Supplementary Information (SI) for RSC Advances.

CO_2 Adsorption and Activation on $AuO(CO_2)_n^{-/+}$ (n = 1 – 3) Clusters: A Theoretical Study

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Table S1 Method sensitivity summary for $AuO(CO_2)_n^{-/+}$ (n = 1 - 3): ZPE-corrected relative energies across six methods.

Isomer	Relative Energy (eV)					
	comb1	comb2	comb3	comb4	comb5	comb6
$1A^-$	0.00	0.00	0.00	0.00	0.00	0.00
$1B^-$	0.12	0.19	0.13	0.13	0.09	0.10
$1C^-$	0.60	0.79	1.06	1.23	0.64	0.87
$1D^-$	0.92	1.30	1.39	1.32	1.31	1.35
$2A^-$	0.00	0.00	0.00	0.00	0.00	0.00
$2B^-$	0.38	0.24	0.27	0.14	0.57	0.41
$2C^-$	0.62	0.52	-0.02	-0.13	0.47	0.31
$2D^-$	1.49	1.38	1.62	1.44	1.74	1.74
$3A^-$	0.00	0.00	0.00	0.00	0.00	0.00
$3B^-$	0.14	0.11	0.84	0.85	0.77	0.58
$3C^-$	0.42	0.40	1.22	1.22	0.86	0.89
$3D^-$	1.35	1.35	2.22	2.29	1.81	1.91
$1A^+$	0.00	0.00	0.00	0.00	0.00	0.00
$1B^+$	1.02	0.97	0.19	0.14	0.99	0.98
$1C^+$	1.50	1.44	1.74	1.66	1.64	1.56
$1D^+$	1.75	1.77	1.92	1.88	1.81	1.86
$2A^+$	0.00	0.00	0.00	0.00	0.00	0.00
$2B^+$	0.63	0.61	0.81	0.87	0.69	0.64
$2C^+$	1.09	1.01	0.06	0.05	0.00	0.03
$2D^+$	2.67	2.58	3.06	3.07	3.21	1.53
$3A^+$	0.00	0.00	0.00	0.00	0.00	0.00
$3B^+$	0.09	0.11	0.13	0.23	0.04	0.04
$3C^+$	1.18	1.16	0.98	0.98	1.42	1.16
$3D^+$	3.54	3.43	2.85	2.78	3.38	3.74

Methods:

comb1: B3LYP-D3/Def2-TZVP

comb2: B3LYP-D3/LANL2DZ/6-311+G(3df)

comb3: M06-2X /Def2-TZVP

comb4: M06-2X/LANL2DZ/6-311+G(3df)

comb5: ωB97X-D/ Def2-TZVP

comb6: ωB97X-D /LANL2DZ/6-311+G(3df)

Table S2 Percent differences of Au-O bond length and O-C-O angle for each method combination relative to B3LYP/def2-TZVP

Isomer	percent change in Au-O bond length P_{bond}					percent change in O-C-O angle P_{angle}				
	comb1	comb2	comb3	comb4	comb5	comb1	comb2	comb3	comb4	comb5
$1A^-$	0.50%	-0.50%	-0.50%	-1.50%	-1.00%	-0.20%	-0.74%	-0.68%	-0.08%	-0.33%
$1B^-$	2.16%	-3.90%	-1.73%	-2.60%	-0.43%	-0.29%	1.05%	0.92%	0.71%	0.45%
$1C^-$	1.09%	-0.54%	0.54%	-1.09%	0.00%	0.30%	1.14%	2.11%	0.02%	0.45%
$1D^-$	0.98%	1.47%	2.45%	-0.49%	0.98%	-0.53%	1.21%	1.03%	1.87%	1.87%
$2A^-$	1.98%	-0.99%	-0.50%	-0.99%	-0.50%	0.48%	1.82%	2.60%	0.16%	0.72%
$2B^-$	0.81%	-0.24%	-0.11%	-1.25%	-0.61%	-0.02%	-0.66%	-0.50%	-0.30%	-0.19%
$2C^-$	1.07%	0.15%	0.28%	-0.90%	-0.51%	-0.25%	1.12%	1.08%	0.31%	0.26%
$2D^-$	1.16%	3.14%	4.23%	0.22%	1.33%	0.71%	0.98%	1.50%	0.73%	1.08%
$3A^-$	0.00%	0.96%	1.44%	-0.48%	0.00%	-0.05%	0.92%	0.87%	0.03%	0.05%
$3B^-$	0.67%	-0.01%	0.13%	-1.18%	-0.89%	0.08%	-0.69%	-0.56%	-0.50%	-0.34%
$3C^-$	2.25%	-3.80%	-2.00%	-2.44%	-0.44%	0.02%	-0.33%	-0.24%	-0.15%	-0.09%
$3D^-$	1.39%	3.65%	4.13%	-0.30%	1.69%	0.34%	0.62%	0.91%	0.67%	0.58%
$1A^+$	0.69%	1.99%	3.69%	-0.14%	0.82%	0.29%	0.22%	0.95%	0.03%	0.98%
$1B^+$	0.55%	-1.80%	-0.19%	-3.85%	2.26%	-0.01%	-0.54%	0.22%	-0.67%	0.16%
$1C^+$	0.73%	-3.43%	-2.13%	-2.04%	-1.05%	-0.23%	1.87%	1.51%	0.95%	0.62%
$1D^+$	0.67%	-0.16%	1.05%	-0.77%	0.10%	0.02%	-0.39%	0.02%	-0.57%	0.02%
$2A^+$	0.87%	1.88%	3.81%	-0.23%	1.14%	-0.01%	0.14%	0.18%	0.02%	0.04%
$2B^+$	0.86%	-3.45%	-2.30%	-2.30%	-1.17%	-0.07%	0.20%	0.21%	0.05%	0.00%
$2C^+$	0.72%	-1.64%	1.13%	-3.94%	-2.51%	0.00%	-0.28%	-0.22%	-0.63%	0.15%
$2D^+$	0.59%	-3.66%	-2.64%	-2.33%	-1.63%	-0.22%	1.15%	0.78%	0.23%	-0.03%
$3A^+$	0.93%	1.72%	3.66%	-0.25%	1.15%	0.93%	0.09%	0.14%	-0.01%	0.04%
$3B^+$	0.82%	-2.72%	-1.71%	-1.95%	-1.05%	-0.03%	0.08%	0.10%	-0.03%	-0.06%
$3C^+$	1.46%	8.41%	8.86%	4.43%	5.21%	1.46%	0.00%	-0.03%	-0.17%	-0.19%
$3D^+$	0.46%	7.91%	8.91%	3.05%	5.01%	0.46%	3.23%	3.29%	1.06%	2.29%

Methods:

comb1: B3LYP-D3/LANL2DZ/6-311+G(3df)

comb2: M06-2X /Def2-TZVP

comb3: M06-2X/LANL2DZ/6-311+G(3df)

comb4: ωB97X-D/ Def2-TZVP

comb5: ωB97X-D /LANL2DZ/6-311+G(3df)

$P_{bond} = [r_{comb\ n} - r_{ref}] / r_{ref}$

Where $r_{comb\ n}$ is the internal Au–O bond length of the AuO unit from the optimized structure at method combination comb *n*, and r_{ref} is the B3LYP-D3/def2-TZVP value. Positive means longer than the reference.

$P_{angle} = [\theta_{comb\ n} - \theta_{ref}] / \theta_{ref}$

Where $\theta_{comb\ n}$ is the O–C–O angle of the coordinated CO_2 from the optimized structure at method combination comb *n*, and θ_{ref} is the B3LYP-D3/def2-TZVP value. Positive means longer than the reference.

The coordinates of the low-lying $AuO(CO_2)_n^{-/+}$ isomers, optimized at the B3LYP-D3 level with Def2-TZVP, are as follows:

$1A^-$

C	-2.13820000	0.09626500	-0.00001000
O	-1.95147600	1.31428700	-0.00000300
O	-3.17825800	-0.59309300	-0.00000200
O	-1.04707200	-0.79526400	-0.00000800
Au	0.78789400	0.00019000	0.00000200

$1B^-$

O	-1.29528100	-1.09524400	-0.00006700
Au	0.74229200	0.00000000	0.00002800
C	-2.00379000	-0.00000700	-0.00006600
O	-1.29543400	1.09533000	-0.00006700
O	-3.23657500	-0.00008200	-0.00009500

$1C^-$

C	0.29372100	-1.69979200	0.00000000
O	1.48809800	-1.37425500	0.00000000
O	-0.44594700	-2.63888500	0.00000000
O	-1.26244100	1.70537600	0.00000000
Au	0.00000000	0.36279600	0.00000000

$1D^-$

O	2.02376200	-0.00002600	1.23320100
Au	0.55813000	0.00001500	-0.18034400
C	-2.67268500	-0.00003500	0.18506700
O	-2.76523100	-1.16052800	0.20441300
O	-2.76554700	1.16043200	0.20448500

$2A^-$

C	-2.36479300	0.18693600	-0.00029500
O	-1.84079300	-1.00703000	0.00035400
O	-3.54363900	0.49235200	-0.00026900
C	2.18195200	0.30854500	-0.00002900
O	2.16542400	-0.95478800	-0.00046600
O	2.94714300	1.22416600	0.00018300
O	-1.39032500	1.14442400	-0.00047800
Au	0.18221000	-0.12868200	0.00009300

$2B^-$

C	1.20857400	0.69852100	0.00019400
O	2.00468700	1.65860400	0.00084900

O	1.41112500	-0.52388200	-0.00077300
C	4.06461100	-0.47278700	-0.00008800
O	4.14460600	-0.49107200	1.15892700
O	4.14529600	-0.48854500	-1.15909400
O	-0.09683300	1.19761200	0.00066800
Au	-1.57607800	-0.15412800	-0.00006700

$2C^-$

C	1.47538900	1.36678200	-0.03055300
O	0.28740000	1.68578800	-0.39737300
O	2.26839700	2.06878400	0.55940100
C	1.70421200	-1.17820600	-0.00559400
O	2.56263900	-2.01236200	-0.21659000
O	1.97369600	0.10451500	-0.48245100
O	0.58640100	-1.40717500	0.60315900
Au	-1.01906200	-0.05883400	-0.00395300

$2D^-$

O	0.93667900	-0.00028800	-0.00000100
C	1.80641100	2.27124800	-0.00000100
O	1.85376700	2.37625900	-1.15898500
O	1.85376600	2.37625800	1.15898400
Au	-1.11966900	0.00038100	0.00000000
C	1.80478400	-2.27249500	0.00000000
O	1.85206300	-2.37752800	1.15898500
O	1.85205600	-2.37753200	-1.15898500

$3A^-$

C	-0.00015700	1.65482500	0.23987300
O	-0.00056800	1.75833500	1.43661900
O	1.11104400	1.64971800	-0.53924100
C	2.26675300	0.82014200	-0.18855300
O	2.01702900	-0.42185400	0.02674500
O	3.33353800	1.36756800	-0.23317500
O	-2.01707600	-0.42200700	0.02665900
Au	0.00002600	-0.95391200	0.01607000
C	-2.26674400	0.81986200	-0.18934900
O	-1.11078400	1.64925100	-0.54000100
O	-3.33333200	1.36774700	-0.23277300

$3B^-$

C	3.85620500	-0.51912000	-0.12555700
O	3.79181200	0.16947500	0.80865300
O	4.06372700	-1.18403700	-1.05363900

C	1.43942600	2.20489500	0.17543000
O	2.06718400	2.46346300	-0.76708300
O	0.81667300	2.08022200	1.14707600
O	-0.47118200	-1.38438000	0.53573500
Au	-1.78539600	-0.01232400	-0.09972200
C	0.86009800	-1.21335700	0.17929800
O	1.19679600	-0.26790200	-0.55798300
O	1.54898400	-2.10945500	0.70011900

$3C^-$

C	-3.76106600	-1.52406600	-0.24692700
O	-3.05467700	-2.05189900	-0.99971000
O	-4.54272300	-1.04718300	0.46718000
C	-0.55482900	-0.23850000	0.70426900
O	-1.73142800	-0.32231000	1.07626800
O	0.37849300	-1.04952200	1.10942500
O	-0.14767100	0.67936300	-0.12803200
C	-2.79166200	1.94323300	-0.23886200
O	-3.11659800	1.30301100	-1.15178800
O	-2.53338300	2.65808300	0.63675000
Au	2.03328200	-0.03089000	-0.11888100

$3D^-$

C	2.99979500	0.14535500	0.68555300
O	3.25493000	0.43396000	-0.40988800
O	2.82007200	-0.12833200	1.79821500
C	0.72752800	2.58057700	-0.45005300
O	0.36168000	2.75821800	-1.53934300
O	1.22323600	2.56429400	0.60412400
O	-0.89664800	0.78687700	0.02461100
C	-3.26189000	0.71817500	0.62554200
O	-3.65534800	0.70626600	-0.47017300
O	-3.08254200	0.73699200	1.77592200
Au	-0.03791900	-1.05735200	-0.24600000

$1A^+$

O	2.33511400	-0.29490200	-0.00001200
Au	0.50475000	0.02185100	0.00000200
C	-2.67368300	0.01108200	-0.00000400
O	-1.55398700	0.39351500	-0.00000900
O	-3.76026900	-0.32270400	0.00000100

$1B^+$

O	-0.45410800	1.24182300	-0.00023200
Au	0.96130300	-0.06911900	0.00004300
C	-3.29515400	-0.19835100	-0.00005000
O	-4.41159600	0.06875600	0.00043000
O	-2.15579800	-0.47926200	-0.00058400

$1C^+$

C	-1.84396800	0.00006500	-0.00014200
O	-1.08664100	-1.07413100	0.00012300
O	-3.03979100	0.00001000	0.00006100
O	-1.08651200	1.07411900	0.00010600
Au	0.66794100	-0.00000500	-0.00001900

$1D^+$

C	-0.00348100	-2.73735800	0.00000000
O	-0.01227200	-1.55651300	0.00000000
O	0.00420100	-3.87374800	0.00000000
O	0.01068200	2.33083400	0.00000000
Au	0.00000000	0.52176700	0.00000000

$2A^+$

O	2.03550400	-1.57900500	-0.00145800
C	-2.95217800	-1.33467800	0.00000700
O	-3.83555300	-2.06850300	0.00076800
O	-2.04957200	-0.58845700	-0.00055800
Au	0.96081400	-0.06553500	0.00008800
C	-1.26864600	2.12703100	0.00007400
O	-2.31251600	2.57776800	-0.00189200
O	-0.16028200	1.71108800	0.00221000

$2B^+$

C	2.32849000	0.60139300	0.02787200
O	3.42712900	1.05983800	0.04071100
O	1.22415800	1.30978200	-0.16594600
C	-3.07854100	0.46300900	0.00570200

O	-2.11888500	-0.19353200	-0.21805500
O	-4.01984100	1.06958000	0.20436600
O	1.97539200	-0.65898500	0.19653100
Au	0.00755300	-0.34278300	-0.00838400

$2C^{+}$

O	-0.00375300	0.13327700	1.29327800
C	-2.73762500	-1.62877600	-0.10197400
O	-3.69347400	-2.24221100	0.07292500
O	-1.76405000	-1.00337600	-0.28325600
Au	1.32526100	-0.13890600	-0.07643500
C	-2.03343400	2.07785000	-0.09122100
O	-0.86375800	2.06674100	-0.06770900
O	-3.18362600	2.08045500	-0.11554400

$2D^{+}$

C	-1.68852800	1.22734500	-0.00014400
O	-0.38128900	1.41780500	-0.00021800
O	-2.33986500	2.22481400	-0.00035000
C	-1.68853000	-1.22735900	-0.00076600
O	-2.33993300	-2.22477400	0.00003400
O	-2.26646400	0.00001900	0.00006100
O	-0.38130500	-1.41780000	-0.00029000
Au	1.03712900	-0.00000500	0.00014600

$3A^{+}$

C	1.97662600	-2.57085400	-0.80089400
O	1.33207500	-1.76880500	-0.24401000
O	2.60960800	-3.35754700	-1.35004200
C	1.97703600	2.57054600	-0.80094500
O	2.61032300	3.35695100	-1.35015400
O	1.33217100	1.76879000	-0.24400400
O	-2.36326200	0.00033600	-1.40554100
C	1.18976700	-0.00002000	1.99301800
O	0.03194300	-0.00011500	1.74748100
O	2.28887100	0.00007000	2.28610500
Au	-1.18473900	0.00005700	0.02701600

$3B^{+}$

C	2.63693500	-1.72728900	0.00011900
O	1.46173900	-1.59436800	-0.00003500
O	3.76462400	-1.89002200	-0.00032000
C	-2.60825700	-1.76884900	-0.00010000
O	-1.43508900	-1.61898900	0.00019300

O	-3.73348400	-1.94788800	-0.00022500
O	1.06078400	1.74524000	-0.00000700
Au	-0.00004100	0.05851200	0.00003000
C	-0.02205900	2.53864300	0.00002500
O	-1.09062300	1.72610300	0.00003000
O	-0.03251200	3.72023400	0.00003000

$3C^{+}$

C	-2.83845700	-1.23955300	-0.09360900
O	-1.70410900	-1.44891100	-0.34193600
O	-3.94750000	-1.08455300	0.12111400
C	3.83105600	1.08810900	-0.15369200
O	2.65650800	1.13258300	-0.37681800
O	4.94948500	1.06593100	0.04515200
O	2.02035200	-0.23682400	0.52659900
Au	0.22628600	-0.65173800	0.01613700
C	-2.53290200	2.59477700	0.01937700
O	-2.13283300	1.49912100	-0.04870900
O	-2.92125300	3.67606900	0.08619200

$3D^{+}$

C	-0.21808600	1.79588100	0.46919300
O	-0.05518100	1.62530700	1.61832400
O	0.75135300	1.94825100	-0.49256800
C	1.92893500	1.28064300	-0.30381300
O	1.98468100	0.05943600	-0.10151400
O	2.97785000	1.94902800	-0.42925600
O	-1.90318200	-0.34077300	0.00920500
Au	0.15477400	-1.12754500	0.01356400
C	-2.23753400	0.83236500	-0.20718900
O	-1.44662500	1.90977600	-0.16458100
O	-3.44227800	1.05181400	-0.54219900