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Ta^+ and $Nb^+ + CO_2$: Intersystem crossing in ion-molecule reactions

Electronic Supplementary Information

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- Figure S1: Comparison of integrated energy distribution for whole scattering range and pie cut
- Figure S2: Integrated energy distributions from velocity distributions
- Figure S3: Kinetic traces from SIFT experiments for $Ta^+ + CO_2$
- Figure S4: Representative mass traces for $Ta^+ + CO_2$ from SIFT experiments
- Figure S5: Kinetic traces from SIFT experiments for $Nb^+ + CO_2$
- Figure S6: Representative mass traces for $Nb^+ + CO_2$ from SIFT experiments
- Figure S7: Calculated unimolecular rate curves for the product complex $MO^+(CO)$
- Figure S8: Representation of modes for $TaO^+ + CO$ as used in the SVP analysis
- Table S1: $Ta^+ + CO_2$ rate constants
- Table S2: $Nb^+ + CO_2$ rate constants
- Table S3: Energies of stationary points displayed for $Nb^+ + CO_2 \longrightarrow NbO^+ + CO$ reaction coordinate in figure 1
- Table S4: Comparison of relative energies of stationary points for $Nb^+ + CO_2$ at DFT (B3LYP), MP2, CCSD level of theory
- Table S5: Bond lengths and angles for exemplary structures along the reaction coordinate for $Nb^+ + CO_2$ and Ta^+CO_2
- Cartesian coordinates and energies for optimized structures for $Nb^+ + CO_2$ at DFT (B3LYP), MP2 and CCSD level of theory.

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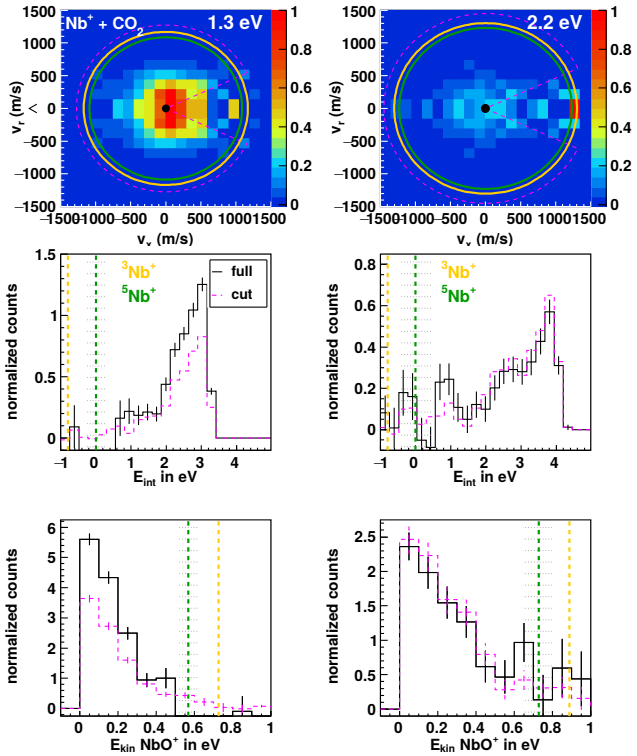

Fig. S1 Integrated energy distributions for the whole scattering range ($\theta = 0° - 180°$, black solid line) and applied pie cut ($\theta = 0° - 160°$, pink dashed line). The top panel (a,b) shows the product ion velocity distributions with the kinematic cut-offs (green: ground state, orange: first electronically excited state) and the applied pie cut (pink dashed line) superimposed. The middle panel (c,d) shows the internal energy distributions and the bottom panel (e,f) the kinetic energy distributions of NbO^+. The vertical lines illustrate the respective kinematic cut-offs. The hashed areas show the 1σ-error from Gaussian error propagation

Table S1 Rate constants for the indicated reactions derived from SIFT data. Uncertainties are dominated by systematic effects, estimates at $\pm 20\%$

	k ($x10^{-10}$ cm^3 s^{-1})	
T(K)	$Ta^+ + CO_2 \longrightarrow TaO^+ + CO$	$TaO^+ + CO_2 \longrightarrow TaO_2{}^+ + CO$
200	4.9	6.7
300	4.5	5.3
400	4.3	4.2
500	4.3	3.6
600	4.0	3.1

Table S2 Rate constants for the indicated reactions derived from SIFT data. Uncertainties are dominated by systematic effects, estimates at $\pm 20\%$

	k($x10^{-10}$ cm^3 s^{-1})	
T(K)	$Nb^+ + CO_2 \longrightarrow NbO^+ + CO$	$NbO^+ + CO_2 \longrightarrow NbO_2{}^+ + CO$
200	4.5	0.33
300	3.1	0.17
400	2.6	0.13
500	2.4	0.09
600	2.0	0.12

Table S3 Energies of stationary points for preparing figure 1 using the computational approach described in the main text. All values given relative to $^5Nb^+ + CO_2$

	Energy (eV)		
	Quintet	Triplet	Singlet
$Nb^+ + CO_2$	0.00	0.51	1.90
Pre-reaction well (LM1) $[NbCO_2]^+$	-1.01	-0.66	-0.63
Transition state (TS)	0.84	± 0.00	0.15
Post-reaction well (LM2) $[ONbCO]^+$	0.45	-3.13	-3.05
$NbO^+ + CO$	1.87	-1.99	-1.87

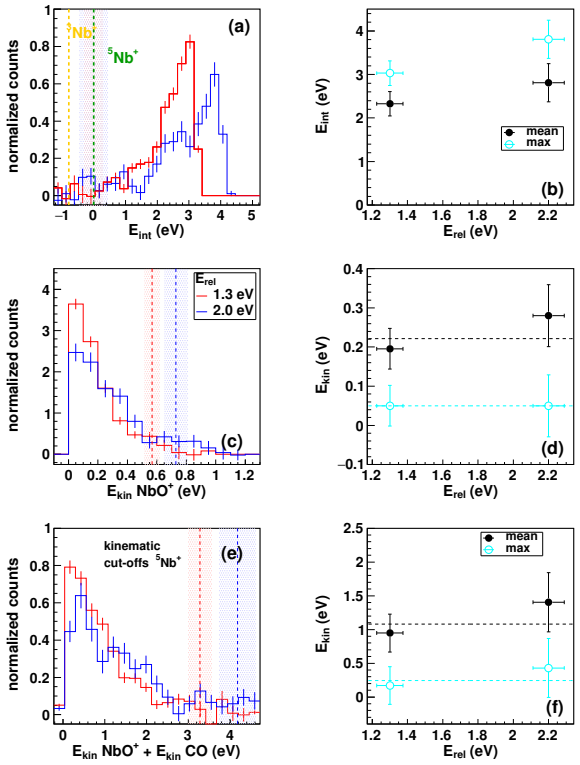

Fig. S2 Comparisons of integrated energy distributions for (a,b) internal, (c,d) NbO^+ kinetic energy and (e,f) product kinetic energy. The left column directly compares the results for both collision energies. The coloured columns indicate the 1σ-error from Gaussian error propagation and are centred around the respective kinematic cut-offs. The right column shows the mean bin and the bin with maximum intensity of the respective distributions including errors. The error of the relative collision energy stems from the widths of the velocity distributions from the input beams. The error of the respective integrated energy distributions is determined via Gaussian error propagation.

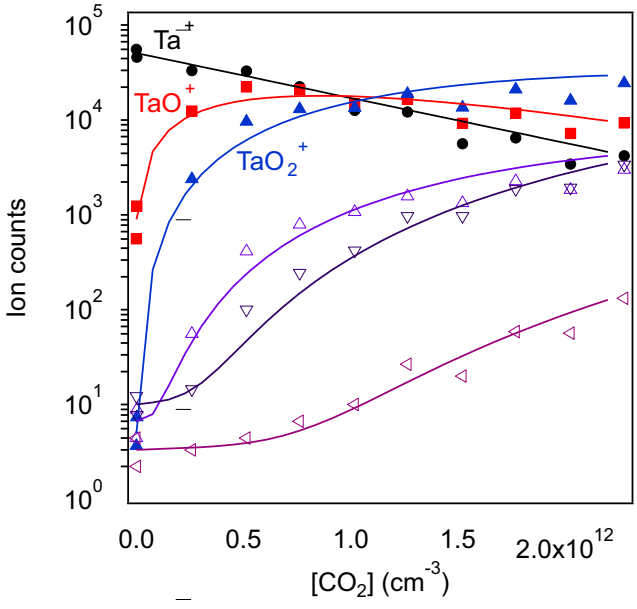

Fig. S3 Representative SIFT data for the $Ta^+ + CO_2$ reaction. Data shown is at 300 K, 0.34 Torr, with a reaction time of 2.6 ms. Experimental data are Ta^+ (black solid circles), TaO^+ (red solid squares), TaO_2^+ (blue solid triangles), $TaO_2^+(CO_2)$ (purple open up triangles), $TaO_2^+(CO_2)_2$ (darker purple open down triangles), and $TaO_2^+(CO_2)_3$ (mauve open side triangles). Curves are fits from kinetic modeling.

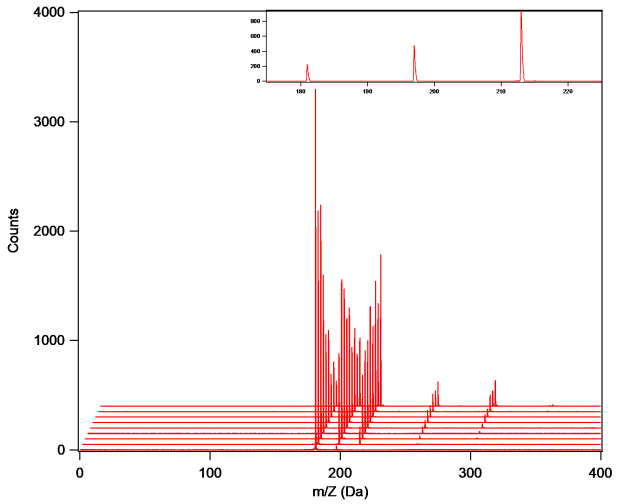

Fig. S4 Representative SIFT time-of-flight spectra for the $Ta^+ + CO_2$ data shown in figures 4 and S3. Inset shows representative peak shapes.

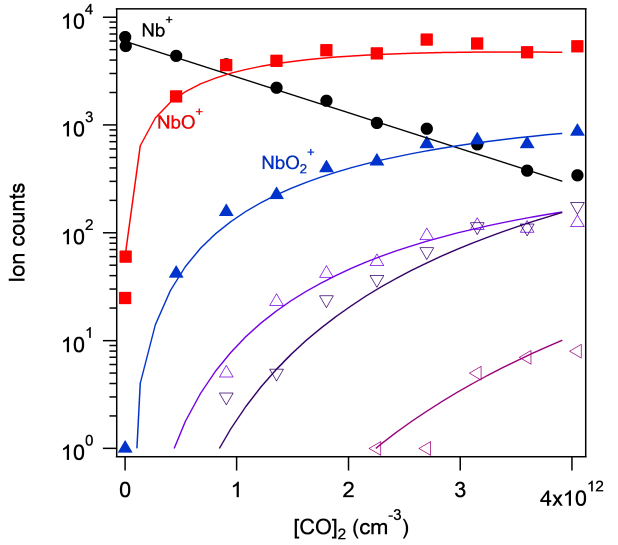

Fig. S5 Representative SIFT data for the $Nb^+ + CO_2$ reaction. Data shown is at 300 K, 0.33 Torr, with a reaction time of 2.6 ms. Experimental data are Nb^+ (black solid circles), NbO^+ (red solid squares), NbO_2^+ (blue solid triangles), $NbO_2^+(CO_2)$ (purple open up triangles), $NbO_2^+(CO_2)_2$ (darker purple open down triangles), and $NbO_2^+(CO_2)_3$ (mauve open side triangles). Curves are fits from kinetic modelling.

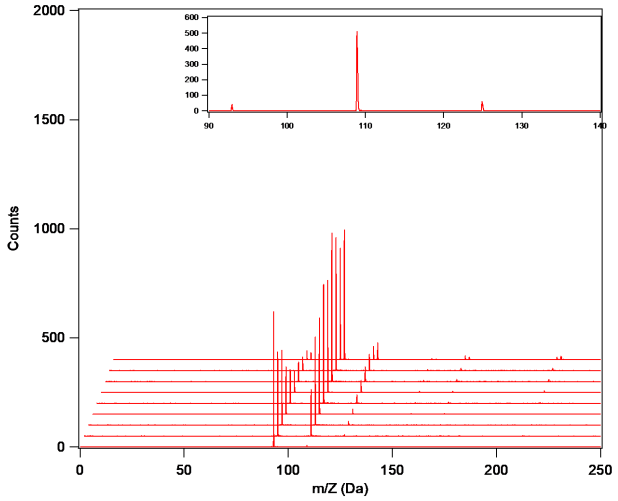

Fig. S6 Representative SIFT time-of-flight spectra for the $Nb^+ + CO_2$ data shown in figures 4 and S5. Inset shows representative peak shapes.

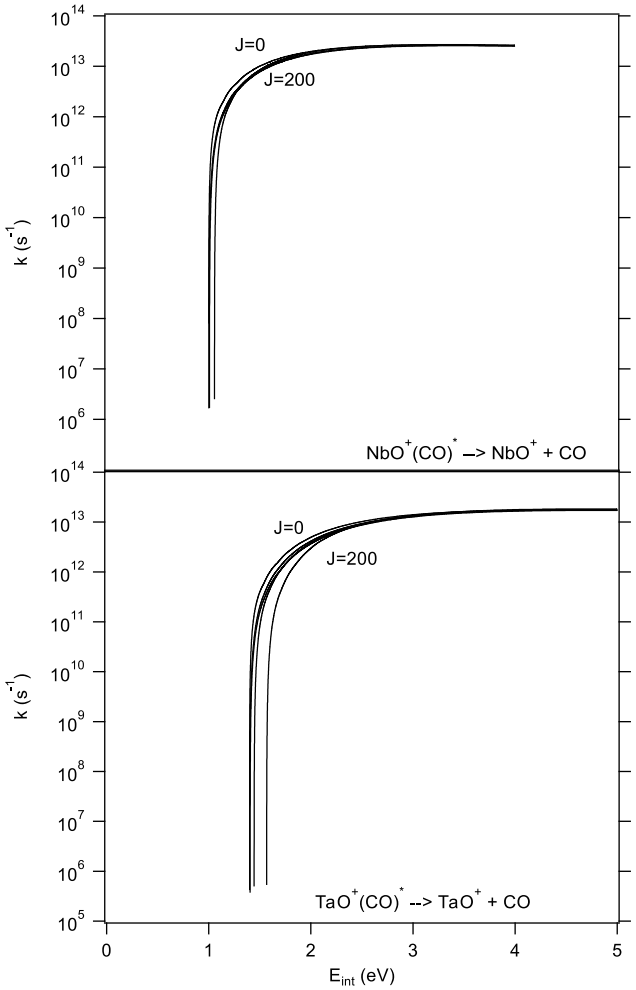

Fig. S7 Calculated unimolecular rate curves for the product complex (as Figure 5). Top) $NbO^+(CO)$ and Bottom)$TaO^+(CO)$ dissociations as a function of internal energy for J = 0, 50, 100, 150, and 200

Table S4 Relative energy (in eV) along the $Nb^+ + CO_2$ reaction pathway in three different spin multiplicities, relative to the $^5Nb^+ + CO_2$ limit. Optimization was performed using either DFT (B3LYP), MP2 or CCSD method, CCSD(T) energies are shown, including the zero-point energy as calculated within the respective optimization method. The aug-cc-pVTZ basis set was used for C, O, the ECP28MDF_AVTZ basis set was employed for Nb

		DFT (B3LYP)	MP2	CCSD
Reactants	$^1Nb^+ + CO_2$	1.90	1.90	1.90
	$^3Nb^+ + CO_2$	0.51	0.51	0.51
	$^5Nb^+ + CO_2$	0	0	0
Pre-reaction well (LM1)	$^1[NbOCO]^+$	-0.53	-0.63	-0.63
	$^3[NbOCO]^+$	-0.63	-0.66	-0.66
	$^5[NbOCO]^+$	-0.96	-1.01	-1.01
Transition state (TS)	$^1[NbCO_2]^+$	0.17	0.10	0.15
	$^3[NbCO_2]^+$	0.03	0.00	–
	$^5[NbCO_2]^+$	0.86	0.87	0.84
Post-reaction well (LM2)	$^1[ONbCO]^+$	-3.04	-3.06	-3.05
	$^3[NbOCO]^+$	-3.12	-3.11	-3.13
	$^5[NbOCO]^+$	0.48	0.46	0.45
Products	$^1NbO^+ + CO$	-1.87	-1.89	-1.87
	$^3NbO^+ + CO$	-1.98	-1.97	-1.99
	$^5NbO^+ + CO$	1.92	1.87	1.87

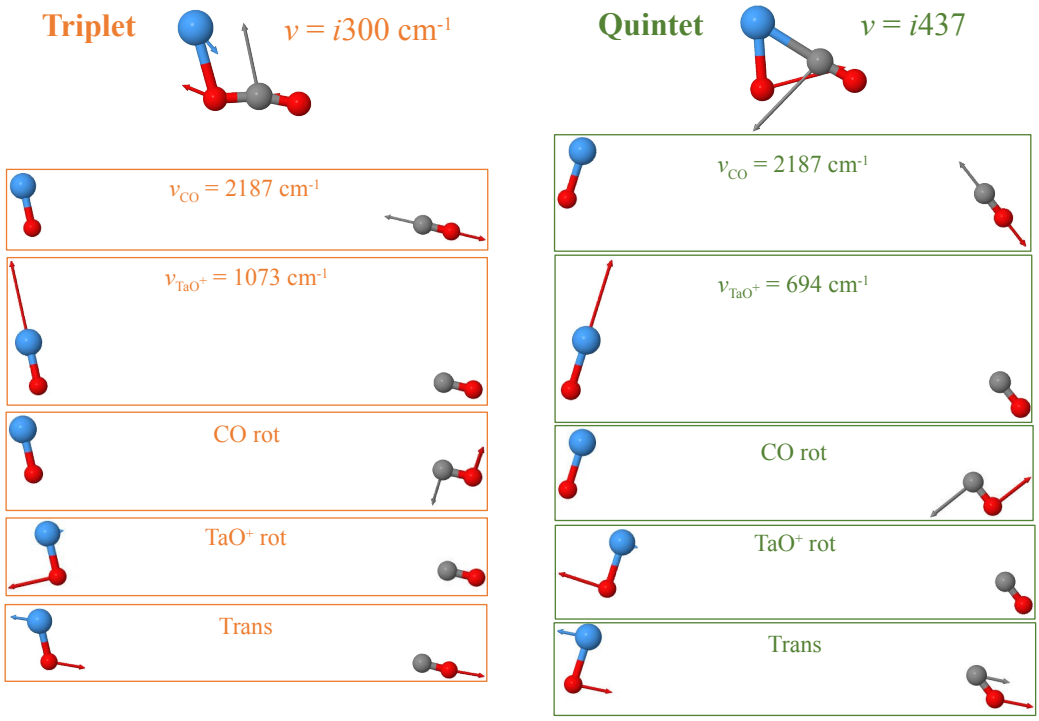

Fig. S8 Graphical illustration of modes for the products $TaO^+ + CO$ for the reaction $Ta^+ + CO_2$ together with the imaginary mode at the transition state which represents the dissociation coordinate at the transition state (triplet: orange; quintet: green))

Table S5 Comparison of bond lengths and bond angles for $M^+ + CO_2$ (M = Nb, Ta) as optimized at the CCSD level of theory along with the aug-cc-pVTZ basis set was used for C, O, the ECP28MDF_AVTZ basis set for Nb, and ECP60MDF_AVTZ for Ta. Transition states were calculated at the B3LYP level with the same basis set.

		Bond length (Å)				Bond angles (°)	
		M–O_1	O_1–C	C–O_2	M–C	∠(MOC)	∠(OCO)
CO_2			1.160	1.160			180
pre-reaction well ^{5}[MOCO]$^+$	Nb	2.328	1.184	1.141			180
	Ta	2.209	1.177	1.140			180
Quintet transition state (^{5}TS)	Nb	1.932	1.894	1.126	2.203	70.3	124.0
	Ta	1.922	1.841	1.130	2.138	69.2	124.6
Triplet transition state (^{3}TS)	Nb	2.117	1.220	1.150	2.568	96.9	163.6
	Ta	2.047	1.227	1.142	2.585	101.3	164.5
CP (quintet → triplet)	Nb	1.957	1.313	1.159	2.114	77.8	145.8
	Ta	1.961	1.295	1.158	2.228	83.7	147.1
Post-reaction well ^{3}[OMCO]$^+$	Nb	1.659		1.118	2.330		
	Ta	1.666		1.119	2.201		
$^3MO^+$	Nb	1.651					
	Ta	1.654					
CO				1.129			

Cartesian coordinates (in Angstrom) of optimized structures along with their zero-point corrected electronic energies calculated at the respective level (in Hartree)

DFT (B3LYP)

CO_2

$E = -188.651729$

O	0.000000	0.000000	1.160469
C	0.000000	0.000000	0.000000
O	0.000000	0.000000	-1.160469

CO

$E = -113.353802$

O	0.000000	0.000000	0.482499
C	0.000000	0.000000	-0.643331

$^1[NbCO_2]^+$, LM1

$E = -245.056694$

Nb	0.000000	0.000000	1.175071
O	0.000000	0.000000	-1.025194
C	0.000000	0.000000	-2.202791
O	0.000000	0.000000	-3.344950

$^3[NbCO_2]^+$, LM1

$E = -245.067084$

Nb	0.000000	0.000000	1.180411
O	0.000000	0.000000	-1.035451
C	0.000000	0.000000	-2.212344
O	0.000000	0.000000	-3.354895

$^5[NbCO_2]^+$, LM1

$E = -245.089813$

O	2.548513	-0.585438	0.001061
C	1.613785	0.085345	-0.002380
O	0.867917	1.050114	0.000692
Nb	-0.902784	-0.103158	0.000006

$^1[NbCO_2]^+$, TS

$E = -245.042789$

Nb	0.866351	-0.106594	-0.000068
C	-0.840045	1.099316	-0.000876
O	-1.496800	0.036312	0.003539
O	-2.477403	-0.580254	-0.001429

$^3[NbCO_2]^+$, TS

$E = -245.053496$

O	-2.592156	0.569017	-0.000443
C	-1.644197	-0.081556	0.000997
O	-0.874231	-1.027293	-0.000325
Nb	0.916983	0.101355	0.000004

$^5[NbCO_2]^+$, TS

$E = -245.018122$

O	1.232377	-0.686319	0.000000
C	-0.548077	-1.332134	0.000000
O	-0.821319	-2.424689	0.000000
Nb	-0.000000	0.801972	0.000000

$^1[NbCO_2]^+$, LM2

$E = -245.157147$

C	-0.743551	-1.403893	0.000000
O	-1.052322	-2.484879	0.000000
Nb	0.000000	0.641532	0.000000
O	1.609985	0.249945	0.000000

$^3[NbCO_2]^+$, LM2

$E = -245.159356$

C	-0.778298	-1.468417	0.000000
O	-1.046240	-2.555424	0.000000
Nb	0.000000	0.647316	0.000000
O	1.629964	0.339242	0.000000

$^5[NbO]^+$, LM2

$E = -245.036735$

C	-0.868244	-1.362848	0.000000
O	-1.261791	-2.417606	0.000000
Nb	0.000000	0.606541	0.000000
O	1.912974	0.331222	0.000000

$^1[NbO]^+$

$E = -131.751190$

Nb	0.000000	0.000000	0.269203
O	0.000000	0.000000	-1.379667

$^3[NbO]^+$

$E = -131.758230$

Nb	0.000000	0.000000	0.269555
O	0.000000	0.000000	-1.381468

$^5[NbO]^+$

$E = -131.623554$

Nb	0.000000	0.000000	0.310122
O	0.000000	0.000000	-1.589375

CP (Quintet/Triplet); no ZPE

$E = -245.073515, -245.073521$

Nb	-0.827690	-0.110158	-0.000040
O	2.444928	-0.521155	-0.000610
C	1.395265	-0.016464	0.001476
O	0.750532	1.098065	-0.000294

MP2

CO_2

$E = -188.310147$

O	0.000000	0.000000	1.170226
C	0.000000	0.000000	0.000000
O	0.000000	0.000000	-1.170226

CO

$E = -113.137605$

O	0.000000	0.000000	0.488125
C	0.000000	0.000000	-0.650833

$^1[NbCO_2]^+$, LM1

$E = -244.256797$

Nb	0.000000	0.000000	1.224775
O	0.000000	0.000000	-1.109474
C	0.000000	0.000000	-2.292785
O	0.000000	0.000000	-3.447908

$^3[NbCO_2]^+$, LM1

$E = -244.272098$

Nb	0.000000	0.000000	1.209211
O	0.000000	0.000000	-1.078476
C	0.000000	0.000000	-2.266017
O	0.000000	0.000000	-3.419220

$^5[NbCO_2]^+$, LM1

$E = -244.300917$

Nb	0.000000	0.000000	1.211917
O	0.000000	0.000000	-1.081809
C	0.000000	0.000000	-2.271934
O	0.000000	0.000000	- 3.425316

$^1[NbCO_2]^+$, TS

$E = -244.235842$

Nb	0.833629	-0.110092	-0.000172
O	-0.781730	1.115361	-0.001430
C	-1.402005	-0.002616	0.006748
O	-2.439114	-0.549179	-0.002751

$^3[NbCO_2]^+$, TS

$E = -244.251285$

Nb	-0.891569	-0.103938	0.000006
O	0.839563	1.054378	0.000081
C	1.552159	0.028503	-0.000335
O	2.565609	-0.543075	0.000137

$^5[NbCO_2]^+$, TS

$E = -244.206774$

Nb	-0.000000	0.824531	0.000000
O	1.172872	-0.728175	0.000000
C	-0.556806	-1.362967	0.000000
O	-0.755267	-2.475323	0.000000

$^1[NbCO_2]^+$, LM2

$E = -244.387368$

C	-0.753362	-1.409755	0.000000
O	-1.053803	-2.505712	0.000000
Nb	-0.000000	0.658062	0.000000
O	1.618824	0.190458	0.000000

$^3[NbCO_2]^+$, LM2

$E = -244.386371$

C	-0.775357	-1.502856	0.000000
O	-1.035096	-2.603169	0.000000
Nb	0.000000	0.665322	0.000000
O	1.616613	0.320537	0.000000

$^5[NbO]^+$, LM2

$E = -244.226517$

C	-0.874707	-1.413068	0.000000
O	-1.255754	-2.477971	0.000000
Nb	0.000000	0.636120	0.000000
O	1.911785	0.277656	0.000000

$^1[NbO]^+$

$E = -131.202282$

Nb	0.000000	0.000000	0.273858
O	0.000000	0.000000	-1.403523

$^3[NbO]^+$

$E = -131.204543$

Nb	0.000000	0.000000	0.269284
O	0.000000	0.000000	-1.380080

$^5[NbO]^+$

$E = -131.037168$

Nb	0.000000	0.000000	0.318538
O	0.000000	0.000000	-1.632507

CCSD

CO_2

$E = -188.298907$

O	0.000000	0.000000	1.159629
C	0.000000	0.000000	0.000000
O	0.000000	0.000000	-1.159629

CO

$E = -113.139474$

O	0.000000	0.000000	0.483757
C	0.000000	0.000000	-0.645009

$^1[NbCO_2]^+$, LM1

$E = -244.271167$

Nb	0.000000	0.000000	1.238169
O	0.000000	0.000000	-1.143892
C	0.000000	0.000000	-2.319508
O	0.000000	0.000000	-3.462094

$^3[NbCO_2]^+$, LM1

$E = -244.277241$

Nb	0.000000	0.000000	1.217605
O	0.000000	0.000000	-1.102435
C	0.000000	0.000000	-2.283980
O	0.000000	0.000000	-3.424806

$^5[NbCO_2]^+$, LM1

$E = -244.296544$

Nb	0.000000	0.000000	1.221051
O	0.000000	0.000000	-1.106832
C	0.000000	0.000000	-2.291185
O	0.000000	0.000000	-3.432664

$^1[NbCO_2]^+$, TS

$E = -244.242879$

Nb	0.866351	-0.106594	-0.000068
O	-0.840045	1.099316	-0.000876
C	-1.496800	0.036312	0.003539
O	-2.477403	-0.580253	-0.001429

$^5[NbCO_2]^+$, TS

$E = -244.222314$

Nb	0.000000	0.822890	0.000000
O	1.205425	-0.712086	0.000000
C	-0.514011	-1.383704	0.000000
O	-0.819917	-2.467447	0.000000

$^1[NbCO_2]^+$, LM2

$E = -244.356034$

C	-0.767515	-1.480727	0.000000
O	-1.040667	-2.566786	0.000000
Nb	0.000000	0.660348	0.000000
O	1.616303	0.293046	0.000000

$^3[NbCO_2]^+$, LM2

$E = -244.361131$

C	-0.783497	-1.529999	0.000000
O	-1.043021	-2.617573	0.000000
Nb	-0.000000	0.664660	0.000000
O	1.630644	0.358690	0.000000

$^5[NbO]^+$, LM2

$E = -244.240456$

C	-0.874623	-1.410369	0.000000
O	-1.254022	-2.465341	0.000000
Nb	-0.000000	0.643502	0.000000
O	1.909989	0.225172	0.000000

$^1[NbO]^+$

$E = -131.176089$

Nb	0.000000	0.000000	0.269278
O	0.000000	0.000000	-1.380051

$^3[NbO]^+$

$E = -131.182472$

Nb	0.000000	0.000000	0.269477
O	0.000000	0.000000	-1.381069

$^5[NbO]^+$

$E = -131.051881$

Nb	0.000000	0.000000	0.319471
O	0.000000	0.000000	-1.637289

CP (Quintet/Triplet); not fully converged

$E = -244.266313, -244.266495$

Nb	-0.660979 -	0.065529	0.003668
O	2.460321	-0.604005	-0.003699
C	1.453202	-0.031124	-0.000576
O	0.874888	1.147521	-0.000013