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Mingfei Zhou, Ling Jiang, and Qiang Xu

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Reactions of silicon atoms and small clusters with CO: Experimental and theoretical characterization of Si_nCO $(n=1-5)$, $Si_2(CO)_2$, *c*-$Si_2(\mu$-O$)(\mu$-CSi$)$, and *c*-$Si_2(\mu$-O$)(\mu$-CCO$)$ in solid argon

Mingfei Zhou[a)]
Department of Chemistry & Laser Chemistry Institute, Shanghai Key Laboratory of Molecular Catalysts and Innovative Materials, Fudan University, Shanghai 200433, People's Republic of China

Ling Jiang and Qiang Xu[b)]
National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka 563-8577, Japan

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Reactions of silicon atoms and small clusters with carbon monoxide molecules in solid argon have been studied using matrix isolation infrared absorption spectroscopy. In addition to the previously reported SiCO monocarbonyl, $Si_2(CO)_2$ and Si_nCO $(n=2-5)$ carbonyl molecules were formed spontaneously on annealing and were characterized on the basis of isotopic substitution and theoretical calculations. It was found that Si_2CO, Si_3CO, and Si_5CO are bridge-bonded carbonyl compounds, whereas Si_4CO is a terminal-bonded carbonyl molecule. The $Si_2(CO)_2$ and Si_3CO molecules photochemically rearranged to the more stable *c*-$Si_2(\mu$-O$)(\mu$-CCO$)$ and *c*-$Si_2(\mu$-O$)(\mu$-CSi$)$ isomers where Si_2 is inserted into the CO triple bond. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1811078]

I. INTRODUCTION

The CO molecule plays a central role in chemisorption, catalysis, and organometallic chemistry. Numerous experimental and theoretical investigations on the interactions of CO with transition metal and main group element atoms, clusters, and surfaces have been accomplished. The interaction of CO with a silicon center is one such study.

Experimentally, the matrix isolation technique has been applied to characterize the reaction products of a silicon atom and CO. In 1977, Weltner and co-workers reported electron spin resonance (ESR) and optical spectra of silicon carbonyls SiCO and $Si(CO)_2$, which were prepared by the vaporization and reaction of silicon atoms with CO in various matrices at 4 K.[1] Absorptions at 1899 and 1928 cm^{-1} were assigned to the C–O stretching frequencies of the SiCO and $Si(CO)_2$ molecules in solid argon. The ground state of SiCO was determined to be a $^3\Sigma^-$. The $Si(CO)_2$ molecule was claimed to have a linear or slightly bent geometry because of the missing symmetric C–O stretching vibration in the IR spectrum. The structure and bonding of various SiCO isomers and $Si(CO)_2$ have been the subject of several theoretical calculations.[2–7] In contrast to the experiment, theoretical calculations indicated that $Si(CO)_2$ has a bent ground state structure with two intense C–O stretching vibrations.[7] In addition, the charged $SiCO^+$ and $SiCO^-$ carbonyls have been characterized.[7,8]

Considerable attention has also been focused on the interactions of CO with silicon surfaces,[9–16] but much less is known about the structure and properties of the Si_nCO $(n\geqslant 2)$ species, which are often invoked as models for CO absorption on silicon surfaces. Studies on the reactions of silicon clusters in the gas phase showed that CO does not react with silicon clusters at room temperature, although a series of $Si_n(CO)_m^+$ products where CO is very weakly bound to the clusters was observed when the temperature was lowered to 77 K.[17] Recently, carbon monoxide adsorption on small silicon clusters has been studied theoretically. The results showed that the binding energies of Si_nCO $(n=2-7)$ decreased successively and rapidly as the number of silicon atoms increased.[18]

In this paper, we report a combined matrix isolation infrared spectroscopic and theoretical study of the reactions of silicon atoms and small clusters with CO in solid argon. We will show that Si_nCO $(n=1-5)$ and $Si_2(CO)_2$ are formed on sample deposition and on annealing. Photoinduced rearrangement of Si_3CO and $Si_2(CO)_2$ to *c*-$Si_2(\mu$-O$)(\mu$-CSi$)$ and *c*-$Si_2(\mu$-O$)(\mu$-CCO$)$ molecules where CO is activated is also observed.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

The experiment for laser ablation and matrix isolation infrared spectroscopy is similar to those used previously.[19] Briefly, a Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate with 10 ns pulse width) was focused on the rotating silicon target. The laser-ablated silicon atoms were codeposited with CO in excess argon onto a CsI window cooled normally to 7 K by means of a closed-cycle helium refrigerator. The matrix gas deposition rate was typically 2–4 mmol h^{-1}. Carbon monoxide, $^{13}C^{16}O$ (99%) and $^{12}C^{18}O$ (99%) were used to prepare the CO/Ar mixtures. In general, matrix samples were deposited for 1–2 h. After sample deposition, IR spectra were recorded on a BIO-RAD FTS-6000e spectrometer at 0.5 cm^{-1} resolution using a liq-

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[a)] Electronic mail: mfzhou@fudan.edu.cn
[b)] Electronic mail: q.xu@aist.go.jp

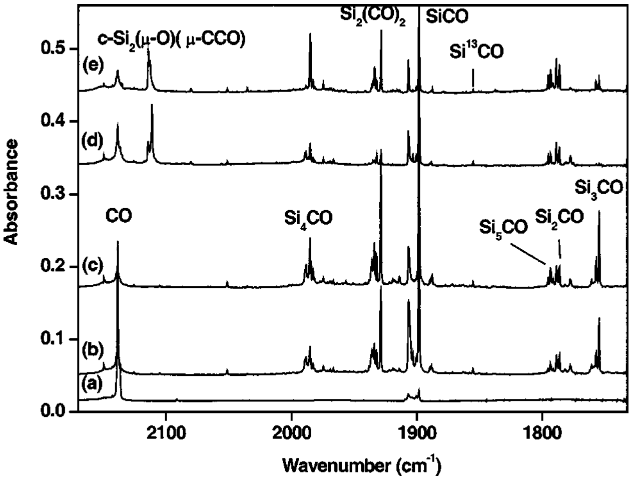

FIG. 1. Infrared spectra in the 2170–1730 cm^{-1} region from codeposition of laser-ablated silicon atoms with 0.025% CO in Ar. (a) 1 h of sample deposition at 7 K, (b) after annealing to 30 K, (c) after annealing to 34 K, (d) after 20 min of broad-band irradiation, and (e) after annealing to 38 K.

uid 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 GAUSSIAN98 program.[20] The Becke three-parameter hybrid functional with the Lee-Yang–Parr correlation corrections (B3LYP) was used.[21,22] The 6-311+G(d) basis sets were used for Si, C, and O atoms.[23] Geometries were fully optimized and vibrational frequencies calculated with analytical second derivatives.

III. RESULTS AND DISCUSSION

A. Infrared spectra

A series of experiments has been done using different CO concentrations (ranging from 0.025% to 0.5% in argon) and different laser energies (ranging from 5 mJ/pulse to 20 mJ/pulse) to control the relative concentrations of Si and CO. The experiments with low CO concentrations and high laser energies are of particular interest here. The infrared spectra in the 2170–1730, 1220–1170, and 820–730 cm^{-1} regions with 0.025% CO in argon using relatively high laser energy (18 mJ/pulse) are illustrated in Figs. 1 and 2, respectively, and the band positions are listed in Table I. The stepwise annealing and photolysis behavior of these new product absorptions will be discussed below. In addition to the absorptions listed in the table, absorptions for Si_2, Si_3, and Si_4 (not shown) are also observed.[24,25] Weak absorptions (458.0, 853.4, 998.6, and 1390.5 cm^{-1}) in the $A\,^3\Pi_u \leftarrow X\,^3\Sigma_g$ system of Si_2 (Ref. 24) appeared on 25 K annealing, increased on 30 K annealing, but markedly decreased on 34 K annealing. The Si_3 (525.7 cm^{-1}) and Si_4 (501.2 cm^{-1}) (Ref. 25) absorptions also appeared on 25 K annealing, increased on 30 K annealing, and remained almost unchanged on 34 K annealing. Different isotopic carbon monoxides, $^{13}C^{16}O$, $^{12}C^{18}O$ and $^{12}C^{16}O + ^{13}C^{16}O$, $^{12}C^{16}O + ^{12}C^{18}O$ mixtures, were employed for product identification through isotopic shifts and splittings. The isotopic counterparts are also listed in Table I. The mixed $^{12}C^{16}O + ^{13}C^{16}O$ spectra in the C–O stretching frequency region are shown in Figs. 3 and 4, and the mixed $^{12}C^{16}O + ^{12}C^{18}O$ spectra in the C–O stretching frequency region are illustrated in Figs. 5 and 6, respectively. Figures 7 and 8 show the spectra in the 1220–1120 and 820–720 cm^{-1} regions for different isotopic CO samples after 20 min of broad-band irradiation.

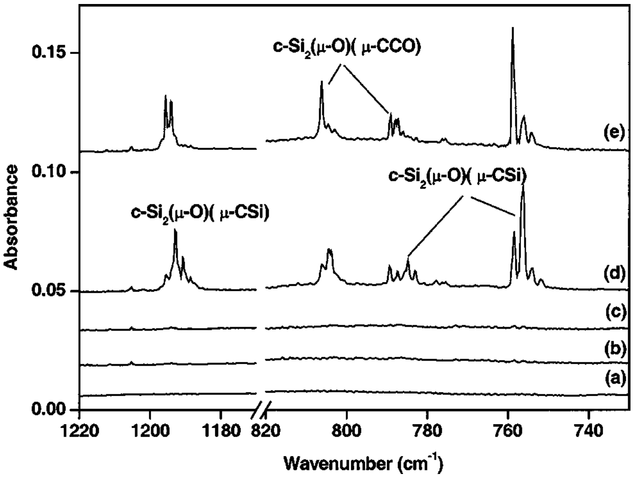

FIG. 2. Infrared spectra in the 1220–1170 and 820–730 cm^{-1} regions from codeposition of laser-ablated silicon atoms with 0.025% CO in Ar. (a) 1 h of sample deposition at 7 K, (b) after annealing to 30 K, (c) after annealing to 34 K, (d) after 20 min of broad-band irradiation, and (e) after annealing to 38 K.

B. Calculation results

Quantum chemical calculations were performed on the potential product molecules. The optimized structures are shown in Fig. 9. The vibrational frequencies and intensities are listed in Table II. Table III provides a comparison of observed and calculated isotopic frequency ratios for the observed vibrational modes.

1. SiCO

As reported previously,[1,7] the bands at 1898.4 and 1906.8 cm^{-1} are due to the C–O stretching vibration of the SiCO molecule at different trapping sites. A weak band at 3771.8 cm^{-1} was observed to track with the 1898.4 cm^{-1} band and is assigned to the overtone ($2v_1$) of the C–O stretching mode. This band shifted to 3686.3 cm^{-1} with $^{13}C^{16}O$ and to 3688.2 cm^{-1} with $^{12}C^{18}O$. The isotopic frequency ratios are almost the same as those of the v_1 fundamental. The anharmonicity constant was deduced to be -12.5 cm^{-1}.

2. $Si_2(CO)_2$

The sharp band at 1928.7 cm^{-1} with nearby matrix site-split bands at 1932.2 and 1934.1 cm^{-1} appeared on annealing but disappeared on broad-band irradiation. The 1928.7 cm^{-1} band was previously assigned to the linear $Si(CO)_2$ molecule.[1] However, recent theoretical calculations indicated that $Si(CO)_2$ has a singlet ground state with a bent C_{2v}

TABLE I. Infrared absorptions (cm^{-1}) from codeposition of laser-ablated silicon atoms with CO in excess argon.

$^{12}C^{16}O$	$^{13}C^{16}O$	$^{12}C^{18}O$	$^{12}C^{16}O + ^{13}C^{16}O$	$^{12}C^{16}O + ^{12}C^{18}O$	$R(12/13)$	$R(16/18)$	Assignment
1898.4	1855.2	1855.9	1898.4, 1855.2	1898.4, 1855.9	1.0233	1.0229	SiCO
1906.8	1863.4	1863.8	1906.8, 1863.4	1906.8, 1863.8	1.0233	1.0231	Site
3771.8	3686.3	3688.2	3771.8, 3686.3	3771.8, 3688.2	1.0232	1.0227	SiCO $2v_{CO}$
1928.7	1886.7	1882.6	1970.3, 1928.7, 1900.1, 1886.7	1970.5, 1928.7, 1897.7, 1882.6	1.0223	1.0245	$Si_2(CO)_2$
1932.2	1890.1	1886.0	1972.5, 1932.2, 1903.0, 1890.1	1972.8, 1932.2, 1900.6, 1886.0	1.0223	1.0245	Site
1934.1	1891.9	1887.8	1973.6, 1934.1, 1904.0, 1891.8	1973.7, 1934.1, 1901.5, 1887.8	1.0223	1.0245	Site
1788.7	1747.7	1750.0	1788.7, 1747.7	1788.7, 1750.0	1.0235	1.0221	Si_2CO
1786.3	1745.4	1747.6	1786.3, 1745.4	1786.3, 1747.6	1.0234	1.0221	Site
1777.5	1736.6	1738.2	1777.5, 1736.6	1777.5, 1738.2	1.0236	1.0226	Site
1754.5	1715.8	1713.0	1754.5, 1715.8	1754.5, 1713.0	1.0226	1.0242	Si_3CO
1756.9	1718.6	1715.3	1756.9, 1718.6	1756.9, 1715.3	1.0223	1.0243	Site
1985.2	1940.9	1939.2	1985.2, 1940.9	1985.2, 1939.2	1.0228	1.0237	Si_4CO
1988.7	1944.4	1942.5	1988.7, 1944.4	1988.7, 1942.5	1.0228	1.0238	Site
1793.2	1753.9	1750.7	1793.2, 1753.9		1.0224	1.0243	Si_5CO
1795.3	1755.9	1752.7	1795.3, 1755.9	1795.3, 1752.8	1.0224	1.0243	Site
1192.8	1157.2	1187.7	1192.8, 1157.2	1192.8, 1187.7	1.0308	1.0043	c-$Si_2(\mu$-$O)(\mu$-$CSi)$
1195.6	1159.8	1190.5	1195.6, 1159.8	1195.6, 1190.5	1.0309	1.0043	Site
784.8	784.5	757.2			1.0004	1.0365	c-$Si_2(\mu$-$O)(\mu$-$CSi)$
789.5	789.3	761.4			1.0003	1.0369	Site
756.1	751.2	736.6	756.2, 751.2	756.2, 736.6	1.0065	1.0265	c-$Si_2(\mu$-$O)(\mu$-$CSi)$
758.9	754.0	739.0	758.9, 754.0	758.9, 739.0	1.0065	1.0269	Site
2111.5	2048.6	2087.2	2111.5, 2106.3, 2055.8, 2048.6	2111.3, 2087.0	1.0307	1.0116	c-$Si_2(\mu$-$O)(\mu$-$CCO)$
2114.3	2051.2	2089.9	2114.4, 2110.2 2058.4, 2051.2	2114.1, 2089.4	1.0308	1.0117	Site
1391.9	1358.6	1364.9			1.0245	1.0198	c-$Si_2(\mu$-$O)(\mu$-$CCO)$
1394.8	1361.3	1367.7			1.0246	1.0198	Site
803.7	793.7	789.0	804.5, 802.8, 795.4, 793.8	803.7, 789.5	1.0126	1.0186	c-$Si_2(\mu$-$O)(\mu$-$CCO)$
806.2	796.0	791.3	806.2, 804.7, 797.1, 796.0	805.8, 791.3	1.0128	1.0188	Site
783.0	782.4	754.5			1.0008	1.0378	c-$Si_2(\mu$-$O)(\mu$-$CCO)$
787.3							Site

symmetry.[6,7] The linear structure lies about 60 kcal/mol higher in energy than the bent structure and is only a transition state based on the presence of an imaginary calculated frequency. The bent ground state $Si(CO)_2$ molecule was computed to have two C–O stretching vibrations at 2004.9 and 2073.0 cm^{-1} with 1166:504 relative intensities.[7] In the present experiments using pure isotopic CO samples, no obvious absorptions in the C–O stretching frequency region were observed to track with the 1928.7 cm^{-1} band, which suggests that the previous assignment to $Si(CO)_2$ is incorrect. Our results show that the 1928.7 cm^{-1} band is favored relative to the SiCO absorption in higher laser energy experiments. The intensity ratio of the 1928.7 cm^{-1} and 1898.4 cm^{-1} bands after 34 K annealing changes from 0.193:0.230 in the experiment shown in Fig. 1 to 0.424:0.689 in another experiment with 0.25% CO and 15 mJ/pulse laser energy. This observation implies that the molecule with the 1928.7 cm^{-1} band involves more Si atoms than SiCO, and accordingly, we assign the 1928.7 cm^{-1} band to $Si_2(CO)_2$. The observation of only one C–O stretching mode suggests that the molecule is centrosymmetric. In the mixed $^{12}C^{16}O + ^{13}C^{16}O$ spectra (Fig. 3), a triplet at 1928.7, 1900.1, and 1886.7 cm^{-1} and a weak associated band at 1970.3 cm^{-1} were observed. The 1970.3 cm^{-1} band is due to the symmetric C–O stretching mode of the $Si_2(^{12}C^{16}O)(^{13}C^{16}O)$ molecule. The symmetric C–O stretching mode of the centrosymmetric $Si_2(^{12}C^{16}O)_2$ and $Si_2(^{13}C^{16}O)_2$ molecules is IR inactive, but this mode of $Si_2(^{12}C^{16}O)(^{13}C^{16}O)$ is IR active because of the reduced symmetry. Similar isotopic splitting was observed in the mixed $^{12}C^{16}O + ^{12}C^{18}O$ experiments, as shown in Fig. 5.

The assignment is strongly supported by DFT calculations. As shown in Fig. 9, the $Si_2(CO)_2$ molecule was predicted to have a singlet ground state with a C_{2h} symmetry. The antisymmetric C–O stretching mode (b_u) was computed at 2015.2 cm^{-1}, which should be multiplied by 0.957 to fit the observed frequency. The calculated $^{12}C/^{13}C$ and $^{16}O/^{18}O$ isotopic frequency ratios of 1.0228 and 1.0247 agree well with the experimental ratios, 1.0223 and 1.0245. The IR inactive symmetric C–O stretching mode (a_g) of $Si_2(CO)_2$ was calculated at 2064.8 cm^{-1}, but this mode of $Si_2(^{12}C^{16}O)(^{13}C^{16}O)$ and $Si_2(^{12}C^{16}O)(^{12}C^{18}O)$ was calculated at 2050.3 and 2050.6 cm^{-1} with appreciable IR intensities (each has a 331 km/mol IR intensity, and the corresponding antisymmetric modes have IR intensities of 1911 and 1935 km/mol, respectively), completely consistent with the experiment.

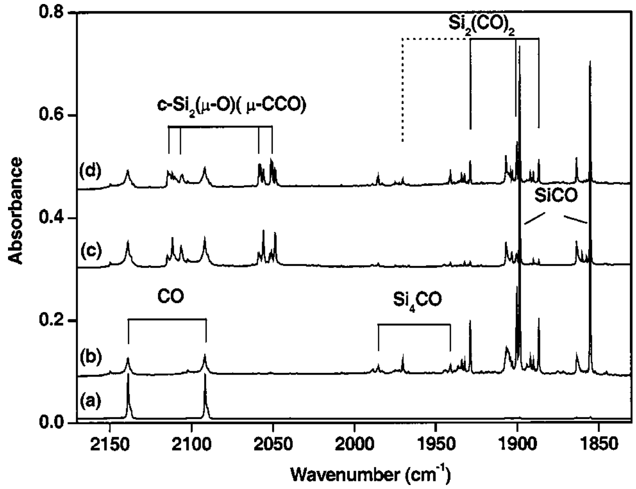

FIG. 3. Infrared spectra in the 2150–1830 cm^{-1} region from codeposition of laser-ablated silicon atoms with 0.02% $^{12}C^{16}O + 0.02\%$ $^{13}C^{16}O$ in Ar. (a) 2 h of sample deposition at 7 K, (b) after annealing to 34 K, (c) after 20 min of broad-band irradiation, and (d) after annealing to 38 K.

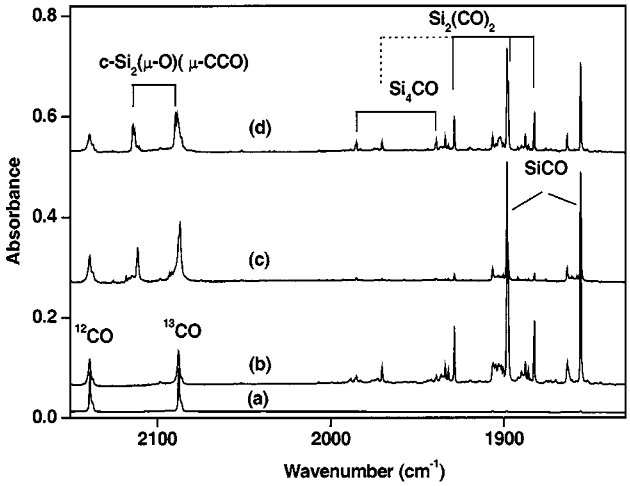

FIG. 5. Infrared spectra in the 2170–1830 cm^{-1} region from codeposition of laser-ablated silicon atoms with 0.02% $^{12}C^{16}O + 0.02\%$ $^{12}C^{18}O$ in Ar. (a) 2 h of sample deposition at 7 K, (b) after annealing to 34 K, (c) after 20 min of broad-band irradiation, and (d) after annealing to 38 K.

3. Si_nCO ($n=2-5$)

Besides the SiCO and $Si_2(CO)_2$ absorptions, four new bands at 1985.2, 1793.2, 1788.7, and 1754.5 cm^{-1} were observed in the C–O stretching frequency region. Each band has minor site absorptions that are 1–3 cm^{-1} apart. All four of these bands increased markedly on annealing, and the yields relative to SiCO increased with lower CO concentration and higher laser energy. As listed in Table I, each band exhibited $^{12}C/^{13}C$ and $^{16}O/^{18}O$ isotopic frequency ratios that are characteristic of C–O stretching vibrations. In the mixed $^{12}C^{16}O + ^{13}C^{16}O$ and $^{12}C^{16}O + ^{12}C^{18}O$ spectra (Figs. 3–6), each band splits into a doublet, indicating that only one CO subunit is involved in these vibrations. Therefore, these bands are due to C–O stretching vibration of the Si_nCO clusters with $n \geqslant 2$. The 1793.2, 1788.7, and 1754.5 cm^{-1} bands lie in the region expected for the bridge-bonded C–O stretching vibrations, while the 1985.2 cm^{-1} band is due to a terminal-bonded C–O stretching vibration. These four bands exhibited quite different isotopic frequency shifts, different annealing and photolysis behavior, and therefore can be assigned to Si_nCO with $n=2-5$ with the help of density functional frequency calculations.

The 1788.7 cm^{-1} band appeared on 25 K annealing and increased on broad-band irradiation, during which the $Si_2(CO)_2$ absorption and the 1985.2, 1793.2, and 1754.5 cm^{-1} bands were almost destroyed. This band is weaker but was still observed in the experiment with 0.25% CO and 15 mJ/pulse laser energy, during which the 1985.2, 1793.2, and 1754.5 cm^{-1} bands did not appear. These observations imply that the 1788.7 cm^{-1} absorption involves fewer silicon atoms than the 1985.2, 1793.2, and 1754.5 cm^{-1} absorptions, and therefore, we assign the 1788.7 cm^{-1} band to the C–O stretching mode of the bridge-bonded Si_2CO molecule. The 1754.5 cm^{-1} band also appeared on 25 K annealing and markedly increased on subsequent 30 and 34 K annealing. This band was destroyed on broad-band irradiation. The

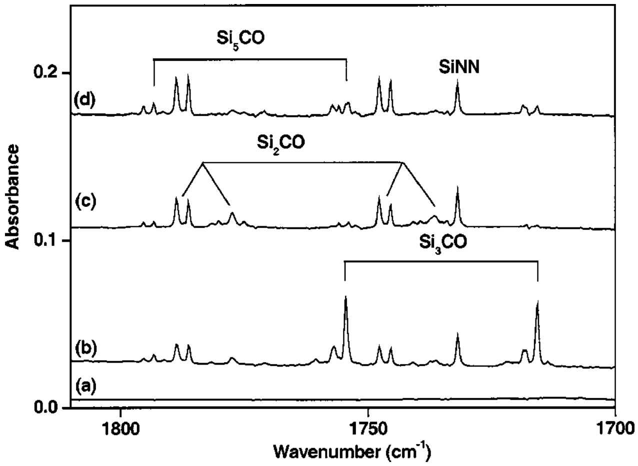

FIG. 4. Infrared spectra in the 1810–1700 cm^{-1} region from codeposition of laser-ablated silicon atoms with 0.02% $^{12}C^{16}O + 0.02\%$ $^{13}C^{16}O$ in Ar. (a) 2 h of sample deposition at 7 K, (b) after annealing to 34 K, (c) after 20 min of broad-band irradiation, and (d) after annealing to 38 K.

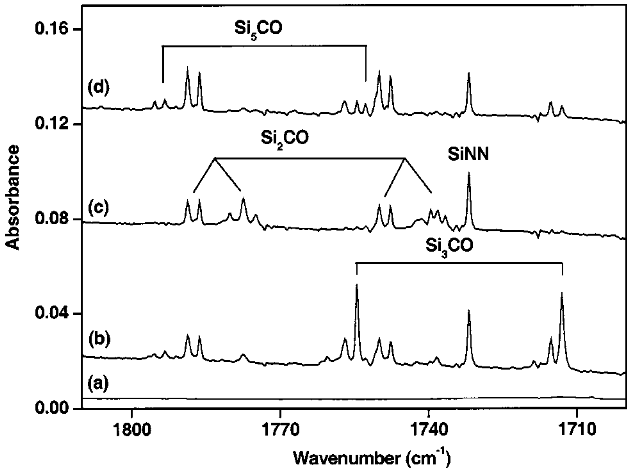

FIG. 6. Infrared spectra in the 1810–1700 cm^{-1} region from codeposition of laser-ablated silicon atoms with 0.02% $^{12}C^{16}O + 0.02\%$ $^{12}C^{18}O$ in Ar. (a) 2 h of sample deposition at 7 K, (b) after annealing to 34 K, (c) after 20 min of broad-band irradiation, and (d) after annealing to 38 K.

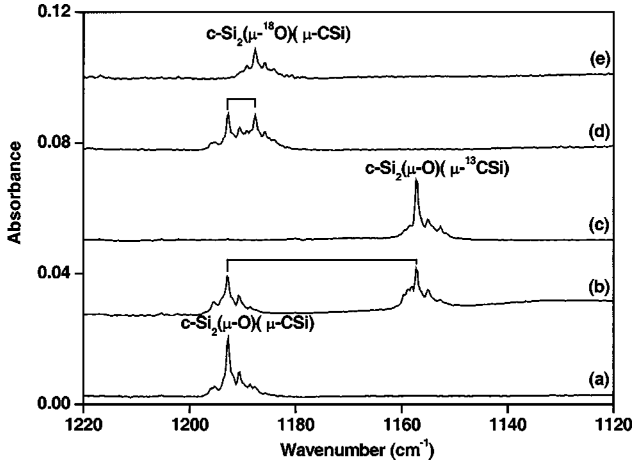

FIG. 7. Infrared spectra in the 1220–1120 cm^{-1} region from codeposition of laser-ablated silicon atoms with isotopic CO samples in excess Ar. Spectra were recorded after sample deposition followed by 34 K annealing and 20 min of broad-band irradiation. (a) 0.025% $^{12}C^{16}O$, (b) 0.02% $^{12}C^{16}O$ + 0.02% $^{13}C^{16}O$, (c) 0.025% $^{13}C^{16}O$, (d) 0.02% $^{12}C^{16}O$ + 0.02% $^{12}C^{18}O$, and (e) 0.025% $^{12}C^{18}O$.

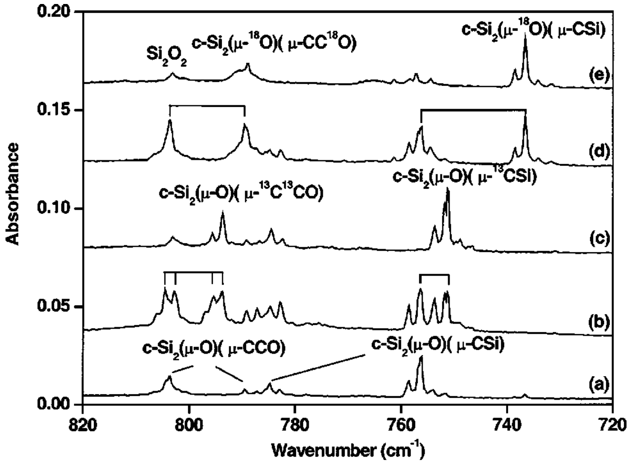

FIG. 8. Infrared spectra in the 820–720 cm^{-1} region from codeposition of laser-ablated silicon atoms with isotopic CO samples in excess Ar. Spectra were recorded after sample deposition followed by 34 K annealing and 20 min of broad-band irradiation. (a) 0.025% $^{12}C^{16}O$, (b) 0.02% $^{12}C^{16}O$ + 0.02% $^{13}C^{16}O$, (c) 0.025% $^{13}C^{16}O$, (d) 0.02% $^{12}C^{16}O$ + 0.02% $^{12}C^{18}O$, and (e) 0.025% $^{12}C^{18}O$.

band intensity was not recovered on further annealing to 38 K, which is quite different from the 1985.2 and 1793.2 cm^{-1} bands. This band is assigned to the C–O stretching mode of bridge-bonded Si_3CO. As will be discussed below, the Si_3CO molecule photochemically rearranged to the c-$Si_2(\mu\text{-}O)(\mu\text{-}CSi)$ isomer under broad-band irradiation. The remaining 1985.2 and 1793.2 cm^{-1} bands are assigned to the C–O stretching modes of the terminal-bonded Si_4CO and bridge-bonded Si_5CO molecules, respectively. These two bands appeared after the Si_2CO and Si_3CO absorptions and increased more on high temperature annealing. Both bands decreased markedly on broad-band irradiation but were recovered after subsequent 38 K annealing.

The assignments are strongly supported by theoretical calculations. Molecular dynamics simulations for carbon monoxide adsorption on small silicon clusters have been recently performed using a full-potential linear-muffin-tin orbital method.[18] The most stable structures of each of the Si_nCO $(n=2-5)$ clusters are in good agreement with our DFT/B3LYP calculations, as shown in Fig. 9. The Si_2 cluster has a triplet ground state, but the interaction of Si_2 with CO results in a singlet ground state Si_2CO molecule having a semibridge- bonded structure with two inequivalent Si–C bonds (1.792 and 2.227 Å). The Si–Si and C–O bond lengths are 2.235 and 1.171 Å, respectively, which are 0.045 Å shorter and 0.043 Å longer than those of Si_2 and CO calculated at the same level. Both Al_2CO and Ga_2CO have been observed in solid argon and characterized to have similar semibridge-bonded structures.[26–28] Previous *ab initio* calculations, and infrared and optical investigations in solid matrices indicated that the most stable structure of Si_3 has a C_{2v} symmetry with a singlet ground state.[25,29–31] From the rotational spectrum,[32] the geometric structure was determined to have a Si–Si bond length of 2.177 Å with an apex angle of 78.10°. Our B3LYP calculation gave a Si–Si bond length of 2.186 Å with an apex angle of 82.3°. A CO molecule interacts with Si_3 to form the Si_3CO carbonyl, which was predicted to have a planar bridge-bonded C_{2v} structure involving a four-membered Si_3C ring. The C–O bond length was predicted to be slightly (0.005 Å) longer than that of Si_2CO. Another stable Si_3CO isomer having a Si_3 ring with CO terminal-bonded to one of the Si atoms was predicted to be 26.2 kcal/mol higher in energy than the planar bridged-bonded structure. The ground state structure of Si_4 is a planar rhombus with D_{2h} symmetry.[33,34] The only stable structure of Si_4CO monocarbonyl with respect to Si_4+CO was predicted to be nonplanar with C_s symmetry (Fig. 9). The Si_4 subunit remains nearly planar, and the CO subunit is almost perpendicular to the Si_4 plane. The CO molecule interacts terminally with one of the apex Si atoms of rhombus Si_4 with the Si–C and C–O bond lengths of 1.872 and 1.144 Å, re-

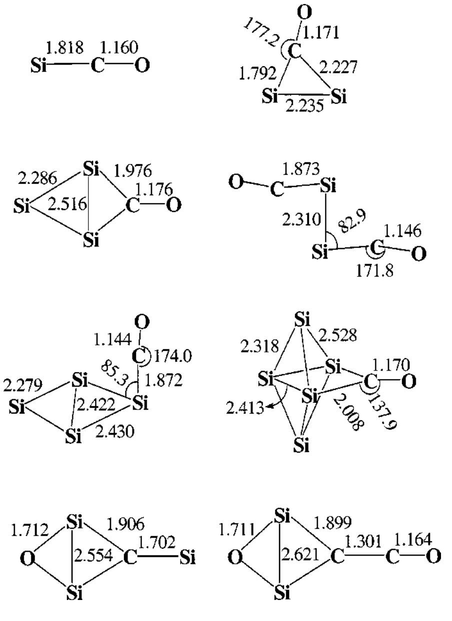

FIG. 9. Optimized structures (bond lengths in angstroms, bond angles in degrees) of the reaction products.

TABLE II. Calculated vibrational frequencies (cm^{-1}) and intensities (km/mol) of the product molecules.

	Frequency (intensity, mode)
SiCO	1953.7 (759, σ), 572.3 (0.2, σ), 322.9 (0.4, π)
Si_2CO	1891.4 (632,a'), 632.2 (5,a'), 487.6 (20,a'), 482.8 (30,a'), 426.9 (2,a''), 132.9 (1,a')
$Si_2(CO)_2$	2064.8 (0,a_g), 2015.2 (2304,b_u), 576.5 (0,a_g), 490.6 (31,b_u), 453.2 (0,a_g), 443.7 (1,a_u), 430.2 (62,), 415.4 (0,b_u), 323.9(0,b_g), 103.1 (0,a_g), 76.1 (2,b_u), 59.7 (0.5,a_u)
Si_3CO	1831.7 (681,a_1), 490.0 (16,a_1), 448.2 (0,b_2), 441.3 (11,a_1), 439.3 (3,b_1), 403.6 (1,b_2), 355.1 (26,a_1), 270.6 (0.3,b_2), 97.9(2,b_1)
Si_4CO	2059.0 (939,a'), 538.7 (22,a'), 506.4 (9,a'), 418.8 (14,a'), 407.8 (10,a'), 403.7 (0.5,a''), 382.5 (1,a''), 312.6 (4,a'), 190.0(2,a''), 144.0 (3,a'), 87.8 (0.3,a''), 71.6 (1,a')
Si_5CO	1866.4 (701,a_1), 505.9 (3,b_1), 451.7 (0,a_1), 446.0 (10,b_1), 430.8 (0,b_2), 427.0 (8,a1), 367.2 (6,a1), 356.4 (1,b2), 337.1 (5,a_1), 272.1 (0,b_2), 268.8 (0,a_2), 243.5 (5,b_1), 208.4 (0,a_1), 102.4(0,b_2), 51.3 (0,b_1)
c-$Si_2(\mu$-O)(μ-CSi)	1187.4 (363,a_1), 773.6 (129,a_1), 746.5 (315,b_2), 478.6 (30,b_2), 474.4 (26,a_1), 390.8 (3,a_1), 234.3 (4,b_1), 146.0 (0,b_2), 78.2 (0,b_1)
c-$Si_2(\mu$-O)(μ-CCO)	2183.9 (1934,a_1), 1388.3 (70,a_1), 812.1 (387,b_2), 769.1 (86,a_1), 691.0 (35,b_2), 640.1 (19,b_1), 493.2 (51,a_1), 446.4 (21,b_2), 414.4 (11,a_1), 188.9 (1,b_1), 121.9 (2,b_2), 120.2 (1,b_1)

spectively. The C–O bond length is significantly shorter than those of Si_2CO and Si_3CO and is very close to that of $Si_2(CO)_2$. The Si_5CO monocarbonyl was predicted to have a nonplanar structure with C_{2v} symmetry. It can be regarded as CO bridge bonded with two of the equatorial silicon atoms of Si_5, which was predicted to have a trigonal bipyramid structure with a D_{3h} symmetry.[35]

No evidence was found for the formation of the $Si_n(CO)_2\,(n\geqslant 3)$ species in the present experiments. The $Si_3(CO)_2$ molecule was predicted to be unbound with respect to Si_3CO+CO. The $Si_4(CO)_2$ molecule was predicted to have a D_{2d} symmetry with both COs bridge-bonded having a strong doubly degenerated C–O stretching vibration at 1866 cm^{-1}.

The C–O stretching vibrational frequencies of the ground state $Si_nCO\,(n=2-5)$ monocarbonyls were predicted at 1891.4, 1831.7, 2059.0, and 1866.4 cm^{-1}, which should be scaled (observed frequency/calculated frequency) by factors of 0.946, 0.958, 0.964, and 0.961 to fit the observed frequencies. Moreover, the calculated isotopic frequency ratios are in quite good agreement with the experimental values, as listed in Table III. The large $^{12}C/^{13}C$ and small $^{16}O/^{18}O$ ratios for the Si_2CO monocarbonyl, which are quite different from those of the other $Si_nCO\,(n=3-5)$ monocarbonyls, are correctly predicted by DFT calculations. The B3LYP/6-311+G* harmonic frequency analysis indicated that, for each Si_nCO, the CO stretching mode has the largest IR intensity, and all of the other modes have intensities less than 3% of the C–O stretching intensity.

In previous Raman and IR studies in solid matrices, the Si_6 and Si_7 clusters were characterized, whereas the Si_5 cluster was not observed presumably because of the low concentration of Si_5 in the vapor.[25,34] Previous calculations indicate that the binding energies of $Si_nCO\,(n=2-7)$ decrease successively and rapidly as the number of silicon atoms increases.[18] Our B3LYP/6-311+G* calculations predicted that the $Si_nCO\,(n=2-5)$ species are bound by 34.4, 32.7, 7.8, and 18.4 kcal/mol, respectively, with respect to Si_n+CO, but Si_6CO and Si_7CO are unbound with respect to Si_6+CO and Si_7+CO. As will be discussed, the silicon clusters were formed in solid argon on annealing, and the formation of large silicon clusters is in competition with the reactions to form carbonyls; therefore, the concentrations of the larger clusters Si_6 and Si_7 are expected to be low. The Si_6 and Si_7 absorptions were barely observed in the present experiments.

The structures of the present characterized Si_nCO are quite different from that of the carbon oxides $C_{n+1}O\,(n=2-5)$.[36–39] The larger atomic radius of silicon compared to that of carbon, for example, generally restricts silicon to single bonding, resulting in cyclic or three-dimensional structures. In contrast, carbon can readily form multiple bonds, and consequently, carbon oxides possess linear structures. The C–O stretching frequency of Si_4CO observed here in solid argon, 1985.2 cm^{-1}, is about 100 cm^{-1} lower than the 2081 cm^{-1} frequency for CO normally adsorbed on a Si(100) surface.[14] The C–O stretching frequencies of bridge-bonded Si_nCO ($n=2$, 3, and 5) clusters observed here are about 50–100 cm^{-1} higher than the 1701 cm^{-1} frequency for CO bridge-coordinated on a Si(100) surface.[16]

4. *c*-$Si_2(\mu$-O)(μ-CSi)

The bands at 1192.8, 784.8, and 756.1 cm^{-1} appeared together on broad-band irradiation. Each band was blueshifted by several wave numbers on subsequent annealing to 38 K. The 1192.8 cm^{-1} band showed a very small shift with

TABLE III. Comparison of the observed and calculated isotopic frequency ratios of the reaction products.

Molecule	Mode	$^{12}C/^{13}C$		$^{16}O/^{18}O$	
		Obs.	Calc.	Obs.	Calc.
SiCO	C—O stretching	1.0233	1.0236	1.0229	1.0234
Si_2CO	C—O stretching	1.0235	1.0238	1.0221	1.0230
$Si_2(CO)_2$	C—O stretching	1.0223	1.0228	1.0245	1.0247
Si_3CO	C—O stretching	1.0226	1.0226	1.0242	1.0249
Si_4CO	C—O stretching	1.0228	1.0232	1.0237	1.0241
Si_5CO	C—O stretching	1.0224	1.0226	1.0243	1.0249
c-$Si_2(\mu$-O$)(\mu$-CSi$)$	Si═C stretching	1.0308	1.0332	1.0043	1.0003
	Si—O—Si stretching (a_1)	1.0004	1.0000	1.0365	1.0378
	Ring puckering (b_2)	1.0065	1.0076	1.0265	1.0265
c-$Si_2(\mu$-O$)(\mu$-CCO$)$	C—O stretching	1.0307	1.0313	1.0116	1.0122
	C—C stretching	1.0245	1.0285	1.0198	1.0171
	Ring puckering (b_2)	1.0126	1.0198	1.0186	1.0131
	Si—O—Si stretching (a_1)	1.0008	1.0001	1.0378	1.0392

$^{12}C^{18}O$ (5.1 cm^{-1}) but shifted to 1157.2 cm^{-1} with $^{13}C^{16}O$. The $^{12}C/^{13}C$ isotopic frequency ratio of 1.0308 implies that this band is mainly due to a Si–C stretching vibration. In the mixed $^{12}C^{16}O+^{13}C^{16}O$ and $^{12}C^{16}O+^{12}C^{18}O$ experiments (Fig. 7, traces *b* and *d*), only the pure isotopic counterparts were observed, indicating that only one C atom and one O atom are involved in this mode. The 784.8 and 756.1 cm^{-1} bands showed very small shifts (0.3 and 4.9 cm^{-1}) with $^{13}C^{16}O$ but large shifts with $^{12}C^{18}O$ (27.6 and 19.5 cm^{-1}). The mixed $^{12}C^{16}O+^{13}C^{16}O$ and $^{12}C^{16}O+^{12}C^{18}O$ spectra (Fig. 8, traces *b* and *d*) clearly showed that only one O atom and one C atom are involved in the molecule. The band positions and isotopic frequency shifts suggest the involvement of a cyclic four-membered c-$Si_2(\mu$-O$)(\mu$-C$)$ structure. Accordingly, we assign the 1192.8, 784.8, and 756.1 cm^{-1} bands to the c-$Si_2(\mu$-O$)(\mu$-CSi$)$ molecule. As a reference point, the rhombus Si_2O_2 molecule was observed at 802.9 and 781.8 cm^{-1} in solid argon.[40] B3LYP calculation predicted the c-$Si_2(\mu$-O$)(\mu$-CSi$)$ molecule to have a planar structure with C_{2v} symmetry (Fig. 9). The terminal C–Si bond length was computed to be 1.702 Å and appears to be a double bond. Experimentally, the Si–C bonds of H_2CSiH_2 and $H_2CSi(CH_3)_2$ were determined to be 1.704 and 1.692 Å, respectively.[41,42] The three experimentally observed modes of c-$Si_2(\mu$-O$)(\mu$-CSi$)$ were calculated at 1187.4, 773.6, and 746.5 cm^{-1} with 363:129:315 km/mol relative intensities. The calculated isotopic frequency ratios are also in reasonable agreement with the experimental values (Table III) and provide strong support for the experimental assignment for the c-$Si_2(\mu$-O$)(\mu$-CSi$)$ molecule.

5. c-$Si_2(\mu$-O$)(\mu$-CCO$)$

The bands at 2111.5, 1391.9, 803.7, and 783.0 cm^{-1} appeared together on broad-band irradiation and are assigned to different vibrational modes of the c-$Si_2(\mu$-O$)(\mu$-CCO$)$ molecule. All of these bands were blueshifted by several wave numbers on annealing analogous to the c-$Si_2(\mu$-O$)(\mu$-CSi$)$ absorptions. The 2111.5 cm^{-1} band lies in the region expected for a C–O stretching vibration. This band shifted to 2048.6 cm^{-1} with $^{13}C^{16}O$ and to 2087.2 cm^{-1} with $^{12}C^{18}O$, giving a $^{12}C/^{13}C$ isotopic frequency ratio of 1.0307 and an $^{16}O/^{18}O$ ratio of 1.0116. These ratios are significantly larger and smaller, respectively, than diatomic CO ratios, suggesting strong coupling with another C atom. In the mixed $^{12}C^{16}O+^{13}C^{16}O$ experiment (Fig. 3), a quartet at 2111.5, 2106.3, 2055.8, and 2048.6 cm^{-1} with ≈1:1:1:1 relative intensities was observed, while in the mixed $^{12}C^{16}O+^{12}C^{18}O$ experiment (Fig. 5), a doublet at 2111.3 and 2087.0 cm^{-1} was produced. The isotopic shifts and splittings imply the involvement of a CCO subunit in the molecule. The 1391.9 cm^{-1} is much weaker than the 2111.5 cm^{-1} band and is due to the C–CO stretching mode. The 803.7 and 783.0 cm^{-1} bands exhibited very similar isotopic shifts as the 756.1 and 784.8 cm^{-1} bands of c-$Si_2(\mu$-O$)(\mu-$CSi$)$ (Table I), which is suggestive of the involvement of a cyclic four-membered c-$Si_2(\mu$-O$)(\mu$-C$)$ unit in the molecule.

The c-$Si_2(\mu$-O$)(\mu$-CCO$)$ molecule was predicted to have a singlet ground state with a planar C_{2v} symmetry (Fig. 9). The C–O stretching (a_1), C–CO stretching (a_1), ring puckering (b_2), and Si–O–Si stretching (a_1) modes were computed at 2183.9, 1388.3, 812.1, and 769.1 cm^{-1} with 1934:70:387:86 km/mol relative intensities, which are in excellent agreement with the observed frequencies. The calculated isotopic frequency ratios for the low modes are not in very good agreement with the experimental values. The normal modes of the ring system are not well modeled by the harmonic calculations, and anharmonicity in the vibrations may contribute to this.

C. Reaction mechanism

Under the present experimental conditions, silicon atoms are the predominant species produced by laser ablation of the silicon target. The absorptions of small silicon clusters Si_2, Si_3, and Si_4 appeared only on sample annealing in experiments with low CO concentrations, which indicate that these small silicon clusters were formed in solid argon upon annealing but not during the laser ablation process.

Table IV lists the energetics for possible reactions in the present experiments calculated at the B3LYP/6-311+G* level. As can be seen in Table IV, the processes [reactions (1)–(6)] of successive formation of silicon clusters from Si_2 to Si_5 all are exothermic, indicating that the formation of

TABLE IV. Energetics (in kcal/mol) for possible reactions of silicon atoms and small clusters with CO calculated at the B3LYP/6-311+G* level.

	Reaction	Reaction energy[a]
1	$\mathrm{Si}(^3P)+\mathrm{Si}(^3P) \rightarrow \mathrm{Si}_2(^3\Sigma_g^-)$	−70.0
2	$\mathrm{Si}_2(^3\Sigma_g^-)+\mathrm{Si}(^3P) \rightarrow \mathrm{Si}_3(^1A_1)$	−82.9
3	$\mathrm{Si}_2(^3\Sigma_g^-)+\mathrm{Si}_2(^3\Sigma_g^-) \rightarrow \mathrm{Si}_4(^1A_g)$	−107.9
4	$\mathrm{Si}_3(^1A_1)+\mathrm{Si}(^3P) \rightarrow \mathrm{Si}_4(^1A_g)$	−95.1
5	$\mathrm{Si}_2(^3\Sigma_g^-)+\mathrm{Si}_3(^1A_1) \rightarrow \mathrm{Si}_5(^1A_1')$	−100.1
6	$\mathrm{Si}(^3P)+\mathrm{Si}_4(^1A_g)+ \rightarrow \mathrm{Si}_5(^1A_1')$	−75.0
7	$\mathrm{Si}(^3P)+\mathrm{CO}(^1\Sigma_g^+) \rightarrow \mathrm{SiCO}(^3\Sigma^-)$	−35.2
8	$\mathrm{Si}_2(^3\Sigma_g^-)+\mathrm{CO}(^1\Sigma_g^+) \rightarrow \mathrm{Si}_2\mathrm{CO}(^1A')$	−34.4
9	$\mathrm{Si}_3(^1A_1)+\mathrm{CO}(^1\Sigma_g^+) \rightarrow \mathrm{Si}_3\mathrm{CO}(^1A_1)$	−32.7
10	$\mathrm{Si}_4(^1A_g)+\mathrm{CO}(^1\Sigma_g^+) \rightarrow \mathrm{Si}_4\mathrm{CO}(^1A')$	−7.8
11	$\mathrm{Si}_5(^1A_1')+\mathrm{CO}(^1\Sigma_g^+) \rightarrow \mathrm{Si}_5\mathrm{CO}(^1A_1)$	−18.4
12	$\mathrm{SiCO}(^3\Sigma^-)+\mathrm{CO}(^1\Sigma_g^+) \rightarrow \mathrm{Si(CO)}_2(^1A_1)$	−21.2
13	$\mathrm{SiCO}(^3\Sigma^-)+\mathrm{SiCO}(^3\Sigma^-) \rightarrow \mathrm{Si}_2\mathrm{(CO)}_2(^1A_g)$	−48.8
14	$\mathrm{Si}_2\mathrm{CO}(^1A')+\mathrm{CO}(^1\Sigma_g^+) \rightarrow \mathrm{Si}_2\mathrm{(CO)}_2(^1A_g)$	−14.7
15	$\mathrm{Si}_3\mathrm{CO}(^1A_1) \rightarrow c\text{-}\mathrm{Si}_2(\mu\text{-}\mathrm{O})(\mu\text{-}\mathrm{CSi})(^1A_1)$	−24.5
16	$\mathrm{Si}_2\mathrm{(CO)}_2(^1A_g) \rightarrow c\text{-}\mathrm{Si}_2(\mu\text{-}\mathrm{O})(\mu\text{-}\mathrm{CCO})(^1A_1)$	−52.0

[a] A negative value of energy denotes that the reaction is exothermic.

these small silicon clusters from silicon atoms is attainable. The silicon monocarbonyl SiCO and small silicon cluster carbonyls $\mathrm{Si}_n\mathrm{CO}\,(n=2-5)$ were produced on annealing. These carbonyl species were formed by the reactions of silicon atoms and small clusters with CO in solid argon [reactions (7)–(11) in Table IV].

The $\mathrm{Si}_2(\mathrm{CO})_2$ absorption increased on annealing, and the yield relative to SiCO increased with higher laser energy. This implies that $\mathrm{Si}_2(\mathrm{CO})_2$ was mainly formed by the reaction of $\mathrm{Si}_2\mathrm{CO}$ with CO, reaction (14), which was predicted to be exothermic by about 14.7 kcal/mol. However, the formation of $\mathrm{Si}_2(\mathrm{CO})_2$ via SiCO dimerization [reaction (13)] cannot be excluded. In our recent investigation of boron and CO reaction, the linear OCBBCO molecule was formed by BCO dimerization but not via the BBCO+CO reaction.[43] It is interesting to note that $\mathrm{Si(CO)}_2$ was not observed in the experiments. The SiCO molecule has been well studied to have a $^3\Sigma$ ground state, while the $\mathrm{Si(CO)}_2$ molecule was predicted to have a singlet ground state with a bent structure. Although the SiCO+CO reaction [reaction (12)] is exothermic, it involves spin change and probably requires some activation energy. In the similar $\mathrm{Si}+\mathrm{N}_2$ reaction system, the $\mathrm{Si(NN)}_2$ molecule was also not observed.[1] Both the $\mathrm{Si}_2\mathrm{CO}$ and $\mathrm{Si}_2(\mathrm{CO})_2$ molecules have singlet ground states, and the formation of $\mathrm{Si}_2(\mathrm{CO})_2$ from $\mathrm{Si}_2\mathrm{CO}$ preserves spin.

The absorptions due to the $c\text{-}\mathrm{Si}_2(\mu\text{-}\mathrm{O})(\mu\text{-}\mathrm{CSi})$ and $c\text{-}\mathrm{Si}_2(\mu\text{-}\mathrm{O})(\mu\text{-}\mathrm{CCO})$ molecules appeared on broad-band irradiation, during which the $\mathrm{Si}_3\mathrm{CO}$ and $\mathrm{Si}_2(\mathrm{CO})_2$ absorptions were destroyed. It appears that broad-band irradiation initiates the isomerization reactions (15) and (16). DFT calculations indicated that the $c\text{-}\mathrm{Si}_2(\mu\text{-}\mathrm{O})(\mu\text{-}\mathrm{CSi})$ and $c\text{-}\mathrm{Si}_2(\mu\text{-}\mathrm{O})(\mu\text{-}\mathrm{CCO})$ molecules are more stable than the $\mathrm{Si}_3\mathrm{CO}$ and $\mathrm{Si}_2(\mathrm{CO})_2$ carbonyl isomers by about 24.5 and 52.0 kcal/mol, respectively.

One of the most remarkable aspects of the present experiments is the production of the $c\text{-}\mathrm{Si}_2(\mu\text{-}\mathrm{O})(\mu\text{-}\mathrm{CSi})$ and $c\text{-}\mathrm{Si}_2(\mu\text{-}\mathrm{O})(\mu\text{-}\mathrm{CCO})$ molecules where CO is activated by the reactions of silicon atoms and carbon monoxide. Carbon monoxide is regarded as a good ligand both as a σ donor and a π acceptor, and generally, the reactions of carbon monoxide with transition metal atoms as well as main group metal atoms form carbonyl complexes. A variety of transition metal carbonyl and main group carbonyl complexes have been synthesized in this way.[44] Recent infrared spectroscopic investigations of the reactions of laser-ablated early transition metal and actinide metal atoms with CO have also demonstrated CO activation via transition metal and actinide metal carbonyl complexes.[45–48] The monocarbonyls of Nb, Th, and U can be isomerized to the inserted carbide-oxide molecules on visible light irradiation. The dicarbonyls of the Ti group, the V group, and the actinide metals Th and U undergo photoinduced isomerization to the OMCCO (M=Ti, Zr, Hf, V, Nb, Ta, U, and Th) molecules with visible or UV photons. The OMCCO molecules can undergo further photochemical rearrangement to the $\mathrm{OTh}(\eta^3\text{-}\mathrm{CCO})$ or $(\eta^2\text{-}\mathrm{C}_2)M\mathrm{O}_2$ (M=Nb, Ta, and U) molecules with UV photons. In the present silicon case, the CSiO molecule was predicted to lie significantly higher in energy than the SiCO isomer,[5] and this rearranged molecule was not observed here.

IV. CONCLUSIONS

Reactions of silicon atoms and small clusters with carbon monoxide molecules in solid argon have been studied using matrix isolation infrared absorption spectroscopy. In addition to the previously reported SiCO monocarbonyl, absorptions at 1928.7 cm^{-1} are assigned to the antisymmetric C–O stretching vibration of $\mathrm{Si}_2(\mathrm{CO})_2$ with C_{2h} symmetry. Small silicon cluster monocarbonyls, $\mathrm{Si}_n\mathrm{CO}\,(n=2-5)$, were also produced on annealing at low CO concentrations. On the basis of isotopic substitution and theoretical calculations, absorptions at 1788.7, 1754.5, and 1793.2 cm^{-1} are assigned to the bridge-bonded $\mathrm{Si}_2\mathrm{CO}$, $\mathrm{Si}_3\mathrm{CO}$, and $\mathrm{Si}_5\mathrm{CO}$ carbonyls, while absorption at 1985.2 cm^{-1} is assigned to the terminal-bonded $\mathrm{Si}_4\mathrm{CO}$ molecule. The $\mathrm{Si}_2(\mathrm{CO})_2$ and $\mathrm{Si}_3\mathrm{CO}$ molecules underwent photochemical rearrangement to the more stable $c\text{-}\mathrm{Si}_2(\mu\text{-}\mathrm{O})(\mu\text{-}\mathrm{CCO})$ and $c\text{-}\mathrm{Si}_2(\mu\text{-}\mathrm{O})(\mu\text{-}\mathrm{CSi})$ isomers, which provides an unprecedented mechanism for CO activation. The theoretical analysis found that both $c\text{-Si}_2(\mu\text{-O})(\mu\text{-CCO})$ and $c\text{-Si}_2(\mu\text{-O})(\mu\text{-CSi})$ have four-membered ring structures and lie lower in energy than the respective $\text{Si}_2(\text{CO})_2$ and Si_3CO isomers.

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