## Supporting Information: Slow electron velocity-map imaging of Al<sub>2</sub>O<sub>2</sub> and Al<sub>3</sub>O<sub>3</sub>

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**Figure S1.** Peak areas of features a-d in the cryo-SEVI spectrum of  $Al_2O_2^-$  normalized to the area of peak S1 as a function of (a) photon energy and (b) eKE.



**Figure S2**. Results of the application of the code of Liu and Ning<sup>1</sup> to detachment from the HOMOs of the two different isomers of  $Al_3O_3^-$ . (a) Calculated anisotropy parameters for low-eKE detachment from the book and kite anion HOMOs are shown as solid red and black lines, respectively, and compared to the experimental PADs for the  $0_0^0$  transition attributed to each (A1 and B1 for kite and book, respectively). (b) Calculated total detachment cross sections for the book (red) and kite (black) anion isomers. The dashed vertical lines show the eKEs of peaks A1 and B1 (black and red, respectively) at the photon energy used to acquire the green trace in Figure 6.



**Figure S3.** Three cryo-SEVI scans of  $Al_3O_3^{-1}$  focusing on the higher-eBE region of the photoelectron spectrum. The eKEs and peak widths for the vibrational origin in the two lower-energy scans are provided, demonstrating that decreasing the photon energy does not result in narrower features.



Figure S4. Vibrational modes of  $Al_2O_2$ , as well as their symmetries within the  $D_{2h}$  point group.



**Figure S5.** Vibrational frequencies of the neutral Al<sub>3</sub>O<sub>3</sub> **3a** (left) and **3b** (right) isomers invoked in the vibrational assignments of the Al<sub>3</sub>O<sub>3</sub><sup>-</sup> cryo-SEVI spectrum. All modes have  $a_1$  symmetry within the  $C_{2\nu}$  point group.



**Figure S6.** The top panel shows the intrinsic reaction coordinate path calculated for the book/kite isomerization of neutral  $Al_3O_3$ . The transition state geometry is pictured, as are several intermediate geometries. The dashed lines show the (non-ZPE corrected) energies of neutral isomers **3a** and **3b** relative to the transition state. The bottom panel shows the density of **3a** vibrational states using the same energy scale. Vertical lines are used to indicate the energies of the neutral **3b** isomer and the transition state.

**Table S1.** Cartesian coordinates (in Å) and relative energies (in eV) for the anion and neutral states of  $Al_2O_2$  involved in this work calculated at the B3LYP/aug-cc-pVTZ level. Energies are relative to the anion ground state and are zero-point corrected.

$\tilde{X}^{2}B_{3u}$ ( <b>2a</b> anion, $D_{2h}$ ) <b>E</b> = <b>0.000</b>							
Al	1.246489	0.00000	0.00000				
0	0.00000	1.276998	0.00000				
0	0.00000	-1.276998	0.000000				
Al	-1.246489	0.00000	0.00000				
$ ilde{X}^{-1}A_{_g}$	$(2a \text{ neutral}, D_{2h})$		E = 2.189				
Al	1.213801	0.00000	0.00000				
0	0.00000	1.273649	0.00000				
0	0.00000	-1.273649	0.00000				
Al	-1.213801	0.00000	0.00000				
$\tilde{a}^{3}B_{3u}$ (2a neutral, $D_{2h}$ ) E = 2.447							
Al	1.211351	0.00000	0.00000				
0	0.00000	1.279760	0.00000				
0	0.00000	-1.279760	0.000000				
Al	-1.211351	0.00000	0.00000				

**Table S2.** Cartesian coordinates (in Å) and relative energies (in eV) for the lowest-energy anion and neutral states of the book and kite isomers of  $Al_3O_3$ , calculated at the B3LYP/aug-cc-pVTZ level. Energies are relative to the lowest-energy anion state and are zero-point corrected.

$\tilde{X}^{-1}A_{_{1}}$	$(3a \text{ anion}, C_{2v})$	E = 0.000	
Al	0.00000	0.00000	-0.122474
Al	0.00000	0.00000	-2.600977
0	0.00000	1.285031	-1.258241
0	0.00000	-1.285031	-1.258241
0	0.00000	0.00000	1.602762
Al	0.00000	0.00000	3.285740
$\tilde{X}^{-1}A$	(3h anion Ca)		E = 0.005

Λ	$A_1$ ( <b>SD</b> alloll, $C_{2\nu}$ )		E = 0.003
Al	0.00000	0.00000	0.868074
Al	0.00000	1.930638	-0.798390
Al	0.00000	-1.930638	-0.798390
0	0.00000	1.684254	1.051909
0	0.00000	0.00000	-0.919668
0	0.00000	-1.684254	1.051909

$ ilde{X}^{-2}A_{_{ m I}}$	( <b>3a</b> neutral, $C_{2\nu}$ )		E = 2.078
Al	0.00000	0.00000	-0.110949
Al	0.00000	0.00000	-2.524745
0	0.00000	1.272736	-1.312032
0	0.00000	-1.272736	-1.312032
0	0.00000	0.00000	1.570316
Al	0.00000	0.00000	3.284154

$ ilde{X}^{2}$	$B_2$ ( <b>3b</b> neutral, $C_{2\nu}$ )		E = 2.584
Al	0.00000	0.00000	0.916806
Al	0.00000	1.866137	-0.786967
Al	0.00000	-1.866137	-0.786967
0	0.00000	1.693535	1.004235
0	0.00000	0.00000	-0.940637
0	0.00000	-1.693535	1.004235

		<b>3</b> a		3	3b
		$ ilde{X}^{-1}A_1$	$ ilde{X}^{-2}A_{1}$	$ ilde{X}^{-1}A_1$	$ ilde{X}^{-2}B_2$
$v_1$	$a_1$	1051	1073	739	726
$v_2$	$a_1$	843	802	682	644
<i>V</i> 3	$a_1$	594	746	540	573
$v_4$	$a_1$	544	586	414	432
$v_5$	$a_1$	325	343	208	246
$v_6$	$b_1$	335	360	163	174
$v_7$	$b_1$	151	175	329	331
$v_8$	$b_1$	57	64	107	102
V9	$b_2$	819	765	994	979
$v_{10}$	$b_2$	491	640	578	577
<i>v</i> <sub>11</sub>	$b_2$	234	240	461	561
$v_{12}$	$b_2$	50	57	361	307

**Table S3.** B3LYP/aug-cc-pVTZ harmonic frequencies (in cm<sup>-1</sup>) for the anionic and neutral states of both isomers of Al<sub>3</sub>O<sub>3</sub>. The symmetries of each mode within the  $C_{2\nu}$  point group are also provided.

**Table S4.** Results of the TDDFT calculation performed on the  ${}^{3}B_{3u}$  electronic state of the Al<sub>2</sub>O<sub>2</sub> neutral cluster, calculated at the B3LYP/aug-cc-pVTZ level. For each of the three states, the excitation energy (in eV, relative to the closed-shell singlet) and orbital occupation are provided. The excitation energies (in eV) calculated at the MRMP2 level by Sarker and coworkers<sup>2</sup> are also provided for comparison.

State	Orbital Occupation	TDDFT	MRMP2 <sup>2</sup>
${}^{3}B_{1g}$	$\dots (2b_{1u})^2 (4b_{2u})^1 (1b_{3g})^2 (7a_g)^2 (5b_{3u})^1$	2.64	3.72
$^{3}A_{u}$	$\dots (2b_{1u})^2 (4b_{2u})^2 (1b_{3g})^1 (7a_g)^2 (5b_{3u})^1$	2.71	2.78
${}^{3}B_{2g}$	$\dots (2b_{1u})^1 (4b_{2u})^2 (1b_{3g})^2 (7a_g)^2 (5b_{3u})^1$	3.62	2.09

Isomer	eKE (eV)	$f_0$	$f_1$	$f_2$	$f_3$	$f_4$	$f_5$
<b>3</b> a	0.001	0.868	0.128	0.003	0.000	0.000	0.000
3b	0.001	0.993	0.005	0.001	0.000	0.000	0.000
<b>3</b> a	0.633	0.009	0.750	0.105	0.070	0.046	0.020
3b	0.633	0.448	0.074	0.434	0.023	0.020	0.001
<b>3</b> a	2.001	0.062	0.691	0.055	0.073	0.056	0.063
3b	2.001	0.099	0.073	0.658	0.060	0.101	0.007

**Table S5**. Partial wave analysis extracted from the PAD calculations for the  $Al_3O_3^-$  anion HOMOs. The fractional character  $f_l$  represents the fraction of the outgoing electron with angular momentum l, and is calculated as described in previous work.<sup>3</sup> For each eKE, the dominant contributions are shown in bold.

## References

<sup>1</sup>Y. Liu and C. Ning. Calculation of photodetachment cross sections and photoelectron angular distributions of negative ions using density functional theory. *J. Chem. Phys.* **143**, 144310 (2015). <sup>2</sup>M. I. M. Sarker, C.-S. Kim, and C. H. Choi. Ground and excited states of Al<sub>2</sub>O<sub>2</sub> and its anion. *Chem. Phys. Lett.* **411**, 297 (2005).

<sup>3</sup>J. A. DeVine, M. L. Weichman, M. C. Babin, and D. M. Neumark. Slow photoelectron velocity-map imaging of cold tert-butyl peroxide. *J. Chem. Phys.* **147**, 013915 (2017).