Infrared Spectra of the Reaction Products of Laser-Ablated Titanium Atoms and Oxides with Carbon Monoxide in Solid Argon

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Abstract: Pulsed laser ablated Ti atoms react readily with CO on condensation with excess argon. Infrared spectra with ^{13}CO and $C^{18}O$ substitution are presented for the $Ti(CO)_y$ species ($y = 1-4$). The carbonyl frequency in TiCO at 1854.4 cm^{-1} denotes a strong interaction. Titanium oxides are also reactive with CO; the molecule OTiCO, with the carbonyl frequency at 1866.7 cm^{-1}, has been prepared by the TiO + CO and Ti + CO_2 reactions. Evidence is also presented for $O_2Ti(CO)_y$ molecules, which exhibit higher carbonyl frequencies than the analogous $Ti(CO)_y$ species.

Introduction

Reactions of titanium atoms with small molecules such as CO, CO_2, O_2, H_2, N_2 are of great interest as models for catalytic, chemisorption, and oxidation processes. However, information about these simple reactions and the molecular products is sparse. On the macroscopic scale, the metal surface–CO interaction and metal coordination compounds are important as many studies attest.[1,2] This work is devoted to the investigation of Ti atom reactions with carbon monoxide and dioxide. Investigations of the Ti + O_2, N_2, and H_2 systems also have been done and will be reported separately.

In spite of the importance of titanium carbonyl complexes only two experimental studies have been devoted to the Ti + CO system. A $Ti(CO)_y$ complex binding energy was determined by chemiluminescence spectroscopy (1.75 eV),[3] and infrared spectra assigned to the $Ti(CO)_6$ molecule were obtained with 10% CO in solid Ar, Kr, and Xe.[4] Note that titanium hexacarbonyl was the only reaction product observed. Several electronic structure calculations have dealt with the TiCO and $Ti(CO)_2$ molecules.[5-9] For the TiCO molecule, a $^5\Delta$ ground state with somewhat lower (0.62 and 0.70 eV) binding energy was calculated using the CASSCF/MRCI and density function methods, respectively.[7,9] For the $Ti(CO)_2$ molecule, a higher total binding energy (1.02 eV) was calculated.

Most first-row M–CO molecules have been observed experimentally with the notable exception of TiCO, and the C–O stretching frequencies for a series of MCO molecules (excluding Ti) have been compared.[10] Codeposition of transition metals with CO produces mono- and dicarbonyls, as well as higher carbonyls, and a step-by-step mechanism for these reactions is expected.[10-12] The lack of experimental data on the lower Ti carbonyls, in contrast to later transition metal carbonyls, prompted a re-examination of the Ti + CO system using laser-ablated Ti atoms.

It has been shown recently from studies in this laboratory that laser ablation is an effective method for producing metal atoms for chemical reactions during condensation in excess argon.[13-15] Due to high reagent kinetic energy the initial product distribution is different from that produced by ordinary thermal evaporation reactions. The new molecules TiCO, $Ti(CO)_2$, $Ti_2(CO)_2$, OTiCO, and O_2TiCO obtained here are of chemical interest for their roles in catalytic and chemisorption processes.

Experimental Section

The apparatus for laser ablation and matrix isolation has been described previously.[13-15] The titanium target (Goodfellow Metals 99.6+%) was filed clean and mounted on a rotating rod (1 rpm). The Nd:YAG laser fundamental (1064 nm, 6 Hz repetition rate, 10 ns pulse width) was focused on the target (10 cm f.l.) through the hole in the CsI cryogenic window. Laser power was varied from 50 to 150 mJ/pulse at the sample. Even though the target area was evacuated to better than 10^{-5} Torr, the Ti target surface exhibited TiO_2 after ablation. A pellet pressed (10 tons) from TiO_2 powder (Aldrich) and a TiO pellet (Strem Chemicals) were similarly ablated.

Titanium, TiO, and TiO_2 ablation products[16] were codeposited with carbon monoxide (Air Products, ultra high purity) and isotopic modifications (Cambridge Isotope, 99% ^{13}CO, 98% $C^{18}O$), diluted in argon at 2–4 mmol/h for 1–2 h periods. Concentrations of mixtures

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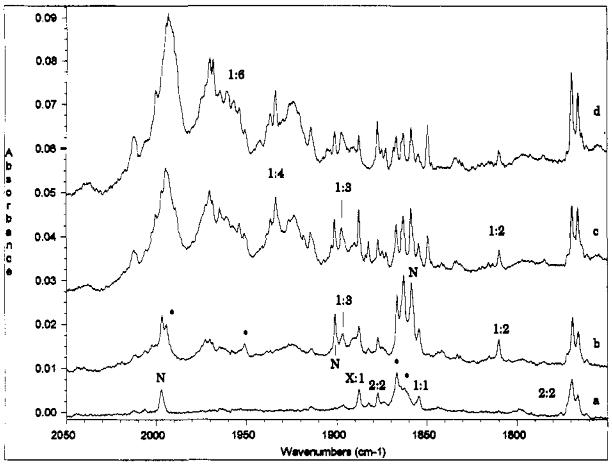

Figure 1. Infrared spectra in the 2050−1750 cm^{-1} region for pulsed laser ablated Ti atoms codeposited with CO in argon at 12 K: (a) Ti + CO/Ar = 1/300 codeposited for 2 h, (b) after annealing to 25 K, (c) after annealing to 30 K, and (d) after annealing to 35 K.

were varied from 1/600 to 1/50 for CO/Ar. Similar experiments were done with carbon dioxide (Matheson and Cambridge Isotope). FTIR spectra were recorded at 0.5 cm^{-1} resolution on Nicolet 750 and 60SXR and with 2 cm^{-1} resolution on Nicolet 5DXB instruments. Reported frequencies are accurate to ±0.2 cm^{-1}.

Results

Infrared spectra of the Ti + CO, TiO_2 + CO, TiO + CO, and Ti + CO_2 systems will be reported.

Ti + CO. Infrared spectra of the atomic titanium and CO system in argon are presented in Figures 1−3 and Table 1. After codeposition of Ti atoms with dilute CO/Ar mixtures (1/600 to 1/300) new bands were observed at 1997.0 (labeled N), 1887.7 (labeled X:1), 1877.2 (labeled 2:2), 1866.7 (labeled *), 1862.8 (labeled *), 1854.4 (labeled 1:1), and 1769.1 cm^{-1} (labeled 2:2) as shown in Figure 1a for the 1/300 sample. Although the 1862.8 cm^{-1} band may contain some HCO absorption,[17] another product absorbs in this region.[18] Annealing to 20 K (Figure 1b) increased all bands and produced new 1810.0 (labeled 1:2), 1858.7 (labeled N), 1897.5 (labeled 1:3), 1901.1 (labeled N), 1951 (labeled *), and 1995 cm^{-1} (labeled *) bands. Further annealing to 30 K (Figure 1c) continued these trends, but decreased the 1:2 band and produced new 1933.8 (labeled 1:4) and 1849.5 cm^{-1} bands. Final annealing to 35 K (Figure 1d) further decreased the 1:1 and 1:2 bands and revealed a broad feature near 1956 cm^{-1} (labeled 1:6) and the strong band at 1995 cm^{-1}. The lower frequency region contained TiO_2 at 946.9 and 917.1 cm^{-1}, TiO at 988.8 cm^{-1},[16] and a new 952.8 cm^{-1} band. Annealing produced a prominent 847 cm^{-1} band at the expense of all other absorptions in this region.

In contrast the relative intensities are different for the more concentrated 1/200 mixture shown in Figure 2. After deposition, the 1854.4 cm^{-1} band (1:1) and weaker 1:2 and 1:3 bands were detected in the 2000−1900 cm^{-1} region. The 1000−800 cm^{-1} region revealed TiO, TiO_2, and the 952.8 cm^{-1} band (labeled *). Again annealing increased the absorptions by varying degrees including the 1:2, 1:3, and 1:4 bands, and most particularly the 1956 (labeled 1:6) and 1995 cm^{-1} (labeled *) bands.

With 2% CO, Figure 3, the 1:1 and 1:2 bands were barely detected, the 2:2 bands were stronger, and the 1897.5, 1933.8, 1964.7, and 1995 cm^{-1} bands were observed on deposition.

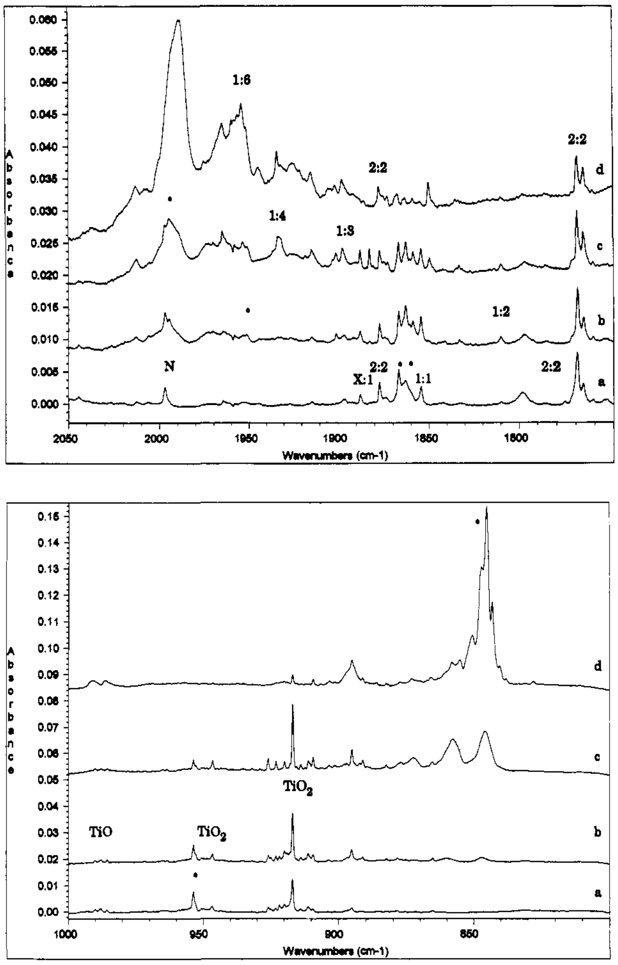

Figure 2. Infrared spectra in the 2050−1750 and 1000−800 cm^{-1} regions for pulsed laser ablated Ti atoms codeposited with CO in argon at 12 K: (a) Ti + CO/Ar = 1/200 codeposited for 2 h, (b) after annealing to 20 K, (c) after annealing to 25 K, and (d) after annealing to 30 K.

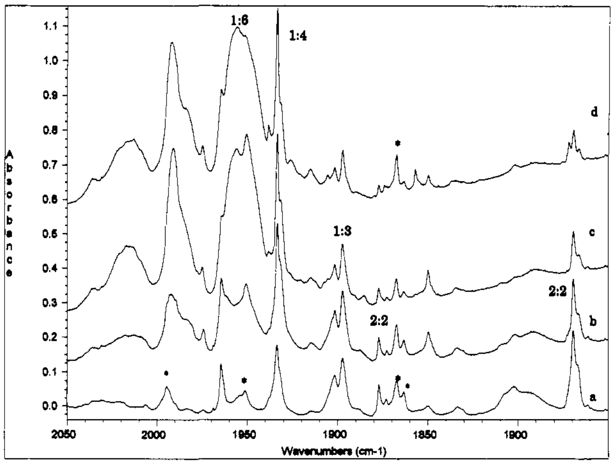

Figure 3. Infrared spectra in the 2050−1750 cm^{-1} region for pulsed laser ablated Ti atoms codeposited with CO in argon at 12 K: (a) Ti + CO/Ar = 1/50 codeposited for 1 h, (b) after annealing to 25 K, (c) after annealing to 35 K, and (d) after broadband full arc photolysis for 20 min.

Annealing (25 K) now decreased the 2:2 bands, again increased the 1849.5 and 1897.5 cm^{-1} bands, doubled the sharp 1933.8 cm^{-1} absorption, increased the 1951 and 1995 cm^{-1} bands, and produced a broad 2017 cm^{-1} band. Further annealing to 35 K continued these trends, decreased the 1951 and 1964.7 cm^{-1} bands, shifted the 1995 cm^{-1} band to 1992 cm^{-1}, and produced

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[18] Chertihin, G. V.; Andrews, L. *J. Phys. Chem.* **1994**, *98*, 5891. The 1810.6 cm^{-1} band is reassigned to $Ti(N_2)_2$.

Table 1. Absorptions (cm^{-1}) Observed in the Reaction of Titanium Atoms with CO on Condensation with Excess Argon

^{12}CO[a]	^{12}CO/^{13}CO	^{13}CO	A/P[d]	C^{18}O	Ident
2017 broad		1974 broad	+/	1970 broad	$Ti_x(CO)_y$
$\underline{1997.0}$	none	1952.8	0/0	1950.2	$O_2Ti(N_2)(CO)$
1995	1968	1951	++/0	1947	$O_2Ti(CO)_4$
1974.5	cannot obs	1931.5	++/	1926.6	$Ti_x(CO)_y$
1964.7	1951.6, 1936.9	1920.0	−	1920.0	X−$Ti(CO)_3$
1956 broad	1931 broad	1913 broad	++/	1909 broad	$Ti(CO)_6$
1951[b]	1929	1909	+/−	1904	$O_2Ti(CO)_2$
1933.8	1922, 1915, 1906	1891.7	++/+	1887.3	$Ti(CO)_4$
1914		1873			$Ti_x(CO)_y$
1897.5	1883	1856.4	+	1851.9	$Ti(CO)_3$
$\underline{1887.7}$	none	1845.2	+/+	1844.4	(O_2TiCO)
$\underline{1877.2}$, 1875.3	1860.1	1834.5	+/−	1835.6	$Ti_2(CO)_2$
1867.2		1826.2	+/+	1823.4	X−$Ti(CO)_3$
$\underline{1866.7}$[b,c]	none	1823.7	−/−	1826.1	OTiCO
1862.8	1839.4	1822.1	+/−	1818.9	$OTi(CO)_2$
1857.1	1842, 1832	1816.8	0/++	1812.2	Ti(CO)Ti(CO)
$\underline{1854.4}$	none	1813.5	+/0	1814.5	TiCO
1849.5	none	1809.4	++/− −	1804.8	X−TiCO
1833	?	1795		1793	$Ti_x(CO)_y$
1810.0	1788.6	1771.6	+/−	1766.0	$Ti(CO)_2$
$\underline{1769.1}$, 1766.1	1745.3	1729.3	+/−	1729.1	$Ti_2(CO)_2$
988.8[b,c]		988.8	−	(946.2)[c]	TiO
952.8[b,c]		952.8	−/−	(911.9)[c]	OTiCO
917.1[b]		917.1	−	(881.8)[c]	TiO_2
895.3[b]		895.3		860.4	(TiO_2)X
882.6[b]		882.6		848.2	(TiO_2)X
866[b]		866.2	+/	(833)	$O_2Ti(CO)_y$
847[b]		847	++/0	(813)	$O_2Ti(CO)_4$

[a] Underlined bands are present in the 1/600 Ti + CO experiment on deposition; second band listed is matrix site splitting. [b] Bands favored in TiO_2+CO experiments labeled with an asterisk in Figures 1−4. [c] Major products in Ti + CO_2 experiments. [d] Annealing and photolysis behavior indicated: 0 = no change, + = increase, − = decrease.

a dominant broad band at 1956 cm^{-1}. A final 20 min broadband photolysis decreased the 2:2 bands, produced a new 1857.1 cm^{-1} band, increased bands at 1867.2 and 1933.8 cm^{-1}, and decreased the 1849.5 and 1862.8 cm^{-1} bands. Photolysis and annealing behavior are summarized in Table 1. An experiment with 5% CO gave spectra similar to those in Figure 3, but the 2:2 bands were relatively weaker. With 10% CO, the major initial bands were observed at 1992, 1963, 1953, 1933, and 1897 cm^{-1} with weaker broad bands at 1867, 1852, 1802, and 1766 cm^{-1}. Annealing to 20 and 30 K left dominant sharper 1992 and broader 1953 cm^{-1} bands, a broad 2015 cm^{-1} band, and some remaining 1933 cm^{-1} absorption.

Another experiment was done on the next day identical to the 1/200 study shown in Figure 2 except that the laser power was tripled in order to increase the Ti concentration relative to the CO concentration. The yield of all product bands increased with the 3-fold laser power increase but in different proportions. Bands noted 1:y increased a factor of 4−5, bands due to titanium oxide complexes increased a factor of 5−6, and bands identified as 2:y increased a factor of 7−9. In the lower region TiO_2 was enhanced relative to TiO.

Isotopic substitution was employed for characterization of these absorptions using 2%, 1%, and 0.5% samples; the ^{13}CO and C^{18}O isotopic frequencies are listed in Table 1. Weak new bands were observed at 1826.6 and 1823.4 cm^{-1} with ^{13}CO and C^{18}O, respectively, on annealing, which indicated another absorption near 1867 cm^{-1} with the ^{12}C^{16}O reagent at higher concentrations. Both 1:1 mixtures of ^{12}CO:^{13}CO and C^{16}O:C^{18}O and mixtures richer in one component were used. Due to overlapping of bands it is difficult to determine isotopic counterparts for every band. Concentration and annealing behavior of the absorptions allowed the following conclusions: the bands at 1769.1, 1810.0, 1862.8, and 1877.2 cm^{-1} produced triplets, while the 1887.7, 1866.7, and 1854.4 cm^{-1} absorptions gave doublets; these multiplets are illustrated in Figure 4. The 1897.5 cm^{-1} band produced a doublet with at least one weak intermediate component and the 1933.8 cm^{-1} band gave an apparent doublet with three weak intermediate components; in contrast the 1964.7 cm^{-1} band produced a quartet with stronger intermediate components. The 1951 cm^{-1} band gave a triplet in oxide experiments.

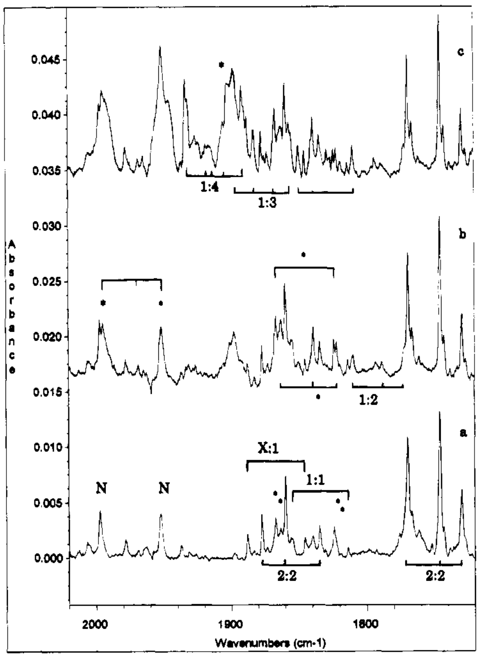

Figure 4. Infrared spectra in the 1920−1720 cm^{-1} region for Ti atoms codeposited with ^{12}CO and ^{13}CO in argon at 12 K: (a) Ti + ^{12}CO/^{13}CO/Ar = 1/1/200 codeposited for 2 h, (b) after annealing to 20 K, and (c) after annealing to 25 K.

Ti + CO + N$_2$. An experiment was done analogous to that in Figure 1, but with N_2 added at the same concentration as the CO. A band at 1997.0 cm^{-1} in the deposited sample and bands growing on annealing at 1901.0, 1858.5, 1815.6, and 1810.0

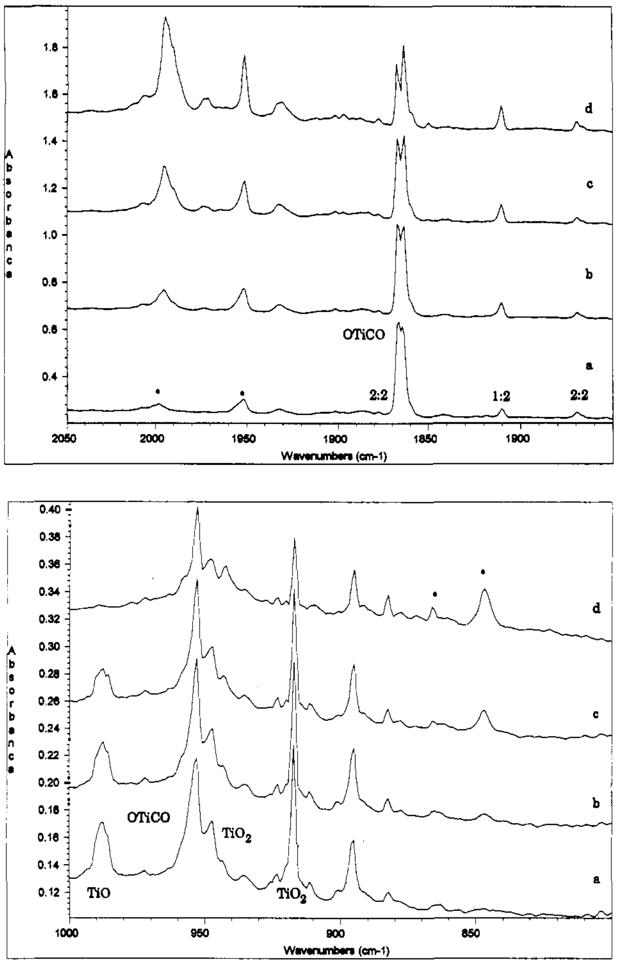

Figure 5. Infrared spectra in the 2050–1750 and 1000–800 cm^{-1} regions for pulsed-laser ablated TiO_2 pellet codeposited with CO in argon: (a) TiO_2 ablation products codeposited with CO/Ar = 1/100 for 1 h, (b) after annealing to 20 K, (c) after annealing to 25 K, and (d) after annealing to 35 K.

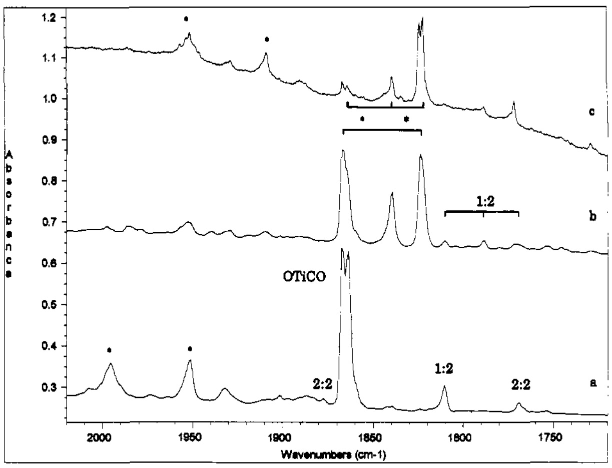

Figure 6. Infrared spectra in the 2020–1720 cm^{-1} region for pulsed-laser ablated TiO_2 pellet codeposited with isotopic CO in argon: (a) $^{12}CO/Ar$ = 1/100, (b) $^{12}CO/^{13}CO/Ar$ = 1/1/400, and (c) $^{13}CO/Ar$ = 1/200.

cm^{-1} were enhanced by the addition of nitrogen. The latter bands were observed in the Ti/N_2 study.[18]

TiO_2 + CO. The behavior of the 1866.7 cm^{-1} band in the above Ti + CO system was unusual. This band appeared with the lowest concentration of CO and is intensity depended very strongly on laser power. Moreover when this band was intense, a new 952.8 cm^{-1} band with the same behavior appeared. The lower 1000–800 cm^{-1} region contains vibrations of titanium oxides[16] and a new band in this region may belong to a reaction product of titanium oxides and carbon monoxide.

Accordingly, pulsed laser evaporated TiO_2 was codeposited with 1% CO and spectra are shown in Figure 5. The yield of TiO and TiO_2 was high in experiments with a TiO_2 target. After deposition the 1866.7 cm^{-1} band and 1862.8 cm^{-1} satellite were the most intense in the upper region. Annealing increased broad bands at 1995, 1951, and 1933 cm^{-1} and sharp bands at 1877.2, 1810.0, and 1769.1 cm^{-1}, while the 1866.7 cm^{-1} band decreased and the 1862.8 cm^{-1} band increased, as shown in Figure 5. Below the bands of TiO (988.2 cm^{-1}) and TiO_2 (917.1 cm^{-1}),[16] several new bands (952.8, 984.9, 882.2, and 866 cm^{-1}) were observed. After annealing, the 952.8 cm^{-1} and titanium oxide bands decreased, and a weak 847 cm^{-1} band increased markedly. Note that in this system bands of titanium oxides were more intense than in the Ti + CO system. Clearly laser ablation of TiO_2 pellets gives more TiO and TiO_2 presumably from recombination of Ti and O atoms. The production of Ti atoms from ablation of TiO_2 has been verified by the formation of $Ti^{18}O_2$ from $^{18}O_2$ added to the sample.[16]

In a similar TiO_2 ablation experiment with 1/200 CO/Ar, the 1887.7 and 1854.4 cm^{-1} bands were observed as in Figure 1; however, on annealing the 1854.4 cm^{-1} band decreased and the 1887.7 cm^{-1} band increased, reaching an absorbance double that in Figure 1.

With $^{12}CO/^{13}CO$ isotopic mixtures, the 1866.7 cm^{-1} band gave a doublet with a counterpart at 1823.7 cm^{-1}, and the 1810.0 cm^{-1} band produced a triplet with counterparts at 1788.7 and 1771.9 cm^{-1}. Isotopic spectra are shown in Figure 6. The new 1839.4 cm^{-1} band is shown to be the mixed 12/13 component of a triplet with the ^{12}CO counterpart at 1862.8 and the ^{13}CO counterpart at 1822.1 cm^{-1}. Broad bands in the upper region also produced shifts, but due to overlapping it is difficult to determine counterparts for each band; however, weak intermediate components were found for the 1951 and 1995 cm^{-1} absorptions. The bands below 1000 cm^{-1} did not reveal any ^{13}CO shifts.

TiO + CO. Ablation experiments were done with a TiO pellet and CO in argon. The TiO target gave similar spectra to the TiO_2 target; however, Ti atom reaction products were stronger with the TiO target. Annealing behavior was the same as in Ti/CO experiments. After annealing, photolysis decreased O_3 1867.7 and 1862.8 cm^{-1} bands while 1887.7 cm^{-1} increased and 1854.4 cm^{-1} was unchanged.

Ti + CO_2. Spectra of the Ti + CO_2 reaction are shown in Figure 7. After deposition only one strong band at 1866.7 cm^{-1} with shoulders at 1863 and 1858 cm^{-1} was found in the upper region of the spectrum. Annealing led to slightly decreasing 1866.7 cm^{-1} and increasing 1858.7 cm^{-1} and ozone band intensities. Weak bands at 1951 and 1810 cm^{-1} also increased. Below 1000 cm^{-1}, titanium oxides and 952.8, 895.1, and 882.5 cm^{-1} absorptions were observed. The intensities of these bands decreased after annealing and a weak 866.2 cm^{-1} band increased in intensity.

Experiments were done with $C^{18}O_2$ and $^{13}CO_2$. Enriched carbon monoxide was formed in each experiment. The strong product band shifted to 1826.1 and 1823.7 cm^{-1}, respectively. Annealing increased the 1818.9 and 1822.1 cm^{-1} bands, respectively, at the expense of the strong bands. The lower region revealed shifted bands for $C^{18}O_2$ reaction products but unshifted bands for $^{13}CO_2$ reaction products as given in Table 1.

Reaction of isotopic $C^{16,18}O_2$ produced a strong doublet at 1866.7 and 1826.1 cm^{-1} and a triplet at 1862.8, 1837.6, and 1818.9 cm^{-1}. Below 1000 cm^{-1} the new 952.8 cm^{-1} band

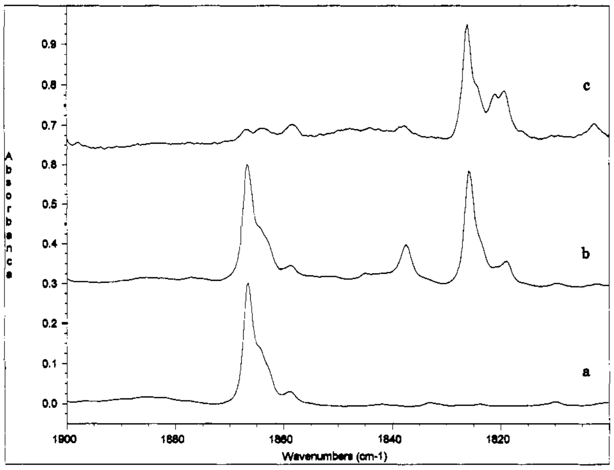

Figure 7. Infrared spectra in the 1900–1800 cm^{-1} region for pulsed laser ablated Ti atoms codeposited with isotopic CO$_2$ in argon: (a) $C^{16}O_2$/Ar = 1/100, (b) $C^{16,18}O_2$/Ar = 1/200, and (c) $C^{18}O_2$/Ar = 1/200.

produced a strong doublet with the ^{18}O counterpart at 911.9 cm^{-1}, and a doublet was also observed for TiO at 988.8 and 946.2 cm^{-1}. New 895.1, 889.0, 882.5, 881.8, 869.6, 860.4, and 848.2 cm^{-1} bands were also observed; the 899.0 and 881.8 cm^{-1} bands are due to the $Ti^{16}O^{18}O$ and $Ti^{18}O_2$ molecules.[16] Finally, CO and $C^{18}O$ were observed in the upper region in experiments with isotopic mixtures; $C^{18}O$ can only be formed as the product of $C^{16}O^{18}O$ or $C^{18}O_2$ decomposition or reaction.

Discussion

The new product absorptions will be identified on the basis of concentration dependence and annealing behavior and reactions with oxide systems. It is clear that titanium oxide complexes are produced in addition to lower titanium carbonyls absorbing below 1890 cm^{-1} and higher carbonyls absorbing above 1890 cm^{-1}. Unfortunately the Ti experiments contain oxides and the oxide experiments contain Ti atoms, so both types of products are expected in all experiments.

Lower Titanium Carbonyls. The 1887.7 and 1854.4 cm^{-1} bands were the first absorptions produced in dilute CO experiments with Ti and both exhibited doublets with mixed isotopic CO reagents indicating single CO oscillators. Hence both bands could be due to the first and most reactive carbonyl in this system, namely TiCO. Close examination of Figures 1 and 2 (and a similar 1/600 experiment) shows that both bands increase on 20 K annealing along with the 1:2 band, but that the 1887.7 cm^{-1} band increases and the 1854.4 cm^{-1} band decreases on 25 K annealing, and that both decrease on annealing to 35 K. Furthermore, photolysis increases the 1887.7 cm^{-1} band with little effect on the 1854.4 cm^{-1} band. In addition the 1887.7 cm^{-1} band is favored in experiments with substantial TiO$_2$ present. It appears that the 1854.4 cm^{-1} band is due to the more reactive simple monocarbonyl species.

Another difference between the two absorptions concerns the CO isotopic counterparts. As shown in Table 1, for 1887.7 cm^{-1} the $C^{18}O$ counterpart is lower than the ^{13}CO counterpart as for ^{13}CO (2091.5 cm^{-1}) and $C^{18}O$ (2087.4 cm^{-1}), whereas for 1854.4 cm^{-1} the reverse relationship is found. Although the differences are small, there is more ^{13}C shift than ^{18}O shift (by 1.0 cm^{-1}) for the 1854.4 cm^{-1} band; in contrast there is more ^{18}O shift than ^{13}C shift (by 0.8 cm^{-1}) for the 1887.7 cm^{-1} band. Expressed in terms of isotopic frequency ratios, the CO diatomic exhibits a $^{12}CO/^{13}CO$ ratio of 1.0224 and a $C^{16}O/C^{18}O$ ratio of 1.0244. The 1887.7 cm^{-1} band exhibits more "diatomic like" ratios (12/13 ratio 1.0225, 16/18 ratio 1.0232) than the 1854.4 cm^{-1} band (12/13 ratio 1.0226, 16/18 ratio 1.0220).

Recent CASSCF/MRCI calculations[7] predict the linear ground state Ti–CO molecule to be bound with respect to dissociation into Ti and CO and to sustain a carbonyl frequency red shift of 280 cm^{-1} while density function calculations[9] predict a smaller carbonyl red shift of 231 cm^{-1}. Both 1887.7 and 1854.4 cm^{-1} bands are in reasonable agreement with the theoretical predictions for TiCO. In addition, the density function calculations[9] predict the Ti–C vibration at 467 cm^{-1} with 0.6% of the infrared intensity of the C–O fundamental. This explains the failure to observe any Ti–C stretching absorptions in this work. In addition, the ^{13}CO shift for TiCO is predicted to exceed the $C^{18}O$ shift by 0.2 cm^{-1}.[9] This means that carbon is vibrating between oxygen and another atom and provides further evidence for assignment of the 1854.4 cm^{-1} band to TiCO. A tentative assignment for the 1887.7 cm^{-1} band, then, is to the O$_2$TiCO complex, which is favored on annealing in TiO$_2$ experiments. The observation of O$_2$Ti(CO)$_y$ (y = 2, 4) in the 1950–1995 cm^{-1} region suggests that the y = 1 species should absorb near 1900 cm^{-1}.

Furthermore, the same high-level calculations predict V–CO to be less strongly bound than Ti–CO, and the C–O fundamental to be accordingly less red shifted, which is in reasonable agreement with the 1904 cm^{-1} argon matrix assignment to VCO.[19,20] The CrCO and NiCO compounds are still less strongly bound with carbonyl frequencies at 1977 and 1996 cm^{-1}, respectively,[10,11] which is in accord with theoretical predictions of less effective back donation to CO $2\pi^*$ orbitals going across the transition series.[7-10]

Titanium Dicarbonyls, Ti(CO)$_2$ and Ti$_2$(CO)$_2$. The 1877.2 and 1769.1 cm^{-1} bands labeled 2:2 were also observed under the lowest CO concentration conditions, and they tracked together on annealing and photolysis as CO concentration was increased to 2%. The 2:2 bands showed different annealing behavior depending on concentration: at 1/600 the bands increased substantially, at 1/100 the bands decreased slightly, and at 1/50 the bands decreased markedly. Such behavior is appropriate for lower carbonyls. Another band labeled 1:2 at 1810.0 cm^{-1} increased markedly on annealing in the dilute CO experiments. Both band sets gave mixed isotopic triplets, which indicates two equivalent carbonyl groups. The isotopic ratios for the 1810.0 cm^{-1} band (1.0217 and 1.0249 for 12/13 and 16/18, respectively) are near the diatomic values given above, which are in accord with fundamental C–O vibrations. In contrast the 1877.2 and 1769.1 cm^{-1} bands exhibit isotopic ratios of 1.023 for both ^{13}CO and $C^{18}O$, which indicates more C and less O participation in the latter vibrational modes.

The same high level calculations predict the dicarbonyl to be linear with a shorter CO bond than TiCO owing to less donation to π^* per CO submolecule and less binding per CO (1.02 eV total).[7] The 1877.2 and 1769.1 cm^{-1} bands with an average frequency (1823 cm^{-1}) below TiCO (1854 cm^{-1}) are not in accord with the Ti(CO)$_2$ calculations. On the other hand, the 1810.0 cm^{-1} band is appropriate for the antisymmetric CO stretching fundamental of linear OCTiCO with a symmetry forbidden symmetric counterpart. (Unfortunately, the 1810 cm^{-1} frequency is common[18] to Ti(N$_2$)$_2$ and some of this band may be due to the nitrogen species, but the major absorption here shows a ^{13}CO shift: see Figure 6.)

Harmonic force constant refinement calculations were performed with the ASYM20 program[21] using the 1788.6 and 1771.6 cm^{-1} isotopic frequencies for Ti(^{12}CO)(^{13}CO) and Ti(^{13}CO)$_2$, respectively. The force constants K_r = 14.8 mdyn/Å

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and K_{rr} = 1.6 mdyn/Å fit the frequencies to ±0.8 cm^{-1} and predicted the forbidden symmetric C−O stretching mode at 2018 cm^{-1}. The average $Ti(CO)_2$ frequency (1914 cm^{-1}) is clearly above the TiCO fundamental (1854 cm^{-1}) and in accord with the quantum chemical calculations.

The 1810 cm^{-1} band observed here for the antisymmetric C−O stretching fundamental of $Ti(CO)_2$ is in agreement with other substituted titanium dicarbonyl compounds,[22,23] which exhibit an infrared band in the 1850 cm^{-1} range. These compounds also show another band in the 1940 cm^{-1} region for the symmetric C−O stretching mode since the OC−Ti−CO structure is nonlinear in these compounds.

What species then is required to account for the 1877.2 and 1769.1 cm^{-1} band pair? The region below 1800 cm^{-1} is often attributed to bridging carbonyls,[24] and two such species, $OC(Ti)_2CO$ and $Ti(CO)_2$, must be considered here. The former 4-membered ring would have to be nonplanar to exhibit both symmetric and antisymmetric carbonyl stretching motions whereas the latter 3-membered ring has both modes allowed. However, the 2:2 bands require more than one Ti atom and assignment to $Ti_2(\mu_2\text{-}CO)_2$ is indicated. This nonplanar (butterfly) species involves CO bridging to orthogonal d orbitals on the initial Ti_2 molecule, which may result in removing any Ti−Ti bonding interaction in the $OC(Ti)_2CO$ species. This molecule is the dimer $(TiCO)_2$ of the simplest carbonyl. Finally, the 2:2 bands decreased while a 1857 cm^{-1} band increased on photolysis, suggesting a possible ring opening to give a species with two inequivalent CO subgroups.

OTiCO. The strongest of four carbonyl bands favored in TiO_2 + CO experiments (noted with an asterisk in Figures 1−3 and footnote b in Table 1) and the strongest absorption produced in Ti + CO_2 reactions was at 1866.7 cm^{-1}. This band was observed in all Ti + CO experiments, but its intensity depended more on laser power than on CO concentration, and Ti + O recombination and subsequent TiO complex formation was suspected.

The 1866.7 and 952.8 cm^{-1} bands exhibited approximately constant relative intensity in Ti+ dilute CO, TiO_2 + CO, TiO + CO and Ti + CO_2 experiments and are thus assigned to the same molecule. The bands decreased on annealing in favor of the 1862.8 cm^{-1} band in CO experiments. With $^{12}CO/^{13}CO$ the upper band exhibited a doublet (1.0236 ratio) and the lower band was unshifted. For Ti + $C^{16,18}O_2$, both bands exhibited doublets (16/18 ratios 1.0222 and 1.0449) which identifies vibrations of single C−O and Ti−O oscillators. These isotopic ratios are near CO and TiO (1.0450)[17] values, which identifies new C−O and Ti−O fundamental vibrations and accordingly the OTiCO molecule. The 12/13 ratio is slightly larger and the 16/18 ratio slightly smaller than diatomic values, which shows interaction between CO and another vibrational motion. Furthermore, observation of only these two major new bands in Ti + CO_2 experiments confirms the identification of the OTiCO molecule. Note that the CO fundamental is red shifted 12 cm^{-1} less by interaction with TiO than with Ti.

Higher Oxide Carbonyls. The 1862.8 cm^{-1} band increases on annealing at the expense of the 1866.7 cm^{-1} band in all experiments and is favored in TiO and TiO_2 experiments. The 1862.8 cm^{-1} band exhibits triplet absorptions in isotopic experiments with mixed $^{12}CO,^{13}CO$ at 1839.4 cm^{-1} and mixed $C^{16}O,C^{18}O$ at 1837.4 cm^{-1}. We favor assignment of the 1862.8 cm^{-1} band to $OTi(CO)_2$.

The 1951 and 1995 cm^{-1} bands are observed after annealing in all Ti experiments and on deposition in TiO and TiO_2 studies. The 1951 cm^{-1} band exhibits a 1909 cm^{-1} ^{13}CO counterpart with a stronger 1929 cm^{-1} intermediate component in mixed $^{12}CO,^{13}CO$ experiments and a 1904 cm^{-1} $C^{18}O$ counterpart with a stronger 1926 cm^{-1} mixed isotopic component. This absorption appears to involve two equivalent CO subgroups. The 1951 cm^{-1} band is probably due to $O_2Ti(CO)_2$. The $O_2Ti(CO)_2$ species is analogous to similar Cr, Mo, and W intermediates prepared by photooxidation of the hexacarbonyls in argon matrix samples containing O_2.[25−28] For these cases dioxide dicarbonyls are observed with antisymmetric C−O stretching frequencies near 2065, 2041, and 2018 cm^{-1} respectively for Cr, Mo, and W. The analogous 1951 cm^{-1} frequency for $O_2Ti(CO)_2$ indicates a much stronger interaction between CO and TiO_2 than with CrO_2, MoO_2, or WO_2.

The major band after annealing in TiO_2 experiments with CO at 1995 cm^{-1} (Figure 5) exhibits isotopic ratios for ^{13}CO (1.0222) and $C^{18}O$ (1.0244) in excellent agreement with diatomic CO ratios. One mixed isotopic component was observed at 1968 cm^{-1} and more are not precluded. The associated 847 cm^{-1} band in the TiO_2 region does not shift on isotopic CO substitution. Since annealing shows that these bands are due to the highest carbonyl that can be formed with TiO_2, the molecule is probably $O_2Ti(CO)_4$, with presumably a distorted octahedral structure.

Again, analogous dioxide tetracarbonyls have been prepared for Mo and W and these compounds exhibit strong C−O absorptions at 2110 and 2096 cm^{-1}, respectively. The 1995 cm^{-1} band for the analogous $O_2Ti(CO)_4$ compound shows a stronger interaction with TiO_2. In the Mo and W cases, the isolated metal dioxide molecules are bent, but the OMO subunit in the tetracarbonyls is thought to be linear.[26−28] In the Ti case the 16/18 ratio for the 847 cm^{-1} band (prepared from $^{18}O_2$) appears slightly larger (1.042) than for isolated TiO_2 so it must be concluded that the TiO_2 subunit remains bent and CO submolecules occupy the axial and two equatorial sites in a distorted octahedron.

Higher Titanium Carbonyls. There remain major bands in the 1 and 2% CO experiments at 1897.5 and 1933.8 cm^{-1} that grow on annealing and are clearly due to higher carbonyls. These bands are observed on codeposition with 5 and 10% CO samples and are very weak in TiO and TiO_2 + CO experiments. For the highest expected carbonyl, a strong band at 1950 cm^{-1} in previous 10% CO experiments[4] has been identified as $Ti(CO)_6$, and the broad band that appears at 1956 cm^{-1} and dominates the spectrum on annealing in the present 2% experiments (Figure 3) exhibits broad ^{13}CO and $C^{18}O$ counterparts that support the original $Ti(CO)_6$ assignment.[4] However, the sharper 1987 cm^{-1} band assigned earlier to $Ti(CO)_6$ and attributed to symmetry lowering by the matrix is probably due to the $O_2Ti(CO)_4$ species identified here at 1992−1995 cm^{-1} depending on CO concentration. Force constant calculations[21] for the ^{12}CO (1956 cm^{-1}) and all ^{13}CO (1913 cm^{-1}) isotopic molecules give K_r = 17.2 mdyn/Å with fixed K_{rr} = 1.7 mdyn/Å. The unresolved central mixed isotopic component is appropriate for the octahedral hexacarbonyl.[29] Thus, the new 1897.5 and 1933.8 cm^{-1} bands are most likely associated with

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Ti(CO)$_y$ molecules for $2 < y < 6$. A close examination of Figures 1–3 with increasing CO concentration and annealing temperature reveals an evolution of band intensity going up the series, and the straightforward assignment $y = 3$ and 4 is proposed.

The 1897.5 and 1933.8 cm^{-1} bands exhibit ^{12}CO/^{13}CO and C^{16}O/C^{18}O ratios in excellent agreement with diatomic CO values. Furthermore, these bands exhibit weak intermediate mixed ^{12}CO/^{13}CO isotopic absorptions as expected[29] for trigonal planar Ti(CO)$_3$ and tetrahedral Ti(CO)$_4$ molecules although band overlap in these complicated systems makes the isolation of only one set of isotopic bands impossible. Force constant refinement calculations[21] were performed for trigonal planar Ti(CO)$_3$ and tetrahedral Ti(CO)$_4$ using the ^{12}CO/^{13}CO data given in Table 1. For Ti(CO)$_3$ the force constants $K_r = 15.8$ mdyn/Å and $K_{rr} = 1.3$ mdyn/Å reproduced the data including mixed ^{12}CO/^{13}CO to ± 1.8 cm^{-1}. For Ti(CO)$_4$ the force constants $K_r = 16.4$ mdyn/Å and $K_{rr} = 1.3$ mdyn/Å reproduced the ^{12}CO/^{13}CO isotopic data to ± 1.0 cm^{-1}. Taken as a whole, the good fit to the force constant calculations supports the assignments to Ti(CO)$_3$ and Ti(CO)$_4$.

The hexacarbonyl is probably formed by addition of CO to the pentacarbonyl yet no band is obvious in the spectrum for assignment to Ti(CO)$_5$. It is likely that the strongest band of Ti(CO)$_5$ is included in the broad 1950–1960 cm^{-1} band growing on annealing, but this hypothesis cannot be documented.

The Ti(CO)$_3$ and Ti(CO)$_4$ compounds observed here may be compared to other zerovalent titanium carbonyls which contain coordinating ligands.[30] Substituted carbonyls give lower frequency carbonyl absorptions in the 1750–1800 cm^{-1} region owing to extra electron density available from the coordinating ligand. Such extra electron density is manifested in Ti(CO)$_6^{2-}$ relative to Ti(CO)$_6$ with their intense C–O stretching bands at 1750 and 1950 cm^{-1}, respectively.[4,31]

It is of interest to compare the carbonyl frequencies assigned here for Ti(CO)$_y$ to those for Ni(CO)$_y$ ($y = 1-4$) where Ni(CO)$_4$ is a known compound. DeKoch identified NiCO at 1996 cm^{-1} as the major product in Ar/CO = 500/1 samples codeposited with Ni atoms.[11] Annealing first increased a weak band at 1967 cm^{-1}, assigned to Ni(CO)$_2$, then increased bands at 2017 and 2052 cm^{-1} for the tricarbonyl and tetracarbonyl, in agreement with earlier assignments to Ni(CO)$_3$ produced by photodissociation of Ni(CO)$_4$.[32] The same behavior was observed here for the Ti carbonyls formed in the Ti and CO reactions. Furthermore, the relative frequencies are similar for the four Ti and Ni carbonyl bands, which supports the present identification of titanium carbonyls.

Other Absorptions. The 1964.7 cm^{-1} band exhibits the same 1920.0 cm^{-1} ^{13}CO and C^{18}O counterpart, which gives slightly higher 12/13 and lower 16/18 ratios (1.023) than the diatomic molecule. This again denotes more C and less O participation than for the diatomic oscillator. Stronger intermediate components were observed at 1951 and 1937 cm^{-1}, giving an approximately 1/3/3/1 quartet, which is not the case for higher carbonyls of high symmetry.[29] A straightforward explanation for the quartet is a nondegenerate vibration of three equivalent CO groups. New absorptions appear on annealing at 1826.2 cm^{-1} in ^{13}CO and at 1823.4 cm^{-1} in C^{18}O experiments which point to another absorption growing at 1867.2 cm^{-1} on annealing in >1% ^{12}CO experiments. This annealing product is due to a higher carbonyl species. The 1964.7 and 1867.2 cm^{-1} bands in high concentration CO experiments are tentatively assigned to Ti(CO)$_3$ perturbed and made nonplaner by another atom or molecule. The O$_2$Ti(CO)$_3$ species is a possibility.

A sharp band appears at 1974.4 cm^{-1} on annealing in 2% CO experiments. Photolysis after annealing increases the band. The isotopic ratios are near CO values so this must be a carbonyl vibration, but mixed isotopic components were masked by other bands. This species probably involves more than one Ti atom, but no definitive identification is possible. Finally, the broad 2017 cm^{-1} band that appears on annealing shows proper carbonyl isotopic shifts and its earlier assignment[4] to a higher carbonyl Ti$_x$(CO)$_y$ cluster species is reasonable.

The sharp 1849.5 cm^{-1} band that appears on annealing to 25 K involves one CO group. It is probably due to a perturbed TiCO species, possibly TiTiCO.

Nitrogen complexes readily with Ti and TiO$_2$, as shown in a recent study, [18] and several weak bands observed here are due to such species. Bands at 1901.0 and 1858.5 cm^{-1} have been identified as O$_2$TiN$_2$ and O$_2$Ti(N$_2$)$_2$. Part of the 1810 cm^{-1} band observed here is due to a nitrogen species[18] containing two N$_2$ molecules, but absorption at 1810 cm^{-1} also exhibits ^{13}CO and C^{18}O shifts as assigned above. The nitrogen species absorbing at 1810 cm^{-1} is probably due to Ti(N$_2$)$_2$ rather than the (O$_2$TiN$_2$)$_2$ dimer suggested earlier.[18] Finally, the weak 1997.0 cm^{-1} band is a single carbonyl vibration enhanced by nitrogen, which suggests a mixed O$_2$Ti(N$_2$)(CO) species.

Reaction Mechanisms. The reaction to form titanium carbonyls is straightforward as the first and second additions of CO to Ti are exothermic[7] and the third through sixth successive additions are expected to be exothermic as well. These reactions proceed spontaneously on annealing to 25–35 K as CO diffuses and reacts in solid argon at these temperatures in stepwise reactions summarized by reaction 1. Although the pentacarbonyl was not characterized here, its presence is manifested by observation of the highest carbonyl formed, Ti(CO)$_6$.

$$\mathrm{Ti} + y\mathrm{CO} \rightarrow \mathrm{Ti(CO)}_y \quad (y = 1-6) \tag{1}$$

Titanium clusters apparently play a minor role in these experiments. It is expected that Ti$_x$ species will also bind CO molecules. The sharp bands assigned here include one small cluster species for $x = 2$ and $y = 2$.

$$x\mathrm{Ti} + y\mathrm{CO} \rightarrow \mathrm{Ti}_x\mathrm{(CO)}_y \tag{2}$$

Laser ablation of the Ti metal target is always accompanied by the formation of trapping of TiO and TiO$_2$ in the matrix sample,[16] and these oxides also react with CO.

$$\mathrm{TiO} + \mathrm{CO} \rightarrow \mathrm{OTiCO} \tag{3}$$

$$\mathrm{TiO}_2 + y\mathrm{CO} \rightarrow \mathrm{O}_2\mathrm{Ti(CO)}_y \tag{4}$$

In the laser ablation of TiO and TiO$_2$ pellets, the yield of TiO and TiO$_2$ was increased over that from the Ti target, and the yield of oxide carbonyls was also increased. It is important to note that the greater CO absorbance for OTiCO relative to TiCO in all titanium ablation experiments, where Ti surely exceeds TiO concentration, indicates the greater reactivity of TiO for CO. In addition, the O$_2$Ti(CO)$_2$ and O$_2$Ti(CO)$_4$ species produced here are analogous to the Cr, Mo, and W species produced by photooxidation of the hexacarbonyls.[25–28]

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Table 2. Harmonic Force Constants (mdyn/Å) Calculated for Titanium Carbonyls Using the ASYM20 Program.[a]

	K_r	K_π
TiCO	13.9[b]	
$Ti(CO)_2$	14.8	1.6
$Ti(CO)_3$	15.8	1.3
Ti(CO)4	16.4	1.3
$Ti(CO)_6$	17.2	1.7[c]
CO	18.5	

[a] Reference 21; $K_r = K(CO)$ and $K_\pi = K(CO,CO)$. [b] Diatomic approximation. [c] K_π opposite fixed with K_π adjacent at 0.85.

The reaction of Ti and CO_2 was done to support the formation of OTiCO as Ti atoms from laser ablation[13,33] contain more than enough excess kinetic energy to react with CO_2.

$$Ti + CO_2 \rightarrow [OTiCO]^* \xrightarrow{relax} OTiCO \qquad (5)$$

$$Ti + CO_2 \rightarrow TiO + CO \qquad (6)$$

$$O_3 + OTiCO \xrightarrow{h\nu} O_2TiCO + O_2 \qquad (7)$$

In some cases the energized $[OTiCO]^*$ intermediate is relaxed by the matrix and the OTiCO molecule is stabilized, reaction 5. Note that the same product molecule is made by reactions 3 and 5. However, the yield of TiO was enhanced in the CO_2 experiments, and CO was observed as well, so in other cases the energized intermediate decomposes to diatomic products, reaction 6. Finally, photolysis decreases O_3 and OTiCO absorptions and increases O_2TiCO in oxide experiments as shown in reaction 7.

Finally, it should be noted that the laser powers employed here produce electrons and ions in addition to metal atoms. However, in Ti + O_2 work, the TiO_2 signal at 917.1 cm^{-1} was one to two orders of magnitude stronger than O_4^- at 953.7 cm^{-1}.[16] At lower laser powers, the O_4^- signal is stronger, and the O_4^- species may contribute to the 952.8 cm^{-1} product absorption in TiO_2 + CO experiments. It follows that charged species play, at most, a minor role in the matrix metal atom chemistry reported here.

Conclusions

Titanium atoms react readily with CO molecules on condensation with excess argon, and infrared spectroscopic evidence with ^{13}CO and $C^{18}O$ substitution is presented for the identification of $Ti(CO)_y$ species ($y = 1-4$ and 6). The higher carbonyls are formed by successive additions of CO on annealing in 25–35 K argon matrices. Force constants are given in Table 2 for the Ti carbonyls. Note the lowest C–O force constant for TiCO where the bonding interaction per carbonyl is the strongest and the highest force constant for $Ti(CO)_6$. All $Ti(CO)_y$ force constants are, of course, reduced from the free CO value owing to the Ti–CO bonding interaction through d-orbital back-bonding.

A major problem with titanium is the ever presence of the oxide, and all titanium atom samples contain TiO and TiO_2 from oxidation during the ablation process. Although the presence of oxides complicates interpretation of the spectra, more chemical information is provided in the spectra of oxide complexes. Titanium oxides are also reactive with CO, and the high yield of OTiCO relative to TiCO in Ti ablation experiments, where the Ti concentration must exceed the TiO concentration, suggests that TiO is more reactive toward CO than Ti atoms. The formation of the same OTiCO molecule from the Ti + CO_2 reaction confirms the identification of this molecule. Evidence is also presented for several CO complexes with TiO_2 including the dicarbonyl and tetracarbonyl, which are analogous to Cr, Mo, and W compounds produced by photooxidation of the hexacarbonyls.[25–28]

The C–O stretching frequency decreases from 1887.7 (tentative assignment) to 1866.7 to 1854.4 cm^{-1} in the series of proposed complexes with O_2Ti, OTi, and Ti, respectively, a relatively small difference. This is in contrast to the NiN_2 and O_2NiN_2 species and the TiN_2 and O_2TiN_2 species where the metal complexes exhibit somewhat more red shift of the N_2 fundamental,[34,35] but the difference between O_2TiN_2 (1901.3 cm^{-1}) and TiN_2 (1847.1 cm^{-1})[18] is comparable to that proposed for the analogous CO species. Although d-orbital back-donation from the metal center adequately explains the carbonyl frequency trends in a group of high-spin M–CO species,[7,9] competitive σ and π bonding effects are in operation, and bonding to oxygen is expected to reduce the d-electron density available for back-bonding as is observed here. The effect is small and π molecular orbitals involving the oxygen atoms are probably involved in the back-donation to the CO $2\pi^*$ molecular orbitals in the above O_2Ti, OTi, and Ti carbonyl series.

The matrix isolation technique provides a means to study the metal and metal oxide–carbon monoxide interaction so important in catalysis on the molecular level. Furthermore, the stability of the $Ti(CO)_y$ molecules observed here, coupled with the preparation of substituted titanium carbonyls,[22,23,30] suggests renewed efforts to synthesize higher titanium carbonyls.

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Note Added in Proof: Similar experiments reacting Zr and Hf with CO give analogous major bands within ±20 cm^{-1}.

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