Bonding Analysis

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Carbon Monoxide Bonding With BeO and $BeCO_3$: Surprisingly High CO Stretching Frequency of $OCBeCO_3$**

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Dedicated to Professor Christian Reichardt on the occasion of his 80th birthday

Abstract: *The complexes $OCBeCO_3$ and $COBeCO_3$ have been isolated in a low-temperature neon matrix. The more stable isomer $OCBeCO_3$ has a very high C–O stretching mode of 2263 cm^{-1}, which is blue-shifted by 122 cm^{-1} with respect to free CO and 79 cm^{-1} higher than in OCBeO. Bonding analysis of the complexes shows that OCBeO has a stronger OC–BeY bond than $OCBeCO_3$ because it encounters stronger π backdonation. The isomers $COBeCO_3$ and COBeO exhibit redshifted C–O stretching modes with respect to free CO. The inverse change of C–O stretching frequency in OC–BeY and CO–BeY is explained with the reversed polarization of the σ and π bonds in CO.*

The isolation of reactive species in low-temperature matrices is a very important method for investigating molecules which are otherwise difficult to study experimentally. By combining spectroscopic results of matrix-isolated compounds with quantum-chemical calculations it becomes possible to investigate molecules which possess unusual bonding situations.[1] A striking example is the first neutral argon compound HArF, which was synthesized and identified in an argon matrix by Kriachtchev et al. in 2000.[2] Another example is the family of compounds XBeO where X is a σ donor ligand. Theoretical studies predicted that monomeric BeO is an unusually strong Lewis acid, which binds rather strongly even with noble gas atoms He–Xe[3] and with the ligands CO and N_2.[4] The theoretical findings were confirmed by low-temperature matrix studies, in which the molecules XBeO with X = Ar, Kr, Xe, N_2, and CO could be synthesized.[5] A remarkable aspect of the latter species is that both isomers OCBeO and COBeO could be identified.[5b] The identification was made possible by comparing the calculated and observed oxygen 16/18 and carbon 12/13 isotopic frequency ratios in the stretching fundamentals. The carbonyl complex OCBeO was measured with a C–O stretching frequency of 2190 cm^{-1} that corresponds to a blueshift of 52 cm^{-1} with respect to CO, which has an observed stretching mode of 2138 cm^{-1} in solid argon.[5b]

Carbonyl complexes $OC\rightarrow A$ (A = acceptor moiety), which possess C–O stretching frequencies that are higher than in free CO, have been termed “abnormal carbonyls ” by Strauss,[6] because the majority of carbonyl complexes shows a redshift with respect to CO. It has been shown that the OC–A bond in abnormal carbonyls exhibits very little $OC\leftarrow A$ π backdonation and that the bonding interactions come mainly from $OC\rightarrow A$ σ-donation.[7] $OC\leftarrow A$ π backdonation leads to a redshift of the C–O stretching mode, because the antibonding π* orbital of CO becomes occupied. The driving force for the blueshift of the $OC\rightarrow A$ σ donation has been the topic of a debate some years ago. It was first suggested that the HOMO (highest occupied molecular orbital) of CO which is a σ orbital has antibonding character.[8] The shape of the σ-HOMO and the finding that σ donation from the oxygen end in COH^+ leads to a strong redshift of the C–O stretching mode speak against an antibonding character of the orbital.[9] An alternative explanation which rationalizes the C–O blueshift in HCO^+ and the redshift in COH^+ has been given in terms of the opposing polarization of the σ and π orbitals of CO when a positive charge approaches the molecule from either end.[10] Whatever explanation is used, it is clear that BeO is a strong σ acceptor. This becomes apparent by the unusually strong bonding in the noble gas complexes XBeO (X = He–Xe), which are devoid of π backdonation.[3,5a]

The finding that BeO is an unusually strong σ acceptor led to a search for other species BeY, which might further enhance the Lewis acidity of the acceptor fragment. Until today, no such molecule was found. Here we report about beryllium carbonate $BeCO_3$ which exhibits unusual acceptor properties. We isolated the carbonyl complex $OCBeCO_3$ along with the isomer $COBeCO_3$ in a neon matrix. The former species has a C–O stretching frequency of the donor CO moiety of 2263 cm^{-1}. This is a further blueshift of 79 cm^{-1} compared with OCBeO, which has a value of ν(C–O) = 2184 cm^{-1} in solid neon. To the best of our knowledge, the observed value of ν(C–O) = 2263 cm^{-1} is the second highest C–O stretching frequency which has ever been reported for a neutral[11] carbonyl complex. A slightly larger value of ν(C–

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O) = 2267 cm^{-1} was found for the boron complex OCB($CF_3)_3$.[12] The much higher C–O stretching frequency in $OCBeCO_3$ suggests that the bonding might be stronger than in OCBeO, which raises the question about the nature of the bonding in the two molecules. Here we report about experimental and theoretical investigations of $OCBeCO_3$ and OCBeO and the isomers $COBeCO_3$ and COBeO.

The XBeO and $XBeCO_3$ (X = CO or OC) complexes were experimentally studied by matrix isolation infrared absorption spectroscopy, which has been described in detail previously.[1a,d] The complexes were prepared by co-deposition of laser-evaporated Be atoms with CO_2/Ne mixtures onto a CsI window at 4 K. Infrared spectra were recorded on a Bruker Vertex 80 V spectrometer at 0.5 cm^{-1} resolution using a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector. Figure 1 shows the spectra in selected regions from co-deposition of laser-evaporated beryllium atoms with 0.05 % CO_2 in neon. Besides the known CO_2 (2347.7 and 668.0 cm^{-1}), CO (2140.8 cm^{-1}), and CO_2^- (1658.3, 1253.8, and 714.1 cm^{-1}) absorptions,[13] new product absorptions were produced either on sample deposition or on annealing or photolysis, which can be classified into several groups based on their annealing and photochemical behaviors (labeled as **A**–**D** in Figure 1). Species **A** has one strong band at 2183.6 cm^{-1} and a weak band at 1493.8 cm^{-1}. These two bands were observed on sample deposition and remain almost unchanged on subsequent sample annealing and broad-band irradiation using the high-pressure mercury arc lamp ($250 < \lambda < 580$ nm). Species **B** involves eight absorptions at 2263.1, 1846.8, 1182.3, 1121.8, 890.0, 804.9, 796.4, and 775.3 cm^{-1}. These absorptions were weak on sample deposition, increased on annealing, and were almost destroyed on broad band UV-visible irradiation. Species **C** involves two absorptions at 2061.1 and 1557.3 cm^{-1}. Both bands appeared on sample deposition, slightly decreased on annealing, but markedly increased on UV-visible irradiation ($250 \text{ nm} < \lambda < 580$ nm).

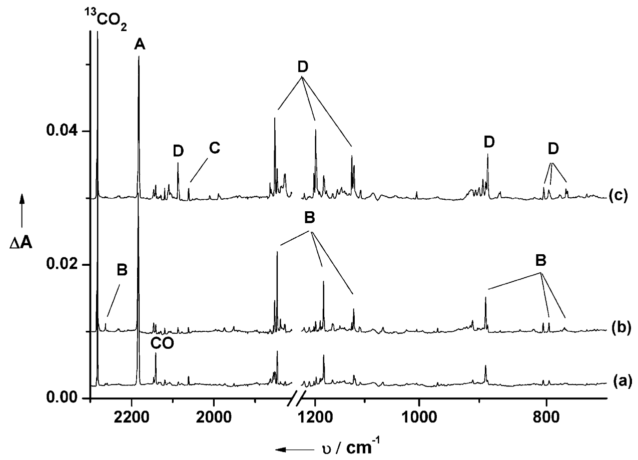

Figure 1. Infrared spectra in the 2300–1810 and 1230–720 cm^{-1} regions from co-deposition of laser-evaporated beryllium atoms with 0.05 % CO_2 in neon: a) 0.5 h of sample deposition at 4 K, b) after 12 K annealing, and c) after 15 min of UV-visible light ($580 > \lambda > 250$ nm) irradiation. **A**: OCBeO; **B**: $OCBeCO_3$; **C**: COBeO, and **D**: $COBeCO_3$.

The group **D** absorptions were produced upon broad-band UV-visible irradiation with the disappearance of the group **B** absorptions. The experiments were repeated using isotopic-labeled $^{13}CO_2$ and $C^{18}O_2$ samples, and the $^{12}CO_2 + {}^{13}CO_2$ (1:1), $C^{16}O_2 + C^{18}O_2$ (1:1), and $C^{16}O_2 + C^{16}O^{18}O + C^{18}O_2$ (61 % ^{18}O) mixtures. The spectra in selected regions with different isotopic samples are shown in Figures S1–S4 of the Supporting Information (SI).

The group **A** absorptions at 2183.6 and 1493.8 cm^{-1} correspond to the absorptions reported at 2189.5 and 1498.2 cm^{-1} that were previously assigned to the OCBeO molecule in solid argon.[5b] The upper band is due to the CO stretching vibration, and the low band represents the BeO stretching mode. The group **C** absorptions at 2061.1 and 1557.3 cm^{-1} are attributed to the CO and BeO stretching modes of the COBeO molecule in solid neon. The same modes were observed at 2056.5 and 1533.9 cm^{-1} in solid argon.[5b]

The group **B** absorptions are assigned to different vibrational modes of the $OCBeCO_3$ molecule. The 2263.1 cm^{-1} absorption exhibits isotopic frequency shifts (52.0 cm^{-1} with $^{13}CO_2$ and 51.5 cm^{-1} with $C^{18}O_2$) that are characteristic of a CO stretching vibration, which is blue-shifted by 122.3 cm^{-1} from that of diatomic CO in solid neon. Such a large blueshift indicates that the CO molecule is coordinated to a positively charged metal center. No intermediate absorptions were observed in the spectra with the mixed $^{12}CO_2 + {}^{13}CO_2$, $C^{16}O_2 + C^{18}O_2$, and $C^{16}O_2 + C^{16}O^{18}O + C^{18}O_2$ samples (see Figure S1), indicating that only one C atom and one O atom is involved in this vibrational mode. This is further supported by the components of the calculated C–O stretching mode, which show significant components at C (0.16 mass$^{-0.5}$) and O (0.22 mass$^{-0.5}$) of the CO donor species. There is a very small component at Be (0.01 mass$^{-0.5}$), whereas the other atoms have negligibly small components of < 0.0005 mass$^{-0.5}$. The spectral features of the 1846.8, 1182.3, 1121.8, 890.0, and 796.4 cm^{-1} absorptions imply that species **B** is due to a carbonate complex with the CO_3 unit coordinated to Be in a bidentate fashion forming a four-membered BeO_2C ring. The isotopic shift ($^{12}C/^{13}C$:1.0226, $^{16}O/^{18}O$:1.0191) and splitting indicate that the 1846.8 cm^{-1} absorption is due to a C=O stretching vibration and only one CO subunit is involved. The 1121.8 cm^{-1} absorption has isotopic frequency ratios of $^{12}C/^{13}C$:1.0050 and $^{16}O/^{18}O$:1.0194, which suggests that this absorption belongs to the symmetric OBeO stretching vibration. The 890.0 cm^{-1} absorption exhibits a small ^{13}C shift ($^{12}C/^{13}C$:1.0034) but quite large oxygen isotopic shift ($^{16}O/^{18}O$:1.0525), and is mainly due to the symmetric OCO stretching vibration. This mode splits into four bands with approximately equal intensities in the experiment with the $C^{16}O_2 + C^{18}O_2$ sample, whereas six bands were resolved in the experiment with the $C^{16}O_2 + C^{16}O^{18}O + C^{18}O_2$ mixture (Figure S2). These mixed isotopic spectral features confirm the involvement of a CO_3 fragment with two equivalent oxygen atoms. The $OCBeCO_3$ molecule is formed by the reaction of Be atom with two carbon dioxide molecules. The $OCBeCO_3$ absorptions increase on annealing, which implies that the reaction is spontaneous and requires negligible activation energy.

Absorber **D** was produced under irradiation with UV-visible light ($250 < \lambda < 580$ nm) at the expense of the group **B** absorptions, suggesting that the absorber of group **D** absorptions is due to a structural isomer of species **B**. Eight absorptions were observed for species **D**. The band position and isotopic frequency shifts indicate that the 2087.8 cm^{-1} absorption is a CO stretching vibration. The band positions of the other seven absorptions at 1852.2, 1199.2, 1125.2, 886.7, 804.2, 796.8, and 773.3 cm^{-1} are very close to those of $OCBeCO_3$ with very similar isotopic frequency shifts and splittings. Accordingly, the group **D** absorptions are assigned to different vibrational modes of the $COBeCO_3$ complex, a structural isomer of $OCBeCO_3$.

We carried out quantum chemical calculations using DFT and ab initio methods to investigate the structures, bond energies, and vibrational spectra of the molecules. Details of the theoretical methods are given in the SI. Figure 2 shows the calculated geometries of the molecules BeO, $BeCO_3$, and CO, and the complexes XBeO and $XBeCO_3$ (X = CO or OC) at M06-2X/def2-TZVPP, MP2/cc-pVTZ, and CCSD(T)/cc-pVTZ. The agreement between the theoretically predicted bond lengths and angles at different levels of theory is quite good. All theoretical methods suggest that the C–O distance of the CO donor molecule becomes shorter in OCBeX with respect to free CO, whereas it becomes longer in COBeX. The C–O bond shortening in $OCBeCO_3$ is more distinct than in OCBeO, whereas the C–O bond in COBeO is slightly longer than that in $COBeCO_3$.

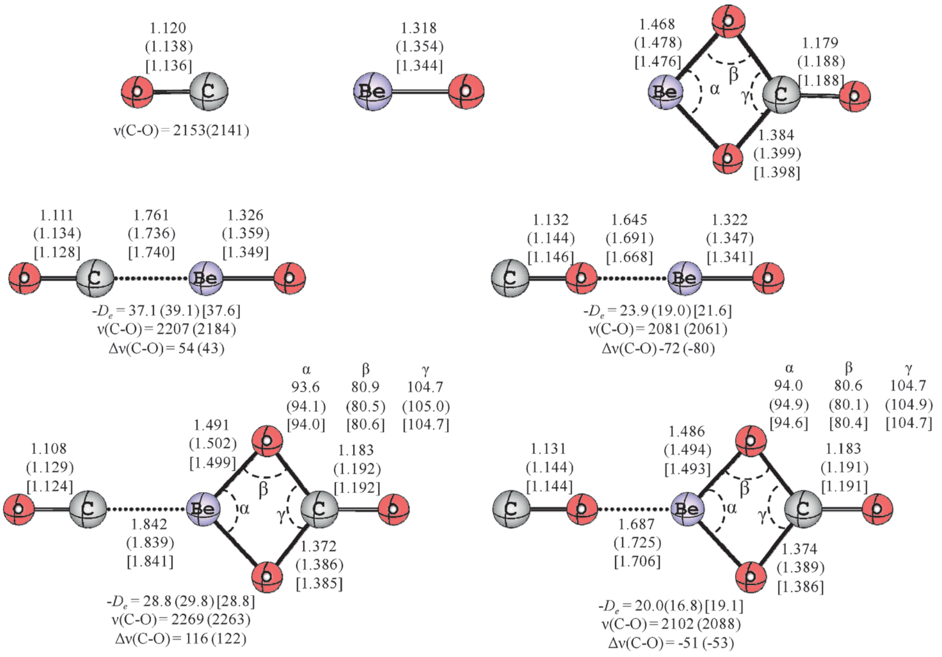

Figure 2. Optimized geometries at M06-2X/def2-TZVPP, MP2/cc-pVTZ (in parentheses), and CCSD(T)/cc-pVTZ [in brackets]. The bond lengths and angles are in [Å] and [°], respectively. Calculated bond dissociation energies (D_e) for the C–Be and O–Be bond are given in kcal mol^{-1}. Theoretical CCSD(T)/cc-pVTZ (and experimental) stretching frequencies ν(C–O) and their shift $\Delta\nu$(C–O) with respect to free CO [cm^{-1}].

Figure 2 shows also the theoretically predicted bond dissociation energies (BDEs) D_e of the CO ligand and the calculated and experimental C–O stretching frequencies ν(C–O) as well as the frequency shifts $\Delta\nu$(C–O) with respect to free CO. The BDEs at the three levels of theory are very similar to each other. The calculated D_e values show the trend OCBeO > $OCBeCO_3$ and COBeO > $COBeCO_3$. The calculations thus predict that the CO ligand in the carbonyl complexes OCBeO and $OCBeCO_3$ is more strongly bonded than in the isomers COBeO and $COBeCO_3$. The BDEs also suggest that beryllium carbonate is a weaker Lewis acid than beryllium oxide. A very interesting aspect concerns the vibrational frequencies for the C–O stretching mode. The experimental and theoretical frequencies ν(C–O) and frequency shifts $\Delta\nu$(C–O) at CCSD(T)/cc-pVTZ are in excellent agreement with each other. Both sets of values show that the carbonyl complexes OCBeO and $OCBeCO_3$ exhibit a blue-shifted frequency shift $\Delta\nu(C–O) > 0$, whereas the isomers COBeO and $COBeCO_3$ have red-shifted C–O modes $\Delta\nu(C–O) < 0$. Theory and experiment agree that the frequency shift $\Delta\nu$(C–O) in $OCBeCO_3$ is much higher than in OCBeO. But CO is more strongly bonded in the latter species than in the former complex!

We analyzed the nature of the donor–acceptor interactions in XBeO and $XBeCO_3$ (X = CO or OC) with the EDA (energy decomposition analysis) in conjunction with the NOCV (natural orbitals for chemical valence) method, which gives a detailed insight into the bonding situation. Table 1 gives the numerical results of the X–BeO and X–$BeCO_3$ interactions at BP86/TZ2P+. The calculated values for the intrinsic interactions ΔE_{int} exhibit the same trend as the BDEs, which means that the relative energies come from the strength of the donor–acceptor bonds and not from the relaxation of the fragments. The data for OCBeO and $OCBeCO_3$ show that the stronger bond in the former species ($\Delta\Delta E_{int} = 14.4$ kcal mol^{-1}) can be attributed to the bigger orbital interactions in OCBeO than in $OCBeCO_3$ ($\Delta\Delta E_{orb} = 15.2$ kcal mol^{-1}). Surprisingly, the OC→BeX σ donation in OCBeO is slightly stronger ($\Delta E_{orb}(a1) = -24.5$ kcal mol^{-1}) than in $OCBeCO_3$ ($\Delta E_{orb}(a1) = -22.5$ kcal mol^{-1}), which is puzzling in view of the C–O stretching mode of the two species. Further inspection of the orbital components of ΔE_{orb} reveals a striking difference in the strength of the OC←BeX π backdonation. The π contribution of $\Delta E_{orb}(b1) + \Delta E_{orb}(b2)$ in OCBeO is much larger (39.4 % of

Table 1: EDA-NOCV results of the chemical bonding in OC—BeY and CO—BeY (Y = O, CO_3) at BP86/TZ2P+//CCSD(T)/cc-pVTZ. Energy values are given in kcal mol^{-1}.

Fragments	OC—BeO CO and BeO	OC—$BeCO_3$ CO and $BeCO_3$
ΔE_{int}	−45.3	−30.9
ΔE_{Pauli}	32.7	25.8
ΔE_{elstat}[a]	−31.2 (40.0%)	−25.1 (44.2%)
ΔE_{orb}[a]	−46.8 (60.0%)	−31.6 (55.8%)
ΔE_{orb}(a1)[b] σ	−24.5 (52.4%)	−22.5 (71.2%)
ΔE_{orb}(b1)[b] $\pi_{\parallel}$	−9.2 (19.7%)	−4.3 (13.6%)
ΔE_{orb}(b2)[b] $\pi_{\perp}$	−9.2 (19.7%)	−2.8 (8.8%)
ΔE_{orb}(rest)[b]	−3.9 (8.3%)	−2.2 (7.0%)
Fragments	**CO—BeO CO and BeO**	**CO—$BeCO_3$ CO and $BeCO_3$**
ΔE_{int}	−24.0	−16.9
ΔE_{Pauli}	23.6	20.5
ΔE_{elstat}[a]	−14.7 (30.8%)	−11.3 (30.3%)
ΔE_{orb}[a]	−32.9 (69.2%)	−26.0 (69.7%)
ΔE_{orb}(a1)[b] σ	−14.9 (45.3%)	−15.0 (57.7%)
ΔE_{orb}(b1)[b] $\pi_{\parallel}$	−6.3 (19.1%)	−4.3 (16.5%)
ΔE_{orb}(b2)[b] $\pi_{\perp}$	−6.3 (19.1%)	−4.5 (17.3%)
ΔE_{orb}(rest)^b	−5.4 (16.5%)	−2.2 (8.5%)

[a] The values in parentheses give the percentage contribution to the total attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$. [b] The values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb}.

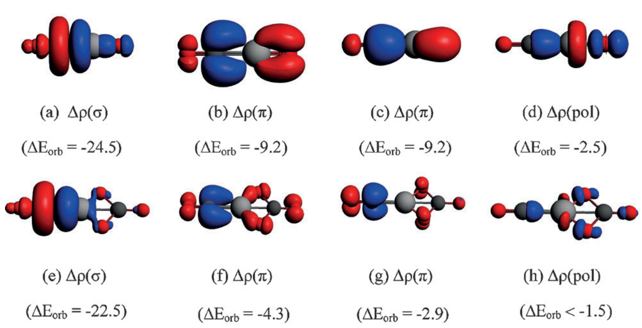
(a) Δρ(σ) (ΔE_{orb} = -24.5)
(b) Δρ(π) (ΔE_{orb} = -9.2)
(c) Δρ(π) (ΔE_{orb} = -9.2)
(d) Δρ(pol) (ΔE_{orb} = -2.5)
(e) Δρ(σ) (ΔE_{orb} = -22.5)
(f) Δρ(π) (ΔE_{orb} = -4.3)
(g) Δρ(π) (ΔE_{orb} = -2.9)
(h) Δρ(pol) (ΔE_{orb} < -1.5)

Figure 3. Plot of deformation densities $\Delta\rho$ of the pairwise orbital interactions and the associated interaction energies ΔE_{orb} (in kcal mol^{-1}) between CO and BeO moieties in OCBeO and $OCBeCO_3$. The direction of the charge flow is red→blue. a) σ donation OC→BeO. b and c) π backdonation OC←BeO. d) Polarization in OCBeO. e) σ donation OC→$BeCO_3$. f and g) π backdonation OC←$BeCO_3$. h) Polarization in $OCBeCO_3$.

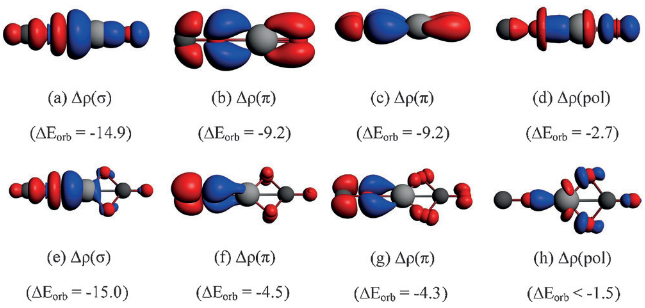
(a) Δρ(σ) (ΔE_{orb} = -14.9)
(b) Δρ(π) (ΔE_{orb} = -9.2)
(c) Δρ(π) (ΔE_{orb} = -9.2)
(d) Δρ(pol) (ΔE_{orb} = -2.7)
(e) Δρ(σ) (ΔE_{orb} = -15.0)
(f) Δρ(π) (ΔE_{orb} = -4.5)
(g) Δρ(π) (ΔE_{orb} = -4.3)
(h) Δρ(pol) (ΔE_{orb} < -1.5)

Figure 4. Plot of deformation densities $\Delta\rho$ of the pairwise orbital interactions and the associated interaction energies ΔE_{orb} (in kcal mol^{-1}) between CO and BeO in COBeO and $COBeCO_3$. The direction of the charge flow is red→blue. a) σ donation CO→BeO. b and c) π backdonation CO←BeO. d) Polarization in COBeO. e) σ donation CO→$BeCO_3$. f and g) π backdonation CO←$BeCO_3$. h) Polarization in $COBeCO_3$.

ΔE_{orb}) than in $OCBeCO_3$ (22.4% of ΔE_{orb}). It is known from previous studies[7] that OC←A π backdonation has a stronger impact on the C—O stretching than OC→A σ donation.[14] Thus, the stronger donor–acceptor bond and lower C—O stretching frequency in OCBeO than in $OCBeCO_3$ can be explained with the bigger contribution of OC←BeX π backdonation in the former species, which enhances the donor–acceptor interactions but weakens the C—O bond.

Which explanation is given by the EDA-NOCV results for the redshift $\Delta\nu$(C—O) of the isomers COBeO and $COBeCO_3$? Table 1 shows that there is no dramatic change in the relation of σ donation and π backdonation in comparison with the more stable isomers OCBeO than in $OCBeCO_3$. The percentage contribution of OC→A σ donation in COBeO and $COBeCO_3$ is a bit less than in OCBeO than in $OCBeCO_3$, but the modest alteration does not explain the substantial difference of the frequency shifts $\Delta\nu$(C—O) between the two pairs of isomers. Relevant information is provided by the deformation densities $\Delta\rho$ which are associated with the pairwise orbital interactions are considered. They are shown in Figure 3 and Figure 4.

Figure 3 displays the deformation densities $\Delta\rho(\sigma)$ and $\Delta\rho(\pi)$ which are connected to the σ donation and π backdonation in OCBeO and $OCBeCO_3$. The direction of the charge flow, which is indicated by the colors red→blue, nicely illustrates the change in the electronic structure of the molecules. The shape of $\Delta\rho(\sigma)$ indicates that the charge flow comes mainly from the lone-pair electrons at carbon (Figure 3a) or oxygen (Figure 3e) to the beryllium atom. Note that the π backdonation OC←BeO (Figure 3b,c) and OC←$BeCO_3$ (Figure 3f,g) leads to charge accumulation only at the carbon atom of CO (blue region), whereas electronic charge at the oxygen end (red region) is depleted. The deformation densities $\Delta\rho(\pi)$ for OCBeO and $OCBeCO_3$ thus reveal not only the impact of the π backdonation but also the change in the polarization of the C—O bond, which has been suggested as driving force for the bond shortening when a positive charge approaches the carbon atom of CO.[10] Such polarization in the C—O σ bond is not directly obvious from the shapes of $\Delta\rho(\sigma)$. Inspection of the remaining deformation densities showed that there is an orbital pair in both compounds, which is associated with the polarization of the C—O σ bond. The shape of $\Delta\rho$(pol) (Figure 3d,h) displays the charge flow O→C and Be→Y, which comes from the polarization of the σ charge in both molecules. The same situation is found when the deformation densities $\Delta\rho(\sigma)$, $\Delta\rho(\pi)$, and $\Delta\rho$(pol) of the isomers COBeO and $COBeCO_3$ are analyzed, which are shown in Figure 4. The deformation densities of OCBeY and COBeY (Y = O, CO_3) support the suggestion[10] that the inverse change of the bond length and stretching frequency of CO, which is encountered by σ donation at carbon or oxygen in complexes OC→A and CO→A comes from the induced polarization of the σ and π bonds in CO.

Table 2: Calculated NBO partial charges q, charge separation in CO Δq(C–O), and Wiberg bond orders P of the CO moiety at M06-2X/def2-TZVPP.

Compound	q(C)	q(O)	q(CO)	Δq(C–O)	P(CO)
CO	+0.52	−0.52	0	1.04	2.23
OCBeO	+0.52	−0.32	+0.20	0.84	2.30
COBeO	+0.69	−0.61	+0.08	1.30	2.01
$OCBeCO_3$	+0.62	−0.32	+0.30	0.94	2.41
$COBeCO_3$	+0.70	−0.59	+0.11	1.29	2.04

The inverse polarization of the CO bond in the complexes comes clearly to the fore when the calculated partial charges of carbon and oxygen are considered. Table 2 shows that the charge separation in free CO ($\Delta q = 1.04$ e) becomes smaller in OCBeO ($\Delta q = 0.84$ e) and $OCBeCO_3$ ($\Delta q = 0.94$ e), whereas it increases in COBeO ($\Delta q = 1.30$ e) and $COBeCO_3$ ($\Delta q = 1.29$). The smaller positive charge of CO in OCBeO (+0.20 e) than in $OCBeCO_3$ (+0.30 e) is in agreement with the significant π backdonation on the former molecule. Note that the partial charge at carbon in OCBeO is the same as in free CO (+0.52 e). The direct charge donation OC→BeO, which comes from the carbon lone-pair orbital, is compensated by the polarization within the CO moiety which shifts electronic charge from oxygen to carbon. The actual net charge transfer OC→BeO thus takes place from the oxygen atom on CO to BeO. An even more counterintuitive change of the partial charges is observed for the isomer COBeO (Table 2). The direct charge donation CO→BeO from the oxygen lone-pair orbital is overcompensated by the induced polarization. The oxygen atom in COBeO carries an even higher negative charge of $q = -0.61$ e than in free CO (−0.52 e). The same trends can be observed in the complexes $OCBeCO_3$ and $COBeCO_3$. The alteration in the charge polarization of CO leads to larger bond order P(CO) in $OCBeCO_3$ and OCBeO and to smaller values in $COBeCO_3$ and COBeO.

In summary, we report the isolation of the complexes $OCBeCO_3$ and $COBeCO_3$ in a low-temperature neon matrix. The more stable isomer $OCBeCO_3$ has a very high C–O stretching mode of 2263 cm^{-1}, which is blue-shifted by 122 cm^{-1} with respect to free CO and 79 cm^{-1} higher than in OCBeO. Quantum chemical calculations show that the donor–acceptor bonds OC–BeY (Y = O, CO_3) come mainly from OC→BeY σ donation. OCBeO has a stronger OC–BeY bond than $OCBeCO_3$ because it encounters stronger π backdonation. The isomers $COBeCO_3$ and COBeO exhibit redshifted C–O stretching modes with respect to free CO. The inverse change of C–O stretching frequency in OC–BeY and CO–BeY is explained with the reversed polarization of the σ and π bonds in CO.

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