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Structural and Photoelectron Spectroscopic Study on the Heterotrinuclear Nickel-Titanium Dioxide Carbonyl Complexes $Ni_2TiO_2(CO)_n^-$ (n = 2-4)

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Theoretical supplement

The simulated photoelectron spectrum for a given isomer is based on the generalized Koopmans' theorem in the text. This theory was chosen for simulation because generalized Koopmans' theorem enhances the accuracy of simulated photoelectron spectra by adding a correction term compare with other methods (simple FC calculations, namely). The simulations are done by fitting the distribution of calculated vertical detachment energies with unit-area Gaussian functions of 0.1 eV width. In our experiment, the experimental temperature is generally between 200 K and 300 K, and the anion that has not been stripped of electrons has certain stability and the ground state structure is undoubtedly. The starting geometries in this work are built manually since the cluster size is small and the potential energy surface is simple. The frequency analyses at the same level of theory with geometry optimizations were performed to confirm that each optimized structure is a true minimum on potential energy surface without imaginary frequency. The vibrational frequencies are harmonic without augmented or scaled.

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Table S1 The total energies of several anion isomers of $Ni_2TiO_2(CO)_n^-$ (n = 2-4) clusters with different spin multiplicities.

Isomers	Spin multiplicities of anion		
	2	4	6
2*b*	-4244.348743	-4244.262552	-4244.242933
3g	-4357.701052	-4357.658169	-4357.589649
4g	-4471.154167	-4471.119377	-4471.046811

Table S2 The total energies of several neutral isomers of $Ni_2TiO_2(CO)_n$ (n = 2, 3) clusters with different spin multiplicities.

Isomers	Spin multiplicities of neutral		
	1	3	5
2*b*	-4244.286485	-4244.233634	-4244.142455
2*c*	-4244.249117	-4244.221672	-4244.146018
3*a*	-4357.697821	-4357.658967	-4357.582955
3*b*	-4357.689148	-4357.637411	-4357.549248
3*d*	-4357.672637	-4357.626822	-4357.543071

Table S3 Experimental and theoretical vertical detachment energies (VDEs) and adiabatic detachment energies (ADEs) as well as theoretical relative energies (ΔE) of the higher energy structures of $Ni_2TiO_2(CO)_n^-$ (n = 3, 4) clusters.

n	Isomers	ΔE (eV)	VDE (eV)		ADE (eV)	
			Theo.	Exp.	Theo.	Exp.
3	3*d*	0.6	2.87	2.76(4)	2.61	2.43(5)
	3*e*	1.17	2.60		2.49	
	3*f*	1.48	3.20		3.02	
	3*g*	1.88	3.09		2.22	
4	4*d*	0.56	3.15	2.86(3)	2.64	2.60(5)
	4*e*	0.72	3.13		2.88	
	4*f*	0.73	3.64		2.76	
	4*g*	0.84	3.24		1.87	
	4*h*	0.93	3.00		2.70	
	4*i*	1.18	3.06		2.91	
	4*j*	1.18	3.00		2.85	
	4*k*	1.75	3.10		2.84	

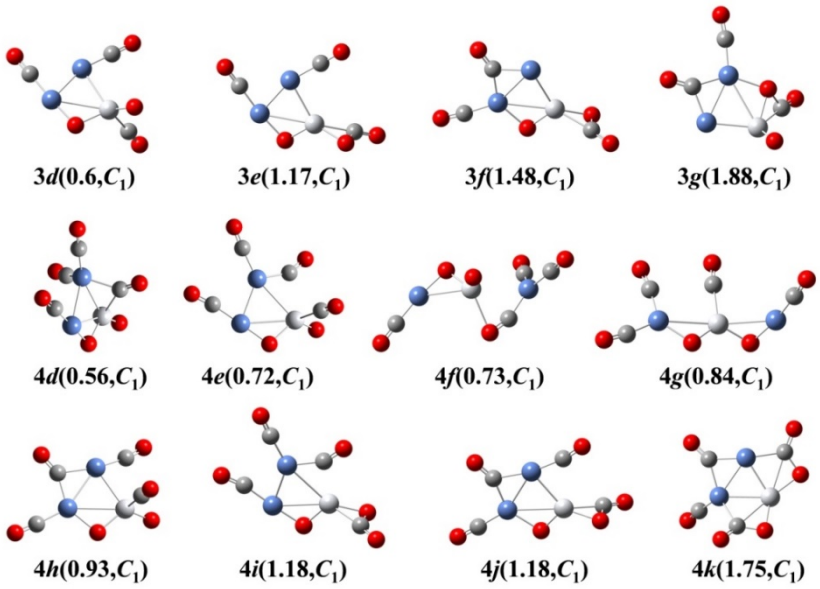

Figure S1 Schematic diagrams of the isomers with higher energies of $Ni_2TiO_2(CO)_n^-$ (n = 3, 4) clusters (Ti, white; Ni, blue; C, gray; O, red). The relative energy (in units of eV) and symmetry of each cluster are in parentheses.

Cartesian coordinates of all carbonyl isomers of $Ni_2TiO_2(CO)_n^-$ (n = 2-4) are shown below. The calculations were performed at the BP86 level of theory.

2*a*

Ti	-0.00008500	-0.25860700	0.00002900
Ni	2.63190000	-0.21260200	-0.28861700
Ni	-2.63192500	-0.21274100	0.28846800
O	1.21552100	-1.22174400	-0.83161600
O	-1.21555600	-1.22187400	0.83171100
C	-3.81119500	0.87724500	-0.25087200
O	-4.59144600	1.66404300	-0.64269900
C	3.81131400	0.87713000	0.25093400
O	4.59171700	1.66366000	0.64300000

2*b*

Ti	1.32027800	-1.15561200	-0.08892800
Ni	0.13305100	1.07093800	0.05241300
Ni	-1.32873500	-0.77274600	-0.19895500
O	2.23824500	-1.92298600	1.07324800
O	-0.14278600	-2.05560100	-0.64633800
C	-2.42898500	0.44843800	0.23294300
O	-3.15931100	1.30649000	0.57410800
C	1.41624700	2.17650800	-0.15445400
O	2.37753700	2.83765000	-0.30243900

2*c*

Ti	-1.89535700	-0.57984300	-0.20942800
Ni	-0.63716200	1.49589600	-0.16638000
Ni	0.86285000	-0.49976200	0.01437800
O	-3.22943300	-0.94066100	0.73469800
O	-0.57633100	-1.75051200	-0.12371800
C	2.47535100	-1.16647100	-0.00631100
O	3.59317100	-1.50185300	-0.01866200
C	1.15944200	1.28842100	0.21204300
O	1.90882400	2.20966400	0.36131900

3a

Ti	0.25724000	-0.32385100	-0.14572400
Ni	2.85357700	-0.06601100	-0.40402200
Ni	-2.34404200	-0.43786400	0.25440300
O	1.46268400	-0.54468100	-1.45492500
O	-0.87349600	-1.55400900	0.41578400
C	-3.96620200	0.14289000	0.31284500
O	-5.06769700	0.52837700	0.35598900
C	3.95226600	0.41162300	0.79034700
O	4.68111800	0.74429600	1.65018500
C	-1.32620700	1.13114400	-0.31277900
O	-1.68828200	2.21592800	-0.63543500

3b

Ti	-1.32290100	-1.22185700	0.00013500
Ni	-0.67766500	1.13774900	0.00001400
Ni	1.32059400	-0.32749800	-0.00013400
O	-2.62679000	-2.27419300	-0.00046500
O	0.28894100	-1.94192400	-0.00012900
C	3.04644500	-0.60330300	0.00019800
O	4.20777400	-0.70459800	0.00052800
C	1.21444400	1.47035100	-0.00022900
O	1.71483900	2.55493900	-0.00042300
C	-2.42488200	1.13937100	0.00025300
O	-3.57404200	1.38519200	0.00036900

3c

Ti	0.18789900	-0.01360500	-0.02098100
Ni	2.77528900	-0.41398400	-0.36494300
Ni	-2.42578000	0.06830000	0.08784000
O	1.22130500	-0.86469300	-1.18335000
O	-0.97612700	-0.99104200	0.84869200
C	-4.13035300	-0.39398800	0.19062700
O	-5.28796600	-0.53375500	0.25878200
C	4.06503600	0.15383100	0.57062400
O	4.93119900	0.57243300	1.24570500
C	-1.48679500	1.47540100	-0.41783700
O	-0.46433000	2.13793300	-0.39983200

3d

Ti	1.27756700	-0.63664800	0.46700000
Ni	-0.58427600	1.05850700	-0.00422800
Ni	-1.44647200	-1.09013100	-0.04913700
O	2.23663900	-0.63007600	1.83599200
O	0.03971600	-1.99408700	0.25628500
C	-2.82223100	-0.13257300	-0.33259200
O	-3.78442300	0.51530500	-0.53102600
C	0.51863800	2.34321700	0.13748800
O	1.26138200	3.23963200	0.25850500
C	2.71658700	-0.51881100	-1.10770700
O	3.53125100	-0.53818300	-1.94011600

3e

Ti	1.12375000	-0.56123200	0.24187200
Ni	-0.73555700	1.03499200	0.06388700
Ni	-1.49809700	-1.16654500	-0.11364900
O	2.83153600	-0.64251200	1.01146800
O	0.11089600	-1.98659100	-0.10014300
C	-2.90196800	-0.20653800	-0.10971300
O	-3.88509600	0.44078500	-0.07647100
C	0.34214400	2.35306400	-0.05235500
O	1.07327200	3.26776900	-0.06069500
C	3.09241900	-0.42388500	-0.37531300
O	4.19741900	-0.36760800	-0.86210600

3f

Ti	-1.45742000	-0.16432200	0.20553700
Ni	0.10057300	1.63948700	-0.05133800
Ni	1.26406800	-0.56906000	-0.00035300
O	-3.20216000	0.35435100	0.98216900
O	-0.40519100	-1.53267200	0.14232700
C	2.69737400	-1.56814200	-0.09928500
O	3.71643000	-2.12845100	-0.16486400
C	1.89331400	1.13380600	-0.02886400
O	2.78639400	1.92593500	-0.06109900
C	-3.44608000	-0.42622900	-0.36645800
O	-4.52226800	-0.55964600	-0.91188700

3*g*

Ti	1.79877800	-0.38171700	0.17495600
Ni	-0.09952100	-1.76021500	-0.45418600
Ni	-0.88380400	0.50889300	0.14153500
O	2.79034000	-0.84419500	1.41823200
O	0.90021000	1.33670000	0.35270500
C	-2.17859900	1.67920500	0.31225100
O	-3.10920600	2.36866400	0.42092200
C	-1.75800000	-1.08131800	-0.08139200
O	-2.79527200	-1.67181200	-0.11338900
C	1.99436400	1.55732700	-0.64030200
O	2.16560300	2.62358300	-1.15823700

4*a*

Ti	-0.00005700	-0.51450000	-0.00029900
Ni	2.62456500	-0.30828500	-0.33500800
Ni	-2.62482100	-0.30902500	0.33461800
O	1.23417700	-1.30780300	-1.00769100
O	-1.23444500	-1.30993000	1.00521600
C	-4.21845400	0.29960100	0.07964900
O	-5.30163800	0.70110100	-0.08628200
C	4.21849000	0.29963400	-0.08006300
O	5.30185500	0.70078200	0.08559400
C	-1.55021500	0.76994600	-0.87553100
O	-1.85723300	1.59632400	-1.66450000
C	1.55081100	0.76774900	0.87767100
O	1.85786400	1.59228900	1.66855500

4*b*

Ti	1.13852200	-1.65478800	-0.22581400
Ni	0.73215500	1.02847100	0.40683600
Ni	-1.32777400	-0.28925600	-0.11081600
O	2.22037200	-2.17460300	-1.38438700
O	-0.55776100	-1.98751000	-0.56561400
C	-3.07777600	-0.44503100	-0.06869900
O	-4.23848100	-0.47295200	-0.00280800
C	1.69926500	2.23185600	-0.47793600
O	2.37470200	2.95558400	-1.08831700
C	1.35618000	-0.16876200	1.54484800
O	1.71407500	-1.27028200	1.91618200
C	-1.13307500	1.51873100	0.02249900
O	-1.69261900	2.56057900	-0.05567300

4*c*

Ti	1.22158500	-1.41759800	0.08428900
Ni	0.70874200	1.01476500	-0.01794000
Ni	-1.38533700	-0.38587600	0.00583600
O	2.39348000	-2.59150400	-0.08231000
O	-0.40771500	-2.04999800	0.09324600
C	-3.11933200	-0.60899800	-0.00209500
O	-4.28170200	-0.67633200	-0.01135100
C	-1.21419200	1.43611600	-0.07040200
O	-1.79099200	2.46955600	-0.12186600
C	1.47994600	1.13027700	1.57926600
O	1.99899400	1.27995200	2.61935000
C	1.53935800	0.99511100	-1.58918500
O	2.08232400	1.05123000	-2.62468600

4*d*

Ti	-1.93030100	0.00090200	0.10530600
Ni	0.55906600	0.81349400	-0.11257200
Ni	0.21828500	-1.74091600	-0.10428800
O	-3.51831800	0.51888300	0.17497500
O	-1.57241700	-1.76766900	0.00926300
C	1.91275100	-1.74144500	-0.27114200
O	3.07364100	-1.81171700	-0.39836200
C	-0.31886400	1.35368800	-1.55439200
O	-0.79367900	1.83246900	-2.51188000
C	2.13506000	1.54859700	0.23242100
O	3.13191000	2.10236800	0.45970400
C	-0.43958600	0.72295400	1.59792000
O	-0.20055800	0.95631900	2.73211300

4*e*

Ti	-1.70733800	-0.44425000	-0.34762800
Ni	0.83672700	0.73416900	-0.10732200
Ni	0.74054000	-1.65759600	0.12576100
O	-2.88255700	-0.45547600	-1.53420200
O	-0.98288000	-2.05675100	0.11255100
C	2.40808800	-1.30904000	0.08461000
O	3.57739900	-1.21627800	0.05345600
C	-0.54413000	1.64660400	-0.75275000
O	-1.02460800	2.60553900	-1.23633400
C	-2.73656100	0.45279400	1.31485400
O	-3.33394400	0.90129000	2.20058600
C	2.10687900	1.86722200	0.31245200
O	2.89562800	2.68217200	0.57600900

4f

Ti	-0.31123400	-0.80558000	0.30873900
Ni	-2.78948600	0.36768700	0.50712800
Ni	2.33769000	0.32138800	-0.47569500
O	-1.22128700	0.29986000	1.37080700
O	-0.11780200	-2.32241000	0.93914400
C	3.56550200	-0.81587000	0.16199500
O	4.34041100	-1.55896700	0.60109000
C	-4.16115900	0.23271800	-0.48069300
O	-5.08976400	0.11919800	-1.18989500
C	1.06973900	-0.24143300	-1.56038800
O	0.02518400	-0.69804400	-1.94368400
C	2.36535300	2.00210600	0.14054500
O	2.37086300	3.08080400	0.56739300

4g

Ti	0.39925400	-0.19981400	-0.59948000
Ni	3.04428200	-0.43023300	-0.25610600
Ni	-2.32268600	-0.32890600	0.11344400
O	1.82237600	-0.68038800	-1.55714400
O	-0.84414000	-1.40706100	-0.28374300
C	-2.60919200	1.39687300	0.22715600
O	-2.97928100	2.49772000	0.33424600
C	3.95666100	-0.18356600	1.15136800
O	4.56015600	-0.00776200	2.14196600
C	0.29465400	1.89215300	-0.36493500
O	0.30921200	3.05371000	-0.28032100
C	-3.81038100	-1.22964700	0.44909900
O	-4.86566500	-1.65660400	0.69587000

4h

Ti	-1.24768400	-0.96349800	-0.47186300
Ni	-0.37537200	1.28642700	0.12267900
Ni	1.49145100	-0.33814800	-0.15694000
O	-2.47889500	-1.42551800	-1.52039000
O	0.35008000	-1.75266500	-0.66882000
C	3.18436700	-0.78216300	-0.13648400
O	4.32820400	-0.99287300	-0.09253700
C	1.53784000	1.36792600	0.39301400
O	2.10372300	2.34729500	0.76916400
C	-2.00304700	1.63712700	-0.40235900
O	-3.02967900	2.09095300	-0.72160700
C	-1.95592600	-1.35149300	1.53591700
O	-2.32100400	-1.59009500	2.60915900

4i

Ti	1.57885400	-0.21061900	-0.34639100
Ni	-1.09011600	0.65410200	-0.00545700
Ni	-0.65705600	-1.67568300	-0.02240000
O	3.36996100	0.18235100	-0.78074700
O	1.10709800	-1.91104500	-0.26266200
C	-2.32830200	-1.37233400	0.19749200
O	-3.49034400	-1.45574900	0.35011500
C	0.29860700	1.73868000	-0.23617600
O	0.78704400	2.80700600	-0.38069800
C	-2.50052100	1.68105100	0.14359500
O	-3.40093400	2.41437800	0.23291200
C	3.34412400	0.21481500	0.62186400
O	4.28999900	0.42113600	1.34607300

4j

Ti	-1.20534900	-0.64430900	-0.32479800
Ni	0.03626700	1.42097600	0.00326300
Ni	1.54444600	-0.53682000	-0.00661000
O	-2.92047200	-1.25925200	-0.87960500
O	0.09950500	-1.77276300	-0.24949500
C	3.11080600	-1.31963400	0.06423700
O	4.18548000	-1.76189200	0.12154200
C	1.93902200	1.19952700	0.18432400
O	2.69251100	2.11157200	0.33086400
C	-1.62309700	1.96932400	-0.06437300
O	-2.64693300	2.53544300	-0.10840100
C	-2.99852900	-1.26798700	0.50531800
O	-3.94903000	-1.61172700	1.17287300

4k

Ti	0.80035300	1.24702200	0.36942400
Ni	1.02991800	-0.88038800	-0.45172300
Ni	-1.21419600	-0.22153800	-0.04181900
C	2.65899100	-0.15077500	0.33628200
C	-1.21079400	1.69795500	-0.69437200
O	2.57888700	1.07006700	0.99564200
O	-2.13913400	1.94814000	-1.45018900
O	3.69971100	-0.79981600	0.27659100
O	-0.25411200	2.63279500	-0.35932400
C	-2.58956000	-0.51687800	1.01287900
C	-0.51879300	-1.92826200	-0.51389600
O	-3.44397100	-0.66520500	1.79103200
O	-0.75225900	-3.08508100	-0.64794000