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Molecular versus Dissociative Chemisorption of Nitric Oxide on Co_2 and Co_3 (Neutral and Cationic). A Density Functional Study

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The reactivity of nitric oxide with small cobalt clusters (Co_2 and Co_3) is investigated with all electron linear combination of Gaussian type orbitals Kohn−Sham density functional theory. Full geometry optimization has been performed without symmetry constraints, starting from several initial geometries to locate different minima on the potential energy surface. Several spin configurations were considered for each case. The equilibrium geometries are characterized by their bonding energies and harmonic frequencies. A comparison with other experimental and theoretical values has been made. Bond distances, equilibrium geometries, harmonic frequencies, adduct formation energies, net atomic charges from Mulliken populations, Mayer bond orders, and ionization potentials are presented. In particular, some bridged structures are predicted. The NO molecule is molecularly bonded to Co_2^+ whereas Co_2, Co_3, and Co_3^+ show dissociative chemisorption. For Co_2NO^+, two low-lying states, a singlet and a triplet, are found, consistent with the deduction from experimental values that a reactive and an unreactive form are present. A comprehensive description of each adduct (Co_nNO) is provided. To explain the experimental behavior of these systems, we calculated the $Co_nO_2^+$ systems. The values of the adduct formation energies that we found are −68.7, −92.0, −81.7, and −106.9 kcal/mol for Co_2NO^+, $Co_2O_2^+$, Co_3NO^+, and $Co_3O_2^+$, respectively. With these results, we can conclude that $Co_nO_2^+$ systems are more stable than Co_nNO^+, which provides an explanation of the experimental results.

Introduction

Nitric oxide is one of many toxic molecules able to destroy ozone, a potential carcinogen, and one of the precursors of acid rain. The adsorption of nitric oxide on metallic surfaces can constitute the initial step of corrosive processes. On the other hand, contrary to this role as a noxious chemical, nitric oxide has been found to be of important and unforeseen significance in biology. Understanding the reactions of NO is crucial, as it could help in the design of automobile exhaust catalysts and, therefore, help to prevent the destructive processes, and perhaps improve knowledge of the role of NO in biological systems.

The surface chemistries of CO and NO have been extensively studied[1] in relation to factors such as substrate geometry, electronic structures, dissociation, and activation. An interesting fact is that NO is dissociatively chemisorbed on surfaces such as Rh, Cr, Fe and Co, whereas Pt does not dissociate the NO molecule.[1,2] A number of experimental[3] and theoretical[4−8] studies exist on different transition metal complexes of nitric oxide and carbon monoxide, but very little is known about chemisorption on transition-metal clusters.

Progress in cluster research has been spectacular in recent years. Developments in both theory and experiments will provide more knowledge of many of the properties of atomic aggregates, particularly those that reflect the transition from molecular to bulk behavior. There have been many previous studies of transition-metal clusters and their reactivity with small molecules (see, for example, ref 9). An area of major interest is the study of the reactivity of clusters through such processes as physisorption, chemisorption, and absorption.[10−14] One of the most important questions is the change in reactivity as a function of cluster size. Particularly, the reactivity of transition-metal clusters shows a dramatic size dependence. For example, Geusic et al.[15] reported that Co and Co_2 do not react with D_2 whereas Co_3−Co_5 react completely, and Co_6−Co_9 are again practically unreactive.

The chemisorption of NO on cobalt clusters has been investigated by Klaassen and Jacobson.[16,17] They reported experiments on the competition of dissociative versus molecular chemisorption of NO on small cobalt clusters, using gas-phase ion techniques to distinguish, select, and study different cobalt ion clusters. They used $^{18}O_2$ to monitor the different oxygen isotopic distributions that occur when it reacts with either dissociatively or molecularly chemisorbed NO. Their main interest was centered on uncovering the nature of the structure of NO chemisorbed on Co_n^+ ($n = 2−4$) clusters, examining displacement reactions with $^{18}O_2$. They reported the following isotopic reaction for Co_nNO^+

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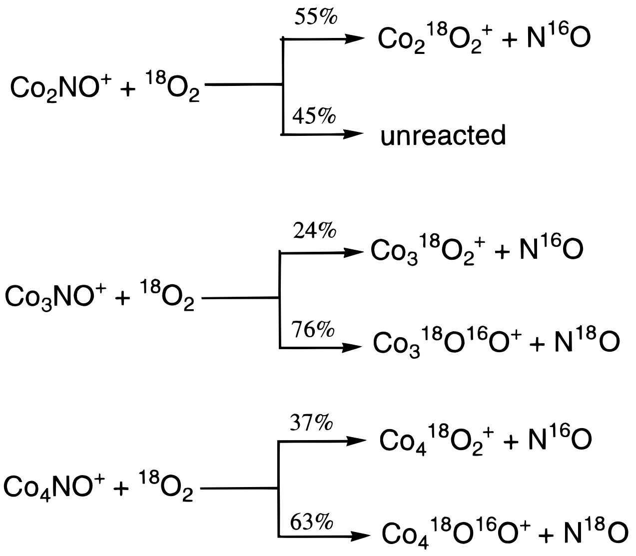


With these experiments, they suggested that the reactive form of Co_2NO^+ consists of molecular nitric oxide bound to $Co_2{}^+$. The unreactive portion of Co_2NO^+ might consist of NO dissociatively attached to $Co_2{}^+$ or to different bonding modes that are unreactive with O_2. Co_3NO^+ and Co_4NO^+ yield substantial scrambling with ${}^{18}O_2$. They rationalized this scrambling by invoking initial dissociative attachment of dioxygen to a cluster-nitride-oxide species generating a trioxide nitrido intermediate which subsequently eliminates nitric oxide as either $N^{18}O$ or $N^{16}O$. They reported that if both Co_3NO^+ and Co_4NO^+ consisted of molecular nitric oxide clusters, then little or no scrambling could be expected.

Trying to rationalize the results of Klaassen and Jacobson, Robles *et al.*[18,19] reported a theoretical study in which they presented a procedure that systematically generates adduct geometries with a simplified molecular mechanics that served as input geometries for the electronic structure calculations with the Extended-Huckel molecular orbital formalism. Using this simple theoretical procedure, they proposed a number of bridged structures and also reported ionization potentials and adduct formation energies. However, full geometry optimizations of these systems are desirable in order to make more meaningful comparisons between theoretical and experimental results.

To explain the behavior of the Co clusters, we performed a theoretical density functional study of the interaction of NO with cobalt dimers and trimers (neutral and cationic). Experimental results show that these clusters present a very interesting change in reactivity as a function of the cluster size. It is possible to understand this phenomenon on structural grounds. Therefore, reliable electronic and molecular structure calculations are of great interest for these systems. In this work, we report bond distances, equilibrium geometries, harmonic frequencies, adduct formation energies, net atomic charges from Mulliken population, and Mayer bond orders for Co_2NO and Co_3NO (neutral and cationic). To explain the experimental behavior of these systems, we calculated the $Co_2O_2{}^+$ and $Co_3O_2{}^+$ systems. The present results allow the experimental data of Klaassen and Jacobson to be rationalized, providing a better understanding of the electronic structure and geometry of the adducts and a possible reaction mechanism as well.

Computational Details

The deMon-KS program was used to perform all the calculations. The Linear Combination of Gaussian-type orbitals Kohn–Sham Density Functional Theory (LCGTO-KSDFT) method is implemented in this program. The local spin density approximation (LSDA) was included as in Vosko, Wilk, and Nusair,[20] while the generalized gradient approximation (GGA) was that of Perdew and Wang for exchange[21] and that of Perdew for correlation.[22,23] Full geometry optimization was performed at the LSDA level, and the GGA was included self-consistently for the final energy evaluation.

The Gaussian orbital basis sets that we have used are (63321/5211*/41+) for cobalt, (621/41/1*) for nitrogen, and (621/41/1*) for oxygen. The basis sets have been optimized as described in Godbout et al.[24] The auxiliary basis set used to fit the charge density and the exchange-correlation potential is (5,5;5,5) for cobalt, (4,3;4,3) for nitrogen, and (4,3;4,3) for oxygen. In this notation, the charge density and the exchange-correlation auxiliary function sets are separated by a semi-colon. Following the notation (k_1,k_2 ; l_1,l_2), the number of s-type Gaussians in the charge density (exchange-correlation) basis is represented by k_1 (l_1), while k_2 (l_2) gives the number of sets of s-, p-, and d-type Gaussians with common exponents in the charge density (exchange-correlation) auxiliary function set.

The charge density was fitted analytically, while the exchange-correlation potential was fitted numerically on a grid (deMon-KS option FINE)[25] composed of 32 radial shells and 26 angular points per shell.[26] At the end of each SCF procedure, the exchange-correlation contribution to the energy gradients was calculated by numerical integration on an augmented set of grid points consisting of the same 32 radial shells with 50, 110, or 194 angular grid points. The radial grid in deMon-KS was inspired by Becke,[26] differing only in the fact that it uses the Gaussian–Legendre quadrature scheme instead of Gauss–Chebyshev.

Full geometry optimization without symmetry constraints has been performed starting from several initial geometries to locate different minima on the potential energy surface (PES). Geometries were optimized using analytical gradients and the optimization method of Broyden–Fletcher–Goldfarb–Shanno (BFGS).[27] Different spin "multiplicities" ($2S_z+1$) were considered in all calculations in order to find the most stable spin state. To find the global minimum, one must consider several multiplicities and several initial structures for each adduct. We cannot exclude the possibility that true global minima were missed in the optimization procedure, but the number of different initial geometries and spin multiplicities that were considered is sufficiently high for us to feel confident that the global minimum has been identified.

To discriminate minima from other critical points on the potential energy surface, a vibrational analysis was performed using numerical differentiation (two-point finite-differences) of the gradients, for the most stable structures of each spin state. The harmonic frequencies were obtained by diagonalizing the Cartesian force constant matrix. The elements of this matrix are evaluated by numerical differentiation of the analytical gradient using a displacement (GSTEP) equal to 0.02 atomic units (au) from the optimized geometry for all 3N coordinates and a density convergence threshold equal to 10^{-5}. It was found that the convergence of the self-consistent field procedure should be tighter if properties such as vibrations are calculated. The effects of the GSTEP and the density convergence threshold in the vibrational analysis have been discussed elsewhere.[28] Since the geometry optimization is only at the local level, the vibrations were calculated in the LSDA approximation. All

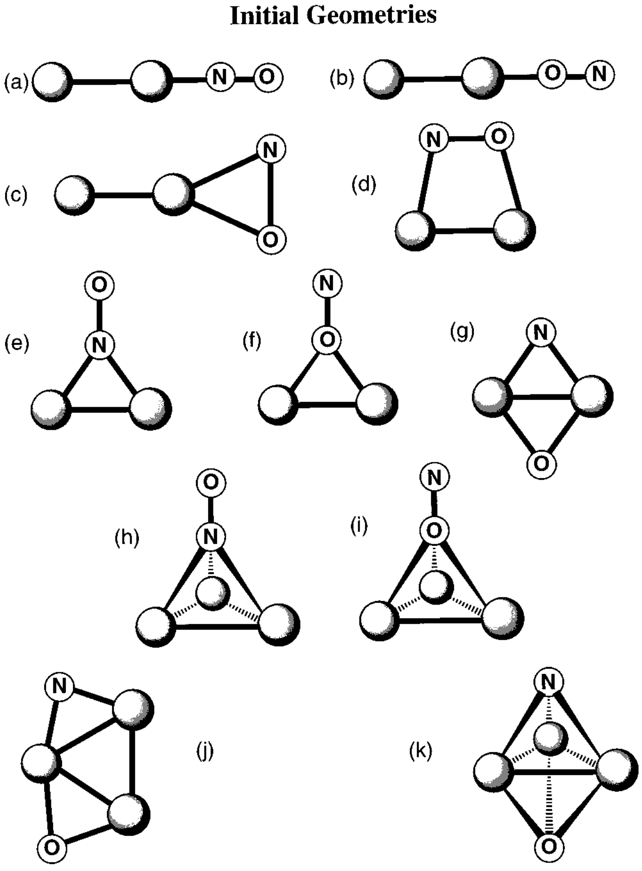


Figure 1. Initial geometries used in the geometry optimization. These geometries were used with all the spin multiplicities that were tested and with the different bond distances and angles.

equilibrium geometries and harmonic frequencies reported here are LSDA values. Only energy differences include the GGA corrections.

Results and Discussion

This section is organized in three subsections. Section A describes the geometry optimization of Co_2NO and Co_3NO (neutral and cationic). Section B discusses the vibrations of these systems. In section C we present an analysis of the cluster−NO interaction and a comparison with the results for $Co_2O_2^+$ and $Co_3O_2^+$.

A. Geometry Optimization. Co_2NO and Co_2NO^+. The initial geometries that were used are shown in Figure 1. We tested different bond distances and angles for each structure. For Co_2NO and Co_2NO^+, several critical points on the different PES were found. Figures 2 and 3 present the more stable structures for Co_2NO and Co_2NO^+, respectively. Bond distances at the LSDA level and energy differences at the GGA level compared to the most stable structure in each case are also shown.

For the Co_2NO system, two different minima with similar stability were found, both with the NO dissociatively bonded to the cobalt dimer. These are doubly bridged structures with different "multiplicities" (doublet and quartet) and both present similar bond distances. The doublet−quartet splitting is 0.7 kcal/mol. This energy difference is very small and we cannot say with certainty that one structure is more stable than the other. In Figure 2, there is also one structure with the NO molecularly bonded to the cobalt cluster, which is 17.3 kcal/mol less stable than the doubly bridged structures. This geometry was calculated with different "multiplicities", but the resulting minima are less stable. We also tried to calculate the same geometry with the oxygen atom directly bonded to the cobalt cluster (Figure 1f) and with different spin states, but the minima were also less stable. Linear geometries are even more unstable. For all the structures that we tested, the system is more stable when the NO molecule is bonded to the cobalt cluster by the nitrogen atom. We do not show structures that are less stable than those shown in Figure 2.

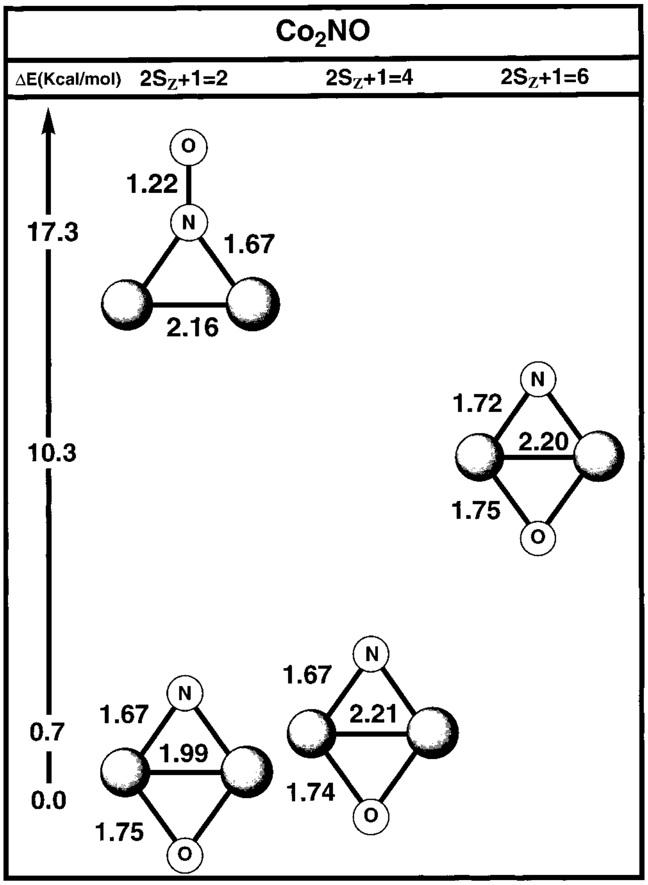


Figure 2. Most stable structures for Co_2NO. Bond distances at the LSDA level and energy differences at the GGA level compared to the most stable structure are also shown. LSDA calculations were done by the method of Vosko, Wilk, and Nusair.[20] GGA calculations were done by the method of Perdew and Wang for exchange[21] and by that of Perdew for correlation.[22,23]

In all structures in Figure 2, the N−Co bond distances are shorter than the O−Co bond distances. When the spin changes from doublet to quartet on the doubly bridged structures, the bond distance between cobalt atoms gets longer. It seems that the electron is transferred to an antibonding orbital between the cobalt atoms when the spin multiplicity changes from 2 to 4. Figure 4 shows the molecular orbital picture for the most stable structure of Co_2NO. The lowest unoccupied molecular orbital (LUMO) is an antibonding orbital between the two cobalt atoms. When the spin changes from doublet to quartet, this molecular orbital becomes occupied, and the bond distance between the cobalt atoms increases. For the neutral Co_2NO system, we can say that the NO molecule is dissociatively chemisorbed.

For the Co_2NO^+ system, it can be seen in Figure 3 that the most stable structure is a triplet with NO molecularly chemisorbed on the cobalt cluster. In this system, the NO bond distance is 1.19 Å, a value which is close to that of the isolated NO molecule. (The calculated NO bond distance for the isolated molecule is 1.17 Å.) We also tried to obtain the singlet with this structure, but we could not fully converge the geometry

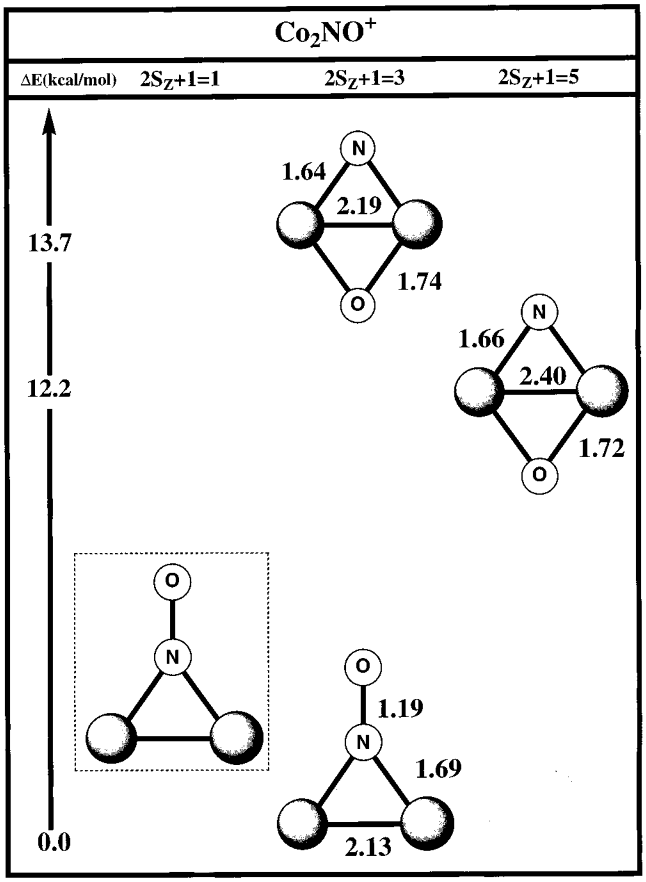


Figure 3. Most stable structures for Co_2NO^+. Bond distances at the LSDA level and energy differences at the GGA level compared to the most stable structure are also shown. LSDA calculations were done with Vosko, Wilk and Nusair.[20] GGA calculations were done by the method of Perdew and Wang for exchange[21] and by that of Perdew for correlation.[22,23] The singlet is not fully optimized (see text).

optimization of this open-shell singlet. However, the lowest energy we found for the singlet is within 6 kcal/mol of the triplet. So we suggest that these two states correspond to the reactive and unreactive forms deduced from the experiment. Deciding which is reactive and which unreactive would, of course, involve kinetic considerations which are beyond the scope of this work (although one might intuitively expect the triplet to be more reactive toward triplet O_2). The quintet system with this geometry is less stable than the structures shown in Figure 3. The structures with the oxygen atom directly bonded to the cobalt clusters (Figure 1f) are not reported, as they are less stable.

In Figure 3, there is one structure with the NO dissociatively chemisorbed on the dimer, but it is 12.2 kcal/mol less stable. It seems that, when the Co_2NO system is ionized, chemisorption is quite different. As a general trend, we found linear systems less stable and structures with the NO molecule bonded to the cobalt dimer directly by the nitrogen atom more stable. We do not report all the structures that we obtained which are less stable than those shown in Figure 3.

Figure 3 shows that the N−Co bond distances are shorter than the O−Co bond distances. If we compare the doubly bridged structures, triplet and quintet, it can be seen that the bond distance between the cobalt atoms shortens when the multiplicity changes from quintet to triplet. As in the neutral system, it seems that the electron moves from an antibonding orbital between the cobalt atoms of the quintet structure. The quintet−triplet splitting for the doubly bridged structures is 1.5 kcal/mol.

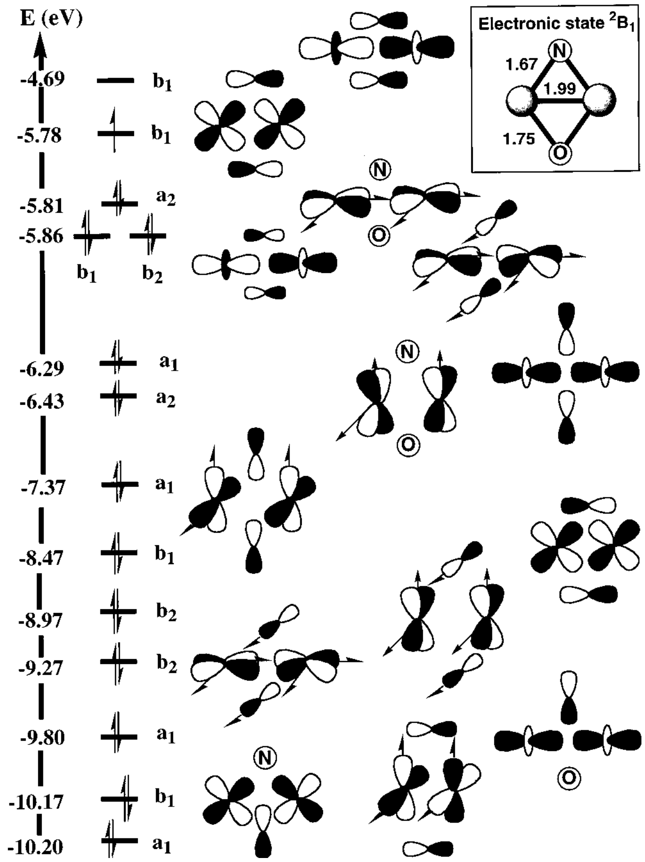


Figure 4. Molecular orbital picture for the most stable structure of Co_2NO.

In Figure 5 is presented the molecular orbital picture for the most stable structure of Co_2NO^+. The highest occupied orbitals are d orbitals of the cobalt atoms, and the orbitals with appreciable NO character are consistent with "molecular chemisorption".

Co_3NO and Co_3NO^+. These systems were optimized by using the initial geometries reported in Figure 1 with different bond distances and angles. Some linear structures were also calculated, and as for the dimers, they are less stable. For this reason, they will not be included in the following discussion. Several critical points on the different PES were found. In Figures 6 and 7 we show the more stable structures that we found for Co_3NO and Co_3NO^+, respectively. Bond distances at the LSDA level and energy differences at the GGA level compared to the most stable structure in each case are also shown.

For Co_3NO, three different minima with similar stability were found. They are all trigonal bipyramidal structures with the NO molecule dissociatively bonded to the cobalt cluster. The most stable system is a triplet with C_s symmetry. The triplet−quintet splitting is 3.9 kcal/mol, and the energy difference between the septet and the triplet is 4.5 kcal/mol, as can be seen in Figure 6. The currently available density functionals and techniques typically have uncertainties in the 5−10 kcal/mol range for relative energies for transition metal systems. Therefore, we cannot state categorically that one structure is more stable than the others. The singlet bridge structure is less stable by 15.6 kcal/mol.

In Figure 6, there is one structure with NO molecularly bonded to the cobalt trimer that is 29.9 kcal/mol less stable than

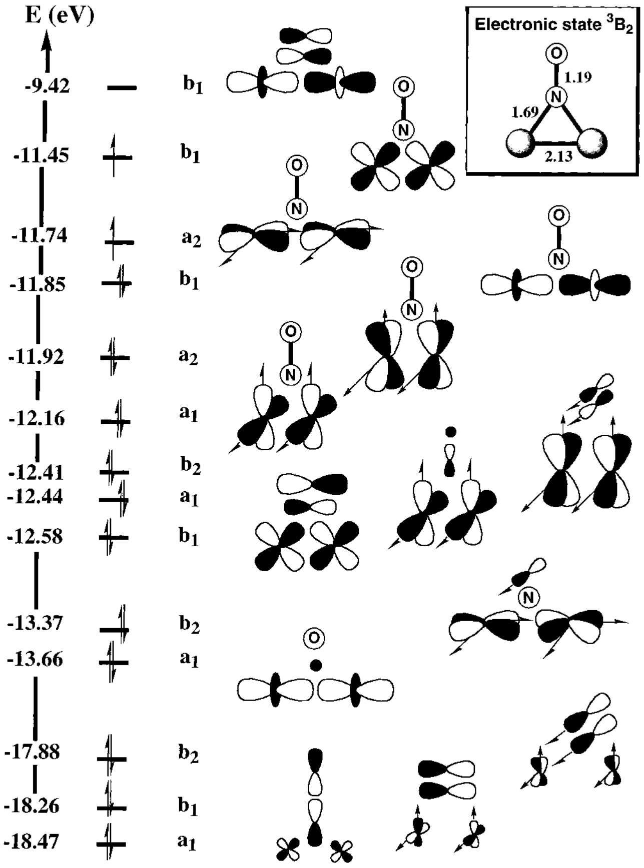


Figure 5. Molecular orbital picture for the most stable structure of Co_2NO^+.

the triplet. It is a singlet state, and this is the most stable structure with molecularly bonded NO that we found. The structures with the oxygen atom directly bonded to the cobalt cluster (Figure 1i) and different spin multiplicities are also less stable.

On the singlet PES, the energy difference between the two structures that we show in Figure 6 is 14.3 kcal/mol. With these results we can say that the reaction between the NO molecule and the trimer is dissociative.

As we saw for the dimer, in all the trimer structures shown in Figure 6, the N−Co bond distances are shorter than the O−Co ones. In this system, when the spin multiplicity changes from triplet to quintet, the symmetry is modified from C_s to C_{3v}. The longer Co−Co bond distance in the triplet shortens, and the other bond distances remain almost equal.

In a previous work,[9c] we found an equilateral triangle that is subject to a first-order Jahn−Teller deformation for the trimer cobalt clusters This structure could lead to two possible structures of C_{2v} symmetry, namely, the acute and obtuse isosceles triangles. As we reported before, the most stable structure of Co_3 at this level is the quartet obtuse triangle, which is 0.5 kcal/mol lower than the D_{3h} structure. For Co_3NO, the cobalt cluster is also an obtuse triangle. This system presents a second-order Jahn−Teller distortion, leading to a distorted structure of C_s symmetry. With these results, we can say that the NO molecule is dissociatively chemisorbed on the cobalt trimer.

For Co_3NO^+, two different minima with similar stability were found. They both are trigonal bipyramidal structures where the NO molecule is dissociated. In this case, the most stable system is a quartet with C_{3v} symmetry. We could not obtain a quartet distorted structure for this system. The quartet−doublet splitting is 4.4 kcal/mol. As we can see in Figure 7, when the spin multiplicity changes from quartet to doublet, the symmetry is modified from C_{3v} to C_s. Considering the neutral system as a distorted trigonal bipyramid, we expect that the most probable structure for Co_3NO^+ is the C_{3v} one because the Jahn−Teller distortion is avoided if one electron is removed. However, we cannot ensure that the doublet is less stable than the quartet since the energy difference is smaller than the accuracy of the calculation.

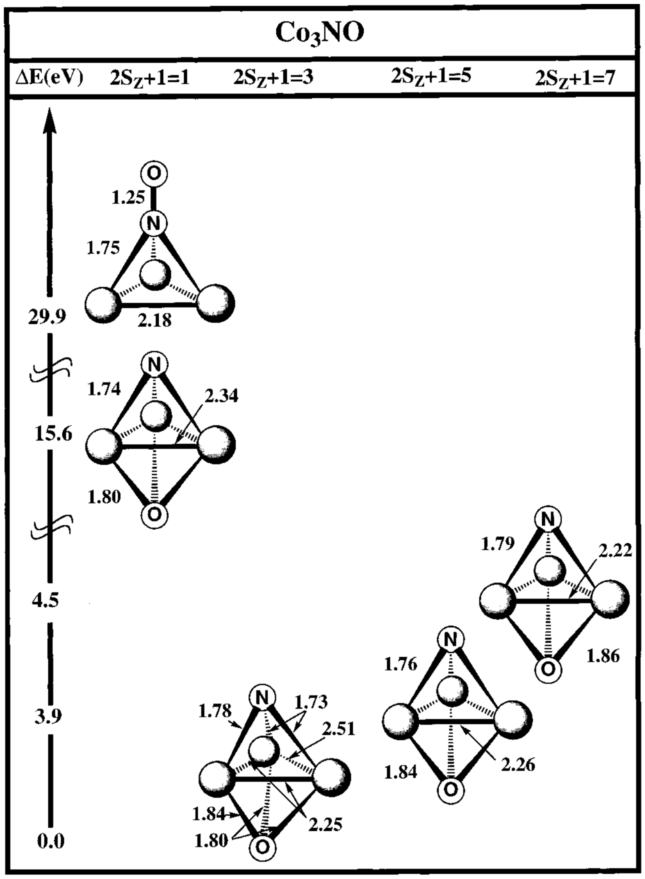


Figure 6. Most stable structures for Co_3NO. Bond distances at the LSDA level and energy differences at the GGA level compared to the most stable structure are also shown. LSDA calculations were done by the method of Vosko, Wilk, and Nusair.[20] GGA calculations were done by the method of Perdew and Wang for exchange[21] and by that of Perdew for correlation.[22,23]

In Figure 7 there are two trigonal bipyramidal structures, with spin multiplicity equal to 6 and 8. These two systems are less stable by 10.0 and 18.5 kcal/mol, respectively. The planar structure that we also report in this figure is less stable by 15.8 kcal/mol. We calculated this geomery with the other three spin multiplicity values, and the results were less stable.

All the structures that we found with the NO molecule molecularly bonded are less stable by more than 30 kcal/mol. For this reason, they are not shown in Figure 7. For molecularly bonded NO systems, the structures with the oxygen atom directly bonded to the cobalt cluster are less stable than the structures with the nitrogen atom directly bonded to the cluster.

In this system, the N−Co bond distances are shorter than the O−Co bond lengths in all the structures. Comparing the results for Co_3NO and Co_3NO^+, we can say that both systems present a similar bonding situation with the NO molecule.

Our results are in good agreement with the experimental results, which establish that for Co_2NO^+ the reactive form consists of molecularly chemisorbed NO, while for Co_3NO^+,

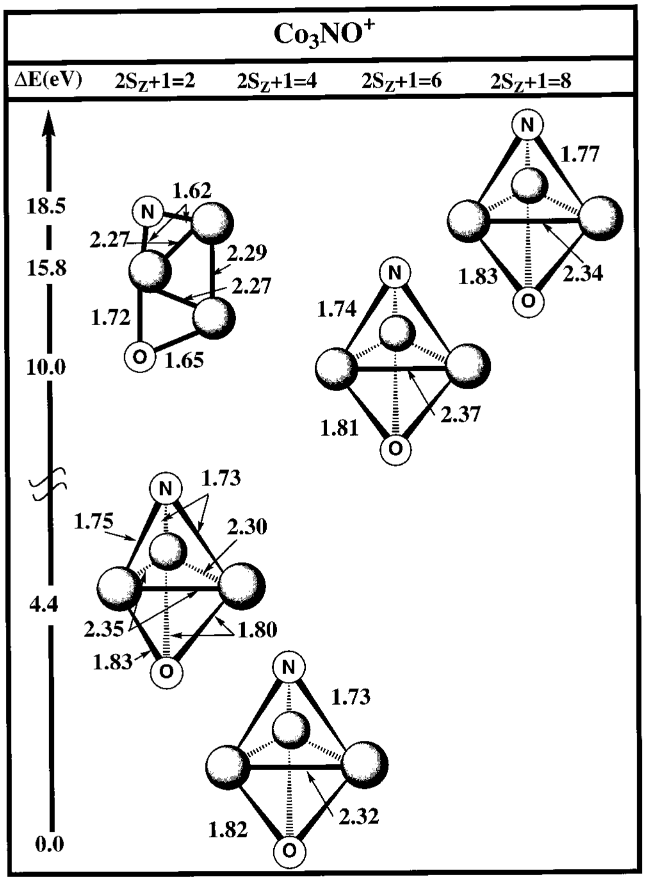


Figure 7. Most stable structures for Co_3NO^+. Bond distances at the LSDA level and energy differences at the GGA level compared to the most stable structure are also shown. LSDA calculations were done by the method of Vosko, Wilk, and Nusair.[20] GGA calculations were done by the method of Perdew and Wang for exchange[21] and by that of Perdew for correlation.[22,23]

NO is mainly attached to the cobalt clusters through dissociative chemisorption, in analogy to the metal surface process.

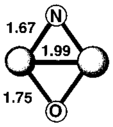
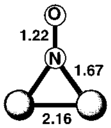
B. Vibrational Analysis. In Tables 1−4 we report the results obtained from the vibrational study performed for the more stable structures in each case. For all structures, the values are positive, and this confirms that the structures shown are local minima on the potential energy surface.

In these tables, we also report each irreducible representation for every normal mode. As far as we know, there are no experimental results for these systems. The lowest frequencies indicate that the potential energy surfaces are not very flat.

Considering the most stable structures in each case, it can be seen that the harmonic frequencies of the neutral Co_2NO system are bigger than those for the cationic system, except for the N−O harmonic frequency of the cationic system (1798 cm^{-1}) that we present in Table 2. This harmonic frequency is close to that calculated for the isolated NO (1932 cm^{-1}). It should be recalled that the NO molecule is dissociated on the neutral system, so the N−O normal mode must be smaller. Larger values of the frequencies are in accordance with the fact that the Co−Co and Co−N bond lengths are smaller for the neutral than for the cationic system. It seems that, in going to the cationic system from the neutral system, an electron is removed from an antibonding orbital.

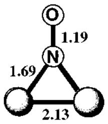
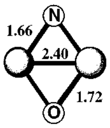
Comparing the results for Co_3NO (neutral and cationic), we notice that the frequencies are similar. The most relevant fact when an electron is removed is the change in symmetry from C_s to C_{3v}.

TABLE 1. Molecular Structures, Spin Multiplicity ($2S_z+1$), Harmonic Frequencies (in cm^{-1}), Assignment by Symmetry (A), Relative Energies (ΔE), Adduct Formation Energies (ΔE_f), Net Atomic Charges from the Mulliken Population, and Mayer Bond Order of the More Stable Structures of Co_2NO with NO Dissociatively and Molecularly Chemisorbed[a]

Structure	$2S_z+1$	ν (cm^{-1})	A	ΔE (kcal/mol) GGA	ΔEf (kcal/mol) GGA	Net atomic charges	Mayer bond order
	2	425 445 549 601 792 952	b_2 b_1 a_1 b_1 a_1 a_1	0.0	-78.3	Co=0.54 Co=0.54 N=-047 O=-0.61	Co-Co=1.6 Co-N=1.4 Co-O=1.0 N-O=0.3
	2	277 296 381 646 732 1656	b_1 a_1 b_2 a_1 b_1 a_1	17.3	-61.0	Co=0.23 Co=0.23 N=-0.29 O=-0.17	Co-Co=1.7 Co-N=0.9 N-O=1.5

[a] All the calculations of the vibrational study were performed at the LSDA level (Vosko, Wilk, and Nusair[20]). GGA calculations were done with Perdew and Wang[21] for exchange and by that of Perdew for correlation.[22,23] For the adduct formation energies, $\Delta E_f = E(Co_2NO) - [E(Co_2) + E(NO)]$.

TABLE 2. Molecular Structures, Spin Multiplicity ($2S_z+1$), Harmonic Frequencies (in cm^{-1}), Assignment by Symmetry (A), Relative Energies (ΔE), Adduct Formation Energies ($\Delta E_f^{(+)}$), Net Atomic Charges from the Mulliken Population, and Mayer Bond Order of the More Stable Structures of Co_2NO^{+1} with NO Molecularly and Dissociatively Chemisorbed[a]

Structure	$2S_z+1$	ν (cm^{-1})	A	ΔE (kcal/mol) GGA	ΔEf (+) (kcal/mol) GGA	Net atomic charges	Mayer bond order
	3	283 300 379 639 702 1798	b_1 a_1 b_2 a_1 b_1 a_1	0.0	-68.7	Co=0.61 Co=0.61 N=-0.22 O=-0.0	Co-Co=1.9 Co-N=0.8 N-O=1.7
	5	199 304 544 648 720 848	b_2 a_1 b_1 b_1 a_1 a_1	12.2	-56.5	Co=0.95 Co=0.95 N=-0.38 O=-0.52	Co-Co=1.2 Co-N=1.4 Co-O=1.0 N-O=0.1

[a] All the calculations of the vibrational study were performed at the LSDA level (Vosko, Wilk, and Nusair[20]). GGA calculations were done by the method of Perdew and Wang for exchange[21] and by that of Perdew for correlation.[22,23] For the adduct formation energies, $\Delta E_f^{(+)} = E(Co_2NO^{+1}) - [E(Co_2^{+1}) + E(NO)]$.

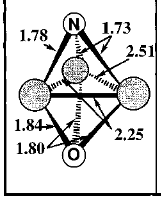
C. Cluster-NO interaction. In Tables 1−4 we report relative energies (ΔE), adduct formation *energies* (ΔE_f, $\Delta E_f^{(+)}$), net atomic charges from Mulliken populations, and Mayer bond orders for the more stable structures in each system. The adduct formation energies were computed from

$$\Delta E_f = E(Co_xNO) - E(Co_x) - E(NO) \qquad (1)$$

The cationic adduct formation energies ($\Delta E_f^{(+)}$) are similarly defined.

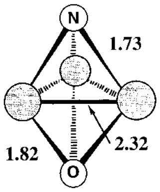
From the Mulliken population one can see that, in all systems, cobalt clusters undergo electron transfers toward the NO molecule. The larger the transfer, the stronger the chemisorption seems to be. Since the initial electron transfer from the pure

TABLE 3. Molecular Structure, Spin Multiplicity ($2S_z$+1), Harmonic Frequencies (in cm^{-1}), Assignment by Symmetry (A), Relative Energy (ΔE), Adduct Formation Energy (ΔE_f), Net Atomic Charges from the Mulliken Population, and Mayer Bond Order of the Most Stable Structure of Co_3NO[a]

Structure	$2S_Z$+1	ν (cm^{-1})	A	ΔE (kcal/mol) GGA	ΔEf (kcal/mol) GGA	Net atomic charges	Mayer bond order
	3	184 227 322 347 460 486 583 617 802	a' a'' a' a' a' a'' a' a'' a'	0.0	-86.9	Co=0.44 Co=0.44 Co=0.36 N=-0.60 O=-0.64	Co-Co=1.0 Co-Co=0.5 Co-Co=1.0 Co-N=1.0 Co-N=0.8 Co-N=1.0 Co-O=0.7 Co-O=0.6 Co-O=0.7 N-O=0.0

[a] The calculations of the vibrational study were performed at the LSDA level (Vosko, Wilk, and Nusair[20]). GGA calculations were done by the method of Perdew and Wang for exchange[21] and by that of Perdew for correlation.[22,23] For the adduct formation energies, $\Delta E_f = E(Co_3NO) - [E(Co_3) + E(NO)]$.

TABLE 4. Molecular Structure, Spin Multiplicity ($2S_z$+1), Harmonic Frequencies (in cm^{-1}), Assignment by Symmetry (A), Relative Energy (ΔE), Adduct Formation Energy ($\Delta E_f^{(+)}$), Net Atomic Charges from the Mulliken Population, and Mayer Bond Order of the More Stable Structure of Co_3NO^+ [a]

Structure	$2S_Z$+1	ν (cm^{-1})	A	ΔE (kcal/mol) GGA	ΔEf(+) (kcal/mol) GGA	Net atomic charges	Mayer bond order
	4	202 203 329 435 437 576 577 606 836	e e a_1 e e e e a_1 a_1	0.0	-81.7	Co=0.69 Co=0.69 Co=0.69 N=-0.49 O=-0.58	Co-Co=1.0 Co-N=1.0 Co-O=0.7 N-O=0.0

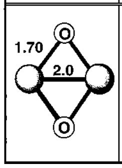
[a] The calculations of the vibrational study were performed at the LSDA level (Vosko, Wilk, and Nusair[20]). GGA calculations were done by the method of Perdew and Wang for exchange[21] and by that of Perdew for correlation.[22,23] For the adduct formation energies, $\Delta E_f^{(+)} = E(Co_3NO^+) - [E(Co_3^+) + E(NO)]$.

TABLE 5. Pure Cluster Adiabatic Ionization Potentials and Neutral Adduct Formation Energies of the Most Stable Systems[a]

system	adiabatic ionization potential (kcal/mol)	system	adduct formation energies (kcal/mol)
Co_2	172.72	Co_2NO	−78.3
Co_3	152.15	Co_3NO	−86.9

[a] The calculations are at the GGA level, by the method of Perdew and Wang for Exchange[21] and by that of Perdew for correlation.[22,23]

TABLE 6. Optimized Geometry, Spin Multiplicity ($2S_z$+1), Harmonic Frequencies (cm^{-1}), Assignment by Symmetry (A), Adduct Formation Energy ($\Delta E_f^{(+)}$), Net Atomic Charges from the Mulliken Population, Mayer Bond Order, GGA and Experimental Dissociation Energy (D^0 ($Co_2^+ - 2O$)) of the More Stable Structures of $Co_2O_2^+$ [a]

Structure	$2S_Z$+1	ν (cm^{-1})	A	ΔEf(+) (kcal/mol) GGA	Net atomic charges	Mayer bond order	D^0 (Co_2^+-2O) (kcal/mol) GGA	EXP(29)
	2	440 461 545 562 795 920	b_{2u} b_{1u} b_{2g} a_g b_{3u} a_g	-92.0	Co=0.93 Co=0.93 O=-0.43 O=-0.43	Co-Co=1.8 Co-O=1.1	227.5	221

[a] GGA calculations were done by the method of Perdew and Wang[21] for exchange and by that of Perdew for correlation.[22,23] For the adduct formation energy, $\Delta E_f^{(+)} = E(Co_2O_2^+) - [E(Co_2^+) + E(O_2)]$. Dissociation energy computed from $D^0(Co_2^+ - 2O) = E(Co_2^+) - E(Co_2O_2^+) + 2E(O)$.

cluster is determined by its ionization potential (IP), it seems possible that a lower IP allows for a larger electron transfer and, thus, a stronger chemisorption of NO for such a cluster. In Table 5, pure cluster adiabatic ionization potentials and neutral adduct formation energies (ΔE_f) of the most stable systems are reported. As can be seen, there is a correlation between these two quantities, namely, as the adiabatic ionization potentials decrease, the adduct formation energies become more negative. These results are in agreement with the previous idea.

In general, the Mayer bond orders indicate the strength of the bond. For Co_2NO^+, the Mayer bond orders for the most stable structure that we found indicate that the N−Co bond is the weakest part of the structure. As already mentioned, for this system, Klaassen and Jacobson[16] reported the following isotopic reaction

$$Co_2NO^+ + {}^{18}O_2 \xrightarrow{55\%} Co_2{}^{18}O_2^+ + N^{16}O$$

The Co_2NO^+ structure that is reactive with dioxygen could be the triplet structure that we found most stable. The weak N−Co bond is broken, and the O−Co bond is formed. It is possible that the reaction between Co_2NO^+ and O_2 yields $Co_2O_2^+$ because the stability of the $Co_2O_2^+$ system is greater than that of the Co_2NO^+ system. If this is the case, the reaction will lead to the more stable product. To confirm this idea, we calculated the $Co_2O_2^+$ system. The results are shown in Table 6. In this table, we present the more stable structure, spin multiplicity ($2S_z$+1), harmonic frequencies and the assignment by symmetry, adduct formation energy ($\Delta E_f^{(+)}$), net atomic charges from the Mulliken population analysis, Mayer bond orders, and the dissociation energy of the following reaction:

$$Co_2O_2^+ \rightarrow Co_2^+ + 2O$$

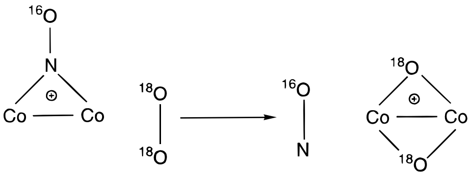
We calculated this dissociation energy in order to compare it to the experimental results previously reported by Jacobson and Freiser[29] which are also shown in this table.

As can be seen, the most stable structure is a doubly bridged one, similar to the Co_2NO structure that we found. The most stable structure with O_2 molecularly chemisorbed is 68 kcal/mol less stable. With the experimental results, Jacobson and Freiser[29] suggest formation of the doubly bridged oxide species, in analogy to bridging oxides commonly observed for transition-metal oxide compounds. Our results confirm this suggestion.

From the results of the vibrational study, we can see that this structure is a local minimum on the potential energy surface.

Comparing the adduct formation energies of $Co_2O_2^+$ and Co_2NO^+, we can see that the first system is more stable than the second. This confirms the idea concerning the relative stability of the two systems. The Mulliken population analysis shows a charge-transfer process from the cluster to the O_2 molecule, as obtained for the Co_2NO^+ system previously reported. The O−Co bond of $Co_2O_2^+$ is stronger than the N−Co bond of Co_2NO^+. Our results for the dissociation energy are in good agreement with the experimental results.

From these results we expect the reaction between Co_2NO^+ and O_2 to proceed according to the following reaction



In this reaction, weak N−Co bonds are broken in order to form stronger O−Co bonds.

For Co_3NO^+, we found in all structures that the N−Co bond distances are shorter than the O−Co bond lengths. Considering the Mayer bond orders that we report in Table 4, it seems that the N−Co bond is stronger than the O−Co bond. On this basis, one might expect to observe an isotopic reaction for these structures such as:

$$Co_3NO^+ + {}^{18}O_2 \rightarrow Co_3N^{18}O^+ + {}^{16}O^{18}O$$

but this reaction has not been reported by Klaassen and Jacobson[16] as we mentioned in the Introduction. It seems likely that the reaction between Co_3NO^+ and O_2 is governed by thermodynamics, yielding $Co_3O_2^+$ because the stability of the $Co_3O_2^+$ system is greater than that of the Co_3NO^+ system. If this is the case, then the reaction will lead to the most stable product, regardless of the fact that the reaction mechanism calls for the breaking of the N−Co and O−Co bonds. To confirm this idea, we calculated the $Co_3O_2^+$ system. The results we obtained are shown in Table 7. As can be seen, the most stable structure is a trigonal bipyramid, similar to that found for the Co_3NO^+ system. From the results of the vibrational study, we can see that this structure is a local minimum on the potential energy surface.

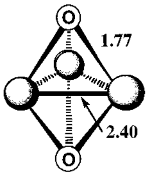
If we compare the adduct formation energies of $Co_3O_2^+$ to those of Co_3NO^+, we can see that the first system is more stable than the second one. This confirms the idea concerning the relative stability of both systems. With the Mulliken population analysis, we can see a charge-transfer process from the cluster to the O_2 molecule. The Mayer bond orders indicate, indeed, that the N−Co bond of Co_3NO^+ is stronger than the O−Co bond of $Co_3O_2^+$. To obtain $Co_3O_2^+$ from Co_3NO^+, strong N−Co bonds must be broken, and O−Co bonds must be formed. Therefore, the explanation in terms of thermodynamic stability seems to be appropiate. Of course, a full characterization of the reaction mechanism would require further calculation of activation barriers and reaction paths, which is beyond the scope of the present work.

Conclusions

We found that the linear Co_2NO and Co_3NO systems (neutral and cationic) are less stable than the other structures. As a general trend, we found that the structures with the NO molecule bonded to the cobalt clusters directly by the nitrogen atom are more stable than the structures with the NO molecule bonded to the cobalt clusters directly by the oxygen atom. For all the structures that we found, the N−Co bond distances are shorter than the O−Co bond distances.

We conclude that for the neutral Co_2NO system, chemisorption is mainly dissociative, while for the cationic system the chemisorption seems to be mainly molecular. For Co_2NO^+ we find two low-lying states, a singlet and a triplet, that likely correspond to the unreactive and reactive forms deduced experimentally. For Co_3NO (neutral and cationic), the chemisorption is dissociative.

TABLE 7. Optimized Geometry, Spin Multiplicity ($2S_z$+1), Harmonic Frequencies (cm^{-1}), Assignment by Symmetry (A), Adduct Formation Energy ($\Delta E_f^{(+)}$), Net Atomic Charges from the Mulliken Population, and Mayer Bond Order of the Most Stable Structures of $Co_3O_2^+$ [a]

Structure	$2S_z$+1	ν (cm^{-1})	A	$\Delta E_f^{(+)}$ (kcal/mol) GGA	Net atomic charges	Mayer bond order
	3	64 87 380 473 473 554 557 578 817	e e a_1 e e e e a_1 a_1	-106.9	Co=0.74 Co=0.73 Co=0.73 O=-0.60 O=-0.60	Co-Co=0.9 Co-O=0.8 O-O=0.0

[a] GGA calculations were done by the method of Perdew and Wang for exchange[21] and by that of Perdew for correlation.[22,23] For the adduct formation energy, $\Delta E_f^{(+)} = E(Co_3O_2^+) - [E(Co_3^+) + E(O_2)]$.

In all systems, cobalt clusters undergo electron transfers toward the NO molecule. The larger the transfer, the stronger the chemisorption. Since the initial electron transfer from the pure cluster is determined by its IP value, it seems possible that a lower IP allows for a larger electron transfer and, thus, a stronger chemisorption of NO in such a cluster. Our results confirm this idea.

The dissociation energy that we obtained for $Co_2O_2^+$ is in good agreement with the experimental value.[29]

The experimental reaction between Co_xNO^+ and O_2 yields $Co_xO_2^+$. As our results show, this *could be* because the stability of the $Co_xO_2^+$ system is higher than that of the Co_xNO^+ system.

Our results are in good agreement with the experimental results,[16] which establish that for Co_2NO^+, the reactive form consists of molecularly chemisorbed NO, while for Co_3NO^+, NO is mainly attached to the cobalt clusters through dissociative chemisorption in analogy to its behavior on metal surfaces. We rationalized the experimental data, providing a better understanding of the electronic structure and geometry of the adducts and of aspects of a possible reaction mechanism as well.

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