Supporting information for publication

Mechanistic insights into CO_2 Reduction to CO by Group 5 Transition Metal Monoxide Cations

Haili Yu,[1,†] Jia Han,[2,†,*] Quyan Su,[1] Pengcheng Liu,[3] Shilin Liu,[1,2] Xiaoguo Zhou[1,2,*]

1. *Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China*
2. *Hefei National Research Center for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, China*
3. *Anhui Institute of Optics and Fine Mechanics, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei 230031, China*

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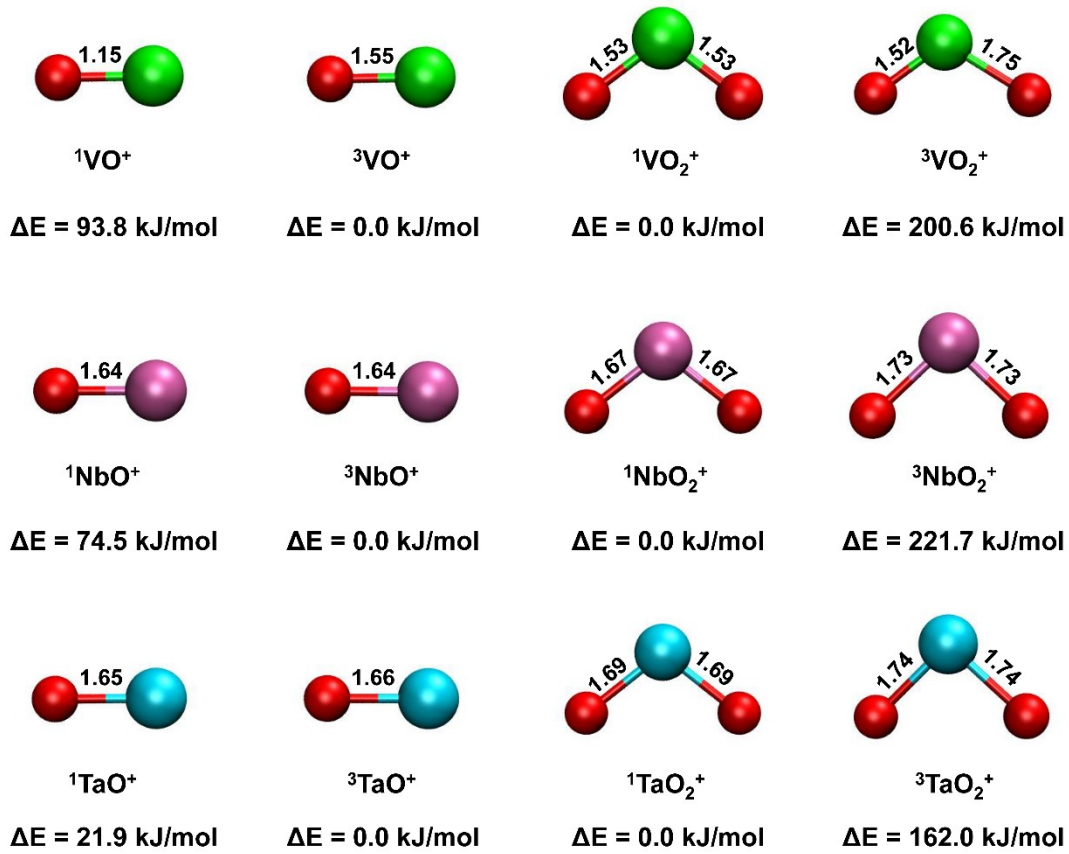

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Table S1. Triple spin contamination $\langle S^2 \rangle$ values for the relevant complexes were calculated at the PBE0-D3(BJ)/def2-TZVP level of theory.

	$\langle S^2 \rangle$ value			
	^{3}RC	^{3}TS	^{3}MECP	^{3}PC
$^3VO^+$-OCO	2.054	2.027	2.039	2.012
$^3NbO^+$-OCO	2.019	2.016	2.018	2.011
$^3TaO^+$-OCO	2.014	2.014	2.014	2.014

Table S2. Cartesian coordinates for all optimized geometry of reactants, intermediates, transition states, products, and minimum energy crossing points at the PBE0-D3(BJ)/def2-TZVP level of theory.

$^1VO^+$

	x	y	z
V	0.00000000	0.00000000	0.39108400
O	0.00000000	0.00000000	-1.12436700

$^3VO^+$

	x	y	z
V	0.00000000	0.00000000	0.39946300
O	0.00000000	0.00000000	-1.14845600

$^1VO_2^+$

	x	y	z
V	0.00000000	0.37970400	0.00000000
O	1.22387600	-0.54580200	0.00000000
O	-1.22387600	-0.54584700	0.00000000

$^3VO_2^+$

	x	y	z
V	0.00000000	0.37933000	0.00000000
O	1.34054000	-0.74677200	0.00000000
O	-1.34054000	-0.34380100	0.00000000

$^1RC(VO^+\text{-}CO_2)$

	x	y	z
V	1.18092300	-0.28626100	-0.00000900
O	2.29898100	0.75271500	0.00000700
C	-2.08543800	0.03146700	0.00000700
O	-0.94098800	-0.24931300	0.00002900
O	-3.18906900	0.29599900	-0.00001600

$^1TS(VO^+\text{-}CO_2)$

	x	y	z
V	0.74298600	0.18487500	-0.34360500
O	1.40374400	-0.88828900	0.52064400
C	-1.17144600	-0.18677600	-0.12301700
O	-0.39130400	0.96652500	0.62014800
O	-2.26994100	-0.46967200	-0.06066500

^{1}PC(VO^{+}-CO_2)

	x	y	z
V	0.64230100	0.00004600	-0.37437100
O	0.94945600	-1.23506900	0.50361100
O	0.94481000	1.23681500	0.50299800
C	-1.51921900	-0.00109500	-0.09946700
O	-2.60146500	-0.00105900	0.14430700

^{3}RC(VO^{+}-CO_2)

	x	y	z
V	-1.19947900	-0.32358200	0.00000100
O	-2.13260000	0.89480400	-0.00000100
C	2.04311700	0.02103900	-0.00000100
O	3.13430900	0.33431000	0.00000200
O	0.91445400	-0.31459400	-0.00000400

^{3}TS(VO^{+}-CO_2)

	x	y	z
V	0.78506100	0.12856200	-0.33277000
O	1.44744000	-0.91644500	0.56781900
C	-1.29951300	-0.29271500	-0.16731400
O	-0.35138100	1.26970900	0.48817000
O	-2.37847300	-0.50334300	0.02621100

^{1}PC(VO^{+}-CO_2)

	x	y	z
V	-0.60984000	-0.08442500	-0.35630200
O	-1.14116400	1.40958300	0.41637500
O	-0.84953400	-1.31451300	0.52247700
C	1.52072200	0.04997700	-0.08826500
O	2.60344600	0.11016900	0.15171500

MECP (V)

	x	y	z
V	0.73380820	0.14672348	-0.37627841
O	1.33683748	-0.79796979	0.62767443
C	-1.09543209	-0.03621188	0.05804728
O	-0.54558239	1.02104363	0.55822178
O	-2.07937961	-0.61774495	-0.14763126

^{1}NbO^{+}

	x	y	z
Nb	0.00000000	0.00000000	0.26698300
O	0.00000000	0.00000000	-1.36828800

$^3NbO^+$

	x	y	z
Nb	0.00000000	0.00000000	0.26698300
O	0.00000000	0.00000000	-1.36828800

$^1NbO_2^+$

	x	y	z
Nb	0.00000000	0.28980100	0.00000000
O	1.30325300	-0.74261400	0.00000000
O	-1.30325300	-0.74261400	0.00000000

$^3NbO_2^+$

	x	y	z
Nb	0.00000000	0.33428900	0.00000000
O	1.25584200	-0.85559400	0.00000000
O	-1.25584200	-0.85763500	0.00000000

$^1RC(NbO^+\text{-}CO_2)$

	x	y	z
Nb	0.93281700	-0.22484400	-0.00022300
O	2.02053400	1.00969100	0.00030600
C	-2.48775400	0.05653500	0.00029200
O	-3.59220000	0.32240400	-0.00081000
O	-1.34320700	-0.22216900	0.00142800

$^1TS1(NbO^+\text{-}CO_2)$

	x	y	z
Nb	-0.80117700	-0.21093700	-0.16631900
O	-1.19326400	1.26113800	0.44730100
C	1.89658700	-0.02816900	0.10473100
O	2.73965300	0.53642400	-0.41778300
O	1.13720200	-0.69538200	0.74432100

$^1IM(NbO^+\text{-}CO_2)$

	x	y	z
Nb	-0.65417300	-0.20070700	-0.20482100
O	-1.19186500	1.16513100	0.53056800
C	1.48762400	0.06314900	0.02452200
O	2.47330400	0.54091300	-0.36903900
O	0.95548000	-0.72478400	0.86978500

^{1}TS2(NbO^{+}-CO_2)

	x	y	z
Nb	-0.61518300	-0.21187400	-0.19760000
O	0.75738200	-0.66162400	0.92822400
O	-1.22374700	1.18810500	0.44198700
C	1.43372400	0.16327000	-0.14933400
O	2.54388600	0.43692200	-0.24551300

^{1}PC(NbO^{+}-CO_2)

	x	y	z
Nb	-0.53541700	0.00022000	-0.29491100
O	-0.74452200	-1.31578400	0.72364400
O	-0.73409400	1.31911900	0.72217900
C	1.79095200	-0.00266300	-0.08671800
O	2.87941300	-0.00246300	0.13063600

^{3}RC(NbO^{+}-CO_2)

	x	y	z
Nb	-0.97644400	-0.24815500	-0.00008800
O	1.22606400	-0.40091800	0.00056900
O	-1.39411600	1.34679800	0.00015300
C	2.33905900	-0.01645700	-0.00000700
O	3.41803400	0.33825800	-0.00026700

^{3}TS(NbO^{+}-CO_2)

	x	y	z
Nb	-0.65343400	-0.14254500	-0.21282500
O	0.70644600	-1.21476200	0.69028900
O	-1.11684100	1.19908700	0.64721500
C	1.52878600	0.28246300	-0.20568800
O	2.61265400	0.53437000	-0.09250900

^{3}PC(NbO^{+}-CO_2)

	x	y	z
Nb	0.45624400	-0.06326700	-0.28058700
O	1.14954400	1.46557800	0.58208200
O	0.65827400	-1.38827600	0.70158900
C	-1.74735600	0.09467700	-0.04565100
O	-2.83554900	0.17593400	0.18857400

MECP(Nb)

	x	y	z
Nb	-0.67131791	-0.19751573	-0.20539938
O	-1.19814151	1.16174089	0.54995712
C	1.54222535	0.04437916	0.04809414
O	2.48694996	0.56497047	-0.38051784
O	0.99502682	-0.74772761	0.84716191

$^{1}TaO^{+}$

	x	y	z
Ta	0.00000000	0.00000000	0.16301900
O	0.00000000	0.00000000	-1.48754800

$^{3}TaO^{+}$

	x	y	z
Ta	0.00000000	0.00000000	0.16379600
O	0.00000000	0.00000000	-1.49463800

$^{1}TaO_2^{+}$

	x	y	z
Ta	0.00000000	0.19227700	0.00000000
O	1.34512000	-0.87726300	0.00000000
O	-1.34512000	-0.87726300	0.00000000

$^{3}TaO_2^{+}$

	x	y	z
Ta	0.00000000	0.21654700	0.00000000
O	1.25423500	-0.98809700	0.00000000
O	-1.25423500	-0.98789500	0.00000000

$^{1}RC(TaO^{+}\text{-}CO_2)$

	x	y	z
Ta	0.66852100	-0.12950300	0.00001400
O	0.58754300	1.53205900	-0.00005800
O	-1.35798300	-0.58639600	-0.00013600
C	-2.44691400	-0.10379600	-0.00002100
O	-3.49462500	0.31389700	0.00007900

^{1}TS(TaO^+-CO_2)

	x	y	z
Ta	-0.57192600	-0.14704100	-0.07295700
O	-0.81412100	1.46726200	0.24730800
O	1.26378700	-0.43258400	0.76516400
C	2.17281600	-0.01349500	0.07973500
O	3.13954400	0.31719000	-0.40654100

^{1}PC(TaO^+-CO_2)

	x	y	z
Ta	-0.38679400	-0.00002600	-0.18906100
O	-0.42341400	1.33632000	0.86530400
O	-0.42311700	-1.33629000	0.86533300
C	1.87355800	0.00037200	-0.09894200
O	2.97085400	-0.00006900	0.06875400

^{3}RC(TaO^+-CO_2)

	x	y	z
Ta	0.67937000	-0.14352000	-0.00001200
O	0.79546000	1.52332600	0.00004400
O	-1.45185600	-0.48170100	0.00011100
C	-2.55644700	-0.06204900	0.00005600
O	-3.62552000	0.31453600	-0.00008600

^{3}TS(TaO^+-CO_2)

	x	y	z
Ta	-0.47271100	-0.08719300	-0.11464300
O	-0.60698900	1.41545700	0.64418500
O	0.86005300	-1.24632100	0.71605900
C	1.69320700	0.23486200	-0.19105300
O	2.79051800	0.45035100	-0.17083800

^{3}PC(TaO^+-CO_2)

	x	y	z
Ta	-0.29092400	0.01767900	-0.19118000
O	-0.53721700	1.40774400	0.73264600
O	-1.26566000	-1.27069400	0.74137900
C	1.93368600	-0.11453300	-0.01361300
O	3.00729200	-0.21247300	0.28069900

MECP(Ta)

	x	y	z
Ta	-0.48989700	-0.13802500	-0.10417400
O	-0.85970900	1.39144400	0.44912000
O	1.19175900	-0.61118700	0.91456200
C	1.81283900	0.03310200	0.02990900
O	2.77862600	0.45439800	-0.43553100