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Reactions of Pulsed-Laser-Evaporated Be Atoms with CO_2. Infrared Spectra of OCBeO and COBeO in Solid Argon

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Abstract: Pulsed-laser-evaporated Be atoms and CO_2 react during condensation in excess argon to form CO, ArBeO, BeOBe, and two new molecules with CO and BeO stretching absorptions. Ab initio calculations at the MBPT(2) level reveal two stable isomeric products OC–BeO and CO–BeO and predict vibrational frequencies. The OC–BeO and CO–BeO molecules are identified by matching calculated and observed 16/18 and 12/13 isotopic frequency ratios in both submolecule stretching fundamentals. The BeO molecule is an extremely strong Lewis acid as attested by the formation of ArBeO and the blue shift in the CO fundamental for OC–BeO.

Introduction

Reactions of metal atoms with carbon dioxide give several different types of products depending on the metal. In the case of alkali metals a principal product is the $M^+CO_2^-$ ion pair with C_{2v} symmetry, in which the alkali metal cation is symmetrically located between the oxygen atoms;[1–3] lithium gives also the LiOCO species (C_s symmetry), which photoisomerizes to the cyclic isomer.[2,4] The alkali metals (except sodium) yield, in addition, the $M_2^{2+}CO_2^{2-}$ ion pairs;[2,3] two geometric isomers are obtained for the potassium and cesium adducts, of which the symmeric (C_{2v}) species is the less stable and photoisomerizes to an unsymmetrical (C_s) species. In the case of aluminum both cyclic AlO_2C and trans AlOCO species are formed and undergo a reversible isomerism.[5] Boron, however, behaves differently and inserts to give a bent OBCO molecule, which is more stable than B + CO_2 by 58 kcal/mol.[6] The trans BOCO addition product molecule is calculated to be more stable than B + CO_2 by only 25 kcal/mol.[7] The relative stability of the OBCO insertion product is probably due to the boron–carbon bond.

Beryllium atom reactions with CO_2 are of interest for comparison to the above metal–carbon dioxide species for periodic relationships in bonding trends. Theoretical calculations have predicted the stability of BeO complexes with CO owing to the strong Lewis acid strength of BeO; the OC–BeO complex is bound by 40.8 kcal/mol, but the CO–BeO isomer is bound by only 18.4 kcal/mol.[8] Beryllium atom reactions with O_2 produce infrared spectra for the Ar–BeO complex and the BeO_2, Be_2O, and Be_2O_2 molecules.[9,10] On the other hand, beryllium atom reactions with CO give evidence for beryllium carbonyls, ArBeO, and Be_2O.[11] Lithium atom reactions with CO yield both the LiCO and LiCO isomers, in addition to more complex products.[12] It is expected and found that the Be + CO_2 reaction produces the OC–BeO molecule, which is reported here.

Experimental Section

The experimental methods for pulsed-laser ablation, matrix infrared examination of products, and application to beryllium atom reactions have been described earlier.[6,13–16] In the present work pulsed-laser (50–70 mJ/pulse of 1064-nm radiation focused to a 0.1-mm spot on a rotating target) evaporated Be atoms were codeposited with Ar/CO_2 samples (50/1 and 200/1) for 2-h periods at 3 mmol/h, and infrared spectra were recorded at 0.5-cm^{-1} resolution and ±0.1-cm^{-1} accuracy on a Nicolet 750 FTIR instrument. Samples were subjected to broad-band UV photolysis (175 W) and annealing cycles, and additional spectra were recorded. Carbon dioxide (Matheson, bone dry), $C^{18}O_2$ (50% and 97%, Cambridge Isotope Laboratories), and $^{13}CO_2$ (99%, Cambridge Isotope Laboratories) were used as received.

Results

Infrared spectra and ab initio calculations of reaction products in the Be + CO_2 system will be presented.

Be + CO_2. Figure 1a shows the infrared spectrum recorded from a sample prepared by codepositing Be atoms using higher laser power in the above range and a Ar/CO_2 = 200/1 sample for 2 h. The strongest product band in the spectrum is CO at 2138.4 cm^{-1}. Beryllium species observed in previous O_2 studies appear as broad bands at 1568 and 1550 cm^{-1} (XBeO) and sharp bands at 1526.1 cm^{-1} (ArBeO) and 1412.4 cm^{-1} (BeOBe).[9,10] The weak 1944-cm^{-1} band is due to a beryllium carbonyl species.[11] New bands unique to the Be/CO_2 system are the strong 2189.5-cm^{-1} and medium-intensity 1498.2-cm^{-1} bands (labeled 1), sharp 1828.2-, 1455.5-, 1442.3-cm^{-1} and broad 1794-cm^{-1} absorptions, and sharp weak 2056.5- and 1533.9-cm^{-1} bands (labeled 2). The observed bands are collected in Table 1. Broad-band UV photolysis reduced the bands labeled 1 by 10% and increased the bands labeled 2 to 2.5 times their original intensity as is shown in Figure 1b. Subsequent sample annealing to 25 and 30 K had little effect on the product absorptions except those at 1828.2 and 1442.3 cm^{-1}, which increased slightly. Another experiment was done using a Ar/CO_2 = 200/1 sample and lower laser power, and

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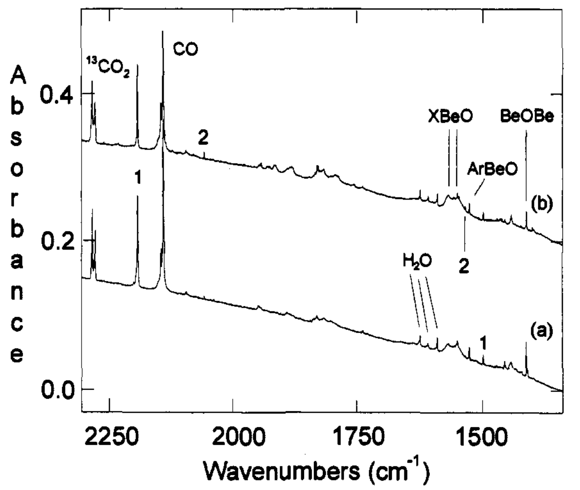

Figure 1. Infrared spectra in the 2300–1340-cm^{-1} region for the pulsed-laser-evaporated Be atom reaction with CO_2: (a) Ar/CO_2 = 200/1 codeposited with Be for 2 h at 10 K and (b) after broad-band photolysis for 30 min. The band due to $^{13}CO_2$ in its natural abundance is indicated.

Table 1. Infrared Absorptions (cm^{-1}) Observed in Solid Argon for Reactions of Be Atoms with Isotopic CO_2 Molecules

$^{12}C^{16}O_2$	$^{12}C^{18}O_2$	$^{13}C^{16}O_2$	identification
2189.5	2139.4	2140.1	species 1, OCBeO
2138.4	2087.4	2091.5	CO
2056.5	2006.8	2011.9	species 2, COBeO
1944	1908		Be_xCO
1828.2	1794.6		aggregate, $(Be_xO_y)(OCO)$
1794	1762		aggregate, $(Be_xO_y)(OCO)_z$
1533.9	1506.8	1533.8	species 2, COBeO
1526.1	1497.7	1526.1	ArBeO[a]
1498.2	1472.5	1498.1	species 1, OCBeO
1455.5	1418.7		aggregate, (BeOBe)(OCO)
1442.3	1405.8		aggregate, $(BeOBe)(OCO)_x$
1412.4	1371.2	1412.4	BeOBe[a]

[a] References 9 and 10.

the yield of bands labeled 1 and 2 was about 20% higher than in Figure 1a, but the 1455.5- and 1412.4-cm^{-1} bands were weaker by the same amount. Photolysis decreased the 1 bands by 10% and increased the 2 bands to 2.5 times their original intensity. Annealing to 20 K had little effect on the 1 and 2 bands, but further annealing to 30 K decreased both sets of bands by about 20%.

A final experiment was done with a Ar/CO_2 = 50/1 sample and lower laser power, and the product band intensities were reduced from those shown in Figure 1a; BeOBe was not observed in the spectrum. In addition to CO at 2138.4 cm^{-1}, a stronger 2143.0-cm^{-1} band due to the $(CO_2)(CO)$ complex[17] was observed, and strong equal intensity bands at 1383.6 and 1279.6 cm^{-1} were observed for the Fermi doublet[18] of CO_2 presumably made allowed in CO_2 clusters trapped in the matrix. Photolysis had the same effect on the bands labeled 1 and 2; the former decreased and the latter increased slightly.

Be + $C^{18}O_2$. Figure 2a illustrates the spectrum from a $C^{18}O_2$ sample codeposited with Be atoms. The strongest product band in the spectrum at 2139.4 cm^{-1} (labeled 1) covers a small amount of $C^{16}O$ at 2138.4 cm^{-1}; note the weak $C^{16}O_2$ product band at 2189.5 cm^{-1} and $C^{18}O$ at 2087.4 cm^{-1}. The sharp band labeled 2 in this region shifts to 2006.8 cm^{-1}, the beryllium carbonyl species appears at 1908 cm^{-1}, and weak sharp and broad bands are found at 1794.6 and 1762 cm^{-1}. In the lower region $ArBe^{18}O$ appears at 1497.7 cm^{-1}, the band labeled 1 at 1472.5 cm^{-1}, the weak band labeled 2 at 1506.8 cm^{-1}, other bands at 1418.7 and 1405.8 cm^{-1}, and $Be^{18}OBe$ at 1371.2 cm^{-1}.[9,10] Annealing to 36 K, shown in Figure 2b, decreased all bands by about 25%, but those at 1794.6 and 1406 cm^{-1}, which increased slightly. A final photolysis (not shown) had the same effect as that described above: bands labeled 1 decreased by 10% and bands labeled 2 increased to 2.5 times their original intensity.

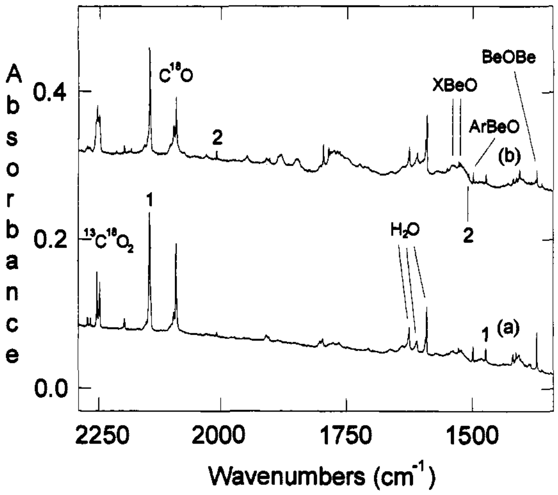

Figure 2. Infrared spectra in the 2280–1340-cm^{-1} region for the pulsed-laser-evaporated Be atom reaction with $C^{18}O_2$: (a) $Ar/C^{18}O_2$ = 200/1 codeposited with Be for 2 h at 10 K and (b) after annealing to 36 K. The peak due to $^{13}C^{18}O_2$ in the $C^{18}O_2$ sample is indicated.

A similar 200/1 experiment was performed with a 50% enriched $C^{16,18}O_2$ sample. The bands labeled 1, 2, ArBeO, and BeOBe were clear doublets in the spectrum. The 1455.5- and 1442-cm^{-1} and 1418.7- and 1406-cm^{-1} bands also appeared as doublets, but the 1828.2- and 1794.6-cm^{-1} bands shifted slightly to 1825.7 and 1802.0 cm^{-1}. This experiment was repeated with a 50/1 sample and lower laser power, and the results parallel those reported above. Weaker bands labeled 1 and 2 were observed as isotopic doublets in the same relative intensities, and a very weak BeOBe doublet was observed at 1412.4 and 1371.2 cm^{-1}. The $(C^{18}O)(CO_2)$ complex was observed at 2091.8 cm^{-1} as a satellite to $C^{18}O$ at 2087.4 cm^{-1}. The Fermi doublet for mixed isotopic $C^{16,18}O_2$ clusters became a 1:2:1:1:2:1 sextet at 1383.5, 1359.2, 1333.1, 1278.3, 1254.2, 1227.0 cm^{-1}.

Be + $^{13}CO_2$. One experiment was done with a $Ar/^{13}CO_2$ = 50/1 sample and lower laser power. The major product band was ^{13}CO at 2091.5 cm^{-1} with a $(^{13}CO)(^{13}CO_2)$ satellite at 2095.5 cm^{-1}. The major new product band appeared at 2140.1 cm^{-1} with a weaker counterpart at 1498.1 cm^{-1} (species 1), and the minor product band appeared at 2011.9 cm^{-1} with a weaker counterpart at 1533.8 cm^{-1} (species 2). Species 1 and 2 bands were observed with the same relative intensities as before. In addition, the Fermi doublet for $^{13}CO_2$ clusters was observed at 1367.8 and 1256.6 cm^{-1} with 6:1 relative intensity.

Calculations. Ab initio calculations at the MP2 and MP4 levels have predicted that the linear isomers COBeO and OCBeO are stable with respect to dissociation into the diatomic products by 18.4 and 40.8 kcal/mol, respectively.[8] These calculations were repeated here at the MBPT(2) level using the 6-311G* basis sets and the ACES II program system[19] in order to generate isotopic frequencies and intensities. Figure 3 shows the geometries and energies for the two isomers, which are in very good agreement with Frenking et al., allowing for the different basis sets employed. The present energy difference, 21.2 kcal/mol, is also in good agreement with the earlier 22.4 kcal/mol value.[8] In addition, energy calculations were done here at the MBPT(2) level for Be (–14.614 05 au), CO (–113.120 00 au), BeO (–89.730 34 au),

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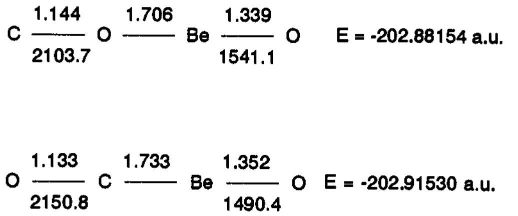

Figure 3. Bond distances (Å), frequencies (cm^{-1}), and energies (au) calculated for CO–BeO and OC–BeO at the MBPT(2) level with 6-311G* basis sets.

Table 2. Harmonic Frequencies (cm^{-1}) and Infrared Intensities (km/mol) Predicted for OCBeO Isotopic Molecules at the MBPT(2) Level with the 6-311G* Basis Sets

16-12-9-16[a]	16-13-9-16	16-12-9-18	18-12-9-16	18-12-9-18
(σ+) 2150.8 (356)	2101.3	2150.8	2101.2	2101.2
(σ+) 1490.4 (124)	1490.3	1465.5	1490.2	1465.2
(σ+) 444.7 (0.4)	441.4	434.4	437.2	426.8
(π) 419.2 (0.4)	409.6	419.0	416.2	416.0
(π) 98.9 (35)	98.4	97.8	98.0	96.9

[a] (Mode symmetry) frequency (intensity).

Table 3. Harmonic Frequencies (cm^{-1}) and Infrared Intensities (km/mol) Predicted for COBeO Isotopic Molecules at the MBPT(2) Level with the 6-311G* Basis Sets

12-16-9-16[a]	13-16-9-16	12-16-9-18	12-18-9-16	12-18-9-18
(σ+) 2103.7 (114)	2057.6	2103.7	2051.9	2051.9
(σ+) 1541.1 (13)	1541.0	1513.4	1541.1	1531.4
(σ+) 366.0 (0.13)	362.9	357.9	360.3	352.1
(π) 281.2 (24)	280.8	280.0	277.4	276.2
(π) 117.0 (19)	115.3	116.1	114.5	113.7

[a] (Mode symmetry) frequency (intensity).

and CO_2 (−188.268 10 au) to predict reaction energetics. These values are also compatible with earlier calculated values.[8,20,21]

Calculated isotopic frequencies are listed in Tables 2 and 3 for the two isomers OCBeO and COBeO. Infrared intensities are given for the common isotopic molecule; little variation was found in the mode intensities upon isotopic substitution.

Discussion

New infrared absorptions will be assigned to product molecules and bonding trends in CO complexes, and reaction mechanisms will be considered.

Assignments. The 1526.1- and 1412.4-cm^{-1} bands have been observed in Be + O_2 experiments. The oxygen-18 shifts to 1497.7 and 1371.2 cm^{-1}, the doublet character of both bands with $^{16,18}O_2$ reagent, and ab initio calculations substantiate their assignment to ArBeO and BeOBe.[9,10,21] Observation of the same 1526.1- and 1412.4-cm^{-1} bands in the present Be + CO_2 experiments supports the earlier assignments, shows that Be abstracts oxygen from CO_2 to produce BeO under the conditions of these experiments, and raises the possibility of the OCBeO and COBeO product molecules in the matrix sample.

Two pairs of new product absorptions were observed in the Be + CO_2 experiments, each with a band in the CO and in the BeO stretching regions of the infrared spectrum. The bands labeled 1 at 2189.5 and 1498.2 cm^{-1} decreased together (10%) on photolysis, and the bands labeled 2 at 2056.5 and 1533.9 cm^{-1} increased together (doubled) on photolysis; no other bands exhibited these changes. The 2189.5- and 1498.2-cm^{-1} bands were also observed in analogous CO experiments[11] with 10% of the present absorbance, but the same relative intensities, and these bands doubled on annealing to 30 K. The 2056.5-cm^{-1} band was also detected after photolysis with 6% of the absorbance in CO_2 experiments.

The observed bands exhibit 16/18 isotopic ratios near those for harmonic CO (1.02443) and BeO (1.02069) stretching vibrations. In the case of species 1, 2189.5/2139.4 = 1.02342 and 1498.2/1472.5 = 1.01745, and in the case of species 2, 2056.5/2006.8 = 1.02477 and 1533.9/1506.8 = 1.01799. Of course, the OCBeO and COBeO molecules involve different participations of oxygen in the normal modes, and slightly different isotopic ratios result. The mixed isotopic experiments show that the CO and BeO stretching modes involve single uncoupled oxygen atoms.

Ab initio calculations at the MBPT(2) level are expected to predict frequencies close to the observed values. However, for highly polar molecules such as BeO, the errors can be substantial. The BeO fundamental is calculated in the 1400–1420-cm^{-1} range depending on the level of theory, and the observed fundamental is 1464 cm^{-1}.[10,20-22] The linear molecules OCBeO and COBeO are also highly polar as the dipole moment of BeO dominates.[21] The ab initio frequency calculations in Tables 2 and 3, then, provide a general guide on frequency position, but the isotopic frequency ratios are expected to be accurate. Calculations predict the OCBeO molecule to have the higher CO stretching mode and the lower BeO stretching mode with 16/18 ratios of 1.023 61 and 1.017 20, respectively. On the other hand, calculations predict the COBeO molecule to have the lower CO stretching mode and the higher BeO stretching mode with 16/18 ratios of 1.025 24 and 1.018 30. It is clearly seen that the observed frequency positions and 16/18 ratios for species 1 match very well with the calculated values for OCBeO and the observed positions and ratios for species 2 match the calculated values for COBeO. The calculations also show that there is practically no coupling between the two oxygen atoms.

The 12/13 isotopic ratios are calculated to be higher (1.023 56) for OCBeO than for COBeO (1.022 40), and the observed species 1 ratio (1.023 08) fits the former and the observed species 2 ratio (1.022 12) fits the latter. Note also the calculated and observed 0.1-cm^{-1} carbon-13 shifts for the Be–O stretching modes of both isomers. Accordingly, species 1 is identified as OCBeO and species 2 as COBeO.

The 1455.5- and 1442.3-cm^{-1} and 1828.2- and 1794-cm^{-1} bands are in accord with (BeOBe)(OCO) aggregate molecules. The lower frequency bands have large 16/18 ratios (1.025 93 and 1.025 96) which are just below that for BeOBe (1.030 05). The decrease at 1455.5 cm^{-1} and growth at 1442.3 cm^{-1} on annealing support tentative assignments of these bands to (BeOBe)(OCO) and (BeOBe)$(OCO)_x$, respectively. The sharp upper frequency mode has a 16/18 ratio (1.018 72) below that of CO (1.024 43) but appropriate for a C–O stretch in a subunit weakly coupled to a second oxygen atom as suggested from the mixed isotopic spectrum. The sharp and broad bands are tentatively assigned to CO_2 and CO_2 clusters with beryllia species, which is in accord with their growth on annealing.

Bonding Trends. Frenking et al. pointed out the unique property of BeO as the strongest diatomic neutral Lewis acid.[7,21] This suggests in a series of X–CO molecules or complexes that OBe should have the largest effect on the CO fundamental as the lone pair on carbon is weakly antibonding.[23] Table 4 collects CO stretching fundamentals for diatomic and CO_2 complexes with CO. In particular, the HF Lewis acid blue shifts the CO fundamental to 2162.4 cm^{-1} and the LiF Lewis acid to 2185 cm^{-1} followed by BeO at 2189.5 cm^{-1}.[24,25] Only small metal difluoride and trifluoride complexes with CO give higher fundamentals.[24]

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Table 4. Stretching Fundamentals (cm^{-1}) for CO–Small Molecule Complexes in Solid Argon

molecule	ν(CO)	molecule	ν(CO)
CO	2138.4	FH–CO	2162.4[b]
$(CO_2)(CO)$	2143.0[a]	FLi–CO	2185[c]
ClH–CO	2154.2[b]	OBe–CO	2189.5

[a] Reference 17. [b] Reference 24. [c] Reference 25.

The CO fundamental has been related to the strength of the electric field near the cation binding to the CO submolecule.[24] The HCO^+ molecular ion with a C–O stretching fundamental at 2183.95 cm^{-1} provides an interesting comparison;[26] this fundamental would probably be slightly higher if it were not for interaction with the H–C stretching fundamental at 3088.74 cm^{-1}.

Reaction Mechanisms. The primary reaction 1 of interest here is endothermic by 20.0 kcal/mol on the basis of MBPT(2) energy calculations and 20 ± 2 kcal/mol on the basis of thermochemical calculations.[27] The pulsed-laser-evaporated Be atoms produced

$$Be + CO_2 \rightarrow BeO + CO \qquad (1)$$

here clearly have more than enough kinetic energy to activate reaction 1 on the basis of the observation of CO, ArBeO, and BeOBe in the spectra.[9,10] Reactions of pulsed-laser-evaporated Al and Be atoms with O_2 in this laboratory give OAlO and OBeO, which require substantial activation energies.[10,14] Similar pulsed-laser evaporation of aluminum gives average kinetic energies measured in the 110 kcal/mol range.[28] It is reasonable for many of the laser-evaporated Be atoms in these experiments to have kinetic energies in the 30–40 kcal/mol range, which should be more than enough energy to activate reaction 1.

The BeO product of reaction 1 has three fates: to form the ArBeO species in the matrix absorbing at 1526.1 cm^{-1}, reaction 2, to add another Be atom to give BeOBe absorbing at 1412.4 cm^{-1}, reaction 3, or to complex with the CO product, reactions 4 and 5, which are exothermic by 40.8 and 19.6 kcal/mol, respectively, on the basis of the present MBPT(2) calculations.

$$Ar + BeO \rightarrow ArBeO \qquad (2)$$

$$BeO + Be \rightarrow BeOBe \qquad (3)$$

$$OC + BeO \rightarrow OC\text{–}BeO \qquad (4)$$

$$CO + BeO \rightarrow CO\text{–}BeO \qquad (5)$$

These results are in excellent agreement with the earlier calculations.[8] Note that the yield of the more stable OC–BeO species far exceeds the yield of the less stable CO–BeO species on the basis of relative CO stretching integrated band intensities (29:1) even after normalizing for calculated intensities (9:1).

Although the overall reaction (eqs 1 and 4) is exothermic by 20.8 kcal/mol, this reaction does not proceed on annealing to allow reaction of cold Be and CO_2, which is expected for a two-step reaction involving an endothermic first step. On the other hand, the exothermic reactions 4 and 5 are expected to proceed without activation energy, and the observation of a very small yield of both product isomers and the growth of OCBeO on annealing in analogous Be + CO experiments[11] supports this postulate.

Broad-band photolysis slightly decreases the OC–BeO absorptions and increases the CO–BeO absorptions. This is probably due in part to photochemical equilibration between populations of OC–BeO and CO–BeO in the matrix. The BeO molcule absorbs blue visible and near-UV radiation,[22] which can dissociate the CO complexes. The matrix apparently relaxes the less stable CO–BeO form more efficiently such that photolysis results in a decrease in OC–BeO and an increase in CO–BeO. Assuming that the calculated C–O stretching intensities (Tables 2 and 3) are correct, the increase in 2 cannot be accounted for solely by the decrease in 1. Accordingly, additional reaction 1 may be activated by UV excitation[29] of Be with preferential relaxation of the CO–BeO isomer.

The two structures for BeO complexes with CO are reminiscent of two HF complexes with CO.[30] Calculations show that OC--HF is more stable than CO--HF by 1 kcal/mol,[31] and the more stable form was observed first in the gas phase[32] and in solid argon at 12 K.[24] Subsequent experiments trapping HF and CO in solid argon at 5 K characterized the more stable OC--HF and the less stable CO--HF forms.[29]

Conclusions

Pulsed-laser-evaporated Be atoms react with CO_2 during condensation with excess argon to form CO, ArBeO, and BeOBe and two new product molecules with CO and BeO stretching absorptions. Ab initio calculations at the MBPT(2) level show that two isomeric products OC–BeO and CO–BeO are stable, in agreement with earlier calculations,[8] and predict isotopic frequencies for each molecule. The OC–BeO and CO–BeO molecules are identified on the basis of matching calculated and observed 16/18 and 12/13 isotopic frequency ratios in both submolecule stretching fundamentals. The more stable OC–BeO isomer is produced in substantially larger yield over the less stable isomer on reagent codeposition; however, broad-band photolysis redistributes the population to increase the less stable isomer at the expense of the more stable isomer. Finally, BeO is an extremely strong Lewis acid, as indicated by the formation of ArBeO[9,10,21] and the large blue shift in the CO fundamental to 2189.5 cm^{-1} for the OC–BeO species.

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