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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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interaction. From the energy level structure found, all three of the intermediates were determined to be diamagnetic, as $Ni(CO)_4$ is known to be.

Electronic Energy Levels of Intermediates in the Nickel Carbonylation Reaction[a)]

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Abstract

Using the multiple scattering $X\alpha$ method, electronic energy levels have been found self-consistently for the intermediates $Ni(CO)_n$, n=1,2,3 in the formation of nickel tetracarbonyl via the Ni-CO surface reaction. Linear geometries have been assumed for NiCO and $Ni(CO)_2$, and a trigonal planar conformation for $Ni(CO)_3$, in accordance with previously published IR spectra. The intermediates were assumed to be in the gas phase, free of surface interaction. From the energy level structure found, all three of the intermediates were determined to be diamagnetic, as $Ni(CO)_4$ is known to be.

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Introduction

Self-consistent field calculations using the multiple scattering Xα (MSXα) technique are reported on the electronic structure of the mono-, di-, tri-, and tetracarbonyls of nickel. The results allow the evolution of the tetracarbonyl level structure to be traced from the point of surface detachment of the Ni+CO complex.

Chemisorption processes in general, and catalysis in particular, have been the subjects of intensive study in recent years. Of special interest is the role played by d-electrons in transition metal substrates; catalytic ability seems, with few exceptions, to be directly correlated with d-band vacancies, filled by covalent bonding with adsorbate molecules. The exact extent and nature of d-electron involvement in this bonding is one of the largely unresolved points of interest in the study of chemisorption. As a prototype for the understanding of nondissociative chemisorption, the nickel-carbon monoxide reaction has received considerable attention. The bonding of the CO molecule to a transition metal substrate such as nickel is considered to be relatively simple, and therefore amenable to investigation; the CO on Ni system has been extensively studied both experimentally [1-6] and theoretically[7-22]. Recently, photoemission spectroscopy of CO adsorbed on a nickel surface has determined the presence of large relative shifts in the CO levels upon adsorption; the use of angle-resolved techniques[3,4] has affirmed that a reversal of the two topmost occupied CO levels, the 1π and 5σ levels, takes place on adsorption, the 5σ level becoming strongly involved in bonding. As the CO 5σ orbital is a carbon "lone pair" orbital extending into the metal surface, we would indeed expect stronger interaction than with the CO 1π orbital or the deeper oxygen "lone pair" orbital, 4σ, which points away from the surface. Theoretical studies, concurrently, have investigated the role of nickel s, p, and d electrons in bonding CO, and the extent to which back donation of nickel electrons into the (normally unoccupied) CO 2π* level takes place. There have been numerous studies of the $Ni(CO)_4$ molecule[7-16], and, more recently, calculations of the level structure of atomic clusters taken to simulate CO bonding to a nickel surface: NiCO[17-19], Ni_4CO[20], Ni_5CO[19-22], and bridge-bonded Ni_2CO[18-20].

Theoretical approaches have included ab initio calculations[7,9,10,17,18], Hartree-Fock-Slater methods[19,22], and MSXα calculations[8,12-14,21,22]. Among the calculations for $Ni(CO)_4$, results as to orbital energies and orbital character are in agreement on general features; namely, the highest occupied ($9t_2$ and 2e) levels are predominantly of nickel 3d character, and the CO 5σ- and 1π-derived levels become nearly coincident or reversed. Calculations for chemisorbed CO using cluster models also predict a near-coincidence[22] or reversal[17-21] of these levels.

There have been several studies of the linear NiCO cluster, one of the intermediates considered here, as a model for chemisorption. Bagus and Hermann[17,18] did Hartree-Fock calculations on NiCO and concluded that the ground state had an open-shell ($12\sigma^1$ $1\delta^3$) structure. Rosen, Baerends and Ellis, in a subsequent Hartree-Fock-Slater calculation[19], showed a closed-shell configuration ($11\sigma^2$ $1\delta^4$), and recently Fenske[23], from a Hartree-Fock configuration-interaction study, has also found NiCO to be closed-shell.

The primary motivation for the present set of calculations was the series of experiments by R.S. Mehta[24] investigating the effect of the magnetic state of a nickel substrate on the gaseous $Ni(CO)_4$ formation rate. It was found that the activation energy ΔE for the breaking away of the Ni+CO complex from the surface is dependent on the para- or ferromagnetic state of the nickel; for example, for a $Ni_{0.72}Cu_{0.28}$ alloy $\Delta E \approx 0.15$eV in the paramagnetic state, while $\Delta E \approx 0.35$eV in the ferromagnetic state. Based on these findings a model for $Ni(CO)_4$ formation was proposed in which the Ni+CO complex was inferred to be diamagnetic upon departure from the surface. Our calculations were undertaken to find the magnetic state of the intermediates $Ni(CO)_n$, n= 1,2,3 and the evolution of their electronic structure as additional carbonyl groups are added. Computations for CO and $Ni(CO)_4$ were included for comparison.

Our results showed that all of the series $Ni(CO)_n$, n = 1,2,3,4 are closed-shell molecules, and that most of the principal level shifts due to bonding occur by the time the second CO group has been added to the nickel atom. This is in accordance with the findings of photoemission studies, which also show large shifts in the CO orbitals for a single isolated molecule bonded to Ni.

Method

The multiple scattering Xα method has been extensively applied to atomic clusters[25,26]. A muffin-tin potential is assumed, constant between atomic spheres surrounding each nucleus and spherically symmetric inside the atomic spheres andoutside a bounding sphere enclosing the entire molecular cluster. The orbital wave function (WF) is expanded inside the atomic spheres in the partial wave representation, using numerically generated solutions to the atomic Schroedinger equation. In the intersphere region the expansion is in terms of modified Bessel functions. The Slater local approximation to the exchange potential, $V_{xch}(r) = -3\alpha[3\rho(r)/8\pi]^{1/3}$ is used, where α is a numerical parameter of the order of 0.7. Using boundary conditions of continuity of the orbital WF and its first derivative across sphere boundaries the scattered wave secular equations can be set up. The generated expansion coefficients are then employed in setting up the new potential, and the process is repeated to self-consistency.

The method has been widely used in finding the electronic structure of molecular species (e.g., refs. 8,26) and of clusters taken to simulate a solid[27]. In calculations of the levels of $Ni(CO)_4$, those obtained by MSXα methods[8,13,14] are in agreement with those found from other, <u>ab initio</u>, methods[7,9] with the possible exception of finding a larger Ni 4s involvement in bonding and a lesser effect of 2π backbonding. Larsson and Braga[12] and Braga, Larsson, and Leite[13] have shown convincingly, however, that the differences lie in the interpretation of the resulting orbital WF's rather than in the reliability of the methods employed.

All the molecules included in our study were taken to be in the gaseous phase, completely desorbed from the surface. The clusters consisted, therefore, of a single Ni atom bonded to 1,2,3 or 4 CO groups. Calculations were carried to a self-consistency of ±0.002 Rydberg for all valence levels over an energy range from -2.5 Ryd to -0.1 Ryd. Symmetry assignments for the intermediates were made in accordance with the IR vibrational mode spectra taken by DeKock[28]. This gives a linear monocarbonyl ($C_{\infty v}$) and dicarbonyl ($D_{\infty h}$) and a trigonal planar (D_{3h}) tricarbonyl as shown in Figure 1. The interatomic distances used for the $Ni(CO)_n$, n = 1-4 were those of Braga, Larsson, and Leite[13] in their calculation of the $Ni(CO)_4$ electron levels. These distances were used in the absence of data on the intermediate carbonyls. The CO molecule equilibrium distance was used for the isolated CO calculation.[29] The radii of the atomic sphere regions were chosen to have a 20% overlap to improve accuracy; previous studies[30,31] have concluded that such an overlapping-spheres model provides an approximate correction for non-muffin tin effects by reducing the volume of the constant-potential intersphere region. The carbon and oxygen atomic sphere radii were determined from the ratio of covalent radii given by Slater[32]. Atomic cores were not frozen.

Results and Discussion

The calculated nickel monocarbonyl valence levels are shown in Figure 2 in comparison with the CO levels. The isolated CO calculation yielded level orderings and characters in agreement with the known CO level structure. Dashed lines connect the monocarbonyl levels to the CO levels from which they are principally derived. To differentiate the CO levels from those of NiCO, which have the same symmetry labelling, NiCO levels will be indicated in the following discussion by a tilde, e.g. $9\tilde{\sigma}$. The lowest NiCO valence levels, $8\tilde{\sigma}$ and $9\tilde{\sigma}$, are the shifted CO 3σ and 4σ levels, respectively. The CO 1π level shows a shift of only .03 Ryd, or 0.4eV, upon becoming $3\tilde{\pi}$, while the 5σ level shifts downward by 3.4eV to become $10\tilde{\sigma}$, the principal NiCO bonding level. This constitutes a reversal of 0.9eV between the $10\tilde{\sigma}$ and $3\tilde{\pi}$ levels; angle-resolved photoemission measurements give a 0.5eV reversal for CO on Ni(100)[4] and a 1.6eV reversal on Ni(111)[3], by way of comparison. As we will see, the addition of successive CO groups to Ni widens this reversal separation. The $10\tilde{\sigma}$ level is an admixture of the 5σ level, the carbon "lone pair" orbital, with Ni s, p_z, and d_z2 orbitals to a virtually equal extent (31% s, 31% p_z, and 38% d_z2).

The highest occupied NiCO orbitals are the $11\tilde{\sigma}$ and $1\tilde{\delta}$,respectively, both nickel d-nonbonding, a feature that persists throughout the series of intermediates. The $4\tilde{\pi}$ level is nickel d (90%) with a CO π (10%) admixture. There are no partially filled orbitals in NiCO; thus it has no static magnetic moment according to our calculation. Had the $5\tilde{\pi}$ (empty) level been more nearly degenerate with the $11\tilde{\sigma}$ and $1\tilde{\delta}$ levels, one might have expected exchange splittings to give partially filled levels and thus a paramagnetic molecule. The gap between $11\tilde{\sigma}$ and $5\tilde{\pi}$, however, is large, about 2eV, so the molecule is diamagnetic.

Dicarbonyl valence levels are compared to those of CO in Figure 3. The CO 3σ and 4σ levels are split into the degenerate (to the accuracy of our calculation) pair $6\sigma_g^+$, $5\sigma_g^+$ and the close-lying pair $7\sigma_u^+$, $6\sigma_u^+$, respectively. The CO 1π level participates in the formation of three occupied valence pi-levels, the $3\pi_u$, $1\pi_g$, and $2\pi_g$. The $3\pi_u$ orbital is virtually completely CO-like, showing only about 1% Ni character. The $1\pi_g$ and $2\pi_g$ orbitals represent combinations of the CO 1π and $2\pi^*$ wavefunctions. $1\pi_g$ is a pure oxygen p-type orbital, with no nickel or carbon character, while $2\pi_g$ has no admixture of oxygen and combines carbon p-character with Ni $d_{xz,yz}$. Thus the $1\pi_g$ and $2\pi_g$ orbitals provide the first direct evidence of occupation of the CO $2\pi^*$ orbital in the $Ni(CO)_n$ series.

The CO 5σ level participates in forming the $8\sigma_g{}^+$, $7\sigma_u{}^+$ orbitals, which again lie below the 1π-derived levels. The reversal splitting between $1\pi_u$, the most "CO 1π-like" orbital and the averaged $8\sigma_g{}^+$, $7\sigma_u{}^+$ pair is now 2.9eV, a 2eV increase over the NiCO analogous separation. The topmost occupied orbitals in $Ni(CO)_2$ are the $9\sigma_g{}^+$ and $1\delta_g$ nonbonding levels, as expected. As these are filled, the dicarbonyl, like the monocarbonyl, is diamagnetic.

The final molecule studied was the tricarbonyl, Figure 4. The same general features are evident here as in $Ni(CO)_2$ and NiCO. The 3σ and 4σ levels of CO split into e', a_1' pairs; the set of levels $7a_2'$, $3a_2''$, 8e' and 7e'', clustered around -0.81 Ryd, comprise the CO 1π-evolved levels (while $2\pi^*$ involvement can be assumed here, given the backbonding present in $Ni(CO)_2$ and $Ni(CO)_4$ it cannot be unambiguously demonstrated within the limits of our calculation). The 5σ level, split into $8a_1'$ and 7e', is an average of 2.6eV below the cluster of 1π-related levels. Nickel d-character is distributed principally on the set of levels 9e', 2e'', and $9a_1'$, the highest occupied orbitals. Again in $Ni(CO)_3$, all occupied orbitals are completely filled.

It is of interest that our results confirm to some extent DeKock's assignment of molecular geometries. Given that NiCO and $Ni(CO)_4$ are closed-shell, the fact that $D_{\infty h}$ and D_{3h} symmetries lead to closed-shell configurations for $Ni(CO)_2$ and $Ni(CO)_3$ tends to substantiate these symmetry assignments.

Figure 5 depicts the evolution of the level structure from CO to $Ni(CO)_4$, showing only the principal CO-derived valence levels. The calculated $Ni(CO)_4$ level structure is in close agreement with that found, for instance, by Braga, Larsson and Leite[13] in their MSXα calculation; we will not elaborate here except for purposes of comparison with an intermediate species. The energy difference between the CO 1π-derived levels ($1t_1$, $8t_2$, and 1e) and the principal 5σ-derived levels ($7t_2$, $8a_1$) is 2.8eV on the averagein $Ni(CO)_4$. (One should not put undue emphasis on these estimates of the reversal shifts, as they are simple averages over the groups of levels containing significant 1π- and 5σ-character. They serve, however, to illustrate the trend as CO groups are added.) The following general conclusions can be drawn from comparison of the $Ni(CO)_n$, n = 1-4 series: 1) the low-lying CO 3σ- and 4σ-derived valence levels shift very little, as expected, during the formation of $Ni(CO)_4$ (the 3σ level, for instance, going from -2.16 Ryd in CO to -2.21 Ryd in $Ni(CO)_2$, and -2.14 Ryd in $Ni(CO)_4$); 2) the nickel nonbonding levels shift slightly toward lower energies as the number of CO groups attached increases (see Table II); 3) most of the shifts associated with the CO 1π and 5σ levels have occurred by the time the second carbonyl group has been added, the reversal shift growing from 0.9eV in NiCO to nearly 3eV in $Ni(CO)_{2-4}$.

Summary

It has been confirmed that the isolated $Ni(CO)_n$ molecule is diamagnetic for any value of $\underline{n}$ from 1 to 4. Thus the Ni+CO complex is expected to be nonmagnetic upon detachment from the Ni substrate during the Ni-CO surface reaction. Reversal of the 5 and 1 CO-derived levels takes place even with only one attached CO group for the interatomic distances used in the present calculations.

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Table I

Calculational Parameters

Interatomic Distances (in a.u.)

R_{co} for CO: 2.132

R_{ni-c} for $Ni(CO)_n$: 3.440

R_{co} for $Ni(CO)_n$: 2.135

α - factors

carbon: 0.75928

oxygen: 0.74447

nickel: 0.70896

intersphere (for CO): 0.75039

intersphere (for $Ni(CO)_n$): 0.72376

Sphere Radii (in a.u.)

CO:	carbon	1.378
	oxygen	1.181
	outer sphere	2.346
$Ni(CO)_n$:		
	carbon	1.380
	oxygen	1.182
	nickel	2.749

outer sphere for NiCO 4.753

outer sphere for $Ni(CO)_{2-4}$ 6.757

Table II

Final Energy Levels for CO and for Ni(CO)$_n$, n=1-4 (Rydbergs)
Levels above dashed lines (_ _ _ _) are unoccupied.

CO	
$2\pi^*$	-0.199
5σ	-0.686
1π	-0.899
4σ	-1.088
3σ	-2.088
$2\sigma(C1s^2)$	-20.161
$1\sigma(O1s^2)$	-37.798
total energy	-224.751

NiCO	
12σ	-0.223
5π	-0.262
11σ	-0.412
1δ	-0.415
4π	-0.434
3π	-0.871
10σ	-0.938
9σ	-1.194
8σ	-2.227
$7\sigma, 2\pi(Ni3p^6)$	-4.882
$6\sigma(Ni3s^2)$	-7.593
$5\sigma(C1s^2)$	-20.383
$4\sigma(O1s^2)$	-37.742
$3\sigma, 1\ (Ni2p^6)$	-61.592
$2\sigma(Ni2s^2)$	-70.495
$1\sigma(Ni1s^2)$	-594.322
total energy	-3236.255

$Ni(CO)_2$	
$10\sigma g^+$	-0.166
$4\pi u$	-0.290
$3\pi g$	-0.380
$9\sigma g^+$	-0.543
$1\delta g$	-0.584
$2\pi g$	-0.637
$1\pi g$	-0.659
$3\pi u$	-0.811
$7\sigma u^+$	-0.972
$8\sigma g^+$	-1.089
$6\sigma u^+$	-1.162
$7\sigma g^+$	-1.203
$5\sigma g^+$ ←	-2.208
$6\sigma g^+$	-2.208
$4\sigma u^+, 2\sigma u^+(Ni3p^6)$	-5.060
$5\sigma g^+(Ni3s^2)$	-7.772
$3\sigma u^+, 4\sigma g^+(C1s^2)$	-20.476
$2\sigma u^+, 3\sigma g^+(O1s^2)$	-37.613
$1\sigma u^+, 1\pi u(Ni2p^6)$	-61.784
$2\sigma g^+(Ni2s^2)$	-70.652
$1\sigma g^+(Ni1s^2)$	-596.500
total energy	-3457.366

Table II, continued

Ni(CO)$_3$	
3e"	-0.047
11e'	-0.058
$3a_2'$	-0.085
$4a_2''$	-0.137
$10a_1'$	-0.155
10e'	-0.176
$2a_2'$	-0.314
9e'	-0.464
$9a_1'$	-0.496
2e"	-0.508
$3a_2''$	-0.800
$1a_1'$	-0.811
1e"	-0.811
8e'	-0.816
7e'	-0.972
$8a_1'$	-1.023
6e'	-1.55
$7a_1'$	-1.164
5e'	-2.175
$6a_1'$	-2.175
$2a_2''$,4e'(Ni3p^6)	-4.961
$5a_1'$(Ni3s^2)	-7.673
$4a_1'$,3e'(C1s^2)	-20.379
$3a_1'$,2e'(O1s^2)	-37.716
$1a_2''$,1e'(Ni2p^6)	-61.690
$2a_1'$(Ni2s^2)	-70.559
$1a_1'$(Ni1s^2)	-596.399
total energy	-3680.925

Ni(CO)$_4$	
$11t_2$	-0.065
$2t_1$	-0.102
$9a_1$	-0.159
3e	-0.168
$10t_2$	-0.196
$9t_2$	-0.490
2e	-0.558
$1t_1$	-0.781
$8t_2$	-0.801
1e	-0.807
$7t_2$	-0.966
$8a_1$	-1.021
$6t_2$	-1.129
$7a_1$	-1.151
$5t_2$	-2.137
$6a_1$	-2.137
$4t_2$(Ni3p^6)	-5.013
$5a_1$(Ni3s^2)	-7.727
4a,$3t_2$(C1s^2)	-20.325
3a,$2t_2$(O1s^2)	-37.650
$1t_2$(Ni2p^6)	-61.756
$2a_1$(Ni2s^2)	-70.626
$1a_1$(Ni1s^2)	-596.448
total energy	-3904.945

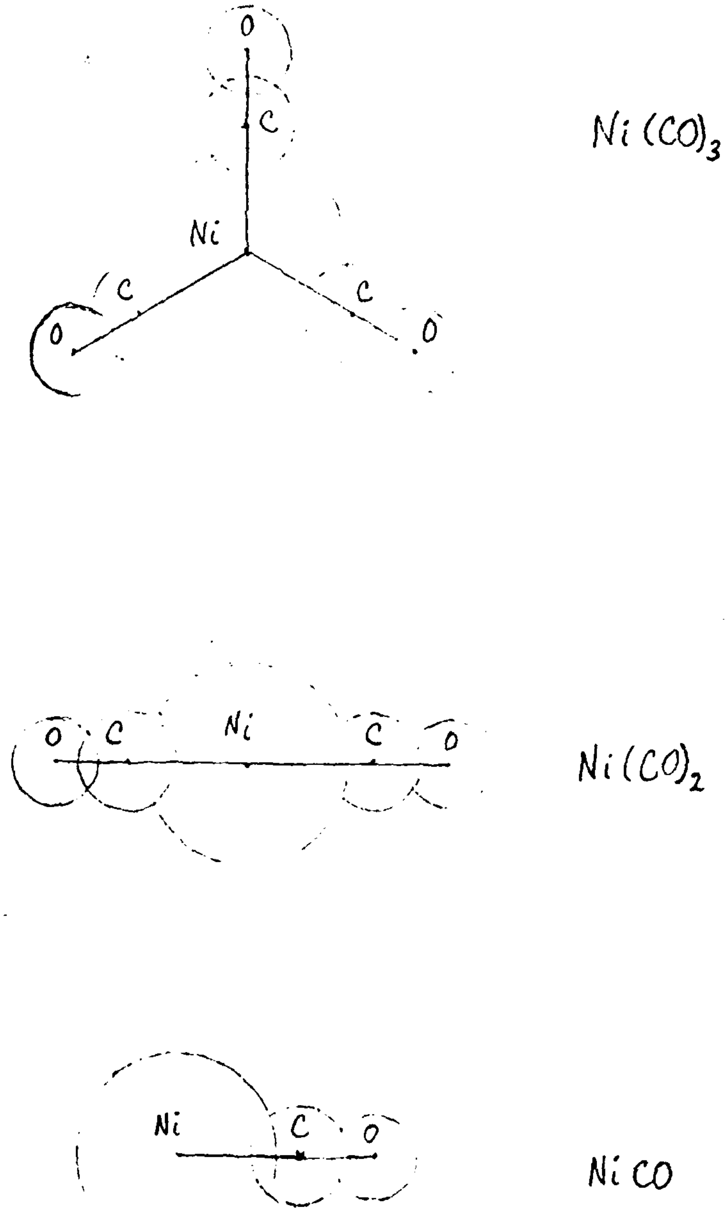


Figure 1.

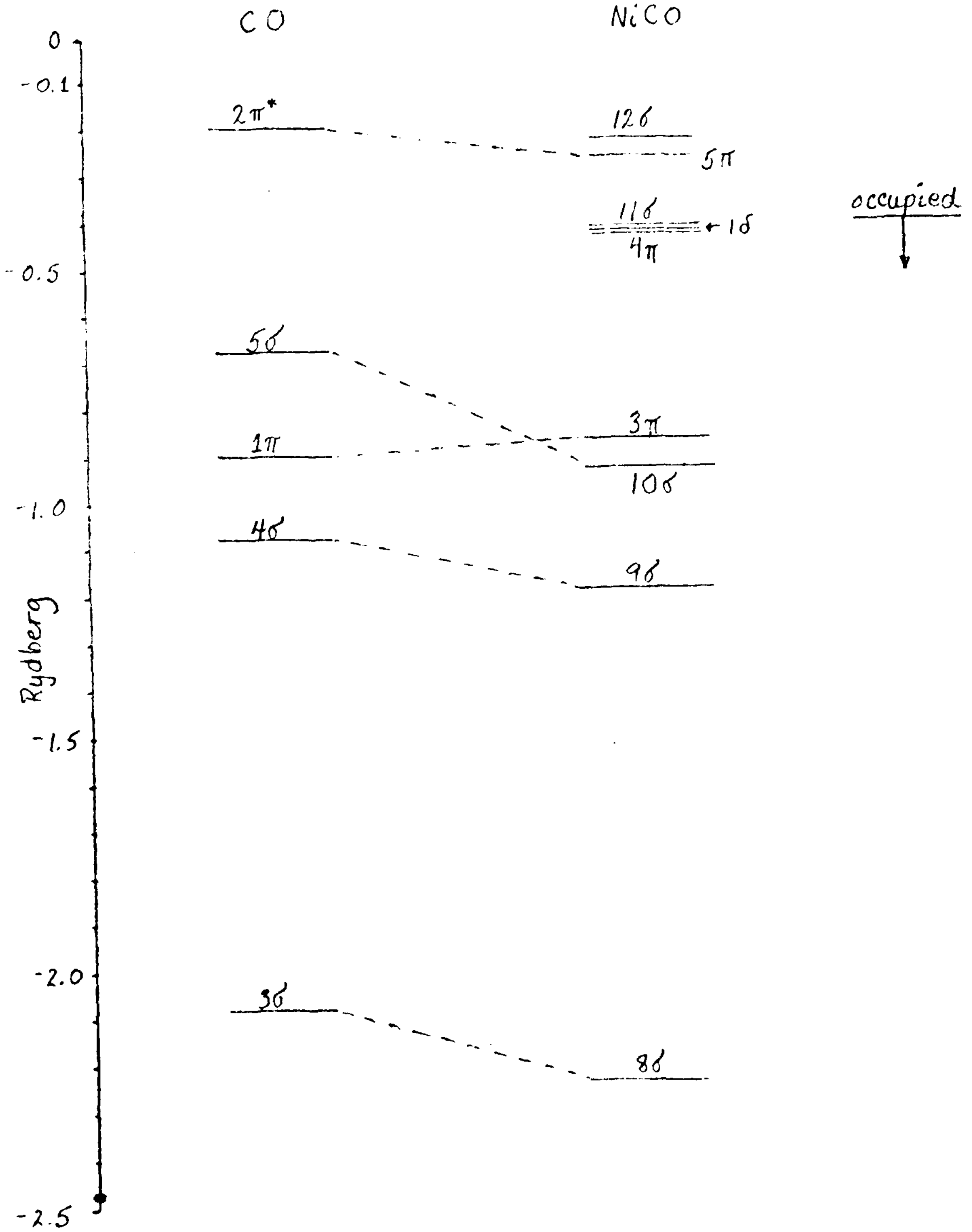
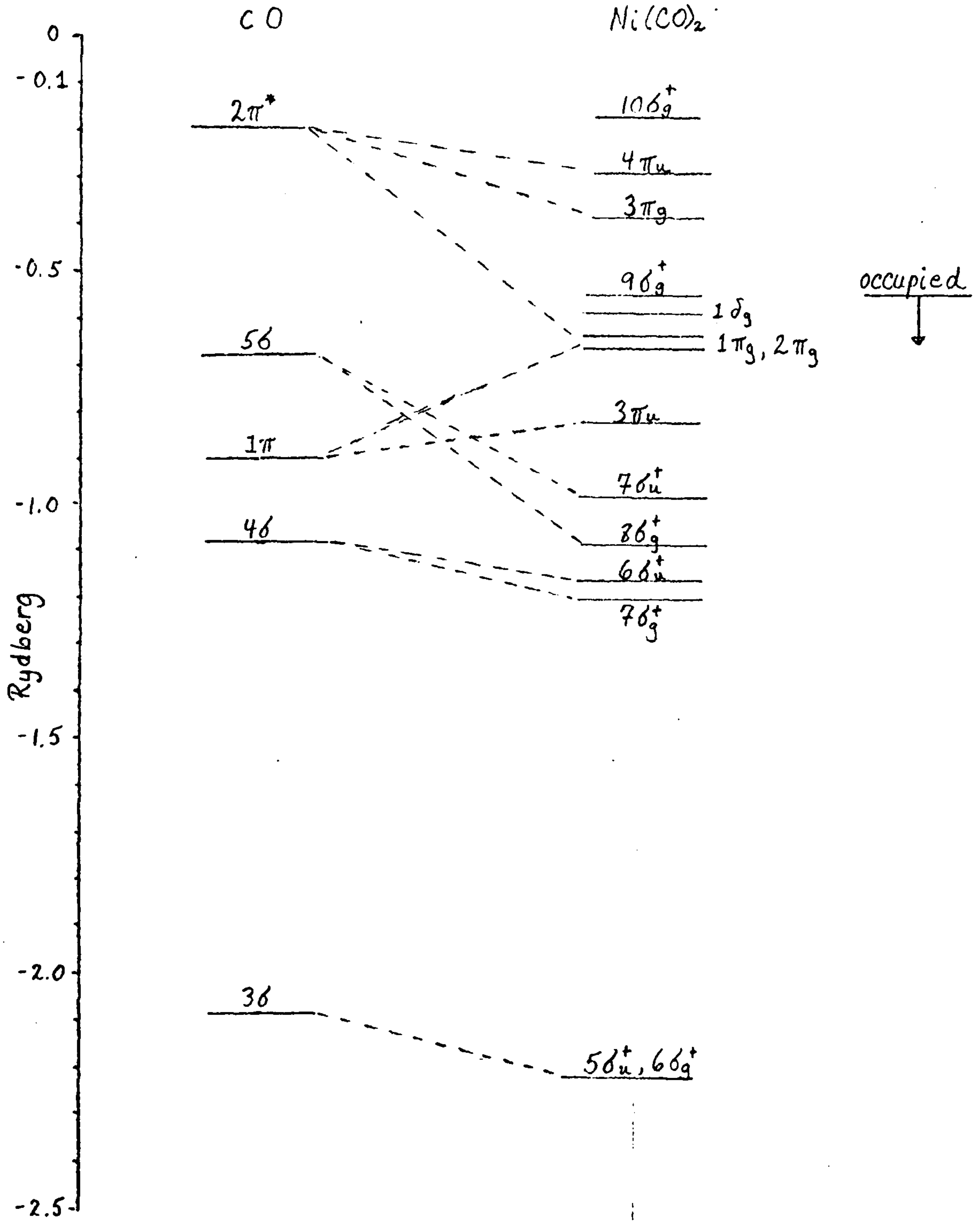

CO
NiCO
0
-0.1
-0.5
-1.0
-1.5
-2.0
-2.5
Rydberg
2π*
12σ
5π
11σ
1δ
4π
occupied
5σ
3π
1π
10σ
4σ
9σ
3σ
8σ

Figure 2.



CO
Ni(CO)₂
0
-0.1
-0.5
-1.0
-1.5
-2.0
-2.5
Rydberg
2π*
5σ
1π
4σ
3σ
10σg+
4πu
3πg
9σg+
1δg
1πg, 2πg
3πu
7σu+
8σg+
6σu+
7σg+
5σu+, 6σg+
occupied

Figure 3.

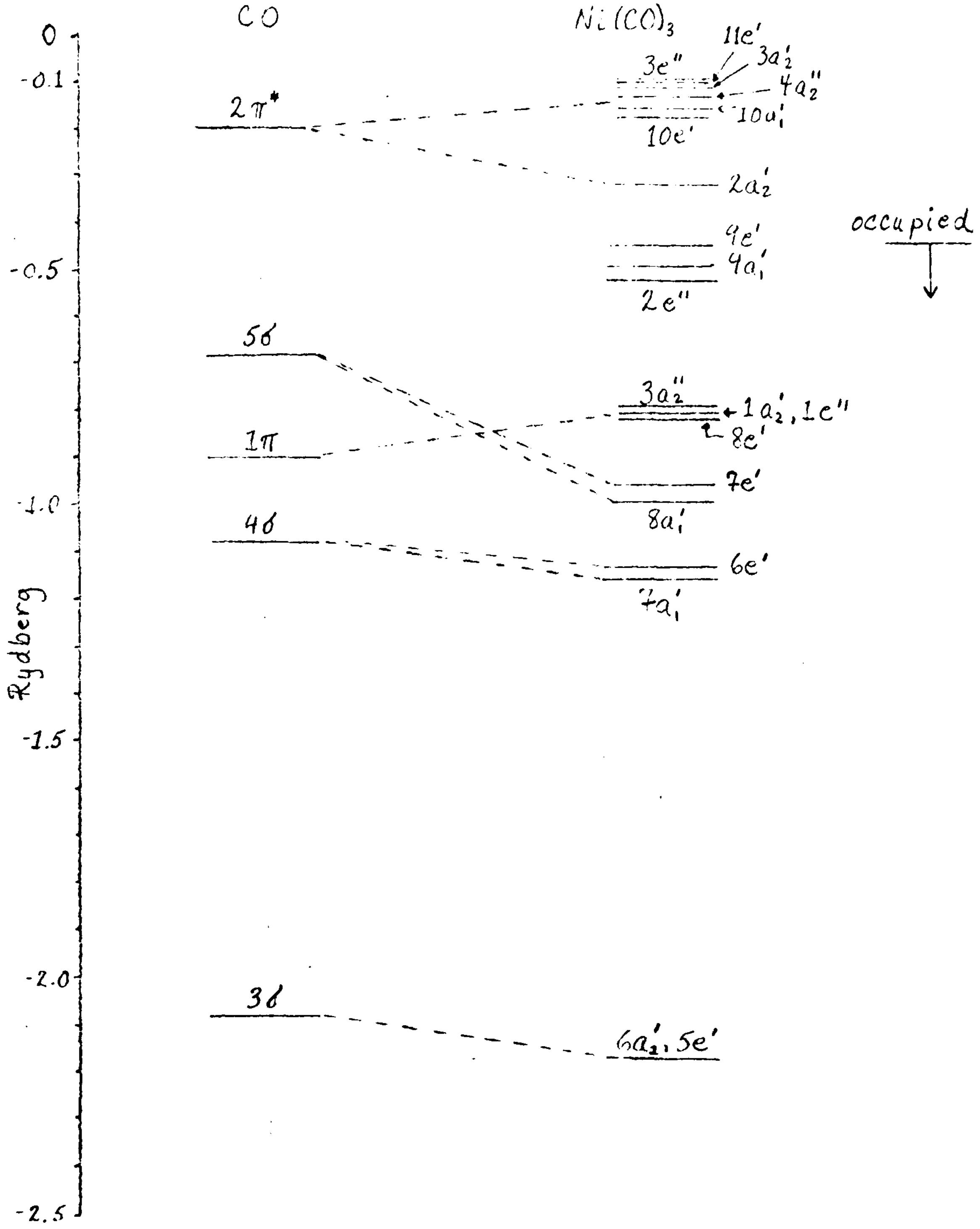

CO
$Ni(CO)_3$
0
-0.1
-0.5
-1.0
-1.5
-2.0
-2.5
Rydberg
$2\pi^*$
5σ
1π
4σ
3σ
$11e'$
$3a_2'$
$3e''$
$4a_2''$
$10a_1'$
$10e'$
$2a_2'$
$9e'$
$9a_1'$
$2e''$
occupied
$3a_2''$
$1a_2', 1e''$
$8e'$
$7e'$
$8a_1'$
$6e'$
$7a_1'$
$6a_1', 5e'$

Figure 4.

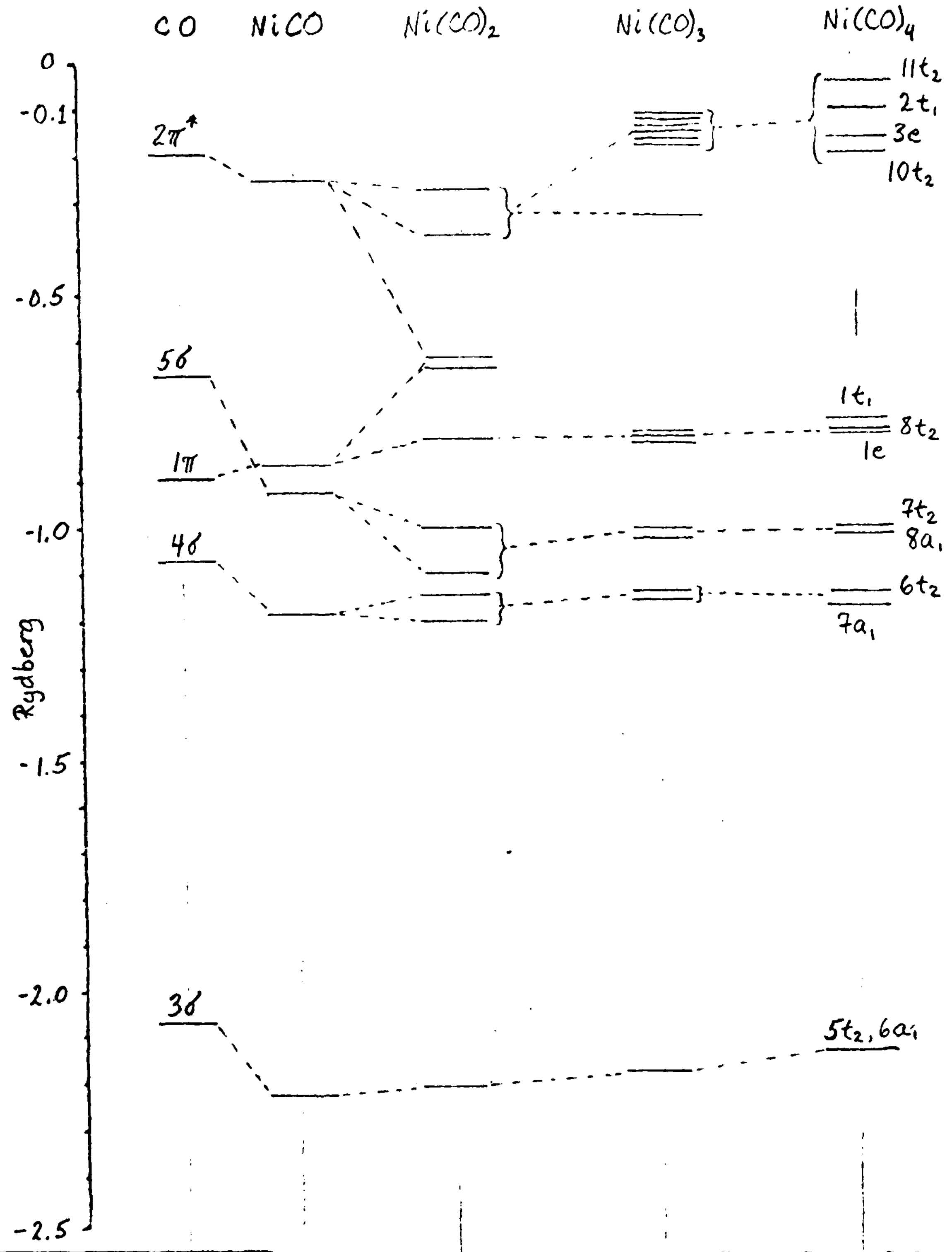

CO
NiCO
Ni(CO)2
Ni(CO)3
Ni(CO)4
0
-0.1
-0.5
-1.0
-1.5
-2.0
-2.5
Rydberg
2π*
5σ
1π
4σ
3σ
11t2
2t1
3e
10t2
1t1
8t2
1e
7t2
8a1
6t2
7a1
5t2, 6a1

Figure 5.

DATE
ILME