Noble Gas−Actinide Compounds: Evidence for the Formation of Distinct CUO(Ar)$_{4−n}$(Xe)$_n$ and CUO(Ar)$_{4−n}$(Kr)$_n$ (n = 1, 2, 3, 4) Complexes

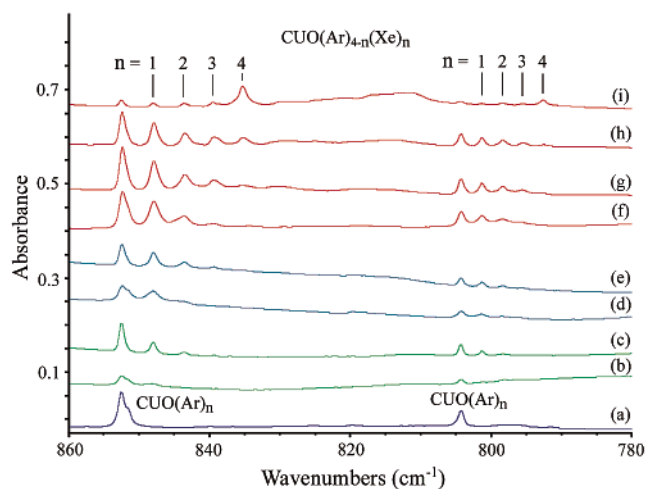Binyong Liang,[†] Lester Andrews,*,[†] Jun Li,[‡] and Bruce E. Bursten*,[§]

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Forty years ago, the preparation of stable xenon fluoride compounds required the reclassification of the inert gases as *noble gases* (Ng).[1,2] Since that time considerable effort has gone into exploring the chemistry of the noble-gas elements. Matrix isolation has played a central role in noble-gas chemistry by facilitating the discovery of many new species, such as KrF$_2$, XeCl$_2$, XeClF, HXeF, and HArF.[3−10] We have recently discovered that Ar, Kr, and Xe atoms stabilize a different electronic state of matrix-isolated CUO than is found in solid neon,[11,12] which has led to the first characterization of weak U−Ng bonds.[13] In that work, calculations using relativistic density functional theory (DFT) and key experiments using 1% Ar in neon showed that small numbers of Ar atoms were sufficient to change the ground state of CUO but that unambiguous characterization of the distinct CUO(Ar)$_n$ complexes could not be achieved.[13] The calculated binding energy of CUO−Xe (6.8 kcal/mol) is more than double that for CUO−Ar (3.2 kcal/mol), however, which suggests that the spectroscopic resolution of different CUO(Xe)$_n$ complexes might be possible. We report here matrix infrared spectroscopic and theoretical characterization of four distinct CUO(Ar)$_{4−n}$(Xe)$_n$ (n = 1, 2, 3, 4) complexes and the analogous complexes for Kr.

The experimental and theoretical methods have been described in previous publications.[11−13] Briefly, laser-ablated U atoms were co-deposited with Ar/Xe/CO and Ar/Kr/CO mixtures at 7 K. Infrared spectra were recorded following deposition, UV photolysis, and extensive annealing cycles. Relativistic DFT calculations were performed on CUO(Ng)$_n$ (Ng = Ar, Kr, Xe; n = 1, 2, 3, 4, 5, 6) and CUO(Ar)$_{4−n}$(Xe)$_n$ (n = 1, 2, 3, 4) complexes using the Amsterdam density functional code (ADF 2000)[14] with the PW91 functional, the Pauli formalism,[11] and frozen core approximations for U 5d, Ar 2p, Kr 3d, and Xe 4d. Triple-ζ Slater basis sets were used for U, Ar, Kr, and Xe atoms, with d- and f-type polarization functions (TZ2P) and 2s2p2d diffuse functions (Vdiff) for the noble gases.[15]

Infrared spectra from a series of experiments with atomic U, CO, and Xe in argon matrices are compared in Figure 1. First, the CUO molecule in pure argon produces two strong IR absorptions at 852.5 and 804.3 cm^{-1} [Figure 1a], which are due to the triplet state CUO(Ar)$_n$ complex.[13] An experiment with U, 1% Xe (mole basis), and 0.2% CO in Ar gives the same two absorptions plus new weaker satellites at 848.0 and 801.3 cm^{-1}, and annealing increases these bands and produces additional satellites at 843.6 and 798.4 cm^{-1} [Figure 1b,c]. Another experiment with 2% Xe

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Figure 1. Infrared spectra in the 860−780 cm^{-1} region for CUO formed by laser-ablated U and CO reaction in excess argon: (a) 0.3% CO in pure argon after sample deposition at 7 K, (b) 0.2% CO, 1% Xe in argon after deposition at 7 K, (c) after annealing to 40 K, (d) 0.2% CO, 2% Xe in argon after deposition at 7 K, (e) after annealing to 40 K, (f) 0.2% CO, 3% Xe in argon after deposition at 7 K, (g) after annealing to 40 K, (h) after annealing to 45 K, and (i) after annealing to 50 K.

provides stronger satellite features, and final annealing produces new members of each progression at 839.4 and 835.4 cm^{-1} and at 795.5 and 792.6 cm^{-1} [Figure 1d,e]. An investigation with 3% Xe yields sharp four-membered progressions below each of the pure argon matrix bands, and their total absorbance is near that for the pure argon matrix bands even though only 3% Xe is present. Annealing this matrix stepwise increases the intensities of the lower-energy bands of each progression. These results clearly show that each new progression terminates with four bands [Figure 1f,g,h,i]. Additional experiments with atomic U, 2% Xe, and 0.3% ^{13}C^{16}O or ^{12}C^{18}O in Ar gave shifted progressions with almost the same isotopic frequency ratios as the bands in pure Ar. This observation indicates that the progressions are due to perturbed CUO vibrational modes related to the strong 852.5 and 804.3 cm^{-1} absorptions for CUO in solid argon.

Experiments generating CUO in mixtures of 1 and 2% Kr in Ar produced results analogous to those from the Xe/Ar experiments (Table 1). The average separations of the four components of the progressions (1.6 cm^{-1} for the first and 1.2 cm^{-1} for the second) are slightly smaller than observed in the Xe/Ar experiments.

Relativistic DFT calculations have provided the total binding energy versus n for the complexes CUO(Ng)$_n$ (Ng = Ar, Kr, Xe). The maximum total binding energy is achieved when n = 5 for Ar, n = 5 for Kr, and n = 4 for Xe. These DFT results are consistent

Table 1. Infrared Absorptions (cm^{-1}) for CUO in Various Solid Noble-Gas Environments

Ng	U–C mode[a]	U–O mode[a]
Ne	1047.3	872.2
Ar	852.5	804.3
Kr	842.3	797.1
Xe	829.8[b]	789.2[b]
Ar and	852.5, 850.9, 849.3,	804.3, 803.1, 801.8,
1% Kr	847.6, 846.0[c]	800.6, 799.4[c]
Ar and	852.5, 848.0, 843.6,	804.3, 801.3, 798.4,
1% Xe	839.4, 835.4[d]	795.5, 792.6[d]

[a] Dominant internal coordinate in the stretching mode. [b] Major site in pure xenon. [c] Last two bands observed with Ar, 2% Kr. [d] Last band observed with Ar, 2% Xe; latter bands stronger with Ar, 3% Xe.

with a simple geometric model which requires that the noble-gas atoms remain at a distance larger than twice their van der Waals radii when at typical U−Ng bond lengths. Five Ar atoms essentially saturate the equatorial plane about CUO: A pentagonal planar arrangement of Ar atoms separated by twice the van der Waals radius of Ar (3.76 Å)[16] requires a U−Ar bond length of 3.20 Å, which is very close to the optimized U−Ar bond length in all of our CUO(Ar)$_n$ calculations. For our calculated U−Xe distances, the complexation of five xenon atoms cannot be accommodated without forcing the xenon atoms to be too close to one another. This model also suggests that the presence of a single Xe atom favors the complexation of a total of four noble-gas atoms, achieving octahedral coordination about U.

The binding energy calculations suggest that the optimum isolated CUO(Ar)$_n$ complex should be CUO(Ar)$_5$. However, the octahedral symmetry expected in the face-centered-cubic solid argon lattice and the effect of secondary solvation could favor CUO(Ar)$_4$ in pure argon. We will therefore refer to the pure argon species as CUO-(Ar)$_n$ where n = 4 or 5. The experiments using a matrix of dilute Xe in Ar show the sequential complexation of 1, 2, 3, and 4 Xe atoms, where Xe atoms displace Ar atoms. We therefore propose that the progressions in Figure 1 are due to the sequential formation of the six-coordinate complexes CUO(Ar)$_{4−n}$(Xe)$_n$ (n = 1, 2, 3, 4) upon annealing of the matrix. The experimental data suggest that the U−C and U−O stretching frequencies decrease by roughly 4 and 3 cm^{-1}, respectively, as each successive Xe atom is complexed.

Calculated binding energies, geometries, and vibrational frequencies for the CUO(Ar)$_{4−n}$(Xe)$_n$ (n = 0, 1, 2, 3, 4) complexes provide strong support for successive substitution of Ar by Xe in these complexes. First, the complexes are all predicted to have a triplet ground state (ignoring spin−orbit effects) and therefore have vibrational properties distinctly different than CUO in solid Ne, which has a singlet ground state.[11,13] Second, the total binding energy increases with increasing Xe substitution. The significance of second-shell solvation effects is indicated in the changes in the two frequencies of CUO(Xe)$_4$ in the Xe/Ar matrix as compared to those in pure Xe (5.6 and 3.4 cm^{-1}). Third, the calculations give cis and trans CUO(Ar)$_2$(Xe)$_2$ frequencies within 1 cm^{-1}, which cannot be resolved in our spectra. Finally, the calculations predict that the replacement of an Ar atom with a Xe atom should lead to a small red-shift in the U−C and U−O stretching frequencies, which is in good agreement with the experimental observation.

As noted earlier, the interaction of Ng atoms with CUO involves a Lewis acid−base interaction in which a lone pair on the Ng atom donates into a vacant U-based orbital of CUO.[13] The strength of these interactions increases as the Ng atom becomes larger; therefore, of these new complexes, CUO(Xe)$_4$ should exhibit the strongest U−Xe bonding, The calculated U−Xe distance of 3.37 Å in CUO(Xe)$_4$ is significantly longer than the experimental Au−Xe distance of 2.74 Å in AuXe$_4$$^{2+}$;[17] the Au−Xe bonding in this dicationic complex (as well as that in AuXe$^+$ and AuXe^{2+}) is strongly enhanced by the charge-induced dipole interactions involving the Au^{2+} cation.[18,19] We can also compare CUO(Xe)$_4$ with the experimentally observed neutral transition-metal complexes XeM-(CO)$_5$ (M = Cr, Mo, W).[20,21] The calculated M−Xe distances in these carbonyl complexes, 2.99 (Cr), 3.10 (Mo), and 3.06 (W) Å,[15] are comparable to the U−Xe distances predicted here, especially when the larger size of U is considered. The measured M−Xe dissociation energies in the XeM(CO)$_5$ complexes, 9.0 (Cr), 8.0 (Mo), and 8.2 (W) kcal/mol,[20,21] are comparable with those calculated here for U−Xe.

The present spectra clearly show that four Ng atoms are involved in the intimate coordination sphere around uranium. This work provides the first characterization of neutral complexes involving four noble-gas atoms on one metal center.

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