Structures of $[CoO(CO_2)_n]^-$ and $[NiO(CO_2)_n]^-$ Clusters Studied by Infrared Spectroscopy – Supporting Information

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Measured and Calculated Frequencies and Assignments for $[CoO(CO_2)_n]^-$ and $[NiO(CO_2)_n]^-$ Cluster Ions (Tables S1 and S2):

We report the assigned experimentally measured frequencies, together with the calculated frequencies and assignments of the observed peaks for $[CoO(CO_2)_3]^-$ and $[NiO(CO_2)_n]^-$ (n = 2, 3).

Coordinates of Calculated Structures:

We report the Cartesian coordinates of the core structures calculated and presented in Figure 2, Figure 4 and Figure 7 (see main text) in units of Bohr.

HOMOs of Dominant Calculated Structures (Figures S1 and S2)

We report the HOMOs of the dominant calculated core structures for $[CoO(CO_2)_3]^-$ and $[NiO(CO_2)_n]^-$.

Table S1.

Experimentally measured frequencies, calculated frequencies and assignments of the observed peaks for $[CoO(CO_2)_3]^-$.

Experimental Frequency [cm^{-1}]	Relative Intensity	Calculated Frequency [cm^{-1}]	Calculated Intensity [$km \cdot mol^{-1}$]	Assigned to Isomer(s)
1656	0.1	1654	384.9	^{1}D(1a)
1708	1	1704	950.4	^{1}A(1a)
1815	0.6	1822	629.4	^{1}A(1a)
1841	0.3	1839	758.5	^{1}D(1a)
2343	N/A[a]	2339 – **2340**[b]	586.9	^{1}A(1a) and ^{1}D(1a)

[a] The solvent peak at 2343 cm^{-1} is on a different scale than the other peaks, and we cannot report relative intensity for this peak.

[b] The **bold** number indicates the frequency of the solvent peak due to the most dominant core structure present for $[CoO(CO_2)_3]^-$. See the main text for a discussion of the assignment and Figure 4 for the assigned structures.

Table S2.

Experimentally measured frequencies, calculated frequencies and assignments of the observed peaks for $[NiO(CO_2)_n]^-$.

Number of CO_2 units, n	Experimental Frequency [cm^{-1}]	Relative Intensity	Calculated Frequency [cm^{-1}]	Calculated Intensity [$km \cdot mol^{-1}$]	Assigned to Isomer(s)
2	1671	1	1607	969.9	G(1)
	1754	0.3	1774	690.1	H(1)
	2339	N/A[a]	**2325** – 2344[b]	583.9	G(1) and H(1)
3	1646	0.1	1665	374.6	D(1a)
	1687	1	1685 – 1688	848.6 – 872.4	A(1a) and A(1b)
	1746	0.1	1721	973.8	E(1)
	1839	0.1	1861	598.3	A(1b)
	1880	0.7	1892 – 1903	570.3 – 730.5	A(1a) and D(1a)
	2340	N/A[a]	**2335** – 2348[b]	593.0	All Isomers

[a] The solvent peaks at 2339 cm^{-1} and 2340 cm^{-1} are on a different scale than the other peaks, and we cannot report relative intensity for them.

[b] The **bold** numbers indicate the frequency of the solvent peak due to the most dominant core structure present for a given number of CO_2 units. See the main text for a discussion of the assignment and Figure 7 for the assigned structures.

Coordinates:

$CoO(CO_2)_n^-$

Structure ^{1}A

0.39712223873987	1.33482890221287	-1.06056424075757 Co
-0.08387334416097	-2.09577827538192	-1.43603067771019 O
1.71597194647284	-2.59610731947496	0.25800698458302 C
2.56468268142436	-0.35734503129525	1.06026381716753 O
2.44429142780628	-4.65959694778586	0.93105928333852 O
-1.78589887271409	3.72181702652453	0.19527822860219 C
-3.37024823856621	4.29006891626798	1.70779554795605 O
-0.57784883900218	4.72871272893253	-1.65580894317962 O

Structure ^{3}A

0.32907427702752	1.31346850104496	0.34367794407208 Co
-0.39464646307563	-2.11801446225895	0.72104595586118 O
1.94060132934880	-2.78166629092263	-0.08613774700044 C
3.22506186888565	-0.69928338839435	-0.65665876337358 O
2.69090492863326	-4.94570840729095	-0.24636422147664 O
-2.16641013029268	3.99226159115094	-0.09798205975134 C
-4.23452954171608	4.70446710568755	-0.67689800235931 O
-0.08585726881085	4.90107535098343	0.69931689402809 O

Structure ^{1}B

-0.00000565139406	-0.00001069546181	-0.49002691921838 Co
0.00000090628792	-0.00000719271491	-3.91707200730861 C
-0.00000028724587	0.00000088621861	3.79693101285514 C
2.04582885807356	-0.00001153037889	2.31522948925761 O
-2.04583425786577	-0.00001198466607	2.31523523777915 O
0.00000657066815	0.00001869790583	6.09417055113014 O
2.23062843240546	0.00001070121155	-4.41246173476084 O
-2.23062457092940	0.00001111788569	-4.41247087599228 O

Structure ^{3}B

-0.00004022500543	-0.00008869911107	-0.41628609230421 Co
0.00001591257813	-0.00001482084522	-4.23045232065580 C
-0.00000322776405	0.00006117054826	4.00356024879509 C
2.08372991263221	-0.00000314659360	2.55305899098784 O
-2.08376588159025	-0.00000306112798	2.55310628484488 O
0.00003328158418	-0.00000694268325	6.30459769909834 O
2.18864100369834	0.00002779735756	-4.97681081685064 O
-2.18861077613318	0.00002770245533	-4.97681218804636 O

Structure ^{1}C

0.05466588100429	0.66179409988112	-0.56850433478141	Co
-1.83515591969342	-2.32201504009252	-0.88874747199216	O
0.01412712540385	-3.60642150103266	0.18746964791268	C
1.86074190059637	-1.91374624386145	0.74891903952081	O
0.13120749401811	-5.85128046897597	0.60573599304864	O
-0.33716985586516	4.75695857965287	0.65141059630133	C
1.75255710380173	3.87133382361330	-0.31179515493695	O
-1.86770190925268	2.91935107067530	1.21856117970055	O

Structure ^{3}C

-0.00233718106671	0.55426731564453	0.00604449120878	Co
0.03445421829178	-2.28063762159695	-2.05092622601705	O
-0.00044843265162	-3.79333222065973	-0.02499828444263	C
-0.03448346932533	-2.31384645866411	2.02222662555393	O
-0.00161759753776	-6.08854752394765	-0.04464626672233	O
-0.00071901097404	4.94475131638807	0.04114913541092	C
-0.03584625811059	3.91242597924149	-2.07193135201485	O
0.03095770350830	3.86939579012376	2.13446709931139	O

Structure ^{1}D

0.25687733649391	4.50200598582146	-0.00514380232607	C
0.65461133213275	5.26576720165136	-2.15656417754080	O
0.68671238669335	5.27603313699125	2.13632302892033	O
-0.93949050431001	-1.01378648968538	0.01088988358817	Co
-1.13335345747288	2.12611055174173	0.01055720148810	O
1.53990456744090	-3.44424357497342	-0.00413642922802	C
3.69512333953450	-4.09867103139375	-0.01552351536417	O
-0.68947958373840	-4.46393904125496	0.00696155525508	O

Structure ^{3}D

0.25262879913220	4.61099954145519	-0.00969553057264	C
0.59328270800970	5.38247674504554	-2.16532749660932	O
0.80608496533692	5.31567606575277	2.12392741471482	O
-0.98709033501114	-0.98033729753137	-0.01462232067413	Co
-1.27652013894000	2.20492316744356	0.02568531802814	O
1.56835385823947	-3.63111779315126	0.01580735607472	C
3.74214732532592	-4.18560749978876	0.07137106157573	O
-0.62798176531892	-4.56773619032733	-0.06378205774471	O

Structure ^{1}E

-1.70402501757871	-0.41722728518352	-2.63825399636787	Co
-3.94995298045141	1.14560763320592	-3.88075141666322	O
3.21638944610294	0.08730246800798	-1.80241721848320	C
5.47092446896829	0.35357147272062	-2.06159288817509	O
1.62018044419345	-0.38528023079364	-3.64854802579219	O
1.87373050737227	0.18091629201505	0.82911183145919	C
2.99833240494325	0.51157694938642	2.79045717618822	O
-0.57394635884236	-0.21619979054533	0.64372696355036	O

Structure ^{3}E

-1.72323875998342	0.12161884259611	-2.67104574586768	Co
-4.39479424992737	0.47670787758670	-4.07598249204193	O
3.30160914479930	0.07042999827633	-1.76738339136750	C
5.57508222329256	0.03950776986883	-1.99282718114531	O
1.67169964506160	0.01924722593118	-3.63798728759950	O
1.94860230801000	0.16115348059360	0.87619054022709	C
3.09526013176733	0.21544052932517	2.85157335218088	O
-0.52258752831237	0.15616178463565	0.64919463133009	O

Structure ^{1}F

-4.18437965375663	1.00865227930482	-0.60516951133749	Co
-6.53938770147088	-1.42978935654529	-0.24007949073225	O
0.47866030090285	-0.59833668847461	-1.47994514608492	C
2.31633076912284	-1.42565948359749	-2.53751004727676	O
-1.69713833969466	-0.15110352221538	-2.63785958928701	O
0.39835491079657	0.15636401336299	1.36465850684577	C
2.19784742706367	-0.03479846441263	2.75396502180612	O
-1.82543222626673	1.06264111943502	1.98527822493040	O
-8.10454441052309	-0.31284150647396	-1.92204479452378	C
-10.16016657833313	-1.07379851570653	-2.53087513992678	O
-6.91147049784354	1.75797212532380	-2.69123903441381	O

Structure ^{3}F

-4.13742838830052	-0.09815097834941	-0.95641703884439	Co
-7.25172027402057	-0.18705375117945	0.56515124884959	O
0.87833490934803	-0.10573956813726	-1.58586091464121	C
2.97051994893912	-0.13053067543231	-2.48634912799746	O
-1.23966127782143	-0.07243990078454	-2.90885807771753	O
0.37519071316605	-0.10798457794163	1.32157452671733	C
2.04341783227441	-0.08174187464333	2.87250351118906	O
-2.06423142833246	-0.14249644231098	1.85663067827534	O
-8.40565062551864	-0.07453577623555	-1.69661602768562	C
-10.64399376788691	-0.06039551639989	-2.08488473743694	O
-6.55610364184705	0.02037106141440	-3.43769504070823	O

$NiO(CO_2)_n^-$

Structure A

0.26454316750716	1.28090348804046	-1.05512436829086	Ni
-0.31310639786832	-2.20983495592847	-1.09396544328878	O
1.79160423163158	-2.63888552044550	0.25689506815992	C
2.91182503399442	-0.44971817441746	0.77982305427161	O
2.54374934718440	-4.72455271885357	0.88195726553561	O
-1.90053113230011	3.90596999615393	0.11532628244689	C
-3.68507163667960	4.29656551341989	1.42935481231561	O
-0.30881361346954	4.90615237203070	-1.31426667115004	O

Structure D

0.24744521396789	4.43928395723654	0.04614074315775	C
0.51891351692795	5.34711792366959	-2.08048115097975	O
1.00490185330330	5.06020844042900	2.16088772746462	O
-1.03472863427882	-0.96912204475981	0.13166687677619	Ni
-1.33304359403517	2.24190694920939	0.08327993323223	O
1.47823527997669	-3.49096971441738	-0.08402024199034	C
3.66505578926931	-3.92301274418921	-0.33861132204012	O
-0.65916083783054	-4.49560925915748	0.21495348345071	O

Structure E

-1.83346924953900	0.25409562588746	-2.40855429188264	Ni
-4.12816596768732	0.30758114452458	-4.50535555572959	O
3.19441183126635	0.07455691194152	-1.76908215475636	C
5.45183700313494	-0.01688798243398	-2.13023514310469	O
1.48877301557758	0.12120947687509	-3.56808575457028	O
1.99749596007438	0.15082470458225	0.93217543899813	C
3.25361768978869	0.12520757716285	2.84517364523435	O
-0.47286736790791	0.24368005027378	0.83569624152714	O

Structure F

-4.12106696196098	-0.07003602559091	-0.97524033395090	Ni
-7.18466907951599	-0.14462422556614	0.52737058309747	O
0.86150006050928	-0.08493350233226	-1.55949690297869	C
2.93811249579254	-0.08006800522193	-2.48914006433419	O
-1.26599424797318	-0.04645158676061	-2.88971719248777	O
0.36401924934897	-0.13652396175908	1.34502624885134	C
2.05522287285620	-0.16937326483860	2.87989078721988	O
-2.05187089719095	-0.14073945903942	1.88153901702674	O
-8.38534130044100	-0.07774673610401	-1.73877054920140	C
-10.64103644101212	-0.08502071234948	-2.03583420639172	O
-6.60020175041296	-0.00518052043760	-3.48644838685069	O

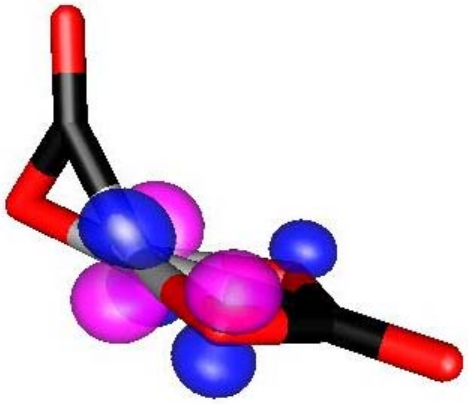
Structure G

-0.00077471170212	-2.17466148633698	0.00096836100828	Ni
-2.09214063181075	0.78146223804789	0.00104814080758	O
0.00019289061004	2.20085943472219	0.00034954351793	C
0.00078465297800	4.52163610206157	-0.00092986072360	O
2.09186785785469	0.78045303291453	0.00105153728115	O

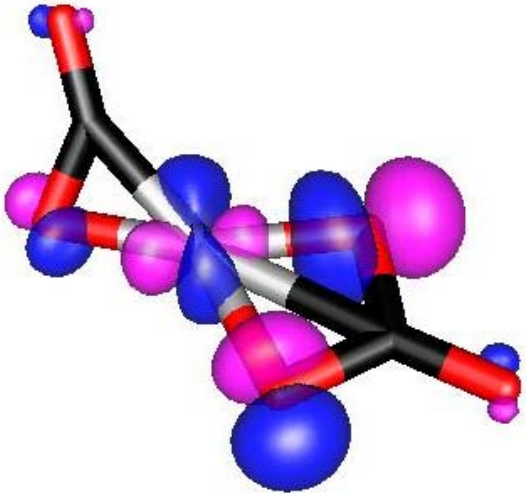
Structure H

-1.12705732145813	-0.30815573563822	-0.12903082225465	Ni
-3.74000176882123	1.37927958390878	-0.14113101437094	O
2.34135889318886	0.24239624050533	-0.04665215574626	C
4.06802340281786	1.71990672572377	0.02176300768367	O
2.01135589603458	-2.13704663761702	-0.10616297629745	O

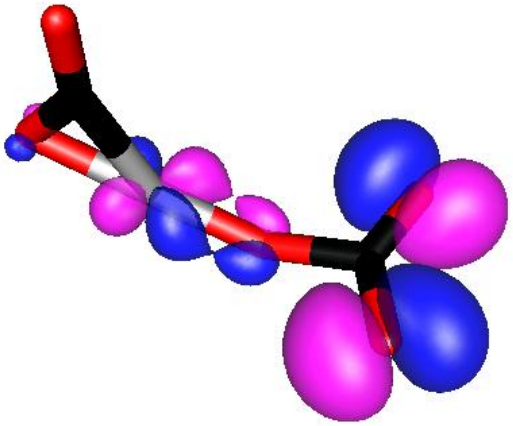
Figure S1: HOMOs of the dominant core structures of $[CoO(CO_2)_n]^-$ clusters.



^{1}A

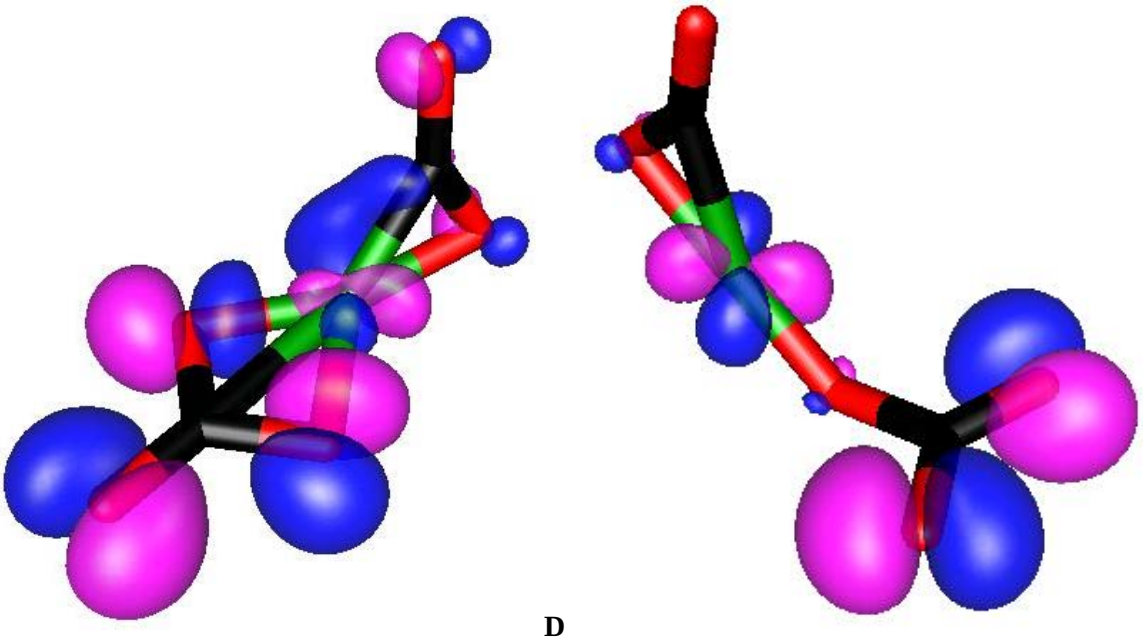


^{3}A



^{1}D

Figure S2: HOMOs of the dominant core structures of $[NiO(CO_2)_n]^-$ clusters.



A **D**