

On the Noble-Gas-Induced Intersystem Crossing for the CUO Molecule: Experimental and Theoretical Investigations of CUO(Ng)_n (Ng = Ar, Kr, Xe; n = 1, 2, 3, 4) Complexes in Solid Neon

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Uranium atoms excited by laser ablation react with CO in excess neon to produce the novel CUO molecule, which forms distinct Ng complexes (Ng = Ar, Kr, Xe) when the heavier noble gases are added. The CUO(Ng) complexes are identified through CO isotopic and Ng substitution on the neon matrix infrared spectra and by comparison to DFT frequency calculations. The U–C and U–O stretching frequencies of CUO(Ng) complexes are slightly red-shifted from frequencies for the $^1\Sigma^+$ CUO ground state, which identifies singlet ground state CUO(Ng) complexes. In solid neon the CUO molecule is also a complex CUO(Ne)_n, and the CUO(Ne)_{n-1}(Ng) complexes are likewise specified. The next singlet CUO(Ne)_x(Ng)₂ complexes in excess neon follow in like manner. However, the higher CUO(Ne)_x(Ng)_n complex (n = 3, 4) stretching modes approach pure argon matrix CUO(Ar)_n values and isotopic behavior, which are characterized as triplet ground state complexes by DFT frequency calculations. This work suggests that the singlet–triplet crossing occurs with 3 Ar, 3 Kr, or 4 Xe and a balance of Ne atoms coordinated to CUO in the neon matrix host.

Introduction

We have recently reported that the reaction of laser-ablated uranium atoms with CO leads to the formation of the novel CO-insertion product CUO,¹ which is isoelectronic to the uranyl dication UO₂²⁺ that is so prevalent in uranium chemistry.^{2,3} We have discovered that the CUO molecule has a remarkably rich electronic structure with a $^3\Phi$ triplet state very close in energy to the $^1\Sigma^+$ ground state of linear CUO. In particular, we found that CUO is trapped as a singlet molecule in solid neon, but in solid argon the molecule exists

as a triplet CUO(Ar)_n complex.^{4,5} The singlet and triplet electronic states are distinguished experimentally by very different U–C and U–O stretching vibrational frequencies for the singlet (1047.3, 872.2 cm⁻¹) and triplet (852.5, 804.3 cm⁻¹) states, as has been successfully modeled by relativistic density functional theory (DFT) calculations.^{1,4,5} The fact that CUO changes ground state from $^1\Sigma^+$ to $^3\Phi$ when the matrix environment changes from neon to argon led to our discovery of actinide–noble gas bonding.⁵

Although CUO in solid neon has a singlet ground state, the inclusion of small amounts of argon in the neon matrix leads predominantly to a triplet complex. This observation

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leads to a fundamentally important question about the interaction between noble-gas (Ng) atoms and CUO: How many Ar atoms must be complexed to CUO to induce the crossover from a singlet to a triplet state? Initial relativistic DFT calculations (PW91) in the absence of spin-orbit coupling found $^3A''$ CUO(Ar) to be lower in energy than $^1A'$ CUO(Ar) by about 1 kcal/mol, but our confidence in this result is limited by the small energy difference between states and difficulties using DFT to calculate energies of noble-gas complexes.⁵ The above question could best be answered experimentally by preparing CUO(Ar)_n complexes in excess neon to determine the coordination numbers for which the frequencies and isotopic shifts change from singlet to triplet state values. CUO produced with 1% Ar in neon led to absorptions at 854.0, 806.5 cm⁻¹, which are very close to the 852.5, 804.3 cm⁻¹ bands observed in solid argon. In both of these sets of experiments, we propose that the absorptions are associated with a triplet CUO(Ar)_n complex where the specific value of *n* was not determined.⁵ Recent experiments in which CUO was formed in argon with small amounts of Xe led to the characterization of distinct CUO(Ar)_{4-n}(Xe)_n (*n* = 1, 2, 3, 4) complexes where Xe atoms replace Ar atoms in the intimate coordination sphere around CUO.^{6,7} The straightforward interpretation of these spectra suggests that CUO(Ar)₄ is formed in pure argon.

There are only a few examples of argon complexes in neutral molecules, namely, ArW(CO)₅,⁸⁻¹⁰ ArBeO,^{11,12} and ArMX (M = Cu, Ag, Au; X = F, Cl).¹³⁻¹⁵ Positive ions, of course, bind noble gas atoms more strongly because of the strong charge-induced dipole interactions, as found for the AuXe⁺, AuXe₂⁺, and AuXe₄²⁺ complexes¹⁶⁻¹⁸ and the FeAr_n⁺, SrAr_n⁺ and NiAr_n⁺ clusters, for example.¹⁹⁻²²

We report here extensive new experiments and calculations for CUO with dilute heavy noble gases Ar, Kr, and Xe in excess neon. These studies conclusively identify the mono-Ng adducts CUO(Ar), CUO(Kr), and CUO(Xe), which are found as singlet molecules that also contain coordinated Ne atoms in the coordination sphere. It appears that the singlet-

to-triplet crossover occurs when 3 Ar, 3 Kr, or 4 Xe atoms are coordinated to CUO.

Experimental and Computational Methods

The laser-ablation and matrix-isolation experiment has been described previously.^{1,23,24} Focused Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate, 10 ns pulse width) on the rotating uranium metal target (Oak Ridge National Laboratory) using low energy (1–5 mJ/pulse) gave a faint target emission. 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 IR transparent window at 2–4 mmol/h for one hour. Carbon monoxide (Matheson), ¹³C¹⁶O and ¹²C¹⁸O (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, 175W, 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.

DFT calculations of the $^1\Sigma^+$ ($^1A'$) and $^3\Phi$ ($^3A''$) states of CUO, CUO(Ng)₄, CUO(Ne)₃(Ng) (Ng = Ne, Ar, Kr, Xe), and CUO(Ne)_{4-n}(Ar)_n (*n* = 0, 1, 2, 3, 4) molecules were performed using the NWChem program.²⁵ To avoid the symmetry-breaking issue for the triplet states, only C_s symmetry was imposed on the calculations of CUO(Ng)₄, CUO(Ne)₃(Ng) (Ng = Ne, Ar, Kr, Xe), and CUO(Ne)_{4-n}(Ar)_n (*n* = 0, 1, 2, 3, 4) molecules. The DFT calculations used the PW91 exchange-correlation functional,²⁶ which shows relatively small error in calculating noble-gas complexes. The small-core Stuttgart–Dresden–Bonn (SDB) pseudo-potential and basis sets for U atom²⁷ and large-core SDB pseudo-potentials and basis sets for Ne, Ar, Kr, and Xe²⁸ were employed to account for the scalar relativistic effects. The aug-cc-pVTZ basis sets were used for C and O atoms.²⁹ Because the potential energy surfaces involving noble gas atoms are very flat, an ultrafine grid was used for integrations and very tight criteria were used for energy and gradient convergence to determine the optimal geometries and frequencies as accurately as possible.

Owing to the underestimation of the triplet–singlet energy difference by DFT we also performed coupled-cluster calculations for CUO and the CUO(Ng) model molecules at the CCSD(T) level using the MOLPRO program.³⁰ To accurately evaluate the small triplet–singlet energy difference, we fully optimized the geometries

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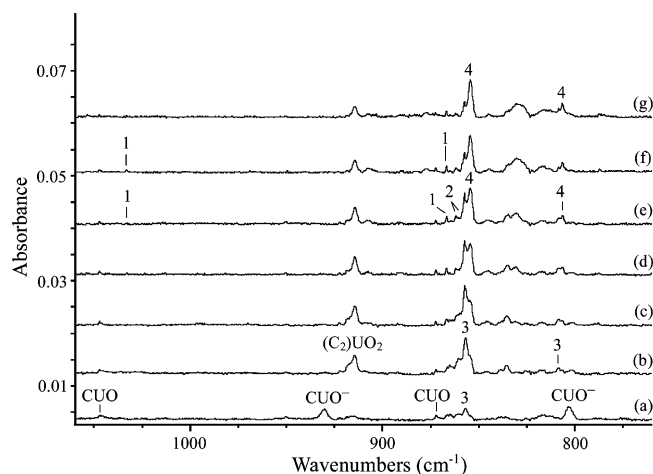


Figure 1. Infrared spectra in the 1060–760 cm^{-1} region for laser-ablated U atom, 0.1% CO, 1% Ar reaction products in excess neon at 3.5 K: (a) after sample deposition for 60 min, (b) after 240–700 nm photolysis for 15 min, and (c) after sample annealing to 8 K, (d) 10 K, (e) 11 K, (f) 12 K, and (g)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

of CUO and CUO(Ng) to obtain meaningful comparisons. The CCSD(T) calculations were thus limited to smaller basis sets. We used Hay's effective core potential and the LANL2DZ basis sets for U atom,³¹ and SDB pseudopotentials and basis sets for C, O, and the noble gas atoms, with d-type polarization functions and p-type diffuse functions added for C and O atoms.^{28,32}

Results

We will report infrared spectra for each CUO and noble gas system in excess neon and new computations on CUO-(Ng) complexes. As will be clear, we believe that "isolated" CUO in a pure neon matrix is better described as a CUO-(Ne)_n complex. The electronic properties of this neon complex are nearly identical to those predicted for the free CUO molecule, and we will continue to denote the neon-complexed CUO molecule simply as CUO.

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. The deposited sample reveals the familiar CUO (1047.3, 872.2 cm^{-1}) and CUO^- (930.0, 803.1 cm^{-1}) neon-matrix absorptions plus weak 866 and 857.2 cm^{-1} bands (labeled 3) (Figure 1a). In these experiments the CUO absorptions appear unshifted $\pm 0.1 \text{ cm}^{-1}$ from the values in a pure neon matrix, but the CUO^- peaks are displaced up to 1 cm^{-1} . Ultraviolet photolysis destroys CUO^- and produces $(\text{C}_2)\text{UO}_2$ and OUCCO absorptions at 914.6 and 835.7 cm^{-1} , shifted 7.3 and 5.3 from the pure neon-matrix values,¹ and markedly increases the 857.2 cm^{-1} absorption. Weak new features are apparent at 865, 861 cm^{-1} and at 808.3, 806.4 cm^{-1} (Figure 1b). Annealing to 8 and 10 K (Figure 1c,d) increased sharp new weak 1033.3, 866.6 cm^{-1} features (labeled 1), increased 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, 4) suggesting two modes of two different product complex

Table 1. Infrared Absorptions (cm^{-1}) from Reactions of Laser-Ablated U Atoms with CO and Ar in Excess Neon

$^{12}\text{C}^{16}\text{O}$	$^{13}\text{C}^{16}\text{O}$	$^{12}\text{C}^{18}\text{O}$	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	$(\text{C}_2)\text{UO}_2$ in neon
914.6	914.6	868.8	$(\text{C}_2)\text{UO}_2$
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	XUO in neon ^a
843.2	843.2	795.4	OUCCO in neon
835	835	787	OUCCO
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^-

^a X is not determined: see text.

species $\text{CUO}(\text{Ar})_{n-1}$ and $\text{CUO}(\text{Ar})_n$ (30% net growth in the 3, 4 band pairs). Further annealing to 11 and 12 K maximized the sharp 1033.3, 866.6 cm^{-1} pair, and the 861.9 and 858.8 cm^{-1} bands, increased the bands of 4 relative to those of 3, and produced a broad OUCCO absorption near 831 cm^{-1} (Figure 1e,f). Final annealing to 13 K slightly increased the bands of 4 and decreased all other product bands (Figure 1g). Table 1 presents the product absorptions. The number labels represent the *n* value in the proposed $\text{CUO}(\text{Ng})_n$ complexes to be identified in this work.

We found that reducing the argon concentration increased the relative yield of the sharp new 866.6 cm^{-1} band. With 0.2% Ar and 0.1% CO the isolated CUO bands in neon dominated the spectrum of the deposited sample, but photolysis and annealing produced the bands of 1 at 1033.3 and 866.6 cm^{-1} where the latter was almost equal in intensity to the 872.2 cm^{-1} band of CUO and much stronger than very weak bands at 861.9, 858.8, 857.2, and 854.3 cm^{-1} . Figure 2 shows the spectra obtained using 0.5% Ar in neon. Note the increase in intensities of the CUO bands relative to the 1, 2 and 3, 4 bands, as compared to 1% Ar, and the increase in the relative intensity of the bands of 1, particularly on annealing. Because of the lower intensity of the bands for 3, the two bands labeled 2 at 861.9 and 858.8 cm^{-1} can be observed more clearly. Again further annealing increased the bands of 4 relative to those for 3. With 3% argon and 0.1% CO, the only CUO absorptions observed were the matched pair of $\text{CUO}(\text{Ar})_{n-1}$ and $\text{CUO}(\text{Ar})_n$ absorptions at 857.2, 854.3 cm^{-1} and at 808.3, 806.4 cm^{-1} , and the lower-energy component of each pair increased markedly on annealing. The infrared spectra for CUO in pure neon and for CUO with dilute Ar, Kr, and Xe in neon are compared in Figure 3. The presence of Ng atoms in the neon host reduces the yield of isolated CUO as $\text{CUO}(\text{Ng})_n$ complexes are formed in preference.

An experiment was performed with 0.1% ^{13}CO and 0.7% Ar in neon, and the IR bands are listed in Table 1. The isotopically shifted bands behaved the same as their ^{12}CO counterparts. Figure 4 illustrates diagnostic spectra recorded for 0.07% ^{12}CO + 0.07% ^{13}CO and 0.7% Ar in neon, which

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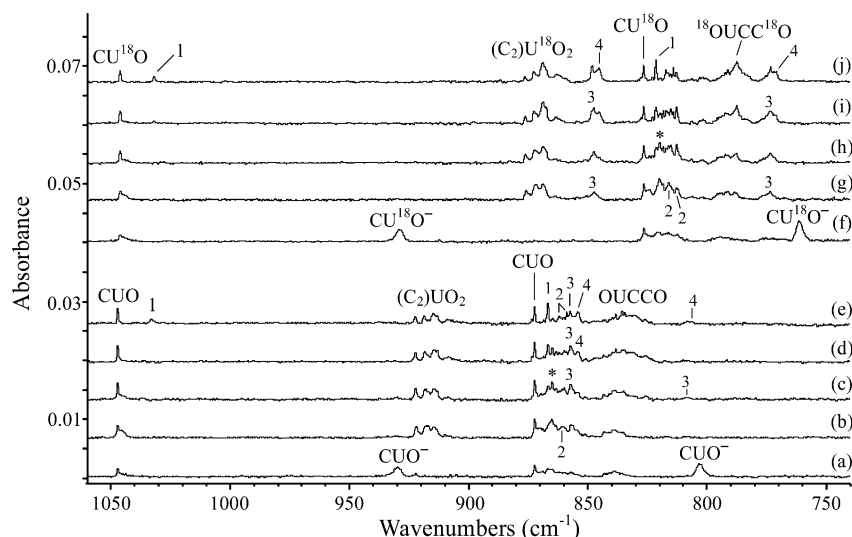


Figure 2. Infrared spectra in the 1060–740 cm^{-1} region for laser-ablated U atom, 0.1% CO, 0.5% Ar reaction products in excess neon at 3.5 K: (a) after sample deposition with $^{12}\text{C}^{16}\text{O}$ for 60 min, (b) after 240–700 nm photolysis for 15 min, and (c) after sample annealing to 8 K, (d) 10 K, and (e) 12 K; (f) after sample deposition with 0.1% $^{12}\text{C}^{18}\text{O}$ and 0.5% Ar in excess neon for 60 min, (g) after 240–700 nm photolysis for 15 min, and (h) after sample annealing to 8 K, (i) 10 K, and (j) 12 K.

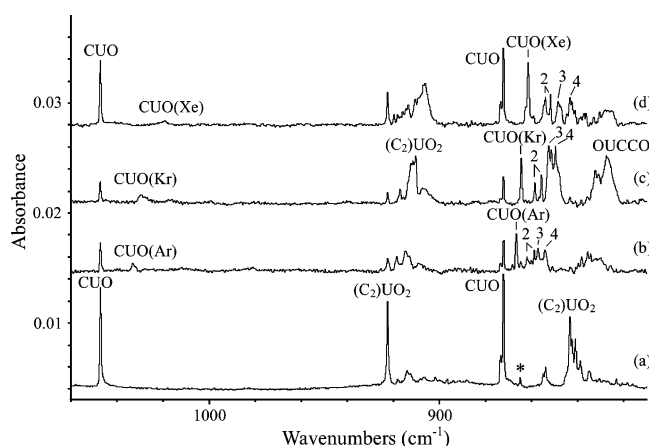


Figure 3. Infrared spectra in the 1060–810 cm^{-1} region for laser-ablated U atom, 0.1% CO, Ng reaction products in excess neon at 3.5 K after sample deposition, photolysis, and annealing to 12–13 K: (a) pure neon, (b) 1% Ar in neon, (c) 0.5% Kr in neon, and (d) 0.3% Xe in neon.

are the sum of ^{12}CO and ^{13}CO product spectra. The major products give doublet peaks containing ^{12}CO and ^{13}CO components except for $(\text{C}_2)\text{UO}_2$ and OUCCO, which exhibit strong UO_2 and UO stretching modes, respectively. The product evolution on photolysis is the same as described above for Ar doped neon and previously for pure neon.¹ Note two important observations: (1) the bands labeled CUO(Ar) mimic isolated CUO in that the doublet at 1033.3, 998.0 cm^{-1} is red-shifted 14.0, 12.8 cm^{-1} and a doublet at 866.6, 864.6 cm^{-1} is red-shifted 5.6, 5.9 cm^{-1} from the neon matrix isolated absorptions, and (2) the stronger bands labeled 3 and 4 also exhibit doublets at 857.2, 842.7 cm^{-1} and at 854.3, 839.7 cm^{-1} , and the weaker band for 3 is observed only for ^{12}CO at 808.3 cm^{-1} , but a 4 doublet for ^{12}CO and ^{13}CO is found at 806.4, 798.4 cm^{-1} . This large difference in ^{12}CO – ^{13}CO shifts for the 866.6, 864.6 cm^{-1} doublet (2.0 cm^{-1}) on one hand, and the 857.2, 842.7 cm^{-1} and 854.3, 839.7 cm^{-1} doublets (14.5 and 14.6 cm^{-1}) on the other hand, clearly associates the CUO(Ar) product with pure-neon-isolated

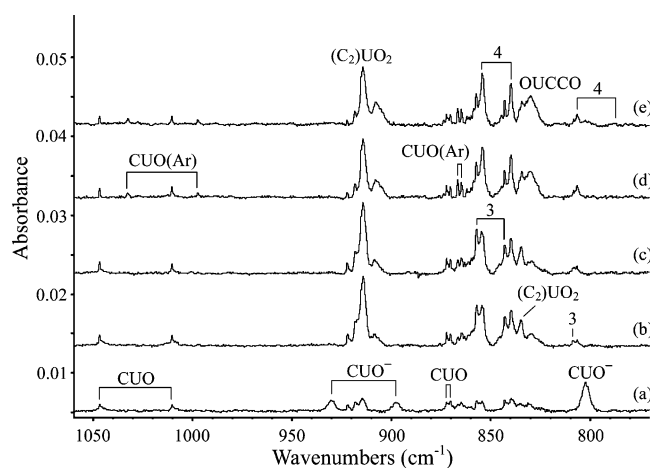


Figure 4. Infrared spectra in the 1060–780 cm^{-1} region for laser-ablated U atom, 0.07% $^{12}\text{C}^{16}\text{O}$, and 0.07% $^{13}\text{C}^{16}\text{O}$, and 0.7% Ar reaction products in excess neon at 3.5 K: (a) after sample deposition for 60 min, (b) after 240–700 nm photolysis for 15 min, and (c) after sample annealing 8 K, (d) 12 K, and (e) 13 K.

singlet CUO whereas the products 3 and 4 exhibit behavior similar to pure-argon-isolated triplet CUO. The weaker features labeled 2 appear to give a doublet at 861.9 and 858.8 cm^{-1} .

A similar experiment was done with $^{12}\text{C}^{18}\text{O}$ substitution, and shifted frequencies are listed in Table 1. The most important observations are that the behaviors of the bands labeled 1 at 1032.2 and 821.3 cm^{-1} parallel those of isolated CU^{18}O at 1046.3 and 826.4 cm^{-1} , but the bands labeled 3 and 4 shift to 848.2 and 845.3 cm^{-1} and have weaker associated 773.5 and 771.4 cm^{-1} bands. Again the bands of 1 show $^{12}\text{C}^{18}\text{O}$ shifts of 1.1 and 45.3 cm^{-1} , which are almost the same as isolated CUO (1.0 and 45.8 cm^{-1}) whereas the shifts for the bands of 3 (9.0 and 34.8 cm^{-1}) and 4 (9.0 and 35.0 cm^{-1}) are nearly the same as those for CUO(Ar)_n (7.8 and 36.0 cm^{-1}). The 820–810 cm^{-1} region in the $^{12}\text{C}^{18}\text{O}$ experiment is a good place to search for singlet CUO(Ng)_n complexes as the isotopically shifted U–O mode is well

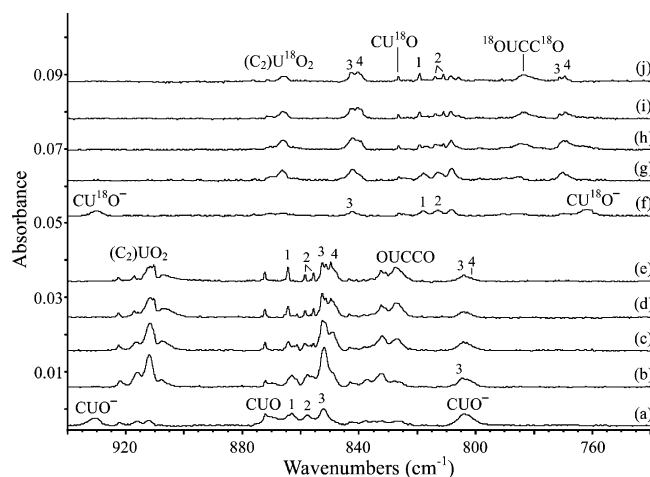


Figure 5. Infrared spectra in the 940–740 cm^{-1} region for laser-ablated U atom, 0.5% Kr, reaction products in excess neon at 3.5 K: (a) after sample deposition with $^{12}\text{C}^{16}\text{O}$ for 60 min, (b) after 240–700 nm photolysis for 15 min, and (c) after annealing to 10 K, (d) 12 K, and (e) 13 K; (f) after sample deposition with $^{12}\text{C}^{18}\text{O}$ for 60 min, (g) after 240–700 nm photolysis for 15 min, and (h) after annealing to 10 K, (i) 12 K, and (j) 13 K.

below the U–C mode for triplet complexes, which are represented by only the 848.2 and 845.3 cm^{-1} (3 and 4) bands; in essence, the isotopic substitution “unmasks” these singlet U–O bands. Two weak bands at 815.9 and 812.5 cm^{-1} increase on photolysis and shift to 817.1 and 813.9 cm^{-1} on 12 K annealing. These bands appear to track with the 861.9 and 858.8 cm^{-1} bands of the $^{12}\text{C}^{16}\text{O}$ products and the 859.8 and 856.9 cm^{-1} bands for $^{13}\text{C}^{16}\text{O}$ products.

CUO and Kr in Neon. As shown in Figure 3, the IR bands of the products when Kr is added to neon are slightly red-shifted from those in the presence of Ar. Figure 5 compares the infrared spectra obtained for 1% Kr in neon with 0.1% $^{12}\text{C}^{16}\text{O}$ and with 0.1% $^{12}\text{C}^{18}\text{O}$ and shows the evolution of product complexes. In addition to CUO and CUO^- , new bands are observed at 863, 858, and 852 cm^{-1} . As in Figure 1 for 1% Ar, photolysis destroys the CUO^- anion absorptions and gives new product bands labeled 3, now at 852.2 and 804.7 cm^{-1} . Annealing produces new 848.9 and 802.7 cm^{-1} features along with sharp new bands below CUO (872.2 cm^{-1}) at 864.4, 858.6, and 855.7 cm^{-1} (labeled 1, 2). The $^{12}\text{C}^{18}\text{O}$ substitution separates the product bands into two sets: first, 842.3 and 839.3 cm^{-1} (labeled 3, 4), which have smaller ^{18}O shifts and follow the pure argon (triplet) product, and second, 826.4 cm^{-1} (CU^{18}O in neon), 819.2, 813.8, and 811.0 cm^{-1} (labeled 1 and 2), which have larger ^{18}O shifts. A 808.1 cm^{-1} band increases on photolysis and then decreases on annealing while the 1, 2, 3, and 4 absorptions increase. Similar behavior was observed with $^{13}\text{C}^{16}\text{O}$, and the frequencies are listed in Table 2. A third band at 808 cm^{-1} , observed in the Kr spectrum with $^{12}\text{C}^{18}\text{O}$, decreases on annealing. This band could suggest another singlet complex, but without more isotopic data a case cannot be made.

CUO and Xe in Neon. The spectra obtained when Xe is added to neon are remarkably rich and detailed. As shown in Figure 3, the product peaks with Xe are slightly red-shifted from those with Kr, where more dilute Xe (0.3%) was

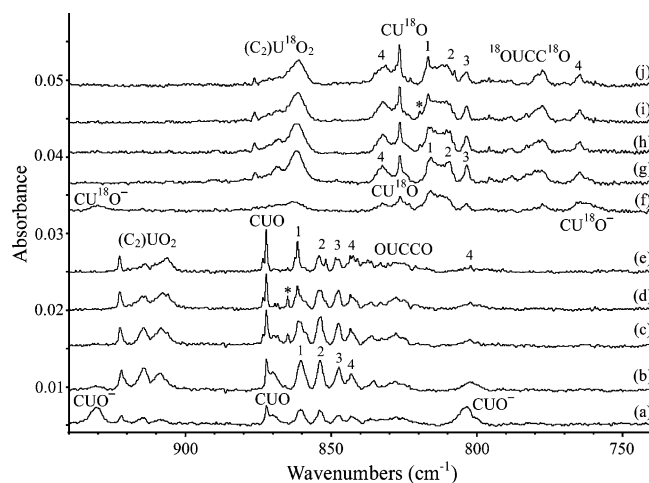


Figure 6. Infrared spectra in the 940–740 cm^{-1} region for laser-ablated U atom, 0.5% Xe, reaction products in excess neon at 3.5 K: (a) after sample deposition with $^{12}\text{C}^{16}\text{O}$ for 60 min, (b) after 240–700 nm photolysis for 15 min, and after annealing to (c) 10 K, (d) 12 K, and (e) 13 K; (f) after sample deposition with $^{12}\text{C}^{18}\text{O}$ for 60 min, (g) after 240–700 nm photolysis for 15 min, and after annealing to (h) 10 K, (i) 12 K, and (j) 13 K.

Table 2. Infrared Absorptions (cm^{-1}) from Reactions of Laser-Ablated U Atoms with CO and Kr in Excess Neon

$^{12}\text{C}^{16}\text{O}$	$^{13}\text{C}^{16}\text{O}$	$^{12}\text{C}^{18}\text{O}$	identification
2046	1984	2020	OUCCO
1047.3	1010.8	1046.3	CUO in neon
1029.6	995.9	1028.4	1, CUO(Kr)
930.9	898.0	929.8	CUO^-
922.1	922.1	875.9	$(\text{C}_2)\text{UO}_2$ in neon
912.0	912.0	866.5	$(\text{C}_2)\text{UO}_2$
872.2	870.5	826.4	CUO in neon
864.4	862.4	819.2	1, CUO(Kr)
864.9	863.1	819.8	CUO(CO) in neon
858.6	856.5	813.8	2a, CUO(Kr) ₂
855.7	853.5	811.0	2b, CUO(Kr) ₂
	850.4	808.1	?
852.2	838.0	842.3	3, [T], CUO(Kr) ₃
848.9	835.6	839.3	4, [T], CUO(Kr) ₄
854.6	854.5	809.6	XUO in neon
843.2	843.2	795.4	OUCCO in neon
832	832	784	OUCCO
804.7		771.2	3, [T], CUO(Kr) ₃
802.7		769.3	4, [T], CUO(Kr) ₄
804.2	802.3	762.0	CUO^-

employed to favor the lower Xe substitution complexes. Figure 6 compares sets of five spectra for 0.5% Xe with 0.1% $^{12}\text{C}^{16}\text{O}$ or $^{12}\text{C}^{18}\text{O}$. Isolated CUO (872.2 cm^{-1}) is followed by four bands at 861, 854, 847.4, and 843.3 cm^{-1} (labeled 1, 2, 3, 4). Using 1% Xe favors the lower frequency members of this series. The corresponding CU^{18}O spectra, however, show isolated CU^{18}O (826.4 cm^{-1}) followed by only three bands at 816.6, 810.0, and 803.7 cm^{-1} (labeled 1, 2, 3) since the fourth band shifted much less to 832.4 cm^{-1} (labeled 4). Annealing sharpens the first band to 861.5 cm^{-1} with the $^{12}\text{C}^{18}\text{O}$ counterpart at 816.6 cm^{-1} , and the second band splits into two features at 854.1, 851.8 cm^{-1} with $^{12}\text{C}^{18}\text{O}$ counterparts at 810.0, 807.5 cm^{-1} . The second 4 band increases in intensity on annealing at 798.6 and 764.6 cm^{-1} for $^{12}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$, respectively. A similar experiment with $^{13}\text{C}^{16}\text{O}$ gave analogous results, and the frequencies are listed in Table 3.

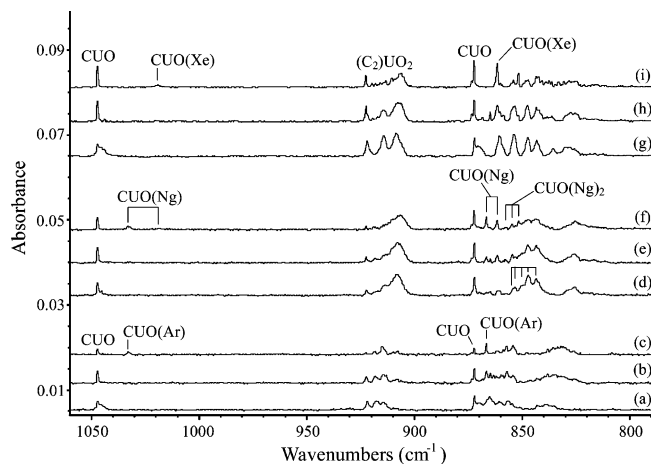


Figure 7. Infrared spectra for CUO in neon doped with Ar (a–c), Ar + Xe (d–f), and Xe (g–i). Spectra are grouped in sets of three: the bottom three are 0.1% CO and 0.5% Ar in neon; the middle three are 0.1% CO, 0.15% Ar, and 0.4% Xe in neon; and the top three are 0.1% CO and 0.3% Xe in neon. In every set, the three spectra are full-arc photolysis, 10 K and 14 K annealing in the order from bottom to top.

Table 3. Infrared Absorptions (cm^{-1}) from Reactions of Laser-Ablated U Atoms with CO and Xe in Excess Neon

$^{12}\text{C}^{16}\text{O}$	$^{13}\text{C}^{16}\text{O}$	$^{12}\text{C}^{18}\text{O}$	identification
2046	1984	2020	OUCCO
1047.3	1010.8	1046.3	CUO in neon
1019.4	986.8		1, CUO(Xe)
930	898	929	CUO ⁻
922.1	922.1	875.9	(C ₂)UO ₂ in neon
908	908	862	(C ₂)UO ₂
872.2	870.5	826.4	CUO in neon
864.9	863.1	819.8	CUO(CO) in neon
861.5	859.5	816.6	1, CUO(Xe)
854.6	854.5	809.6	XUO in neon
854.1	851.7	810.0	2a, CUO(Xe) ₂
851.8	849.5	807.5	2b, CUO(Xe) ₂
847.4	844.7	803.7	3, CUO(Xe) ₃
843.3	829.6	832.4	4, [T], CUO(Xe) ₄
829		778	OUCCO
798.6		764.6	4, [T], CUO(Xe)
803	802	761	CUO ⁻

CUO and Ar and Xe in Neon. Experiments involving mixtures of Ar and Xe in neon were carried out. Figure 7 presents the spectra obtained when a mixture of 0.1% $^{12}\text{C}^{16}\text{O}$, 0.15% Ar and 0.4% Xe was used, along with the corresponding spectra obtained with single Ng dopants. Several observations about the mixed Ar/Xe spectra are important. After full-arc photolysis four bands are observed 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 (Figure 7f), labeled CUO(Ng)₂. Recall that 858.8 cm^{-1} appeared with Ar in neon and 851.8 cm^{-1} with Xe in neon, but the intermediate 854.7 cm^{-1} component that *increases* on annealing requires the Ar, Xe mixture. Annealing also produced the bands labeled CUO(Ar) and CUO(Xe) in Figures 3b,d and 7c,i, and noted as doublets labeled CUO(Ng) in Figure 7f.

Calculations. New DFT calculations have been performed using NWChem for isolated CUO in $^1\Sigma^+$ and $^3\Phi$ states and for CUO(Ng)₄ in $^1A'$ and $^3A''$ states with Ng = Ne, Ar, Kr, and Xe, where the $^1A'$ and $^3A''$ states are derived from the

Table 4. 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	$^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{16}\text{O}$ freq ratio ^a
1.0010	1.0011	1.0012		$^{12}\text{C}^{16}\text{O}/^{12}\text{C}^{18}\text{O}$ 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	$^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{16}\text{O}$ freq ratio
1.0554	1.0552	1.0552	1.0550	$^{12}\text{C}^{16}\text{O}/^{12}\text{C}^{18}\text{O}$ 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	$^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{16}\text{O}$ freq ratio
	1.0106	1.0106	1.0544	$^{12}\text{C}^{16}\text{O}/^{12}\text{C}^{18}\text{O}$ freq ratio
	854.3	848.9	843.3	4, CUO(Ng) ₄
	1.0174	1.0159	1.0165	$^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{16}\text{O}$ freq ratio
	1.0106	1.0114	1.0131	$^{12}\text{C}^{16}\text{O}/^{12}\text{C}^{18}\text{O}$ freq ratio
	808.3	804.7		3, CUO(Ng) ₃
	1.0455	1.0434		$^{12}\text{C}^{16}\text{O}/^{12}\text{C}^{18}\text{O}$ freq ratio
	806.4	802.7	798.6	4, CUO(Ng) ₄
	1.0455	1.0434	1.0445	$^{12}\text{C}^{16}\text{O}/^{12}\text{C}^{18}\text{O}$ freq ratio

^a For the immediately preceding frequency.

$^1\Sigma^+$ and $^3\Phi$ states of CUO as a result of using the C_s symmetry. The calculated structural parameters, frequencies, and binding energies (relative to $^1\Sigma^+$ CUO + 4 Ng) are listed in Table 5. Note the steady decrease in frequencies for increasing Ng size and the clear distinction between frequencies for the singlet and triplet states. As expected, the binding energies for the singlet and the triplet series all increase when the Ng atoms become heavier. Even though $^1\Sigma^+$ CUO is more stable than the $^3\Phi$ CUO, all the triplet CUO(Ng)₄ species are more stable than their corresponding singlet, i.e., the coordination of Ar, Kr, and Xe atoms indeed stabilizes the triplet more than does the singlet. It is interesting to find that the differential stabilization of $^3A''$ CUO(Ng)₄ relative to $^1A'$ CUO(Ng)₄ (i.e., the difference in the U–Ng binding energies in the triplet and singlet states) is 4.5, 5.6, 5.9, 6.0 kcal/mol for Ne, Ar, Kr, Xe, respectively. That is, by comparing with the singlet CUO(Ng)₄, the Ar, Kr, and Xe atoms have larger differential stabilization effects for the triplet than the Ne atoms have.

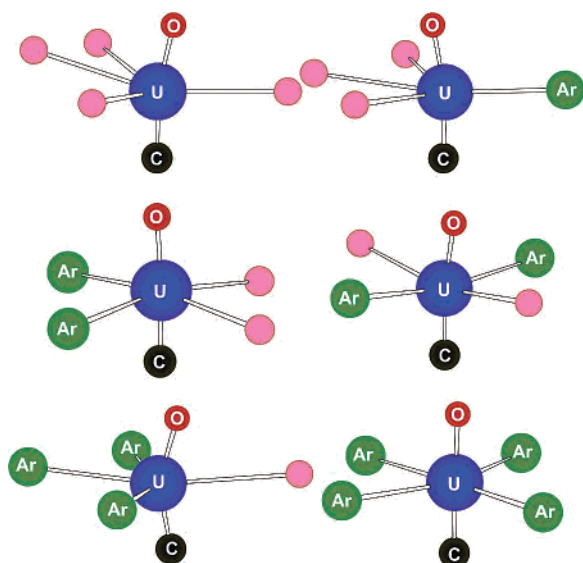
Similar calculations were done for the CUO(Ne)₃(Ng) (Ng = Ne, Ar, Kr, Xe) and CUO(Ne)_{4–n}(Ar)_n ($n = 0, 1, 2, 3, 4$) series, and the results are given in Table 6. Our calculations for CUO(Ar) and CUO(Ne)₃(Ar) reveal 0.002–0.005 Å increases in CUO bond lengths and 9–5 cm^{-1} decreases in stretching frequencies when three Ne atoms are included. Computed structures of the CUO(Ne)_{4–n}(Ar)_n ($n = 0, 1, 2, 3, 4$) complexes are illustrated in Figure 8. Our calculations of the total binding energy as a function of n in CUO(Ne)_n complexes indicate that the saturated CUO(Ne)_n complex likely has $n = 6$, and that the CUO(Ne)_n(Ar)₃ complex can contain up to two Ne atoms.

In addition, CCSD(T) energy calculations were performed for CUO and CUO(Ng) in singlet and triplet states. The CCSD(T) calculations are far more computationally demanding than DFT calculations, and we have not pursued

Table 5. Vibrational Frequencies (cm^{-1}), Bond Lengths (\AA), Angles, and Binding Energies Calculated by NWChem for CUO and CUO(Ng)₄ Complexes^{a,b}

molecule	state	E_b (kcal mol ⁻¹)	U–C	U–O	U–Ng ₄	U–Ng _{5,7}	U–Ng ₆	$\angle\text{CUO}$ (deg)	$\angle\text{CUNg}_4$ (deg)	$\nu_{\text{U–C}}$	$\nu_{\text{U–O}}$
CUO	¹ Σ^+	0	1.757	1.798				180		1089	870
CUO(Ne) ₄	¹ A'	4.52	1.769	1.805	3.313	3.164	3.333	167.7	90.8	983	847
CUO(Ar) ₄	¹ A'	6.51	1.774	1.811	3.401	3.237	4.027	155.5	107.1	963	840
CUO(Kr) ₄	¹ A'	8.87	1.775	1.812	3.374	3.325	4.391	149.8	95.7	947	839
CUO(Xe) ₄	¹ A'	11.48	1.782	1.813	3.476	3.439	4.566	147.6	91.9	942	839
CUO	³ Φ	-1.15	1.857	1.825				180		893	828
CUO(Ne) ₄	³ A''	9.01	1.862	1.828	3.090	3.105	3.283	179.5	90.8	884	819
CUO(Ar) ₄	³ A''	12.08	1.871	1.833	3.256	3.261	3.244	176.9	89.9	869	814
CUO(Kr) ₄	³ A''	14.75	1.874	1.835	3.333	3.344	3.325	177.2	89.3	864	810
CUO(Xe) ₄	³ A''	17.47	1.879	1.836	3.452	3.471	3.451	178.6	87.5	860	808

^a The atoms in CUO(Ng)₄ are numbered as U(1), C(2), and O(3), with the Ng atoms labeled as atoms 4 and 6 along the C_s plane, and atoms 5 and 7 off the C_s plane. ^b The differential stabilization of the triplet relative to the singlet is 4.5, 5.6, 5.9, and 6.0 kcal/mol, respectively, for CUO(Ng)₄ (Ng = Ne, Ar, Kr, Xe).

**Figure 8.** Structures of CUO(Ne)_{4-n}(Ar)_n ($n = 0, 1, 2, 3, 4$). For simplicity Ne atoms are not labeled.**Table 6.** Vibrational Frequencies (cm^{-1}), Bond Lengths (\AA), and Angles Calculated by NWChem for Two Series of CUO Complexes with Four Mixed Noble Gas Atoms: CUO(Ne)₃(Ng) (Ng = Ne, Ar, Kr, Xe) and CUO(Ne)_{4-n}(Ar)_n ($n = 0, 1, 2, 3, 4$)

molecule	state	U–C	U–O	$\angle\text{CUO}$ (deg)	$\nu_{\text{U–C}}$	$\nu_{\text{U–O}}$
CUO(Ne) ₃ (Ne)	¹ A'	1.769	1.805	167.7	983	847
CUO(Ne) ₃ (Ar)	¹ A'	1.773	1.807	168.6	978	842
CUO(Ne) ₃ (Kr)	¹ A'	1.774	1.808	166.1	976	843
CUO(Ne) ₃ (Xe)	¹ A'	1.775	1.809	157.4	970	846
<i>cis</i> -CUO(Ne) ₂ (Ar) ₂	¹ A'	1.773	1.809	177.2	971	842
<i>trans</i> -CUO(Ne) ₂ (Ar) ₂	¹ A'	1.774	1.810	168.6	973	843
CUO(Ne)(Ar) ₃	¹ A'	1.774	1.811	154.0	965	840
CUO(Ar) ₃ (Ar)	¹ A'	1.774	1.811	155.5	963	840
CUO(Ne) ₃ (Ne)	³ A''	1.862	1.828	179.5	884	819
CUO(Ne) ₃ (Ar)	³ A''	1.865	1.830	174.1	878	820
CUO(Ne) ₃ (Kr)	³ A''	1.866	1.831	172.7	876	818
CUO(Ne) ₃ (Xe)	³ A''	1.868	1.831	170.9	873	817
CUO(Ar) ₃ (Ar)	³ A''	1.871	1.833	176.9	869	814

calculations with more than one noble-gas atom bonded to CUO at this time. The ³ Φ state for linear CUO is calculated to be 15.8 kcal/mol above the ¹ Σ^+ state. For the CUO(Ng) molecules, the ³ A'' state is calculated to be 15.0, 14.4, 14.4, and 14.3 kcal/mol above the ¹ A' for Ng = Ne, Ar, Kr, and Xe, respectively.

Discussion

The bands for the new noble-gas complexes observed here will be assigned on the basis of Ar, Kr, Xe and ¹²C¹⁶O, ¹²C¹⁸O, ¹³C¹⁶O substitution, comparison to the spectrum of CUO in pure neon, which is taken as the reference complex, and the DFT calculations. Recall that CUO is produced upon the reaction of excited U atoms (via laser ablation or UV photolysis)^{1,7} and that excited triplet CUO binds Ng atoms more strongly than does ground state singlet CUO.⁵ The CUO(Ng)_n complex distribution on deposition is not statistical because excited CUO* is formed initially, and during relaxation excited triplet CUO will bond Ar more strongly (and thus more extensively) than ground state CUO.

Noble-gas clusters with metal positive ions have been investigated extensively by using both experiment and theory. Miller and co-workers have found FeAr_n⁺ clusters favored for up to six argon atoms with a special stability for FeAr₆⁺ in a presumed octahedral symmetry.¹⁹ Velegrakis et al. have observed noble-gas clusters for a number of metal cations. For argon clusters with K⁺, Mg⁺, and Sr⁺ there is significant population into and above the $n = 10$ range, but for Ni⁺ and Pt⁺ the population decreases after $n = 6$.^{20–22} Although the CUO molecule is neutral overall, we can reasonably expect an intimate first layer of coordinated noble gas atoms followed by a more weakly interacting secondary shell. This model emerges from our investigations with CUO in mixtures of Ar, Kr, and Xe.^{6,7}

CUO in Neon. Our calculations on CUO(Ne)_n indicate that Ne atoms are also capable of binding to CUO, just as Ar, Kr, and Xe can, although the U–Ne bonds are quite weak. This computational result provides support for the notion that CUO in solid neon is likely a CUO(Ne)_n complex that results from coordination of Ne atoms to the CUO molecule. Unlike Ar, Kr, and Xe, the coordination of Ne atoms does not perturb the electronic structure of CUO enough to cause a singlet–triplet crossover. As a result, the predicted DFT frequencies for the isolated ¹ Σ^+ CUO molecule (1049, 874 cm^{-1} from ADF calculations)^{1,4,5} are in excellent agreement with the observed frequencies for CUO in solid neon (1047.3 and 872.2 cm^{-1}).¹

Like the bonding of other Ng atoms to CUO, the binding of Ne atoms to CUO is due to a Lewis acid–base interaction in which a lone pair on a Ne atom donates into an empty orbital on the uranium center. These interactions are facilitated by the high positive charge on the U atom, which has a Mulliken charge of +1.35 at the ADF/PW91 level of calculation. Nevertheless, the U–Ne interactions are quite weak because of the small polarizability of neon. Our current NWChem calculations (Table 5) find a binding energy of 1.1 kcal/mol per U–Ne bond in CUO(Ne)₄, which is small enough to justify further calculations before characterizing the U–Ne interaction. Our initial theoretical studies of the binding of multiple Ne atoms to CUO lead to the prediction that the maximum total binding energy is achieved for CUO(Ne)₆. The coordination of six Ne atoms is in accord with our previous predictions that CUO will coordinate four or five heavy Ng atoms,^{6,7} for the smaller size of Ne allows a greater number to be accommodated in the coordination sphere.

Our calculations support the explanation that the binding of Ne atoms to CUO does not provide enough differential stabilization of the triplet state to cause the spin crossover in the molecule, which is consistent with the experimental observation that the U–C and U–O vibrations of CUO(Ne)_n are well modeled by the isolated CUO molecule. Thus, it seems clear that Ne is serving as an innocent “ligand” that does not greatly perturb the CUO molecule. As noted earlier, we will refer to CUO(Ne)_n complex in solid neon simply as CUO.

The question of the magnitude of the singlet–triplet splitting in CUO is of great current interest. Our initial DFT calculations on isolated CUO found the ¹Σ⁺ state below the ³Φ state by about 1 kcal/mol.^{1,4,5} This value is small enough to cast some doubt on the predicted ordering of the states, especially in view of the fact that spin–orbit coupling would stabilize the triplet state relative to the singlet state, as we noted earlier.⁵ The more accurate CCSD(T) calculations predict that the triplet state is 15.8 kcal/mol above the singlet ground state, although these calculations also did not include spin–orbit effects. Roos et al.³³ have recently applied the CASPT2/SO method, which explicitly includes spin–orbit effects, to the CUO molecule. They find that the inclusion of spin–orbit coupling lowers the triplet state relative to the singlet state by 8–10 kcal/mol. Applying this magnitude for the spin–orbit effects to the splitting we found from the CCSD(T) calculations would place the triplet state 6–8 kcal/mol above the singlet state. This is in reasonable agreement with very recent preliminary calculations of Visscher et al.,³⁴ which find triplet above singlet by 17 kcal/mol at the DC-CCSD level, where the contribution of the coupled-cluster triple excitations is too expensive to be included. We have previously found that the singlet–triplet splitting decreases upon complexation of noble-gas atoms.⁵ The experimental observation that CUO in pure neon exhibits the properties of the singlet molecule indicates that any differential

stabilization of the triplet state by coordination of Ne atoms is not great enough to overcome the initial state splitting in the isolated molecule. Our CCSD(T) calculations predict that the T–S separation is 0.8 kcal/mol smaller for CUO(Ne) than for CUO in the gas-phase, which implies that the T–S separation for CUO(Ne)₆ would be about 4.8 kcal/mol smaller than for CUO. If spin–orbit coupling is unchanged for CUO in the CUO(Ne)₆ complex, our calculations are consistent with the above experimental observation for the Ne matrix.

The 850 cm⁻¹ region is very important for the noble-gas-doped systems, so more attention must be paid to the neon-matrix spectrum of CUO. On deposition the sharp CUO absorptions at 1047.3 and 872.2 cm⁻¹ exhibit red shoulders about 5 cm⁻¹ wide. On annealing these shoulders disappear revealing sharp, weak satellite absorptions at 1044.3 cm⁻¹ (identified as “CUO site” in ref 1) and a similar peak at 869.0 cm⁻¹ that must also be identified as a CUO site absorption. In addition, a sharp 864.9 cm⁻¹ absorption labeled with an asterisk (*) in the figures increases on 8 K annealing, decreases on 12 K annealing, and *does not* show a counterpart near 1040 cm⁻¹. Hence, this 864.9 cm⁻¹ peak cannot be due to a CUO site, as suggested previously,¹ although it exhibits nearly the same isotopic frequency ratios. A CUO complex that leaves the C–U stretching mode unperturbed but the U–O stretching mode slightly red-shifted appears likely for the 864.9 cm⁻¹ absorption. The weak 854.6 cm⁻¹ absorption increases on photolysis and shows virtually no carbon-13 shift and a larger oxygen-18 shift approaching that for UO itself. Thus, the 854.6 cm⁻¹ absorption is due to a U–O vibration in a molecule XUO where X cannot be identified: another matrix site of OUCCO is a possibility. The sharp 864.9 cm⁻¹ peak is probably due to a weak CUO(CO) complex of unreacted CO and CUO: ultraviolet photolysis destroys this complex in favor of OUCCO. Weak interaction at oxygen is suggested by the absence of a new U–C stretching mode in the spectrum. The presence of extra Ng diminishes the 864.9 cm⁻¹ band in favor of CUO(Ng) complexes. The pure neon matrix and noble-gas doped neon matrix CUO systems all reveal the 864.9 cm⁻¹ absorption on deposition. In pure neon it increases on annealing, but with added Ar and Kr (Figures 1, 2, 5) the 864.9 cm⁻¹ absorption increases on 8 K but decreases on 12 K annealing in favor of sharp peaks at 866.6 and 864.4 cm⁻¹ that will be assigned below to singlet CUO(Ar) and CUO(Kr), respectively. With added Xe (Figure 6) the 864.9 cm⁻¹ peak increases on annealing to 10 K and is replaced on annealing to 12 K by the 861.5 cm⁻¹ peak that will be assigned to singlet CUO(Xe).

CUO(Ng). The bands labeled 1 are assigned to the complexes CUO(Ng), which are proposed to be formed upon the replacement of one or more Ne atoms of CUO(Ne)_n by an Ar, Kr, or Xe atom. Conclusive evidence that these bands are due to the addition of a single heavy noble-gas atom is provided by the experiments with mixtures of isotopomers of CO and with the mixtures of Ar and Xe. The mixed ¹²C¹⁶O + ¹³C¹⁶O experiment (Figure 4) reveals doublet absorptions at 1033.3, 998.0 and 866.6, 864.6 cm⁻¹ and shows that these

(33) Roos, B.; Widmark, P.-O.; Gagliardi, L. *Faraday Discuss. Chem. Soc.* **2003**, *124*, 57.

(34) Visscher, L., 2003, personal communication.

bands are due to vibrations involving a single carbon atom. In a mixed $^{12}\text{C}^{16}\text{O} + ^{12}\text{C}^{18}\text{O}$ isotopic experiment, the CUO absorptions also gave doublets, which demonstrates the involvement of a single oxygen atom.¹ The very low laser energy employed here, the sharp CUO product bands, and the excellent fit of the DFT calculated frequencies for the $^1\Sigma^+$ CUO state^{1,4} all argue that this molecule contains a single U atom. Finally, the mixed Ar, Xe in neon experiments give sharp unshifted doublet absorptions for CUO(Ar) and CUO(Xe) without intermediate components and show that these absorptions arise from complexes containing a single heavy Ng atom. This last experiment in particular tells us that the complexes contain one, and only one, Ng atom.

The bands for CUO(Ng) are red-shifted relative to those of CUO, and the red-shift increases from Ar to Kr to Xe (Figure 3). The bands for the CUO(Ng) complexes are favored by Ng dilution, consistent with monosubstitution, and the bands increase in intensity upon annealing. The bands for complexes 3 are stronger on deposition and reaction of U excited by laser-ablation (Figure 1a) and UV photolysis (Figure 1b) owing to the greater stability of the higher triplet CUO complexes (see below). The coordination of a single noble-gas atom has a greater effect on the U–C stretching frequency than on the U–O stretching frequency: The U–C modes of CUO(Ng) are red-shifted relative to CUO by 14.0, 17.7, and 27.9 cm^{-1} , respectively, with Ar, Kr, and Xe, whereas the U–O mode is red-shifted by 5.6, 7.8, and 10.9 cm^{-1} (Table 4). The isotopic frequency ratios indicate that the U–C and U–O stretching normal modes of CUO change only very slightly upon complexation with an Ng atom. The 1047.3 cm^{-1} band of singlet CUO is an almost pure U–C stretching mode for which the isotopic ratio $^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{16}\text{O} = 1.0361$. For the CUO(Ng) complexes, this ratio decreases to 1.0354 with Ar, to 1.0342 with Kr, and to 1.0330 with Xe. This slight decrease in the U–C stretching character is accompanied by a slight increase in the $^{12}\text{C}^{16}\text{O}/^{12}\text{C}^{18}\text{O}$ ratio and U–O stretching character. In analogous manner, the 872.2 cm^{-1} band of singlet CUO is an almost pure U–O stretching mode with $^{12}\text{C}^{16}\text{O}/^{12}\text{C}^{18}\text{O} = 1.0554$. This ratio decreases very slightly to 1.0552, 1.0552, and 1.0550 in the Ng series while the $^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{16}\text{O}$ ratio increases from 1.0020 to 1.0023. The slight decrease in U–O stretching character for the lower band is associated with a slight increase in U–C stretching character. In conclusion, the two modes of each CUO(Ng) complex are close in position and normal mode character to the modes of singlet CUO(Ne)_n. This close comparison provides strong evidence that the CUO(Ng) complexes are also trapped in singlet ($^1A'$ under C_s symmetry) ground states that are electronically similar to the $^1\Sigma^+$ state of isolated CUO. As is observed for the triplet CUO(Ng)_n complexes,^{4–6} the U–C mode is perturbed more than the U–O mode by the CUO–Ng interaction in the singlet CUO(Ng) complexes. Hence, we have identified the CUO(Ng) complexes by neon-matrix infrared spectroscopy and characterized their ground state as singlet through comparison to DFT calculated frequencies for $^1\Sigma^+$ CUO.^{1,4}

Our initial DFT calculations without spin–orbit coupling predicted that the complexation of CUO by Ng atoms would

stabilize the triplet more than the singlet, but also suggest that a single heavy noble-gas would be sufficient to cause a spin crossover from CUO to CUO(Ng). For example, the scalar-relativistic DFT calculations on CUO(Ar) predicted that the $^3A''$ state would be below the $^1A'$ state by about 1 kcal/mol.⁵ As noted earlier, this energy separation is questionable, particularly because the DFT calculations did not include spin–orbit coupling. Roos et al. have pointed out that, were spin–orbit effects included, our earlier DFT results would most certainly find the triplet below the singlet for CUO as well as CUO(Ar).³³ Our CCSD(T) calculations on CUO, discussed earlier, indicate that DFT is underestimating the singlet–triplet splitting in CUO, and, by extension, is placing the triplet too low in CUO(Ar) and other multiple-coordinated CUO complexes. Our CCSD(T) calculations on the mono-Ng adducts CUO(Ng) indicate that the $^1A'$ state is still below the $^3A''$ state by 15.0, 14.4, and 14.3 kcal/mol for Ar, Kr, and Xe, respectively. These CCSD(T) calculations did not include spin–orbit effects, but if we use the differential stabilization of the triplet state found by Roos et al.,³³ we see that the singlet state of CUO(Ng) will still be below the triplet state. Thus, at this higher level of theory, we find the experimentally consistent result that coordination of a single Ng atom to CUO is not sufficient to change the ground state from singlet to triplet.

Note the changes in relative U–C and U–O stretching absorption band profiles and relative intensities as CUO is complexed successively by Ar, Kr, and Xe (Figure 3). For CUO isolated in neon the 1047.3 (U–C) and 872.2 (U–O) cm^{-1} bands are sharp and the relative intensity is about 1:1. However, for the Ng complexes the U–C stretching band is broadened and the intensity decreases relative to the U–O stretching band, and this effect increases from Ar to Kr to Xe, as does the red-shift of the U–C and U–O bands relative to CUO. Furthermore, the red-shift of the U–C mode upon Ng coordination is significantly larger than that of the U–O mode (Table 4). These observations indicate that the Ng atom in the CUO(Ng) complex interacts more strongly with the U–C bond than with the U–O bond, and that this interaction increases with the Ng size and polarizability. This observation is completely in agreement with the results of our earlier DFT calculations, which showed that the Ng atom in CUO(Ng) interacted much more strongly with the C atom than with the O atom, and increasing binding energies with Ar, Kr, and Xe (2.2, 3.1, and 4.1 kcal/mol).

The earlier DFT results were obtained using the ADF method. We have performed new DFT calculations using NWChem, which can make use of symmetry in frequency calculations. As was the case for our earlier ADF calculations, the calculated stretching frequencies for the $^1\Sigma^+$ and $^3\Phi$ states of isolated CUO from the NWChem calculations (Table 5) show the dramatic changes in the U–C and U–O stretching frequencies upon the change in electronic state. The agreement between the NWChem calculated frequencies of the $^1\Sigma^+$ state (1089, 870 cm^{-1}) and the observed frequencies in the pure neon matrix (1047.3, 872.2 cm^{-1}) is not quite as good as for the ADF calculations (1049, 874 cm^{-1}), but overall these calculations provide additional

support for the notion that CUO in neon behaves much like isolated $^1\Sigma^+$ CUO. The coordination of four Ne atoms, to form $\text{CUO}(\text{Ne})_4$, lowers the U–C and U–O stretching modes by about 100 and 20 cm^{-1} , respectively, relative to isolated CUO. The calculated frequencies for $\text{CUO}(\text{Ne})_4$ are in poorer agreement with the experimental values than those for isolated CUO. Nevertheless, these model complexes can be used to show the trends in stretching frequencies as Ne is replaced by an Ar, Kr, or Xe atom.

The series of complexes $\text{CUO}(\text{Ng})_4$ ($\text{Ng} = \text{Ne}, \text{Ar}, \text{Kr}, \text{Xe}$) show a steady decrease in the U–C and U–O stretching modes as the Ng atom gets heavier. The calculated stepwise red-shifts (4–15 cm^{-1} and 2–9 cm^{-1} for the triplet U–C and U–O modes, respectively) are comparable to those observed experimentally (10–14 cm^{-1} and 2–6 cm^{-1}). It is satisfying that the calculated red-shift of the U–C mode is larger than that for the U–O mode. The trend in the frequencies of the $\text{CUO}(\text{Ne})_3(\text{Ng})$ ($\text{Ng} = \text{Ne}, \text{Ar}, \text{Kr}, \text{Xe}$) complexes is very similar, although the U–O stretch does not decrease monotonically progressing through the series.

In general, the NWChem DFT calculations seem to model much of the behavior of the $\text{CUO}(\text{Ng})_n$ complexes with reasonable accuracy. We will be investigating improved means for modeling the very weak U–Ne interactions, which we hope will improve the quantitative agreement between the calculated and the experimental values.

CUO(Ng)₂. The sharp bands labeled 2 for each Ng atom (Tables 1–3) resolve out of the band immediately below the bands for 1 upon annealing and are thus more difficult to characterize. For the Ar/Ne experiments, the bands for 2 increase in intensity relative to those of 1 when the Ar concentration is increased from 0.5% to 1%. Further, the unmasked band labeled 2b gives a triplet feature with an intermediate component in the mixed Ar, Xe neon experiment, which provides evidence for two Ng atoms. Hence, bands labeled 2 are assigned to $\text{CUO}(\text{Ng})_2$ complexes in two different neon matrix sites or isomer structures. We believe that at least two Ne atoms are still coordinated to the U atom in the $\text{CUO}(\text{Ng})_2$ complexes, so if the noble-gas atoms all lie in the equatorial plane, these complexes will have geometric isomers. We have separately calculated the properties of *cis*- and *trans*- $\text{CUO}(\text{Ne})_2(\text{Ar})_2$ (Table 6), and these two complexes are predicted to have slight differences in their stretching frequencies. With the experimental evidence at hand, we cannot confirm or rule out the presence of multiple geometric isomers in the matrix.

The CO isotopic frequency ratios for both bands of 2 are virtually the same as for the U–O mode in the $\text{CUO}(\text{Ng})$ complex and isolated CUO in neon (there is a very slight decrease in $^{12}\text{C}^{16}\text{O}/^{12}\text{C}^{18}\text{O}$ ratio and increase in $^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{16}\text{O}$ ratio). This observation along with the observed frequencies shows that the $\text{CUO}(\text{Ng})_2$ complexes have a singlet electronic state related to the ground state of isolated CUO. Apparently the coordination of two heavy noble-gas atoms is still not enough to lower the energy of the triplet state of $\text{CUO}(\text{Ng})_2$ below that of the singlet state.

CUO(Ng)_{3,4}. Our previous studies with Xe in argon have identified the proposed octahedral complexes $\text{CUO}(\text{Ar})_{4-n}(\text{Xe})_n$ ($n = 0, 1, 2, 3, 4$), which first conclusively demonstrated that CUO could bind multiple noble-gas atoms.^{6,7} The present studies of Ng in neon continue this trend, and we propose that the bands labeled 3 and 4 are due to $\text{CUO}(\text{Ng})_3$ and $\text{CUO}(\text{Ng})_4$, where an indeterminate number of neon atoms are still bonded to the U atom. The bands labeled 3 and 4 are clearly favored by higher Ng concentrations, and by the reaction of excited U to form excited CUO (Figure 1 a,b). For $\text{Ng} = \text{Ar}$ or Kr , the CO isotopic frequency ratios for these bands are substantially different from those for CUO, $\text{CUO}(\text{Ng})$, and $\text{CUO}(\text{Ng})_2$; rather, the frequencies and isotopic frequency ratios of the bands of 3 and 4 resemble those for $\text{CUO}(\text{Ar})_n$ in pure argon.^{4–6} In particular, the isotopic data distinguishes the characters of the strong bands in the 870–850 cm^{-1} region for these various species. As discussed below, for CUO and $\text{CUO}(\text{Ng})$, the vibration in this spectral region is U–O in character, but for 3 (with Ar and Kr) and 4 (with Ar, Kr, and Xe) the mode is primarily a U–C vibration.

The isotopic frequency ratios for the strong 852.5 cm^{-1} fundamental for CUO in a pure argon matrix are $^{12}\text{C}^{16}\text{O}/^{12}\text{C}^{18}\text{O} = 1.0092$ and $^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{16}\text{O} = 1.0188$. The magnitudes of these ratios make it clear that this vibration is predominantly U–C stretch in character, as compared to the 872.2 cm^{-1} vibration of neon-isolated CUO, which is a nearly pure U–O stretch. For the experiment in which Ar is doped into the Ne (Table 1), the ratios for the 857.2 cm^{-1} band labeled 3 and the 854.3 cm^{-1} band labeled 4 are nearly the same as those for CUO in argon (1.0106, 1.0172 and 1.0106, 1.0174, respectively). Thus, these vibrations are also primarily U–C in character. We therefore propose that the $\text{CUO}(\text{Ar})_3$ and $\text{CUO}(\text{Ar})_4$ complexes are triplet molecules similar to CUO in pure argon.^{4–6} These results suggest that the S → T crossover for $\text{CUO}(\text{Ar})_n$ occurs at $n = 3$, i.e., $\text{CUO}(\text{Ar})_2$ has a singlet ground state whereas $\text{CUO}(\text{Ar})_3$ has a triplet ground state.

In addition the isotopic frequency ratios reveal a slight increase in oxygen and decrease in carbon mass dependence for the vibration, which indicates a slight change in normal mode character. The primary difference between the $\text{CUO}(\text{Ar})_4$ species, absorbing at 852.5 cm^{-1} in pure argon, and the present 4 bands is the secondary solvent shell of argon in the former and neon in the latter, which causes a small 1.8 cm^{-1} shift. This is close to the differences observed for the $\text{CUO}(\text{Ng})_4$ ($\text{Ng} = \text{Kr}, \text{Xe}$) complexes with neon and argon secondary solvent shells.^{6,7} The U–O, U–C mode mixing changes slightly on going from $\text{CUO}(\text{Ar})_n$ in pure argon to $\text{CUO}(\text{Ar})_4$ in neon.

These trends continue for the Kr-doped neon matrix (Table 4). The U–C stretches of $\text{CUO}(\text{Kr})_3$ and $\text{CUO}(\text{Kr})_4$ 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 as those for the Ar complexes. It therefore appears that the behavior of these Kr complexes is entirely parallel

to that of the Ar complexes, and $\text{CUO}(\text{Kr})_3$ and $\text{CUO}(\text{Kr})_4$ have triplet ground states.

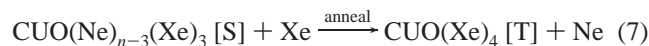
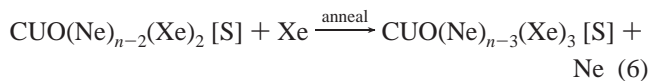
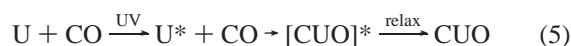
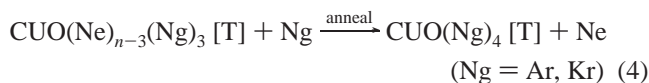
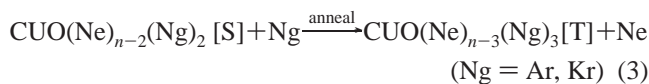
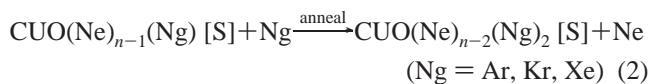
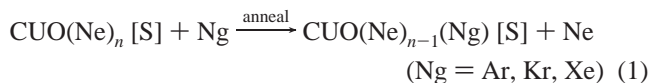
The situation is somewhat different for CUO with Xe in neon. The band assigned to $\text{CUO}(\text{Xe})_3$ exhibits isotopic frequency ratios that are close to those of the singlet complexes, whereas that for $\text{CUO}(\text{Xe})_4$ has isotopic frequency ratios that indicate that it is a triplet complex. Further, there is no $\text{CUO}(\text{Xe})_3$ counterpart to the lower frequency band for $\text{CUO}(\text{Xe})_4$. These observations seem to indicate that the $S \rightarrow T$ crossover for the $\text{CUO}(\text{Xe})_n$ complexes requires the coordination of four Xe atoms as compared to three Ar or Kr atoms. The band for $\text{CUO}(\text{Xe})_4$ is red-shifted by 5.6 cm^{-1} from that for $\text{CUO}(\text{Kr})_4$, and the isotopic frequency ratios continue the trend of decreasing U–C and increasing U–O character in the vibrational mode. Finally, we note that the $\text{CUO}(\text{Kr})_4$ complex absorbs at 846.0 cm^{-1} in solid argon, 2.9 cm^{-1} lower than the neon-matrix value presented here. Likewise, $\text{CUO}(\text{Xe})_4$ absorbs at 835.4 cm^{-1} in solid argon, which is 7.9 cm^{-1} lower than the present neon-matrix value. These shifts are indicative of larger secondary argon–neon solvent effects than was found for $\text{CUO}(\text{Ar})_4$. Clearly the $\text{CUO}(\text{Xe})_4$ complex is more vulnerable to matrix effects.

Fewer data are available for the weaker, lower, mostly U–O mode of the larger complexes. These bands show $^{12}\text{C}^{16}\text{O}/^{12}\text{C}^{18}\text{O}$ ratios consistent with a decrease in U–O character relative to the argon-matrix 804.3 cm^{-1} absorption.

CUO(Ng)_n Complex Formation. These experiments clearly show that the weaker singlet complexes $\text{CUO}(\text{Ng})_{1,2}$ are formed by successive addition of Ng atoms to $^1\Sigma^+$ CUO on diffusion in the solid neon matrix. We believe that the intimate coordination sphere is completed by neon. We will assume, for convenience only, that the relevant reactions involve a one-to-one replacement of coordinated Ne atoms by heavier Ng atoms; as will be noted later, it seems likely that the number of coordinated Ne atoms varies with different Ng dopants.

Intermediate annealing (8–10 K) shows a net decrease in $\text{CUO}(\text{Ne})_n$ and a net increase in $\text{CUO}(\text{Ng})_{1,2,3}$ absorptions (eqs 1–3), and late annealing (12–14 K) decreases the latter and increases $\text{CUO}(\text{Ng})_4$ (eq 4). In pure neon, ultraviolet photolysis increases $\text{CUO}(\text{Ne})_n$ absorptions about 4-fold,¹ but with extra Ng atoms present, much of the CUO growth is found in $\text{CUO}(\text{Ng})_n$ complexes. Ultraviolet photolysis ($\lambda > 290 \text{ nm}$) is sufficient to activate CO insertion reaction (eq 5). With 1% Ar (Figure 1) most of the increase (4-fold) is $\text{CUO}(\text{Ar})_3$, but with 0.5% Ar, $\text{CUO}(\text{Ar})_n$ ($n = 0, 1, 2, 3, 4$) all increase. With 1% Kr (Figure 5) most of the increase (3-fold) is in $\text{CUO}(\text{Kr})_4$, but with 0.5% Xe (Figure 6) all $\text{CUO}(\text{Xe})_n$ ($n = 0, 1, 2, 3, 4$) increase about 2-fold. With 0.5% Ar, annealing increases all $\text{CUO}(\text{Ar})_n$ ($n = 1, 2, 3, 4$) complexes at the expense of isolated CUO. Therefore, it appears that the change from singlet $\text{CUO}(\text{Ar})_2$ to triplet $\text{CUO}(\text{Ar})_3$ is spontaneous in solid neon at 10–14 K. Figure 1 shows clearly the net growth of triplet species and the effect of eq 4 on the two $\text{CUO}(\text{Ar})_3$ and $\text{CUO}(\text{Ar})_4$ fundamental

absorption bands (labeled 3, 4). Equations 6 and 7 highlight the difference in the spin crossover point for the $\text{CUO}(\text{Xe})_n$ complexes.



We recall that the reaction of U and CO is exothermic and that both laser-ablation and UV photolysis promote this reaction.¹ Note that reaction to form triplet $\text{CUO}(\text{Ne})_n(\text{Ar})_3$ is markedly favored under these high energy conditions, which form the energized CUO product. Hence quenching of excited CUO will involve a considerable diffusion range in the matrix during the deposition–condensation process or local heating during photoexcitation–relaxation, and thus increase the encounters with argon atoms and favor the higher triplet complexes. We found the CCSD(T) CUO–Ng bond energies to be 1.4 kcal/mol per bond higher for the triplet state complexes. On the other hand, diffusion in solid neon at 8–12 K is a more controlled process where simple Ng for Ne exchange occurs in the primary coordination sphere around CUO. The reactions under annealing conditions take place stepwise to give steady growth in the absorption bands.

The picture of primary intimate and secondary coordination spheres of Ng atoms around CUO emerges from our work. We have observed the U–C and U–O stretching modes of $\text{CUO}(\text{Ar})_4$ in solid argon at 852.5 and 804.3 cm^{-1} , and in solid neon at 854.3 and 806.4 cm^{-1} . These $\sim 2 \text{ cm}^{-1}$ differences (1.8 and 2.1 cm^{-1}) arise from the difference in neon and argon secondary solvent shells $\text{CUO}(\text{Ar})_4[\text{Ne}]_x$ and $\text{CUO}(\text{Ar})_4[\text{Ar}]_x$. Larger $2\text{--}4 \text{ cm}^{-1}$ shifts derive from changing the secondary shell around $\text{CUO}(\text{Kr})_4$ from $[\text{Ar}]_x$ to $[\text{Kr}]_x$. For comparison the effect of replacing *each* primary Ar atom in the $\text{CUO}(\text{Ar})_4$ complex with Xe atoms to form $\text{CUO}(\text{Xe})_4$ is $3\text{--}4 \text{ cm}^{-1}$, but the total effect of exchanging the *complete* secondary $[\text{Ar}]_x$ shell for $[\text{Xe}]_x$ is 3.4 and 5.6 cm^{-1} for the U–O and U–C stretching modes, respectively.

In like fashion $\text{CUO}(\text{Xe})_4$ has been observed at 835.4 and 792.6 cm^{-1} in solid argon, at 832.2 and 790.5 cm^{-1} in solid krypton, and at 829.8 and 789.2 cm^{-1} in solid xenon.^{6,7} These

2–3 cm⁻¹ shifts are due to changing the secondary solvent shell around CUO(Xe)₄ from [Ar]_x to [Kr]_x to [Xe]_x. Similarly CUO(Kr)₄ has been observed at 846.0 and 799.4 cm⁻¹ in solid argon and at 842.3 and 797.1 cm⁻¹ in pure solid krypton. Likewise CUO(Kr)₄ in solid neon at 848.9 and 802.7 cm⁻¹ shifts to 842.3 and 797.1 cm⁻¹ in pure krypton revealing larger 6.3 and 5.6 cm⁻¹ secondary solvent effects on replacing neon with krypton. Again CUO(Xe)₄ in solid neon at 843.3 and 798.6 cm⁻¹ is displaced to 829.8 and 789.2 cm⁻¹ in pure xenon showing still larger 13.5 and 9.4 cm⁻¹ shifts for CUO(Xe)₄[Ne]_x to CUO(Xe)₄[Xe]_x.

Why Is the Spin Crossover Point Different for CUO(Xe)_n? The results presented here provide strong evidence that the crossover from singlet to triplet occurs for CUO(Ar)₃ and CUO(Kr)₃, but that the coordination of four Xe atoms is needed to effect spin crossover. This result seems initially nonintuitive, especially given that the U–Ng binding energy increases from Ar to Kr to Xe (Table 5). We will propose here a possible explanation for this apparent anomaly. At present, detailed calculations to support this proposal are prohibitively large but will likely be pursued in the future.

As noted throughout this paper, we assume that CUO in neon has Ne atoms directly coordinated to the CUO molecule. Our binding energy studies lead us to conclude that CUO(Ne)₆ is the likely species in which six Ne atoms are weakly bound to CUO in the first coordination sphere. The number of Ne atoms bonded to CUO after Ng substitution is indeterminate; for example, the complex CUO(Ar)₄ in neon might better be formulated as CUO(Ar)₄(Ne) or CUO(Ar)₄(Ne)₂. Based on the sizes of the noble-gas atoms, we expect the maximum number of remaining Ne atoms to be found for CUO(Ar)_n and the smallest number for CUO(Xe)_n. Thus, it might very well be the case that, for a given value of *n*, the Xe complexes have a smaller overall coordination number than do the Kr complexes, which in turn might be smaller than for the Ar complexes.

The reason that the triplet state of CUO eventually drops below the singlet state is because the triplet state is better able to bind Ng atoms than is the singlet state.⁵ If this differential preference for Ng binding to the triplet state is great enough to overcome the inherent singlet–triplet splitting in isolated CUO, crossover will occur. From the NWChem DFT results in Table 5, we can obtain the following values for the differential binding energy preference for the triplet states relative to the singlet states of the CUO(Ng)₄ series, which are the differences in the U–Ng binding energies listed in footnote *b*: 4.5 (Ne), 5.6 (Ar), 5.9 (Kr), and 6.0 (Xe) kcal/mol. Smaller values are obtained from the CCSD(T) calculations on the CUO(Ng) series: 0.8 (Ne), 1.4 (Ar), 1.4 (Kr), and 1.5 (Xe) kcal/mol. In each case, the differential triplet binding energy is remarkably constant for all of the Ng adducts.

As noted earlier, we believe that with the inclusion of the spin–orbit effects (using the estimates of Roos et al.³³) the triplet state of isolated CUO will lie 6–8 kcal/mol above the singlet state. Thus, in order for crossover to occur, there

must be 6–8 kcal/mol differential stabilization of the triplet state. If we assume the CCSD(T) numbers and the same differential binding energy for multiple Ng substitution, we suggest that triplet CUO(Ng)₄ (Ng = Ar, Kr, Xe) complexes would gain 5–6 kcal/mol differential stabilization, which is very close to the expected value for the initial singlet–triplet splitting. If there are still Ne atoms coordinated to the CUO(Ng)₄ complexes, they will provide additional, albeit small, stabilization of the triplet state. The experimental data indicate that all of the CUO(Ng)₄ complexes (Ng = Ar, Kr, Xe) are triplets, including the mixed noble-gas complexes CUO(Ng)_{4-n}(Ng')_n.^{6,7}

We propose that the unusual behavior of the CUO(Ng)₃ (Ng = Ar, Kr, Xe) complexes in neon is likely due to a variable number of Ne atoms in the first coordination sphere of the complex. In the case of Ar and Kr, the differential stabilization of the triplet provided by three Ar or Kr atoms plus the differential stabilization of any remaining Ne atoms is apparently enough to cause spin crossover. In the case of Xe, however, there probably are a smaller number of Ne atoms bonded to CUO(Xe)₃ because of steric crowding and there may therefore not be enough stabilization of the triplet to cause crossover. The small numbers involved in this argument pose a future challenge to the accuracy of electronic structure calculations in order to model correctly the energetic “knife-edge” between the singlet and triplet states.

Conclusions

The CUO product of the reaction of laser-ablated U and CO in excess neon gives a singlet CUO(Ne)_n complex in solid neon. When dilute Ar, Kr, or Xe are added as “reagents,” CUO(Ne)_x(Ng)_{1,2,3,4} complexes are formed.

We have shown conclusively that the CUO(Ne)_x(Ng) complexes are singlet states only slightly perturbed from CUO(Ne)_n using both U–C and U–O bond stretching frequencies and isotopic shifts as a description of the normal modes. We have also shown in the more gas-phase-like neon matrix that three or four Ar, Kr, or Xe atoms and a balance of Ne atoms coordinate with CUO and change the CUO spin state from singlet to triplet. The CUO(Ng)_n complex distribution on deposition is not statistical because excited CUO* is formed initially and during relaxation excited CUO triplet will bond Ar more strongly (and thus more extensively) than ground state singlet CUO.

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. We obtain information on the nature of solvation shells around matrix-isolated guest molecules by using heavier Ng matrix atoms (Ar, Kr, Xe) as reagents in the lighter Ne matrix host.

We believe the unique ground state reversal of CUO molecule is caused by two major stabilizing effects to the triplet state: the U–Ng bonding and the spin–orbit coupling. The spin–orbit coupling splits the CUO triplet state so that the low-energy component of the triplet becomes closer in energy to the singlet ground state. The coordination of Ne, Ar, Kr, and Xe atoms stabilizes both the singlet and the triplet states of CUO, but the triplet states are stabilized more than the singlet. The difference of the binding energies for Ng atoms bonded to CUO triplet and singlet states is larger for Ar, Kr, and Xe than for Ne, which explains why Ne atom coordination is not enough to reverse the ground state of CUO from singlet to triplet. The present paper provides solid experimental evidence that the ground state reversal of CUO only becomes feasible when multiple Ng atoms are coordinated to the CUO molecule.

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