Communication

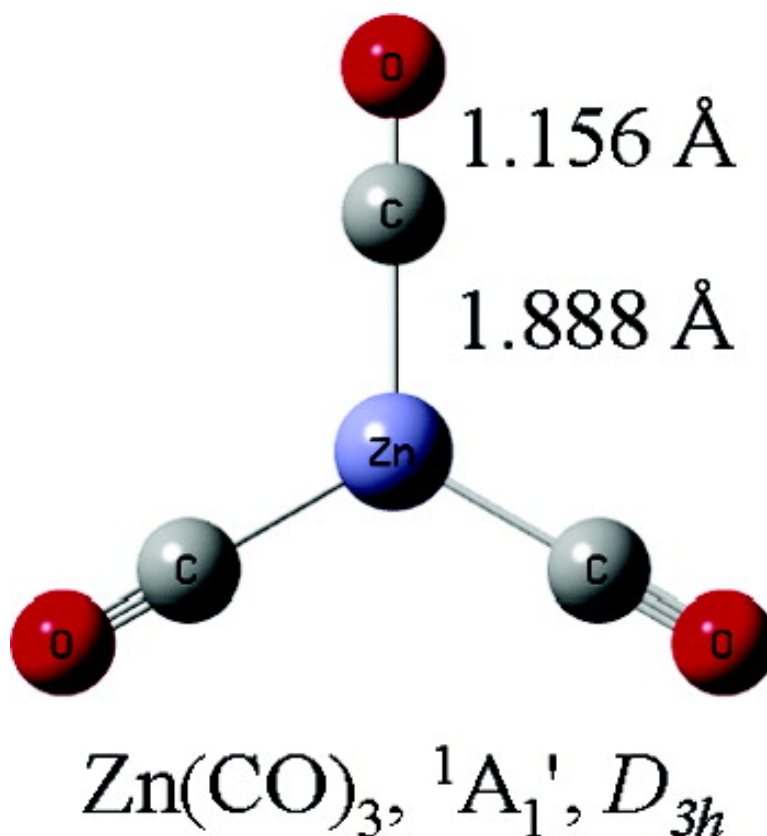# Experimental and Theoretical Evidence for the Formation of Zinc Tricarbonyl in Solid Argon

Ling Jiang, and Qiang Xu

$Zn(CO)_3$, $^1A_1'$, D_{3h}

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 9 articles that cite this article, as of the time of this article download
- Access to high resolution figures

ACS Publications
High quality. High impact.

View the Full Text HTML

Experimental and Theoretical Evidence for the Formation of Zinc Tricarbonyl in Solid Argon

Ling Jiang 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 April 11, 2005; E-mail: q.xu@aist.go.jp

The interaction of carbon monoxide with metal atom is of considerable interest from an academic or an industrial viewpoint.[1] It is generally accepted that the bonding scheme of transition-metal carbonyls involves a σ-type dative interaction between the lone-pair electrons of CO and the vacant orbitals of the metal atom and π-type back-donation from the filled d_π orbitals of the metal atom to the vacant π^* orbitals of CO molecules.[1,2] In contrast with the extensive experimental and theoretical studies of the interactions of CO molecules with the transition-metal and main-group-element atoms,[3] however, almost nothing is known about a simple zinc carbonyl molecule. Here we report a study of the reactions of laser-ablated zinc atoms with CO molecules in excess argon. IR spectroscopy coupled with theoretical calculations provides obvious evidence for the formation of an unprecedented zinc tricarbonyl, $Zn(CO)_3$, the next member of the series of 18-electron metal carbonyls $Cr(CO)_6 \rightarrow Fe(CO)_5 \rightarrow Ni(CO)_4$, but no evidence for the formation of the zinc mono- and dicarbonyls $Zn(CO)_n$ ($n = 1, 2$).

The matrix-isolated $Zn(CO)_3$ molecules were produced by co-deposition of laser-ablated Zn atoms with CO in excess argon at 7 K and investigated using FTIR spectroscopy.[4] Recent studies have shown that, with the aid of an 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.[3,5,6] The IR spectra in the 2000–1960 cm^{-1} region are shown in Figure 1. The 1986.1 and 1975.8 cm^{-1} bands were produced on sample annealing (Figure 1a,b), almost unchanged after broad-band irradiation, and slightly decreased upon further annealing. On the basis of the growth/decay characteristics as a function of changes of experimental conditions, the absorptions in the 2000–1960 cm^{-1} region can be grouped together to one species in different matrix trapping sites. The 1975.8 cm^{-1} absorption, with larger intensity relative to the 1986.1 cm^{-1} band, is used for discussions. Doping with CCl_4 as an electron scavenger has no effect on these bands, indicating that the product is neutral (Figure 1).

The main 1975.8 cm^{-1} absorption shifted to 1931.1 cm^{-1} with $^{13}C^{16}O$ and to 1931.0 cm^{-1} with $^{12}C^{18}O$, respectively (Table 1),[7] exhibiting isotopic frequency ratios ($^{12}C^{16}O/^{13}C^{16}O$, 1.0231; $^{12}C^{16}O/^{12}C^{18}O$, 1.0232) characteristic of C–O stretching vibrations. In the $^{12}C^{16}O + ^{13}C^{16}O$ and $^{12}C^{16}O + ^{12}C^{18}O$ experiments, the mixed isotopic spectra are quartets with approximately 2:1:1:2 relative intensities, which demonstrates the doubly degenerate vibrational mode for a trigonal species.[8] The 1975.8 cm^{-1} band is therefore assigned to the antisymmetric C–O stretching vibrations (e′) of the $Zn(CO)_3$ molecule with D_{3h} symmetry.

To support the experimental assignment and to provide insight into the structure and bonding in $Zn(CO)_3$, we have performed quantum chemical calculations at the BP86/6-311++G(3df,3pd) level of theory with the Gaussian 03 program system.[9,10] Geometries were fully optimized, and vibrational frequencies were calculated
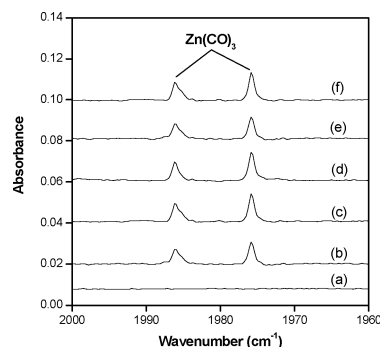

Figure 1. IR spectra in the 2000–1960 cm^{-1} region for laser-ablated Zn atoms co-deposited with 0.5% CO in argon at 7 K: (a) 60 min of sample deposition, (b) after annealing to 30 K, (c) after annealing to 34 K, (d) after 20 min of broad-band irradiation, (e) after annealing to 36 K, and (f) doping with 0.05% CCl_4, after annealing to 34 K.

Table 1. Observed and Calculated Vibrational Frequencies (cm^{-1}) and Isotopic Frequency Ratios for the $Zn(CO)_3$ Molecule

	$^{12}C^{16}O$	$^{13}C^{16}O$	$^{12}C^{18}O$	$^{12}C/^{13}C$	$^{16}O/^{18}O$
obs^a	1975.8	1931.1	1931.0	1.0231	1.0232
calc^b	1974.7	1928.5	1930.2	1.0240	1.0231

^{a} Two matrix trapping sites were observed, and only the major site absorption is listed here. ^{b} Only the IR-active antisymmetric CO stretching mode (e′) is listed. Details are reported in the Supporting Information.
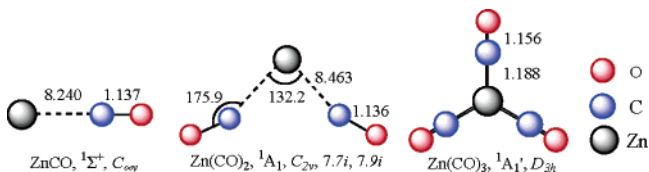

Figure 2. Optimized structures (bond lengths in angstrom, bond angles in degree), electronic ground states, and point groups of the $Zn(CO)_n$ ($n = 1–3$) molecules. For $Zn(CO)_2$, the letter "i" denotes the imaginary frequency (in cm^{-1}).

with analytical second derivatives. The natural bond orbital (NBO)[11] approach was employed to elucidate the electron configuration and the bonding characteristics.[7] The calculated C–O stretching vibrational frequencies and isotopic frequency ratios of $Zn(CO)_3$ are presented in Table 1. The optimized structures, along with the ground states and point groups, are illustrated in Figure 2. Meanwhile, the calculations for the $Zn(CO)_n$ ($n = 1, 2$) species have also been considered at the same theory level, and salient results are showed in Figure 2.

Our DFT calculations predict that the $Zn(CO)_3$ molecule has a singlet ground state with D_{3h} symmetry, whereas a triplet state exhibits no geometry convergence. The geometry optimization procedures starting with C_1, C_{2v}, and C_{3h} symmetry all result in a structure closer to D_{3h} symmetry. The correctness of this predicted ground state and structure for $Zn(CO)_3$ is evident in the calculated
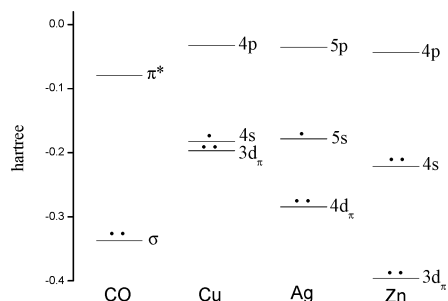
Figure 3. Energy levels of the valence $(n − 1)$d, ns, and np orbitals of the Cu, Ag, and Zn atoms and those of the lone-pair electrons of CO and its vacant π^* orbitals.

frequencies and relative intensities:[7] the calculated antisymmetric stretching frequency, 1974.7 cm^{-1}, agrees within 1.1 cm^{-1} with the experimental argon matrix value (11.4 cm^{-1} for 1986.1 cm^{-1})! Equally importantly, the calculated $^{12}C^{16}O/^{13}C^{16}O$ and $^{12}C^{16}O/$ $^{12}C^{18}O$ isotopic frequency ratios of 1.0240 and 1.0231 agree well with the experimental observations, 1.0231 and 1.0232, respectively. In the mixed isotopic spectra, the calculated symmetric C−O stretching mode (i.e., Zn($^{12}C^{16}O$)($^{13}C^{16}O$)$_2$, 2047.6 cm^{-1}, 82 km/ mol) has an intensity much lower than the antisymmetric one (Zn-($^{12}C^{16}O$)$_3$, 1974.7 cm^{-1}, 1707 km/mol),[7] in agreement with the absence of this absorption in the mixed isotopic spectra. These excellent agreements substantiate the identification of this novel zinc tricarbonyl, Zn(CO)$_3$, from the matrix IR spectrum.

The present DFT calculations show that the singlet Zn(CO)$_n$ (n = 1, 2) molecules lie 50.68 and 37.01 kcal/mol, respectively, in energy lower than the triplet ones. The $R_{Zn−C}$ in zinc monocarbonyl, ZnCO, is 8.240 Å (Figure 2), implying that ZnCO is not bound. A NBO analysis reveals that the natural electron configurations of the Zn, C, and O orbitals are almost unchanged with respect to the isolated Zn and CO, indicating that there is almost no charge transfer from Zn to CO or vice versa.[7] Similar results have also been obtained for zinc dicarbonyl, Zn(CO)$_2$. In contrast, the natural charge of the zinc atom in Zn(CO)$_3$ is 1.26754, exhibiting a large charge transfer from Zn to CO and lowering the CO stretching frequency. It can also be found that the HOMO−LUMO gap of Zn(CO)$_3$ remarkably decreases to 25.49 kcal/mol relative to those of ZnCO and Zn(CO)$_2$ (88.35 and 88.09 kcal/mol), supporting the observation of Zn(CO)$_3$ and the absence of Zn(CO)$_n$ (n = 1, 2). The energies for the formation of Zn(CO)$_3$ from Zn ^1S and ^3P states are +5.23 and −89.92 kcal/mol, respectively, suggesting that the formation of Zn(CO)$_3$ involves the electronic excitation of the Zn atom to the ^3P state during laser ablation (vide infra), similar to the reactions of group 12 metal atoms with H$_2$ and CH$_4$.[3b,12]

Figure 3 shows schematically the energy levels of the valence 4d, 4s, and 4p orbitals of the Zn atom and those of the lone-pair electrons of CO and its vacant π^* orbitals compared with those of the Cu and Ag atoms. Taking the Cu−CO pair as an example, the Cu 3d$_\pi$ and CO π^* levels are close (73.37 kcal/mol), but the Cu 4s and CO lone-pair levels are far apart (96.85 kcal/mol), and thus the contribution for the formation of CuCO is mainly from the d$_\pi$ → π^* back-donation, consistent with the previous reports.[13] The gap of metal $(n − 1)$d$_\pi$ and CO π^* levels follows the order Cu < Ag < Zn, suggesting that the thermal stability of these carbonyls is in the order Cu > Ag > Zn, in good agreement with the observations for Cu(CO)$_n$ (n = 1−3),[13] Ag(CO)$_n$ (n = 2−3),[14] and Zn(CO)$_3$. The electron configuration of Zn in Zn(CO)$_3$ is [core] 4s(0.54) 3d(9.90) 4p(0.29),[7] suggesting that the formation of Zn-(CO)$_3$ involves 4s → 4p promotion of the Zn atom. The HOMO is the Zn−C π bonding orbital,[7] which comprises the Zn sp hybrid orbitals → CO π^* back-donation, satisfying the frontier molecular

orbital (FMO) theory.[15] This promotion increases the Zn−CO bonding by decreasing the σ repulsion and significantly increasing the Zn 4sp hybrid orbitals → CO π^* back-donation. NBO analysis shows that the quenching from Zn ^3P atom to ^1S in Zn(CO)$_3$ corresponds to the stabilization by the overlapped C$_3$ orbitals (see the MO pictures), and the sp^2 hybrid orbitals of Zn atom are favored to bond three CO molecules. It is also found that the absorption of Zn(CO)$_3$ does not disappear until the argon matrix evaporates upon heating, demonstrating its thermal stability.

In summary, the reaction of laser-ablated zinc atoms with CO has produced the Zn(CO)$_3$ molecule, which has the favored 18-electron configuration as the next member of the series Cr(CO)$_6$, Fe(CO)$_5$, and Ni(CO)$_4$.

Supporting Information Available: Isotopic IR data, NBO analysis results, molecular orbital pictures, and the complete ref 9. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999.
(2) Blyholder, G. *J. Phys. Chem.* **1964**, *68*, 2772.
(3) (a) Zhou, M. F.; Andrews, L.; Bauschlicher, C. W., Jr. *Chem. Rev.* **2001**, *101*, 1931. (b) Himmel, H. J.; Downs, A. J.; Greene, T. M. *Chem. Rev.* **2002**, *102*, 4191 and references therein.
(4) The experiment for laser ablation and matrix isolation spectroscopy is similar to the previous reports: Burkholder, T. R.; Andrews, L. *J. Chem. Phys.* **1991**, *95*, 8697. 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. Briefly, Zn atoms ablated with the Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate) were co-deposited with CO in excess argon onto a 7 K CsI window. 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 range of 5000−400 cm^{-1}. Samples were annealed at different temperatures and subjected to broad-band irradiation (λ > 250 nm) using a high-pressure mercury arc lamp (Ushio, 100 W).
(5) Li, J.; Bursten, B. E.; Liang, B.; Andrews, L. *Science* **2002**, *295*, 2242. Andrews, L.; Wang, X. *Science* **2003**, *299*, 2049.
(6) 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.
(7) See Supporting Information.
(8) Darling, J. H.; Ogden, J. S. *J. Chem. Soc., Dalton Trans.* **1972**, 2496.
(9) Frisch, M. J.; et al. *Gaussian 03*, revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.
(10) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822. 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. Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033. Hay, P. J. *J. Chem. Phys.* **1977**, *66*, 4377.
(11) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold. F. *NBO*, version 3.1.
(12) 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. Greene, T. M.; Andrews, L.; Downs, A. J. *J. Am. Chem. Soc.* **1995**, *117*, 8180.
(13) Huber, H.; Kunding, E. P.; Moskovits, M.; Ozin, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 2097. Kasai, P. H.; Jones, P. M. *J. Am. Chem. Soc.* **1985**, *107*, 813. Chemier, J. H. B.; Hampson, C. A.; Howard, J. A.; Mile, B. *J. Phys. Chem.* **1989**, *93*, 114. Blitz, M. A.; Mitchell, S. A.; Hackett, P. A. *J. Phys. Chem.* **1991**, *95*, 8719. Zhou, M. F.; Andrews, L. *J. Chem. Phys.* **1999**, *111*, 4548.
(14) McIntosh, D.; Ozin, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 3167. Kasai, P. H.; Jones, P. M. *J. Phys. Chem.* **1985**, *89*, 1147. Kasai, P. H.; Jones, P. M. *J. Am. Chem. Soc.* **1985**, *107*, 6385. Marian, C. M. *Chem. Phys. Lett.* **1993**, *215*, 582. Liang, B.; Andrews, L. *J. Phys. Chem. A* **2000**, *104*, 9156.
(15) Fukui, K. *Acc. Chem. Res* **1971**, *4*, 57. Woodward. R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Chemie: Weinheim, 1970.

JA052329W