269.9	1.253	1.5	-98.8	[64]
$[CuOOH]^+$ – L35a	900	3.98	1.4072	264.2	1.239	1.0	95.7	[56]
Organic:O_2	899 873							[64]
Organic:O_2	898 870	3.96	1.4080	263.1	1.237	1.0	94.6	[64]
Organic:O_2	896 858	3.94	1.4088	261.9	1.234	1.0	93.5	[64]
Organic:O_2	895 857	3.93	1.4093	261.3	1.232	1.0	93.0	[64]
Organic:O_2	894 855	3.92	1.4097	260.7	1.231	1.0	92.4	[64]
Organic:O_2	894 840	3.92	1.4097	260.7	1.231	1.0	92.4	[64]
UnOH $[Cu_2Li(OOH)]^+$	892	3.9	1.4105	259.5	1.228	1.0	91.3	[60]
Molecule 9	892	3.9	1.4105	259.5	1.228	1.0	91.3	[52]
Cu:O_2 complex – UnOH	892	3.90	1.4105	259.5	1.228	1.0	91.3	[60]
Molecule 7	891	3.90	1.4105	259.5	1.228	1.0	91.3	[52]

O_2^x complex	ν_{O-O} (cm^{-1})	Calculated K (mdyn $Å^{-1}$)	Calculated B_L (Å)	Calculated H (kJ mol^{-1})	Calculated B_o	Closest B_o	Calculated e- covalency %	Ref.
$[CuOOR]^+$ – L42a	887	3.85	1.4126	256.6	1.221	1.0	88.5	[56]
$[CuOOR]^+$ – L69	887	3.85	1.4126	256.6	1.221	1.0	88.5	[56]
$[CuOOR]^+$ – L18d	885	3.83	1.4135	255.4	1.218	1.0	87.4	[56]
$[CuOOR]^+$ – L39a	884	3.83	1.4139	254.8	1.217	1.0	86.8	[56]
$[Cu:O_2]$– L40e (in MeCN)	883	3.82	1.4143	254.2	1.216	1.0	86.3	[56]
Organo:O_2 Complex	883	3.81	1.4148	253.5	1.214	1.0	85.7	[64]
DiEthyl:O_2	882	3.81	1.4148	253.5	1.214	1.0	85.7	[64]
Organo:O_2 Complex	881	3.80	1.4152	252.9	1.213	1.0	85.1	[64]
$[Cu:O_2]$ – L53 (in Ac)	881	3.80	1.4152	252.9	1.213	1.0	85.1	[56]
$[CuOOH]^+$ – L66a	881	3.80	1.4152	252.9	1.213	1.0	85.1	[56]
$[CuOOH]^+$ – L70b	880	3.79	1.4156	252.3	1.211	1.0	84.6	[56]
H_2O_2	880	3.79	1.4156	252.3	1.211	1.0	84.6	[64,65]
H_2O_2	876	3.75	1.4174	249.9	1.206	1.0	82.3	[66]
H_2O_2	875	3.74	1.4178	249.2	1.204	1.0	81.7	[67]
CF_4O_2	875	3.74	1.4178	249.2	1.204	1.0	81.7	[64]
SrO_2 (0.9/0.1)	873	3.72	1.4187	248.0	1.201	1.0	80.6	[68]
$[Cu:O_2]$– L54 (in EtCN)	870	3.69	1.4200	246.1	1.197	1.0	78.9	[56]
SrO_2 (0.96/0.04)	870	3.69	1.4200	246.1	1.197	1.0	78.9	[68]
$[Cu:O_2]$ – L40f (in MeCN)	868	3.67	1.4209	244.9	1.194	1.0	77.7	[56]
SrO_2 (0.98/0.02)	865	3.64	1.4223	242.9	1.190	1.0	76.0	[68]
MgO_2	864 934	3.63	1.4228	242.3	1.189	1.0	75.4	[32]
SrO_2	863	3.62	1.4232	241.7	1.187	1.0	74.9	[32]
CF_3O_2D	863	3.62	1.4232	241.7	1.187	1.0	74.9	[64]
$[CuOOH]^+$ – L40e	860	3.59	1.4246	239.7	1.183	1.0	73.1	[56]
$Cu:O_2$ – L65b (in MeCN)	860	3.59	1.4246	239.7	1.183	1.0	73.1	[56]
CF_3O_2H	860	3.59	1.4246	239.7	1.183	1.0	73.1	[64]
$LiOOH.H_2O$	860	3.59	1.4246	239.7	1.183	1.0	73.1	[69]
$[CuOOR]^+$ – L18b	855	3.54	1.4269	236.5	1.176	1.0	70.2	[56]
$[CuOOH]^+$ – L43a	853	3.53	1.4279	235.1	1.173	1.0	69.0	[56]
BaO_2 (0.79/0.21)	853	3.53	1.4279	235.1	1.173	1.0	69.0	[68]
$[CuOOH]^+$ – L40b	851 835	3.51	1.4288	233.8	1.170	1.0	67.9	[56]
$[CuOOH]^+$ – L45	851	3.51	1.4288	233.8	1.170	1.0	67.9	[56]
BaO_2 (0.86/0.14)	851	3.51	1.4288	233.8	1.170	1.0	67.9	[68]
$[CuOOH]^+$ – L43b	848	3.48	1.4302	231.8	1.165	1.0	66.1	[56]
$[Cu:O_2]$ – L78a (in THF)	848	3.48	1.4302	231.8	1.165	1.0	66.1	[56]
$bisp_2xyl^g$	847	3.47	1.4307	231.1	1.164	1.0	65.5	[60]

O_2^x complex	ν_{O-O} (cm^{-1})	Calculated K (mdyn $Å^{-1}$)	Calculated B_L (Å)	Calculated H (kJ mol^{-1})	Calculated B_o	Closest B_o	Calculated e- covalency %	Ref.
ZnO_2	847	3.47	1.4307	231.1	1.164	1.0	65.5	[32]
$[CuOOR]^+$ – L42a	846	3.46	1.4312	230.5	1.162	1.0	64.9	[56]
$[CuOOR]^+$ – L39c	844	3.44	1.4322	229.1	1.159	1.0	63.7	[56]
$MePy_2Pz$	844	3.44	1.4322	229.1	1.159	1.0	63.7	[60]
$[CuOOH]^+$ - L39a	843	3.43	1.4327	228.4	1.158	1.0	63.1	[56]
$[CuOOR]^+$ - L39a	843	3.43	1.4327	228.4	1.158	1.0	63.1	[56]
BaO_2 (0.97/0.03)	843	3.43	1.4327	228.4	1.158	1.0	63.1	[68]
L3CuOOH excited	843	3.43	1.4327	228.4	1.158	1.0	63.1	[58]
BaO_2	842	3.42	1.4331	227.7	1.156	1.0	62.6	[32]
$bisp^g$ (in EtCN)	840	3.40	1.4341	226.4	1.153	1.0	61.4	[60]
$bisp_2pr^g$ (in EtCN)	837	3.38	1.4356	224.3	1.149	1.0	59.6	[60]
$[Cu:O_2]$ – L30 (in CH_2Cl_2)	837	3.38	1.4356	224.3	1.149	1.0	59.6	[56]
$[Cu:O_2]$ – L40d (in THF)	835	3.36	1.4366	222.9	1.146	1.0	58.4	[56]
CaO_2	835	3.36	1.4366	222.9	1.146	1.0	58.4	[32]
$[P\text{-}tmpa][O_2]$	832	3.33	1.4381	220.8	1.141	1.0	56.6	[60]
$[Cu:O_2]$ – L41a (in EtCn)	832	3.33	1.4381	220.8	1.141	1.0	56.6	[56]
$[Cu:O_2]$ – L28a (in DMF/THF)	832	3.33	1.4381	220.8	1.141	1.0	56.6	[56]
$[Cu:O_2]$ – L60 (in Ac)	832	3.33	1.4381	220.8	1.141	1.0	56.6	[56]
oxy-Hc	832	3.33	1.4381	220.8	1.141	1.0	56.6	[58]
Bpman (CH_2Cl_2)	831	3.32	1.4386	220.1	1.140	1.0	56.0	[60]
$[CuOOH]^+$ - L33c	831	3.32	1.4386	220.1	1.140	1.0	56.0	[56]
$[CuOOR]^{+b}$ – L42c	831	3.32	1.4386	220.1	1.140	1.0	56.0	[56]
Organo:O_2 Complex	830	3.31	1.4391	219.4	1.138	1.0	55.4	[64]
$[Cu:O_2]$ – L82 (in MeTHF)	828	3.29	1.4401	218.0	1.135	1.0	54.2	[56]
Cu^{II}:O_2 complex (in EtO)	827	3.28	1.4406	217.2	1.134	1.0	53.6	[60]
$[Cu:O_2]$ – L69	827	3.28	1.4406	217.2	1.134	1.0	53.6	[56]
$[Cu:O_2]$ – L41a (MeTHF)	827	3.28	1.4406	217.2	1.134	1.0	53.6	[56]
Me_6trend	825	3.27	1.4417	215.8	1.131	1.0	52.3	[60]
$[Cu:O_2]$ – L42a	825	3.27	1.4417	215.8	1.131	1.0	52.3	[56]
$bisp_2et^g$	824	3.26	1.4422	215.1	1.129	1.0	51.7	[60]
$iPr_2Py^{5\ Me}tacn^f$	823	3.25	1.4427	214.4	1.128	1.0	51.1	[60]
tmpaMeO	822	3.24	1.4432	213.6	1.126	1.0	50.5	[60]
$iPr_2PyHtacn$	822	3.24	1.4432	213.6	1.126	1.0	50.5	[60]
$[CuOOH]^+$ - L83	822	3.24	1.4432	213.6	1.126	1.0	50.5	[56]
$[Cu:O_2]$ – L40a (in MeTHF)	822	3.24	1.4432	213.6	1.126	1.0	50.5	[56]
$[Cu:O_2]$ – L67 (in MeTHF)	817	3.19	1.4458	210.0	1.119	1.0	47.4	[56]
$[Cu:O_2]$ – L31a (in Ac)	816	3.18	1.4464	209.2	1.117	1.0	46.8	[56]

O_2^x complex	ν_{O-O} (cm^{-1})	Calculated K (mdyn $Å^{-1}$)	Calculated B_L (Å)	Calculated H (kJ mol^{-1})	Calculated B_o	Closest B_o	Calculated e- covalency %	Ref.
BeO_2	815	3.18	1.4469	208.5	1.116	1.0	46.2	32
tmpaMe_2N	812	3.15	1.4485	206.2	1.111	1.0	44.4	60
[Cu:O_2] – L31a (in MeTHF)	811	3.14	1.4490	205.5	1.109	1.0	43.7	56
[Cu:O_2] complex	803	3.07	1.4534	199.4	1.097	1.0	38.8	60
[Cu:O_2] – L65b	803	3.07	1.4534	199.4	1.097	1.0	38.8	56
Heme:O_2 complex	803	3.07	1.4534	199.4	1.097	1.0	38.8	58
Oxy-Hc	803	3.07	1.4534	199.4	1.097	1.0	38.8	58
triperox- idediamine	800	3.04	1.4551	197.1	1.092	1.0	36.9	63
Li_2O_2	800	3.04	1.4551	197.1	1.092	1.0	36.9	8
Cu:O_2 complex	799	3.04	1.4556	196.3	1.091	1.0	36.2	56
Li_2O_2	796	3.01	1.4573	193.9	1.086	1.0	34.4	70
Rb:O_2 complex	795	3.00	1.4579	193.2	1.084	1.0	33.7	71
Li_2O_2	791	2.97	1.4602	190.0	1.078	1.0	31.2	72
Li_2O_2	790	2.96	1.4608	189.2	1.076	1.0	30.5	32
Li_2O_2	790	2.96	1.4608	189.2	1.076	1.0	30.5	9
Li_2O_2	789	2.95	1.4613	188.4	1.075	1.0	29.9	73
Li_2O_2	788	2.94	1.4619	187.6	1.073	1.0	29.3	57
Li_2O_2	788	2.94	1.4619	187.6	1.073	1.0	29.3	42
Li_2O_2	788	2.94	1.4619	187.6	1.073	1.0	29.3	15
Li_2O_2	785	2.92	1.4637	185.1	1.068	1.0	27.3	74
Rb_2O_2	782	2.89	1.4654	182.7	1.064	1.0	25.4	32
Rb_2O_2	782	2.89	1.4654	182.7	1.064	1.0	25.4	57
Organo:O_2 complex	781	2.88	1.4660	181.8	1.062	1.0	24.8	64
Organo:O_2 complex	779	2.87	1.4672	180.2	1.059	1.0	23.5	64
Organo:O_2 complex	774	2.83	1.4702	176.0	1.051	1.0	20.2	64
Organo:O_2 complex	771	2.80	1.4721	173.4	1.046	1.0	18.3	64
K_2O_2	762 746	2.73	1.4777	165.6	1.031	1.0	12.3	32
K_2O_2	759	2.71	1.4796	163.0	1.026	1.0	10.3	57
Cs_2O_2	753	2.66	1.4835	157.6	1.016	1.0	6.3	57
Rb_2O_2	750	2.64	1.4855	154.8	1.011	1.0	4.3	75
Cu:O_2 complex	750	2.64	1.4855	154.8	1.011	1.0	4.3	58
Oxy-Hc	749	2.63	1.4861	153.9	1.009	1.0	3.6	58
Cs_2O_2	743	2.59	1.4902	148.4	0.999	1.0	-0.5	76
Co^{III} complex	742	2.58	1.4908	147.4	0.997	1.0	-1.2	77
Cs_2O_2	742	2.58	1.4908	147.4	0.997	1.0	-1.2	40
O_2 complex	742	2.58	1.4908	147.4	0.997	1.0	-1.2	78

O_2^x complex	ν_{O-O} (cm^{-1})	Calculated K (mdyn $Å^{-1}$)	Calculated B_L (Å)	Calculated H (kJ mol^{-1})	Calculated B_o	Closest B_o	Calculated e^- covalency %	Ref.
Na_2O_2	738 793	2.55	1.4936	143.6	0.99	1.0	-3.9	[57]
Na_2O_2	736 791	2.54	1.4950	141.7	0.987	1.0	-5.3	[32]
Co^{II}:O_2 complex	730	2.50	1.4992	135.9	0.976	1.0	-9.4	[79]
Org:O_2 complex	713	2.39	1.5116	118.7	0.947	1.0	-21.4	[64]

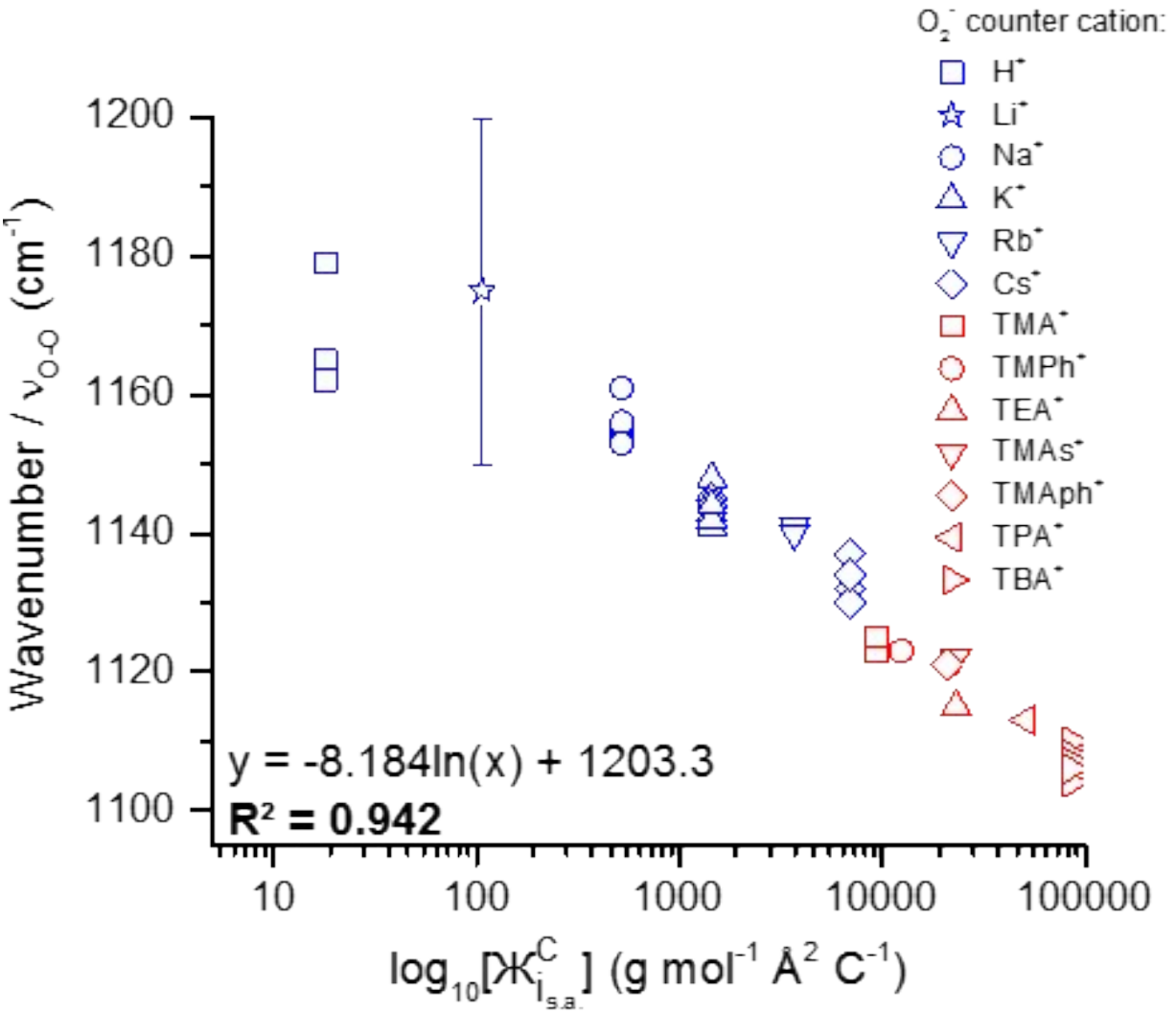

Figure S1. From reports listed in Table S1, the ν_{O-O} Raman bands for $[C^{+}\cdots O_2^{\bullet -}]$ complexes are plotted against $\log_{10}[\mathcal{H}_{i\,s.a.}^{C}]$ of the coordinating cation. Values were calculated in Spartan 15 using a CPK model for single atom cations (blue) and DFT (B3LYP, 6-31G*) for molecular cations (red).

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