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Infrared Spectra of Beryllium Carbonyls from Reactions of Beryllium Atoms with Carbon Monoxide in Solid Argon

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Pulsed laser evaporated beryllium atoms have been reacted with Ar:CO gaseous mixtures during condensation onto a 10 K substrate. Identification of several novel beryllium carbonyls is made on the basis of further reactions on sample warming to 30 K, changes in relative Be/CO concentration, ^{13}CO and $C^{18}O$ isotopic substitution, and ab initio calculations at the SCF level using the 6-311G* basis sets. Although the triplet BeCO molecule has weak bonding character, it is less stable than Be + CO and cannot be formed on annealing in solid argon. The primary product infrared bands from the reaction of Be + CO during condensation are identified as BeBeCO and OCBeBeCO, which are decreased on broadband photolysis and also reproduced on annealing the matrix. Secondary product bands due to higher carbonyls grow strongly on annealing and are identified as the stable $Be(CO)_2$, $Be(CO)_3$, $BeBe(CO)_2$, $(OC)BeBe(CO)_2$, and $(OC)_2BeBe(CO)_2$ molecules. The former four new beryllium carbonyls are characterized by Be−C as well as C−O stretching fundamentals. It is clear that clustering of Be atoms and CO molecules leads to product formation in these experiments.

Introduction

The chemical reactivity of group 1 metal atoms with carbon monoxide has been investigated.[1,2] Lithium atoms were found to be reactive enough to form monolithium carbonyls after codepositing evaporated lithium atoms from a Knudsen cell with carbon monoxide in an argon matrix. Mercury and xenon arcs were used to initiate photochemical processes. In addition to the monometal carbonyls, evidence was also presented for metal cluster−carbonyl complexes. In contrast, Na and K formed metal cluster−carbonyl complexes which photolyzed to give new carbon−carbon-bonded species.

Group 2 metal atom reactions with carbon monoxide have not yet been conducted. In light of chemical reactivity trends for group 1 metals, the best hope for forming group 2 metal carbonyls lies with beryllium. The anomalous behavior of beryllium with respect to the other alkaline earth metals is of considerable interest.[3,4] Since the charge density of beryllium is very similar to that of aluminum, many chemical properties of beryllium are similar to those of aluminum. This relationship is many times referred to as the "diagonal relationship", based on the position of beryllium and aluminum in the periodic table. Aluminum reactions with carbon monoxide and carbon dioxide have been studied in several laboratories;[5−8] therefore, beryllium/carbon monoxide reactions are of interest. While beryllium carbonyls are known to exist on celestial objects,[9,10] very little is known about the nature of the reactivity of beryllium with carbon monoxide. Theoretically, beryllium carbonyls have been investigated in four studies.[11−14] First, Frenking et al. calculated that beryllium oxide forms a stable molecule in union with carbon monoxide. Later Broclawik found the lowest $^1\Sigma$ state of BeCO to be repulsive at all distances and the $^3\pi$ state to have weak bonding character but to be less stable than separated Be and CO.[12] In addition, Sunil predicted from HF and MP calculations that $Be(CO)_2$ and its dimer are stable molecules,[13,14] which suggest stronger binding to Be with increased coordination number.

For close examination of such reaction systems, the matrix isolation technique is well suited. Initial product molecules formed in the gas phase are trapped in a restricted diffusion environment so that spectroscopic techniques can be employed for characterization. Subsequent broadband photolysis and matrix annealings can then be carried out to form and characterize further reaction products.

Recent matrix infrared studies on boron, aluminum, and uranium atom reactions with O_2, CO, CO_2, and N_2 have demonstrated that Nd:YAG laser ablation is a clean and effective source of atomic vapor species.[15−22] The hyperthermal nature

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of pulsed laser evaporated atoms was necessary for many of these reactions to proceed. The primary purposes of this matrix study on beryllium atom reactions with carbon monoxide were to characterize the initial beryllium carbonyls formed and then examine higher carbonyls by annealing the samples to allow reagent aggregation. Reactions of beryllium atoms with H_2, O_2, N_2, and CO_2 have been investigated in this laboratory using the pulsed-laser ablation method.[23-26]

Experimental Section

A beryllium metal (Johnson Matthey, Lump, 99.5%) target was laser evaporated using a Quanta Ray DCR-11 Nd:YAG laser at 1064 nm in the Q switched mode with a 10 ns pulse duration as described previously;[15,16,23] laser power in the 50−80 mJ/pulse range at the sample was used. Beryllium atoms were codeposited with argon and CO, with CO dilutions ranging from 25:1 to 400:1, onto a CsI substrate at 10 K. The laser beam was focused to a spot about 0.1 mm in diameter by a lens (focal length of 10 cm) through a hole in the CsI window onto the metal target, which was rotated at 1 rpm. Carbon monoxide reagent gas (Matheson) and isotopically enriched samples (Cambridge Isotope Laboratories) were used as received. Infrared spectra (Nicolet Model 750 and 60) are averages of 500 scans with spectral resolution of 0.5 cm^{-1} with band position accuracy of ±0.1 cm^{-1}. A 175 W medium-pressure mercury arc lamp (Philips H39KB) with the globe removed (240−1000 nm) was used for broadband photolysis of the matrix samples. To promote higher carbonyl formation, the argon matrix was annealed to between 20 and 45 K and recooled to 10 K. IR spectra were recorded before and after sample deposition and after each photolysis and annealing cycle. The sequence of annealing and photolysis was interchanged in order to correlate product bands.

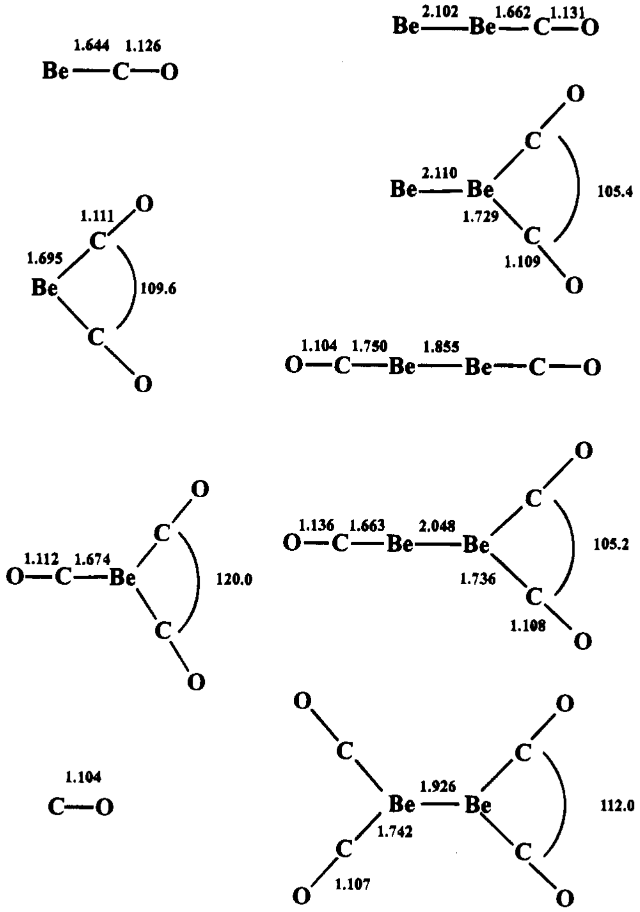
Theoretical Calculations

Theoretical investigations were carried out on the Be and CO system at the SCF level using 6-311G* (6d) basis sets in order to help identify the new product molecules. Triplet molecules required ROHF calculations. For some molecules CI and MBPT(2) level calculations were also performed. Optimized geometries were obtained by analytic first derivative methods, and harmonic vibrational frequencies were obtained using analytic second derivatives at the SCF level. The methods used are contained in the ACESII and PSI codes.[27,28]

Typically, theoretical vibrational frequencies must be scaled down to provide a match with experiment. For SCF frequencies, typical scale factors are about 0.90.[29] Carbon monoxide gave a 2434.8 cm^{-1} fundamentals and 1.104 Å bond length. The former scales by 0.878 to the matrix fundamental, and the latter is shorter by 0.024 Å than the equilibrium CO bond length. The SCF calculations are size consistent, allowing for direct comparison of dissociation energies.

The two simplest monocarbonyls triplet linear BeCO and BeBeCO were examined at the SCF level, and calculated frequencies (not scaled) and bond lengths are given in Table 3. Note that the C−O bond in BeBeCO is 0.005 Å longer than in BeCO and the C−O frequency is 20 cm^{-1} lower. Diberyllium is a formidable theoretical problem,[30-32] and the BeBeCO calculation might suffer from the limited level and basis sets employed here; however, calculations at the CI level give a 1% shorter Be−Be length and slighter lower frequencies, as expected for a well-described molecule (Table 3). At the SCF level the calculations are a guide for identifying the matrix reaction products observed here. Note that the bending modes for these triplet linear molecules are split by Renner−Teller interaction.[33] The Be−Be single bond length calculated here (2.102 Å) for BeBeCO is in reasonable agreement with the experimental value (2.16 Å) for the single bonded B $^1\Sigma_u^+$ state of Be_2.[34] Finally, the Be_3CO molecule was also examined starting with triangular[32] Be_3, which was found to weakly bind CO giving an almost unshifted (2431.7 cm^{-1}) C−O frequency.

Chart 1. Stick Figures with Structural Parameters for Be_xCO_y Molecules from SCF Level Calculations with Distances in Å and Angles in deg



Geometry optimization at the SCF level yields two stable triplet $Be(CO)_2$ molecules which are lower in energy than the lowest energy singlet by 22 kcal/mol. The bent triplet is lower in energy than the linear triplet by 7 kcal/mol. The linear triplet also yields an imaginary frequency for bending motions; thus, at the SCF level the linear molecule is a saddle point in the potential surface. When the level of theory is increased to include configuration interaction, no imaginary frequencies are found for either structure but the bent structure is still lower energy by 3.3 kcal/mol. Frequencies calculated for bent $Be(CO)_2$ are listed in Table 4. Finally, several isocarbonyls were calculated and found to be repulsive.

Two triplet diberyllium dicarbonyls were explored at the SCF level. Linear (OC)BeBe(CO) and the C_{2v} structure $BeBe(CO)_2$ are found with the latter 17 kcal/mol lower in energy. Vibrational frequencies are

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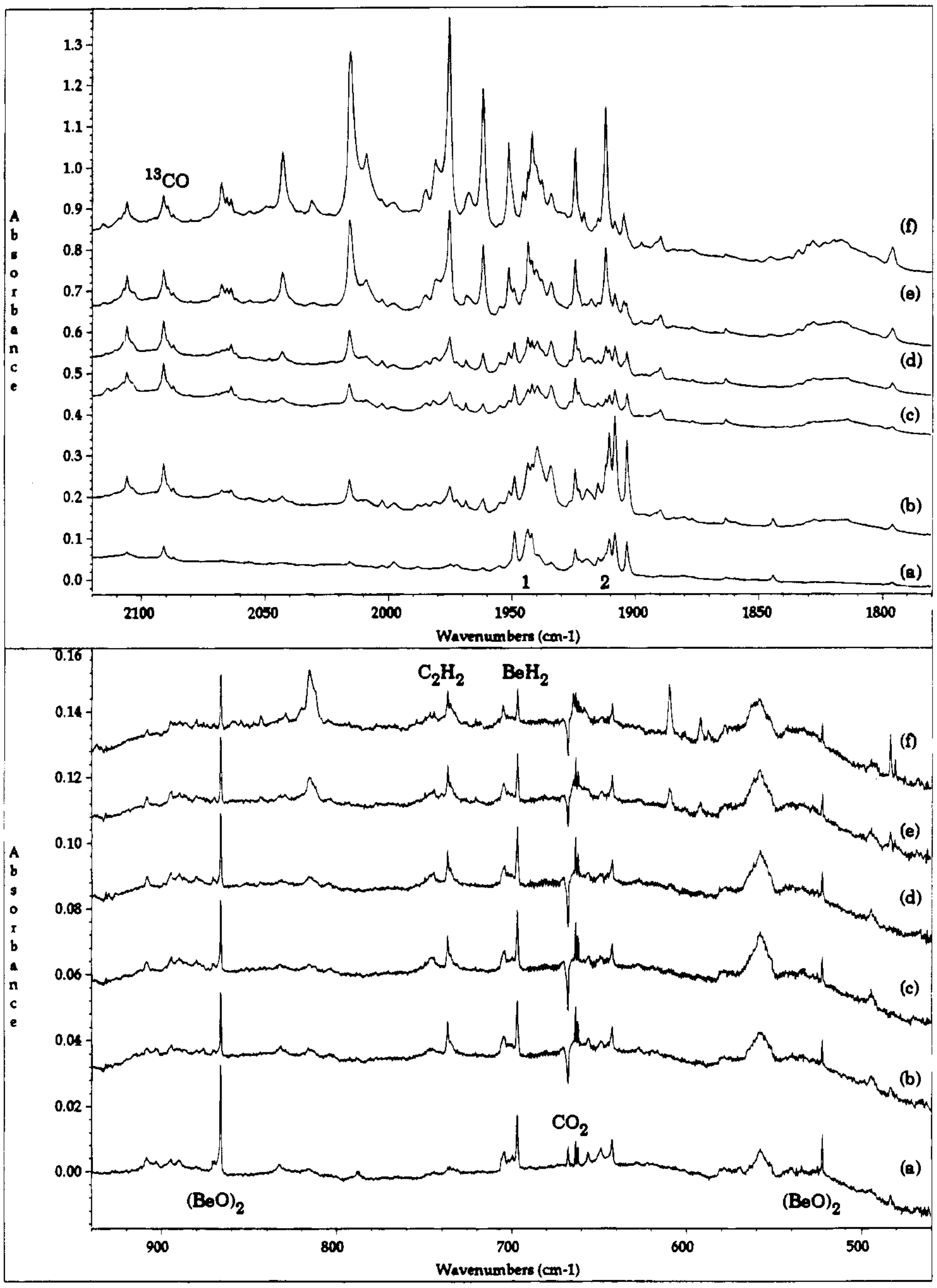

Figure 1. Infrared spectra in the C−O stretching region, 2120−1780 cm^{-1}, and Be−C stretching region, 980−460 cm^{-1}, for a sample prepared by codeposition of beryllium atoms with (a) 400:1 mixture of argon and CO after 2 h of codeposition at 10 K, (b) a 200:1 mixture of argon and CO after 2 h of codeposition at 10 K, (c) 30 m broadband photolysis of the 200:1 sample, (d) after annealing of the matrix to 20 K, (e) after annealing to 25 K, and (f) after annealing to 30 K. Note: Expanded absorbance scale is used for lower frequency region.

listed in Table 5 for these two molecules. Note the unusually short Be−Be bond in the linear molecule. Geometry optimization was also done at the CI level for the linear molecule, and the bond lengths are again close (within 1.8%) to the SCF values (Table 5).

Geometry optimization at the SCF level for $Be(CO)_3$ predicts a stable planar molecule with structural parameters Be−C = 1.674 and C−O = 1.112 Å. Frequency calculations, listed in Table 6, predict two observable infrared bands at 2253.8 and 913.2 cm^{-1}. The hybridization for Be in $Be(CO)_3$ is probably sp^2, where the three planar orbitals are now filled with lone pairs donated from carbon atoms of the CO groups. The beryllium lone pair of electrons now occupies the nonbonding p-orbital, which is appropriate symmetry to donate to the CO $2\pi^*$ molecular orbitals.

Calculations were done for the singlet C_{2v} molecule $(OC)BeBe(CO)_2$ at the SCF level. Structural parameters and the calculated frequencies are listed in Table 7.

The stable $(OC)_2BeBe(CO)_2$ molecule was calculated to form readily from dimerization of $Be(CO)_2$ by Sunil.[13] The former D_{2h} molecule was re-examined, and structural parameters (Be−Be = 1.926 Å, Be−C = 1.742 Å, C−O = 1.107 Å, C−Be−C angle = 112°, Be−C−O angle = 174°) are in excellent agreement with those reported by Sunil.[13] Frequencies were calculated and are listed in Table 8. Because this molecule has D_{2h} symmetry, two strong active modes are expected in the C−O stretching region. Chart 1 compares the structural parameters for the most important beryllium carbonyls explored here.

Results

Infrared spectra for the reaction of pulsed laser evaporated beryllium atoms with carbon monoxide will be presented.

Be + CO. The first experiments were done with higher laser power like that used for O_2 reactions[24] and lower CO concentration. Figure 1a shows the higher frequency C−O stretching region, 2120−1780 cm^{-1}, after 2 h of codeposition of Be atoms with an Ar/CO = 400:1 mixture. Two strong band groups are immediately evident. The first major band group contains bands

Table 1. Infrared Absorptions (cm^{-1}) for Products of Reactions of Be Atoms with CO in Argon

P/A[a]	$^{12}C^{16}O$	$^{13}C^{16}O$	$^{12}C^{18}O$	product molecule
−60/×4	480.5	467.7	478.2	BeBeCO
−60/×4	483.3	470.4	481.1	BeBeCO
-/appears	591.8	588.0	589.4	$BeBe(CO)_2$
-/appears	609.6	604.8	605.1	$Be(CO)_2$
dec/×10	816.1, 843.6	808.1, 820.2	809.0, 833.9	$Be(CO)_3$
(+100/−0.5)[b]	917.2	916.0	911.3	$OCBeBe(CO)_2$
+20/0	1471.1	1469.9	1438.3	BeO complex
−50/×10	1795.9	1755.3	1754.0	aggregate
−60/×6	1903.4	1856.8	1860.2	OCBeBeCO
−60/×6	1908.4	1864.6	1868.4	OCBeBeCO
−30/×4	1924.4	1881.9	1885.0	Be_xCO
(+100/−0.5)[b]	1940.2	1894.0	1898.3	$OCBeBe(CO)_2$
−60/×4	1942.0	1892.6	1901.6	BeBeCO
−60/×2	1943.6	1899.0	1903.1	BeBeCO
−60/×10	1951.4	1907.4	1906.8	$BeBe(CO)_2$ site
−30/×10	1961.7	1918.6	1918.6	$BeBe(CO)_2$
−30/×10	1975.3	1930.7	1930.9	$Be(CO)_2$
−30/×10	2015.9	1970.1	1970.4	$Be(CO)_3$
−/×10	2031.3	1983.6	1984.2	unknown
−30/×10	2043.2	1999.6	2000.6	$(OC)_2BeBe(CO)_2$
−30/×10	2067.6	2020.3	2021.8	$(OC)_2BeBe(CO)_2$
0/×1.5	2106.0	2048.0	2046.2	unknown
∞ abs	2138.4	2091.5	2087.4	CO

[a] P/A indicates % increase or decrease in band intensity after photolysis/growth factor after final annealing to 30 K. [b] A/P for 50:1 experiment.

Table 2. Optimized Geometry Energies for Lowest Energy Beryllium Carbonyl Molecules Using 6-311G* Basis Sets

calcd species	SCF energy (au)
Be	−14.571 890
CO	−112.769 755
^3BeCO	−127.325 524
^3BeBeCO	−141.938 034
$^3Be(CO)_2$ (bent)	−240.118 344
$^3OCBeBeCO$	−254.700 406
$^3BeBe(CO)_2$	−254.727 028
$^1Be(CO)_3$	−352.906 051
$^1Be_2(CO)_3$	−367.515 618
$^1Be(CO)_4$ (D_{2d})	−465.647 480
$^1Be_2(CO)_4$	−480.274 885

from 1949.1 to 1924.4 cm^{-1} with the strongest peak at 1943.6 cm^{-1}, and the second consists of three sharp bands at 1910.6, 1908.4 (strongest), and 1903.5 cm^{-1}. Weaker product bands are also present at 2067.0, 2043.2, 2015.9, 1975.3, 1961.7, and 1795.9 cm^{-1}, which are given in Table 1. Site splitting is common for these product molecules and the most intense band position for a group of sites will be quoted throughout. Two product bands are observed in other regions of the spectrum at 2189.5 and 1471.1 cm^{-1}; the first of these has been identified as OBeCO.[26] In addition, weak BeO complex absorptions are found at 1571.7 and 1549.5 cm^{-1}, and Ar−BeO and BeOBe bands are also evident at 1526.1 and 1412.4 cm^{-1}.[24] Weak $(BeO)_2$ and 483 cm^{-1} bands were detected in the lower frequency region. The CO fundamental at 2138.4 cm^{-1} is not shown. On annealing of the 400:1 sample to 25 and 30 K (not shown), the 2067.6, 2043.2, 2015.9, 1975.1, 1961.7, 1951.4, and 1942.0 cm^{-1} bands increased, the latter 2 bands became the strongest absorptions, and group 1 bands were favored over group 2. In the lower region 816.1, 609.6, 591.8, 483.3, and 480.5 cm^{-1} bands appeared on annealing.

When the CO concentration was increased to Ar/CO = 200:1, the band yield increased slightly, particularly the 2015.9, 1975.1, 1961.7, and 1951.4 cm^{-1} bands; a 1940.2 cm^{-1} band is evident, and the group 2 bands are stronger than group 1 bands as shown in Figure 1b. The photolysis behavior of these bands is shown in Figure 1c and is tabulated in Table 1. Photolysis decreased the first two bands groups by 60%. Weak bands at 2067.6, 2043.2, 2015.9, 1975.3, and 1961.7 cm^{-1} were reduced by 20%.

Upon annealing of the 200:1 sample to 20 K, very little change in peak intensities was observed as shown in Figure 1d. After annealing of the samples to 25 K, all product bands except 1471.1 cm^{-1} increased in intensity, shown in Figure 1e, and weak new bands appeared at 908.5, 816.1, 609.6, and 591.8 cm^{-1} in the low-frequency region along with a sharp weak 483.3, 480.5 cm^{-1} doublet. Further annealing to 30 K increased the above product bands as shown in Figure 1f. Bands in the first two major groups increased by a factor of 2−4 on final annealing along with the associated 908.5, 483.3, and 480.5 cm^{-1} bands. Bands at 2067.6, 2043.2, 2015.9, 1975.1, 1961.7, 1951.4, and 1795.9 cm^{-1} increased more than 10-fold on annealing to 30 K, and bands at 816.1, 609.6, and 591.8 cm^{-1} followed accordingly. A new band is evident at 1644.6 cm^{-1} only after annealing.

Experiments were done with lower laser power and higher CO concentrations, and the 50:1 spectra are shown in Figure 2. Spectra are dominated by very strong 1938.5, 1935.0 cm^{-1} bands, with associated bands at 917.2, 914, and 588 cm^{-1}, and the group 2 bands. The 2015.9 and 1975.3 cm^{-1} bands are strong on deposition, Figure 2a, and the associated bands are observed at 816 and 609 cm^{-1}. Annealing to 25 and 35 K, Figure 2b,c, markedly increases the above bands (shifting the peak to 1940.2 cm^{-1}), produces weak 1961.7, 2043.2, and 2067.6 cm^{-1} bands, and decreases the group 2 bands. Photolysis, Figure 2d, decreases all of the above bands, but nearly destroys the group 2 bands. Annealing to 35 K, Figure 2e, slightly increases the 2015.9, 1975.3, 816, and 609 cm^{-1} bands. A final 45 K annealing (not shown) decreases the group 1 bands and further increases the 2015.9, 1975.3, 816, and 609 cm^{-1} bands. A similar experiment with Ar:CO = 100:1 gave the same trends with weaker product absorbances.

Be was also codeposited with pure CO, and a very strong 1939 cm^{-1} band was observed along with a 918 cm^{-1} band with weaker satellites as in Figure 2. In addition sharp weaker bands were observed at 2048 and 813 cm^{-1}.

Be + ^{13}CO and C^{18}O. Isotopic substitution of ^{13}CO yields a shift of all bands in the CO stretching region, as shown by comparing spectra a and c found in Figure 3 for dilute CO

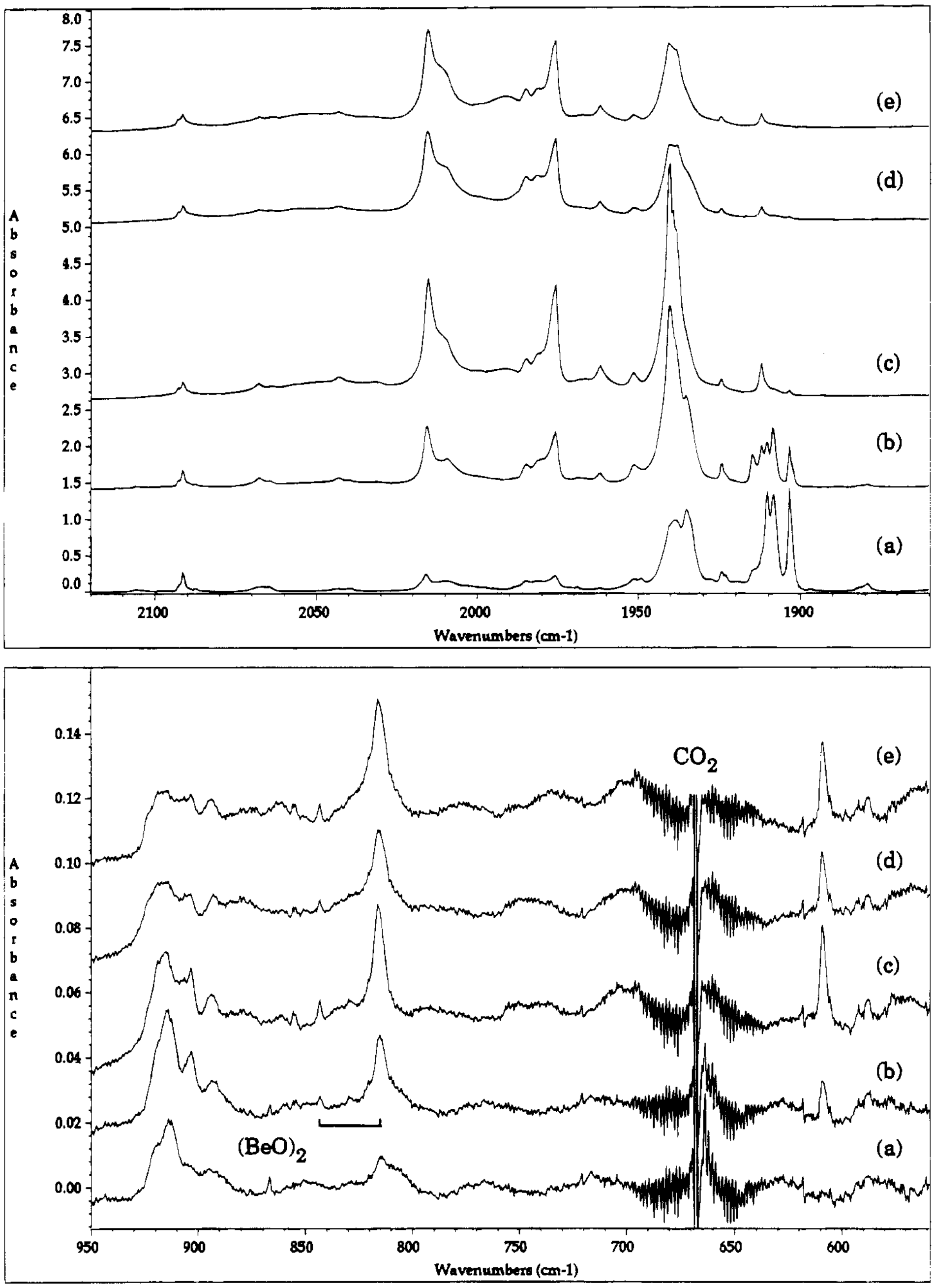

Figure 2. Infrared spectra in the 2120–1860 and 950–550 cm^{-1} regions for beryllium and Ar:CO = 50:1 sample (a) codeposited for 1 h at 10 K, (b) after annealing to 25 K, (c) after annealing to 35 K, (d) after broadband photolysis for 30 m, and (e) after another annealing to 35 K. Note: 50-fold more sensitive absorbance scale is used for lower region.

samples. (Note that these spectra are recorded after annealing to 30 K.) Isotopic substitution of C^{18}O likewise yields a shift of all bands in the CO stretching region, as shown in Figure 3b. New shifted bands also appeared in the lower frequency region on annealing. Similar experiments were done for 50:1 isotopic samples. It is noteworthy that the natural isotopic 816.1 cm^{-1} band became an equal intensity 820.2, 808.1 cm^{-1} doublet with ^{13}CO and the strong 809.0 cm^{-1} band with C^{18}O was accompanied by a 833.9 cm^{-1} satellite analogous to the 843.6 cm^{-1} band for C^{16}O. Isotopic frequencies are given in Table 1.

Be + ^{12}CO/^{13}CO and C^{16}O/C^{18}O. Mixed isotopic experiments were performed to assist in the differentiation of multiple carbonyl containing molecules, as shown in Figure 4. Be + ^{12}CO/^{13}CO experiments yield a doublet for the first band group with the 1943.6 and 1899.0 cm^{-1} band positions unshifted from the separate Be + ^{12}CO and Be + ^{13}CO experiments. The second band group, centered at 1908.4 cm^{-1} in the natural isotopic experiments, gives rise to triplet absorption patternswith the band group centers present at 1908.4, 1882.0, and 1864.8 cm^{-1}, whereas the 1903.4 cm^{-1} site exhibits 1879.0 and 1856.8 cm^{-1} components. Product bands present in the natural abundance experiments at 2067.6, 2043.2, 2015.9, 1975.3, and 1961.7 cm^{-1} grow on annealing and produce a large number of bands between 2067 and 1919 cm^{-1} which can be followed at successive stages of annealing. The 2015 cm^{-1} band produced a quartet with weaker intermediate components at 2002, 1984, and 1972 cm^{-1}, which are clear on 25 K annealing. The 1975 and 1961 cm^{-1} band systems overlap with each other and with the ^{12}CO group one band; any intermediate components in the 1940–1950 cm^{-1} region are masked by ^{12}CO group one bands. The region between 2067 and 2000 cm^{-1} contains bands from the 2067 and 2043 cm^{-1} systems and the 2015, 2002 cm^{-1} bands from the 2015 cm^{-1} system. This complicated band pattern is in accord with the bar spectrum calculated for (CO)$_2$BeBe(CO)$_2$ at the SCF level including intensities and

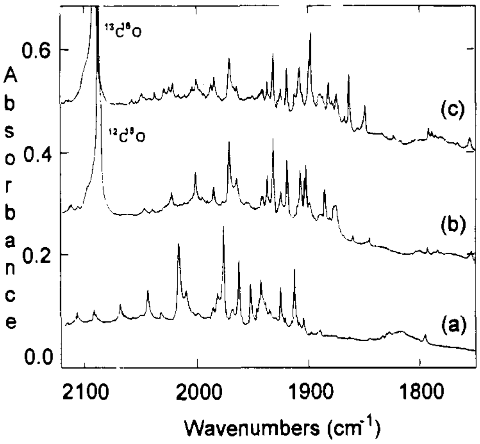

Figure 3. Infrared spectra in the 2120–1780 cm^{-1} region for codeposition of beryllium atoms for 2 h at 10 K followed by annealing to 30 K with mixtures of (a) Ar/$^{12}C^{16}O$ = 200/1, (b) Ar/$^{12}C^{18}O$ = 400/1, and (c) Ar/$^{13}C^{16}O$ = 400/1.

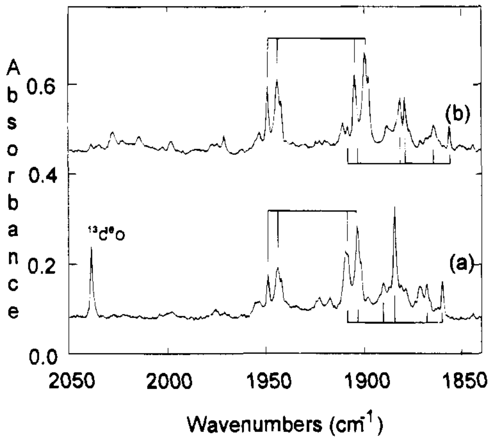

Figure 4. Infrared spectra in the 2050–1840 cm^{-1} region for codeposition of beryllium atoms for 2 h at 10 K with mixtures of (a) Ar/$^{12}C^{16}O$/$^{12}C^{18}O$ = 400/1/1 and (b) Ar/$^{12}C^{16}O$/$^{13}C^{16}O$ = 800/1/1.

statistical weights of each mixed ^{12}CO/^{13}CO isotope. In the lower region intermediate bands appeared for each absorption, except the sharp 483.3, 480.5 and 470.4, 467.7 cm^{-1} doublets were observed without intermediate components.

Be + $C^{16}O$/$C^{18}O$ experiments yield spectra similar to those observed for Be + ^{12}CO/^{13}CO. The first band group appears as an unshifted doublet with group centers at 1943.6 and 1903.1 cm^{-1}. The second band group is present as a 1:2:1 triplet, with centers located at 1903, 1884.7, and 1860.2 cm^{-1}. The band at 1471.1 cm^{-1} has an ^{18}O counterpart at 1438.3 cm^{-1}. As with the ^{12}CO/^{13}CO experiments, a complicated set of bands is present between 2067 and 1919 cm^{-1} after annealing, and the patterns are similar to those described above. In the lower region new absorptions appeared on annealing between the pure isotopic values; weak bands at 807 and 607 cm^{-1} clearly spanned the $C^{16}O$ and $C^{18}O$ peaks. In contrast the 483.3 and 481.1 cm^{-1} bands were observed as in pure isotopic experiments. In a 50:1:1 sample of Ar/$C^{16}O$/$C^{18}O$, the 1903.4, 1884.7, 1860.2 cm^{-1} triplet was clearly resolved on deposition. Annealing produced a strong quartet at 1940.2, 1922.7, 1910.2, and 1898.3 cm^{-1} with components of comparable intensities. The lower frequency bands were observed at 914, 812, and 607 cm^{-1} on annealing.

Discussion

Evidence will be presented for the assignment of new product infrared absorption bands to beryllium carbonyl product molecules on the basis of photolysis and annealing behavior, isotopic shifts, and ab initio calculations. The two band groups formed on codeposition of hyperthermal Be atoms with CO will be assigned to beryllium clusters with one and two CO subunits while bands that grow on annealing the matrix will be identified as higher beryllium carbonyl species.

BeBeCO. The first band group centered at 1943.6 cm^{-1} is a major product formed on sample deposition. Both mixed ^{12}CO/^{13}CO and $C^{16}O$/$C^{18}O$ experiments (Figure 4) show that the first band group exhibits doublet structures indicative of a monocarbonyl product whereas the second group reveals intermediate absorptions suggesting dicarbonyl species. The first band group is therefore due to the major beryllium monocarbonyl product formed in the matrix deposition reaction. The 483.3, 480.5 cm^{-1} doublet and group 1 1943.6, 1942.0 cm^{-1} bands exhibit common behavior on annealing, photolysis, and CO concentration changes in 200/1 and 400/1 experiments. The group 1 bands are clearly due to Be_xCO species. Note that the first two band groups, appearing on sample codeposition, are markedly diminished by broad band photolysis and increase substantially on annealing in the absence of radiation. These increases are due to diffusion and subsequent reaction of cold atoms and molecules in the matrix and are indicative of a spontaneous, presumably exothermic reactions.

The SCF calculations, summarized in Table 3, show that the first band group could be due to BeCO or BeBeCO. Both molecules are predicted to have one very strong infrared band in the 1950 cm^{-1} region. The ^{12}CO/^{13}CO ratios calculated from theoretical frequencies for BeCO (1.0239) and BeBeCO (1.0242) are close to the 1.0235 value observed for dilute experiments. Likewise the predicted $C^{16}O$/$C^{18}O$ ratios for BeCO (1.0229) and BeBeCO (1.0224) are near the observed 1.0213 value. Agreement between observed and calculated harmonic ratios is excellent considering the effect of anharmonicity on the observed isotopic frequency ratio. Note that the observed 12/13 ratio exceeds the ^{12}CO/^{13}CO diatomic ratio (1.0224) and the observed 16/18 ratio is less than the $C^{16}O$/$C^{18}O$ ratio (1.0224). This means that the Be–C–O normal mode involves Be motion and that C is moving with some antisymmetric character between Be and O. The 483.3, 480.5 cm^{-1} bands show isotopic shifts appropriate for a Be–C–O bending mode, and mixed isotopic experiments clearly identify a molecule with one CO subgroup, which supports the assignment to BeBeCO. The SCF calculations in Table 3 predict such a bending mode in the low 400 cm^{-1} region, which is split by Renner–Teller interaction. The Be–Be stretching mode predicted in this region was not observed in the infrared spectrum.

The total energies calculated for Be, triplet BeCO, and BeBeCO given in Table 2 show that reaction 1 is endothermic

$$\mathrm{Be} + \mathrm{CO} \rightarrow \mathrm{BeCO} \qquad \Delta E = +10\ \mathrm{kcal/mol} \qquad (1)$$

$$2\,\mathrm{Be} + \mathrm{CO} \rightarrow \mathrm{Be_2} + \mathrm{CO} \rightarrow \mathrm{BeBeCO} \qquad \Delta E = -15\ \mathrm{kcal/mol} \qquad (2)$$

by 10 kcal/mol whereas reaction 2 is exothermic by 15 kcal/mol. A series of single point energy calculations at the MBPT(2) level show a barrier of approximately 24 kcal/mol for Be + CO to form a stable triplet BeCO molecule. Such an energy requirement could be provided by hyperthermal Be atoms from laser ablation or from radiation emitted from the target surface. *However, the considerable growth of group 1 bands on annealing the cold matrix requires a process with little or no activatiion energy barrier.* Hence, BeCO is ruled out, and the diberyllium product of exothermic reaction 2 is probably the monocarbonyl observed here. The lack of reactivity of Be

Table 3. Frequencies (cm^{-1}) Calculated for the Linear Triplet BeCO and BeBeCO Molecules at the SCF Level Using the 6-311G* Basis Sets[a]

	$^{12}C^{16}O$	$^{13}C^{16}O$	$^{12}C^{18}O$	mode
BeCO	2180.7 (1570)[b]	2129.8	2131.8	σ
	822.8 (4)	820.2	814.6	σ
	410.7 (1)	399.8	406.5	π
	386.5 (39)	376.3	382.6	π
BeBeCO	2161.1 (1942)[b–d]	2110.1	2113.7	σ
	955.9 (0.0)	954.6	950.5	σ
	456.4 (27)	454.6	451.9	σ
	477.3 (1)	436.8	444.2	π
	351.4 (2)	342.2	348.0	π
	141.8 (24)	141.3	140.3	π
	138.5 (6)	138.3	137.4	π

[a] Geometries: BeCO, Be−C = 1.664 Å, C−O = 1.126 Å; BeBeCO, Be−Be = 2.102 Å, Be−C = 1.662 Å, C−O = 1.131 Å. (Be−Be = 2.085 Å, Be−C = 1.660 Å, C−O = 1.147 Å at the CI level.) [b] Infrared intensities in km/mol; relative intensities of isotopic molecules are nearly the same. [c] The σ stretching mode are 95% C−O minus 5% Be−C, 65% Be−C minus 33% Be−Be, and 70% Be−Be plus 30% Be−C. [d] CI level frequencies are 2072.1, 946.5, 454.3, (411.7, 328.2), (131.8, 125.0) cm^{-1}.

Table 4. Frequencies (cm^{-1}) Calculated for the Bent Triplet $Be(CO)_2$ Molecule at the SCF Level Using the 6-311G* Basis Set[a]

$^{12}C^{16}O$	$^{13}C^{16}O$	$^{12}C^{18}O$	mode desc
2365.8 (705)[b]	2311.8	2310.6	sym C−O
2181.2 (4463)	2134.0	2126.7	antisym C−O
743.8 (603)	740.9	739.7	antisym Be−C
611.7 (43)	605.2	608.3	sym Be−C plus Be−C−O bend
479.0 (3)	466.7	470.6	sym Be−C minus Be−C−O bend
420.4 (64)	410.6	416.2	Be−C−O out-of-phase
409.5 (0)	396.8	404.7	Be−C−O twist
380.5 (1)	368.8	375.9	sym C−Be−C
103.1 (1)	102.6	98.9	C−Be−C bend

[a] Geometry: Be−C = 1.695 Å, C−O = 1.111 Å, C−Be−C angle = 109.6°, Be−C−O angle = 176.0°. [b] Infrared intensities in km/mol; relative intensites of isotopic molecules are nearly the same.

and CO is attested by the fact that a weak Ar−BeO band was observed along with BeOBe.[24] Accordingly, unreacted Be can dimerize to give Be_2, which has been observed in previous matrix isolation studies,[34,35] and Be_2 is expected to react with CO according to reaction 2 to form triplet BeBeCO.

OCBeBeCO. The band group centered at 1908.4 and 1903.4 cm^{-1} forms a triplet with stronger intermediate components in both $^{12}CO/^{13}CO$ and $C^{16}O/C^{18}O$ mixed isotopic experiments indicative of two equivalent CO groups. Again the 12/13 ratio (1.0235) is larger than the 16/18 ratio (1.0214) indicating the participation of Be in an antisymmetric type motion involving carbon. Ab initio calculations reveal that three dicarbonyl species can be formed by exothermic reactions, namely bent $Be(CO)_2$, linear (CO)BeBe(CO), and wye $BeBe(CO)_2$,

$$Be + 2CO \rightarrow Be(CO)_2 \qquad \Delta E = -4\ \text{kcal/mol} \qquad (3)$$

$$2Be + 2CO \rightarrow OCBeBeCO \qquad \Delta E = -10\ \text{kcal/mol} \qquad (4)$$

$$2Be + 2CO \rightarrow BeBe(CO)_2 \qquad \Delta E = -27\ \text{kcal/mol} \qquad (5)$$

$$CO + BeBeCO \rightarrow BeBe(CO)_2 \qquad \Delta E = -12\ \text{kcal/mol} \qquad (6)$$

although none of these fit the observed spectra very well. Linear (OC)BeBe(CO) is predicted to absorb higher than the latter two dicarbonyls, but the predicted $^{13}C^{16}O$ and $^{12}C^{18}O$ frequency order is reasonable, whereas the SCF frequencies are lower for bent $Be(CO)_2$ and $BeBe(CO)_2$, but the isotopic shifts are not appropriate. As the SCF level calculations for these species are only first approximations and a guide for making new product identification, the group 2 bands are best identified as the linear diberyllium dicarbonyl OCBeBeCO.

Table 5. Frequencies (cm^{-1}) Calculated for Triplet $Be_2(CO)_2$ and OCBeBeCO Molecules at the SCF Level Using the 6-311G* Basis Sets[a]

	$^{12}C^{16}O$	$^{13}C^{16}O$	$^{12}C^{18}O$	mode
$BeBe(CO)_2$	2381.8 (790)[b]	2327.4	2326.3	sym C−O
	2167.3 (4630)	2120.8	2112.5	antisym C−O
	780.8 (20)	778.3	779.4	Be−Be, Be−C
	655.3 (473)	487.0	497.5	Be−C−O
	436.3 (28)	427.0	433.0	Be−C−O
	416.0 (0)	403.1	411.0	Be−C−O
	404.5 (19)	392.1	400.0	Be−C−O
	390.9 (0)[c]	387.6	384.2	sym Be−C
OCBeBeCO	2401.1 (0)	2346.3	2345.0	σ
	2295.4 (11143)	2245.0	2238.8	σ
	1050.2 (0)	1049.7	1049.0	σ
	551.3 (1410)	548.7	547.0	σ
	442.1 (77)	430.5	438.1	π
	417.4 (0)	407.3	413.8	π
	276.5 (0)[c]	271.9	267.2	σ
	128.7 (0)	128.1	127.8	π
	48.2 (3)	48.0	47.1	π

[a] Geometries: $BeBe(CO)_2$ is C_{2v}; Be−Be = 2.111 Å, Be−C = 1.729 Å, C−O = 1.109 Å, C−Be−C angle = 105.4°, Be−C−O angle = 176.3°. OCBeBeCO is linear; Be−Be = 1.855 Å, Be−C = 1.750 Å, C−O = 1.104 Å (Be−Be = 1.862 Å, Be−C = 1.720 Å, C−O = 1.122 Å at the CI level). [b] Infrared intensities in km/mol. [c] Calculated frequencies at 120.8, 113.3, and 98.6 cm^{-1} omitted from table.

$Be(CO)_2$ and $BeBe(CO)_2$. Warming the matrix samples to 20−30 K to allow diffusion and association of reagents enable several higher carbonyls to be formed as attested by the strongest 3 product bands at 1961.7, 1975.3, and 2015.9 cm^{-1} in the C−O stretching region. These bands are associated, respectively, with weaker bands at 591.8, 609.6, and 816.1 cm^{-1} in the Be−C stretching region in dilute CO studies (Figure 1) but only the latter two band sets were observed in the more concentrated CO experiments (Figure 2). The first members of each set, 1961.7 and 591.8 cm^{-1}, are favored in the 400/1 experiment, and the second members, 1975.3 and 609.6 cm^{-1}, are favored in the 200/1 experiment; therefore the first members appear to be due to the more Be-rich species. The third members, 2015.9 and 816.1 cm^{-1}, are favored in the more concentrated CO experiments and will be assigned below to $Be(CO)_3$.

The 1961.7 and 591.8 cm^{-1} bands are assigned to $BeBe(CO)_2$ on the basis of isotopic shifts and agreement with SCF calculations. The calculated antisymmetric C−O and Be−C stretching frequencies at 2167.3 and 655.3 cm^{-1}, scaled by the same 0.905 factor, agree with the observed frequencies. The calculated symmetric C−O stretching frequency scales to a position under the very strong, broad CO absorption and, therefore, cannot be observed in these experiments.

The 1975.3 and 609.6 cm^{-1} absorptions are tentatively assigned to $Be(CO)_2$ for analogous reasons. The calculated antisymmetric C−O stretching frequency at 2181.2 cm^{-1}, scaled by 0.906, fits the observed band; however, the Be−C stretching mode calculated at 743.8 cm^{-1} requires a lower 0.82 scale factor, but the calculated and observed ^{13}CO and $C^{18}O$ shifts match within 0.7 cm^{-1}. The calculated C−Be−C bond angle is sensitive to the level of theory (110° at SCF and 124° at MP2),[36] and the calculated Be−C stretching frequencies will vary accordingly. A better fit to the observed 609.6 cm^{-1} funda-

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Table 6. Frequencies (cm^{-1}) Calculated for the Singlet D_{3h} Molecule $Be(CO)_3$ at the SCF Level Using the 6-311G* Basis Sets[a]

$^{12}C^{16}O$	$^{13}C^{16}O$	$^{12}C^{18}O$	mode
2397.9 (0)[b]	2342.1	2343.7	a_1', sym C−O
2253.8 (3042)	2203.1	2200.4	e′, antisym C−O
913.2 (172)	910.3	908.8	e′, antisym Be−C
567.1 (98)	556.1	563.4	a_2'', Be−C_3 def
466.0 (0)	451.1	461.0	e′, Be−C−O bend
464.7 (0)	450.4	459.2	e″, Be−C−O bend
391.4 (0)	384.9	377.5	a_1', sym Be−C
377.3 (0)	365.7	372.8	a_2'
92.8 (3)	92.4	90.9	a_2''
86.5 (4)	86.0	82.5	e′

[a] Geometry: Be−C = 1.674 Å and C−O = 1.112 Å. [b] Infrared intensities in km/mol; relative intensities for isotopic molecules are nearly the same.

mental may be found at a higher level of theory. Again the calculated symmetric C-O stretching frequency scales to fall under the CO precursor band.

$Be(CO)_3$. The strong 2015.9 cm^{-1} and weak 816.1 cm^{-1} bands exhibit parallel growth on photolysis and annealing in all experiments and are assigned to singlet $Be(CO)_3$. In the mixed isotopic experiments, two mixed isotopic bands are evident between the pure isotopic C−O bands indicating three equivalent carbonyl groups.[37] The lower frequency band reveals evidence of isotopic mixing. Frequency calculations at the SCF level, expected to be of higher quality for a singlet monoberyllium species, predict only one observable C−O stretching band at 2253.8 cm^{-1} (0.894 experiment/theory ratio) for the antisymmetric C−O stretching mode. For the Be + ^{13}CO experiments, the observed band is at 1970.1 cm^{-1} compared with the calculated value of 2203.4 cm^{-1} (0.894 ratio). Finally, the Be + $C^{18}O$ experiments yield a frequency of 1970.4 cm^{-1} versus the theoretical value of 2200.4 cm^{-1} (0.895 ratio). The theoretical $^{12}C/^{13}C$ isotopic ratio of 1.0230 fits well with the experimental ratio of 1.0232, but the theoretical $^{16}O/^{18}O$ ratio of 1.0243 is slightly higher than the experimental value of 1.0231; the $C^{18}O$ shift is predicted to be slightly more than observed.

The observed 816.1 cm^{-1} band may be compared with the 913.2 cm^{-1} SCF prediction (0.894 ratio) for the next strongest infrared band, namely the antisymmetric Be−C stretching mode. The ^{13}CO spectrum gives a doublet at 808.1, 820.2 cm^{-1}; neither component matches the calculated 3 cm^{-1} isotopic shift. However, the e′ Be−C−O bending mode calculated at 466.0 cm^{-1} has an overtone in the same region capable of Fermi resonance with the e′ Be−C stretching mode. Since the ^{13}CO shift in the bending mode is much larger than for the stretching fundamental (Table 6), the overtone falls below the fundamental only in the ^{13}CO case giving rise to the observed 1:1 doublet. Weaker bands at 843.6 and 833.9 cm^{-1} in $C^{16}O$ and $C^{18}O$ experiments complete the Fermi doublets in these cases where the interaction is weaker. In addition the observed $C^{18}O$ shift in the Be−C stretching fundamental is increased slightly by the Fermi resonance interaction as the Be−C−^{18}O bending mode overtone is closer to the Be−$C^{18}O$ stretching mode fundamental than in the Be−$C^{16}O$ case. Finally, the weak 2048 and 813 cm^{-1} bands in the Be + pure CO experiment are probably due to CO perturbed $Be(CO)_3$.

$Be(CO)_3$ can be formed by CO addition to $Be(CO)_2$, which is exothermic by 11 kcal/mol at the SCF level, reaction 7. On

$$CO + Be(CO)_2 \rightarrow Be(CO)_3 \qquad \Delta E = -11 \text{ kcal/mol} \qquad (7)$$

$$Be + 3CO \rightarrow Be(CO)_3 \qquad \Delta E = -16 \text{ kcal/mol} \qquad (8)$$

the other hand, direct union of the appropriate subunits, reaction 8, is exothermic by 16 kcal/mol on the basis of present SCF calculations and by 40−50 kcal/mol at higher levels of theory.[36] The observed decrease on photolysis is most likely due to photodissociation yielding Be and CO. The 10-fold growth on annealing is reasonable considering the exothermic reaction to form stable $Be(CO)_3$.

$OCBeBe(CO)_2$. The strong 1940 and 917 cm^{-1} bands and weaker 588 cm^{-1} absorption favored in 50:1 experiments are assigned to the singlet $OCBeBe(CO)_2$ molecule for the following reasons. First, this molecule is even more stable than the previously reported diberyllium tetracarbonyl[13] and it will not react further with CO on the basis of SCF energies.

$$2Be + 3CO \rightarrow OCBeBe(CO)_2 \qquad \Delta E = -40 \text{ kcal/mol} \quad (9)$$

$$2Be + 4CO \rightarrow (OC)_2BeBe(CO)_2 \qquad \Delta E = -33 \text{ kcal/mol} \quad (10)$$

$$Be + OCBeBe(CO)_2 \rightarrow (OC)_2BeBe(CO)_2 \qquad \Delta E = +7 \text{ kcal/mol} \quad (11)$$

It can also be made by CO addition to either diberyllium dicarbonyl:

$$CO + BeBe(CO)_2 \rightarrow OCBeBe(CO)_2 \qquad \Delta E = -12 \text{ kcal/mol} \quad (12)$$

$$CO + OCBeBeCO \rightarrow OCBeBe(CO)_2 \qquad \Delta E = -29 \text{ kcal/mol} \quad (13)$$

Thus the major product in high concentration CO (and pure CO) experiments is expected to be $OCBeBe(CO)_2$ and not $(OC)_2BeBe(CO)_2$. Weak analogous bands at 1938 and 909 cm^{-1} were observed in the 200:1 experiments.

The very strong 1940 cm^{-1} band becomes a strong quartet in $C^{16}O/C^{18}O$ experiments which requires 2 inequivalent CO subgroups. The only energetically reasonable such molecule is $OCBeBe(CO)_2$. The observed bands are compatible with the SCF predictions (Table 7). The strongest 2 bands calculated at 2177 and 2165 cm^{-1} are too close to resolve, and the calculated 2386 cm^{-1} band scales to fall under CO precursor absorption. The 917 and 588 cm^{-1} bands are appropriately below Be−C stretching frequencies calculated at 982 and 645 cm^{-1}. Finally, the strong quartet is compatible with SCF calculations for mixed isotopic diberyllium tricarbonyl molecules.

$(OC)_2BeBe(CO)_2$. Bands at 2067.6 and 2043.2 cm^{-1} are assigned to singlet $(OC)_2BeBe(CO)_2$. The SCF frequency calculations reveal the two strongest bands at 2355.9 (0.878 experiment/theory ratio) and 2312.4 (0.884) cm^{-1}. The theoretical $^{12}C/^{13}C$ isotopic ratios for the 2067.6 and 2043.2 cm^{-1} bands (1.0232 and 1.0229, respectively) compare favorably to the experimental values of 1.0234 and 1.0218, although the theoretical $^{16}O/^{18}O$ isotopic ratios for 2067.6 and 2043.2 cm^{-1} (1.0241 and 1.0246, respectively) are higher than the experimental values of 1.02265 and 1.02129. To ensure that these two bands do belong to the same molecule, the relative band intensity was determined to be within 10% during stepwise annealing. Support for the identification of $(OC)_2BeBe(CO)_2$ is found in the general agreement between the observed and calculated mixed isotopic spectra. Unfortunately, the yield was not sufficient to observe weaker Be−C stretching modes.

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Table 7. Frequencies (cm^{-1}) Calculated for the Singlet C_{2v} Molecule $OCBeBe(CO)_2$ at the SCF Level Using the 6-311G* Basis Sets[a]

$^{12}C^{16}O$	$^{13}C^{16}O$	$^{12}C^{18}O$	mode
2386.7 (719)[b]	2332.2	2331.1	sym C−O
2177.9 (4367)	2131.2	2123.0	antisym C−O
2165.9 (1468)	2114.3	2119.3	unique C−O
982.0 (90)	980.9	977.0	unique Be−C
706.9 (7)	702.2	702.6	Be−Be, Be−C
645.5 (516)	642.3	642.8	antisym Be−C
479.0 (1)	466.9	473.6	Be−C−O
476.1 (8)	465.2	473.0	Be−C−O
428.0 (37)	417.9	424.6	Be−C−O
414.8 (0)	401.9	409.8	Be−C−O
409.3 (18)	397.4	404.8	Be−C−O
330.7 (1)	322.2	327.6	
270.7 (4)[c]	266.2	262.2	

[a] Geometry: unique O−C = 1.136 Å and C−Be = 1.663 Å, Be−Be = 2.048 Å, Be−C = 1.736 Å, C−O = 1.108 Å, angle C−Be−C = 105.2°, angle Be−C−O = 176.5°. [b] Infrared intensities in km/mol. [c] Frequencies at 183.9, 187.9, 87.9, 72.0, and 44.9 cm^{-1} omitted.

Table 8. Frequencies (cm^{-1}) Calculated for the Singlet D_{2h} Molecule $(OC)_2BeBe(CO)_2$ at the SCF Level Using the 6-311G* Basis Sets[a]

$^{12}C^{16}O$	$^{13}C^{16}O$	$^{12}C^{18}O$	mode
2417.3 (0)[b]	2362.1	2360.9	sym C−O
2361.3 (2914)	2307.8	2305.7	antisym C−O
2357.4 (0)	2304.0	2302.1	sym C−O
2319.9 (6284)	2268.0	2264.3	antisym C−O
920.3 (0)	919.4	919.7	sym Be−Be
812.1 (0)	810.2	808.0	sym Be−C
746.6 (94)	744.6	741.7	antisym Be−C
579.1 (257)	569.7	576.9	C−Be−C, Be−C
490.4 (0)	480.9	487.0	Be−C−O
484.4 (0)	469.1	479.3	Be−C−O
478.2 (0)	462.7	473.6	Be−C−O
464.8 (86)	454.2	460.9	out-of-plane
427.0 (0)	413.6	422.1	Be−Be−C
420.0 (98)	411.5	411.8	C−Be−C
414.2 (0)	401.4	409.3	Be−Be−C
405.4 (1)[c]	392.6	400.9	Be−Be−C

[a] Geometry: Be−Be = 1.926 Å, Be−C = 1.742 Å, C−O = 1.107 Å, angle C−Be−C = 112.0°, angle Be−C−O = 173.8°. [b] Infrared intensities in km/mol. [c] Frequencies at 271.9, 119.3, 101.1, 100.8, 66.7, 62.8, 39.1, and 31.1 cm^{-1} omitted.

The diberyllium tetracarbonyl molecule is clearly more difficult to make than the diberyllium tricarbonyl on the basis of reactions 9−11. However, the $Be(CO)_2$ dimerization reaction is exothermic,[13] and tertiary reactions like (15) are also possible. The 10-fold growth on annealing in the more dilute CO experiments follows from such reactions.

$$2Be(CO)_2 \rightarrow (OC)_2BeBe(CO)_2 \quad \Delta E = -12 \text{ kcal/mol} \tag{14}$$

$$2CO + OCBeBeCO \rightarrow (OC)_2BeBe(CO)_2 \quad \Delta E = -22 \text{ kcal/mol} \tag{15}$$

Since it can be argued that one of these product bands might be due to $Be(CO)_4$, calculations were performed for $Be(CO)_4$. The lowest energy structure is a singlet molecule with D_{2d} symmetry. This makes the formation via reaction (16) endothermic by 18 kcal/mol, which is not in accord with the increase observed on annealing. Clearly $Be(CO)_4$ is a less stable molecule (1 kcal/mol above Be + 4CO) than $Be(CO)_3$ (16 kcal/mol below Be + 3CO). Accordingly, $Be(CO)_4$ is ruled out.

$$Be(CO)_3 + CO \rightarrow Be(CO)_4 \quad \Delta E = +18 \text{ kcal/mol} \tag{16}$$

Sunil predicted that the $(OC)_2BeBe(CO)_2$ product of reaction 14 should be stable with a calculated Be−Be bond distance of 1.938 Å following the methylene−ethylene analogy.[13] The shortening of the Be−Be bond from the weak van der Waals bond length of 2.45 Å and the $B^1\Sigma_u^+$ state net single bond[34] value of 2.16 Å certainly involves σ and π bonding interactions between the individual triplet $Be(CO)_2$ precursors. The triplet OCBeBeCO molecule is calculated here to have an even shorter Be−Be bond length of 1.855 Å. This Be−Be bond has more "double bond" character—$(\sigma)^2(\pi_x)^1(\pi_y)^1$—than the diberyllium tetracarbonyl.

Bridge-Bonded Carbonyls. Bands at 1795.9 and 1644.6 cm^{-1} grow markedly on annealing and are in the region expected for bridge-bonded carbonyl stretching motions. These bands are probably due to carbonyls bridge bonded to higher order beryllium clusters.

BeO Complex. The band at 1471.1 cm^{-1} shows a very small ^{13}C shift but a significant ^{18}O shift and is present as a doublet in the $^{16}O/^{18}O$ mixed isotope experiments indicating a single O atom species. There is no band in the CO region that behaves like this band although a slightly shifted band would be masked by CO itself. Additionally, OBeCO and OBeOC have been previously identified from the Be + CO_2 reaction.[26] The 1471.1 cm^{-1} band is probably due to an aggregate species containing a BeO subgroup in a higher complex.

Conclusions

Beryllium reactions with carbon monoxide yield beryllium carbonyl products in solid argon. Ab initio calculations show that BeCO has higher energy than Be + CO and thus BeCO cannot be formed on annealing of cold matrix samples. Accordingly, the simple beryllium carbonyl compounds formed on annealing are due to small clusters of reagents and are identified as beryllium cluster carbonyl and a beryllium cluster dicarbonyl, BeBeCO and OCBeBeCO, which are formed by exothermic association reactions. The activation energy for higher beryllium carbonyl formation is very small as evidenced by the 10-fold increase in higher carbonyl bands on annealing from 10 to 30 K. Ab initio calculations and isotopic substitution of ^{13}CO and $C^{18}O$ sugget that the most likely higher carbonyls formed here are the most stable monoberyllium carbonyls $Be(CO)_2$ and $Be(CO)_3$ and diberyllium dicarbonyl, tricarbonyl, and tetracarbonyl, $BeBe(CO)_2$, $OCBeBe(CO)_2$, and $Be_2(CO)_4$. Other beryllium carbonyls may be formed in smaller yield. It is noteworthy that Be−C as well as C−O stretching modes were observed for the former four molecules. In spite of the fact that Be−CO is repulsive in the ground state, $Be(CO)_2$ and $Be(CO)_3$ are stable molecules with average CO binding energies of 5 and 14 kcal/mol, respectively, calculated at the MP4 level.[36] Cooperative effects in the binding of CO to Be are clearly observed.

The best agreement between SCF calculations and experiment was found here for $Be(CO)_3$ with strong antisymmetric C−O and Be−C stretching fundamentals. Clearly, the SCF level of theory is expected to provide a better description for a strongly bound, singlet, monoberyllium carbonyl than for the more weakly bound, triplet, diberyllium species.

Preliminary results from this laboratory for matrix reactions of Mg, Ca, Sr, and Ba with CO also suggest that metal clusters are required to complex CO molecules.[38] This is in agreement with beryllium cluster monocarbonyls but differs from the higher carbonyls such as $Be(CO)_3$ where no heavier metal analog has been found. The beryllium carbonyl observations also differ

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with the results for lithium but are in accord with the results for heavier group 1 reactions.[1,2] In addition the heavier group 2 metals support the formation of carbon–carbon-bonded species, which beryllium does not.

In all of the new beryllium carbonyl species characterized here, the observed $^{12}CO/^{13}CO$ ratios are slightly higher than the diatomic CO value and the observed $C^{16}O/C^{18}O$ ratios are slightly lower than the diatomic value. This means that the CO subgroups are bonded to a small Be_x subunit that participates in the Be–C–O vibrational motion, allowing C to move with some antisymmetric character, thus gaining contribution to the reduced mass of the vibration at the expense of O.

Finally, the chemical parallel with H and CO addition to Be_2 is noteworthy.[23,39] As described above, Be_2 is a van der Waals molecule with a long weak bond.[34,35] On the addition of slightly more electronegative substituents, like H and CO, antibonding electron density is withdrawn and bonding between beryllium atoms increases with a concomitant decrease in bond length, and the BeBeH and HBeBeH molecules have been characterized.[23,29] The BeBeCO and OCBeBeCO molecules also exhibit stabilization of the Be–Be bond. The OCBeBeCO molecule reported here has a short SCF calculated Be–Be bond (1.855 Å), which exhibits more double bond character than the ethylene analog $(OC)_2BeBe(CO)_2$ with a longer SCF calculated Be–Be bond (1.926 Å).

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