Bonding of Multiple Noble-Gas Atoms to CUO in Solid Neon: CUO(Ng)$_n$ (Ng = Ar, Kr, Xe; n = 1, 2, 3, 4) Complexes and the Singlet – Triplet Crossover Point

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Abstract: Laser-ablated U atoms co-deposited with CO in excess neon produce the novel CUO molecule, which forms distinct Ng complexes (Ng = Ar, Kr, Xe) with the heavier noble gases. The CUO(Ng) complexes are identified through CO isotopic and Ng reagent substitution and comparison to results of DFT frequency calculations. The U – C and U – O stretching frequencies of CUO(Ng) complexes are slightly red-shifted from neon matrix $^1\Sigma^+$ CUO values, which indicates a $^1A'$ ground state for the CUO(Ng) complexes. The CUO(Ng)$_2$ complexes in excess neon are likewise singlet molecules. However, the CUO(Ng)$_3$ and CUO(Ng)$_4$ complexes exhibit very different stretching frequencies and isotopic behaviors that are similar to those of CUO(Ar)$_n$ in a pure argon matrix, which has a $^3A''$ ground state based on DFT vibrational frequency calculations. This work suggests a coordination sphere model in which CUO in solid neon is initially solvated by four or more Ne atoms. Up to four heavier Ng atoms successively displace the Ne atoms leading ultimately to CUO(Ng)$_4$ complexes. The major changes in the CUO stretching frequencies from CUO(Ng)$_2$ to CUO(Ng)$_3$ provides evidence for the crossover from a singlet ground state to a triplet ground state.

Keywords: density functional calculations · matrix-isolation · noble gases · uranium

Introduction

The synthesis and properties of the CUO molecule, a novel product of the reaction of laser-ablated uranium atoms with CO trapped in solid noble-gas (Ng) matrices, have recently been explored in our laboratories.[1] The CUO molecule is a neutral species that is isoelectronic to the uranyl dication, UO_2^{2+}, which is prevalent in uranium chemistry.[2, 3] Experiments on CUO in solid neon and solid argon led to remarkable differences in the spectroscopic properties of CUO in the two hosts. We have proposed that CUO in solid neon is a linear molecule with a $^1\Sigma^+$ ground state. By contrast, CUO in solid argon forms a noble-gas complex CUO(Ar)$_n$, which apparently has a triplet ground state as determined by experimental and theoretical probes.[4, 5] The singlet and triplet states of CUO have very different U – C and U – O stretching vibrational frequencies (singlet: 1047.3, 872.2 cm^{-1}; triplet: 852.5, 804.3 cm^{-1}), an observation that has been successfully modeled by relativistic DFT calculations that indicate the formation of direct bonds between the Ar atoms and the U atom of the CUO molecule.[5] These findings were the first report of bonds between noble-gas and actinide atoms. Prior to our studies, there were only a few examples of argon complexes in neutral molecules, namely ArW(CO)$_5$,[6–8] ArBeO,[9, 10] and ArMX (M = Cu, Ag, Au; X = F, Cl).[11–14]

The fact that CUO changes ground state when the matrix host changes from neon to argon is quite remarkable; in fact, it is the spectroscopic differences upon this drastic change that led to our discovery of U – Ng bonding. Two other observations indicate clearly that the U – Ng bonding becomes stronger as one proceeds to heavier noble gases. First, we found that when CUO is trapped in a neon matrix with 1 % Ar added, the dominant species are triplet molecules similar to CUO(Ar)$_n$, thus indicating that CUO "seeks out" the Ar atoms.[5] Second, we have recently reported that Kr and Xe atoms can successively replace the Ar atoms in CUO(Ar)$_n$ to form mixed noble-gas complexes CUO(Ar)$_{4-n}$(Ng)$_n$ (Ng = Kr,

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Xe; $n = 1, 2, 3, 4$). Based on the observed IR spectra, all of these complexes have triplet ground states, as evidenced by the relatively small frequency shifts upon the replacement of Ar atoms by Kr or Xe atoms.[15, 16] The increasing strength of the U–Ng interactions as Ng changes from Ar to Kr to Xe is corroborated by our DFT calculations.

The fact that CUO in solid neon has a singlet ground state, whereas the presence of even 1% Ar in the neon favors the triplet form of the molecule leads to a fundamental question about the interaction of CUO with Ng atoms: How many Ar atoms need to be complexed to CUO to cause the crossover from a singlet ground state to a triplet ground state? Our initial DFT calculations (PW91) on CUO(Ar) predicted that the $^3A''$ state of the complex would be lower in energy than $^1A'$ CUO(Ar) by about 1 kcal mol^{-1}.[5] Our confidence in this theoretical result was somewhat tempered by the very small difference in energy between the states, the potential difficulties of using DFT to calculate the state energies, and the fact that these calculations did not include spin-orbit coupling. Indeed, the likely best ways to address the above question would be experimental studies in which CUO(Ar)$_n$ ($n = 1,2,3,4$) complexes are prepared in excess neon to find out where the frequencies and isotopic shifts change from the singlet to the triplet state values, or theoretical studies involving higher-level methods that can provide more reliable state energies.

Herein we report extensive new experiments in which CUO is formed in excess neon with dilute amounts of the heavy noble gases Ar, Kr, and Xe. These experiments conclusively identify the single-noble-gas complexes CUO(Ar), CUO(Kr), and CUO(Xe), which exist as singlet molecules in the neon matrix. Studies of the successive complexation of additional Ng atoms suggest that the singlet-triplet crossover occurs in CUO(Ng)$_n$ between $n = 2$ and $n = 3$ for the Ar and Kr complexes.

Experimental and Computational Methods

The experiment for laser ablation and matrix isolation spectroscopy has been described previously.[1] Briefly, the Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate with 10 ns pulse width) was focused on the rotating uranium metal target (Oak Ridge National Laboratory) using low energy (1–5 mJ per pulse) such that a target plume was barely observed. Laser-ablated metal atoms were codeposited with carbon monoxide (0.1%) in excess neon doped with 0.2-3% Ar, Kr or Xe onto a 3.5 K CsI window at 2–4 mmol h^{-1} for one hour. Carbon monoxide (Matheson), $^{13}C^{16}O$ and $^{12}C^{18}O$ (Cambridge Isotopic Laboratories), and mixtures were used in different experiments. Infrared spectra were recorded at 0.5 cm^{-1} resolution on a Nicolet 750 spectrometer with 0.1 cm^{-1} accuracy using a HgCdTe detector. Matrix samples were subjected to

broadband photolysis by a medium-pressure mercury arc (Philips, 175 W, globe removed, 240–700 nm) and annealed at different temperatures to allow diffusion and further association of Ng atoms with the CUO products in solid neon matrix.

New calculations of the $^1\Sigma^+$ ($^1A'$) and $^3\Phi$ ($^3A''$) states of CUO and CUO(Ng) (Ng = Ne, Ar, Kr, Xe) complexes were carried out at DFT levels with the NWChem program[17] by using the PW91 exchange-correlation functional.[18] The small-core Stuttgart–Dresden–Bonn (SDB) pseudopotential and basis sets for U atom,[19] large-core SDB pseudopotentials and basis sets for Ne, Ar, Kr, and Xe,[20] and aug-cc-pVTZ basis sets for C and O atoms[21] were employed. Because the potential energy surfaces involving noble gas atoms are very flat, the ultra fine grid was used for integrations and very tight criteria were used for energy and gradient convergence.

Results

CUO and Ar in neon: Infrared spectra for laser-ablated U, 0.1% ^{12}CO, and 1% Ar in neon are illustrated in Figure 1. Upon initial deposition, the spectrum (Figure 1 a) reveals the familiar absorptions of CUO (1047.3, 872.2 cm^{-1}) and CUO$^-$ (930.0, 803.1 cm^{-1}) in solid neon[1] plus a weak band at 866 cm^{-1} and a sharp absorption (labeled 3) at 857.2 cm^{-1}. The CUO absorptions are within ± 0.1 cm^{-1} of the values for CUO in pure neon, but the CUO$^-$ peaks are displaced by as much as 1 cm^{-1}. Ultraviolet photolysis destroys CUO$^-$ and produces $(C_2)UO_2$ and OUCCO absorptions at 914.6 and 835.7 cm^{-1}, which are shifted 7.3 and 5.3 cm^{-1} from the pure-neon-matrix values,[1] and markedly increases the absorption at 857.2 cm^{-1}. Weak new features appear at 861.9 cm^{-1} and at 808.3, 806.4 cm^{-1} (Figure 1 b). Annealing to 8 and 10 K (Figure 1 c,d) revealed new sharp bands at 1033.3 and 866.6 cm^{-1} (labeled 1), led to an increase of the weak features at 861.9 and 858.8 cm^{-1} (labeled 2), and increased the lower component in the 857.2, 854.3 cm^{-1} and 808.3, 806.4 cm^{-1} band pairs (labeled 3 and 4, respectively). The positions and growth patterns of the latter bands suggest pairs of modes arising from two different complexes that differ by one Ar atom, that is CUO(Ar)$_{n-1}$ and CUO(Ar)$_n$. Further annealing to 11 and
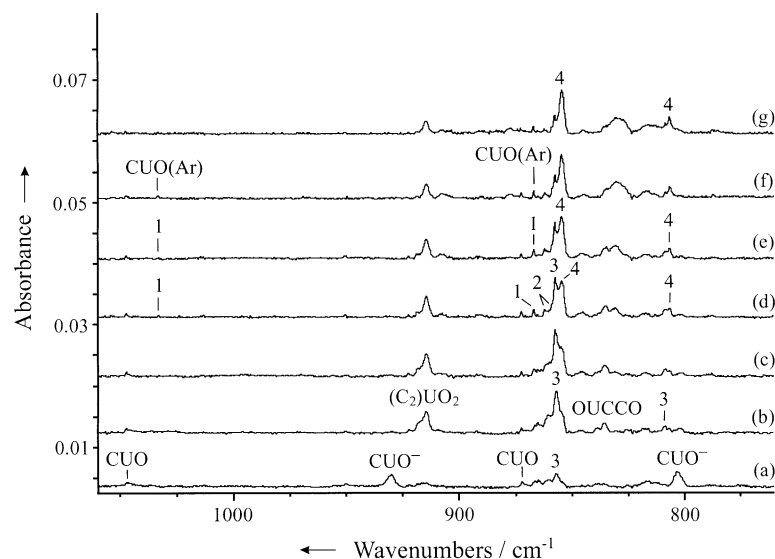

Figure 1. Infrared spectra in the 1060–760 cm^{-1} region for laser-ablated U atom, 0.1% CO, 1% Ar reaction products in excess neon at 3.5 K. a) after sample deposition for 60 min, b) after 240–700 nm photolysis for 15 min, and after sample annealing to c) 8 K, d) 10 K, e) 11 K, f) 12 K, and g) 13 K.

12 K maximized the weak sharp 1033.3, 866.6 cm^{-1} pair and the 861.9 and 858.8 cm^{-1} bands, increased the amount of species **4** relative to species **3**, and produced a broad OUCCO complex absorption near 831 cm^{-1} (Figure 1 e,f). Final annealing to 13 K slightly increased the band for **4** and decreased all other product bands (Figure 1 g). The observed absorption bands are tabulated in Table 1, along with assignments that

Table 1. Infrared absorptions [cm^{-1}] from reactions of laser-ablated U atoms with CO and Ar in excess neon.

$^{12}C^{16}O$	$^{13}C^{16}O$	$^{12}C^{18}O$	Identification
2046	1984	2020	OUCCO
1047.3	1010.8	1046.3	CUO in neon
1033.3	998.0	1032.2	1, CUO(Ar)
930.0	897.7	929.0	CUO$^-$
922.1	922.1	875.9	(C$_2$)UO$_2$ in neon
914.6	914.6	868.8	(C$_2$)UO$_2$
872.2	870.5	826.4	CUO in neon
866.6	864.6	821.3	1, CUO(Ar)
864.9	863.1	819.8	CUO(CO) in neon
861.9	859.8	817.1	2a, CUO(Ar)$_2$
858.8	856.9	813.9	2b, CUO(Ar)$_2$
857.2	842.7	848.2	3, [T], CUO(Ar)$_3$
854.3	839.7	845.3	4, [T], CUO(Ar)$_4$
854.6	854.5	809.6	OUC(OC)
843.2	843.2	795.4	OUCCO in neon
835	835	787	OUCCO (Ar)$_n$
808.3	-	773.1	3, [T], CUO(Ar)$_3$
806.4	798.4	771.3	4, [T], CUO(Ar)$_4$
803.1	801.6	761.0	CUO$^-$

will be discussed later. The number labels in Figure 1 represent the proposed n values for the CUO(Ng)$_n$ complexes identified in this work.

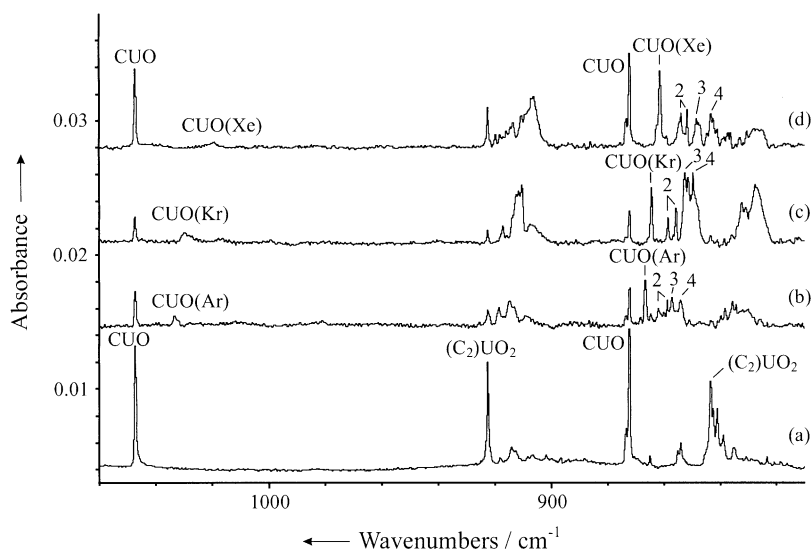Reducing the Ar concentration increases the relative yields of the sharp new bands at 1033.3 and 866.6 cm^{-1} and the isolated CUO bands: At 0.2 % Ar these bands are almost equally intense and much stronger than the bands at 857.2 and 854.3 cm^{-1}.

Infrared spectra for CUO in pure neon and for CUO with dilute Ar, Kr, and Xe in neon are compared in Figure 2. As found in earlier studies, the presence of a heavier noble gas in the neon matrix greatly reduces the yield of isolated CUO in neon as CUO(Ng)$_n$ (Ng = Ar, Kr, Xe) complexes are formed in preference.

To provide a more definitive assignment of the IR spectra, we repeated the experiments using isotopomers of CO. Table 1 lists the frequencies observed when laser-ablated U atoms react with 0.1 % ^{13}CO and 0.7 % Ar in neon. The behavior of the istopically shifted bands parallel that observed for the ^{12}CO counterparts. Figure 3 illustrates the spectra obtained using a mixture of 0.07 % ^{12}CO + 0.07 % ^{13}CO and 0.7 % Ar in neon. The resultant spectra are the sum of the ^{12}CO and ^{13}CO product spectra. The major products give doublet peaks containing ^{12}CO and ^{13}CO components except for (C$_2$)UO$_2$ and OUCCO, which exhibit strong UO$_2$ and UO stretching modes, respectively.[1] The doublet peaks show that one CO molecule contributes to these reactions to form CUO species.

The spectra in Figure 3 provide the most definitive information about the spin states of the products involved. In our previous studies of neon-isolated CUO, the high-energy band at 1047.3 cm^{-1} exhibited a large ^{13}C/^{12}C isotope shift, whereas the low-energy 872.2 cm^{-1} had a much smaller ^{13}C/^{12}C isotope shift.[5] For triplet CUO(Ar)$_n$, which was observed in a pure argon matrix, the 852.5 and 804.3 cm^{-1} showed large and small ^{13}C/^{12}C isotope shifts, respectively. Thus, the 1047.3 cm^{-1} band of singlet CUO in neon and the 852.5 cm^{-1} band of triplet CUO(Ar)$_n$ are predominantly U–C vibrational modes. The lower energy member of each pair is mainly due to the U–O stretch, as has been confirmed by our present and previous studies with C^{18}O and C^{18}O/C^{16}O mixtures.[1] These lower energy bands show a much greater isotope shift with C^{18}O than do the higher energy bands, as expected for a predominantly U–O vibrational mode (Table 1).

We now note the following two important observations in Figure 3: i) The bands labeled CUO(Ar) are at positions similar to those of neon-isolated CUO, with similar isotope shifts. The bands in the ^{12}C/^{13}C doublet at 1033.3, 998.0 cm^{-1} (large isotope shift) are red-shifted by 14.0, 12.8 cm^{-1} from the values of CUO in neon, whereas the bands in the doublet at 866.6, 864.6 cm^{-1} (small isotope shift) are red-shifted by 5.6, 5.9 cm^{-1}. ii) The stronger bands labeled 3 and 4 exhibit decidedly different behavior. There are clear ^{12}C/^{13}C doublets for **3** and **4** at 857.2, 842.7 cm^{-1}, and at 854.3, 839.7 cm^{-1}, and, based on their
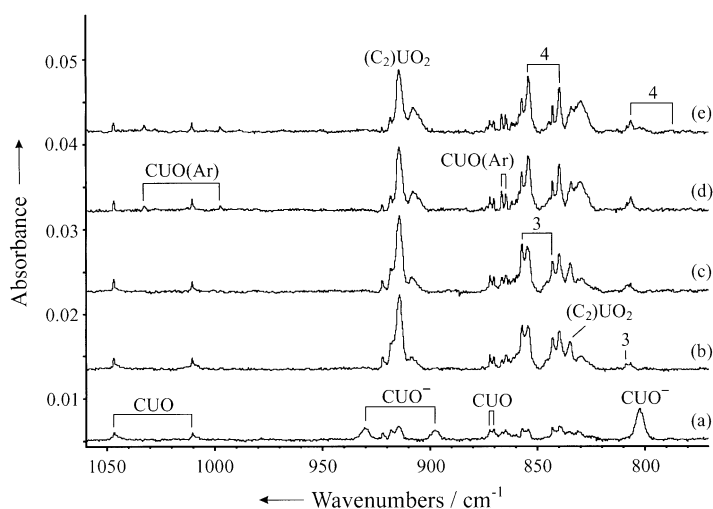

Figure 2. Infrared spectra in the 1060 – 810 cm^{-1} region for laser-ablated U atom, 0.1 % CO, Ng reaction products in excess neon at 3.5 K after sample deposition, photolysis and annealing to 12 – 13 K. a) Pure neon, b) 1 % Ar in neon, c) 0.5 % Kr in neon, and d) 0.3 % Xe in neon.

Figure 3. Infrared spectra in the 1060–780 cm^{-1} region for laser-ablated U atom, 0.07% ^{12}C^{16}O, and 0.07% ^{13}C^{16}O, and 0.7% Ar reaction products in excess neon at 3.5 K. a) After sample deposition for 60 min, b) after 240–700 nm photolysis for 15 min, and after sample annealing to c) 8 K, d) 12 K and e) 13 K.

positions and isotope shifts, we propose that these bands are analogous to the 852.5 cm^{-1} band of CUO(Ar)$_n$. The weaker lower energy mode 3 is observed only for ^{12}CO at 808.3 cm^{-1}, but for the bands labeled 4, we observe a weak ^{12}C/^{13}C doublet at 806.4, 798.4 cm^{-1} (Figure 3e). Thus, we believe that these mixed isotopomer studies show conclusively that CUO(Ar) is a singlet species analogous to CUO in pure neon, whereas species **3** and **4**, which we believe to be CUO(Ar)$_3$ and CUO(Ar)$_4$ respectively, are triplet molecules like CUO(Ar)$_n$ in pure argon.

The Ar-substitution species that has been the most difficult to detect thus far is CUO(Ar)$_2$, which we denote species **2**. Figure 1 and Figure 2b show two weak, sharp features for species **2** at 861.9 and 858.8 cm^{-1}. These bands exhibit very small isotope shifts (2 cm^{-1}) when ^{13}CO is used, which suggests that they correspond to the lower energy predominantly U–O mode of CUO.

CUO and Kr or Xe in neon: New experiments were performed with dilute amounts of Kr or Xe are added to the neon matrix gas. The results of these experiments mirror those in Ar. As shown in Figure 2 and listed in Table 2, CUO(Kr) and CUO(Xe) produce vibrational pairs of bands at 1029.6, 864.4 cm^{-1} and 1019.4, 861.5 cm^{-1}, respectively. These values demonstrate the small but monotonic red shift in the U–C and U–O stretching frequencies as one proceeds from CUO (pure neon) to CUO(Ar) to CUO(Kr) to CUO(Xe). The frequencies and ^{12}CO/^{13}CO isotope ratios of these bands are close to those of CUO in pure neon, which strongly suggests that all of the CUO(Ng) molecules are singlets.

In addition to the mono-Ng adducts, there are prominent spectral features that correspond to multiple Ng atoms bonded to CUO. These Kr-containing species parallel those formed with Ar and exhibit further slight redshifts, as is evident in Figure 2 and Table 2. In particular, annealing produces pairs of bands at 852.2, 804.7 cm^{-1} and 848.9,

802.7 cm^{-1}, which, by comparison to the Ar products, are associated with CUO(Kr)$_3$ and CUO(Kr)$_4$, respectively. We believe that the sharp pair of bands at 858.6 and 855.7 cm^{-1} correspond to CUO(Kr)$_2$ The isotopic ratios of the bands assigned to CUO(Kr)$_3$ and CUO(Kr)$_4$ with ^{13}CO and C^{18}O follow the same pattern as that of triplet CUO(Ar)$_n$.

We have previously found that Xe has the highest affinity for CUO among the noble gases and that it induces the largest red shifts relative to CUO(Ar)$_n$.[15, 16] The greater affinity for Xe made it desirable to use a lower concentration in the dilute mixture. The results in Figure 2d with 0.3% Xe in neon parallel those of Kr with slightly greater redshifts. The bands labeled 2, 3, and 4 are assigned to CUO(Xe)$_n$ ($n = 2, 3, 4$), respectively.

CUO and Ar and Xe in neon: To confirm the assignments, we also ran experiments in which two different dilute mixtures of both Ar and Xe in neon were used. Our previous studies of CUO using dilute Xe in argon showed that the mixed CUO(Ar)$_{4-n}$(Xe)$_n$ complexes have vibrational bands that are intermediate between those of CUO(Ar)$_n$ and CUO(Xe)$_4$.[15, 16] The present results are consistent with that earlier study. Full-arc photolysis of CUO with 0.15% Ar and 0.4% Xe in neon leads to bands at 853.3, 850.2, 847.2, and 843.3 cm^{-1} with a shoulder at 854.3 cm^{-1}. Annealing decreased these broader features and produced three sharp 858.8, 854.7, 851.8 cm^{-1} absorptions for CUO(Ng)$_2$. Recall that the 858.8 cm^{-1} band appeared with Ar and 851.8 cm^{-1} with Xe, but the intermediate 854.7 cm^{-1} component that *increases* on annealing requires the Ar, Xe mixture. The fact that there is only one intermediate band, which would correspond to CUO(Ar)(Xe), suggests that these are adducts of two heavy Ng atoms. The mixed Ar and Xe in neon experiments provide the most definitive evidence for identification of the mono-Ng adducts: annealing of the mixture

Table 2. Comparisons of frequencies [cm^{-1}], shifts, and isotopic frequency ratios for CUO(Ng) complexes.

Ne	Ne + Ar	Ne + Kr	Ne + Xe	Comment
1047.3	1033.3	1029.6	1019.4	CUO(Ng)
	14.0	17.7	29.9	shift from Ne
1.0361	1.0354	1.0342	1.0330	^{12}C^{16}O/^{13}C^{16}O freq. ratio[a]
1.0010	1.0011	1.0012	–	^{12}C^{16}O/^{12}C^{18}O freq. ratio[a]
872.2	866.6	864.4	861.5	CUO(Ng)
	5.6	7.8	10.7	shift from Ne
1.0020	1.0023	1.0023	1.0023	^{12}C^{16}O/^{13}C^{16}O freq. ratio
1.0554	1.0552	1.0552	1.0550	^{12}C^{16}O/^{12}C^{18}O freq. ratio
	861.9	858.6	854.1	2a, CUO(Ng)$_2$
	858.8	855.7	851.8	2b, CUO(Ng)$_2$
	857.2	852.2	847.4	3, CUO(Ng)$_3$
	1.0172	1.0174	1.0032	^{12}C^{16}O/^{13}C^{16}O freq. ratio
	1.0106	1.0106	1.0544	^{12}C^{16}O/^{12}C^{18}O freq. ratio
	854.3	848.9	843.3	4, CUO(Ng)$_4$
	1.0174	1.0159	1.0165	^{12}C^{16}O/^{13}C^{16}O freq. ratio
	1.0106	1.0114	1.0131	^{12}C^{16}O/^{12}C^{18}O freq. ratio
	808.3	804.7		3, CUO(Ng)$_3$
	1.0455	1.0434		^{12}C^{16}O/^{12}C^{18}O freq. ratio
	806.4	802.7	798.6	4, CUO(Ng)$_4$
	1.0455	1.0434	1.0445	^{12}C^{16}O/^{12}C^{18}O freq. ratio

[a] For the immediate above frequencies.

produced the bands assigned to CUO(Ar) and CUO(Xe) in Figure 2 with *no* intermediate components.

Discussion

The experiments presented here, in conjunction with DFT and higher level calculations, add new insight into the chemistry of CUO and its interactions with noble gas atoms. The work here reinforces the notion that multiple noble gas atoms can bind to CUO. In fact, what we describe as neon-isolated CUO is almost certainly a complex of CUO with neon, CUO(Ne)$_n$. We have not determined whether this molecule is better described as a discrete complex (definite n value) or as a neon-solvated molecule without distinct U−Ne bonds. Our DFT calculations find that for singlet CUO(Ne), the U−Ne bond length is 3.18 Å and without basis sets superposition correction (BSSE) the U−Ne binding energy is 1.3 kcal mol^{-1}, a small enough value to warrant further theoretical investigations before drawing a conclusion as to whether a U−Ne bond exists. Further, we have found that the maximum U−Ne binding energy occurs when $n = 6$, corresponding to an eight-coordinate hexagonal-bipyramidal structure. It is evident that CUO(Ne)$_n$, which we shall continue to denote simply as CUO, has a singlet ground state corresponding to a linear f^0 U(VI) CUO molecule. As noted earlier, the vibrational modes at 1047.3 cm^{-1} (mainly U−C) and 872.2 cm^{-1} (mainly U−O) are diagnostic for the singlet form of CUO.[1, 4, 5]

Dilute amounts of Ar, Kr, and Xe in the neon matrix produce a consistent pattern of reactivity and determine the electronic state for CUO. We shall discuss these species in order of increasing number of heavy noble-gas atoms, then we will present our conclusions about the formation of these complexes and their spin states. We remind the reader that excited U (from laser ablation or UV photolysis) is required for the insertion reaction, [1, 16] and that Ng atoms are more strongly bound to triplet CUO than to singlet CUO. [4, 5] Hence, the singlet complexes tend to be formed on annealing in the cold matrix and the triplet complexes are favored when excited U atoms produce excited triplet CUO.

CUO(Ng): As is evident in the spectra in Figure 2, the heavy noble gases form complexes with CUO that have pairs of IR bands very close to the 1047.3 and 872.2 cm^{-1} bands of CUO: 1033.3, 866.6 cm^{-1} (Ar), 1029.6, 864.4 cm^{-1} (Kr), and 1019.4, 861.5 cm^{-1} (Xe). The experiment with both dilute Ar and Xe in the neon matrix shows no intermediate band between the 1033.3 cm^{-1} and 1019.4 cm^{-1} bands. This provides very strong evidence that the absorbing species has a single noble-gas atom; if there were more than one Ng atom in the complex, we would expect to see intermediate absorptions corresponding to mixed CUO + Ar + Xe adducts. Furthermore the CUO(Ar) bands are favored on dilution of Ar as are the isolated CUO absorptions. We therefore propose that the bands listed above are due to CUO(Ar), CUO(Kr), and CUO(Xe), respectively. We envision that these more weakly bound singlet CUO complexes are formed via the displacement of Ne atoms from CUO(Ne)$_n$ by a heavier Ng atom. The reaction to form this and other Ng substitution complexes is

driven by the greater binding energy of Ng to CUO as one proceeds from Ne to Ar to Kr to Xe, which we calculate at 1.3, 2.2, 3.1, and 4.1 kcal mol^{-1}, respectively.

The increasing red shift of the U – C and U – O vibrations of CUO(Ng) relative to those of CUO are also reflective of the increased U – Ng bonding, which very slightly weakens the U – C and U – O bonding. Note that for all of the CUO(Ng) species, the U – C vibrations are redshifted more than the U – O vibrations. For CUO(Xe), for example, the U – C stretch is 27.9 cm^{-1} lower than that in CUO, whereas the U – O stretch is lowered by only 10.7 cm^{-1}. This observation suggests that the interaction of CUO with an Ng atom has a greater impact on the U – C bonding than on the U – O bonding.

The experiments with ^{13}CO and C^{18}O show that the isotopic frequency ratios of the CUO(Ng) species are nearly the same as those of CUO. The 1047.3 cm^{-1} band of CUO is an almost pure U – C stretching mode with a ^{12}C^{16}O/^{13}C^{16}O ratio of 1.0361. For CUO(Ng) this ratio decreases to 1.0354 with Ar, to 1.0342 with Kr, and to 1.0330 with Xe. This slight decrease in U – C stretching character is accompanied by a slight increase in the ^{12}C^{16}O/^{12}C^{18}O ratio and U – O stretching character. In analogous manner, the 872.2 cm^{-1} band of CUO is an almost pure U – O stretching mode with a ^{12}C^{16}O/^{12}C^{18}O frequency ratio 1.0554. This ratio decreases very slightly for the CUO(Ng) molecules: 1.0552 (Ar), 1.0552 (Kr), and 1.0550 (Xe). We see that the vibrational frequencies and isotopic frequency ratios of CUO(Ng) closely correspond to those of singlet CUO. Given that the frequencies and isotopic ratios of triplet forms of CUO, such as CUO(Ar)$_n$, are very different from those of singlet CUO, it follows that the CUO(Ng) species are also singlet molecules. The binding of one heavy Ng atom is not yet sufficient to cause a crossover of the electronic state of CUO from a singlet to a triplet.

CUO(Ng)$_2$: The weak, sharp bands labeled 2 (Figure 1 and Figure 2, and Table 1 and Table 2) are observed at frequencies slightly lower than the lower energy bands (U – O stretch) of the CUO(Ng) molecules, and the bands of **2** exhibit behaviors that are very similar to these low-energy bands of CUO(Ng). The bands for **2** exhibit red shifts from Ar to Kr to Xe, and the magnitudes of these red shifts are slightly greater than those for CUO(Ng), indicating a greater Ng influence on the U – C and U – O bonding. When the concentration of Ar in neon is increased from 0.5 % to 1 %, the intensities of the bands for **2** increase relative to those of CUO(Ar), which suggests that the formation of **2** is more favored as the concentration of Ar increases. It is also notable that when both Ar and Xe are present, the band labeled 2b shows a vibrational feature that is intermediate between the values observed for Ar in neon and Xe in neon. All of these observations suggest that the species **2** is the bis-Ng adduct CUO(Ng)$_2$. The intermediate band in the mixed Ar/Xe experiment is then due to the mixed complex CUO(Ar)(Xe).

The CO isotopic frequency ratios for both bands of CUO(Ar)$_2$ are virtually the same as those for the U – O modes of CUO and CUO(Ng). We therefore propose that, like CUO and CUO(Ng), the CUO(Ng)$_2$ complexes are singlet molecules; the binding of two heavy noble-gas atoms still does not induce the singlet-triplet crossover for CUO. We

would expect each CUO(Ng)$_2$ species to have a higher-energy U–C vibration at roughly 1000–1030 cm^{-1}, but we have not observed these weaker bands.

Finally, it is curious that the CUO(Ng)$_2$ complexes show two vibrational bands in the U–O stretch region. It is possible that the two bands are due to site effects in the matrix, but a more likely explanation is that we are observing two isomers of the CUO(Ng)$_2$ molecules. Given that the molecules also contain two (or more) Ne atoms, and are more correctly formulated as CUO(Ne)$_2$(Ng)$_2$, it is possible that we are seeing separate vibrations due to the *cis* and *trans* isomers of the six-coordinate complexes.

CUO(Ng)$_3$ and CUO(Ng)$_4$: The bands labeled 3 and 4 increase in relative intensity when the concentration of Ng is increased, and also increase upon annealing. The dominant feature due to species **3** is an absorption at 857.2 (Ar), 852.2 (Kr), or 847.4 (Xe) cm^{-1}, and the dominant band for species **4** is at 854.3 (Ar), 848.8 (Kr), and 843.3 (Xe) cm^{-1}. These frequency values are close to those of the primarily U–O stretching frequency of CUO, CUO(Ng), and CUO(Ng)$_2$ (852–872 cm^{-1}) and to those of the primarily U–C stretching frequency of CUO(Ar)$_n$ in pure argon (852.5 cm^{-1}).[4, 5, 15, 16] The isotopic frequency ratios of the strong bands of species **3** and **4** for Ar clearly indicate that these species are more closely related to CUO(Ar)$_n$ than they are to CUO, CUO(Ng), and CUO(Ng)$_2$.

Recall that the 872.2 cm^{-1} band of CUO shows small ^{12}C^{16}O/^{13}C^{16}O and large ^{12}C^{16}O/^{12}C^{18}O isotopic frequency ratios. The strong 852.5 cm^{-1} band of CUO(Ar)$_n$ exhibits the opposite behavior inasmuch as the ^{12}C^{16}O/^{13}C^{16}O frequency ratio (1.0188) is larger than the ^{12}C^{16}O/^{12}C^{18}O ratio (1.0092). Species **3** and **4** with dilute Ar in neon, which we believe are neon-complexed CUO(Ar)$_3$ and CUO(Ar)$_4$, respectively, exhibit ratios that are nearly the same as those of CUO(Ar)$_n$ (**3**: 1.0172, 1.0106; **4**: 1.0174, 1.0106). These results indicate that the 852.5 cm^{-1} band of CUO(Ar)$_n$ and the strong bands of CUO(Ar)$_3$ and CUO(Ar)$_4$ are predominantly U–C stretching modes, a result that is consistent with the calculated DFT vibrational modes of ^{3}A″ CUO(Ar). These comparisons suggest that CUO(Ar)$_3$ and CUO(Ar)$_4$ are triplet molecules, like CUO(Ar)$_n$.[4, 5] The presence of more than two heavy Ng atoms in species **3** and **4** is consistent with the behavior of the bands for **3** and **4** in the experiments that involved mixtures of Ar and Xe in neon. These bands generate complex multiplets when both Ar and Xe are present, which suggests a mixture of CUO(Ar)$_{3-n}$(Xe)$_n$ and CUO(Ar)$_{4-n}$(Xe)$_n$ substitution products.
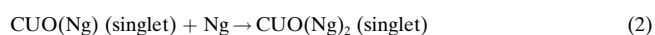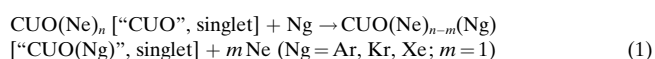
The assignments of species **3** and **4** for Ar in neon to CUO(Ar)$_3$ and CUO(Ar)$_4$ is based primarily on the spectroscopic observations and two logical extensions of previous work. First, earlier in this paper, we have provided evidence for CUO(Ar)$_2$ that was corroborated by the mixed Ar + Xe experiments. Second, our previous work on the mixed noble-gas complexes CUO(Ar)$_{4-n}$(Ng)$_n$ (Ng = Kr, Xe) provides a precedent for the stepwise coordination of noble-gas atoms to CUO. Further, the frequencies of CUO(Ar)$_4$ in neon (854.3 and 806.4 cm^{-1}) are very close to those observed for CUO(Ar)$_n$ in pure argon (852.5 and 804.3 cm^{-1}). Based on

our calculations and the spectra of the mixed Ar/Kr and Ar/Xe complexes, we believe that $n = 4$ is most likely for CUO(Ar)$_n$, although in a pure argon matrix there might be second-shell solvation effects that involve additional non-negligible U–Ar interactions. The small redshifts for the frequencies of CUO(Ar)$_n$ relative to those of CUO(Ar)$_4$ in neon are consistent with this notion of slightly greater U–Ar interaction in the argon matrix.

These trends continue with Kr and Xe. The major bands assigned to CUO(Kr)$_3$ and CUO(Kr)$_4$ in neon are shifted 5.0 and 5.4 cm^{-1} lower than the corresponding Ar complexes, and the CO isotopic frequency ratios are almost the same (Table 2). The strong band for CUO(Xe)$_4$ is 5.6 cm^{-1} below that of CUO(Kr)$_4$. The isotopic frequency ratios for CUO(Kr)$_4$ and CUO(Xe)$_4$ indicate slightly decreasing U–C and increasing U–O character in the vibrational mode.

Finally, we can compare the frequencies for CUO(Kr)$_4$ and CUO(Xe)$_4$ in solid neon to those we reported earlier in solid argon.[15, 16] The strong bands for CUO(Kr)$_4$ and CUO(Xe)$_4$ are shifted lower by 2.9 and 7.9 cm^{-1}, respectively, in solid argon relative to solid neon. These shifts indicate somewhat larger secondary argon–neon solvent effects than found for CUO(Ar)$_4$. Clearly CUO(Xe)$_4$ is more vulnerable to matrix effects than CUO(Ar)$_4$ and CUO(Kr)$_4$, probably because of the longer U−Xe bonds, which lead to a larger effective volume for the Xe complex.

CUO(Ng)$_n$ complex formation: These experiments clearly show that singlet complexes CUO(Ng) and CUO(Ng)$_2$ are formed by stepwise addition of Ng atoms to singlet CUO on diffusion in the solid neon matrix or by substitution of Ne by heavier Ng atoms [Eq. (1) and (2)]. As noted earlier, we believe that the intimate coordination sphere in these "coordinatively unsaturated" Ng complexes is completed by an indeterminate number of neon atoms.

CUO(Ne)$_n$ ["CUO", singlet] + Ng → CUO(Ne)$_{n-m}$(Ng)
["CUO(Ng)", singlet] + m Ne (Ng = Ar, Kr, Xe; $m = 1$)   (1)

CUO(Ng) (singlet) + Ng → CUO(Ng)$_2$ (singlet)   (2)

Intermediate annealing (8–10 K) shows a net decrease in CUO and a net increase in **1**, **2**, **3** CUO(Ng)$_n$, and late annealing (12–14 K) decreases the latter in favor of species **4**. This, given the low concentrations of the Ng atoms, seems to indicate facile diffusion of the Ng atoms in the neon host. The addition of a third Ng atom is accompanied by a change in the spin-state of the system from singlet to triplet [Eq. (3)], a state that is preserved upon addition of a fourth Ng atom [Eq. (4)], because these triplet states are more stable than their singlet analogues.

CUO(Ng)$_2$ (singlet) + Ng → CUO(Ng)$_3$ (triplet)   (3)

CUO(Ng)$_3$ (triplet) + Ng → CUO(Ng)$_4$ (triplet)   (4)
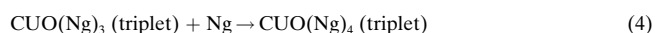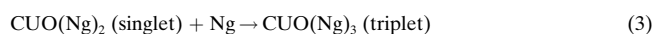
In pure neon, ultraviolet photolysis increases the absorptions due to CUO about fourfold,[1] but with extra Ng atoms present, much of the growth is found in triplet CUO(Ng)$_n$ complexes (Figure 1b). This occurs because the excited CUO

states formed on photolysis bind Ng more strongly than ground state CUO. As expected, the product distribution among the $CUO(Ng)_n$ complexes is highly dependent on the concentration of Ng in the neon matrix. With 1% Ar (Figure 1) most of the increase (fourfold) is in $CUO(Ar)_3$, but with 0.5% Ar, $CUO(Ar)_n$ ($n = 0, 1, 2, 3, 4$) all increase. With 1% Kr most of the increase (threefold) is in $CUO(Kr)_4$, but with 0.5% Xe all $CUO(Xe)_n$ ($n = 0, 1, 2, 3, 4$) increase about twofold. Therefore, it appears that the addition of an Ar atom to singlet $CUO(Ar)_2$ to form triplet $CUO(Ar)_3$ [Eq. (3)] is spontaneous in solid neon at 10 – 14 K. Figure 1 shows clearly the favorable nature of reactions (3) and (4) upon annealing. Note that UV photoexcitation followed by relaxation in the matrix cage greatly assists crossover to the triplet manifold.

Conclusion

The studies reported here add valuable new insight into the remarkable chemistry of CUO with noble-gas atoms. Prior to this report, we had shown that CUO has different spin states in solid neon and solid argon, that U–Ar bonds formed in the argon matrix, and that Ar atoms could be displaced by Kr or Xe atoms. The present studies, in which dilute amounts of Ar, Kr, or Xe are used as reagents in a neon host, provide strong experimental evidence that a minimum of three Ar or Kr atoms are needed to reach the singlet – triple crossover point. The analysis of the U–C and U–O stretching modes show conclusively that the CUO(Ng) and $CUO(Ng)_2$ complexes are singlet molecules only slightly perturbed from $CUO(Ne)_n$, whereas $CUO(Ng)_3$ and $CUO(Ng)_4$ are closely related to triplet $CUO(Ar)_n$.

The results presented here show a remarkable dichotomy in the interaction of Ne atoms with CUO relative to those of the heavy Ng atoms Ar, Kr, and Xe. In cases where there are fewer than four heavy Ng atoms, we propose that Ne atoms complete the coordination sphere about CUO. Our calculated U–Ng binding energies increase smoothly and monotonically from Ne to Ar to Kr and Xe. In fact, the calculated U–Xe binding energy is nearly twice the U–Ar binding energy, so the formation of two U–Xe bonds provides more total binding energy than do three U–Ar bonds. However, we see that it is the *number* of the Ng ligands, not the *type* of heavy Ng atoms that determines the spin state. This conclusion is in perfect agreement with our previous findings that both the singlet and triplet states of CUO are stabilized upon coordination by Ar, Kr, and Xe atoms, but the triplet state of CUO is stabilized more by these Ng atoms than does the singlet state so that more Ng ligands help to turn the triplet into a ground state.[5] All of the CUO(Ng) and $CUO(Ng)_2$ - molecules are singlet molecules that have not yet reached the crossover point.

The $CUO(Ng)_n$ complex distribution on deposition is not statistical because excited CUO* is formed in the initial reaction, and during relaxation excited CUO* will bond Ar more strongly (and thus more extensively) than ground state CUO.

The experimental results here present new challenges in the use of theory to describe the delicate state energetics involved. Our previous scalar-relativistic DFT calculations predicted that naked CUO has a $^1\Sigma^+$ ground state, and that the triplet state of CUO is stabilized more by argon coordination than the singlet state. These preliminary results were not able to determine the state crossover point with argon coordination, which is not surprising given the limitations of the methods we used, particularly no treatment of the spin-orbit interaction, and the intrinsic difficulty in describing bonds involving noble-gas atoms.[4, 5] Spin-orbit coupling (mainly due to the U atom) can stabilize the triplet relative to the singlet,[22] but these effects are expected to change little for $CUO(Ng)_n$ complexes with different number of the Ng ligands. Higher-level electronic structure calculations are currently in progress to provide theoretical insight into the U–Ng bonding.[23]

Finally, this work provides a model of four Ar, Kr or Xe atoms interacting with CUO in the intimate solvation shell followed by a weaker interaction with a larger secondary solvent shell. This effect is demonstrated by the 4.2 cm^{-1} shift in the U–C stretching mode of $CUO(Ar)_4$ on replacing one Ar atom by Xe as compared to the change from 843.3 to 835.4 to 832.6 to 829.8 cm^{-1} when $CUO(Xe)_4$ is solvated by secondary $[Ne]_x$, $[Ar]_x$, $[Kr]_x$ and $[Xe]_x$ shells, respectively. Our work provides insight into the nature of solvation shells around matrix isolated molecules by using heavier Ng matrix atoms (Ar, Kr, Xe) as reagents in the lighter Ne matrix.

Acknowledgement

[1] U + CO in neon: M. F. Zhou, L. Andrews, J. Li, B. E. Bursten, *J. Am. Chem. Soc.* **1999**, *121*, 9712.
[2] M. Gal, P. L. Groggin, J. Mink, *Spectrochim. Acta A* **1992**, *48*, 121.
[3] N. Ismail, J.-L. Heully, T. Saue, P.-J. Daudey, C. J. Marsden, *Chem. Phys. Letts.* **1999**, *300*, 296.
[4] L. Andrews, B. Liang, J. Li, B. E. Bursten, *Angew. Chem.* **2000**, *112*, 4739; *Angew. Chem. Int. Ed.* **2000**, *39*, 4565.
[5] J. Li, B. E. Bursten, B. Liang, L. Andrews, *Science* **2002**, *295*, 2242..
[6] J. R. Wells, E. Weitz, *J. Am. Chem. Soc.* **1992**, *114*, 2783.
[7] X.-Z. Sun, M. W. George, S. G. Kazarian, S. M. Nikiforov, M. Poliakoff, *J. Am. Chem. Soc.* **1996**, *118*, 10525.
[8] A. W. Ehlers, G. Frenking, E. J. Baerends, *Organometallics* **1997**, *16*, 4896.
[9] C. A. Thompson, L. Andrews, *J. Am. Chem. Soc.* **1994**, *116*, 423.
[10] A. Veldkamp, G. Frenking, *Chem. Phys. Lett.* **1994**, *226*, 11.
[11] C. J. Evans, A. Lesarri, M. C. L. Gerry, *J. Am. Chem. Soc.* **2000**, *122*, 6100.
[12] C. J. Evans, M. C. L. Gerry, *J. Chem. Phys.* **2000**, *112*, 9363.
[13] C. J. Evans, M. C. L. Gerry, *J. Chem. Phys.* **2000**, *112*, 1321.
[14] D. C. Grills, M. W. George, *Adv. Inorg. Chem.* **2001**, *52*, 113.
[15] B. Liang, L. Andrews, J. Li , B. E. Bursten, *J. Am. Chem. Soc.* **2002**, *124*, 9016.
[16] L. Andrews, B. Liang, J. Li , B. E. Bursten, *J. Am. Chem. Soc.* **2003**, *125*, 3126.

[17] High Performance Computational Chemistry Group, *NWChem, A Computational Chemistry Package for Parallel Computers, Version 4.1* **2002**, Pacific Northwest National Laboratory, Richland, Washington 99352, USA.

[18] a) J. P. Perdew, Y. Wang, *Phys. Rev. B* **1992**, *45*, 13 244; b) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Foilhais, *Phys. Rev. B* **1992**, *46*, 6671.

[19] W. Küchle, M. Dolg, H. Stoll, H. Preuss, *J. Chem. Phys.* **1994**, *100*, 7535.

[20] A. Nicklass, M. Dolg, H. Stoll, H. Preuss, *J. Chem. Phys.* **1995**, *102*, 8942.

[21] a) T. H. Dunning, Jr., *J. Chem. Phys.* **1989**, *90*, 1007; b) R. A. Kendall, T. H. Dunning, Jr., R. J. Harrison, *J. Chem. Phys.* **1992**, *96*, 6796.

[22] B. Roos, P.-O. Widmark, L. Gagliardi, *Faraday Discuss. Chem. Soc.* **2003**, *124*, 1.

[23] B. E. Bursten, M. L. Drummond and J. Li, *Faraday Discuss. Chem. Soc.* **2003**, *124*, 57.