

## Detection of Free Nickel Monocarbonyl, NiCO: Rotational Spectrum and Structure

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Unsaturated transition metal carbonyls are important in processes such as organometallic synthesis, homogeneous catalysis, and photochemical decomposition of organometallics.<sup>1</sup> In particular, a metal monocarbonyl offers a zeroth-order model for interpreting the chemisorption of a CO molecule on a metal surface in catalytic activation processes.<sup>2</sup> Thus, quite large numbers of theoretical papers which predict spectroscopic and structural properties of transition metal carbonyls have appeared. In general, the strong bonding between a transition metal and CO is interpreted as arising from the synergistic combination of  $\sigma$  donation from the filled CO  $5\sigma$  orbital to the metal and  $\pi$  back-donation from the metal  $d\pi$  to CO  $2\pi^*$  orbital.

Historically, the nickel monocarbonyl NiCO has been one of the metal carbonyls most extensively studied by theoretical calculations. At least 50 theoretical studies have been published on this simplest transition metal carbonyl up to the present time. In 1976, Walch and Goddard<sup>2</sup> predicted the ground electronic state of NiCO to be an open-shell  $^3\Delta$  state, but subsequent calculation revealed that it belongs to a closed-shell  $^1\Sigma^+$  state.<sup>3</sup> Later, Bauschlicher et al.<sup>4</sup> concluded that  $\pi$  donation is the most important factor for the Ni–CO bond, and  $\sigma$  bond interaction makes only a minor bonding contribution or is even repulsive. This conclusion was supported by recent high-level calculations.<sup>5</sup> The NiCO molecule has been thought as a prototype molecule when the transition metal–CO bond was studied by the theoretical calculations. However, experimental evidence for NiCO is much more sparse, and the matrix isolation infrared spectroscopy was almost the sole method to study NiCO experimentally.<sup>6–9</sup> Indeed, there has been no prior confirmed observation of free NiCO itself nor direct measurement of its structural properties.

This Communication reports the preparation of free nickel monocarbonyl, NiCO, and the observation of its rotational transitions. The NiCO molecule was generated by the sputtering reaction of a Ni cathode in the presence of carbon monoxide CO. Accurate bond lengths of Ni–C and C–O were experimentally determined from isotopic data. The reliabilities of theoretical calculations mentioned above have been assessed for the first time through comparison between experimental and theoretical results.

The present experiments were carried out using a source modulation microwave spectrometer with a free space discharge cell.<sup>10</sup> As the microwave source, a multiplier following an OKI klystron was employed. The radiation transmitted through the cell was detected by an InSb detector cooled at 4.2 K by liquid He. Line frequencies were estimated to be accurate to better than 30 kHz. CO gas entrained in argon gas was continuously introduced into the free space cell. A 60-cm long nickel cathode was sputtered by a dc glow discharge with current of 200 mA in the presence of 1 mTorr of CO and 4 mTorr of Ar gas. For observation of  $^{13}\text{C}$  or  $^{18}\text{O}$  isotopic species,  $^{13}\text{CO}$  or  $\text{C}^{18}\text{O}$  was used as the precursor instead of normal  $^{12}\text{C}^{16}\text{O}$ . The cell was cooled to about 100 K using circulated liquid nitrogen. When the Ni cathode was fresh, NiCO

**Table 1.** Molecular Constants for Isotopic NiCO in the Ground Vibrational States<sup>a</sup>

	$B_0$ (MHz)	$D_0$ (kHz)
$^{58}\text{Ni}^{12}\text{C}^{16}\text{O}$	4529.97820(17)	1.13419(10)
$^{60}\text{Ni}^{12}\text{C}^{16}\text{O}$	4484.86808(19)	1.11288(11)
$^{58}\text{Ni}^{13}\text{C}^{16}\text{O}$	4496.76022(19)	1.12620(10)
$^{60}\text{Ni}^{13}\text{C}^{16}\text{O}$	4451.06563(42)	1.10467(21)
$^{58}\text{Ni}^{12}\text{C}^{18}\text{O}$	4214.72861(38)	0.96634(18)
$^{60}\text{Ni}^{12}\text{C}^{18}\text{O}$	4170.68500(23)	0.94711(11)

<sup>a</sup> Numbers in parentheses are one standard deviation in units of the last significant figure.

**Table 2.** Molecular Structure of NiCO

method	Ni–C (pm)	C–O (pm)	ref
Experimental <sup>a</sup>			
$r_0$	167.230(41)	115.124(54)	this work
$r_s$	167.0125(17)	115.2546(13)	this work
$r_{1e}$	167.013(14)	115.262(11)	this work
$r_m^{(1)}$	166.938(18)	115.2119(84)	this work
$r_m^{(2)}$	166.89002(90)	115.26057(80)	this work
Theoretical			
BPW91/6-311+G*	167.5	116.6	17
B3LYP/6-311+G*	168.5	115.1	9
CASSCF	168.3	116.1	5
BP86/6-311+G*	167.5	116.7	8
BP86	163.08	117.35	18
B3LYP/DZ	166.6	115.2	14
B3LYP	167.9	115.0	19
GC(rel)	168	117	20
CASPT2	165	117	21
BP	166.3	117.5	22
CCSD(T)	168.7	116.6	23
MP2	164.6	117.8	24

<sup>a</sup> Numbers in parentheses are one standard deviation in units of the last significant figure.

lines were observed strongly enough to be easily observed without data accumulation. The NiCO lines showed diamagnetic properties, and they rapidly disappeared when the discharge current was turned off. This behavior indicated that the carrier was a singlet transient species.

Fifty-six lines of six NiCO isotopomers in total were observed in the frequency range between 161 and 315 GHz. The molecular constants derived from the least-squares analysis of the observed frequencies are listed in Table 1. The rotational and centrifugal distortion constants were determined for each isotopic species. A standard error of the fit is about 10 kHz for each species. The  $\nu_3$  (Ni–C str.) wavenumber was estimated to be  $604\text{ cm}^{-1}$  using  $\omega_3 \approx (4B_0^3/D_0)^{1/2}$ , which agreed well with the matrix-IR value,  $591.1\text{ cm}^{-1}$  (ref 7).

Table 2 lists the bond lengths of NiCO obtained from the present rotational constants by several methods,<sup>11–13</sup>  $r_0$ ,  $r_s$ ,  $r_{1e}$ ,  $r_m^{(1)}$ , and  $r_m^{(2)}$ , together with some of the theoretical predictions. The uncertainty given is estimated from those in the fundamental

**Table 3.** Experimental Molecular Structures of NiCO and Related Molecules

molecule	method	Ni–C (pm)	C–O (pm)	ref
PdCO	$r_m^{(2)}$		114.0	29
PtCO	$r_m^{(2)}$		114.6	30
NiCO	$r_m^{(2)}$	166.9	115.3	this work
FeCO	$r_s$		115.9	28
Ni(CO) <sub>4</sub>	$r_g$	183.8	114.2	15
NiC	$r_0$	163.1		27
CO	$r_e$		112.8	25
CO <sub>2</sub>	$r_e$		116.0	26

constants and rotational constants. The equilibrium NiCO bond length,  $r_e$ , has not been obtained from the present rotational constants because of lack of vibrationally excited data. In this work, the  $r_m^{(2)}$  values are used for qualitative discussions, because the  $r_m^{(2)}$  method often gives a good estimation for the equilibrium structure.<sup>13</sup> Theoretical Ni–C lengths are close to our  $r_m^{(2)}$ (Ni–C) length, but most of them have errors of about 2 pm. The B3LYP calculations give very good predicted values for the C–O length, but other methods tend to overestimate for the C–O length. The closest predictions have been given by B3LYP/DZ calculations (Ni–C 166.6 pm, C–O 115.2 pm).<sup>14</sup>

Table 3 indicates that the Ni–C length of NiCO is about 17 pm shorter than that of the  $r_g$  structure of saturated nickel tetracarbonyl Ni(CO)<sub>4</sub>.<sup>15</sup> The C–O bond length of NiCO is, however, close to that of Ni(CO)<sub>4</sub>. Similar differences in the bond lengths were reported between FeCO and Fe(CO)<sub>5</sub>.<sup>16</sup> These facts suggest that the  $\pi$  back-donation from the Ni  $d\pi$  orbital to the CO  $p\pi^*$  orbital in NiCO is geometrically much more effective than that in Ni(CO)<sub>4</sub>. On the other hand, the C–O bond length of NiCO is closer to that of CO<sub>2</sub> than of CO. In NiCO, the C–O bond seems to have double bond character because of the large electron density of the CO  $p\pi^*$  orbital originating from the Ni  $d\pi \rightarrow$  CO  $p\pi^*$  back-donation.

The C–O bond lengths previously determined for three other transition metal monocarbonyls, FeCO, PdCO and PtCO, are also listed in Table 3. FeCO has the longest C–O distance which is close to that of CO<sub>2</sub>. On the other hand, the C–O distance of PdCO is rather close to that of CO. The C–O bond lengths of NiCO and PtCO have intermediate values, but those of NiCO and PtCO are fairly close to FeCO and NiCO, respectively. The C–O lengths of these metal monocarbonyls probably reflect the ability of  $\pi$  back-donation of the metal atoms. The first-row transition metals such as Fe and Ni seem to have a high propensity for  $\pi$  back-donation, whereas the second- and third-row transition metals such as Pd and Pt show much less propensity. More structural data for metal monocarbonyls are desired to discuss the relationship between the C–O bond length and the ability of  $\pi$  back-donation in detail.

In conclusion, the molecular structure of NiCO has been determined in detail by the measurement of its rotational spectrum. The reliabilities of various theoretical calculations have been assessed for the first time through comparison between the

experimental and theoretical bond distances. The present experimental result will be useful to refine the metal–CO interaction models adopted in the quantum chemical calculations for interpreting the chemisorption of a CO molecule on a metal surface in catalytic activation processes.

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**Supporting Information Available:** Observed rotational transition frequencies of isotopic NiCO (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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