Ground-State Reversal by Matrix Interaction: Electronic States and Vibrational Frequencies of CUO in Solid Argon and Neon**

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The reactions of laser-ablated metal atoms with small molecules during their condensation in frozen noble gas matrices have led to a remarkable number of fundamental small molecules that provide new insights into the structures of and bonding in metal complexes. The coupling of these experiments with state-of-the-art electronic structure calculations provides a combined experimental/theoretical approach to identifying and characterizing transient species in the matrix.[1] We have recently combined frozen matrix experiments with relativistic calculations using density functional theory (DFT) to study the reactions of actinide atoms with small molecules, such as N_2, CO, and CO_2. The relativistic DFT calculations have been powerful tools in the identification of new small molecules, such as NUN, CAnO, $An(CO)_n$, and OAnCO (An = Th, U).[2–5]

It is generally assumed that the noble gas matrix that confines the reaction products is electronically innocent, that is, the reaction products can be treated as isolated molecules. This assumption has been key in using electronic structure theory to characterize the products; it is assumed that the products can be modeled as isolated "gas-phase" molecules when their molecular and electronic properties are calculated. This approach has worked remarkably well for most of the small actinide-containing products that we have studied. For example, the reaction of U atoms with CO during condensation with Ne at 4 K leads to the formation of CUO, among other products.[3] The CUO molecule is of considerable interest as it is isoelectronic to the important uranyl dication UO_2^{2+}, and CUO contains the strongest uranium–carbon bond characterized to date. A key to identifying this molecule within the Ne matrix was the observation that our DFT-calculated stretching frequencies for the isolated ground-state CUO molecule are within 2 cm^{-1} of the experimentally observed frequencies, and the isotopic shifts upon using ^{13}CO or C^{18}O are predicted with high accuracy.

Herein we report surprising new experimental results on the CUO molecule when it is formed during condensation with Ar at 7 K. The properties of CUO in the Ar matrix are apparently very different from those in the Ne matrix, which suggests that the molecule is being influenced by the more polarizable Ar atoms. Relativistic DFT calculations provide preliminary evidence that the form of CUO in the Ar matrix can be ascribed to a low-lying electronic excited state of the isolated CUO molecule that corresponds to a change in the electron configuration of the molecule relative to the ground state.

Previous Hartree–Fock pseudopotential calculations found a stable linear CUO species,[6] and DFT calculations characterized low-lying linear and bent singlet states with frequencies near the 1047.3 and 872.2 cm^{-1} values observed for CUO in solid neon.[3] By using refined DFT calculations in the form of the Amsterdam Density Functional (ADF 2.3) code,[7] which includes scalar relativistic corrections and high-precision numerical integration, we find a $^1\Sigma^+$ ground state for the CUO molecule with calculated ^{12}CU^{16}O bond-stretching frequencies at 1049 and 874 cm^{-1}, which are in excellent agreement with the values obtained in a neon matrix (Table 1). Of equal significance, the calculated ^{13}CU^{16}O and ^{12}CU^{18}O frequencies match the observed values extremely well, as shown by the frequency ratios in Table 1. On the basis of the observed isotopic shifts, the bands at 1047.3 and 872.2 cm^{-1} are assigned to essentially pure U–C and U–O stretching modes, respectively, with the values being in excellent agreement with simple mechanical calculations for "U–C" and "U–O" diatomic molecules. Thus, the $^1\Sigma^+$ state seems well described by the relativistic DFT calculation, and no other state mixes significantly with the ground state.

The formation of CUO in solid argon leads to a species with very different vibrational frequencies. The CUO molecule is

Table 1. Calculated and experimental data for the $^1\Sigma^+$ and $^3\Phi$ states of linear CUO.

	$^1\Sigma^+$	$^3\Phi$[a]
	calculated values	
U–C [Å]	1.747	1.846
U–O [Å]	1.802	1.815
E_{total} [eV]	−20.8714	−20.8039
zero point energy [eV]	0.1270	0.1115
ν_{bend} [cm^{-1}(km mol^{-1})][b]	63 (381)	54 (159)
$\nu_{\mathrm{U-O}}$ [cm^{-1}(km mol^{-1})][b]	874 (199)	843 (115)
$\nu_{\mathrm{U-C}}$ [cm^{-1}(km mol^{-1})][b]	1049 (120)	902 (311)
	experimental values	
noble gas matrix	Ne	Ar
$\nu_{\mathrm{U-O}}$ [cm^{-1}]	872.2	804.3
$\nu_{\mathrm{U-C}}$ [cm^{-1}]	1047.3	852.5
^{16}O/^{18}O (U–O)[c]	1.0549 (*1.0554*)	1.0514 (*1.0469*)
^{12}C/^{13}C (U–O)[c]	1.0023 (*1.0020*)	1.0127 (*1.0196*)
^{12}C/^{13}C (U–C)[c]	1.0357 (*1.0361*)	1.0260 (*1.0188*)
^{16}O/^{18}O (U–C)[c]	1.0019 (*1.0010*)	1.0052 (*1.0092*)

[a] The reported geometry and energy for the $^3\Phi$ state are those for the $^3A''$ component under C_s symmetry, while the frequencies and intensities of the vibrations are averages of the $^3A'$ and $^3A''$ components. [b] Calculated wavenumber; the intensity is given in parenthesis. [c] Isotopic ratios for the stretching frequencies of CUO, presented as calculated (*experimental*). The calculated values are from DFT frequency calculations in which the mass of the appropriate atom has been changed. The values are ratios and of the form n:1.

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prepared by treating laser-ablated U atoms with CO in excess argon during condensation at 7 K. The Nd:YAG fundamental (1064 nm, 10 Hz, 10 ns) focused on a rotating uranium metal target using low energy (1 – 5 mJ pulse) evaporates U atoms as described previously.[2, 3, 8–10] Infrared spectra of the co-deposited samples conclusively enable two absorptions at 852.5 and 804.3 cm^{-1} to be identified as CUO (Figure 1). These bands shift to 836.8 and 788.8 cm^{-1} with ^{13}CO and to 844.7 and 768.3 cm^{-1} with C^{18}O, which shows that both vibrations involve substantial motions of the carbon and oxygen atoms. In addition, no new absorptions are observed with ^{12}CO+^{13}CO and C^{16}O+C^{18}O mixtures, which indicates that a single CO molecule is involved in the primary reaction. The bands increase in intensity upon ultraviolet photolysis, which indicates that the insertion of uranium into CO requires activation. A similar energy requirement was found for the U+N$_2$ insertion reaction.[2] Extensive studies with laser-ablated actinide metals shows that single metal atom reaction products dominate the spectrum at these relatively low metal concentrations.[2–5]

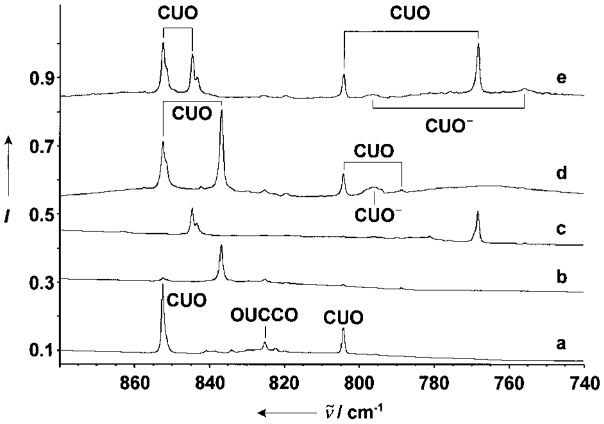

Figure 1. Infrared spectra in the 880 – 740 cm^{-1} region for laser-ablated U atoms co-deposited at 7 K with different CO isotopes diluted in argon: a) 0.3 % ^{12}CO after deposition and photolysis at $\lambda > 240$ nm, b) 0.2 % ^{13}CO after deposition and photolysis at $\lambda > 240$ nm, c) 0.3 % C^{18}O after deposition and photolysis at $\lambda > 240$ nm, d) 0.2 % ^{12}CO + 0.2 % ^{13}CO after deposition, and e) 0.2 % C^{16}O + 0.2 % C^{18}O after deposition.

The large red-shift of 194.8 and 67.9 cm^{-1} in the stretching frequencies of CUO in solid argon relative to the values in solid neon is very unusual. In contrast, the stretching frequencies of the CUO$^-$ ion exhibit red-shifts of only 5.1 and 5.2 cm^{-1} from neon to argon, and the secondary reaction product OUCCO, formed by the addition of another molecule of CO to CUO, gives frequencies 23.7 and 15.8 cm^{-1} lower in solid argon than in solid neon.[3] These small shifts are attributed to normal matrix effects on the ground states of CUO$^-$ and OUCCO owing to the change in polarizability of the host environment.[11]

We believe that the frequencies at 852.5 and 804.3 cm^{-1} for CUO in solid argon arise from a different electronic state of CUO than that observed in solid neon, and that this state corresponds to a low-lying excited state of the isolated CUO molecule. The isotopic shifts and intensities show that the bond-stretching modes are strong mixtures of U–C and U–O internal coordinates as both modes exhibit substantial shifts upon the use of ^{13}CO and C^{18}O. Our DFT calculations on linear CUO reveal a $^3\Phi$ state[12] that is only 1.2 kcal mol^{-1} (420 cm^{-1}) above the $^1\Sigma^+$ ground state, with ^{12}CU^{16}O stretching frequencies predicted at 902 and 843 cm^{-1}. The calculated intensity ratio of these two bands (2.7:1) is in good accord with the experimentally observed intensity ratio (3:1). Further, the calculations on this state with the isotopomers ^{13}CU^{16}O and ^{12}CU^{18}O demonstrate that the observed frequencies involve significant mixing of both the U–C and U–O internal coordinates, which is in contrast to the $^1\Sigma^+$ ground state. The mode mixing is more extensive than predicted by our calculations, as shown by the isotopic frequency ratios in Table 1. We propose that the species observed in the Ar matrix corresponds to the $^3\Phi$ excited state of the isolated CUO molecule, and that the disagreement between the calculated and observed frequencies and isotopic shifts is an indication of a non-negligible interaction between the CUO molecule and the Ar host. Apparently the interaction of the argon matrix makes $^3\Phi$ CUO(Ar)$_n$ the minimum energy species in solid argon whereas $^1\Sigma^+$ CUO is lower in energy in a solid neon matrix, as in the gas phase. Other possible isomers of CUO, such as a triangular form of the molecule, are much too high in energy to be feasible.

The presence of a low-lying excited state for linear CUO is consistent with our previously advanced molecular orbital descriptions of CUO and UO$_2^{2+}$ (see Figure 8 of ref. [3]). The lower electronegativity of C compared to O leads to a much smaller HOMO – LUMO gap in CUO (0.37 eV) than in UO$_2^{2+}$ (2.36 eV). The $^1\Sigma^+$ ground state of CUO corresponds to a U(VI) f^0 molecule with a $(1\pi)^4(3\sigma)^2(2\pi)^4(4\sigma)^2$ electron configuration; the 1π and 3σ molecular orbitals (MOs) are strongly O-localized, U–O bonding orbitals while the 2π and 4σ MOs are C-localized, U–C bonding orbitals. The $^3\Phi$ excited state corresponds to a $(1\pi)^4(3\sigma)^2(2\pi)^4(4\sigma)^1(1\phi)^1$ electron configuration, in which one of the predominantly U–C bonding 4σ electrons has been excited to the nonbonding U 5fϕ orbital, which leads to a formal U(V) f^1 molecule with a much longer (ca. 0.1 Å) calculated U–C bond length. The 19 % reduction in the experimental U–C stretching frequency for CUO in going from Ne to Ar (as compared to an 8 % reduction in the U–O stretching frequency) is consistent with the transfer of an electron from a predominantly U–C bonding orbital to a nonbonding orbital.

It is perhaps surprising that we are proposing that the excited-state triplet form of the isolated CUO molecule is actually the ground state of CUO in an Ar host. We believe that the formation of a pσ "hole" on the carbon atom or the presence of a U-localized electron in the excited state of CUO may facilitate a weak but favorable interaction between $^3\Phi$ CUO and its argon host that is not possible in the harder neon cage. The lower quality of the agreement between the calculated and observed vibrational frequencies in the Ar matrix may be a consequence of interactions between the molecule and the Ar host. Preliminary DFT calculations on model cage molecules CUO(Ng)$_n$ (Ng = Ne, Ar; n = 13, 17, 20, 23) provide support for this proposal inasmuch as there appears to be a significant attractive interaction between the

CUO molecule and the Ar atoms of the model cages. We are examining these interactions carefully, especially in light of the recent report of the new stable argon molecule HArF.[13]

The potential energy surfaces (PES) along the bending coordinate are quite complicated for both the $^1\Sigma^+$ ground state and the $^3\Phi$ excited state of linear CUO. Although CUO is isoelectronic to UO_2^{2+}, the U–O and U–C interactions are much more localized in CUO than are the symmetry-equivalent U–O interactions in UO_2^{2+}. As such, the bending PES for both states are quite shallow, which leads to very small predicted bending frequencies ($<75\ cm^{-1}$) in both the ground and excited state. Upon bending, the $^1\Sigma^+$ and $^3\Phi$ states correlate to $^1A'$ and $^3A'+^3A''$ states under C_s symmetry, and interaction of the $^1A'$ with both the $^3A'$ and $^3A''$ states will be allowed by spin–orbit (SO) coupling. We are currently undertaking higher level calculations on CUO, including SO effects, to better chart the relative energetics of this fascinating molecule.

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[1] Recent examples: a) M. F. Zhou, L. Andrews, *J. Chem. Phys.* **1999**, *110*, 10370 (Fe + CO); b) M. F. Zhou, L. Andrews, *J. Am. Chem. Soc.* **1999**, *121*, 9171 (Rh + CO); c) M. F. Zhou, L. Andrews, *J. Phys. Chem. A* **1999**, *103*, 7785 (Nb, Ta + CO).

[2] U + N_2: a) R. D. Hunt, J. T. Yustein, L. Andrews, *J. Chem. Phys.* **1993**, *98*, 6070; b) G. P. Kushto, P. F. Souter, L. Andrews, *J. Chem. Phys.* **1998**, *108*, 7121.

[3] U + CO: M. F. Zhou, L. Andrews, J. Li, B. E. Bursten, *J. Am. Chem. Soc.* **1999**, *121*, 9712.

[4] Th + CO: M. F. Zhou, L. Andrews, J. Li, B. E. Bursten, *J. Am. Chem. Soc.* **1999**, *121*, 12188.

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[9] R. D. Hunt, L. Andrews, *J. Chem. Phys.* **1993**, *98*, 3690.

[10] M. F. Zhou, L. Andrews, *J. Chem. Phys.* **1999**, *111*, 11044.

[11] M. E. Jacox, *Chem. Phys.* **1994**, *189*, 149.

[12] Strictly speaking, spin is no longer a good quantum number because of spin–orbit coupling and it is not rigorously correct to speak of a "triplet" state. Under spin–orbit coupling, the 4σ HOMO and 1ϕ LUMO transform into the $7e_{1/2}$ and $1e_{5/2}+1e_{7/2}$ spinors, respectively, with the $1e_{7/2}$ spinor greatly destabilized (0.65 eV) relative to the $1e_{5/2}$ spinor. Thus, under spin–orbit coupling, the ground state of the isolated molecule corresponds to the $(7e_{1/2})^2$ configuration, and the first excited state corresponds to the $(7e_{1/2})^1(1e_{5/2})^1$ configuration. Because spin-polarization energy is an important factor in actinide complexes, these two states will be dominantly singlet and triplet in character, respectively, and we will use these descriptors for clarity.

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Visualization of Single Multivalent Receptor–Ligand Complexes by Transmission Electron Microscopy**

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Multivalent ligands have the capacity to interact simultaneously with multiple receptors. The binding of a divalent ligand, for example, can bring two receptors together.[1, 2] Many natural and synthetic ligands are not divalent, however, but rather contain many possible receptor binding sites.[3] The complexation of such multivalent ligands with multiple receptors may be important for their biological activities.[4, 5] Unfortunately, whether multiple receptors bind to a multivalent ligand and how many associate in a complex often can only be inferred. The difficulties associated with investigating such molecular details are exacerbated by the lack of tools available to characterize these binding events.

Previous efforts to study multivalent receptor–ligand complexes have used light scattering,[6] fluorescence resonance energy transfer,[7–9] capillary electrophoresis,[10] or analytical ultracentrifugation. Transmission electron microscopy (TEM) methods are complementary to these indirect measurements as they allow direct visualization of complexes.[11–13] Another advantage of TEM experiments is that since single molecules or complexes can be viewed the amount of material needed is typically less than that required for other techniques. Prior applications of electron microscopy to examine multiple receptors interacting with a ligand have focused on large complexes that can be imaged directly.[14, 15] Many important receptor–ligand complexes, however, are too small or of insufficient density to be directly imaged in this way. Here we report a strategy that extends the range of receptor–ligand complexes that can be imaged by TEM.

We reasoned that a method that increased the contrast of receptors would allow visualization of receptors bound to a given ligand and facilitate the characterization of individual small receptor–ligand complexes. Our solution employs colloidal gold particles as labels to monitor the receptor position in the presence of a ligand. Because of its density, colloidal gold allows high-contrast imaging by electron microscopy. This approach is routinely taken in immunohistochemical applications, in which cellular proteins are located by colloidal gold particles attached to antibodies. Proteins other than antibodies can be attached to colloidal gold, and streptavidin-conjugated gold particles of different sizes are readily available. Such particles are used commonly because

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