Matrix Infrared Spectra and Density Functional Calculations of ScCO, $ScCO^-$, and $ScCO^+$

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Laser-ablated Sc atoms and ions react with CO molecules to give primarily the ScCO, $ScCO^-$, and $ScCO^+$ products, which have been isolated in solid argon and/or neon matrices. Based on isotopic substitution as well as density functional calculations, absorptions at 1834.2 cm^{-1} in argon and 1851.4 cm^{-1} in neon are assigned to C−O stretching vibrations of the ScCO molecule, 1923.5 cm^{-1} in argon and 1962.4 cm^{-1} in neon to the $ScCO^+$ cation, and 1732.0 cm^{-1} in neon to the $ScCO^-$ anion, respectively. Higher carbonyls $Sc(CO)_{2,3,4}$ and $Sc(CO)^+{}_{2,3}$ are also produced on annealing. Similar argon matrix experiments with Y give YCO and YCO^+.

Introduction

The bonding of carbon monoxide with transition metals is of great interest because of the importance of metal carbonyls in catalytic processes.[1] Most first-row transition metal carbonyls have been studied both experimentally[2−13] and theoretically.[14−18] In these cases, the carbonyls were produced by thermal metal atom reactions with CO or photodissociation of the stable saturated carbonyl compound in inert matrices and characterized by infrared or electron spin resonance spectroscopy.[2−9] Several carbonyls have also been observed in the gas phase and their binding energies measured.[10−13] Compared to other first-row transition metal carbonyls, there is relatively little work on scandium carbonyls. However, ScCO, $Sc(CO)_2$, and their cations have been studied theoretically using a variety of computational methods.[14−22] The only experimental work is an infrared and electron spin resonance spectroscopic investigation of ScCO in solid argon.[9,23] A broad band at 1950 cm^{-1} was tentatively assigned to the ScCO molecule; however, this assignment does not agree with recent theoretical calculations.[16,17] The lack of experimental data on the lower scandium carbonyls and the discrepancy between experiment and theory for ScCO prompted this investigation with CO using laser-ablated Sc atoms, cations, and electrons.

Recent studies in this laboratory have shown that laser ablation is an effective method for producing reactive metal atoms for chemical reactions during condensation in excess argon. Compared to thermal metal atom reactions, cation and anions can be produced and trapped using the laser-ablation technique.[24−26] We will show that the previous assignment to ScCO in solid argon is incorrect, and a new assignment will made via isotopic substitution and DFT calculations. In addition, the new ions $ScCO^+$ and $ScCO^-$ and the $Sc(CO)_{2,3,4}$ molecules will also be identified here.

Experimental Section

The experiment for laser ablation and matrix isolation spectroscopy has been described in detail previously.[26,27] Briefly, the Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate with 10 ns pulse width) was focused on the rotating scandium metal target(Johnson Matthey, lump, 99.9%) using low energy (1−5 mJ/pulse). Laser-ablated metal atoms were co-deposited with carbon monoxide (0.05−0.5%) in excess argon or neon onto a 10 or 4 K CsI cryogenic window at 2−4 mmol/h for 1−2 h. Carbon monoxide (Matheson) and isotopic $^{13}C^{16}O$ and $^{12}C^{18}O$ (Cambridge Isotopic Laboratories) and selected mixtures were used in different experiments. FTIR spectra were recorded at 0.5 cm^{-1} resolution on a Nicolet 750 spectrometer with 0.1 cm^{-1} accuracy using a HgCdTe detector. Matrix samples were annealed at different temperatures, and selected samples were subjected to broadband photolysis by a medium-pressure mercury arc (Philips, 175 W) with the globe removed.

Results

Infrared spectra for new scandium carbonyl species in argon and neon matrices and density functional calculations for scandium carbonyls will be presented.

Sc + CO/Ar. Experiments were done using different CO concentrations and ablation laser energies. Figure 1 shows infrared spectra with 0.5% CO in argon on a 10 K CsI substrate using lower laser power, and the absorptions are listed in Table 1. Spectra after deposition exhibited a sharp new band at 1834.2 cm^{-1} and weak bands at 1716.3, 1794.7, 1873.6 and 1923.5 cm^{-1}. Annealing to 25 K decreased the 1834.2 cm^{-1} band, increased the later bands, and produced major bands at 1822.2, 1865.4, and 1968.0 cm^{-1}. Broadband photolysis with a 470 nm long wavelength pass filter destroyed the 1716.3 and 1851.4 cm^{-1} bands and produced a new 1775.6 cm^{-1} band, while final annealing reversed the situation. Further annealing to 35 K decreased the 1834.2 cm^{-1} band, increased the 1716.3, 1851.4, and 1923.5 cm^{-1} absorptions, and markedly increased the 1822.2, 1865.4, and 1968,0 cm^{-1} bands. Experiments were also done using $^{13}C^{16}O$ and $^{12}C^{18}O$ isotopic samples, including annealing and photolysis, and the frequencies are given in Table 1. Figure 2 shows spectra with a mixed $^{12}C^{16}O + {}^{13}C^{16}O$ sample.

Sc + CO/Ne. Experiments were done using 0.3, 0.1, and 0.05% CO concentrations in neon on a 4 K cryogenic window. Figure 3 shows the spectra with 0.1% CO in neon using lower laser power, and the absorptions are listed in Table 2. Sample deposition reveals the $(CO)_2^-$ absorption at 1517.6 cm^{-1} (not shown), weak $(CO)_2^+$ absorption at 2056.2 cm^{-1},[28] and new bands at 1962.4, 1926.0, and 1732.0 cm^{-1}. Annealing to 6 K slightly increased the 1962.4 and 1926.0 cm^{-1} bands and the $(CO)_2^+$ absorption at 2056.2 cm^{-1}, and decreased the $(CO)_2^-$ absorption at 1517.6 cm^{-1}, while the 1732.0 cm^{-1} band

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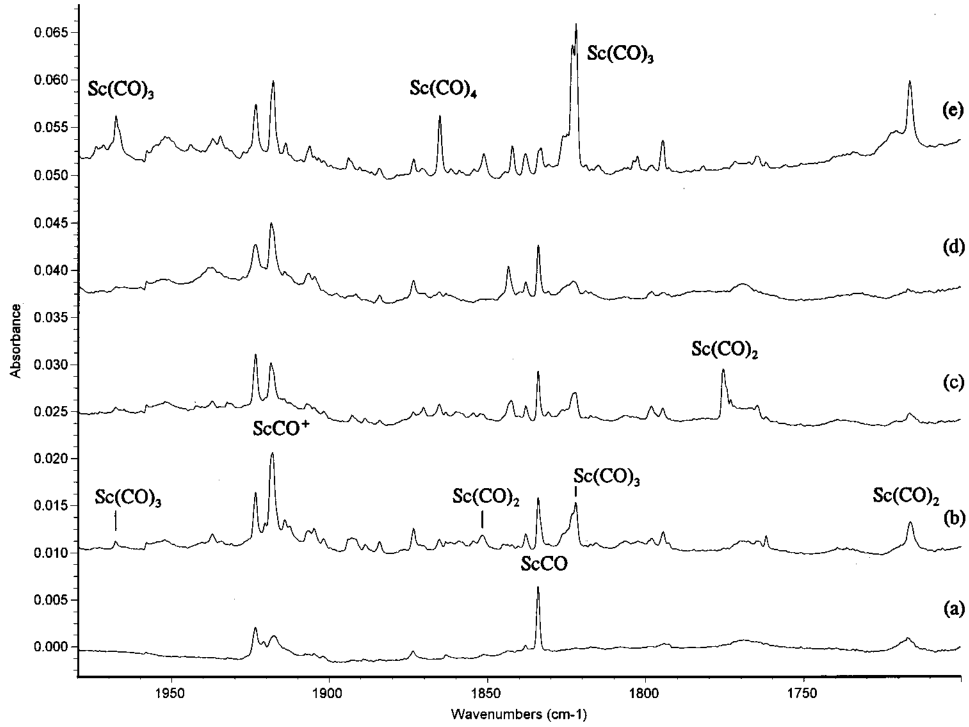

Figure 1. Infrared spectra in the 1980−1700 cm^{-1} region for laser-ablated Sc atoms co-deposited with 0.5%CO in excess argon: (a) after 1 h sample deposition at 10 K, (b) after annealing to 25 K, (c) after 20 min $\lambda > 470$ nm photolysis, (d) after 20 min full-arc photolysis, and (e) after annealing to 35 K.

TABLE 1: Infrared Absorptions (cm^{-1}) from Laser-Ablated Sc Co-deposited with CO in Excess Argon at 10 K

$^{12}C^{16}O$	$^{13}C^{16}O$	$^{12}C^{18}O$	$^{12}C^{16}O + {}^{13}C^{16}O$	$^{12}C^{16}O + {}^{12}C^{18}O$	*R*(12/13)	*R*(16/18)	assignment
2138.2	2091.0	2087.1	2138.2, 2091.0	2138.2, 2087.1	1.02257	1.02448	CO
1968.0	1923.6	1923.2	1968.0, 1955.5, 1941.4, 1923.5	1968.0, 1955.6, 1941.5, 1923.2	1.02308	1.02329	$Sc(CO)_3$
1923.5	1880.7	1879.0	1923.5, 1880.6	1923.5, 1878.9	1.02276	1.02368	$ScCO^+$
1918.4	1877.6	1873.6			1.02172	1.02391	$ScCO^+$ site
1906.4	1865.3	1860.2			1.02203	1.02484	$Sc_x(CO)_y$
1891.7	1851.1	1845.6			1.02193	1.02498	$Sc_x(CO)_y$
1870.4	1829.7	1825.6			1.02224	1.02454	$Sc_x(CO)_y$
1865.4	1824.8	1820.6			1.02225	1.02461	$(Sc(CO)_4)$
1851.4	1809.4	1808.6			1.02321	1.02366	$Sc(CO)_2$ bent
1842.4	1801.0	1800.1			1.02299	1.02350	ScCO site
1838.1	1796.8	1796.4			1.02299	1.02321	ScCO site
1834.2	1792.9	1792.3	1834.2, 1792.9	1834.2, 1792.3	1.02304	1.02338	ScCO
1823.2	1783.4	1779.9	1823.2, 1806.9, 1794.2, 1783.3	1823.1, 1805.5, 1791.7, 1779.8	1.02232	1.02433	$Sc(CO)_3$ site
1822.2	1782.3	1778.8	1822.2, 1805.8, 1793.1, 1782.3	1822.2, 1804.5, 1790.7, 1778.8	1.02239	1.02440	$Sc(CO)_3$
1798.3	1758.9	1756.0			1.02240	1.02409	$(Sc_2(CO)_2)$
1794.5	1756.0	1751.4			1.02192	1.02461	site
1775.5	1736.2	1734.3	1775.5, 1751.6, 1736.0	1775.5, 1750.8, 1734.1	1.02264	1.02376	$Sc(CO)_2$ linear
1764.1	1725.1	1723.1	1764.2, 1740.6, 1724.8	1764.3, 1739.7,1722.9	1.02261	1.02379	$Sc(CO_2)$ site
1762.1	1722.8	1721.0	1762.1, 1738.4, 1722.9	1762.1, 1737.5, 1721.1	1.02281	1.02388	$Sc(CO)_2$ site
1716.3	1679.1	1675.8	1716.2, 1694.6, 1678.9	1716.4, 1693.1, 1676.0	1.02215	1.02417	$Sc(CO)_2$ bent

remained the same. Mercury arc photolysis using $\lambda > 470$ nm radiation decreased the $(CO)_2^-$ 1732.0 and 1926.0 cm^{-1} bands, and produced a new band at 1884.5 cm^{-1}. Full-arc photolysis destroyed the 2056.2 and 1732.0 cm^{-1} bands, decreased the 1962.4 cm^{-1} band, and increased the 1926.0 and 1884.5 cm^{-1} bands. A final 8 K annealing increased the latter bands. Isotopic counterpart absorptions using $^{13}C^{16}O$ and $^{12}C^{18}O$ reagents are also listed in Table 2. Figure 4b shows the spectra of mixed $^{12}C^{16}O + {}^{13}C^{16}O$ experiments where doublets were observed for the 1962.4 and 1732.0 cm^{-1} bands.

CCl_4 Doping. Experiments were done with different concentrations of CCl_4 added to serve as an electron trap in both argon and neon matrices. In argon all the product absorptions exhibited in Figure 1 were also observed with CCl_4; however, the relative intensities were reversed, and the 1923.5 cm^{-1} band became the dominant feature on deposition instead of the 1834.2 cm^{-1} band. Using the same experimental conditions, the initial spectra of deposited samples without CCl_4 and with CCl_4 added are shown in Figure 4 for neon samples. Doping with CCl_4 totally eliminated the 1732.0 cm^{-1} absorption (Figure 4c) and the 1517.6 cm^{-1} $(CO)_2^-$ band (not shown), revealed a new absorption at 1851.4 cm^{-1}, and enhanced the 1962.4 cm^{-1} band *7-fold* compared to the spectrum without CCl_4 doping (Figure 4a). The 1851.4 cm^{-1} band also shows a doublet in the mixed $^{12}C^{16}O + {}^{13}C^{16}O$ spectrum with CCl_4 added (Figure 4d).

Y + CO/Ar. Laser-ablated Y atoms and ions co-deposited with CO in excess argon produced absorptions at 1909.4, 1903.6, and 1893.3 cm^{-1} and a weak doublet at 1874.1, 1869.0 cm^{-1} (trace a in Figure 5). A similar experiment doping with 0.1% CCl_4 had little effect on the 1909.4, 1903.6, and 1893.3 cm^{-1} bands, but greatly intensified the 1874.1, 1869.0 cm^{-1} doublet as shown in trace b of Figure 5. These bands shifted to 1866.7,

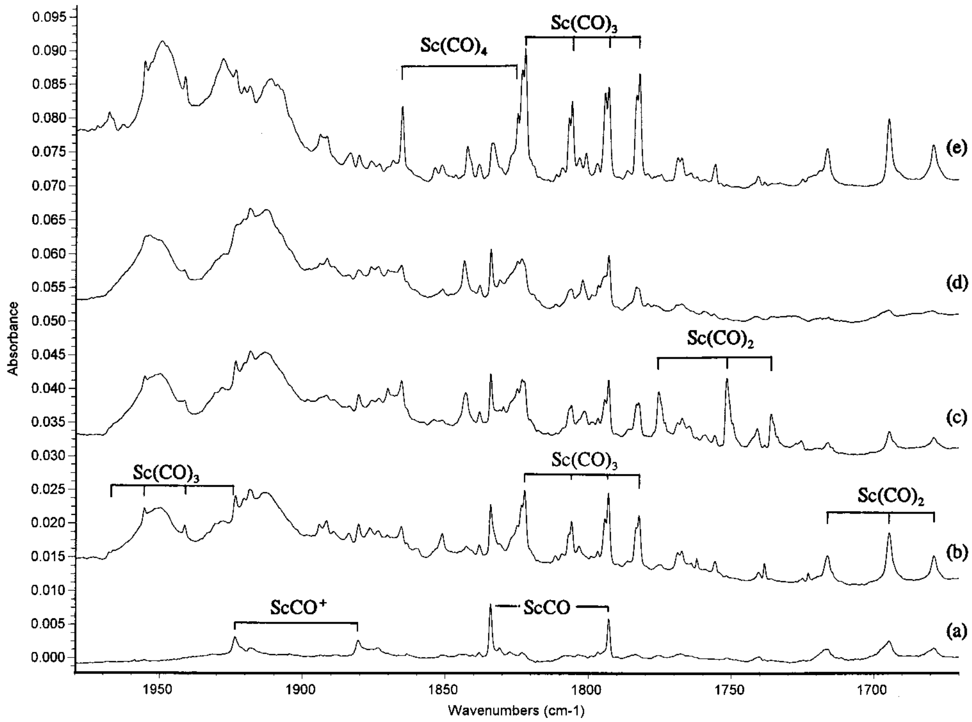

Figure 2. Infrared spectra in the 1980−1670 cm^{-1} region for laser-ablated Sc atoms co-deposited with 0.25% $^{12}C^{16}O$ + 0.25% $^{13}C^{16}O$ in excess argon: (a) after 1 h sample deposition at 10 K, (b) after annealing to 25 K, (c) after 20 min λ > 470 nm photolysis, (d) after 20 min full-arc photolysis, and (e) after annealing to 35 K.

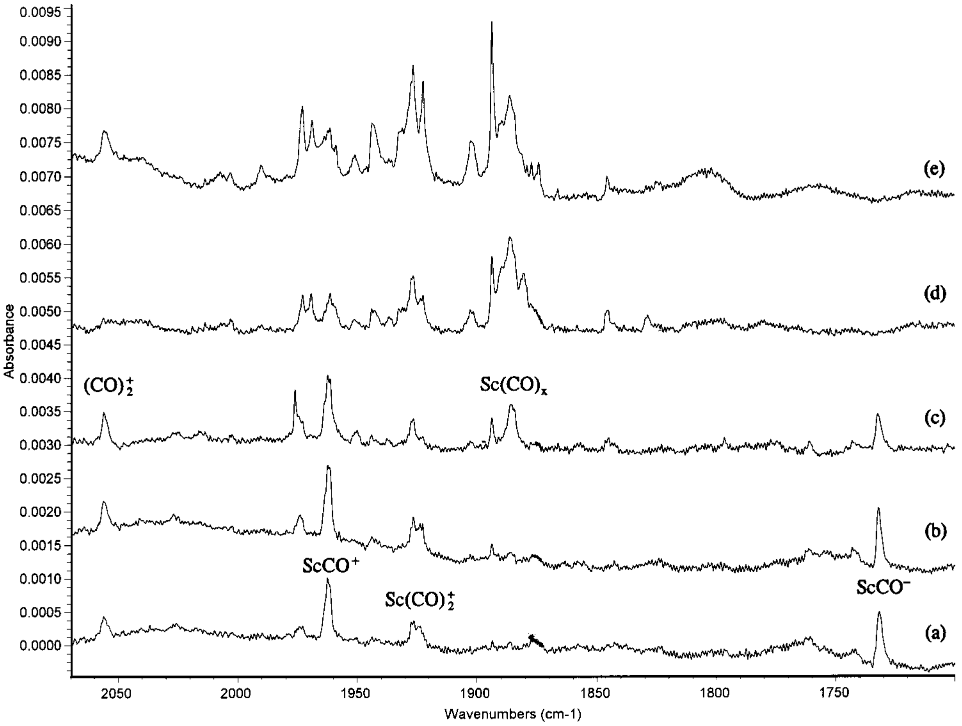

Figure 3. Infrared spectra in the 2070−1700 cm^{-1} region for laser-ablated Sc atoms co-deposited with 0.1% CO in excess neon: (a) after 45 min sample deposition at 4 K, (b) after annealing to 6 K, (c) after 20 min λ > 470 nm photolysis, (d) after 20 min full-arc photolysis, and (e) after annealing to 8 K.

1861.3, 1851.2, 1832.4, and 1827.7 cm^{-1} in the $^{13}C^{16}O$ spectrum as shown in trace d of Figure 5. The mixed $^{12}C^{16}O$ + $^{13}C^{16}O$ spectrum (trace c in Figure 5) shows doublets for all the absorptions.

Calculations. Density functional calculations were done for band identifications using the Gaussian 94 program.[29] The BP86 functional,[30] 6-311+G* basis sets for C and O atoms,[31] and the all-electron set of Wachters and Hay as modified by Gaussian 94 for scandium[32] were used. Calculations were performed on ScCO, ScCO$^-$ and ScCO$^+$, and the results are listed in Table 3. In agreement with previous calculations,[14−17,19,20] the ScCO complex has a $^4\Sigma^-$ ground state derived from $^1\Sigma^+$ CO and atomic Sc with the excited 3d^{2}4s^1 configuration (^{4}F); the $^2\Pi$ excited state, which correlates to ground state CO and

TABLE 2: Infrared Absorptions (cm^{-1}) from Laser-Ablated Sc Co-deposited with CO in Excess Neon at 10 K

$^{12}C^{16}O$	$^{13}C^{16}O$	$^{12}C^{18}O$	$^{12}C^{16}O + ^{13}C^{16}O$	*R*(12/13)	*R*(16/18)	assignment
2159.7	2112.5	2108.9		1.02234	1.02409	$(CO)_x$
2151.9	2104.5	2100.8		1.02252	1.02432	$(CO)_x$
2140.7	2093.6	2089.7	2140.7, 2093.6	1.02250	1.02441	CO
2056.2	2009.8	2033.9		1.02309	1.01096	$(CO)_2^+$
1974.2	1932.7	1924.6	1974.2, 1951, 1943.6, 1932.7	1.02147	1.02577	$Sc(CO)_3^+$
1962.4	1918.8	1916.4	1962.5, 1918.8	1.02272	1.02400	$ScCO^+$
1949.9		1904.8			1.02368	$Sc(CO)^+$ site
1943.6	1901.5	1897.3		1.02214	1.02440	$Sc_x(CO)_y$
1926.0	1884.7	1878.1	1926.0, 1898.9, 1884.6	1.02191	1.02550	$Sc(CO)_2^+$
1922.6	1881.7			1.02174		$Sc(CO)_2^+$ site
1902.2	1860.9	1856.2		1.02219	1.02478	$Sc_x(CO)_y$
1893.7	1852.6	1848.2		1.02219	1.02462	$Sc(CO)_x$
1884.5	1843.8	1839.9		1.02207	1.02424	$Sc(CO)_x$
1851.4	1809.8	1809.3	1851.4, 1809.8	1.02299	1.02327	ScCO
1845.1	1804.7	1801.4	1845.1, 1820.0, 1804.6	1.02239	1.02426	$(Sc_x(CO)_2)$
1732.0	1693.1	1692.9	1731.9, 1693.2	1.02298	1.02310	$ScCO^-$
1694.0						$(Sc(CO)_2^-)$
1517.6	1484.3	1481.2	1517.5, 1499.5, 1484.2	1.02243	1.02457	$(CO)_2^-$
1516.3	1482.9	1480.4	1516.2, 1498.1, 1482.9	1.02252	1.02425	$(CO)_2^-$ site

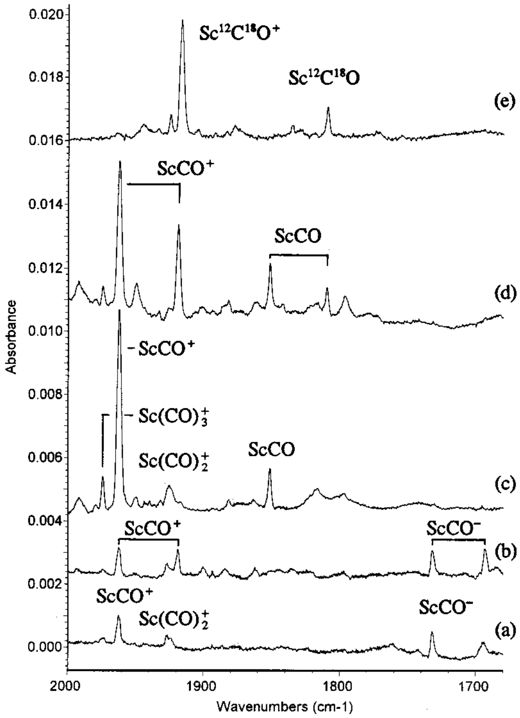

Figure 4. Infrared spectra in the 2000−1680 cm^{-1} region for laser-ablated Sc atoms co-deposited with different CO sample in excess neon after deposition: (a) 0.1% $^{12}C^{16}O$, (b) 0.075% $^{12}C^{16}O$ + 0.075% $^{13}C^{16}O$, (c) 0.1% $^{12}C^{16}O$ + 0.02% CCl_4, (d) 0.075% $^{12}C^{16}O$ + 0.075% $^{13}C^{16}O$ + 0.02% CCl_4, and (e) 0.1% $^{12}C^{18}O$ + 0.02% CCl_4.

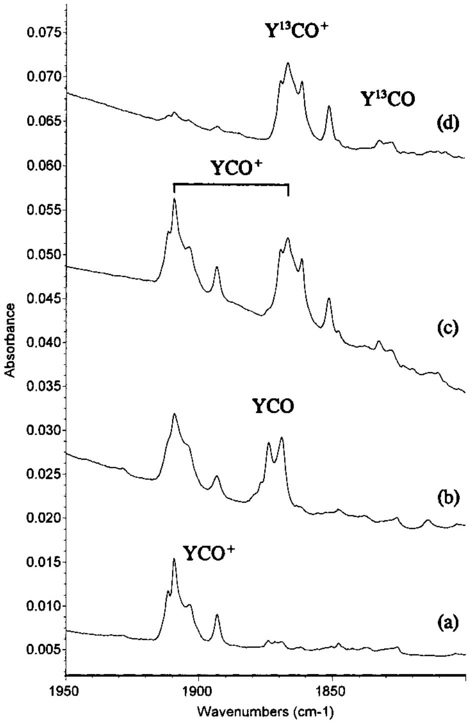

Figure 5. Infrared spectra in the 1950−1800 cm^{-1} region for laser-ablated Y atoms co-deposited with different CO sample in excess argon after deposition: (a) 0.5% $^{12}C^{16}O$, (b) 0.5% $^{12}C^{16}O$ + 0.05% CCl_4, (c) 0.3% $^{12}C^{16}O$ + 0.3%$^{13}C^{16}O$, and (d) 0.5% $^{13}C^{16}O$.

ground state (^2D) Sc atom, is 7.3 kcal/mol higher than the $^4\Sigma^-$ state. The Sc−C bond length (2.075 D) calculated for ground state ScCO is near those obtained by Barnes and Bauschlicher (2.149 D),[15] by Fournier (2.036 D),[16] and by Adamo and Lelj (2.082 D).[17] Both the ScCO$^-$ anion and ScCO$^+$ cation were calculated to have $^3\Sigma^-$ ground states, and the C−O bond length of the anion is longer than for the neutal ScCO molecule, while the cation bond length is shorter. Previous workers found $^3\Sigma^-$ to be the most strongly bound ScCO$^+$ state.[21]

Similar calculations were also done for the $Sc(CO)_2$ molecule, anion and cation, and the results are listed in Table 4. Barnes and Bauschlicher have reported calculations on the $Sc(CO)_2$ molecule with linear geometry, and two states, namely $^4\Sigma^-$ and $^2\Pi_g$, were found to be very close in energy.[15] Four states were converged in the present DFT calculations: these two linear states and two bent states, $^2B_1$ and $^4B_2$. All four of these states are very close in energy, and it is difficult to determine which is the ground state; hence, higher level calculations will be required to answer this question. Similar bent and linear structures were obtained for triplet $Sc(CO)_2^+$ and $Sc(CO)_2^-$ as listed in Table 4.

The $Sc(CO)_3$ molecule was calculated to have a $^4A_1$ ground state with C_{3v} symmetry, and a $^2A''$ state with C_s symmetry is 11.9 kcal/mol higher than the $^4A_1$ state. The calculated isotopic C−O stretching vibrational frequencies and intensities are listed in Table 5.

Discussion

Scandium carbonyl neutral, cation, and anion species will be identified from isotopic substitution and density functional calculations of expected products.

TABLE 3: Geometries, Relative Energies (kcal/mol), Vibrational Frequencies (cm^{-1}), Intensities (km/mol), and Isotopic Frequencies Calculated (BP86/6-311+G*) for ScCO, ScCO$^-$, and ScCO$^+$

molecule	relative energy	geometry	$^{12}C^{16}O$	$^{13}C^{16}O$	$^{12}C^{18}O$
ScCO ($^4\Sigma^-$)	0	Sc−C: 2.075 Å	1841.7(886)	1799.8(842)	1798.8(852)
		C−O: 1.181 Å	416.2(6)	411.9(6)	407.2(5)
		linear	275.1(2)	267.1(2)	271.6(2)
ScCO ($^2\Pi$)	+7.3	Sc−C: 2.068 Å	1832.8(852)	1790.9(810)	1790.2(817)
		C−O: 1.183 Å	424.3(3)	420.0(3)	415.1(3)
		linear	292.6(17)	284.0(16)	288.9(17)
			273.7(3)	265.7(2)	270.2(3)
ScCO$^-$ ($^3\Sigma^-$)	−25.8	Sc−C: 2.078 Å	1730.8(977)	1690.9(937)	1691.1(927)
		C−O: 1.200 Å	418.2(1)	414.0(1)	409.0(1)
		linear	276.2(4)	268.1(4)	272.7(4)
ScCO$^+$ ($^3\Sigma^-$)	+144.0	Sc−C: 2.090 Å	1976.4(502)	1931.7(475)	1929.7(485)
		C−O: 1.159 Å	403.2(0.2)	399.1(0.2)	394.6(0.1)
		linear	282.7(15)	274.5(14)	279.0(15)

TABLE 4: Calculated (BP86/6-311+G*) Geometries, Relative Energies (kcal/mol), C−O Vibrational Frequencies (cm^{-1}), and Intensities (km/mol) for Sc(CO)$_2$, Sc(CO)$_2^-$, and Sc(CO)$_2^+$

state	rel energy	geometry	antisym C−O	sym C−O
Sc(CO)$_2$($^2B_1$)	0	Sc−C: 2.082 Å, C−O: 1.177 Å ∠CScC: 66.5°, ∠ScCO: 178.3°	1808.0(790)	1838.7(2537)
Sc(CO)$_2$ ($^4B_2$)	+3.5	Sc−C: 2.116 Å, C−O: 1.177 Å ∠CScC: 85.7°, ∠ScCO: 179.2°	1830.2(1248)	1859.5(1072)
Sc(CO)$_2$($^4\Sigma_g^-$)	+3.8	Sc−C: 2.197 Å, C−O: 1.165 Å ∠CScC: 180°, ∠ScCO: 180°	1878.3(3471)	1967.3(0)
Sc(CO)$_2$($^2\Pi_g$)	+5.6	Sc−C: 2.126 Å, C−O: 1.182 Å ∠CScC: 180°, ∠ScCO: 180°	1795.5(3226)	1883.2(0)
Sc(CO)$_2^-$($^3\Pi_g$)	−17.6	Sc−C: 2.137 Å, C−O: 1.199 Å ∠CScC: 180°, ∠ScCO: 180°	1691.1(3091)	1776.7(0)
Sc(CO)$_2^-$($^3B_2$)	−25.5	Sc−C: 2.130 Å, C−O: 1.192 Å ∠CScC: 77.5°, ∠ScCO: 178.8°	1747.9(728)	1764.6(2218)
Sc(CO)$_2^+$($^3\Sigma_g^-$)	+142.6	Sc−C: 2.224 Å, C−O: 1.148 Å ∠CScC: 180°, ∠ScCO: 180°	2003.5(2426)	2074.5(0)
Sc(CO)$_2^+$($^3B_1$)	+142.8	Sc−C: 2.172 Å, C−O: 1.150 Å ∠CScC: 77.5°, ∠ScCO: 177.3°	1964.4(1199)	2051.8(263)

TABLE 5: Calculated C−O Isotopic Vibrational Frequencies (cm^{-1}) and Intensities (km/mol) for the $^4A_1$ Sc(CO)$_3$ Molecule and $^3A_1$ Sc(CO)$_3^+$ Cation

		$(^{12}C^{16}O)_3$	$(^{13}C^{16}O)_3$	$(^{12}C^{18}O)_3$
Sc(CO)$_3$[a]	antisym	1870.7(1539×2)	1828.5(1462×2)	1826.3(1478×2)
	sym	1954.6(338)	1909.8(323)	1909.3(323)
Sc(CO)$_3^+$[b]	antisym	2013.7(1688×2)	1969.6(1591×2)	1964.0(1639×2)
	sym	2099.9(68)	2052.3(65)	2050.4(66)

[a] Structure: C_{3v} symmetry, Sc−C: 2.152 Å,C−O: 1.168 Å, ∠CScC: 88.8°, ∠ScCO: 179.1°. [b] Structure: C_{3v} symmetry, Sc−C: 2.254 Å, C−O: 1.144 Å, ∠CScC: 104.8°, ∠ScCO: 179.9°.

ScCO. The prominent 1834.2 cm^{-1} band observed on deposition in all argon matrix experiments subsequently decreased on annealing but increased on photolysis. This band shifted to 1792.9 cm^{-1} in $^{13}C^{16}O$ and to 1792.3 cm^{-1} in $^{12}C^{18}O$ experiments. The 12-16/13-16 ratio 1.023 04 is higher than the diatomic CO ratio (1.022 57), while the 12-16/12-18 ratio 1.023 38 is lower than the corresponding diatomic CO ratio (1.024 48), which means more C and less O motion involvement in this mode. In both mixed $^{12}C^{16}O + {}^{13}C^{16}O$ and $^{12}C^{16}O + {}^{12}C^{18}O$ experiments, only pure isotopic counterparts were observed, which confirms that only one CO subunit is involved in this mode. This band is the major product band on deposition using very low laser power, so only one Sc atom is most likely involved, and hence, this band is assigned to the C−O stretching vibration of the ScCO molecule.

In the neon matrix experiments, no absorption was observed in the 1900−1800 cm^{-1} region on deposition; however, the experiments doping with 0.02% CCl$_4$ produced a sharp band at 1851.4 cm^{-1} after deposition. This band shifted to 1809.8 and 1809.3 cm^{-1} in $^{13}C^{16}O$ and $^{12}C^{18}O$ spectra, and the 12-16/13-16 ratio 1.022 99 and 12-16/12-18 ratio 1.023 27 are almost the same as the argon matrix values. In the mixed $^{12}C^{16}O + {}^{13}C^{16}O$ spectrum, only pure isotopic counterparts were observed. The 1851.4 cm^{-1} band must be the ScCO absorption in a neon matrix. Compared to the argon matrix, the ScCO absorption blue shifted 17.2 cm^{-1} in the neon matrix.

The ScCO assignment is strongly supported by DFT calculations. Earlier calculations found a quartet ground state[14−17] and Fournier[16] reported a C−O stretching vibration at 1916 cm^{-1}. Considering the scale factor, argon matrix effect, and anharmonicity, Fournier predicted the ScCO frequency in an argon matrix at 1834 cm^{-1}, in excellent agreement with our 1834.2 cm^{-1} observed value. The BP86/6-311+G* calculation employed here predicted a 1841.7 cm^{-1} harmonic frequency for ScCO, just 9.7 cm^{-1} lower than the neon matrix value and 7.5 cm^{-1} higher than observed argon matrix value. Of more importance is the excellent agreement between the calculated and observed isotopic frequency ratios: our calculation gave 1.023 28 for 12-16/13-16 and 1.023 85 for 12-16/12-18 ratios, while 1.022 99 and 1.023 04 were observed for 12−16/13−16 and 1.023 27 and 1.023 38 for 12-16/12-18 ratios in neon and argon matrices, respectively. Clearly part of the difference is due to anharmonicity in the observed frequencies. This indicates that DFT calculations predict a normal mode with unique C and O atomic participations that are matched to the observed spectrum. Note also the excellent agreement between ratios in solid argon and neon. Weltner et al.[9] tentatively assigned a broad 1950 cm^{-1} argon matrix band to the ScCO molecule; however, no absorption was observed in this region on deposition, and only a broad band appeared on higher temperature annealing, which might be due to a cluster species.

The ScCO molecule is probably formed by reaction 1 on deposition in argon with laser-ablated metastable Sc atoms, which are 1.43 eV above the ground state. It is noteworthy that the ScCO absorption *does not increase* on annealing as ground state Sc(^{2}D) apparently does not react with CO, although the reaction is exothermic by 4−9 kcal/mol based on calculations.[14–16]

$$\mathrm{Sc^*(^4F) + CO \rightarrow ScCO(^4\Sigma^-)} \tag{1}$$

YCO. The doublet at 1874.1 and 1869.0 cm^{-1} is assigned to YCO at different matrix sites. These bands show carbonyl isotopic ratios 1.0228 and 1.0226, and only doublets were observed in the mixed isotopic experiment. The YCO yield increased markedly in the CCl_4 doped experiment as did ScCO in neon matrix investigations at the expense of ScCO$^-$.

ScCO$^+$. The 1923.5 cm^{-1} band was also observed after deposition in an argon matrix, this band increased on 20 and 25 K annealing, decreased on photolysis, and slightly increased on 30 K annealing, but decreased on higher temperature annealing. In ^{13}C^{16}O and ^{12}C^{18}O experiments, this band shifted to 1880.7 and 1879.0 cm^{-1}. The 12-16/13-16 isotopic ratio 1.022 76 and 12-16/12-18 ratio 1.023 68 are slightly different from ScCO ratios, but still show more C and less O participation than the CO diatomic molecule. In the mixed ^{12}C^{16}O + ^{13}C^{16}O and ^{12}C^{16}O + ^{12}C^{18}O experiments, doublets with pure isotopic counterparts were observed, so only one CO subunit is involved in this mode. Again, this band was present on deposition using lower laser energy, and most likely one Sc atom is involved, so another species with the ScCO formula must be considered.

The relative yield of the 1923.5 cm^{-1} band is about one-fifth of the ScCO absorption at 1834.2 cm^{-1} in normal experiments; however, similar experiments doping with 0.1% CCl_4 changed the relative yield dramatically, and the 1923.5 cm^{-1} band is now almost 5 times more intense than the 1834.2 cm^{-1} band on deposition. This strongly suggests that the 1923.5 cm^{-1} band is due to the ScCO$^+$ cation.

The neon counterpart of the 1923.5 cm^{-1} band is observed at 1962.4 cm^{-1}, which was also present on deposition. The isotopic ratios (12-16/13-16: 1.022 62, 12-16/12-18: 1.023 84) are very close to the argon matrix values. This band was enhanced 6−8 times in CCl_4 doped experiments, which *aids the survival of cations by trapping electrons*. Furthermore, the larger 39 cm^{-1} Ar−Ne shift requires a stronger matrix interaction than for ScCO, which is appropriate for the ScCO$^+$ cation.

The ScCO$^+$ assignment is confirmed by DFT calculations. Our BP86/6-311+G* calculation predicted the $^3\Sigma^-$ ground state ScCO$^+$ cation to have a strong C−O stretching vibration at 1976.4 cm^{-1}, which is 13.9 and 52.9 cm^{-1} higher than the observed neon and argon values. The calculated isotopic ratios 1.023 14 (12-16/13-16) and 1.024 20 (12-16/12-18) are very close to the experimental observations, and of course, slightly different from the calculated ratios for ScCO. The larger red shift for ScCO$^+$ in the argon matrix suggests stronger interaction between ScCO$^+$ and the argon matrix, as has been observed for ScO$^+$.[33]

The ScCO$^+$ cation is produced by reaction 2a on deposition with laser-ablated Sc$^+$ cations in the (^{3}F) excited state, which is 0.56 eV above the ground (^{3}D) state. The ground state reaction is about 9−12 kcal/mol exothermic according to calculations.[21] This is a favorable process: the ScCO$^+$ absorption increased on annealing as the reaction is spin allowed. Note that ground state Sc$^+$(^{3}D) correlates with the $^3\Sigma^+$ excited state of ScCO$^+$, but the ^{3}F excited Sc$^+$ state, which can be produced by laser ablation, correlates with the $^3\Sigma^-$ ground state of ScCO$^+$.[21]

$$\mathrm{(Sc^+)^*(^3F) + CO \rightarrow ScCO^+(^3\Sigma^-)} \tag{2a}$$

$$\mathrm{Sc^+(^3D) + CO \rightarrow ScCO^+(^3\Sigma^+) \xrightarrow{relax} ScCO^+(^3\Sigma^-)} \tag{2b}$$

YCO$^+$. The bands at 1909.4, 1903.6, and 1893.3 cm^{-1} are assigned to YCO$^+$ in different argon matrix sites following the assignment of ScCO$^+$. Recall that these bands were favored by the addition of the CCl_4 electron-trapping molecule.

ScCO$^-$. In neon matrix experiments, a sharp band present at 1732.0 cm^{-1} on deposition, slightly decreased on annealing. This band shifted to 1693.1 and 1692.9 cm^{-1} using ^{13}C^{16}O and ^{12}C^{18}O reagents, and gave the 12-16/13-16 ratio 1.022 98 and 12-16/12-18 ratio 1.023 10. In the mixed ^{12}C^{16}O + ^{13}C^{16}O experiment, a doublet was observed, so another species with ScCO stoichiometry must be considered. This band decreased about 50% on mercury arc photolysis using $\lambda > 470$ nm, disappeared on full-arc photolysis, and did not return on higher temperature annealing. Furthermore, CCl_4 doping eliminated this band, in favor of ScCO, which strongly supports the ScCO$^-$ anion assignment. Our DFT calculation predicted the ScCO$^-$ anion to have a $^3\Sigma^-$ ground state, a strong C−O stretching vibration at 1730.8 cm^{-1}, and isotopic frequency ratios in excellent agreement with observed values.

The ScCO$^-$ anion is produced by reaction 3, and our DFT calculations suggest a 25.8 kcal/mol electron affinity for ScCO, although this energy must be viewed with caution. Note that neon matrices fail to preserve the ScCO absorption without CCl_4 doping (Figure 4), indicating that reaction 3 proceeds readily in a neon matrix, but added CCl_4 *captures electrons* and prevents reaction 3, which allows ScCO to survive the matrix deposition process.

$$\mathrm{ScCO + e^- \rightarrow ScCO^-} \tag{3}$$

All three species ScCO$^+$, ScCO and ScCO$^-$ are observed in the neon matrix, the ScCO$^-$ anion is 119.4 cm^{-1} lower than the neutral ScCO molecule, while the ScCO$^+$ cation is 111.0 cm^{-1} higher than neutral ScCO molecule, which is in line with DFT calculations. The role of added CCl_4 electron trap in these experiments is dramatically demonstrated in Figure 4. The preferential capture of ablated electrons by CCl_4 precludes the formation of ScCO$^-$, allows ScCO to be trapped, and enhances the yield of ScCO$^+$ and higher carbonyl cations. A similar result has been found for FeCO$^+$, FeCO, and FeCO$^-$ and for NiCO and NiCO$^-$ in solid argon.[34,35]

The active (σ) orbital in the ScCO$^+$, ScCO, and ScCO$^-$ series is mostly Sc (4s) in character. For ScCO($^4\Sigma^-$) the orbitals are ---$(\sigma)^1(\pi)^1(\pi)^1$, where ScCO$^+$($^3\Sigma^-$) is formed by removing the σ electron and ScCO$^-$ ($^3\Sigma^-$) results from adding another σ electron. The calculated Mulliken charges[29] for the cation, neutral, and anion follow:

$$\underset{\mathrm{ScCO^+}}{\overset{+1.11}{\mathrm{Sc}}-\overset{-0.03}{\mathrm{C}}-\overset{-0.08}{\mathrm{O}}} \qquad \underset{\mathrm{ScCO}}{\overset{+0.36}{\mathrm{Sc}}-\overset{-0.18}{\mathrm{C}}-\overset{-0.18}{\mathrm{O}}} \qquad \underset{\mathrm{ScCO^-}}{\overset{-0.33}{\mathrm{Sc}}-\overset{-0.40}{\mathrm{C}}-\overset{-0.27}{\mathrm{O}}}$$

The degenerate π orbitals are Sc−C bonding but C−O antibonding. Hence the flow of electron density to C−O results in a reduction of the C−O vibrational frequency as is observed in the series.

It is noted that $ScCO^-$ was observed here in solid neon but not solid argon. The less polarizable neon matrix appears more capable of resolving charges and trapping isolated cations and anions. This may be due to charge delocalization in the more polarizable argon matrix cage which leads to the decomposition of $ScCO^-$ in solid argon. In this regard, the yield of $(CO)_2^-$ was higher in solid neon than in solid argon, and $(CO)_2^+$ was observed here only in solid neon.[28,34,35]

$Sc(CO)_2^+$. The weak broad band at 1926.0 cm^{-1} in neon matrix spectra on deposition increased little on 6K but markedly on 8 K annealing. A triplet was observed in mixed $^{12}C^{16}O + {}^{13}C^{16}O$ experiments, which is suitable for $Sc(CO)_2^+$. Our DFT calculations predict the linear $^3\Sigma_g^-$ state and bent $^3B_1$ state $Sc(CO)_2^+$ to be very close in energy. The linear cation has a strong antisymmetric vibration calculated at 2003.5 cm^{-1} and the bent cation at 1964.4 cm^{-1}. Matrix interaction will favor the bent structure as it has a large dipole moment. Accordingly, the 1926.0 cm^{-1} band is assigned to bent $Sc(CO)_2^+$. The 1926.0 cm^{-1} absorption was slightly enhanced in CCl_4-doped experiments, although less than $ScCO^+$ (Figure 4), which is in accord with the cation identification.

$Sc(CO)_3^+$. The 1974.2 cm^{-1} band in neon experiments increases on annealing and is enhanced by the addition of CCl_4. The isotopic ratios are slightly different from $ScCO^+$ ratios. In mixed isotopic experiments, strong pure isotopic counterparts were observed along with one weaker intermediate component and one shoulder on another band, which is appropriate for a degenerate vibration.[36] This band is assigned to the $Sc(CO)_3^+$ cation. Our DFT calculation predicted a strong antisymmetric C−O stretching vibration at 2013.7 cm^{-1} for the $^3A_1$ state of $Sc(CO)_3^+$ cation.

$Sc(CO)_2$. The scandium dicarbonyl assignment is not as straightforward as ScCO. In a neon matrix, no obvious absorptions due to $Sc(CO)_2$ species are present. However, in an argon matrix, the 1716.3 cm^{-1} band was weak on deposition, but greatly increased on annealing at the expense of ScCO absorption (Figure 1). This band shifted to 1679.1 and 1675.8 cm^{-1} on using $^{13}C^{16}O$ and $^{12}C^{18}O$ samples; the 12-16/13-16 ratio 1.022 15 and 12-16/12-18 ratio 1.024 17 suggest that this band is a terminal C−O stretching mode. In both mixed $^{12}C^{16}O + {}^{13}C^{16}O$ and $^{12}C^{16}O + {}^{12}C^{18}O$ experiments, 1/2/1 triplets were observed, so two equivalent CO subunits are involved in this mode. A weak band at 1851.4 cm^{-1} tracks with the 1716.3 cm^{-1} band and shows slightly higher 12-16/13-16 ratio and lower 12-16/12-18 ratio; these two bands are suitable for antisymmetric and symmetric vibrations of a bent $Sc(CO)_2$ molecule.

The 1775.6 cm^{-1} band was observed only on $\lambda > 470$ nm photolysis when the 1716.3 and 1834.2 cm^{-1} bands decreased. This band decreased on annealing and vanished on full-arc photolysis. In the $^{13}C^{16}O$ and $^{12}C^{18}O$ spectra, this band shifted to 1736.2 and 1734.3 cm^{-1}, respectively, and the 12-16/13-16 ratio 1.022 64 and 12-16/12-18 ratio 1.023 76 characterize a terminal C−O stretching vibration. The clear 1/2/1 triplets were observed in both mixed $^{12}C^{16}O + {}^{13}C^{16}O$ and $^{12}C^{16}O + {}^{12}C^{18}O$ spectra suggest that two equivalent CO subunits participate in this mode.

As already mentioned, both doublet and quartet states of the bent and linear $Sc(CO)_2$ structures are calculated to be very close in energy. For the linear structure, the symmetric C−O stretching vibration is IR inactive, and only the antisymmetric C−O stretching vibration can be observed. For the bent geometry, both symmetric and antisymmetric vibrations have sufficient intensity to be observed. Note for both doublet and quartet, the antisymmetric vibrational frequency for the linear structures are slightly higher than for corresponding bent structures. These calculations suggest that the 1716.3 and 1851.4 cm^{-1} bands are probably due to $Sc(CO)_2$ with bent structure, while the 1775.6 cm^{-1} band is due to the linear molecule. As the bent molecule has a large dipole moment, the argon matrix solvent interaction made the bent molecule more stable than the linear molecule, but during visible light photolysis, the bent molecule can open to linear structure in the matrix cage. Similar results have been observed for the $Fe(CO)_2$ molecule, which is linear in the gas phase, while in the argon matrix, the bent structure is favored due to the matrix solvent interaction.[34]

The increase in bent $Sc(CO)_2$ on annealing follows a decrease in ScCO ($^4\Sigma^-$) which suggests that the bent $Sc(CO)_2$ species observed here is probably the quartet state.

$$ScCO(^4\Sigma^-) + CO \rightarrow Sc(CO)_2(^4B_2) \qquad (4)$$

$Sc(CO)_3$. In the argon matrix, the split band at 1822.2,1823.2 cm^{-1} was observed only on annealing. It decreased on photolysis and increased more on further annealing. In $^{13}C^{16}O$ and $^{12}C^{18}O$ spectra, it shifted to 1782.3, 1783.4 and 1778.8, 1779.9 cm^{-1}, respectively. The 12-16/13-16 ratio (1.0223) and 12-16/12-18 ratio (1.0243) also indicate a C−O stretching vibration. In both mixed $^{12}C^{16}O + {}^{13}C^{16}O$ and $^{12}C^{16}O + {}^{12}C^{18}O$ experiments, quartets with two weaker intermediate components were observed, which is appropriate for the degenerate stretching mode of a trigonal carbonyl species.[36] This split band can be assigned to the antisymmetric C−O vibration of the $Sc(CO)_3$ molecule at different matrix sites.

A weak absorption at 1968.0 cm^{-1} has the same behavior as the doublet at 1822.2,1823.2 cm^{-1}. It shifted to 1923.6 cm^{-1} in $^{13}C^{16}O$ spectra and to 1923.2 cm^{-1} in $^{12}C^{18}O$ spectra, which exhibit a higher 12-16/13-16 ratio (1.0231) and lower 12-16/12-18 ratio (1.0233) compared to the corresponding ratios of the 1822.2,1823.2 cm^{-1} doublet. In both mixed $^{12}C^{16}O + {}^{13}C^{16}O$ and $^{12}C^{16}O + {}^{12}C^{18}O$ experiments, quartets with 1/3/3/1 intensity distribution were produced. This band is appropriate for the nondegenerate symmetric C−O vibration of the $Sc(CO)_3$ molecule. The matrix site is less obvious and not resolved for this mode.

The present DFT calculations predict the $Sc(CO)_3$ molecule with a $^4A_1$ ground state and C_{3v} symmetry. The antisymmetric and symmetric C−O vibration were calculated at 1870.7 (1539 × 2 km/mol) and 1954.6 cm^{-1} (338 km/mol), which are in excellent agreement with the observed spectrum. The marked growth in $Sc(CO)_3$ and $Sc(CO)_2$ on final annealing at the expense of $^4\Sigma^-$ ScCO is in accord with quartet states for the higher carbonyls.

$Sc(CO)_4$. The 1865.4 cm^{-1} argon matrix absorption appeared only on higher temperature annealing after the $Sc(CO)_3$ bands. The isotopic 12-16/13-16 ratio (1.0223) and 12-16/12-18 ratio (1.0246) indicate a terminal C−O stretching vibration. In both mixed isotopic experiments, only pure isotopic bands and no intermediate components were observed, which is in accord with a degenerate vibrational mode.[36] This band is tentatively assigned to $Sc(CO)_4$.

Other Absorptions. In the neon matrix experiments, a 1884.8 cm^{-1} band produced on $\lambda > 470$ nm photolysis and a 1893.6 cm^{-1} band produced on annealing show carbonyl isotopic ratios, but the intermediate components of mixed isotopic spectra are not clear, so these bands can only be assigned to higher carbonyl species. The weaker, broader 1694.0 cm^{-1} band increased slightly on annealing at the expense of the 1732.0 cm^{-1} $ScCO^-$ band, decreased on $\lambda > 470$ nm photolysis, and vanished on full-arc photolysis with the 1732.0 cm^{-1} absorption. Both 1732.0 and 1694.0 cm^{-1} bands were eliminated with CCl_4 present (Figure 4). Unfortunately, the $^{13}C^{16}O$ and $^{12}C^{18}O$ counterparts could not be observed due to CO_2^- in the 1655−1665 cm^{-1} region. The 1694.0 cm^{-1} band is tentatively assigned to $Sc(CO)_2^-$; recall that dicarbonyl anions have been observed in this region for the Fe and Ni systems.[34,35]

The absorptions at 1798.3 and 1794.5 cm^{-1} appeared in solid argon on annealing, and these two bands also show C−O stretching isotopic ratios. In the mixed isotopic experiment, quartets with two close intermediate components were observed. These bands are tentatively assigned to the discandium dicarbonyl $Sc_2(CO)_2$ molecule. The quartet isotopic structure suggests that the two CO subunits are slightly different. Finally, several weak bands observed on annealing cannot be assigned and are listed in Table 1 as $Sc_x(CO)_y$.

Conclusions

Laser-ablated Sc atoms, cations, and electrons react with CO molecules to give primarily the ScCO, $ScCO^+$, and $ScCO^-$ products, which have been isolated in solid argon and neon matrices. On the basis of isotopic substitution as well as density functional calculations, absorptions at 1834.2 cm^{-1} in solid argon and 1851.4 cm^{-1} in solid neon are assigned to the C−O stretching vibration of the ScCO molecule, the higher bands at 1923.5 cm^{-1} in argon and 1962.4 cm^{-1} in neon to the $ScCO^+$ cation, and the lower 1732.0 cm^{-1} band in solid neon to the $ScCO^-$ anion, respectively. This relationship is a general trend among transition metal carbonyl cations, neutrals, and anions[18,34,35] as the increase in electrons from cation to anion increases electron density in π orbitals that are M−C bonding but C−O antibonding.

The larger argon-to-neon blue shift for $ScCO^+$ (39 cm^{-1}) than for ScCO (17 cm^{-1}) indicates a stronger matrix interaction for the cation. Higher carbonyls $Sc(CO)_{2-4}$ and $Sc(CO)^+_{2,3}$ are also produced on annealing where the neon matrix appears to preserve the charged species better than the argon matrix. In this regard $ScCO^-$ is trapped in solid neon but not in solid argon.

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