Supporting Information

Interconvertible Side-On and End-On Bonded Oxo-Superoxo Titanium Ozonide

Complexes

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Table S1. Infrared Absorptions (cm^{-1}) from Co-Deposition of Laser-Evaporated Titanium atoms with Dioxygen in Excess Argon.

$^{16}\text{O}_2$	$^{18}\text{O}_2$	$^{16}\text{O}_2 + ^{18}\text{O}_2$	$^{16}\text{O}_2 + ^{16}\text{O}^{18}\text{O} + ^{18}\text{O}_2$	Assignment (mode) ^a
938.9	896.7	938.9, 896.7		$\text{TiO}_2(\text{O}_2)_2$ (sym TiO_2 stretch)
908.8	873.8	908.8, 873.8		$\text{TiO}_2(\text{O}_2)_2$ (asym TiO_2 stretch)
1131.8	1064.3	1131.5, 1064.5	1131.5, 1096.2, 1064.5	$\text{OTi}(\eta^2\text{-O}_2)(\eta^2\text{-O}_3)$ (O-O stretch)
1022.4	968.5			$\text{OTi}(\eta^2\text{-O}_2)(\eta^2\text{-O}_3)$ (sym O_3 stretch)
999.8	955.3	1004.2, 999.8, 959.4,	1004.2, 999.8, 959.4,	$\text{OTi}(\eta^2\text{-O}_2)(\eta^2\text{-O}_3)$
		955.3	955.3	($\text{Ti}\equiv\text{O}$ stretch)
806.3	761.7	806.1, 796.7, 772.6,	806.1, 796.7, 786.6,	$\text{OTi}(\eta^2\text{-O}_2)(\eta^2\text{-O}_3)$
		762.0	782.4, 772.6, 762.0	(asym O_3 stretch)
686.8	651.6			$\text{OTi}(\eta^2\text{-O}_2)(\eta^2\text{-O}_3)$ (O_3 bending)
561.4	544.8	561.3, 560.2, 558.9, 547.6,	560.2, 550.9, 546.1	$\text{OTi}(\eta^2\text{-O}_2)(\eta^2\text{-O}_3)$ (Ti- O_2 stretch)
		546.1, 545.1		
1341.2	1267.4	1341.4, 1306.8, 1267.2	1341.6, 1306.8, 1268.4	$\text{OTi}(\eta^2\text{-O}_2)(\eta^1\text{-O}_3)$ (O-O stretch)
1117.6	1051.4	1117.4, 1052.1		$\text{OTi}(\eta^2\text{-O}_2)(\eta^1\text{-O}_3)$ (O-O stretch)
993.4	952.0	993.2, 952.2	993.1, 952.4	$\text{OTi}(\eta^2\text{-O}_2)(\eta^1\text{-O}_3)$ ($\text{Ti}\equiv\text{O}$ stretch)
679.8	649.9			$\text{OTi}(\eta^2\text{-O}_2)(\eta^1\text{-O}_3)$ (O_3 bending)
554.2	530.9			$\text{OTi}(\eta^2\text{-O}_2)(\eta^1\text{-O}_3)$ (Ti- O_2 stretch)
516.7	491.5			$\text{OTi}(\eta^2\text{-O}_2)(\eta^1\text{-O}_3)$ (Ti- O_3 stretch)

^a Some modes listed are mixed, and only the major component is listed.

Table S2. Optimized Geometries (as Cartesian Coordinates) of the Structures Mentioned in the Text.

(1) OTi(η^2 -O₂) (η^2 -O₃), ³A, C₁

Ti	0.0508641605	0.0698111495	-0.0600916131
O	-0.057732763	0.1180219576	2.4922329443
O	1.4635094036	-0.0025684791	-0.8011434669
O	-1.4176092764	0.193727692	-1.4068403682
O	-1.3266268838	-1.0598959197	-1.0160554732
O	-0.0422365187	-1.0067942615	1.7630790014
O	0.0478053788	1.2051538592	1.6617661706

(2) OTi(η^2 -O₂) (η^1 -O₃), ³A', C_s

Ti	0.1151455092	-0.0254663035	0.619422429
O	-1.2759207411	0.2821906399	-2.0426843483
O	-1.27626909	0.2822676833	1.3594069381
O	1.7740337748	0.2834335646	1.7282480569
O	1.4890497129	-1.005117591	1.7282480571
O	-1.0743388062	0.2376075138	-3.248315821
O	0.0467949992	-0.0103494759	-1.2283145624

(3) TS, ³A, C₁

Ti	0.0722294653	-0.1748682327	0.4207440444
O	-1.1632817184	0.1877203353	-2.11065925
O	-1.1442156907	0.4429076374	1.254231651
O	1.8799972804	0.1926318518	1.2348841196
O	1.4708510947	-1.0090625041	1.5867351837
O	-0.9576149164	1.3882179916	-1.7473325434
O	-0.2843670791	-0.7215276719	-1.3749052831

Figure S1. Infrared spectra in the 730-500 cm⁻¹ region from co-deposition of laser-evaporated titanium atoms with 0.5% O₂ in argon. (a) 1 h of sample deposition at 6 K; (b) after 35 K annealing; (c) after 40 K annealing; (d) after 15 min 532 nm irradiation; and (e) after 35 K annealing.

Figure S2. Infrared spectra in the 1150-930 cm^{-1} region from co-deposition of laser-evaporated titanium atoms with isotopic-labeled O_2 in excess argon. Spectra were taken after sample deposition followed by 40 K annealing. (a) 0.5% $^{16}\text{O}_2$; (b) 0.5% $^{18}\text{O}_2$; (c) 0.25% $^{16}\text{O}_2$ + 0.25% $^{18}\text{O}_2$; and (d) 0.125% $^{16}\text{O}_2$ + 0.25% $^{16}\text{O}^{18}\text{O}$ + 0.125% $^{18}\text{O}_2$. The asterisk denotes an impurity absorption from the mixed $^{16}\text{O}_2$ + $^{16}\text{O}^{18}\text{O}$ + $^{18}\text{O}_2$ sample.

Figure S3. Infrared spectra in the 830-750 and 580-530 cm^{-1} regions from co-deposition of laser-evaporated titanium atoms with isotopic-labeled O_2 in excess argon. Spectra were taken after sample deposition followed by 40 K annealing. (a) 0.5% $^{16}\text{O}_2$; (b) 0.5% $^{18}\text{O}_2$; (c) 0.25% $^{16}\text{O}_2$ + 0.25% $^{18}\text{O}_2$; and (d) 0.125% $^{16}\text{O}_2$ + 0.25% $^{16}\text{O}^{18}\text{O}$ + 0.125% $^{18}\text{O}_2$.

Figure S4. Infrared spectra in the 1360-1240 and 1150-930 cm^{-1} regions from co-deposition of laser-evaporated titanium atoms with isotopic-labeled O_2 in excess argon. Spectra were taken after sample deposition followed by 15 min 532 nm irradiation. (a) 0.5% $^{16}\text{O}_2$; (b) 0.5% $^{18}\text{O}_2$; (c) 0.25% $^{16}\text{O}_2$ + 0.25% $^{18}\text{O}_2$; and (d) 0.125% $^{16}\text{O}_2$ + 0.25% $^{16}\text{O}^{18}\text{O}$ + 0.125% $^{18}\text{O}_2$. The asterisk denotes an impurity absorption from the mixed $^{16}\text{O}_2$ + $^{16}\text{O}^{18}\text{O}$ + $^{18}\text{O}_2$ sample.