

CO Coordination at XNi₄ Clusters with Impurities X = H, C, O. A Density Functional Study

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We report a computational investigation of CO adsorption on small nickel clusters that contain single impurity atoms H, C, or O. At bare Ni₄ and clusters with H or O impurity, the most stable coordination of the probe molecule is on top of a Ni atom which interacts with the impurity. The CNi₄ cluster is an exception where 3-fold coordination of CO was determined to be more stable than that on top, however, by 4 kJ/mol only. Our results suggest that the heteroatoms X (X = H, C, O) affect only weakly the reactivity of the cluster with respect to CO; the binding energy of CO in the most stable complexes (CO)XNi₄ increases at most by 10% compared to the value for bare Ni₄, 194 kJ/mol. The impurity induces a small decrease of the CO infrared frequency shift for on-top coordinated CO, compared to Ni₄, because of partial oxidation of the metal moiety. A notable difference is predicted for clusters that contain a C impurity because of the different preferred coordination mode which results in a strong CO frequency red shift of ~300 cm⁻¹. The calculated characteristic CO frequency shifts may be helpful in identifying experimentally clusters with impurity atoms.

1. Introduction

Controlled addition of single nonmetal atoms to small transition metal clusters is a promising approach for tailoring their chemical, optical, electronic, and magnetic properties,¹ beyond simply changing the cluster size or the metal.² Such heteroatoms may also be present on clusters because of reactions with gas molecules^{3,4} or surface species during the preparation of heterogeneous catalysts, including supported transition metal clusters.⁵ Reliable detection of impurity atoms in small transition metal clusters is key for understanding cluster properties modified because of the presence of a heteroatom. In our previous computational studies, we explored various indicators of the reactivity of small Ni_n (n = 4–6) clusters that are ligated by single H, C, or O atoms: ionization potential, electron affinity, detachment energy of a Ni atom from the cluster, and total hardness.⁶ The two latter parameters were found to vary at most by 10% compared to the value of the corresponding bare cluster; that is, the presence of the nonmetal impurity atom modifies only weakly the properties of the cluster. In the present work, we studied a direct estimate of the reactivity of ligated clusters, their interaction with a carbon monoxide probe.^{7,8} We calculated structure and stability of (CO)Ni₄ and (CO)XNi₄ complexes. We also explored the possibility of using CO for detecting nonmetal atoms as impurities of small metal clusters and eventually determining the type of impurity atom. Very recently, the effect of additives on the vibrational frequency of CO adsorbed on metal clusters of defined size was studied experimentally for Co_n⁺ clusters, partially covered by hydrogen.⁹ As a general trend, the increase of the CO frequency with the amount of adsorbed hydrogen was rationalized by the gradual oxidation of the metal cluster, and the effective charge of the cluster was estimated from the CO frequency shift. In this connection and for comparison with results with XNi₄ clusters,

we also modeled CO adsorption on the charged bare clusters Ni₄⁺ and Ni₄⁻.

2. Computational Details

We carried out density functional calculations by using the linear combination of Gaussian-type orbitals fitting-functions density functional (LCGTO-FF-DF) method,¹⁰ as implemented in the program PARAGAUSS.^{11,12} We applied the unrestricted Kohn–Sham procedure with the gradient-corrected exchange–correlation functional suggested by Becke (exchange)¹³ and Perdew (correlation).¹⁴ The Kohn–Sham orbitals were represented by the same Gaussian-type basis sets as the ones used in our previous studies:⁶ (15s11p6d) → [6s5p3d] for Ni atoms, (9s5p2d) → [5s4p2d] for C and O atoms, and (6s1p) → [3s1p] for H. The auxiliary basis set employed in the LCGTO-FF-DF method to describe the Hartree part of the electron–electron interaction was derived from the orbital basis sets in the usual fashion¹⁰ and augmented by five p-type and five d-type polarization exponents for each atom. These exponents were constructed as geometric series with a factor 2.5, starting with 0.1 and 0.2 au for p- and d-exponents, respectively; for hydrogen, only the p-type series was applied.

The relative stability of the complexes was estimated by the binding energy (BE) of CO to the cluster (Table 1). The geometry optimizations were started with the most stable structures of XNi₄ (X = H, C, or O) previously obtained.^{6a} On these clusters, we performed a detailed search of possible locations of a CO ligand and verified each structure as local minimum with respect to variations in spin multiplicity and structure (normal-mode analysis without symmetry constraints). For the latter purpose, we estimated second-order energy derivatives as finite differences of analytic gradients.¹⁵ In addition to quantify vibrational frequencies $\nu_{\text{calc}}(\text{CO})$, we provide also frequency values (Table 1), shifted by 40 cm⁻¹. This correction corresponds to the difference between the calculated harmonic frequency, 2103 cm⁻¹, of CO in the gas phase and

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TABLE 1: Calculated Characteristics of CO Adsorbed at Clusters Ni₄, Ni₄⁺, Ni₄⁻, and XNi₄^a

structure	Ns	Ns ₀ ^b	BE	$\nu_{\text{calc}}(\text{CO})$	$\nu_{\text{corr}}(\text{CO})^c$	Int.	$q(\text{X})$	$q(\text{CO})$	$q(\text{Ni}_4)$
(η -CO)Ni ₄	2	4	194	1964	2004	1215		-0.39	0.39
(μ -CO)Ni ₄	4	4	180	1779	1819	538		-0.26	0.26
(μ_3 -CO)Ni ₄	4	4	153	1745	1785	525		-0.35	0.35
[(η -CO)Ni ₄] ⁺	3	3	157	2066	2106	751		0.02	0.98
[(μ -CO)Ni ₄] ⁺	3	3	122	1886	1926	487		-0.15	1.15
[(μ_3 -CO)Ni ₄] ⁺	1	3	94	1713	1753	505		-0.21	1.21
[(μ -CO)Ni ₄] ⁻	5	5	223	1706	1746	656		-0.58	-0.42
(η -CO)HNi ₄	3	5	213	1977	2017	1145	-0.33	-0.37	0.70
(¹ η -CO)HNi ₄	3	5	181	1969	2009	1006	-0.38	-0.31	0.69
(μ -CO)HNi ₄	1	5	167	1801	1841	610	-0.37	-0.46	0.83
(μ_3 -CO)HNi ₄	3	5	167	1705	1745	407	-0.41	-0.37	0.78
(η -CO)CNi ₄	2	2	189	1981	2021	1400	-0.78	-0.45	1.23
(¹ η -CO)CNi ₄	2	2	188	1986	2026	1399	-0.67	-0.41	1.08
(μ -CO)CNi ₄	0	2	185	1819	1859	633	-1.25	-0.71	1.96
(μ_3 -CO)CNi ₄	0	2	193	1721	1761	500	-0.99	-0.47	1.46
(η -CO)ONi ₄	4	4	194	1993	2033	998	-0.69	-0.35	1.04
(¹ η -CO)ONi ₄	4	4	157	1990	2030	999	-0.67	-0.22	0.89
(μ -CO)ONi ₄	2	4	144	1787	1827	576	-0.68	-0.43	1.11
(μ_3 -CO)ONi ₄	2	4	103	1667	1707	410	-0.62	-0.27	0.89

^a Number Ns of unpaired electrons, BE of CO (kJ/mol), CO frequency $\nu_{\text{calc}}(\text{CO})$ and corrected CO frequency $\nu_{\text{corr}}(\text{CO})$ (cm⁻¹), calculated IR intensity Int. (km/mol), PDCs q (e) of the impurity X, CO, and the Ni₄ moiety. ^b Number of unpaired electrons in the cluster before adsorption of CO, ref 6a. ^c Shifted by 40 cm⁻¹ from the calculated value, i.e., $\nu_{\text{corr}}(\text{CO}) = \nu_{\text{calc}}(\text{CO}) + 40$ cm⁻¹; see text. The harmonic vibrational frequency of CO in the gas phase is $\nu_{\text{calc}}(\text{CO}) = 2103$ cm⁻¹.

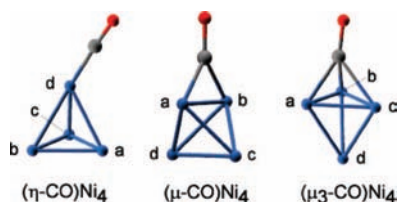


Figure 1. Sketches of various calculated structures of neutral (CO)Ni₄. The structures of the corresponding charged complexes are similar.

the measured CO frequency, 2143 cm⁻¹, which includes an anharmonic contribution.⁷ The electron density distribution in the complexes was estimated by potential-derived atomic charges (PDCs), derived from the electrostatic potential.¹⁶

3. Results and Discussion

3.1. CO Adsorption on Neutral and Charged Ni₄ Clusters.

We were able to identify three stable structures of CO bound to tetrahedral Ni₄, (η -CO)Ni₄, (μ -CO)Ni₄, and (μ_3 -CO)Ni₄ (Figure 1), with BE values of CO decreasing as the coordination of CO increases, 194, 180, and 153 kJ/mol, respectively (Table 1). In the most stable neutral complex, (η -CO)Ni₄, the CO molecule is coordinated with a C–Ni^d distance of 174 pm and slightly tilted toward a triangular face of the tetrahedron. Two Ni–Ni bonds with the Ni^d atom at the top, Ni^b–Ni^d and Ni^c–Ni^d, are ~ 10 pm longer than the other Ni–Ni bonds in the cluster, which hardly change from bare Ni₄ (Table 2).

Similarly to neutral species, in the cationic complexes, the most stable structure is [(η -CO)Ni₄]⁺ with BE(CO) = 157 kJ/mol; here, the on-top coordinated ligand is 37 kJ/mol weaker bound than that in the neutral complex. A similar trend was also calculated for (CO)Pt₄ complexes.¹⁷ In contrast, for CO adsorption on neutral and cationic Rh₄ clusters, only 3-fold coordination was experimentally observed.¹⁸

We obtained only one stable structure for the anionic complex [(μ -CO)Ni₄]⁻; this structure with bridge coordinated CO has the highest BE value of CO, 223 kJ/mol, among all bare or ligated clusters studied here (Table 1).

3.2. CO Adsorption on Ni₄ Clusters with an Impurity Atom. For each type of impurity X = H, C, O, we determined four stable complexes with a CO ligand: (η -CO)XNi₄, (¹ η -

CO)XNi₄, (μ -CO)XNi₄, and (μ_3 -CO)XNi₄. The two η designators label systems where the probe coordinates at Ni centers close to an (η -CO) or farther from an impurity (¹ η -CO), Figures 2–4. The coordination modes of the impurity atom remain as in the initial structures (μ -H)Ni₄, (μ_4 -C)Ni₄, and (μ -O)Ni₄.⁶ For H and O, complexes are most stable where CO is coordinated on top of a Ni atom bound to the impurity; the corresponding complexes with CO at distant Ni atoms are less stable by 32 and 37 kJ/mol, respectively (Table 1). (μ_4 -C)Ni₄ complexes with CO at on-top, bridge, and 3-fold positions are essentially degenerate, BE(CO) = 185–193 kJ/mol; (μ_3 -CO)CNi₄ is most stable (Table 1). The BE values of CO in the most stable structures with O (on-top CO) or C (3-fold CO) impurities are essentially the same, 194 kJ/mol, as in the most stable complex (CO)Ni₄ (on-top CO). However, an H impurity (on-top CO) at Ni₄ increases the CO BE by 19 kJ/mol with respect to Ni₄. An O heteroatom at Ni₄ as well as ionization/oxidation of Ni₄ to Ni₄⁺ strongly destabilize the bonding of CO in bridge and 3-fold coordination, by 36–59 kJ/mol.

Although the overall structure of the XNi₄ clusters is preserved after coordination of CO, the new ligand induces some changes in the interatomic distances in the cluster (Table 2). In the complex with linear coordination of CO to HNi₄, the position of H is more asymmetric with Ni^a–H/Ni^b–H bonds of 170/163 pm in (η -CO)HNi₄ and 169/162 pm in (¹ η -CO)HNi₄, whereas in the initial HNi₄ cluster, both Ni–H bonds are the same, 165/165 pm.^{6a} In addition, the bond Ni^a–Ni^b, to which H is coordinated, is shortened by 9–15 pm compared to the corresponding distance of HNi₄.

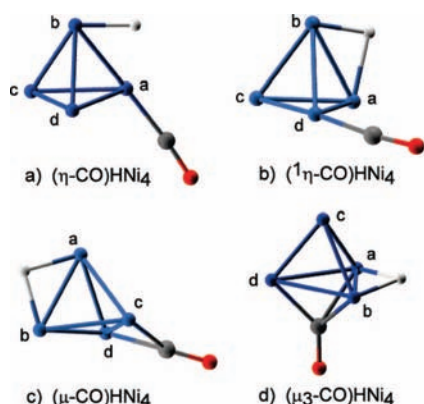
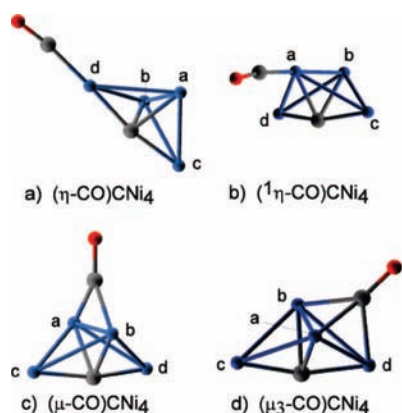
In contrast to complexes with H impurity, the Ni–Ni bond to which the heteroatom O is coordinated is significantly extended in the complex (η -CO)ONi₄, $R(\text{Ni}^a\text{–Ni}^b) = 282$ pm; here, the center Ni^a coordinates two ligands (Figure 4(a)). In the structure (¹ η -CO)ONi₄, this bond is 251 pm, close to the corresponding Ni–Ni bond of ONi₄, 252 pm. In all carbonyl complexes of ONi₄, the distances Ni–O, 175–180 pm, are close to those in the initial cluster ONi₄, 178/178 pm.

In complexes with a C impurity, particularly in (η -CO)CNi₄ and (¹ η -CO)CNi₄, linear coordination of CO correlates with extended Ni–Ni bonds, by 9–17 pm, in that part of the metal

TABLE 2: Interatomic Distances (pm) Calculated for (CO)Ni₄ and (CO)XNi₄ Species, X = H, C, and O^a

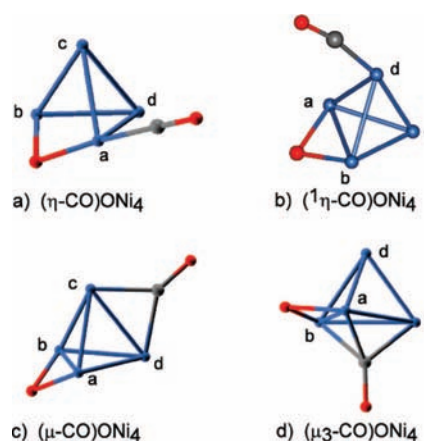
	C–O	C–Ni ^a	C–Ni ^b	C–Ni ^c	C–Ni ^d	Ni ^a –X	Ni ^b –X	Ni ^{c,d} –X	Ni ^a –Ni ^b	Ni ^a –Ni ^c	Ni ^a –Ni ^d	Ni ^b –Ni ^c	Ni ^b –Ni ^d	Ni ^c –Ni ^d
free CO	114.0													
bare Ni ₄									228	229				245
(η -CO)Ni ₄	117.0				174				228	228	232	227	239	239
(μ -CO)Ni ₄	119.3	188	188	315					224	234	234	234	234	261
(μ_3 -CO)Ni ₄	119.6	188	207	207					228	228	239	240	233	233
[(η -CO)Ni ₄] ⁺	114.9				181				228	230	234	228	236	236
[(μ -CO)Ni ₄] ⁺	117.4	188	188	327					227	235	235	235	235	246
[(μ_3 -CO)Ni ₄] ⁺	120.2	184	191	191					247	247	234	236	232	232
[(μ -CO)Ni ₄] ⁻	120.7	187	187	314					256	232	232	232	232	236
(η -CO)HNi ₄	116.5	175				170	163		232	246	235	231	234	222
(¹ η -CO)HNi ₄	116.6				175	169	162		226	234	230	230	251	233
(μ -CO)HNi ₄	119.2			182	187	161	159		229	240	237	239	237	232
(μ_3 -CO)HNi ₄	120.6	198	198		186	166	166		222	233	255	233	255	229
(η -CO)CNI ₄	116.4				176	186	182	184/185	229	235	261	233	256	
(¹ η -CO)CNI ₄	116.3	176				185	195	176/176	237	253	253	236	236	
(μ -CO)CNI ₄	118.8	187	186			183	184	175/175	241	252	252	252	252	
(μ_3 -CO)CNI ₄	120.6	195	194		195	188	190	176/182	227	242	248	243	248	
(η -CO)ONi ₄	116.3	175				176	178		282	243	243	231	231	227
(¹ η -CO)ONi ₄	116.1				178	178	178		251	234	240	234	240	231
(μ -CO)ONi ₄	119.4			183	183	175	175		244	239	239	238	238	243
(μ_3 -CO)ONi ₄	121.4	194	194	183		180	180		241	233	263	233	263	229

^a For the labeling of the Ni atoms see Figures 1–4.

Figure 2. Sketches of calculated structures of (CO)HNi₄ species.Figure 3. Sketches of calculated structures of (CO)CNI₄ species.

moiety where coordination occurs, whereas the Ni–Ni bonds distant of CO are 9–11 pm shorter than in the initial CNI₄ cluster. The Ni–X distances, X = C, in complexes with CO are similar or even somewhat shorter than the distances in the initial CNI₄ cluster.^{6a}

In summary, an impurity atom X at Ni₄ hardly modifies the BE of CO, at most by 10%. Phrased differently, a heteroatom X affects only weakly the reactivity of Ni₄ with respect to CO and similar reactants. This finding corroborates our earlier

Figure 4. Sketches of calculated structures of (CO)ONi₄ species.

conclusions regarding the reactivity of XNi_n clusters on the basis of estimates of the hardness.^{6b} A notable difference with respect to bare Ni₄ is the relative order of the stability of the structures with different coordination of CO on the cluster CNI₄: 3-fold coordination is more stable than on-top.

3.3. Electronic Properties. On-top coordination of CO at the bare Ni₄ cluster results in a strong stabilization of the 5 σ orbital of CO, which shifts 0.23 eV below the 1 π levels because of a destabilization of the latter (Figure 5). The orbitals located at the Ni moiety are weakly affected by the interaction with the ligand; only the type of the HOMO changes from minority spin in the bare cluster to majority spin in (η -CO)Ni₄. Concomitantly, the number of unpaired electrons in the complex decreases by 2 compared to the bare cluster. In the cationic (η -CO)Ni₄⁺ cluster, the orbital energy picture is similar, except for a stabilization of all CO related orbitals because of the charge of the cluster. The same holds for clusters with a hydrogen impurity and different location of the η -CO ligand; in all cases, the 5 σ orbital of CO is slightly more stable than the 1 π orbitals. In addition, in the complex (η -CO)HNi₄ with CO bound close to the impurity, the H–Ni bonding majority and minority spin orbitals are destabilized by 0.78 and 0.57 eV, respectively, whereas in the complex with distant location of CO, the destabilization of these orbitals is only 0.18 and 0.23 eV, respectively.

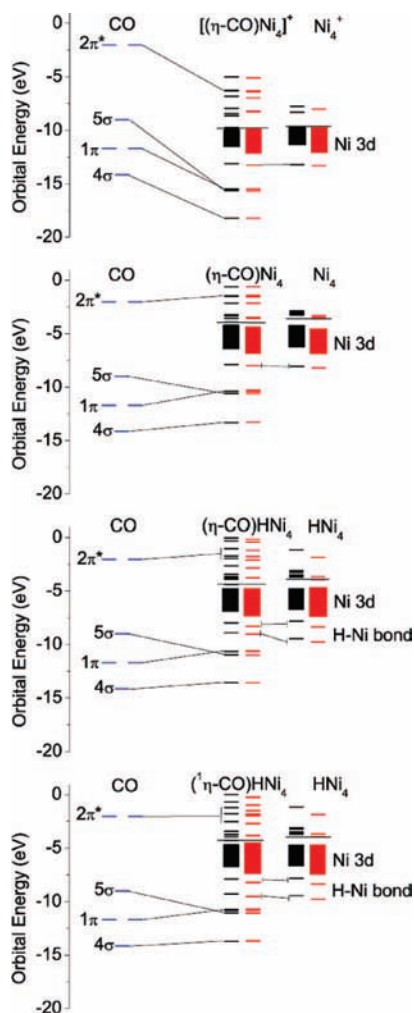


Figure 5. Orbital energies in selected complexes with on-top coordinated CO: $[(\eta\text{-CO})\text{Ni}_4]^+$, $(\eta\text{-CO})\text{Ni}_4$, $(\eta\text{-CO})\text{HNi}_4$, and $({}^1\eta\text{-CO})\text{HNi}_4$. Minority and majority levels shown in black and red, respectively. The HOMO of each cluster is shown as a horizontal black line.

Essentially in all complexes, the charge of the CO molecule is negative, even for bridge and 3-fold coordination to the cationic cluster Ni_4^+ . This result suggests that π back donation from the metal moiety to CO dominates over σ donation from the CO ligand. For all species with impurity atoms, complexes with bridge coordination of CO feature the highest negative charge of CO: -0.46 , -0.71 , and -0.43 e for H, C and O, respectively. Similarly to the clusters XNi_4 , the impurity atoms in the complexes with CO are negatively charged. For example, in the complexes with linearly coordinated CO, the negative charge of the impurity atoms is $q(\text{H}) = -0.38$ to -0.33 e, $q(\text{C}) = -0.78$ to -0.67 e, and $q(\text{O}) = -0.67$ to -0.69 e (Table 1). These values agree within ± 0.1 e with the corresponding impurity charges of clusters without CO ligand.^{6a}

Typically, the coordination of CO at transition metal clusters reduces the magnetism of the cluster.^{1a,19,20} This change of the magnetic moment was rationalized by a destabilization of the valence *s* levels of the metal atom interacting with the ligand(s), which fills of the partially empty *d* manifold of the bare cluster. This trend is also observed in the complexes reported; however, there are exceptions because some of the metal atoms do not interact with the ligand (Table 1). For bare Ni_4 , the CO ligand reduces the number *N_s* of unpaired electrons by two only for on-top coordination, whereas for $\mu\text{-CO}$ and $\mu_3\text{-CO}$, the value,

N_s = 4, does not change. For the complexes with C or O impurity, the trend is opposite: the value of *N_s* is reduced by two for bridge and 3-fold coordination, whereas *N_s* does not change for on-top coordination. For HNi_4 , the CO adsorption results always in a decrease of *N_s* by 2 or 4 electrons.

3.4. Vibrational Frequencies. As expected, we calculated red-shifted (relative to free CO) vibrational frequencies for CO adsorbed at Ni_4 , Ni_4^+ , and Ni_4^- . The higher coordination of CO in neutral and cationic complexes results in larger frequency shifts (Table 1), in agreement with the trend observed previously for CO bound at Pt_4 .¹⁷ In addition, for CO at on-top or bridge positions, the frequency red-shift decreases with increasing positive charge of the cluster. For $(\eta\text{-CO})\text{Ni}_4$, we calculated a red-shift of $\nu(\text{CO})$, 139 cm^{-1} , stronger than that for $(\eta\text{-CO})\text{Ni}_4^+$, 37 cm^{-1} . The red-shift decreases when $\mu\text{-CO}$ binds to the bare clusters in the order Ni_4^- , Ni_4 , and Ni_4^+ (Table 1). For 3-fold coordination, however, the red-shift of CO at the cationic cluster is by 32 cm^{-1} larger than at the neutral cluster. The C–O bond is 0.6 pm longer in the former complex than in the neutral complex, at the expense of much shorter C–Ni bonds; concomitantly, the average C–Ni distance is 12 pm shorter in the cationic species.

For the complexes $(\eta\text{-CO})\text{XNi}_4$ with linear CO coordination at Ni atoms close to the impurity atom, the calculated reduction of the CO frequency red-shift can be rationalized by the reduced electron density on the Ni_4 moiety in consequence of the oxidation due to the impurity atom. The PDCs¹⁶ of the Ni_4 moiety of HNi_4 , CNi_4 , and ONi_4 are 0.33 , 0.82 , and 0.78 e, respectively; the CO frequency red-shifts for on-top coordination, 126 , 122 , and 110 cm^{-1} (Table 1), fall between the values for Ni_4 and Ni_4^+ (see above). There does not seem to be a clear correlation between the CO frequency shift and the charge of the Ni atoms at which CO binds.^{6a}

As in bare Ni_4 , the CO frequency shift of complexes with a bridge or 3-fold coordinated CO probe on XNi_4 is larger than in the complexes with linear coordination (Table 1). We calculated CO frequency red-shifts of 302 , 284 , and 316 cm^{-1} for the complexes $(\mu\text{-CO})\text{XNi}_4$ with $\text{X} = \text{H}$, C , and O , respectively; these shifts are $8\text{--}40\text{ cm}^{-1}$ smaller than that of bridge bonded CO on bare Ni_4 . The red-shifts of CO 3-fold coordinated at clusters with H and C impurities, 398 and 382 cm^{-1} , are higher than for the corresponding complex of CO at bare Ni_4 , 358 cm^{-1} . The CO frequency of $(\mu_3\text{-CO})\text{ONi}_4$ is even more red-shifted, 436 cm^{-1} . In summary, the CO frequency red-shift depends more strongly on the coordination mode of the probe at the cluster than on the presence and the type of the impurity atoms.

The small changes in the BE of CO in the most stable complexes in clusters with impurities and the small variations of the corresponding frequency shifts may be rationalized with similarities in the HOMO and LUMO of bare Ni_4 and the clusters XNi_4 .⁶ HOMO and LUMO of all clusters are strongly dominated by Ni contributions.

The vibrational frequencies of free and adsorbed CO molecules correlate linearly ($R^2 = 0.991$) with the C–O distance (Figure 6(a)). Whereas there is no correlation between charges of the Ni_4 moiety or of CO, with neither the BE of CO nor the CO vibrational frequency, the calculated CO frequencies were found to correlate well with the C(2p) population of the carbonyl in adsorption complexes (Figure 6(b), $R^2 = 0.978$ for all, including charged complexes). This correlation is due to the dominant role of π back donation in the interaction between the carbonyl and the metal cluster. As mentioned above, this

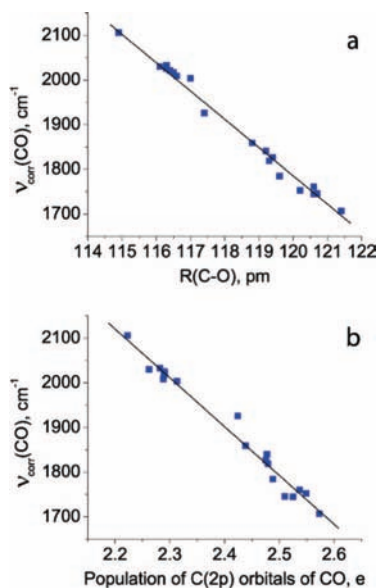


Figure 6. Correlation between the corrected CO frequencies ν_{corr} and (a) the C–O distances and (b) the C(2p) population of the carbonyl, calculated for CO adsorbed on neutral and ionic Ni₄ species and various XNi₄ clusters.

conclusion is supported by the negative charge of CO in the complexes and the overall red-shift of the CO frequency.

Experimental information on the CO vibrational frequency is available only for one of the modeled structures, (η -CO)Ni₄⁺, for which resonance enhanced infrared multiple phonon excitation spectroscopy yielded $2087 \pm 6 \text{ cm}^{-1}$.²¹ Thus, the experimental red-shift is $56 \pm 6 \text{ cm}^{-1}$. For this complex, we calculated a red-shift of 37 cm^{-1} [$\nu_{\text{calc}}(\text{CO}) = 2066 \text{ cm}^{-1}$, $\nu_{\text{corr}}(\text{CO}) = 2106 \text{ cm}^{-1}$, Table 1], that agrees quite well with the experimental result.

As additional comparison, we mention experimental results for clusters of similar metals in the gas phase^{9,18,21} or supported small nickel clusters.^{22–24} Adsorption of two hydrogen atoms on Co₄⁺ leads to a CO vibrational blue-shift of $29 \pm 6 \text{ cm}^{-1}$ compared to CO adsorbed on bare Co₄⁺.⁹ Invoking a simple model, this shift was rationalized by partial oxidation of the metal moiety, estimated at $0.20 \pm 0.02 \text{ e}$ per H atom.⁹ Our model (η -CO)HNi₄ yields a CO blue-shift of 13 cm^{-1} ; the calculated PDC of the Ni₄ moiety of HNi₄, 0.33 e ,⁶ is notably larger than the experimental estimate, but our model system is neutral.

Frequency values measured for CO on small Ni clusters, supported on silica^{22,23} or magnesia,²⁴ fall in the region $2040\text{--}2060 \text{ cm}^{-1}$. The corresponding red-shifts of $80\text{--}100 \text{ cm}^{-1}$ are smaller than our value calculated for (CO)Ni₄, 139 cm^{-1} . This should be due to the smaller size of our model and, in special cases, also to partial charging of the supported cluster. Indeed, the measured CO frequency on Ni₁₁/MgO,²⁴ 2048 cm^{-1} , is very similar to the CO frequency of (CO)Ni₁₁⁺ in the gas phase, $2037 \pm 6 \text{ cm}^{-1}$.²¹ Primet and Sheppard²² reported a vibrational blue-shift of 30 cm^{-1} for CO adsorbed on silica-supported Ni clusters of unknown size after hydrogen had been adsorbed on the sample. This experimental finding agrees qualitatively with our calculated CO blue-shift of 13 cm^{-1} of (CO)HNi₄ in comparison to (CO)Ni₄.

Experimental detection of changes of the CO red-shift due to the presence of an atomic impurity depends both on the intensity of the additional band and the resolution of the measurement, in particular for H and O impurities, where CO

red-shifts change by less than 30 cm^{-1} with respect to the bare cluster. The accuracy of IR measurements on supported metal clusters is about $1\text{--}2 \text{ cm}^{-1}$,⁷ which should allow one to discriminate clearly the CO band on bare clusters from that on clusters with an impurity. Resonance enhanced infrared multiple phonon excitation spectroscopy on size-selected clusters in the gas phase¹⁸ features an accuracy of $2\text{--}20 \text{ cm}^{-1}$; thus, a change in the red-shift due to the presence of an H impurity may not be always discernible. According to our calculations, the CO band in the IR spectra of neutral complexes with a linearly coordinated ligand has an intensity of $1000\text{--}1400 \text{ km/mol}$, similar to that of CO on bare Ni₄ ($\sim 1200 \text{ km/mol}$), whereas the bands of 2- or 3-fold coordinated probes show lower intensities (Table 1) which may make such spectroscopic measurements on CNi₄ clusters more difficult.

4. Conclusions

Heteroatoms X at Ni₄ modify the BE of the probe CO in the most stable isomers of the complexes (CO)XNi₄ at most by 10%. This result confirmed our previous conclusions based on estimates of the hardness of XNi_n.^{6b,c} The charge of the probe was determined to be negative even when coordinated at Ni₄⁺. We interpreted this as a reflection of π back donation dominating over σ donation, as was corroborated by red-shifts of calculated CO vibrational frequencies and their good correlation with the C(2p) populations of the carbonyl. From our calculations, we expect the following characteristics of IR spectra of CO in (CO)XNi₄:

- Single H and O impurities yield similar CO red-shifts, 126 cm^{-1} (H) and 110 cm^{-1} (O), with respect to gas phase CO, that are only slightly smaller than for CO at bare Ni₄, 139 cm^{-1} , because CO is on-top coordinated in all cases.

- Single C impurities yield a strong CO red shift, 382 cm^{-1} , due to preferable bonding of CO at μ_3 sites, but linearly coordinated CO may be also detectable because the calculated CO vibrational intensity is much stronger than that for μ_3 -CO.

Direct quantitative application of these findings for detecting impurity atoms on (supported) metal clusters may be complicated or even impossible because of the influence of the support and variable size of the metal clusters. Nevertheless, the present results should be helpful because they indicate trends on how and to what extent the presence of the impurity atoms considered can modify the vibrational frequency and the BE of a CO probe.

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