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Matrix Infrared Spectra of the Products of Uranium-Atom Reactions with Carbon Monoxide and Carbon Dioxide

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Uranium atoms from pulsed Nd:YAG laser ablation of a uranium metal target were codeposited with carbon monoxide and carbon dioxide in excess argon at 10 K. Infrared spectra following the U + CO reaction revealed strong new absorption bands at 804.4 and 852.6 cm^{-1}, which are assigned to the CUO product on the basis of isotopic shifts, FG matrix calculations, and ab initio pseudopotential calculations. An absorption at 2027.5 cm^{-1} is attributed to the asymmetric secondary reaction product CU(O)CO. In both the U + CO and U + CO_2 reactions, bands at 870.9 and 1963.8 cm^{-1} were observed and assigned to the association product of UO_2 and CO. Lastly, in the U + CO_2 experiments, new absorption band pairs were observed at 804.4 and 1799.6 cm^{-1} and at 801.5 and 2011.7 cm^{-1}. The former pair was almost destroyed on annealing and is assigned to the OUCO insertion product. The latter pair is attributed to an OCU(O)CO species. The direct reaction of U atoms with CO and CO_2 requires an activation energy, which is provided by hyperthermal U atoms from pulsed laser evaporation.

Introduction

Oxidation of uranium carbides,[1,2] carbonization of uranium oxides,[3–5] and solid uranium reactions with carbon monoxide and carbon dioxide[6–9] have been studied extensively. In sharp contrast, their reaction intermediates, uranium oxycarbides, have received little attention even though they have been used as nuclear reactor fuels.[10,11] Experimental studies on the uranium oxycarbides have examined phase transformations[12] and thermal decomposition.[13] In addition, uranium oxycarbides may also be formed in the gas phase during high-temperature uranium-vapor processes where CO and CO_2 are introduced into the system by atmospheric leaks. An earlier matrix infrared study[14] examined the interactions between atomic uranium and CO where uranium carbonyls ranging from U(CO) to $U(CO)_6$ were tentatively characterized. However, spectra were unavailable in the diagnostic 700–900-cm^{-1} region, and no evidence of uranium oxycarbides was presented.

The matrix isolation technique is ideally suited for studying reaction mechanisms since the inert gas matrix prevents initial reaction products from undergoing further reactions until they can be characterized spectroscopically. Additional reaction products can then be formed in a controlled manner by selective photolysis and matrix annealings. Recent matrix IR studies on uranium-vapor reactions with O_2 and N_2[15,16] have demonstrated that Nd:YAG laser ablation of an uranium target is a clean and effective source of uranium vapor. The hyperthermal uranium atoms so produced react readily with both O_2 and N_2 to yield insertion products. Any vapor source must overcome the extreme refractory nature of uranium which requires the solid to be heated to 2200 K for a vapor pressure of 10^{-6} atm. The primary purposes of this matrix study on uranium-vapor reactions with CO and CO_2 are to provide initial characterization of uranium oxycarbides and to further examine uranium carbonyls.

Experimental Section

A uranium metal target was laser evaporated using a Quanta Ray DCR-11 Nd:YAG laser at 1064 nm in the Q swtiched mode with a 10-ns pulse duration. The laser power was typically 70 mJ/pulse at the sample with a 10-Hz repetition rate. Uranium atoms formed as a result of this evaporation were codeposited with mixtures of argon and CO and argon and CO_2 (typical dilutions between 200:1 and 800:1) onto a cold substrate at 10 K. The substrate was a CsI optical window mounted in a copper retainer at the cold tip of a CTI Cryogenics Model 22 closed-cycle refrigerator suspended in a custom-built vacuum chamber as described earlier.[17,18] The laser beam was focused by a lens (focal length of 10 cm) through a hole in the CsI window onto the metal target. The metal target was rotated at 1 rpm to prevent boring and minimize metal cluster formation. The cold head of the refrigerator could be rotated under vacuum so that the substrate faced the target and the gas deposition port or the CsI windows for obtaining transmission FTIR spectra (Nicolet Model 60SXR FTIR spectrometer). The reported spectra are averages of 200 scans with spectral resolution of 0.5 cm^{-1} and band-position accuracy of ±0.1 cm^{-1}. A 175-W medium-pressure mercury arc lamp (Philips H39KB) with the globe removed was used to photolyze the matrix at 0.5-1-h intervals through a quartz window. To further promote aggregation, the argon matrix was annealed to between 20 and 37 K. IR spectra were recorded before and after sample deposition and after each photolysis/annealing. Since annealing must also be occurring during photolysis, the sequence of photolysis and annealing was interchanged in an effort to correlate product bands.

Results

Infrared spectra for the reactions of uranium atoms with CO and CO_2 will be presented.

U + CO. The top spectrum in Figure 1 shows absorption bands in the 900–750-cm^{-1} region that are present after a 3-h codeposition of uranium atoms with a 400:1 argon to carbon monoxide gaseous mixture. Two bands present in the spectrum have been previously assigned; the band at 775.5 cm^{-1} is due to the ν_3 mode of UO_2, and the band at 819.8 cm^{-1} is the stretching mode of UO.[15,19] Another weak band at 1051.1 cm^{-1}, not shown, is due to the ν_3 mode of UN_2.[16] Also present in the top spectrum are strong new absorptions at 852.6 and 804.4 cm^{-1} and a weak band at 870.9 cm^{-1}.

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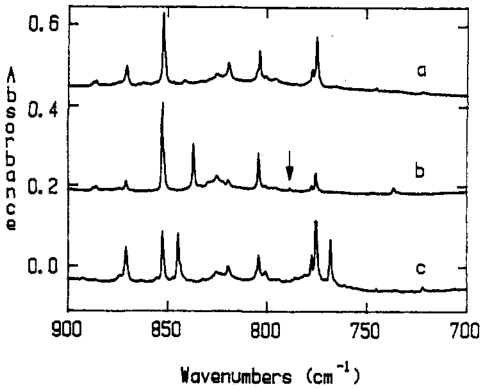

Figure 1. Infrared spectra in the 900–700-cm^{-1} region for samples prepared by codeposition of uranium atoms for 3 h with 400:1 mixtures of argon and (a) $^{12}C^{16}O$, (b) $^{12}C^{16}O$ and $^{13}C^{16}O$ (arrow denotes $^{13}C^{16}O$ absorption), and (c) $^{12}C^{16}O$ and $^{12}C^{18}O$.

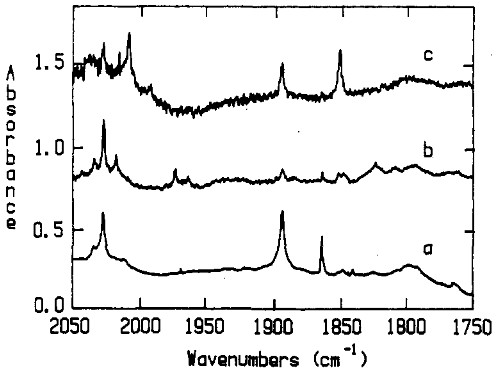

Figure 2. Infrared spectra in the 2150–1750-cm^{-1} region after codeposition of uranium atoms for 3 h with 400:1 mixtures of argon and (a) $^{12}C^{16}O$, (b) $^{12}C^{16}O$, and (c) $^{13}C^{16}O$, and (c) $^{12}C^{16}O$ and $^{12}C^{18}O$.

In the carbon monoxide stretching region, shown in Figure 2, new absorption bands are evident at 1893.4 and 2027.5 cm^{-1} and the CO precursor band is at 2138.4 cm^{-1} (not shown). Additionally, the CO stretching band of HCO is present at 1863.5 cm^{-1}.[20] The 2027.5-cm^{-1} band decreases relative to the other product bands in more dilute samples; in 600:1 samples this band is not observed.

Broad-band ultraviolet photolysis of these samples for 30 min yielded an increase of 15–20% for the 804.4- and 852.6-cm^{-} bands as well as the UO$_2$ band. The bands at 870.9, 874.0, and 1893.4 cm^{-1} were decreased by about 20%, whereas the 2027.8-cm^{-1} band was increased 2-fold upon photolysis. Lastly, the CO band at 2138.4 cm^{-1} was decreased by 25%, as were the carbonyl bands in the 1900–1970-cm^{-1} region.

Annealing of these samples to 28 K yields behavior opposite to that observed for absorption bands after photolysis. The 804.4- and 852.6-cm^{-1} bands decreased by 20%, the bands at 870.9 and 1893.4 cm^{-1} increased by 60–80%, and the 2027.5-cm^{-1} band decreased by about 20% on stepwise annealing. The UO$_2$ band at 775.5 cm^{-1} decreased by 20%, and the 819.8-cm^{-1} band remained unchanged. In addition to these band changes, there are several new bands in the CO stretching region that grow in on annealing. These bands are shown in Figure 3 and correspond qualitatively with those observed by Slater *et al.*[14] The band positions are 1904, 1917, 1934, 1951, and 1967 cm^{-1}.

Isotopic enrichment experiments were conducted where ^{13}CO was substituted for ^{12}CO. For these experiments, the following band positions were observed and recorded in Table I as well as shown in the middle spectrum of Figure 1. The term "shift" is only used when bands undergo similar behavior on photolysis and annealing as well as exhibit similar band shape. The UN$_2$, UO, UO$_2$, and 870.9-cm^{-1} bands are unshifted. The 804.4-cm^{-1} band is now shifted to 788.9 cm^{-1} and the 852.6-cm^{-1} band to 837.1 cm^{-1}. The band at 1893.4 cm^{-1} is shifted to 1851.1 cm^{-1}.

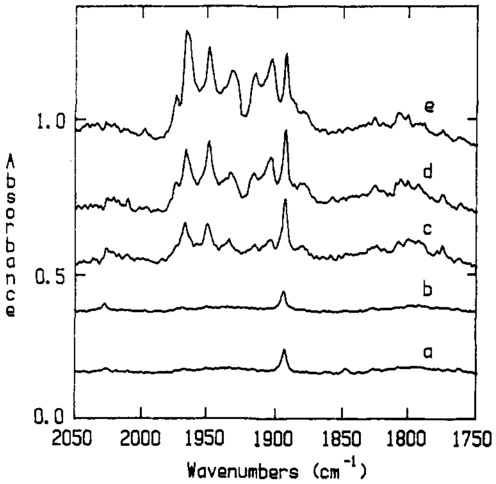

Figure 3. Infrared spectra in the 2150–1750-cm^{-1} region for uranium atoms codeposited with a 600/1 Ar/CO sample at 12 K: (a) spectrum of sample codeposited for 4 h, (b) spectrum after 30 min of ultraviolet photolysis, (c) spectrum after a 12-21-12 K thermal cycle, (d) spectrum after a 12-25-12 K thermal cycle, and (e) spectrum after a 12-30-12 K thermal cycle.

TABLE I: Band Positions (cm^{-1}) for the Reactions of Uranium with Various Isotopic Molecules of Carbon Monoxide and Carbon Dioxide

$^{12}C^{16}O$	$^{13}C^{16}O$	$^{12}C^{18}O$	$^{12}C^{16}O_2$	$^{13}C^{16}O_2$	$^{12}C^{18}O_2$	product molecule
775.5	775.5	775.5	775.5	775.5	737.0[a]	UO$_2$
			804.4	804.4	761.9	OUCO
			801.5	801.5	759.0	OU(CO)$_2$
804.4	788.9	768.7				CUO
819.8	819.8	819.8	819.8	819.8	775.0	UO
			847	844	802	aggregate
852.6	837.1	844.8				CUO
870.9	870.9	870.9	870.9	870.9	827.5	UO$_2$CO
			1799.6	1758.9	1757.0	OUCO
			1870	1829	1827	aggregate
1893.4	1851.1	1849.8	1893.4	1851.1	1849.8	UO$_2$CO
			2011.7	1990.7	1964.5	OU(CO)$_2$
2027.5	1963.8	2008.0				CUO(CO)
2138.4	2091.5	2087.4	2138.4	2091.5	2087.4	CO

[a] Bands for unshifted UO$_2$ and UO are also present at 775.5 and 819.8 cm^{-1}.

The 2027.5-cm^{-1} band is shifted to 1963.8 cm^{-1}, and the CO stretching band is shifted from 2138.4 to 2091.5 cm^{-1}. Two experiments were conducted where a mole ratio of 800:1:1 of Ar/^{13}CO/^{12}CO was used. In addition to those absorption bands observed in the ^{13}CO and ^{12}CO experiments, new bands were observed at 2018.1 and 1973.6 cm^{-1}. The 2027.5-, 2018.1-, 1973.6-, and 1963.8-cm^{-1} band intensities form a 4:2:2:1 pattern as shown in Figure 2b.

Several experiments were also conducted with C^{18}O. In these experiments, UO, UO$_2$, and UN$_2$ were again unshifted. The 804.4-cm^{-1} band was shifted to 768.7 cm^{-1}, and the 852.6-cm^{-1} band was found at 844.8 cm^{-1}, as shown in the bottom spectrum of Figure 1 and listed in Table I. As with the ^{13}CO experiments, the 870.9-cm^{-1} band was unshifted. The 1893.4-cm^{-1} band was shifted to 1849.8 cm^{-1}, and the 2027.5-cm^{-1} band was shifted to 2008.0 cm^{-1}. The CO band was shifted to 2087.4 cm^{-1}. There were no new bands observed for experiments where 1:1 mixtures of C^{18}O and C^{16}O were used as illustrated in Figure 2c.

U + CO$_2$. The bottom spectrum in Figure 4 shows absorption bands in the 700–900-cm^{-1} region that are present after a 3-h codeposition of uranium atoms with a 400:1 argon to carbon dioxide gaseous mixture. Absorption bands are again evident for UO, UO$_2$, and UN$_2$ at 819.8, 775.5, and 1051.1 cm^{-1}, respectively. In these experiments, the UO band is four times more intense than that observed in the U + CO experiments. The growth

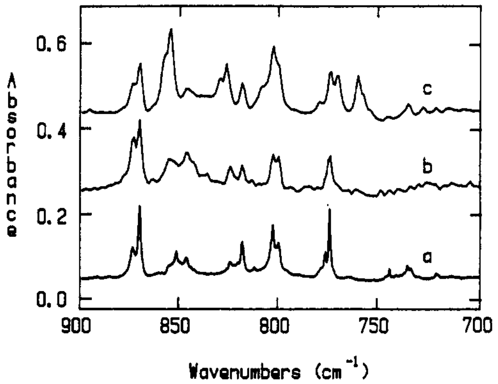

Figure 4. Infrared spectra in the 900–700-cm^{-1} region for codeposition of uranium atoms for 3 h with mixtures of (a) 400/1 Ar/$^{12}C^{16}O_2$, (b) 200/1 Ar/$^{13}C^{16}O_2$, and (c) 300/1 Ar/$^{12}C^{16}O_2$, Ar/$^{12}C^{16}O^{18}O$, and Ar/$^{12}C^{18}O_2$.

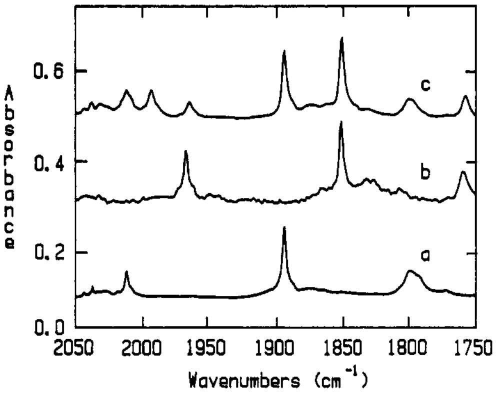

Figure 5. Infrared spectra in the 2150–1750-cm^{-1} region for codeposition of uranium atoms for 3 h with mixtures of (a) 400/1 Ar/$^{12}C^{16}O_2$, (b) 200/1 Ar/$^{13}C^{16}O_2$, and (c) 300/1 Ar/$^{12}C^{16}O_2$, Ar/$^{12}C^{16}O^{18}O$, and Ar/$^{12}C^{18}O_2$.

patterns of UO and CO indicate reaction between U + CO_2 as does the observation of CO in the spectrum. Three new doublet bands are also present with the first at 801.5 and 804.4 cm^{-1}, the second at 847 and 852.6 cm^{-1}, and the third at 870.9 and 874.0 cm^{-1}. In the CO stretching region, new bands were evident at 1799.6, 1893.4, and 2011.7 cm^{-1} (Figure 5a), as well as the CO band at 2138.4 cm^{-1}. The ν_3 mode of CO_2 is very strong at 2339.1 cm^{-1}. These bands are also tabulated in Table I.

Broad-band photolysis of the matrix for 30-min yields a 20% increase in the broad 847-cm^{-1} absorption band and a comparable decrease in the 801.5- and 870.9-cm^{-1} bands. The 804.4- and 852.6-cm^{-1} bands are unchanged. The UO_2 band at 775.5 cm^{-1} is increased on photolysis by 2-fold, while the UO band at 819.8 cm^{-1} is decreased by 50%. In the CO stretching region, the 1893.4- and 2011.7-cm^{-1} bands are decreased by 25%. The CO band at 2138.4 cm^{-1} is decreased by about 15%, and the 1799.6-cm^{-1} band is unchanged.

Annealing the samples to 28 K yielded a 15% reduction in the 852.6-cm^{-1} band and a 90% reduction in the 804.4-cm^{-1} band. The 801.5- and 847-cm^{-1} bands were increased by 15%. The bands at 870.9 and 874.0 cm^{-1} were unchanged during annealing. The UO and UO_2 absorption bands were decreased by about 40%. In the CO stretching region, the band at 1799.6 cm^{-1} was almost destroyed, while the 1893.4-cm^{-1} band and the CO band at 2138.4 cm^{-1} were unchanged. The new band at 2011.7 cm^{-1} was increased by about 20%.

Experiments were conducted where $^{13}CO_2$ was substituted for $^{12}CO_2$, and the band positions are tabulated in Table I and shown as the middle spectra in Figures 4 and 5. The UO_2, UO, and product bands at 801.5, 804.5, 852.6, 870.9, and 874.0 cm^{-1} were unshifted. The broad 847-cm^{-1} band was shifted to 844 cm^{-1}. The band at 1893.4 cm^{-1} shifted to 1851.1 cm^{-1}, while the 2011.7 cm^{-1} band was found at 1964.7 cm^{-1}. The CO fundamental shifted to 2091.5 cm^{-1}.

Two experiments were also conducted where $C^{18}O_2$ was used, and the resultant product band positions are listed in Table I. UO_2 exhibited a shifted counterpart at 737.0 cm^{-1} as well as an unshifted absorption at 775.5 cm^{-1}. $U^{18}O$ appeared at 775.0 cm^{-1}. The 801.5 cm^{-1} band shifted to 759.0 cm^{-1}, and the 804.4 cm^{-1} band shifted to 761.9 cm^{-1}. The broad band at 847 cm^{-1} was displaced to 802 cm^{-1}. The sharp 870.9- and 874-cm^{-1} bands were shifted to 827.5 and 830.5 cm^{-1}, respectively. In the CO region, new bands appear at 1849.8 and 1964.5 cm^{-1} along with $C^{18}O$.

Several experiments were also conducted where 600:1:1 mixture of argon, $C^{18}O_2$, and $C^{16}O_2$ were reacted with the uranium atoms. There were no new bands observed in these mixed reactions. When $C^{16}O^{18}O$ was employed in mixtures with $C^{18}O_2$ and $C^{16}O_2$, new intermediate bands were observed at 855.0 and 1993.0 cm^{-1} as shown in Figures 4c and 5c.

Discussion

Evidence will be presented for the assignment of product bands to five new $U_xC_yO_z$ molecules. The UO_2CO product is formed in both U + CO and U + CO_2 reactions. The products CUO and CU(O)CO are formed only in U + CO experiments, while OUCO and OUC(O)CO are produced only in U + CO_2 reactions.

UO_2CO. The bands at 870.9 and 1893.4 cm^{-1}, present in all experiments, are assigned to a UO_2CO product molecule. These bands follow each other on photolysis and annealing in the U + CO and U + CO_2 experiments. Additionally, the band at 870.9 cm^{-1} and the shoulder at 874.0 cm^{-1} show no ^{13}C shift in either the carbon monoxide or carbon dioxide experiments but do show an ^{18}O shift similar to that observed for UO_2.[15,19] This indicates that the product molecule exhibits an OUO antisymmetric stretching mode that is independent of any carbon participation. The 1893.4-cm^{-1} band shows isotopic shifts (16/18 ratio 1.0235 and 12/13 ratio 1.0229) similar to those for an independent CO molecule (16/18 ratio 1.0244 and 12/13 ratio 1.0224). This suggests that UO_2 molecules scavenge CO molecules to form a new product, $UO_2(CO)$, which is demonstrated in the CO experiments where UO_2 diminished by 50% on annealing while bands at 870.9, 874.0, and 1893.4 cm^{-1} increased by 60–80%. Also, when the amount of UO_2 present in the sample is small, the bands assigned to UO_2CO are weak.

The UO_2CO species absorbing at 870.9 cm^{-1} is reminiscent of $UO_2(O_2)$, $UO_2(NO)$, and $UO_2(N_2)$ absorbing in the 880–892-cm^{-1} region. In these molecules, charge transfer was suggested to give $(UO_2)^+(\text{anion})^-$ pairs in the matrix.[15,21] Since the electron affinity of CO is also probably small like O_2, the UO_2CO species may have $(UO)_2^+(CO)^-$ charge-transfer character as well.

$$UO_2 + CO \rightarrow UO_2(CO) \qquad (1)$$

In the U + CO_2 experiments, there are two mechanisms whereby the small yield of UO_2CO may be formed. First, vibrationally excited UO formed by the U + CO_2 abstraction reaction may insert directly into a CO_2 molecule; recall that the UO reaction product is formed on sample codeposition. This leads to the second mechanism where U + CO_2 reaction gives UO + CO and provides CO for reaction with UO_2 as described above.

CUO. The bands at 852.6 and 804.4 cm^{-1} in the U + CO reactions are assigned to the CUO molecule on the basis of the following evidence. First is the fact that these two bands exhibit a similar growth behavior upon broad-band photolysis as well as a decrease on annealing. Second, isotopic shifts for these bands are in accord with shifts from vibrational analysis for a linear CUO molecule. In fact, FG matrix calculations, shown in Table II, reveal that calculated absorption frequencies for isotopic shifts fit with observed shifts within two wavenumbers. The small

TABLE II: FG Matrix Calculated and Observed Infrared Absorption Band Positions for Isotopes of CUO[a]

calculated (cm^{-1})		observed (cm^{-1})
	$^{12}CU^{16}O$	
853.7		852.6
802.9		804.4
	$^{13}CU^{16}O$	
837.7		837.1
787.6		788.9
	$^{12}CU^{18}O$	
845.7		844.8
767.0		768.7

[a] Potential function F_{CU} = 4.63 mdyn/Å, F_{UO} = 6.00 mdyn/Å, and $F_{CU,UO}$ = 0.02 mdyn/Å.

interaction force constant indicates that only the two stretching mode force constants for CUO adequately reproduce the observed isotopic shifts.

The F_{UO} force constant for UCO (6.00 mdyn/Å) is near the value calculated for UO diatomic (5.93 mdyn/Å), but it is larger than the value for F_{UO} in UO_2 (5.26 mdyn/Å). It is interesting to compare the stretch–stretch interaction force constants for CUO (0.02 mdyn/Å) and UO_2 (0.26 mdyn/Å); both are relatively small, reflecting U impedance to vibrational coupling.

Ab initio pseudopotential calculations were performed on the CUO system.[22] The theoretical results yielded 899- and 1185-cm^{-1} predictions for the 788.9- and 837.1-cm^{-1} bands of ^{13}CUO. The observed/calculated ratios of 0.72 and 0.89 are reasonable for this heavy molecule. While these calculations alone are not conclusive, the total evidence supports this assignment.

The activation energy required to insert into the CO bond is substantial, but it can be provided by the excess kinetic energy the uranium atoms possess after laser ablation.

$$U + CO \rightarrow CUO \qquad (2)$$

Recall that CUO was also increased by mercury arc photolysis as was the analogous NUN molecule, which was produced in a similar reaction of U + N_2.[16]

Another process whereby these insertion reactions can take place is an ionization mechanism. Uranium ions must certainly be formed during laser ablation, and they could arrive at the matrix surface and in principle react with CO or CO_2 to form products. However, such charged products are unlikely to survive, considering the fact that corresponding electrons are ejected during ionization and arrive at the matrix surface first. These electrons then diffuse freely in the matrix, very quickly neutralize any uranium cations, and produce highly reactive excited atoms in the matrix. Additionally, no spectroscopic evidence for the formation of charged-product molecules was found in this investigation.

Several experiments were also conducted where uranium powder and graphite powder were pressed to form a pellet as described previously for boron and graphite.[23] Laser ablation of this pellet and subsequent trapping of the resultant vapors in an argon matrix yielded well-known carbon clusters and bands attributed to UO and UO_2 as impurities. The only product bands evident in the spectra were those for CUO found at 852.6 and 808.4 cm^{-1}. There was very little CO impurity evident in the spectra. The only feasible mechanism for CUO formation in these experiments is the abstraction of a carbon atom from carbon clusters as shown in eq 3.

$$C_n + UO \rightarrow C_{n-1} + CUO \qquad (3)$$

This observation of CUO exemplifies the strength of the uranium–carbon bond and underscores the stability of this species in the carbon–uranium–oxygen system.

OUCO. Bands at 804.4 and 1799.6 cm^{-1} are assigned to the insertion product OUCO. These bands, in the U + CO_2 reaction, decrease slightly on photolysis and markedly on annealing. The band at 804.4 cm^{-1} exhibits a mixed-oxygen isotopic doublet characteristic of the vibration of a single O atom and a 16/18 ratio of 1.0558 that is almost identical to that of UO (1.0571). In addition, no ^{13}C shift was observed for the 804.4-cm^{-1} band. On the other hand, the associated 1799.6-cm^{-1} band was a doublet in scrambled $C^{16,18}O_2$ experiments and exhibited isotopic ratios (16/18 ratio 1.0242 and 12/13 ratio 1.0231) near the values for CO, which is clearly indicative of the vibration of an isolated CO subgroup. Therefore, the 804.4- and 1799.6-cm^{-1} bands are assigned to OUCO.

The OUCO molecule is formed by insertion of a hyperthermal U atom into CO_2 during formation of the matrix.

$$U + CO_2 \rightarrow OUCO \qquad (4)$$

Comparison with the analogous OBCO molecule is of interest. The CO stretching fundamental of OBCO, 1863 cm^{-1}, is slightly higher owing in part to coupling between CO and BO stretching motions.[24] In addition, there is less charge transfer from OB to CO as compared to that from OU to CO.

OCU(O)CO. In the U + CO_2 experiments, the 2011.7- and 801.5-cm^{-1} bands sharpen on annealing and decrease on photolysis. The 801.5-cm^{-1} band exhibits no ^{13}C shift and a 16/18 ratio (1.0560) near that of UO so a terminal UO is again indicated. The 2011.7-cm^{-1} band exhibits isotopic ratios (16/18 ratio 1.0240 and 12/13 ratio 1.0239) appropriate for a terminal CO vibration. However, the scrambled $C^{16,18}O_2$ experiment revealed a sharp mixed isotopic component at 1993.0 cm^{-1}. This indicates the involvement of two equivalent CO subgroups. The molecule is thus identified as the product of the reaction of CO with OUCO.

$$OUCO + CO \rightarrow OCU(O)CO \qquad (5)$$

The linear CUC skeleton is preferred for coupling of the two equivalent CO oscillators. The uncoupled UO vibration at 801 cm^{-1} is slightly higher than the 746-cm^{-1} value for the uncoupled UO vibration in the T-shaped UO_3 molecule.[25] Perhaps O in the linear OUO subgroup in UO_3 donates less electron density to the third O atom than what might be present in the OCUCO subgroup, which is reasonable in view of the electron-donating character of CO.

CU(O)CO. The band at 2027.8 cm^{-1} is identified as a secondary reaction product of CUO and CO on the basis of Ar/CO concentration dependence. This band is assigned to an asymmetric CU(O)CO molecule from $^{12}CO/^{13}CO$ experiments which yielded a 4:2:2:1 relative intensity quartet indicating two inequivalent carbons. The isotopic shift for carbon is too large, 63.7 cm^{-1}, for a CO fundamental vibration of one CO subunit so coupling with a second carbon atom is required. Furthermore, in the mixed $C^{16}{}^{18}O$ experiment, only two bands were observed with a relatively small (19.5 cm^{-1}) shift, indicating less oxygen participation than that in a CO fundamental vibration.

The straightforward reaction of a second CO molecule is

$$CUO + CO \rightarrow CU(O)CO \qquad (6)$$

Since the product was increased by photolysis and decreased by annealing, some activation energy is required. The isotopic data are best explained by a linear CUCO group that couples a CO vibration with another C atom. The remaining O is bonded to U. Therefore, a rearrangement of the reagent CUO to give the CU(O)CO product is required.

Aggregate Formation. There is evidence that product aggregates are also formed in the U + CO_2 experiments. The bands at 1870 and 847 cm^{-1} are broad bands that grow substantially on annealing. These bands also exhibit isotopic shifts that are comparable to those observed for other CO + UO product bands. The increase on photolysis at the expense of OUCO suggests some combination of OUCO and CO_2.

Uranium Carbonyls. Bands that grow in after annealing of the matrix in the U + CO experiments were previously assigned by Slater *et al.*[14] to uranium carbonyls. The tentative assignments for $U(CO)_{1-6}$ were made without the benefit of isotopic substitution. The 1893-cm^{-1} band has been reassigned here to UO_2CO, and weak bands in the mid-1800-cm^{-1} region are not sufficiently well-defined for confident identification. The major bands between 1904 and 1967 cm^{-1} are clearly due to uranium carbonyls, but any attempt to identify them further would be tenuous.

An interesting part of this investigation is that uranium carbonyls were not produced on reagent codeposition using thermal and pulsed laser evaporated U atoms but the carbonyls were formed on annealing the argon matrices to 15–30 K. The major product upon the reaction of energetic U atoms with CO is the insertion product CUO and not the monocarbonyl U(CO). Likewise, the major secondary product is CU(O)CO and not the dicarbonyl $U(CO)_2$. The previous workers also observed 1893.4- and 2027.5-cm^{-1} bands on sample deposition,[14] which are due to the reaction products identified here. It is certainly expected that UO_2 was present in the earlier work. Furthermore, the reaction of U + 2CO to give CU(O)CO as described here could proceed with 2000 K uranium atoms. Unfortunately, the possible presence of CUO in the thermally prepared samples[14] could not be determined. It is suggested that monocarbonyls and dicarbonyls of uranium are unstable with respect to the present reaction products but the higher carbonyls are stable. Photolysis, however, decreases the carbonyl bands in favor of the CUO and CU(O)CO species in accord with their greater stability.

Conclusions

Pulsed laser evaporated U atoms are sufficiently energetic to insert into molecular CO and CO_2 upon condensation with excess argon. Each molecule has been identified through ^{13}C and ^{18}O substitution in two vibrational fundamentals. The UO_2 molecule, present in these experiments, also reacts readily with CO to form UO_2CO. Two secondary reaction products, CU(O)CO and OCU(O)CO, have also been identified. It is clear that energetic uranium atoms and uranium oxides are reactive with CO and CO_2 and that matrix infrared spectroscopy provides new information on the uranium–oxycarbonyl system.

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