( [a] [b]) [a] [a,b] [a,b]

Observation of Anomalous C-O Bond Weakening on Metal Clusters and Activation Process to CO Dissociation (National Institute of Advanced Industrial Science and Technology (AIST)[a] and Kobe University[b]) JIANG, Ling;[a] TENG, Yun-Lei;[a,b] XU, Qiang[a,b]

**[Introduction]** The interaction of carbon monoxide with transition metals may lead to breaking and making chemical bonds and trigger important catalyzed reactions.[1] The long standing goal of elucidating mechanisms of the catalyzed reactions has motivated numerous experimental investigations of CO chemisorption on transition metal surfaces. Remarkably, the chemisorbed CO molecular state with unusual low C-O stretching frequencies ($\nu_{C-O}$) (ca. 1200 cm$^{-1}$) has been found on some transition metal surfaces.[1] However, there has been no report so far on a simple homoleptic metal carbonyl molecule with a side-on-bonded CO and almost none is known about the structural configuration of CO as a precursor to dissociation. Here we report a series of studies of the reactions of laser-ablated small metal clusters with carbon monoxide in excess argon,[2,3] which is a key for explaining the unusually low $\nu_{C-O}$ values (1100-1400 cm$^{-1}$) of the chemisorbed CO molecules on transition metal surfaces and for understanding the activation process to CO dissociation on metal catalysts.

**[Experimental Method]** The experiment employed the laser ablation and matrix isolation infrared spectroscopy. Briefly, the Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate with 10 ns pulse width) was focused on the rotating metal target. The laser-ablated metal atoms were co-deposited with CO in excess argon onto a CsI window cooled normally to 7 K by means of a closed-cycle helium refrigerator. $^{12}C^{16}O$ (99.95%), $^{13}C^{16}O$ (99%, $^{18}O$ < 1%) and $^{12}C^{18}O$ (99%) were used to prepare the CO/Ar mixtures. 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).

**[Theoretical Method]** Quantum chemical calculations were performed to predict the structures and vibrational frequencies of the observed reaction products using the Gaussian 03 program. The BP86, BPW91, and B3LYP density functional methods were used. The 6-311++G(d,p) basis sets were used for C, O, and Sc atoms, and SDD for Y atom.



Fig. 1. IR spectra in the 1210-1180 cm$^{-1}$ and 780-580 cm$^{-1}$ regions for laser-ablated Sc atoms codeposited with 0.06% CO in argon at 7 K. (a) 60 min of sample deposition, (b) after annealing to 28 K, (c) after annealing to 32 K, (d) after 20 min of broad-band irradiation, (e) after annealing to 36 K, (f) doping with 0.01% CCl$_4$, after annealing to 32 K, and (g) after 20 min of broad-band irradiation following (f).

**[Results and Discussion]** Experiments have been done with carbon monoxide concentrations ranging from 0.01% to 1.0% in excess argon. Typical infrared
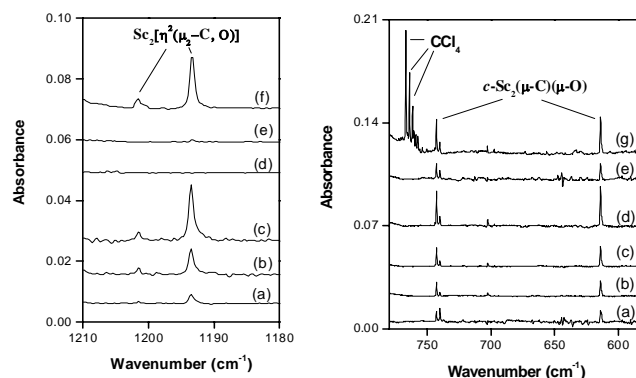
spectra for the reactions of laser-ablated Sc atoms with CO molecules in excess argon in the selected regions are illustrated in Fig. 1. The 1203.1 and 1193.4 cm$^{-1}$ absorptions shifted to 1175.2 and 1165.8 cm$^{-1}$ with $^{13}C^{16}O$, and to 1181.0 and 1171.5 cm$^{-1}$ with$^{12}C^{18}O$, respectively (Fig. 1), exhibiting isotopic frequency ratios ($^{12}C^{16}O/^{13}C^{16}O$:1.0237 and 1.0237; $^{12}C^{16}O/^{12}C^{18}O$: 1.0187 and 1.0187) characteristic of C-O stretching vibrations. In the mixed $^{12}C^{16}O$ + $^{13}C^{16}O$ and $^{12}C^{16}O$ + $^{12}C^{18}O$ experiments (Fig. 1), only pure isotopic counterparts were observed, indicating that only one CO subunit is involved. Accordingly, the absorptions at 1203.1 and 1193.4 cm$^{-1}$ are assigned to the C-O stretching of the $Sc_2[\eta^2(\mu_2\text{-C, O})]$ complex in different matrix sites on the basis of isotopic shifts, mixed isotopic splitting patterns, $CCl_4$-doping experiments, and the comparison with theoretical predictions.[2]

New bands at 742.6 and 614.1 cm$^{-1}$ slightly increased on annealing, markedly increased upon broad-band irradiation at the expense of the 1203.1 and 1193.4 cm$^{-1}$ absorptions of $Sc_2[\eta^2(\mu_2\text{-C, O})]$, and observably decreased on further annealing (Fig. 1). The 742.6 and 614.1 cm$^{-1}$ absorptions are assigned to the Sc-C and Sc-O stretching vibrations of $c$-$Sc_2(\mu\text{-C})(\mu\text{-O})$, respectively.[2]

From the $Sc_2[\eta^2(\mu_2\text{-C, O})]$ molecule, the reaction proceeds by binding oxygen atom with another scandium atom to form a nonplanar intermediate $Sc_2[\eta^2(\mu_2\text{-C, }\mu_2\text{-O})]$ via transition state TS1 (Fig. 2). The barrier height for this process is predicted to be 23.00 kcal/mol, which can be obtained by ultraviolet visible irradiation. From $Sc_2[\eta^2(\mu_2\text{-C, }\mu_2\text{-O})]$, CO can further be activated to form the C-O dissociated $c$-$Sc_2(\mu\text{-C})(\mu\text{-O})$ product via transition state TS2. Interestingly, the structures of $Sc_2CO$ isomers in Fig. 2 represent almost all the main modes of metal-CO coordination to date. The present observation schematically depicts the whole process starting with the interaction of CO with metal to CO dissociation. The present finding is a key for explaining the unusual low $\nu_{C\text{-O}}$ values (1100-1400 cm$^{-1}$) of the chemisorbed CO molecules on transition metal surfaces[1] and for understanding the activation process to CO dissociation on metal catalysts.

References:

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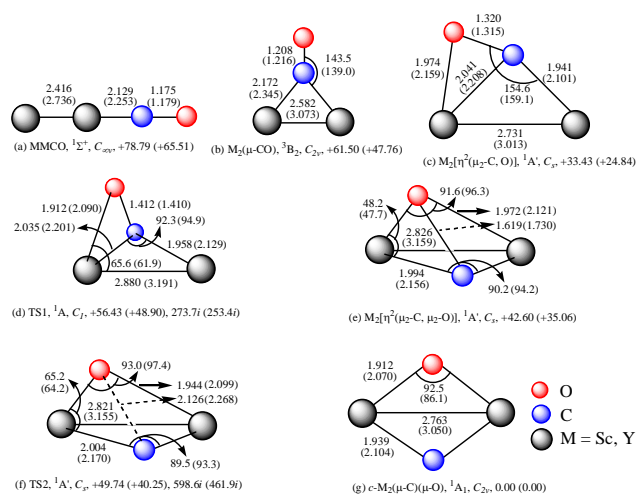(3) Xu, Q.; Jiang, L.; Tsumori, N. *Angew. Chem., Int. Ed*. **2005**, *44*, 4338.

Fig.2. Optimized structures (bond lengths in angstrom, bond angles in degree), electronic ground state, point group, and the relative energies (in kcal/mol) for the $Sc_2CO$ and $Y_2CO$ (in parentheses) isomers. For the transition states (TS, (d) and (f)), the letter "$i$" denotes the imaginary frequency (in cm$^{-1}$).