

Reactions of Laser-Ablated Zinc and Cadmium Atoms with CO: Infrared Spectra of the $\text{Zn}(\text{CO})_x$ ($x = 1-3$), CdCO^- , and $\text{Cd}(\text{CO})_2$ Molecules in Solid Neon

Ling Jiang, Yun-Lei Teng, and Qiang Xu*

National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka 563-8577, Japan and Graduate School of Science and Technology, Kobe University, Nada Ku, Kobe, Hyogo 657-8501, Japan

Received: March 10, 2006; In Final Form: April 13, 2006

Reactions of laser-ablated zinc and cadmium atoms with carbon monoxide molecules in solid neon have been investigated using matrix-isolation infrared spectroscopy. Based on the isotopic substitution, absorptions at 1852.2, 1901.9, 1945.9, and 1995.2 cm^{-1} are assigned to the C–O stretching vibrations of the ZnCO , $\text{Zn}(\text{CO})_2$, and $\text{Zn}(\text{CO})_3$ molecules. Absorptions at 1735.8, 1961.3, and 2035.7 cm^{-1} are assigned to the C–O stretching vibrations of the CdCO^- and $\text{Cd}(\text{CO})_2$ molecules. In contrast with the previous argon experiments, more species and more valuable information about the reaction of zinc and cadmium atoms with CO have been obtained in solid neon. Density functional theory calculations have been performed on these zinc and cadmium carbonyls. The agreement between the experimental and calculated vibrational frequencies, relative absorption intensities, and isotopic shifts substantiates the identification of these carbonyls from the matrix infrared spectrum. The present experiments also reveal that zinc is more reactive with CO than cadmium.

Introduction

Reactions under nontraditional experimental conditions can often yield new and exciting species not accessible from high-temperature typical of traditional techniques.¹ Recent studies have shown that, with an aid of isotopic substitution technique, matrix isolation infrared spectroscopy combined with quantum chemical calculation is very powerful in investigating the spectrum, structure and bonding of novel species.^{2,3} Taking the group 12 metals as an example, it has been found that ^3P excited metal atoms react with H_2 in the matrix to form the metal hydride molecules.^{4,5} To form the monomethylmetal hydride species, CH_3MH ($\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$), excitation to the ^3P metal atom state was also required to promote insertion in to a methane molecule.⁵ This indicates that a number of novel species difficult to form from the reactions of ground-state metals could be generated using the excitation methods such as laser ablation and microwave-powered reactive resonance lamp.

Recently, the reaction of laser-ablated Zn atoms with CO in solid argon has produced the $\text{Zn}(\text{CO})_3$ molecule, the next member of the series of 18-electron metal carbonyls $\text{Cr}(\text{CO})_6 \rightarrow \text{Fe}(\text{CO})_5 \rightarrow \text{Ni}(\text{CO})_4$.⁶ It has been found that the formation of $\text{Zn}(\text{CO})_3$ involves $4s \rightarrow 4p$ promotion of the Zn atom, similar to the reactions of group 12 metal atoms with H_2 and CH_4 .^{4,5} However, the formation of zinc mono- and dicarbonyls $\text{Zn}(\text{CO})_n$ ($n = 1, 2$) was absent from the previous investigations. Interestingly, the CdCO molecule has been observed from the reaction of laser-ablated Cd atoms with CO in excess argon, whereas the cadmium di- and tricarbonyls, $\text{Cd}(\text{CO})_x$ ($x = 2, 3$), have not been observed.⁷ The $5s \rightarrow 5p$ promotion of the Cd atom is primarily responsible for the metastability of CdCO , which increases the Cd–CO bonding by decreasing the σ repulsion and significantly increasing the Cd 5p orbital \rightarrow CO π^* back-donation. Considering that solid neon may stabilize some species difficult to be observed in solid argon,^{2,3} we have modified the experimental equipments and performed the

reactions of laser-ablated zinc and cadmium atoms with CO molecules in excess neon. IR spectroscopy coupled with theoretical calculations provides evidence for the formation of the $\text{Zn}(\text{CO})_x$ ($x = 1-3$), CdCO^- , and $\text{Cd}(\text{CO})_2$ molecules.

Experimental and Theoretical Methods

The experiment for laser ablation and matrix isolation infrared spectroscopy is similar to those previously reported.^{8,9} Briefly, the Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate with 10 ns pulse width) was focused on the rotating Zn and Cd targets. The laser-ablated Zn and Cd atoms were co-deposited with CO in excess neon onto a CsI window cooled normally to 4 K by means of a closed-cycle helium refrigerator. Typically, 1–5 mJ/pulse laser power was used. Carbon monoxide (99.95% CO), $^{13}\text{C}^{16}\text{O}$ (99%, $^{18}\text{O} < 1\%$) and $^{12}\text{C}^{18}\text{O}$ (99%) were used to prepare the CO/Ne mixtures. In general, matrix samples were deposited for 30–60 min with a typical rate of 2–4 mmol/h. After sample deposition, IR spectra were recorded on a BIO-RAD FTS-6000e spectrometer at 0.5 cm^{-1} resolution using a liquid nitrogen cooled HgCdTe (MCT) detector for the spectral range of 5000–400 cm^{-1} . Samples were annealed at different temperatures and subjected to broad-band irradiation ($\lambda > 250$ nm) using a high-pressure mercury arc lamp (Ushio, 100 W).

Quantum chemical calculations were performed to predict the structures and vibrational frequencies of the observed reaction products using the Gaussian 03 program.¹⁰ The BP86 density functional method was used.¹¹ For zinc carbonyls, the 6-311++G(3df,3pd) basis sets were used for C and O atoms¹² and the Wachters–Hay all-electron basis set for Zn atoms.¹³ For cadmium carbonyls, the D95* basis sets was used for C and O atoms,¹⁴ and the Los Alamos ECP plus DZ (LANL2DZ) for Cd atoms.¹⁵ Geometries were fully optimized and vibrational frequencies were calculated with analytical second derivatives. The previous investigations have shown that such a computational scheme can provide reliable information for zinc and cadmium carbonyls, such as infrared frequencies, relative absorption intensities, and isotopic shifts.^{6,7}

* To whom correspondence should be addressed. E-mail: q.xu@aist.go.jp.

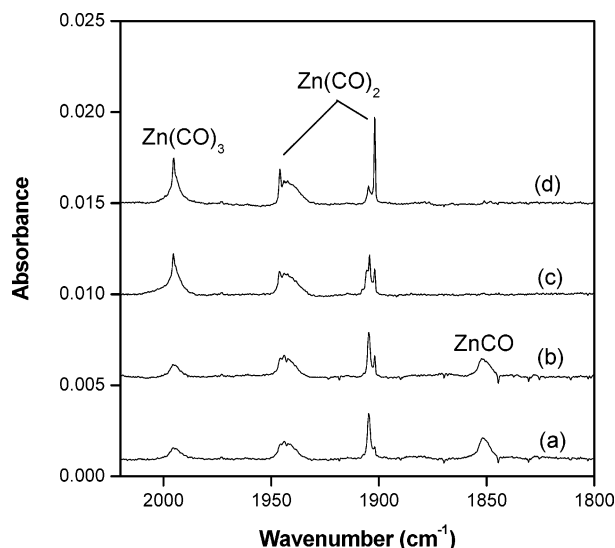


Figure 1. Infrared spectra in the 2050–1800 cm^{-1} region from co-deposition of laser-ablated Zn atoms with 0.3% CO in Ne: (a) 1 h of sample deposition at 4 K; (b) after annealing to 6 K; (c) after 10 min of broad-band irradiation; (d) after annealing to 8 K.

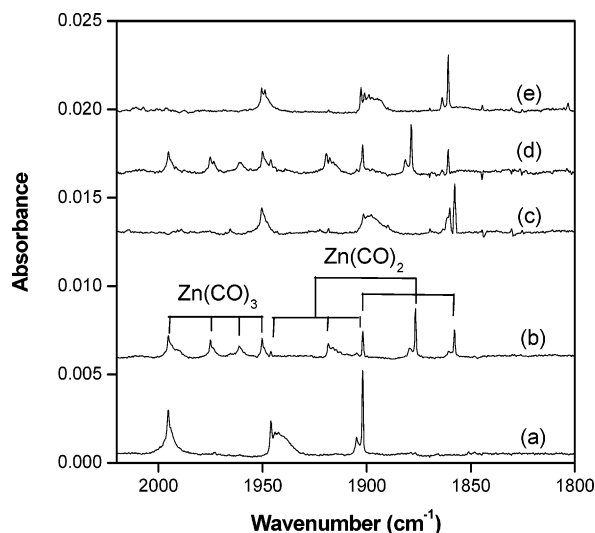


Figure 2. Infrared spectra in the 2050–1800 cm^{-1} region from co-deposition of laser-ablated Zn atoms with isotopic CO in Ne after 10 min of broad-band irradiation and annealing to 8 K: (a) 0.3% $^{12}\text{C}^{16}\text{O}$; (b) 0.15% $^{12}\text{C}^{16}\text{O}$ + 0.15% $^{13}\text{C}^{16}\text{O}$; (c) 0.3% $^{13}\text{C}^{16}\text{O}$; (d) 0.15% $^{12}\text{C}^{16}\text{O}$ + 0.15% $^{12}\text{C}^{18}\text{O}$; (e) 0.3% $^{12}\text{C}^{18}\text{O}$.

Results and Discussion

Experiments have been done with carbon monoxide concentrations ranging from 0.02% to 1.0% in excess neon. Typical infrared spectra for the reactions of laser-ablated Zn and Cd atoms with CO molecules in excess neon in the selected regions are illustrated in Figures 1–3, and the absorption bands in different isotopic experiments are listed in Table 1. The stepwise annealing and photolysis behavior of the product absorptions is also shown in the figures and will be discussed below. Experiments were also done with different concentrations of CCl_4 serving as an electron scavenger in solid neon.

Quantum chemical calculations have been carried out for the possible isomers and electronic states of the potential product molecules. Figure 4 shows the optimized structures of the reaction products. The ground electronic states, point groups, vibrational frequencies and intensities are listed in Table 2. Table 3 reports a comparison of the observed and calculated isotopic frequency ratios for the C–O stretching modes of the reaction

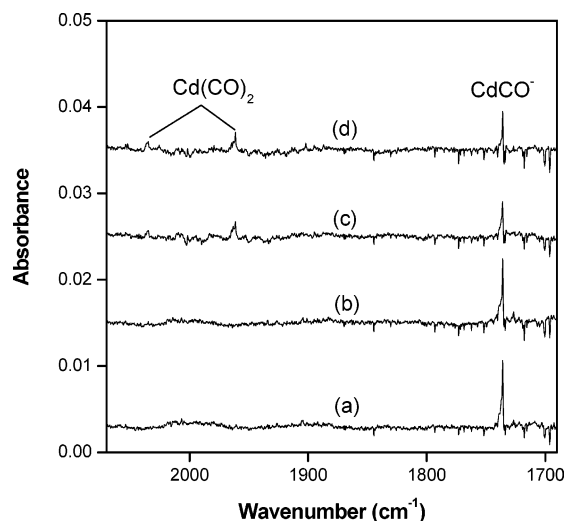


Figure 3. Infrared spectra in the 2050–1700 cm^{-1} region from co-deposition of laser-ablated Cd atoms with 0.3% CO in Ne: (a) 1 h of sample deposition at 4 K; (b) after annealing to 6 K; (c) after 10 min of broad-band irradiation; (d) after annealing to 8 K.

products. Molecular orbital contour surfaces of the highest occupied molecular orbitals (HOMO) of the $\text{Zn}(\text{CO})_n$ ($n = 1-3$), CdCO^- , and $\text{Cd}(\text{CO})_n$ ($n = 1, 2$) molecules are illustrated in Figure 5.

ZnCO, $\text{Zn}(\text{CO})_2$, and $\text{Zn}(\text{CO})_3$. A weak band at 1852.2 cm^{-1} appears after sample deposition, decreases upon annealing, disappears after broad-band irradiation, and does not recover after further annealing (Table 1 and Figure 1). This band shifts to 1811.5 cm^{-1} with $^{13}\text{C}^{16}\text{O}$ and to 1807.8 cm^{-1} with $^{12}\text{C}^{18}\text{O}$, exhibiting isotopic frequency ratios ($^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{16}\text{O}$, 1.0225; $^{12}\text{C}^{16}\text{O}/^{12}\text{C}^{18}\text{O}$, 1.0246) characteristic of C–O stretching vibrations. The mixed $^{12}\text{C}^{16}\text{O} + ^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{16}\text{O} + ^{12}\text{C}^{18}\text{O}$ isotopic spectra only provide the sum of pure isotopic bands, which indicates a monocarbonyl molecule.¹⁶ Doping with CCl_4 has no effect on this band (not shown here), suggesting that the product is neutral.¹⁷ The 1852.2 cm^{-1} band is therefore assigned to the C–O stretching vibration of the neutral zinc monocarbonyl ZnCO. At the BP86/6-311++G(3df,3pd) level of theory, the C–O stretching vibrational frequency ($\nu_{\text{C-O}}$) and $R_{\text{Zn-C}}$ of the singlet ZnCO molecule are predicted to be 2126.4 cm^{-1} and 8.240 Å, respectively, and the singlet lies 50.68 kcal/mol lower in energy than the triplet one ($\nu_{\text{C-O}} = 1906.9 \text{ cm}^{-1}$, $R_{\text{Zn-C}} = 1.957 \text{ Å}$) (Table 2 and Figure 4), indicating that the triplet state drives the Zn–C bond distance closer. Such a longer $R_{\text{Zn-C}}$ distance in the singlet ZnCO molecule than the van der Waals distance may be due to the inefficiency of the XC functional and/or the basis sets used here. The calculated $^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{16}\text{O}/^{12}\text{C}^{18}\text{O}$ isotopic frequency ratios of 1.0239 and 1.0231 are in accord with the experimental observations, 1.0225 and 1.0246, respectively. Analogous to the recently reported CdCO,⁷ the ZnCO excimer may be formed during the co-deposition of CO with “hot” Zn atoms ablated by pulse laser and has fortunately been captured by the neon matrix.

The absorptions at 1945.9 and 1901.9 cm^{-1} are present together after sample deposition, and increase upon annealing and broad-band irradiation (Figure 1). These bands shift to 1901.5 and 1857.9 cm^{-1} with $^{13}\text{C}^{16}\text{O}$ and to 1902.7 and 1860.9 cm^{-1} with $^{12}\text{C}^{18}\text{O}$, exhibiting isotopic frequency ratios ($^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{16}\text{O}$: 1.0233 and 1.0237; $^{12}\text{C}^{16}\text{O}/^{12}\text{C}^{18}\text{O}$: 1.0227 and 1.0220) characteristic of C–O stretching vibrations. As can be seen in Figure 2, two sets of triplet bands have been observed at 1946.0/1918.4/1901.9 and 1901.9/1876.5/1857.8 cm^{-1} in the mixed

TABLE 1: Infrared Absorptions (cm^{-1}) Observed from the Reactions of Laser-Ablated Zinc and Cadmium Atoms with CO in Excess Neon at 4 K

$^{12}\text{C}^{16}\text{O}$	$^{13}\text{C}^{16}\text{O}$	$^{12}\text{C}^{18}\text{O}$	$^{12}\text{C}^{16}\text{O} + ^{13}\text{C}^{16}\text{O}$	$^{12}\text{C}^{16}\text{O} + ^{12}\text{C}^{18}\text{O}$	R(12/13)	R(16/18)	assignment
1995.2	1950.4	1950.1	1995.2, 1975.0, 1961.3, 1950.2	1995.2, 1975.2, 1960.3, 1949.9	1.0230	1.0231	$\text{Zn}(\text{CO})_3$, as-CO str ^d
1945.9	1901.5	1902.7	1946.0, 1918.4, 1901.9	1946.0, 1919.4, 1902.0	1.0233	1.0227	$\text{Zn}(\text{CO})_2$, s-CO str
1904.7	1860.6	1863.7	1904.7, 1879.3, 1860.5	1904.7, 1881.3, 1863.3	1.0237	1.0220	$\text{Zn}(\text{CO})_2$ site, as-CO str
1901.9	1857.9	1860.9	1901.9, 1876.5, 1857.8	1902.0, 1878.6, 1860.9	1.0237	1.0220	$\text{Zn}(\text{CO})_2$, as-CO str
1852.2	1811.5	1807.8	1852.2, 1811.5	1852.2, 1807.7	1.0225	1.0246	ZnCO , CO str
2035.7	1989.2	1986.2			1.0234	1.0249	$\text{Cd}(\text{CO})_2$, s-CO str
1961.3	1917.0	1913.1			1.0231	1.0252	$\text{Cd}(\text{CO})_2$, as-CO str
1735.8	1696.9	1693.3	1735.9, 1696.9	1735.8, 1693.3	1.0229	1.0251	CdCO^- , CO str

^d Abbreviations: as = asymmetric, s = symmetric, str = stretching mode.

TABLE 2: Ground Electronic States, Point Groups, Vibrational Frequencies (cm^{-1}) and Intensities (km/mol) of the Reaction Products

species	elec state	point group	frequencies (intensity, mode)
ZnCO	$^3\Pi$	$C_{\infty v}$	1906.9 (508, σ), 377.3 (20, σ), 262.5 (12, π), 154.7 (5, π)
$\text{Zn}(\text{CO})_2$	3B_1	C_{2v}	1980.1 (108, A_1), 1912.5 (2562, B_2), 506.4 (0.5, B_2), 363.4 (0.4, A_1), 306.9 (0, A_2), 296.4 (10, B_2), 263.9 (1, A_1), 148.2 (8, B_1), 46.2 (0.5, A_1)
$\text{Zn}(\text{CO})_3$	$^1A_1'$	D_{3h}	2059.0 (0, A_1'), 1974.7 (1707 \times 2, E'), 458.6 (2 \times 2, E'), 370.9 (0, A_1'), 367.4 (1 \times 2, E'), 344.9 (0 \times 2, E''), 295.7 (0, A_2'), 166.5 (10, A_2''), 54.4 (0.5 \times 2, E'), 46.4 (1, A_2'')
CdCO^-	$^2A''$	C_s	1748.0 (1735, A'), 190.2 (13, A'), 76.0 (1, A')
$\text{Cd}(\text{CO})_2$	3B_1	C_{2v}	1970.4 (493, A_1), 1881.8 (1920, B_2), 282.4 (25, A_1), 216.5 (1, B_2), 213.5 (2, A_1), 208.8 (0, A_2), 151.7 (3, B_2), 140.6 (0, B_1), 33.5 (1, A_1)

TABLE 3: Comparison of the Observed and Calculated Isotopic Frequency Ratios of the Reaction Products

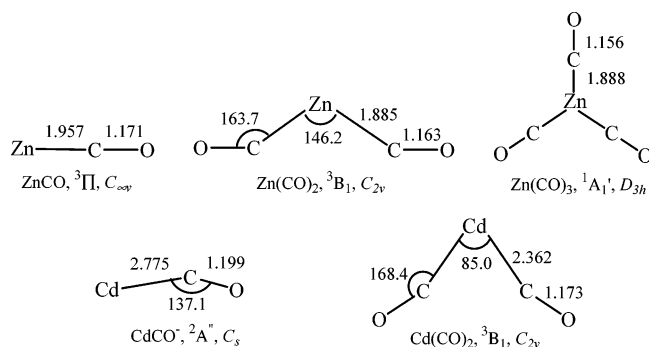
molecule	mode	$^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{16}\text{O}$		$^{12}\text{C}^{16}\text{O}/^{12}\text{C}^{18}\text{O}$	
		obsd	calcd	obsd	calcd
ZnCO	C–O str	1.0225	1.0239	1.0246	1.0231
$\text{Zn}(\text{CO})_2$	C–O sym-str	1.0233	1.0240	1.0227	1.0229
$\text{Zn}(\text{CO})_2$	C–O asym-str	1.0237	1.0238	1.0220	1.0233
$\text{Zn}(\text{CO})_3$	C–O asym-str	1.0230	1.0240	1.0231	1.0231
$\text{Cd}(\text{CO})_2$	C–O sym-str	1.0234	1.0232	1.0249	1.0243
$\text{Cd}(\text{CO})_2$	C–O asym-str	1.0231	1.0226	1.0252	1.0250
CdCO^-	C–O str	1.0229	1.0226	1.0251	1.0250

$^{12}\text{C}^{16}\text{O} + ^{13}\text{C}^{16}\text{O}$ isotopic spectra (Table 1). Similar isotopic spectra in the $^{12}\text{C}^{16}\text{O} + ^{12}\text{C}^{18}\text{O}$ experiments have also been obtained. Accordingly, these bands are assigned to the symmetric and antisymmetric C–O stretching modes of the $\text{Zn}(\text{CO})_2$ molecule. Our density functional theory (DFT) calculations predicted that the singlet $\text{Zn}(\text{CO})_2$ molecule is not bound ($R_{\text{Zn-C}} = 8.463 \text{ \AA}$)⁶ and lies 37.01 kcal/mol in energy lower than the triplet one ($R_{\text{Zn-C}} = 1.885 \text{ \AA}$) (Figure 4). The triplet $\text{Zn}(\text{CO})_2$ molecule has C_{2v} symmetry with a C–Zn–C bond angle of 146.2° (Figure 4). The symmetric and antisymmetric C–O stretching vibrational frequencies are calculated at 1980.1 and 1912.5 cm^{-1} (Table 2), which are in accord with our observed values, 1945.9 and 1901.9 cm^{-1} , respectively. For the antisymmetric C–O stretching mode, the calculated $^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{16}\text{O}/^{12}\text{C}^{18}\text{O}$ isotopic frequency ratios of 1.0238 and 1.0233 (Table 3) are consistent with the experimental observations,

1.0237 and 1.0220, respectively. Similar results have also been obtained for the symmetric C–O stretching mode. These agreements between the experimental and calculated vibrational frequencies, relative absorption intensities, and isotopic shifts substantiate the identification of the $\text{Zn}(\text{CO})_2$ molecule from the matrix IR spectrum.

The 1995.2 cm^{-1} band increase slightly on sample annealing and markedly after broad-band irradiation (Table 1 and Figure 1). The mixed isotopic spectra (Figure 2) are quartets with approximately 2:1:1:2 relative intensities, which are characteristic of doubly degenerate vibrational mode for a trigonal species.¹⁶ The 1995.2 cm^{-1} band is assigned to the antisymmetric C–O stretching vibrations (e') of the $\text{Zn}(\text{CO})_3$ molecule with D_{3h} symmetry. The corresponding C–O stretching frequency of $\text{Zn}(\text{CO})_3$ in argon has been observed at 1975.8 cm^{-1} ,⁶ which is 19.4 cm^{-1} red-shifted from the present neon matrix counterpart. The good agreement between the experimental and calculated vibrational frequencies, relative absorption intensities, and isotopic shifts has also been obtained for the $\text{Zn}(\text{CO})_3$ molecule as reported earlier.⁶ Briefly, the $\text{Zn}(\text{CO})_3$ molecule is predicted to have a singlet ground state with D_{3h} symmetry. The antisymmetric C–O stretching vibrational frequency is calculated at 1974.7 cm^{-1} (Table 2).

CdCO^- and $\text{Cd}(\text{CO})_2$. A sharp band at 1735.8 cm^{-1} appears after sample deposition, decreases after broad-band irradiation (Table 1 and Figure 3). This band shifts to 1696.9 cm^{-1} with $^{13}\text{C}^{16}\text{O}$ and to 1693.3 cm^{-1} with $^{12}\text{C}^{18}\text{O}$, exhibiting isotopic frequency ratios ($^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{16}\text{O}$: 1.0229; $^{12}\text{C}^{16}\text{O}/^{12}\text{C}^{18}\text{O}$: 1.0251) characteristic of C–O stretching vibrations. The mixed $^{12}\text{C}^{16}\text{O} + ^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{16}\text{O} + ^{12}\text{C}^{18}\text{O}$ isotopic spectra only provide the sum of pure isotopic bands, which indicates a monocarbonyl molecule.¹⁶ Doping with CCl_4 decreases this band, suggesting that the product is anionic.¹⁷ The 1735.8 cm^{-1} band is therefore assigned to the C–O stretching vibration of the CdCO^- anion. The corresponding C–O stretching vibration of the neutral CdCO in solid argon has been observed at 1858.2 cm^{-1} ,⁷ which is 122.4 cm^{-1} higher than the present CdCO^- anion in solid neon. Our DFT calculations predict the CdCO^- anion to have an $^2A''$ ground state with C_s symmetry (Table 2 and Figure 4). The calculated C–O stretching mode of the CdCO^- species is 1748.0 cm^{-1} (Table 2), which should be multiplied by 0.993 to

**Figure 4.** Optimized structures (bond lengths in angstroms, bond angles in degrees) of the reaction products.

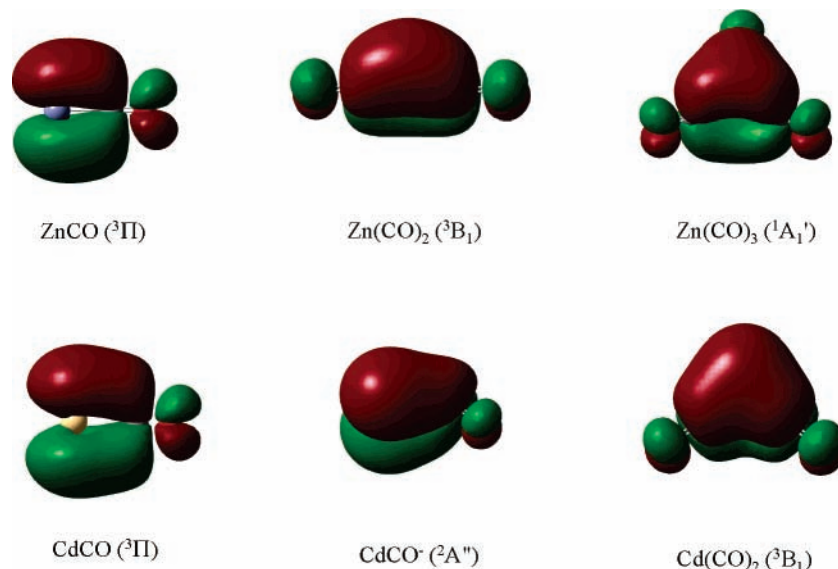
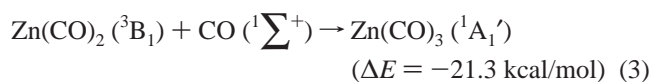
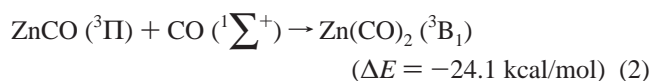
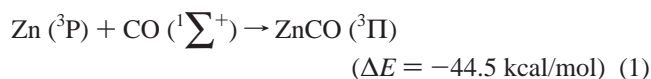


Figure 5. Molecular orbital contour surfaces of the highest occupied molecular orbitals (HOMOs) of the $\text{Zn}(\text{CO})_n$ ($n = 1-3$), CdCO^- , and $\text{Cd}(\text{CO})_n$ ($n = 1, 2$) molecules.

fit the observed frequency. The calculated $^{12}\text{C}/^{13}\text{C}$ and $^{16}\text{O}/^{18}\text{O}$ isotopic frequency ratios of 1.0226 and 1.0250 are consistent with the experimental observations, 1.0229 and 1.0251, respectively (Table 3).

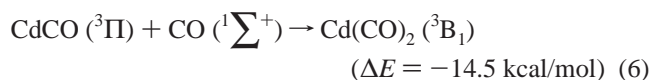
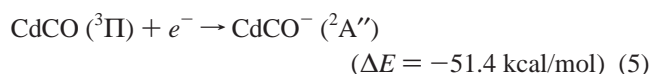
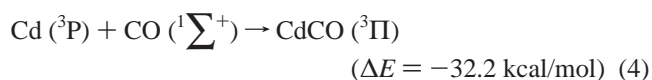
Two weak bands at 2035.7 and 1961.3 cm^{-1} appear together on irradiation and slightly increase after further higher temperature annealing (Table 1 and Figure 3). Both bands exhibit characteristic carbonyl C–O stretching vibrational frequency ratios as listed in Table 1. These two bands are tentatively assigned to the symmetric and antisymmetric C–O stretching modes of the $\text{Cd}(\text{CO})_2$ molecule, due to the fact that the mixed isotopic spectra are too weak to be observed in the present experiments. The calculated results show that the triplet $\text{Cd}(\text{CO})_2$ lies 40 kcal/mol in energy higher than the singlet one with one imaginary frequency at 32.2 cm^{-1} . For the triplet one, the symmetric and antisymmetric C–O stretching vibrations are calculated at 1970.4 and 1881.8 cm^{-1} with 493/1920 relative intensities (Table 2), which is in accord with the $\text{Cd}(\text{CO})_2$ molecule assignment.

Reaction Mechanism. At the present experimental conditions, laser-ablated zinc and cadmium atoms react with carbon monoxide molecules in the excess neon matrixes to produce metal carbonyl species. For the $\text{Zn} + \text{CO}$ reactions, the $\text{Zn}(\text{CO})_x$ ($x = 1, 2$) molecules are the primary products after sample deposition. ZnCO fails to reproduce after irradiation, whereas $\text{Zn}(\text{CO})_2$ and $\text{Zn}(\text{CO})_3$ increase after irradiation and further higher temperature annealing. This suggests that the $\text{Zn}(\text{CO})_x$ ($x = 1, 2$) molecules are formed mainly during the co-deposition of CO with the “hot” Zn atoms generated by pulse laser ablation via reactions 1 and 2, and zinc tricarbonyl $\text{Zn}(\text{CO})_3$ are formed mainly after UV-irradiation by reaction 3,



For the Cd + CO reactions, the CdCO^- anion species is the primary product after sample deposition and the $\text{Cd}(\text{CO})_2$

molecule is weakly observed upon irradiation, whereas CdCO and $\text{Cd}(\text{CO})_3$ are absent from the present experiments. We note that the neutral CdCO molecule has been observed in solid argon.⁷ This suggests that the CdCO^- anion is formed by electron capture by neutral CdCO during co-deposition at the expense of CdCO , reaction 5; the CdCO^- anion is strongly solvated in solid neon,¹⁸ and as a consequence, CdCO^- is “insulated” from the reaction mixture, so that higher cadmium carbonyls are difficult to be formed on annealing. The calculated energy for CdCO^- is below CdCO by 51.4 kcal/mol, whereas the energy for ZnCO^- is below ZnCO by 44.9 kcal/mol. This implies that the formation of CdCO^- from CdCO is energetically favorable than that for ZnCO^- , which supports the above-mentioned analysis.



We also note that the yields of zinc carbonyls are larger than those of cadmium carbonyls (Figures 1 and 3), suggesting that zinc is more reactive with CO than cadmium, as supported by the calculated reaction energies. The trend of the reactivity of zinc and cadmium toward CO is the same as that toward O_2 .¹⁹

As illustrated in Figure 5, the HOMOs in the $\text{Zn}(\text{CO})_n$ ($n = 1-3$), CdCO^- , and $\text{Cd}(\text{CO})_n$ ($n = 1, 2$) molecules are the M–C π bonding orbitals. The formation of these zinc and cadmium carbonyls involves $4s \rightarrow 4p$ promotion of the Zn atom and $5s \rightarrow 5p$ promotion of the Cd atom, respectively, which increase the M–CO bonding by decreasing the σ repulsion and significantly increasing the Zn 4p and Cd 5p orbitals \rightarrow CO π^* back-donation.^{6,7} It has been found that ^3P excited metal atoms react with H_2 in the matrix to form the group 12 metal hydride molecules.^{4,5} To form the monomethylmetal hydride species, CH_3MH ($\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$), excitation to the ^3P metal atom state was also required to promote insertion into a methane molecule.⁵ Along with the aforementioned reports,^{2-7,16,20} the

present finding exhibits that a number of novel species difficult to be formed from the reactions of ground-state metals with small molecules may be generated using the excitation method, such as laser ablation and irradiation by microwave-powered reactive resonance lamp, which are more stabilized in solid neon than in solid argon.

Conclusions

Laser-ablated zinc and cadmium atoms react with carbon monoxide molecules in the excess neon matrixes to produce metal carbonyl species. The ZnCO, Zn(CO)₂, Zn(CO)₃, CdCO⁻ and Cd(CO)₂ molecules have been observed in the present experiments. In the case of Zn + CO reactions, the Zn(CO)_x ($x = 1, 2$) molecules are the primary products after sample deposition and ZnCO disappears after irradiation. In the case of Cd + CO reactions, the CdCO⁻ anion species is the primary product after sample deposition and the Cd(CO)₂ molecule is weakly observed upon irradiation with the absence of CdCO and Cd(CO)₃. Density functional theory calculations have been performed on the zinc and cadmium carbonyls, which lend support to the experimental assignments of the infrared spectra. Furthermore, the plausible reaction mechanism for the formation of the Zn(CO)_x ($x = 1-3$), CdCO⁻, and Cd(CO)₂ molecules has been proposed. The present experiments also reveal that zinc is more reactive with CO than cadmium.

Acknowledgment. We express thanks to the reviewers for valuable suggestions. This work was supported by a Grant-in-Aid for Scientific Research (B) (Grant No. 17350012) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan, and by Marubun Research Promotion Foundation. L.J. thanks the MEXT of Japan and Kobe University for Honors Scholarship.

References and Notes

(1) See, for example: Niu, C.; Lieber, C. M. *J. Am. Chem. Soc.* **1992**, *114*, 3570. Bandy, R. E.; Lakshminarayan, C.; Frost, R. K.; Zwier, T. S. *J. Chem. Phys.* **1993**, *98*, 5362. Wang, L. S.; Cheng, H. S.; Fan, J. *J. Chem. Phys.* **1995**, *102*, 9840. Duncan, M. A. *Int. Rev. Phys. Chem.* **2003**, *22*, 407.

(2) See, for example: Xu, C.; Manceron, L.; Perchard, J. P. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1291. Bondybey, V. E.; Smith, A. M.; Agreiter, J. *Chem. Rev.* **1996**, *96*, 2113. Fedrigo, S.; Haslett, T. L.; Moskovits, M. *J. Am. Chem. Soc.* **1996**, *118*, 5083. Khriachtchev, L.; Pettersson, M.; Runeberg, N.; Lundell, J.; Rasanen, M. *Nature* **2000**, *406*, 874. Himmel, H. J.; Manceron, L.; Downs, A. J.; Pullumbi, P. *J. Am. Chem.*

Soc. **2002**, *124*, 4448. Li, J.; Bursten, B. E.; Liang, B.; Andrews, L. *Science* **2002**, *295*, 2242. Andrews, L.; Wang, X. *Science* **2003**, *299*, 2049.

(3) Zhou, M. F.; Tsumori, N.; Li, Z.; Fan, K.; Andrews, L.; Xu, Q. *J. Am. Chem. Soc.* **2002**, *124*, 12936. Zhou, M. F.; Xu, Q.; Wang, Z.; von Ragué Schleyer, P. *J. Am. Chem. Soc.* **2002**, *124*, 14854. Jiang, L.; Xu, Q. *J. Am. Chem. Soc.* **2005**, *127*, 42. Xu, Q.; Jiang, L.; Tsumori, N. *Angew. Chem., Int. Ed.* **2005**, *44*, 4338.

(4) Himmel, H. J.; Downs, A. J.; Greene, T. M. *Chem. Rev.* **2002**, *102*, 4191 and references therein.

(5) Greene, T. M.; Brown, W.; Andrews, L.; Downs, A. J.; Chertihin, G. V.; Runeberg, N.; Pyykkö, P. *J. Phys. Chem.* **1995**, *99*, 7925. Breckenridge, W. H.; Wang, J. H. *J. Chem. Phys.* **1987**, *87*, 2630. Wang, X.; Andrews, L. *J. Phys. Chem. A* **2004**, *108*, 11006. Wang, X.; Andrews, L. *Inorg. Chem.* **2004**, *43*, 7146.

(6) Jiang, L.; Xu, Q. *J. Am. Chem. Soc.* **2005**, *127*, 8906.

(7) Jiang, L.; Xu, Q. *J. Phys. Chem. A* **2005**, *109*, 9001.

(8) Burkholder, T. R.; Andrews, L. *J. Chem. Phys.* **1991**, *95*, 8697.

(9) Zhou, M. F.; Tsumori, N.; Andrews, L.; Xu, Q. *J. Phys. Chem. A* **2003**, *107*, 2458. Jiang, L.; Xu, Q. *J. Chem. Phys.* **2005**, *122*, 034505.

(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.

(11) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(12) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639. Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(13) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033. Hay, P. J. *J. Chem. Phys.* **1977**, *66*, 4377.

(14) Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum: New York, 1976; Vol. 3, p 1.

(15) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(16) Darling, J. H.; Ogden, J. S. *J. Chem. Soc., Dalton Trans.* **1972**, 2496.

(17) Zhou, M. F.; Andrews, L.; Bauschlicher, C. W., Jr. *Chem. Rev.* **2001**, *101*, 1931.

(18) The ionization energies of neon and argon are 21.56 and 15.76 eV, respectively. Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, Suppl. No. 1, 6.

(19) George, V. C.; Andrews, L. *J. Chem. Phys.* **1997**, *106*, 3457.

(20) Greene, T. M.; Andrews, L.; Downs, A. J. *J. Am. Chem. Soc.* **1995**, *117*, 8180.