Reactions of Laser-Ablated Co and Ni Atoms with Nitrogen Atoms and Molecules. Infrared Spectra and DFT Calculations of Metal Nitride Molecular Species and Complexes

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Laser-ablated Co and Ni atoms, co-deposited with pure nitrogen at 10 K, gave a strong new 795.3 cm^{-1} band with cobalt and a 838.8, 836.1 cm^{-1} isotopic doublet (2.5/1.0) with nickel, which exhibited 14/15 isotopic ratios appropriate for the diatomic CoN and NiN molecules. In solid argon, CoN absorbs at 826.5 cm^{-1} and gives way on annealing to bands at 795.8 and 792.0 cm^{-1}, which are due to $(NN)_xCoN$ complexes. Density functional theory (DFT) calculations predict quintet and quartet ground states for CoN and NiN, respectively, and frequencies in reasonable agreement with the observed values. Evidence is also presented for the dimetal dinitrides, $(CoN)_2$ and $(NiN)_2$, with rhombus structures and metal−metal bonding across the ring. DFT-based calculations and revised assignments are presented for Ni−NN stretching modes in the dinitrogen complexes.

Introduction

The reaction of laser-ablated Fe atoms with nitrogen atoms has prepared the iron nitride molecules FeN and NFeN for characterization by matrix infrared (IR) spectroscopy and density functional theory (DFT) calculations.[1] The relative fundamental frequencies[1,2] of FeN (938 cm^{-1}) and FeO (873 cm^{-1}) show that the iron−nitrogen chemical bond is strong and suggest that Co and Ni should also form stable nitrides. Furthermore, the observation of iron nitride oxides[3] indicates that such terniary compounds can be formed with cobalt and nickel as well.

Thermal Ni atoms form end-bonded complexes with dinitrogen, and the $Ni(NN)_x$ complexes ($x = 1, 2, 3, 4$) have been identified in earlier matrix isolation studies.[4,5] Similar experiments with Co, however, proposed a side-bonded complex with dinitrogen.[6] Such complexes can also be formed after laser-ablated atoms are quenched by the condensing matrix. The analogous NiN_2^+ and CoN_2^+ complexes have been examined by ion cyclotron resonance mass spectrometry and ab initio calculations, which characterize these linear species.[7,8] The metal−dinitrogen interaction is clearly important for the mechanistic understanding of N_2 activation because the reaction of two nickel atoms with N_2 may be able to reduce N_2 as effectively as the metal surface.

Experimental Section

The laser-ablation matrix isolation experiment was identical to that employed for earlier iron, nickel, and cobalt studies with oxygen.[1,2,9,10] Gas samples (nitrogen, Matheson, 99.99%; $^{15}N_2$, Isotec; $^{14}N_2+^{14}N^{15}N+^{15}N_2$, Isotec) were co-deposited for 1−2 h onto a 10 K CsI window at 2−3 mmol/h with Co and Ni atoms ablated using 10−40 mJ pulses of focused 1064 nm radiation. Sample photolysis and annealing cycles were performed as described, and IR spectra were recorded at 0.5 cm^{-1} resolution and ±0.1 cm^{-1} accuracy on a Nicolet 750 spectrometer using a 77 K MCT detector.

Results

Matrix Fourier transform IR (FTIR) spectra will be presented for Co and Ni atoms and N_2 in excess nitrogen and argon.

Co + N₂. Laser-ablated Co atoms co-deposited with pure N_2 give a very strong absorption at 2109 cm^{-1} and other new absorptions that are listed in Table 1. Bands of particular interest are 1873.7, 1016.6, 795.3 cm^{-1} [full-width-at-half-maximum (fwhm) = 1.0 cm^{-1}, labeled $(NN)_xCoN$], and 711.1, 705.1 cm^{-1} [labeled $(CoN)_2$]. Sharp 2003.2 and 1657.7 cm^{-1} bands were observed with Fe and N_2, respectively, and they have been identified as N_3^- and N_3 radical, respectively.[1,11] Sample annealing to 20, 30, and 40 K allowed diffusion and further reaction of the trapped species; most notable is marked increase of absorbance at 705.1 cm^{-1}, and substantial growth in the 1771.6, 1016.6, 795.3, 745.4, 711.1, and 571.0 cm^{-1} bands.

Nitrogen-15 substitution was employed to identify product bands, and shifted absorptions are listed in Table 1. Both mechanical ($^{14}N_2 + ^{15}N_2$) and statistical ($^{14}N_2 + ^{14}N^{15}N + ^{15}N_2$) mixtures were examined to observe isotopic multiplets. Figure 1 shows spectra in the 810−670 cm^{-1} region for the statistical mixture. The strong bands at 795.3, 774.3 cm^{-1} [labeled $(NN)_x$-CoN] increased slightly on annealing and exhibited no displacement from pure isotopic values. A sharp doublet at 1016.6, 985.9 cm^{-1} (not shown) increased markedly on annealing and the strong 745.4, 724.0 cm^{-1} doublet and weak 731.0, 711.4 doublet also exhibited no mixed isotopic effect. The 711.1 and 705.1 cm^{-1} bands [labeled $(CoN)_2$] give rise to isotopic "triplets plus one" isotopic patterns.

In the upper region, the 1873.5 and 1929.1 cm^{-1} bands gave triplets with the statistical mixture, and there was evidence for intermediate components with the 1983.8 and 1992.4 cm^{-1} bands as well.

Co + N₂ in Argon. Cobalt atoms were co-deposited with N_2 (2%) in argon. A weak CoO band was observed at 846.2 cm^{-1} in agreement with earlier work.[10] New bands were

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TABLE 1: Infrared Absorptions (cm^{-1}) Produced by Reactions of Laser-Ablated Co and Nitrogen Isotopic Samples during Condensation at 10 K

$^{14}N_2$	$^{15}N_2$	$^{14}N_2 + {}^{14}N^{15}N + {}^{15}N_2$[a]	anneal[b]	14/15	assignment
2207	2134		++		Co(NN)$_x$
2194	2121		+, −		Co(NN)$_x$
2172	2100		+, −		Co(NN)$_x$
2109	2038	2109, 2073, 2038	−	1.0348	CoNN
2003.2	1937.5	sextet	−	1.0339	N_3^-
1992.4	1926.1	1992, 1958, 1926	+, −	1.0344	Co(N$_2$)$_x$)(NN)$_y$
1983.8	1917.8	1983, 1951, 1918	+, −	1.0344	Co(N$_2$)$_x$)(NN)$_y$
1943.9	1879.2		+, −	1.0344	Co(N$_2$)$_x$)(NN)$_y$
1929.1	1864.6	1929, 1897, 1865	+, −	1.0346	Co(N$_2$)$_x$)(NN)$_y$
1874.8	1841.9	1874.8, 1841.9	−	1.0179	NO
1873.5	1811.4	1873.4, 1842.8, 1811.5	+	1.0344	Co(N$_2$)
1771.6	1734.8	1771.6, 1734.8	+	1.0212	CoNO ?
1657.6	1603.3	sextet	−	1.0339	N_3
1616.0	1581.3		+	1.0219	NO_2
1346.2	1323.6	1346.2, 1323.6	+	1.0171	(Co$^+$)(NO$^-$)
1236.8	1211.8			1.0206	NO_2^-
1204.3	1181.4			1.0196	(Co$^+$)(NO$_2^-$)
1016.6	985.9	1016.6, 985.9	++	1.0311	(CoCoN)
1003.6	973.3		+	1.0311	site
997.8	967.4		+	1.0314	site
969.2					NH_3
943.9	943.7		+		NCo(O$_2$)
857.0	857.0	857.0	+, −		NCoO$_2$
798.0	797.8		+, −		NCoO
795.3	774.3		+	1.0271	(NN)$_x$CoN
765.1	744.2		+	1.0281	?
745.4	724.0	745.4, 724.0	++	1.0294	Co$_2$N
731.0	711.4	730.8, 711	+	1.0276	?
725.4	708.7	(721, 712) 708.9	+	1.0236	(CoNCoN)
711.1	692.1	717.7, 711.1, 700.3, 692.1	+	1.0275	(CoN)$_2$
705.1	686.5	713.1, 705.1, 694.5, 686.5	++	1.0271	(CoN)$_2$ site
571.0	556.1	569.5, 563.7, 557.8	++	1.0268	Co(NN)$_x$
556.3 w	540.8	556.3, 540.8	+	1.0287	site
537.3 w	522.7	537.3, 522.7	+	1.0279	(CoN)$_2$
532.5	518.1	532.5, 578.1	+	1.0278	site
442.0			+		Co(NN)$_x$

[a] Statistical isotopic mixture containing $^{14}N_2$, $^{14}N^{15}N$, and $^{15}N_2$. [b] Annealing behavior: (++) indicates major increase, (+) denotes some increase, (+,−) indicates increase then decrease with successive annealing cycles, and (−) indicates decrease on all annealing cycles.

observed at 826.5, 800.2, 795.8, and 746.8 cm^{-1}; the first decreased and the last three increased on annealing. These bands shifted to 804.1, 800.0, 774.5, and 725.6 cm^{-1}, respectively, with $^{15}N_2$. Both mechanical and statistical mixtures gave 826.5/804.1, 795.5/774.5, and 746.8/725.6 cm^{-1} doublets. Figure 2 shows the spectrum in the 860−700 cm^{-1} region for an experiment with 2% $^{14}N_2$ and 2% $^{15}N_2$ subjected to microwave discharge. After sample deposition for 1.5 h, the spectrum in Figure 2a shows CoO and isotopic doublets at 826.5 and 804.1 cm^{-1} (labeled CoN) and at 795.8 and 774.9 cm^{-1} [labeled (NN)$_x$CoN]. Annealing to 30 K (spectrum b) decreased CoO and CoN bands, increased (NN)$_x$CoN bands, and produced a new 800.0 cm^{-1} band (labeled NCoO) and a new 746.8, 725.6 cm^{-1} doublet (labeled Co$_2$N). Further annealing to 35, 40, and 43 K (Figures 2c, d, and e) continued these trends, but the 795.8/774.7 cm^{-1} bands decreased in favor of 792.0/771.4 cm^{-1} bands [also labeled (NN)$_x$CoN].

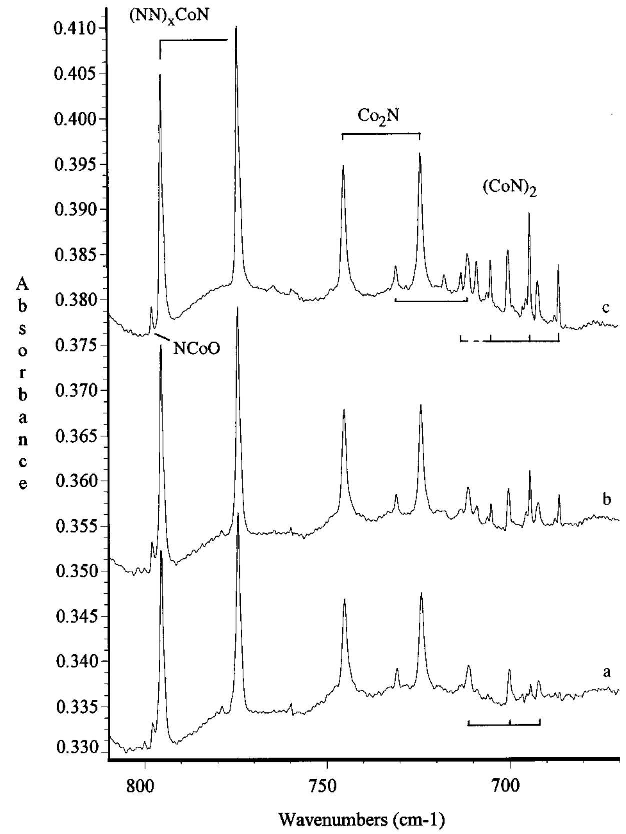

Figure 1. Infrared spectra in the 810−670 cm^{-1} region for laser-ablated Co atoms co-deposited with statistical $^{14}N_2 + {}^{14}N^{15}N + {}^{15}N_2$ at 10 ± 1 K: (a) sample co-deposited for 1 h; (b) after annealing to 25 K; and (c) after annealing to 35 K.

Three features were observed in the low-frequency region at 482.0, 465.1, and 431.9 cm^{-1}. These bands shifted, respectively, to 473.3, 457.3, and 419.9 cm^{-1} with $^{15}N_2$; annealing decreased the former, first increased then decreased the middle, and increased the latter band. The $^{14}N_2 + {}^{15}N_2$ mixture gave a sharp 465.1, 461.5, 457.2 cm^{-1} triplet after annealing. The $^{14}N_2 + {}^{14}N^{15}N + {}^{15}N_2$ mixture produced a pentet after annealing to increase the lowest frequency band with 465.0 (weak), 463.0 (strong), 461.3 (strong), 459.2 (strong), and 457.4 cm^{-1} (weak) components.

In the high-frequency region, sharp bands were observed at 2206.0, 2168.7, 2155.3, 2100.9, and 2047.5 cm^{-1}. Stepwise annealing decreased the 2100.9 cm^{-1} band and increased the others, with the 2206.0 cm^{-1} band dominating. The $^{15}N_2$ experiment shifted all of these bands (Table 2). The mechanical mixture gave a doublet at 2100.9, 2031.9 cm^{-1} and a quartet at 2047.5, 2037.5, 2002.1, 1979.4 cm^{-1}. Annealing decreased these absorptions and produced a forest of bands with the strongest new feature at 2155 cm^{-1}. The statistical mixture gave a triplet at 2100.9, 2066.3, 2031.9 cm^{-1} and a sextet for the sharp 2047.5 cm^{-1} band system. Annealing again gave a forest of bands, but clear central components were observed as listed in Table 2.

Ni + N$_2$. Laser-ablated Ni atoms co-deposited with pure nitrogen gave very strong 2181 and 2170 cm^{-1} bands and weaker 2133.6 and 1902.7, 1893.5 cm^{-1} bands in the upper region; these bands sharpened on annealing. Very weak new features were observed at 1870.6, 1796.9, and 1720.7 cm^{-1}. As before, sharp weak bands were observed at 2003.3 and 1657.7 cm^{-1}. Figure 3 shows the lower frequency region; a new absorption at 996.0 cm^{-1} (labeled NiNiN) sharpened on annealing and revealed splitting at 995.4 cm^{-1} and new split

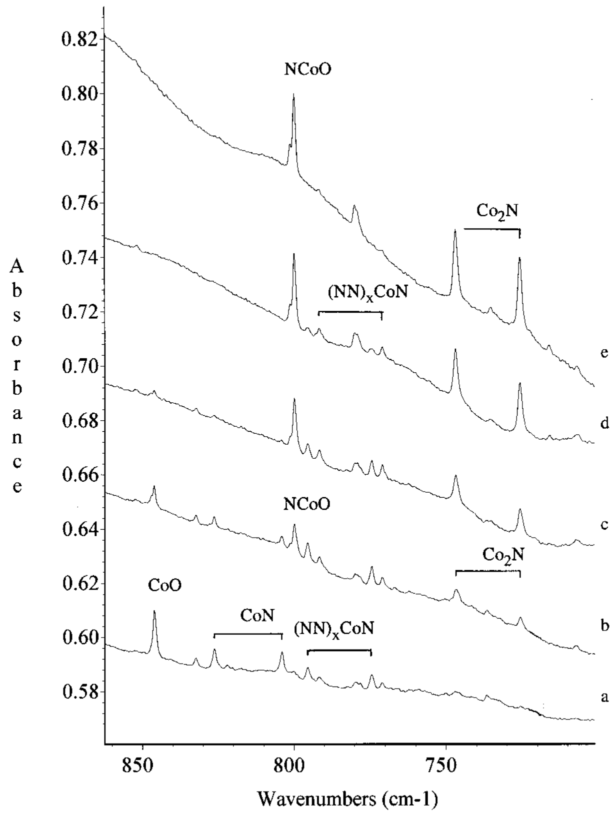

Figure 2. Infrared spectrum in the 860−700 cm^{-1} region for laser-ablated Co atoms co-deposited with 1% $^{14}N_2$ + 2% $^{14}N^{15}N$ + 1% $^{15}N_2$ in argon at 6−7 K: (a) sample co-deposited for 1.5 h; (b) after annealing to 30 K; (c) after annealing to 35 K; (d) after fast annealing; and (e) after fast annealing to 43 K.

TABLE 2: Infrared Absorptions (cm^{-1}) Produced by Reactions of Laser-Ablated Co and N_2 (2%) during Condensation in Excess Argon at 10 K

$^{14}N_2$	$^{15}N_2$	$^{14}N_2$ + $^{14}N^{15}N$ + $^{15}N_2$	anneal[a]	14/15	assignment
2206.0	2132.6	+ 2169 +	++	1.0344	$Co(NN)_x$
2193.3	2119.7			1.0347	$Co(NN)_x$
2168.7	2096.4	+ 2132 +	+	1.0345	$Co(NN)_x$
2155.3	2083.7		+	1.0344	$Co(NN)_x$
2100.9	2031.9	2100.9, 2066.3, 2031.9	−	1.0340	CoNN
2075.0	2006.9		+	1.0339	$Co(NN)_x$
2051.7	1985.1		+	1.0335	$(N_2)Co(N_2)$
2047.5	1979.4	sextet	−	1.0344	$(N_2)Co(N_2)$
1783.7	1747.2		+	1.0209	(CoNO)
1777.6	1740.9		−	1.0211	(CoNO)
852.3	852.3		+		NNCoO
846.2	846.2		−		CoO
826.5	804.1	826.5, 804.1	−	1.0279	CoN
800.2	800.0	800.0	+		NCoO
795.8	774.7	795.8, 774.7	+	1.0272	$(NN)_xCoN$
792.0	771.4	792.0, 771.4	+	1.0267	$(NN)_xCoN$
780.3	780.3		+		? CoO_xN_y
779	779		+		?
746.8	725.7	746.8, 725.7	+	1.0291	Co_2N
482.0	473.3		−	1.0184	$Co(NN)_x$
465.1	457.3	465.0, 463.0, 461.3, 459.2, 457.4	+,−	1.0171	$Co(NN)_x$
431.9	419.9	broad	+	1.0285	$Co(NN)_x$

[a] See Table 1 for key to annealing behavior.

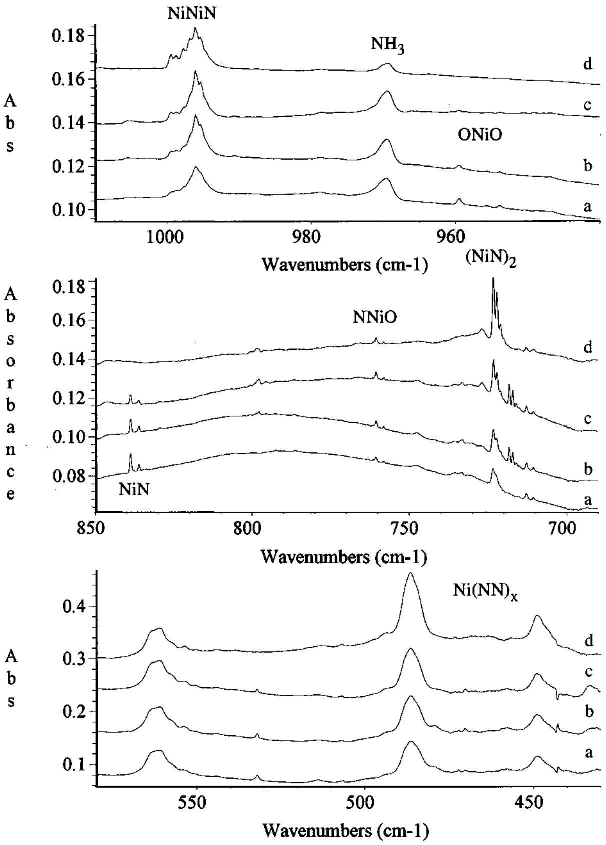

Figure 3. Infrared spectra in the 1000−400 region for laser-ablated Ni atoms co-deposited with N_2 at 10 ± 1 K: (a) sample co-deposited for 1 h; (b) after annealing to 20 K; (c) after annealing to 30 K; and (d) after annealing to 40 K.

bands at 999.4, 998.7 cm^{-1} on the high-frequency side. Sharp, weak nickel isotopic doublets (2.5:1) were observed at 959.5, 953.9 cm^{-1} (ONiO), 894.3, 889.1 cm^{-1} ($ONiO^-$),[9] 838.77, 836.13 cm^{-1} (fwhm = 0.6 cm^{-1}) plus weaker 833.60 cm^{-1} (labeled NiN), 760.5, 758.1 cm^{-1} (labeled NNiO), and 712.9, 710.9 cm^{-1} bands. Sharp nickel isotopic triplets (7:5:1) were resolved at 723.3, 722.2, 721.1 cm^{-1} and produced at 718.3, 717.2, 716.1 on 20 and 25 K annealing [labeled $(NiN)_2$], but destroyed on 30 K annealing. The lower region gave broader bands at 561.0, 486.4, and 449.0 cm^{-1}, which also increased and sharpened on annealing.

Again, $^{15}N_2$ was employed for band identification, and the observed frequencies are compared in Table 3. The strong band shifted to 965.9 cm^{-1}, and annealing allowed resolution of nickel isotopic splittings at 965.3, 964.5 cm^{-1} on the low and 969.3, 968.6 cm^{-1} on the high side of the maximum. The sharp doublet shifted to 816.24, 813.54 cm^{-1} (NiN). Sharp triplets were resolved on annealing and shifted, as given in Table 3. The 693.9, 691.7 cm^{-1} doublet grew slightly on annealing (Figure 4). Finally, the lower frequency bands were also shifted.

An experiment with a $^{14}N_2$ + $^{15}N_2$ mixture gave the sum of pure isotopic counterparts for the 996.0, 965.9 and 838.77, 816.24 cm^{-1} band systems and broadened intermediate bands in the low-frequency region. However, the spectra revealed new intermediate components and 1:2:1 nitrogen isotopic triplets for the 723.3 cm^{-1} band system that sharpened on annealing and the 718.3 band system produced on 20 and 25 K but destroyed on 30 K annealing (Table 4, Figure 4). There is no evidence of any intermediate mixed nitrogen isotopic component for the 712.9, 710.9 cm^{-1} nickel isotopic doublet.

Ni + N_2 in Argon. Similar experiments with 2% N_2 in argon produced absorptions in the upper region at 2089.2, 2104.6, 2136.4, and 2174.5 cm^{-1} that have been assigned to $Ni(NN)_x$ species.[5] A new band at 1879.3 cm^{-1} gave way on annealing to a trio of bands at 1811.1, 1801.8, and 1794.5 cm^{-1}. Weak

TABLE 3: Infrared Absorptions (cm^{-1}) Produced by Reactions of Laser-Ablated Ni and Nitrogen During Condensation at 10 K

$^{14}N_2$	$^{15}N_2$	$^{14}N_2 + {}^{15}N_2{}^a$	anneal^b	14/15	assignment
2181	2107		+	1.0351	$Ni(NN)_4$
2170	2096		+	1.0353	$Ni(NN)_4$
2140	2068		−	1.0348	?
2133.6	2062.7		+,−	1.0344	$Ni(NN)_3$
2003.6	1937.5	quartet	−	1.0340	N_3^-
1902.7	1839.9	1902.7, 1839.9	+,−	1.0341	$Ni(N_2)$
1874.9	1841.8	1874.9, 1841.8	−	1.0179	NO
1870.6	1808.9	1870.6, 1808.9	−	1.0341	$Ni(N_2)$
1796.9	1737.0	1796.9, 1737.0	−	1.0345	?
1720.7	1686.0	1720.7, 1686.0	+,−	1.0206	NiNO ?
1657.7	1603.3	quartet	−	1.0339	N_3
999.4	969.3	999.4, 969.3	++	1.0311	$(^{58}Ni^{58}NiN)$ site
998.7	968.6	998.7, 968.6	++	1.0311	$(^{58}Ni^{60}NiN)$ site
996.0	965.9	996.0, 965.9	+	1.0312	$(^{58}Ni^{58}NiN)$
995.3	965.2	995.4, 965.2	+	1.0312	$(^{58}Ni^{60}NiN)$
994.6	964.5	994.6, 964.5	+	1.0312	$(^{60}Ni^{60}NiN)$
959.5	959.5	959.5	−		$O^{58}NiO$
953.9	953.9	953.9	−		$O^{60}NiO$
894.3	894.3	894.3	−		$O^{58}NiO^-$
889.1			−		$O^{60}NiO^-$
838.77	816.24		−	1.02760	^{58}NiN
836.13	813.54		−	1.02777	^{60}NiN
833.60			−		^{62}NiN
760.5	760.3	760.4	+,−		$N^{58}NiO$
758.1		758.0	+,−		$N^{60}NiO$
723.3	703.9	723.3, 712.3, 703.9	+	1.0276	$(^{58}NiN)_2$
722.2	702.8	722.2, 711.2, 702.8	+	1.0276	$(^{58}Ni^{60}NiN_2)$
721.1	701.8	721.1, 710.1, 701.8	+	1.0275	$(^{60}NiN)_2$
718.3	699.2	707.6	++	1.0273	$(^{58}NiN)_2$ site
717.2	698.1	706.5	++	1.0274	$(^{58}Ni^{60}NiN_2)$ site
716.1	697.0	705.3	++	1.0274	$(^{60}NiN)_2$ site
712.9	693.9	712.9, 693.9	+,−	1.0274	X--^{58}NiN ?
710.7	691.7	710.7, 691.7	+,−	1.0275	X--^{60}NiN ?
560.8	549.9	555 broad	+	1.0200	?
486.3	474.9	484, 479	+	1.0240	$Ni(NN)_4$
449.0	439.1	447, 442	+	1.0225	$Ni(NN)_4$
433.6	423.1		+,−	1.0248	$Ni(NN)_3$

[a] Mixture of $^{14}N_2$ and $^{15}N_2$. [b] Annealing behavior as defined in Table 1.

bands were observed at 1003.2, 875.1, 832.4, and 825.6 cm^{-1} (NiO, $A < 0.002$);[9] stepwise annealing to 40 K increased the first band and decreased the others. A weak triplet at 710.1, 709.0, 707.8 cm^{-1} and doublet at 662.7, 661.0 cm^{-1} increased on stepwise annealing to 35 K (Figure 5a) and decreased on further annealing. These bands shifted with $^{15}N_2$ (Figure 5d), and $^{14}N_2 + {}^{15}N_2$ gave the sum of pure isotopic spectra (Figure 5c) in *contrast* to the nitrogen matrix (Figure 4). The statistical mixture gave a triplet of triplets for the 710.1 cm^{-1} band (Figure 5b). The lower region is dominated by two nickel isotopic doublets at 484.6, 481.0 and 469.5, 465.7 cm^{-1}, a weaker doublet at 563.7, 560.6 cm^{-1}, and a band at 600.2 cm^{-1}. Figure 6 shows the evolution of these bands on annealing; the 469.5, 465.7 cm^{-1} system is strong enough to reveal the ^{62}Ni counterpart at 462.0 cm^{-1}. These bands show $^{15}N_2$ shifts (Figure 6e), and the two stronger systems show clear intermediate components, with $^{14}N_2 + {}^{15}N_2$ (Figure 6a) demonstrating the participation of more than one N_2 subunit in the vibration. The statistical mixture gave a clearly resolved pentet for the 469.5 cm^{-1} band (Table 4).

Finally, it must be mentioned that annealing in all of these experiments is accompanied by a very intense green emission from the matrix.

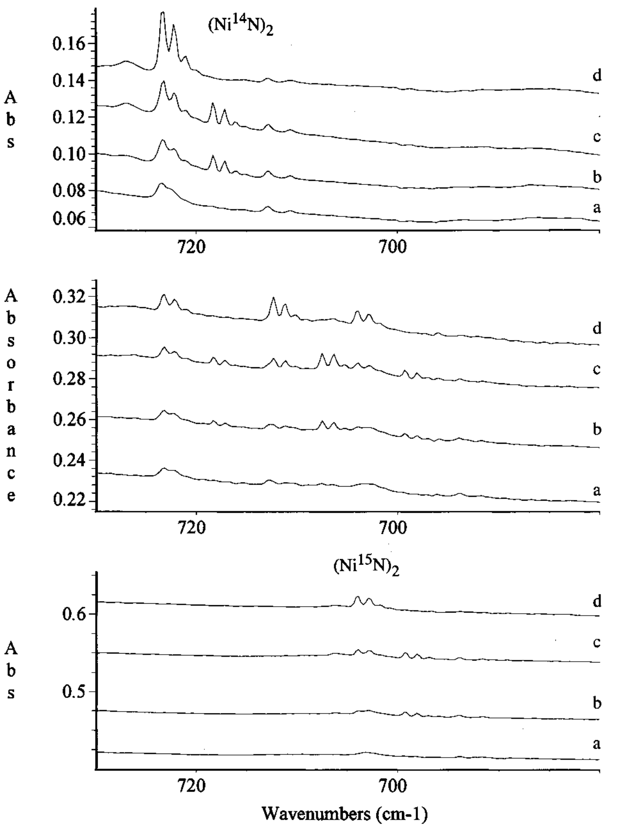

Figure 4. Infrared spectra in the 730−680 cm^{-1} region for laser-ablated Ni atoms co-deposited with $^{14}N_2$ (top), $^{14}N_2 + {}^{15}N_2$ (middle), and $^{15}N_2$ (bottom) at 10 ± 1 K: (a) samples co-deposited for 1 h; (b) after annealing to 20 K; (c) after annealing to 30 K; and (d) after annealing to 40 K.

Calculations

It has been shown that DFT works well in predicting structures and frequencies for small transition metal compounds.[12] Accordingly, all-electron DFT calculations were done initially with the DGauss program developed by Cray Research.[13] The local spin-density-exchange correlation potentials were represented by Vosko-Wilk-Husair potential,[14] whereas nonlocal gradient corrections to the exchange and correlation were determined in situ by self-consistent field (SCF) calculation via exchange and correlation Becke and Perdew potentials, respectively.[15−17] The SCF convergence reported here was 1×10^{-6} au for energy and 1×10^{-3} au/Å for structural optimization. Second derivatives, force constants, and frequencies were determined numerically in the harmonic oscillator approximation. DFT-optimized DZVP quality basis sets were used for both nickel (963321/531/41) and nitrogen (621/41/1).[18]

The NiN, NNiN, NiNi, and $(NiN)_2$ nitride molecules and NiNN and $Ni(N_2)$ complexes were calculated, and results are summarized in Tables 5 and 6. The DGauss DFT calculations predict that the ground state of NiN is a quartet, although the doublet state considered earlier[19] is higher by only 5 kcal/mol. The calculated frequencies for both states (841 and 845 cm^{-1}, respectively) are in excellent agreement with the observed 838.7 cm^{-1} nitrogen matrix value. Similar DFT calculations for CoN in singlet, triplet, and quintet states indicate that the quintets lowest in energy, with a 859 cm^{-1} fundamental, which is in very good agreement with the observed 826.5 cm^{-1} argon matrix values. Calculated parameters for the diatomic metal nitrides are collected in Table 5.

The lowest energy structure for the NiN_2 stoichiometry is the singlet end-bonded NiNN complex, but the singlet side-

TABLE 4: Infrared Absorptions (cm^{-1}) Produced by Reactions of Laser-Ablated Ni and N_2 (2%) during Condensation in Excess Argon at 10 K

$^{14}N_2$	$^{15}N_2$	$^{14}N_2 + {}^{14}N^{15}N + {}^{15}N_2$	anneal[a]	14/15	assignment
2220.4	2146.4		++	1.0345	aggregate
2174.5	2101.5		+	1.0347	$Ni(NN)_4$
2136.4	2064.9		+	1.0346	$Ni(NN)_3$
2104.6	2034.5		+,−	1.0345	$Ni(NN)_2$
2089.2	2019.7	2089.2, 2056.6, 2053.3, 2019.7	−	1.0344	NiNN
2086.0	2016.6		−	1.0344	NiNN site
1907.1	1843.4		−	1.0346	$Ni(N_2)$ site
1879.3	1816.9	1879.3, 1848.6, 1817.0	−	1.0343	$Ni(N_2)$
1811.1	1751.0	1811.0, 1781.4, 1751.0	+	1.0343	$(NiNN)_2$?
1801.8	1741.9	1801.8, 1772.3, 1742.0	+	1.0344	$(NiNN)_2$?
1794.5	1735.0	1794.5, 1765.5, 1735.0	+	1.0343	$(NiNN))_2$?
1003.2	972.6		+	1.0315	NiNiN
961.3	959.9		+, −	1.0014	$NNiO_x$
875.1	854.0	875, 865, 854	−	1.0247	$(N^{58}NiN)$?
871.3	850.3		−	1.0248	$(N^{60}NiN)$?
832.4	809.9		−	1.0279	(NiN)
825.7	789.0		−		NiO
710.1	691.3	710.1, 700.5, 691.3	+	1.0272	$(^{58}NiN)_2$
709.0	690.1	709.0, 699.3, 690.1	+	1.0274	$(^{58}Ni^{60}NiN_2)$
707.8	689.0	707.8, 698.2, 689.0	+	1.0273	$(^{60}NiN)_2$
693.4	675.7		−	1.0262	?
662.7	645.3	662.4, 654.4, 652.8, 645.4	+,−	1.0270	(NiNNiN) ?
661.0	643.9		+,−	1.0266	(NiNNiN) ?
600.2	583.1	599, 591, 584[b]	+	1.0293	$(NiNN)_2$
577.6	560.8	574, 567, 564	+	1.0300	site
563.7	551.0	563.7, 557, 551.0[c]	−	1.0230	$^{58}NiNN$
560.6	547.9		−	1.0233	$^{60}NiNN$
557.8	545.6		−	1.0224	NiNN site
554.6					
484.6	476.3	unresolved	+,−	1.0174	$^{58}Ni(NN)_2$ site
481.0	472.5		+,−	1.0180	$^{60}Ni(NN)_2$ site
469.5	461.6	461.9, 467.2, 465.3, 463.4, 461.5	+,−	1.0171	$^{58}Ni(NN)_2$
465.7	457.8		+,−	1.0173	$^{60}Ni(NN)_2$
462.0	454.1		+,−	1.0174	$^{62}Ni(NN)_2$
417.6	406.1	broad	++	1.0283	$Ni(NN)_3$
409.3	?		++		?

[a] Annealing behavior as defined in Table 1. [b] Broad doublet at 599 and 584 observed with $^{14}N_2 + {}^{15}N_2$. [c] Only pure isotopic bands observed with $^{14}N_2 + {}^{15}N_2$.

bonded $Ni(N_2)$ complex is only 9 kcal/mol higher as determined by DGauss DFT. These complexes are calculated to have one intense IR absorption, the N−N stretching mode, at 2105 and 1807 cm^{-1}, respectively, and much weaker Ni−N stretching modes. Triplet states are higher in energy for both structures. Also substantially higher are obtuse bent open dinitride structures: the quintet state by 127 kcal/mol and the singlet state by 135 kcal/mol. The singlet state has a strong antisymmetric Ni−N stretching mode calculated at 934 cm^{-1}.

The Ni_2N stoichiometry was explored and NiNiN species collapsed to the cyclic C_{2v} structure on the doublet surface. The cyclic Ni_2N molecule has a strong symmetric Ni_2−N stretching mode calculated at 789 cm^{-1}. Singlet and triplet rhombic ring states were calculated for $(NiN)_2$, and the parameters are listed in Table 7. The complexes $Ni(NN)_x$ ($x = 1, 2, 3, 4$) were investigated using the Amsterdam Density Functional (ADF) code for systematic changes in structure and vibrational frequencies, and the results are summarized in Table 6. As expected, the Ni−N bond length increases and the N≡N bond length decreases with increasing number of dinitrogen ligands.

The ADF code (ADF 2.0.1) developed by Baerends and coworkers[20] was used for later calculations of Co_xN_y species. The ADF code employs a series of Slater basis functions, and the adjustable parameter controlling the accuracy of the numerical integration was set at a value of 6.0.[21] The type 4 basis was used for Co (triple-ζ with orbitals frozen up to 2p) and type 5 for N (triple-ζ + polarization with 1s orbital frozen). Accordingly, the lowest energy structure for CoN_2 is the doublet end-bonded CoNN complex, but the doublet side-bonded $Co(N_2)$ complex is only 9 kcal/mol higher. These complexes had strong calculated fundamentals at 2082 and 1842 cm^{-1}, respectively.

The Co_2N stoichiometry was investigated, and doublet, bent, and cyclic species were found to be stable, with the bent structure higher by 27 kcal/mol. To investigate this further, a linear transit calculation was performed where the bond lengths were optimized for a given CoCoN bond angle, and the procedure was repeated for a series of bond angles. The results show how the energy changes as a function of bond angle, and suggests a barrier (4 kcal/mol) between the cyclic and bent forms. The bent quartet closed to the cyclic molecule, which is 36 kcal/mol above the cyclic doublet. Structures and frequencies are summarized in Table 7 for the doublet states. Note that bent CoCoN has a strong Co_2−N stretching mode calculated at 982 cm^{-1} and that cyclic Co_2N has a strong symmetric Co_2−N stretching mode predicted at 856 cm^{-1}. In like fashion, the Co_2N_2 stoichiometry was explored starting with linear CoNNCo, NCoCoN, and *cis* and *trans* isomers, which had imaginary frequencies. The stable rhombus, in singlet, triplet, and quintet states, is included in Table 7. Note the Co−Co distance, 2.342 Å, across the quintet ring. Although the parallelogram was more stable, no evidence for this structure was found.

Finally, three structural isomers of CoNO were examined, and the results are presented in Table 8.

Discussion

The new cobalt and nickel nitride species will be characterized in turn.

Mononitrides: CoN and NiN. Laser-ablated cobalt atoms in pure nitrogen gave a sharp 795.3 cm^{-1} band that increased on annealing and shifted to 774.3 cm^{-1} with $^{15}N_2$. These bands showed no evidence of broadening or intermediate components with $^{14}N_2 + {}^{15}N_2$ and $^{14}N_2 + {}^{14}N^{15}N + {}^{15}N_2$ mixtures. This absorption clearly involves one nitrogen atom. With 2% N_2 in argon, weaker bands at 826.5 and 804.1 cm^{-1} gave way on annealing to stronger 795.8/792.0 and 774.7/771.4 cm^{-1} absorptions, respectively. The observed 14/15 ratio for the strong nitrogen matrix doublet (1.0271) is slightly lower than the harmonic diatomic Co−N value (1.0279), but the higher frequency argon matrix bands gave the 1.0279 ratio.

Laser-ablated nickel atoms in pure nitrogen gave a weaker sharp doublet at 838.77, 836.13 cm^{-1}, with 2.5:1.0 relative intensities, and a much weaker band at 833.60 cm^{-1}, with ~1/20 of the 838.77 cm^{-1} absorbance. These band intensities agree with the distribution of the three major nickel isotopes (^{58}Ni, 67.9%; ^{60}Ni, 26.2%; ^{62}Ni, 3.7%) and show that this absorption involves only one nickel atom. The band became a sharp doublet of doublets with $^{14}N_2 + {}^{15}N_2$, which shows that a single nitrogen atom is involved in this vibration (assuming dissociation

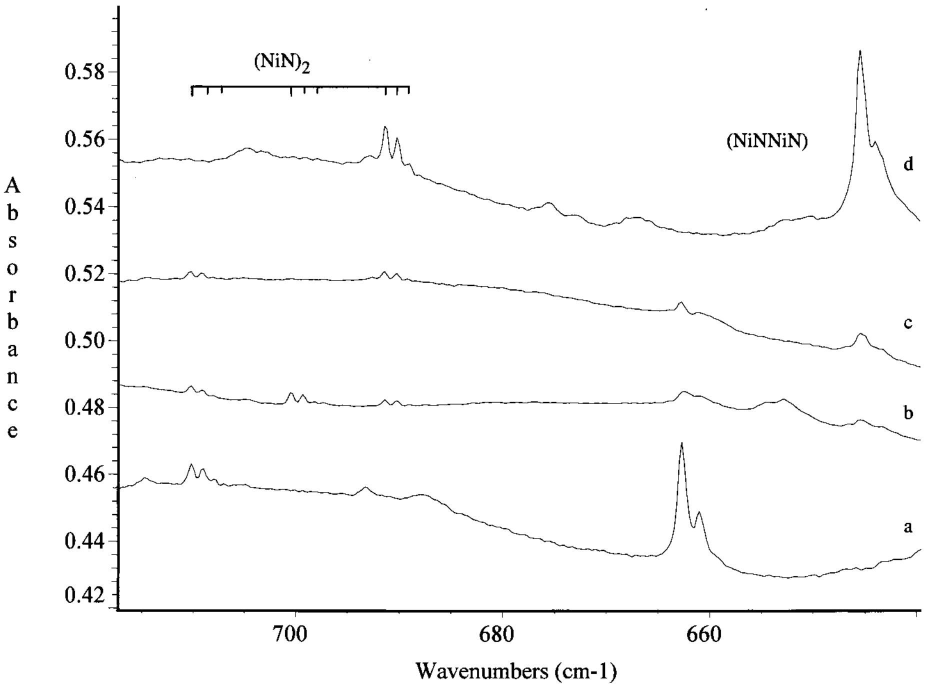

Figure 5. Infrared spectra in the 715−640 cm^{-1} region for laser ablated Ni atoms co-deposited with isotopic N_2 samples in argon at 6−7 K for 1−2 h: (a) 2% $^{14}N_2$; (b) 1% $^{14}N_2$ + 2% $^{14}N^{15}N$ + 1% $^{15}N_2$; (c) 2% $^{14}N_2$ + 2% $^{15}N_2$; and (d) 2% $^{15}N_2$.

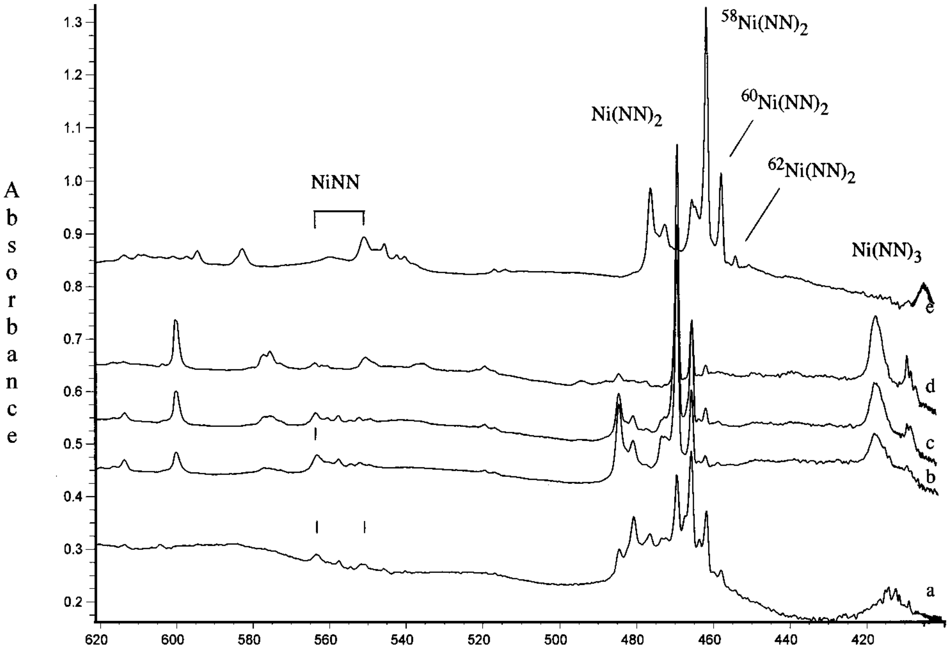

Figure 6. Infrared spectra in the 620−400 cm^{-1} region for laser ablated Ni atoms co-deposited with isotopic N_2 samples in argon at 6−7 K for 1−2 h: (a) 2% $^{14}N_2$ + 2% $^{15}N_2$ after deposition; (b) 2% $^{14}N_2$ after deposition; (c) 2% $^{14}N_2$ after annealing to 30 K; (d) 2% $^{14}N_2$ after annealing to 40 K; and (e) 2% $^{15}N_2$ after deposition.

of N_2). The observed 14/15 ratios for the major nickel isotopes, 1.02760 and 1.02777, are slightly lower than the harmonic diatomic values, 1.02785 and 1.02804. The observed 58/60 and 58/62 ratios for ^{14}N, 1.00316 and 1.00620, are also slightly lower than the harmonic diatomic values, 1.00323 and 1.00632. This deviation is in the direction and of the magnitude expected for normal cubic anharmonicity. In the argon matrix experiments, a very weak band at 832.4 cm^{-1} decreased on annealing and exhibited a 1.0279 nitrogen isotopic ratio. All of the evidence just mentioned substantiates assignment of the 838.8 cm^{-1} band to the $^{58}Ni^{14}N$ fundamental and the 795.3 cm^{-1} band to the $^{59}Co^{14}N$ stretching mode in solid nitrogen, where the metal nitrides may be saturated with dinitrogen ligands at the metal centers, and the argon matrix bands at 832.4 and 826.5 cm^{-1} to the isolated NiN and CoN molecules, respectively. Annealing the CoN samples in solid argon formed the same $(NN)_xCoN$ complex absorbing at 795.8 cm^{-1} (or 792.0 cm^{-1}) as in solid nitrogen absorbing at 795.3 cm^{-1}. As in the case of FeN, further ligation by dinitrogen to the metal center makes little difference in the metal-nitride vibrational frequency; however, the M−N absorptions are stronger in the saturated $(NN)_xMN$ complexes prepared in solid nitrogen.[1]

TABLE 5: Relative Energies, Bond Lengths, and Frequencies Calculated for NiN, NNiN, CoN, and NCoN States by Density Functional Theory

molecule	state	*E*, kcal/mol	bond length, Å	frequency, cm^{-1} (intensity, km/mol)
NiN[a]	$^2\Pi$	+5	1.617	845 (18)
	$^4\Sigma^-$	0	1.617	841 (18)
CoN[a]	$^1\Sigma^+$	+6	1.524	1089 (108)
	$^3\Pi$	+5	1.534	888 (38)
	$^5\Delta$	0	1.588	859 (38)
NNiN	$^1A_1$	+10	1.613 ∠N−Ni−N = 126°	934 (b_1, 46), 883 (a_1, 7), 297 (a_1, 5)
	$^3B_1$	+8	1.640 ∠N−Ni−N = 124°	800 (b_1, 4), 780 (a_1, 0), 259 (a_1, 5)
	$^5A_1$	0	1.693 ∠N−Ni−N = 103°	767 (a_1, 8), 589 (b_1, 0), 223 (a_1, 13)
NCoN	$^2B_1$	+1	1.592 ∠N−Co−N = 118°	965 (a_1, 1), 932 (b_1, 60), 364 (a_1, 1)
	$^4A_2$	0	1.613 ∠N−Co−N = 112°	912 (a_1, 25), 644 (b_1, 31), 223 (a_1, 13)

[a] DGauss, all others ADF; the energy, *E*, is relative to lowest state.

TABLE 6: Relative Energies, Bond Lengths, and Frequencies Calculated for Dinitrogen Complexes of Co and Ni by Density Functional Theory

molecule	state	*E*, kcal/mol	bond length, Å	frequency, cm^{-1} (intensity, km/mol)
Co(N$_2$)	$^2A'$	+9	Co−N = 1.901 N−N = 1.168	1842 (546), 438 (73), 324 (14)
CoNN	$^2\Delta$	0	Co−N = 1.692 N−N = 1.136	2082 (627), 562 (8), 308 (10)
Ni(N$_2$)[a]	$^1A_1$	+9	Ni−N = 1.83 N−N = 1.193	1807 (143), 558 (10), 447 (9)
NiNN[a]	$^1\Sigma^+$	0	Ni−N = 1.675 N−N = 1.150	2105 (433), 590 (10), 295 (18)
58-14-14[b]	$^1\Sigma^+$		Ni−N = 1.670	2124.9 (354), 593.1 (5), 298.0 (14)
60-14-14			N−N = 1.135	2124.9, 589.8, 297.8
58-15-15			$C_{\infty v}$	2033.2, 579.6, 288.2
58-15-14				2086.5, 586.9, 290.8
58-14-15				2092.2, 585.3, 295.4
58-(14-14)$_2$	$^1\Sigma_g^+$		Ni−N = 1.759 N−N = 1.125 $D_{\infty h}$	2207.0 (0), 2138.2 (1309), 511.1 (190), 433.8 (0), 284.0 (268)
60-(14-14)$_2$				2206.9, 2138.2, 506.8, 433.8, 283.6
58-(15-15)$_2$				2132.3, 2066.0, 502.5, 419.2, 275.0
58-(14-14)$_3$	$^1A_1'$		Ni−N = 1.823 N−N = 1.22	2221.9 (0), 2156.1 (821 × 2), 424.5 (22 × 2) 382.2 (0), 364.9 (58 × 2), 344.1 (1)
60-(14-14)$_3$			D_{3h}	2221.9, 2156.1, 423.3, 382.2, 363.2, 343.0
58-(15-15)$_3$				2146.8, 2083.2, 412.7, 369.2, 355.8, 334.8
58-(14-14)$_4$	$^1A_1$		Ni−N = 1.881 N−N = 1.100 T_d	—[c]

[a] DGauss, all others ADF. [b] Isotopic frequencies calculated using ADF. [c] Frequency calculation not successful.

These NiN and CoN fundamentals are near the NiO (825.7 cm^{-1}) and CoO (846.2 cm^{-1}) fundamentals, as FeN (938.0 cm^{-1}) is near the FeO (872.8 cm^{-1}) value,[1,2,9,10] but the small differences within this trio of monoxides and mononitrides will require closer inspection of the molecular orbitals involved and quantum chemical calculations. The present DFT calculations (DGauss) predict a quartet ground state for NiN with a 841 cm^{-1} fundamental, in excellent agreement with the nitrogen 838.8 cm^{-1} matrix value, and a quintet ground state for CoN with a 859 cm^{-1} frequency, some 33 cm^{-1} higher than the argon matrix value. An earlier theoretical study (CASSCF) considered only a doublet ground state[19] for NiN, but the present DFT calculations find the lowest doublet state to be 5 kcal/mol higher than the quintet state.

Previous work with VN, CrN, and MnN gave evidence for several (NN)$_x$MN complexes.[22] For the later transition metal atoms, the presence of more d electrons reduces the capacity for coordination with NN ligands, and the perturbation by NN ligands is less for FeN, CoN, and NiN than with VN and CrN in the saturated (NN)$_x$MN complexes. Finally, as discussed for iron, sufficient dinitrogen is dissociated in these laser-ablation experiments to provide N atoms for reaction with Co and Ni atoms to form the metal nitride molecules.[1] Again, the formation of the N$_3$ radical[1,11] attests the production of N atoms in these experiments.

The weak 2.5:1.0 nickel isotopic doublet at 712.9, 710.7 cm^{-1} in solid nitrogen also shows diatomic 58/60 and 14/15 isotopic ratios and no evidence of a mixed nitrogen isotopic component. This band is likely due to a perturbed NiN species that cannot be identified without more information.

Monometal and Dimetal Dinitrides. Transition metal mononitride and dinitride molecules are both known for two cases; namely, iron[1] and chromium.[22] In solid nitrogen, FeN absorbs at 934 cm^{-1} and the antisymmetric stretching funda-

TABLE 7: Relative Energies, Bond Lengths, and Frequencies Calculated for Dimetal Mono- and Dinitrogen Species by ADFT

molecule	state	bond length, Å	frequency, cm^{-1} (intensity, km/mol)
CoCoN bent + 23 kcal/mol	$^2A'$	Co−Co = 2.168 Co−N = 1.552 ∠Co−Co−N = 113°	982 (58), 282 (11), 54 (1)
Co_2N C_{2v}	$^2A_2$	Co−N = 1.667 ∠Co−N−Co = 82°	856 (a_1, 103), 650 (b_1, 0), 319 (a_1, 5)
$(CoN)_2$ D_{2h}, + 30 kcal/mol	$^1A_{1g}$	Co−N = 1.714 Co−Co = 2.503	824 (0), 701 (39), 628 (109), 588 (0), 335 (0), 119 (36)
$(CoN)_2$ D_{2h}, + 21 kcal/mol	$^5B_{2g}$[a]	Co−N = 1.715 Co−Co = 2.342	842 (0), 695 (207), 494 (0) 469 (97), 409 (0), 286 (21)
$(CoN)_2$ D_{2h}, + 21 kcal/mol	$^3B_{1g}$	Co−N = 1.697 Co−Co = 2.556	816 (0), 774 (51), 636 (0), 610 (90), 331 (0), 231 (42)
Co_2N_2 C_{2v} minimum	$^3B_1$	Co−Co = 2.160 N−N = 1.210 Co−N = 1.754	1540 (321), 644 (7), 533 (0) 340 (27), 283 (0), 247 (0)
Ni_2N C_{2v}	^2X[b]	Ni−N = 1.685 ∠Ni−N−Ni = 87°	789 (a_1, 51), 680 (b_2, 18), 256 (a_1, 3)
$(NiN)_2$ D_{2h}, +2 kcal/mol	$^1A_{1g}$	Ni−N = 1.756 Ni−Ni = 2.063	822 (0), 708 (98), 514 (0), 460 (0), 434 (13), 409 (4)
$(NiN)_2$ minimum D_{2h}	$^3B_{3g}$	Ni−N = 1.764 Ni−Ni = 2.170	796 (0), 634 (83), 464 (45), 447 (0), 442 (0), 304 (20)

[a] The septet rhombus structure had imaginary frequencies. [b] Symmetry not available.

TABLE 8: Relative Energies, Bond Lengths, and Frequencies Calculated for CoNO Isomers

molecule	state	bond length, Å	frequency, cm^{-1} (intensity, km/mol)
Co−NO bent	$^3A'$	Co−N = 1.666 N−O = 1.192	1685 (965), 655 (19), 269 (1)
Co(NO) ring, + 10 kcal/mol	$^1A'$	Co−N = 1.664 Co−O = 1.889 N−O = 1.260	1261 (221), 783 (7), 398 (38)
N−Co−O bent, + 29 kcal/mol	$^1A'$	N−Co = 1.547 Co−O = 1.610 ∠N−Co−O = 131°	1034 (84), 907 (42), 234 (8)
N−Co−O bent, + 34 kcal/mol	$^3A'$	N−Co = 1.566 Co−O = 1.617 ∠N−Co−O = 133°	1015 (61), 896 (34), 239 (8)

mental of bent (114°) NFeN is 904 cm^{-1}, and CrN absorbs at 1044 cm^{-1} and bent (109 ± 4°) NCrN at 875 cm^{-1}. However, DFT calculations for NCoN and NNiN suggest the reverse relationship; namely, that ν_3 of the dinitride may be above the mononitride fundamental. The isoelectronic molecules OMnO and OFeO are bent and have ν_3 fundamentals at 947 ± 1 cm^{-1}.[2,23] For cobalt, two mixed nitrogen isotopic triplets were observed at 711.1 and 705.1 cm^{-1}. Both exhibited slightly asymmetric isotopic triplets denoting interaction with a higher symmetric stretching mode in the 14-M-15 isotopic molecule. These symmetric modes were in fact observed at 717.7 and 713.1 cm^{-1}, respectively. Without cobalt isotopic splittings (^{59}Co is 100.0%) it is difficult to determine the number of Co atoms in each absorber. However, the sharp 705.1 cm^{-1} band increased 10-fold on annealing and the 711.1 cm^{-1} band only increased fourfold. These bands are probably due to $(CoN)_2$.

A similar behavior is observed for nickel. The 723.3 cm^{-1} band, which doubles and resolves into a nickel isotopic triplet (7:5:1) on annealing, is appropriate for the vibration of two equivalent Ni atoms as is the triplet that appears at 718.3, 717.2, 716.1 cm^{-1}. Both of these Ni isotopic triplets exhibit mixed nitrogen isotopic triplets (Figures 4 and 5), indicating the vibration of two equivalent nitrogen atoms. The 14/15 ratios (1.0276 and 1.0273) are essentially diatomic as are the 58/60 ratios (1.00305 and 1.00307; note that the intermediate band is for the 58−60 nickel isotopic species). Thus, these bands are due to two different matrix sites of $(NiN)_2$ as the mixed isotopic nonet patterns so indicate. The argon matrix experiments give a $(NiN)_2$ band system at 710.1 cm^{-1} with identical nickel and nitrogen isotopic splittings. The only difference is the mechanism of formation, based on the $^{14}N_2 + {}^{15}N_2$ experiment; in solid nitrogen, $(NiN)_2$ arises from dimerization of NiN, and in solid argon, $(NiN)_2$ is produced by the reaction of NiNN with a second Ni atom. Note here that further ligation by dinitrogen at the metal centers in $(NiN)_2$ on going from argon to nitrogen environments has a small effect on the b_{2u} mode.

DFT calculations support these assignments. First, the $(CoN)_2$ rhombic ring is predicted to have stable triplet and quintet states with nearly the same energy, but the quintet frequencies fit the observed spectrum better with a strong b_{2u} mode predicted at 695 cm^{-1} and a weaker b_{3u} mode predicted at 469 cm^{-1}, as compared with strong 711 and weak 537 cm^{-1} bands with appropriate 14/15 isotopic ratios. On symmetry lowering to $(Co^{14}NCo^{15}N)$, the higher symmetric stretching mode will couple and lead to asymmetry in the strong triplet plus observation of the symmetric stretching mode. Note the short 2.342 Å Co−Co distance across the ring, which is consistent with weak metal−metal bonding. The $(NiN)_2$ ring has stable singlet and triplet states, and the strongest calculated frequency for the singlet state, the b_{2u} mode at 708 cm^{-1}, is in excellent agreement with the observed spectrum. Note that the calculated 460 cm^{-1} (a_g) band, the Ni−Ni stretching mode, is higher than this mode for Ni_2 (379 cm^{-1}), and the calculated Ni−Ni length, 2.063 Å, is shorter than the 2.20 Å bond length for ground-state Ni_2.[24] Clearly, $(NiN)_2$ is stabilized in part by Ni−Ni bonding across the rhombic ring. Note that the Ni−Ni bond is shorter in $(NiN)_2$ than in $(NiO)_2$ (2.25 Å).[9]

The rhombic $(CoN)_2$ and $(NiN)_2$ molecules are of interest because two transition metal atoms are required to break the dinitrogen bond. However, in the pure $^{14}N_2 + ^{15}N_2$ experiments, the observation of intermediate mixed isotopic components show that these molecules are formed by dimerization of the mononitrides. On the other hand, the observation of only an isotopic

$$CoN + CoN \rightarrow (CoN)_2$$

$$NiN + NiN \rightarrow (NiN)_2$$

doublet with $^{14}N_2 + ^{15}N_2$ for the $(NiN)_2$ species in solid argon demonstrates that a *single dinitrogen molecule* is reduced by two Ni atoms involving the NiNN intermediate, which is a simple nitrogen fixation process.

$$Ni + NN + Ni \rightarrow NiNN + Ni \rightarrow (NiN)_2$$

The 875.1 cm^{-1} band in solid argon is appropriate for tentative assignment to NNiN. The isotopic splittings show one Ni and two equivalent N atoms and the 14/15 and 58/60 isotopic ratios are in accord with a bent molecule (129° upper and 117° lower valence angle limits). The DFT calculations predict singlet, triplet, and quintet states within 10 kcal/mol (Table 5), and the singlet and triplet states have calculated ν_3 frequencies in this region. What then is the case for NCoN? The DFT calculations do not support assignment of the 705.1 cm^{-1} band to NCoN, so this band is probably a matrix site of $(CoN)_2$. No assignment can be made to NCoN from this work.

The 662.7, 661.0 cm^{-1} nickel isotopic doublet shows involvement of one nickel atom and intermediate absorption with $^{14,15}N_2$ for two (most likely inequivalent) nitrogen atoms. This species grows on annealing along with $(NiN)_2$ and exhibits essentially diatomic isotopic ratios. A tentative assignment to an open NiNNiN dimer is suggested.

Dimetal Mononitrides: CoCoN and NiNiN. The sharp band that increases markedly on annealing in cobalt experiments at 1016.6 cm^{-1} and the structured feature at 996.0 cm^{-1} with nickel that increases slightly and shows more structure on annealing both exhibit no evidence of intermediate isotopic components with nitrogen isotopic mixtures. This information indicates that only one N atom participates in this vibration; however, the 14/15 ratios (1.0311 and 1.0312) demonstrate that this N atom is moving against more than one metal mass. Although the resolution is not complete, the 996.0 cm^{-1} band gives the same appearance as the 723.3 cm^{-1} band and a partially resolved 7:5:1 triplet at 996.0, 995.3, 994.6 cm^{-1} the first two components of such a triplet at 999.4, 998.7 cm^{-1} and possibly also at 997.7, 996.9 cm^{-1}. Although this structure does not prove that two nickel atoms are involved in the vibration, it strongly suggests such a possibility. The vibration of *one N atom* against *two nickel masses* would produce a 14/15 ratio 1.0310, almost the same as the 1.0312 observed value. The calculated 58−58 to 58−60 and 60−60 nickel isotopic splittings for such a vibration are 0.9 and 1.8 cm^{-1}, respectively, which is in reasonable agreement with the 0.7 and 1.4 cm^{-1} observed splittings. Hence, the spectroscopic observations are consistent with tentative assignment of the 1016.6 and 996.0 cm^{-1} bands to bent CoCoN and NiNiN, respectively. The DFT calculations offer some support for the observation of bent CoCoN, but the analogous NiNiN species could not be calculated.

Evidence was presented in iron experiments[1] for a cyclic Fe_2N feature with a symmetric Fe_2−N stretching mode at 779 cm^{-1}. The strong bands for cobalt at 745.4 cm^{-1} in solid N_2 and at 746.8 cm^{-1} in solid argon exhibit sharp doublets with statistical isotopic mixtures indicating the vibration of a single N atom. The 14/15 ratios again exceed the CoN diatomic ratio, suggesting that N is vibrating against a mass heavier than a single Co atom. The DFT prediction of a strong symmetric Co_2−N stretching mode at 856 cm^{-1} supports assignment of these bands to cyclic Co_2N. No such species was observed for nickel.

Metal Dinitrogen Complexes MNN and M(N_2). The end-bonded Ni−NN complex was definitively identified by a sharp quartet absorption at 2089.9, 2057.4, 2053.6, 2020.6 cm^{-1} with statistical $^{14,15}N_2$ in solid argon showing two inequivalent nitrogen atoms; however, a triplet absorption at 2101.0, 2066.5, 2029.5 cm^{-1} in the same region was interpreted as side-bonded Co(N_2).[5,6] The present DFT calculations for both NiN_2 and CoN_2 isomers (Table 6) predict both end-bonded species near 2100 cm^{-1} and both side-bonded species in the low 1800 cm^{-1} region. Unfortunately, the lack of coupling between Co−N and N−N in Co−NN complicated the earlier interpretation.[6] The 2101 cm^{-1} band is here reassigned to end-bonded Co−NN.

The present work supports the previous assignment of N−N stretching bands at 2089, 2106, 2139, and 2174 cm^{-1} in solid argon to $Ni(NN)_x$ with $x = 1, 2, 3, 4$ but provides new bands for assignment to the Ni−N stretching modes.[5] Note that our DFT calculations predict the former mode 1−2% too high and a like scale down for the latter mode calculation predicts 580 cm^{-1}, which is >100 cm^{-1} higher than the 466 cm^{-1} band assigned previously.[5]

The spectra in Figure 6 show two band systems with large nickel isotopic splittings characteristic of Ni−NN stretching modes, namely, 563.7, 484.6 (site), and 469.5 cm^{-1}, and a broader 417.6 cm^{-1} band. The 563.7 cm^{-1} band exhibits a minor matrix site splitting at 557.8 cm^{-1}, which disappears on annealing to 35 K just as does the 2086.0 cm^{-1} splitting on the 2089.2 cm^{-1} band of NiNN. Final annealing to 40 K decreases the 2089.2 and 563.7 cm^{-1} bands together. The 563.7 cm^{-1} band shows no mixed isotopic counterpart in $^{14}N_2 + ^{15}N_2$ experiments, and the 484.6 and 469.5 cm^{-1} bands reveal intermediate components at 480.7 and 465.6 cm^{-1}, respectively. However, with the scrambled isotopic sample, a stronger 557 cm^{-1} intermediate band was observed with the 563 and 551 cm^{-1} bands, and a pentet of bands was observed for the 469.5 cm^{-1} absorption system. The isotopic frequency ratios of these bands show that the 563.7 cm^{-1} band involves more Ni and less N motion than Ni−N itself (14/15 ratio 1.0230 and 58/60 ratio 1.00552) and the stronger 484.6 and 469.5 cm^{-1} absorptions exhibit even more Ni and less N motion (58/60 ratios 1.00748 and 1.00816, and 14/15 ratios 1.0174 and 1.0171). The latter bands clearly involve the vibration of Ni between N_2 subunits and show completely resolved nickel isotopic splittings. Stepwise annealing associates the sharp 469.5 and 2104.6 cm^{-1} absorptions, and the broader 417.6 and 2136.4 cm^{-1} bands. Isotopic data show that the 469.5 cm^{-1} band is also due to Ni-$(NN)_2$. The triplet with $^{14}N_2 + ^{15}N_2$ and the pentet with $^{14}N_2 + ^{14}N^{15}N + ^{15}N_2$ are appropriate for the antisymmetric NN−Ni−NN vibration of a linear molecule. It is interesting to note that the antisymmetric stretch of the simple model N_2−Ni−N_2 compound, treating N_2 as a subunit, predicts the 58/60 ratio 1.00748 and the 14/15 ratio 1.0174.

The 563.7 cm^{-1} band involves the vibration between one Ni atom and one N_2 molecule, based on isotopic data, and it is assigned to the Ni−NN stretching mode in this molecule.

Agreement of band position and isotopic frequency ratios with DFT calculated frequencies (Table 6) substantiates this assignment. A similar conclusion has been reached by Manceron et al.[25] In light of the aforementioned association of Ni−NN and N−N stretching modes, the 469.5 cm^{-1} band is assigned to the antisymmetric NN−Ni−NN stretching mode in ^{58}Ni(NN)$_2$. Again the observed 58/60 and 14/15 isotopic ratios are nicely matched by DFT frequency calculations. The DFT calculations predict a 13 cm^{-1} blue shift and an 82 cm^{-1} red shift in the antisymmetric N−N and Ni−N stretching modes in Ni(NN)$_2$ with respect to the fundamentals for NiNN, which are in excellent agreement with the observed 15 and 79 cm^{-1} shifts. The 417.6 cm^{-1} band is assigned to the analogous mode for Ni(NN)$_3$. Note that the much higher 14/15 ratio (1.0283) is matched by the DFT frequency calculation (1.0286) as well as the prediction of a band near 424 cm^{-1}.

Unfortunately the spectrum for Co(NN)$_x$ species is not as straightforward. The 465.1 cm^{-1} band in the Co system shows the same isotopic behavior as the 469.5 cm^{-1} Ni band and it is tempting to assign the 465.1 and 2155 cm^{-1} bands, which show similar annealing behavior, to Co(NN)$_2$. The 431.9 and 2206.1 cm^{-1} bands are strong on final annealing, and coupled with similar bands at 442 and 2207 cm^{-1} in pure nitrogen, Co(NN)$_4$ is suggested.

The antisymmetric N−N stretching fundamental (t_2) of Ni(NN)$_4$ in solid argon at 2174 cm^{-1} is split into 2170 and 2181 cm^{-1} bands on symmetry reduction in solid nitrogen.[5] Likewise it is reasonable to expect the t_2 Ni−NN mode to be split as well. Accordingly the 486.3 and 449.0 cm^{-1} bands in solid nitrogen, which track with the 2181 and 2170 cm^{-1} bands on annealing, are assigned accordingly. Note that such bands were not observed in solid argon. It is possible for the a_1 counterpart assigned to a polarized 303 cm^{-1} Raman band to be correct, but the previous t_2 assignment at 283 cm^{-1} is not correct.[5] A comparison with Ni(CO)$_4$ stretching modes [368 cm^{-1} (a_1), 421 cm^{-1} (t_2)[26]] supports the present assignments. Finally, the weaker 433.6 cm^{-1} band appears and disappears on annealing along with the 2133.6 cm^{-1} band, which are appropriate for assignment to Ni(NN)$_3$ in a nitrogen matrix. We have no evidence for Ni(NN)$_2$ nor NiNN in solid nitrogen, but the 1902.7 and 1870.6 cm^{-1} bands are appropriate for sideways-bound Ni(N$_2$), which is destroyed on annealing.

Both pure N$_2$ experiments show bands in the 1870 cm^{-1} region that could be due to side-bonded species. The coproduct at 1873.5 cm^{-1} gives a triplet with statistical ^{14,15}N$_2$ and the 14/15 ratio 1.0344 for a pure N−N mode, and the Ni product at 1870.6 cm^{-1} gives a doublet with ^{14}N$_2$ + ^{15}N$_2$ (no statistical sample) and the 1.0341 ratio. The argon matrix band at 1879.3 cm^{-1} gives a triplet with a statistical sample and is appropriate for two equivalent nitrogen atoms. These bands are assigned to Co(N$_2$) and Ni(N$_2$), respectively. Finally, the bands that grow strongly on annealing at 1811.1, 1801.8, 1794.5 cm^{-1} with Ni could be due to bridged N$_2$ subunits. The accompanying band at 600.2 cm^{-1} reveals a broad triplet absorption (unresolved nonet pattern) and involves two equivalent N$_2$ subunits. These absorptions are tentatively identified as Ni(μ-N$_2$)$_2$Ni ring species.

NCoO and NNiO. The terniary species NFeO was observed at 798.1 cm^{-1}, below FeO at 872.8 cm^{-1}.[2,3] It is therefore reasonable to find similarly red-shifted Co−O and Ni−O stretching modes for NCoO and NNiO. The sharp, weak band at 798.0 cm^{-1} for Co in ^{14}N$_2$ shifts to 797.8 cm^{-1} in ^{15}N$_2$ and to 762.2 cm^{-1} with ^{18}O$_2$ in ^{14}N$_2$. The 16/18 ratio, 1.0468, is near the observed diatomic Co−O value (1.0465) and the 0.2 cm^{-1} ^{15}N shift shows that nitrogen is involved (if only slightly). Likewise, the 760.5, 758.1 cm^{-1} 2.5:1.0 doublet with Ni in ^{14}N$_2$ revealed the strongest band at 760.3 cm^{-1} with ^{15}N$_2$ and a doublet at 726.3, 723.7 cm^{-1} with ^{18}O$_2$ in ^{14}N$_2$. The 16/18 ratio, 1.0471, is also slightly higher than the observed diatomic Ni−O value (1.0460), and the small ^{15}N shift indicates minimum involvement of nitrogen. The 798.0 and 760.5 cm^{-1} bands are assigned to the metal−oxygen stretching modes of NCoO and NNiO, respectively. The metal-nitrogen stretching fundamental is not observed here, although DFT calculations predict observable intensity as was found for the iron species.

NCo(O$_2$) and NCoO$_2$. Bands at 943.9 and 859.1 cm^{-1} are enhanced by the addition of oxygen, but only the 943.9 cm^{-1} band shifts in ^{15}N$_2$ (to 943.7 cm^{-1}). The 16/18 ratio, 1.0557 and 1.0416, are near values for Co(O$_2$) (1.0575) and OCoO (1.0378), and these bands become triplets with added statistical mixed isotopic oxygen. Hence, the 943.9 cm^{-1} band is probably due to NCo(O$_2$) and the 859.1 cm^{-1} band to NCoO$_2$.

Nitrosyl Complexes MNO. Trace quantities of NO were produced in these nitrogen matrix experiments from oxide impurity and new product bands were observed at 1771.6 cm^{-1} for Co and 1723.0, 1720.7 cm^{-1} for Ni. These bands shifted, respectively, to 1734.8 and 1688.8, 1686.0 cm^{-1} in ^{15}N$_2$ matrixes and showed only the pure isotopic bands (i.e., a doublet) with mixed isotopic nitrogen. Furthermore, these bands were enhanced when ^{16}O$_2$ was added to the nitrogen matrix, and they shifted to 1735.5 and 1686.3, 1683.8 cm^{-1}, respectively, when ^{18}O$_2$ was instead added, and showed only the pure isotopic bands with mixed isotopic oxygen. The mixed isotopic spectra suggest vibrations of a single N−O subgroup and invite consideration of metal nitrosyls.

As was the case for FeNO,[2] the 14−16/15−16 ratios 1.0212 for Co and 1.0206 for Ni and 14−16/14−18 ratios 1.0208 for Co and 1.0218 for Ni are slightly different from the NO diatomic values 1.0179 and 1.0266, respectively. The new nitrosyl product bands show more nitrogen and less oxygen mass dependence than the isolated diatomic molecule, which is consistent with N vibrating between M and O in the M−N−O species.

The present 1723.0, 1720.4 cm^{-1} band for NiNO in solid nitrogen is in agreement with the 1727.3 cm^{-1} observation of Ruschel et al. in solid argon,[27] although we observed no evidence of a lower band near 1670 cm^{-1}. We did however, observe a sharp 1749.6 cm^{-1} band with O$_2$ doping, which increased slightly on annealing and shifted to 1713.5 cm^{-1} with ^{18}O$_2$. A doublet was observed with ^{16,18}O$_2$, which clearly demonstrates that only one oxygen atom is involved in this vibration. A similar 1749.6 cm^{-1} band observed in solid argon was assigned to Ni(NO)$_2$ without supporting evidence for mixed isotopic substitution. These bands are probably due to the same species, which based on the present ^{16,18}O$_2$ observation can involve only one NO subunit. This N−O vibration shows a similar 1.0211 oxygen 16/18 ratio, again characterizing binding at nitrogen. Because the 1749.6 cm^{-1} band yield is much higher in ^{16}O$_2$-doped experiments where nickel oxides are present, this band is probably due to ONiNO.

The present 1771.4 cm^{-1} band for CoNO in solid nitrogen is in good agreement with the 1767.2 cm^{-1} band assigned to CoNO in solid argon.[27] As both Co and NO concentrations were low in our experiments, we did not detect the other product bands reported by Ruschel et al. and ascribed to higher Co$_x$(NO) or Co(NO)$_x$ complexes. Further studies will be required to confirm these assignments.

Charged Species. Weak bands were detected here for N$_3^-$, NO$_2^-$, and O$_3^-$ in solid nitrogen,[1,2,11] so electrons are produced in the ablation process and captured by molecules in the matrix. These bands are weak, and such isolated charged species make a minor contribution to the total product yield.

Two other weak bands in the Co experiments grow on annealing at 1346.2 and 1204.4 cm^{-1}, and with added O_2 another band appeared at 1172.3 cm^{-1}. In contrast to the 1771.6 cm^{-1} band, the 1346.2 cm^{-1} band shows ^{15}N and ^{18}O shifts that define isotopic frequency ratios (1.0171, 1.0272) that agree very well with the NO molecule. Furthermore, mixed isotopic experiments reveal only doublets so only one NO subunit is involved. In contrast, the 1172.3 cm^{-1} band shows a triplet with $^{16,18}O_2$ and is appropriate[28] for $(Co^+)(NO_2^-)$. Hence, charge transfer from Co to an electron-accepting molecule can occur on diffusion and association in the matrix. The 1346.2 cm^{-1} band is in the region expected for $(N-O)^-$ vibrations[29] so it is assigned to a $(Co^+)(NO^-)$ species, which presumably is a side-bonded cyclic molecule with considerable intramolecular charge transfer in contrast to the open Co−N═O nitrosyl species. Similar behavior was found for Fe as both Fe−N═O and $(Fe^+)(NO^-)$ species were observed.[3] In contrast we find no evidence here for $(Ni^+)(NO^-)$, but $(Ni^+)(NO_2^-)$ is identified by weak absorptions at 1214 and 1202 cm^{-1} in O_2-doped experiments.

Conclusions

Laser-ablated Co and Ni atoms co-deposited with pure nitrogen at 10 K gave a strong new 795.3 cm^{-1} band with cobalt and a 838.8, 836.1 cm^{-1} nickel isotopic doublet, which exhibited 14/15 isotopic ratios appropriate for the diatomic CoN and NiN molecules. In solid argon, CoN absorbs at 826.5 cm^{-1} and gives way on annealing to bands at 795.8 and 792.0 cm^{-1}, which are due to $(NN)_xCoN$ complexes. The DFT calculations predict quintet and quartet ground states for CoN and NiN, respectively, and frequencies in reasonable agreement with the observed values. Evidence is also presented for dimetal dinitrides, with rhombus structures and metal−metal bonding across the ring. In the case of nickel, two Ni atoms reduce one N_2 molecule to $(NiN)_2$, which is a simple example of nitrogen fixation.

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