Noble gas–uranium coordination and intersystem crossing for the $CUO(Ne)_x(Ng)_n$ (Ng = Ar, Kr, Xe) complexes in solid neon

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Atomic uranium excited by laser ablation reacts with CO in excess neon to produce the novel CUO molecule, which forms weak complexes $CUO(Ne)_m$ with neon and stronger complexes $CUO(Ne)_x(Ng)_n$ (Ng = Ar, Kr, Xe) when the heavier noble gas atoms are present. The heavier $CUO(Ne)_{m-1}(Ng)$ complexes are identified through the effects of CO isotopic and Ng substitution on the neon matrix infrared spectra and by comparison to DFT frequency calculations on the model complexes CUO(Ng) (Ng = Ne, Ar, Kr, Xe). The U–C and U–O stretching frequencies of $CUO(Ne)_{m-1}(Ng)$ complexes are slightly red shifted from the 1047 and 872 cm^{-1} frequencies for the $^1\Sigma^+$ CUO ground state neon complex, which identifies singlet ground state $CUO(Ne)_{m-1}(Ng)$ complexes in solid neon. The next singlet $CUO(Ne)_x(Ng)_2$ complexes in excess neon follow in like manner. However, stretching modes and the isotopic shifts of the higher $CUO(Ne)_x(Ng)_n$ complexes approach those of the pure argon matrix $CUO(Ar)_n$ complex, which characterizes triplet ground state complexes by comparison to DFT frequency calculations.

Introduction

With the successful application of laser ablation in our laboratory for the investigation of refractory element chemistry using matrix-isolation spectroscopy,[1] it became clear that uranium atom reactions with small molecules could be studied using this method. Fig. 1 shows a schematic diagram of the laser-ablation matrix-isolation apparatus. Briefly, laser-ablated uranium atoms are codeposited at 3.5 K with a reagent molecule, such as CO, in excess noble gas, such as argon or neon, and the reaction products are trapped in the solid noble gas host for infrared spectroscopic analysis.[2] Owing to the extremely high temperature generated by the laser-ablation process, the U atoms contain excess translational and electronic energy and thus are excited and extremely reactive.

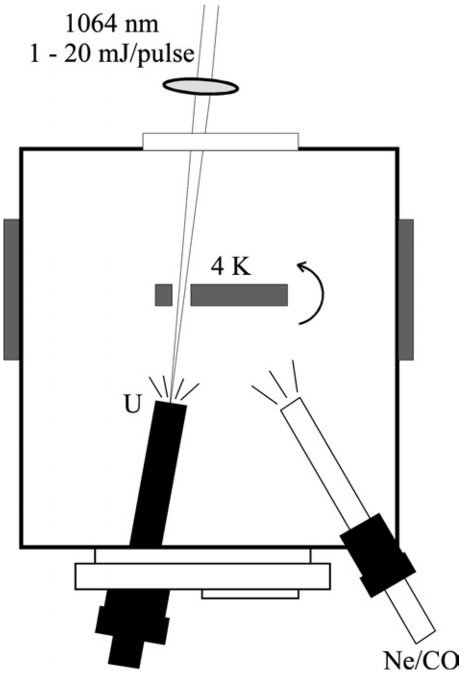

Fig. 1 Schematic diagram of the laser-ablation matrix isolation experiment for infrared spectroscopic investigations.

Our first experiments with U and O_2 in excess argon[3] gave infrared spectra for UO_2 comparable to those recorded for the vapors in equilibrium with UO_2 at 1900 °C trapped in solid argon.[4] We also formed the same NUN species[5] reported previously in the reaction of discharge sputtered U atoms with N_2.[6] The insertion reaction of excited U with N_2 immediately suggested of possibility of the same excited U reaction occurring with the isoelectronic CO molecule.

Ten years ago we observed and assigned new infrared absorptions at 852.6 and 804.4 cm^{-1} to CUO in solid argon formed by the insertion of energetic U atoms into $^{12}C^{16}O$. The $^{13}C^{16}O$ and $^{12}C^{18}O$ isotopic shifts for these bands characterized mixed U–C and U–O stretching vibrational modes.[7] These frequencies were supported by the Hartree–Fock pseudopotential calculations of Pyykkö and coworkers,[8] even though such calculated fundamentals at 1185 and 899 cm^{-1} are considerably higher, due to the limitations of the method. The top three spectra in Fig. 2 show these two absorptions measured 7 years later at 852.5 and 804.3 cm^{-1} in much cleaner argon matrix samples without UO_2 and UN_2 impurities present. The two $CUO(Ar)_n$ absorptions only sharpen on annealing but they increase markedly together on $\lambda > 240$ nm irradiation: clearly excited U is required for the insertion reaction with CO.

This reinvestigation was prompted by the observation of a very different spectrum for CUO in solid neon, which is also shown in Fig. 2. The CUO product exhibits strong 1047.3 and 872.2 cm^{-1} absorptions in solid neon, quite different from

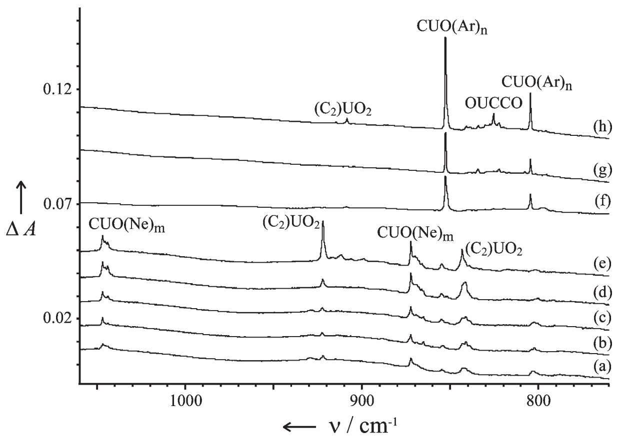

Fig. 2 Comparison of infrared spectra in the 1060–760 cm^{-1} region for laser-ablated U atoms reacting with CO in excess argon and neon: (a) U + 0.2% CO in neon deposited at 4 K for 30 min, (b) after annealing to 8 K, (c) after $\lambda > 470$ nm photolysis, (d) after $\lambda > 290$ nm photolysis, (e) after $\lambda > 240$ nm photolysis, (f) U + 0.3% CO in argon deposited at 7 K for 70 min, (g) after annealing to 30 K, and (h) after $\lambda > 240$ nm photolysis for 15 min.

those in solid argon. The two neon matrix bands for CUO(Ne)$_m$ showed the same sharpening effect on annealing and photolysis as the argon matrix absorptions. However, filtered ultraviolet-visible irradiations were done for the solid neon sample. In a 0.1% CO in neon sample, $\lambda > 380$ nm photolysis doubled the area of the 1047.3 and 872.2 cm^{-1} absorptions; $\lambda > 290$ nm photolysis afforded a further 20% increase, while the final $\lambda > 240$ nm photolysis did not change these absorptions.[9] Spectra a–e in Fig. 2 show the results of a 0.2% CO experiment where initial $\lambda > 470$ nm photolysis increased both absorptions by 50%, a subsequent $\lambda > 290$ nm photolysis doubled both absorptions, and the final $\lambda > 240$ nm photolysis increased both absorptions by 10%. It therefore appears that irradiation in the region around 400 nm is most effective for initiating the U + CO insertion reaction. Now we have two experimental answers for the same question, namely markedly different spectra for CUO in solid argon and neon. This dilemma suggested the theoretical collaboration with Li and Bursten in order to understand these different CUO spectra.[9] The Amsterdam Density Functional (ADF) calculations suggested a $^1\Sigma^+$ ground state for CUO in the gas phase and predicted 1049 and 874 cm^{-1} frequencies for this state. The U/carbon $^{12}C^{16}O/^{13}C^{16}O$ and U/oxygen $^{12}C^{16}O/^{12}C^{18}O$ isotopic frequency ratios are in excellent agreement with the neon matrix values for mostly U–C and U–O stretching modes. Hence, we thought the argon matrix species had to be something "slightly" different.

After additional experiments with $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$ and isotopic mixtures, we became confident that both of these spectra are due to CUO, which is certainly an interesting molecule in its own right. These characterizations of CUO suggested the unusual occurrence of trapping different electronic states of CUO in solid argon and neon, a phenomenon observed earlier for atomic nickel[10] and suggested for UO_2 in another experimental/theoretical collaboration.[11] Accordingly, we found another low-lying state of CUO, the $^3\Phi$ state, about 1 kcal mol^{-1} higher in energy with frequencies of 902 and 843 cm^{-1}, which are much closer to the argon matrix observations. Here we have different frequencies and different normal mode characters (based on isotopic frequencies) for two different CUO electronic states. Hence, matrix infrared spectroscopy can provide a diagnostic of the CUO electronic state and therefore enable us to determine the conditions for the trapping of singlet and triplet CUO states. This ground state reversal has previously been reported,[12] and further investigation on the nature of the argon–CUO interaction led to the discovery of noble gas–actinide complexation as described in our Science article.[13] The ADF calculations showed that multiple argon atoms can bind to CUO[14,15] and left us with the problem of determining the value of m in the CUO(Ne)$_m$ complex and n in the CUO(Ar)$_n$ complex.

Results

New computations and matrix-isolation experiments will be reported.

Calculations

We have performed new calculations on the $^1\Sigma^+$ ($^1A'$) and $^3\Phi$ ($^3A''$) states of CUO and the corresponding singlet and triplet states of the CUO–noble gas model complexes CUO(Ng) (Ng = Ne, Ar, Kr, Xe). While singlet and triplet states will mix in a more proper treatment with intermediate coupling formalism for actinide complexes, the major feature of the non-spin-orbit coupled singlet and triplet states are expected to be maintained. We can therefore discuss the properties of these states at the scalar relativistic level. The calculations were carried out at DFT levels using the PW91 exchange-correlation functional,[16] which has been shown to yield reasonable results for noble-gas-containing systems with weak interactions.[17] The relativistic small-core Stuttgart-Dresden-Bonn (SDB) pseudopotential and basis sets for U atom,[18] large-core SDB pseudopotentials and basis sets for Ne, Ar, Kr, and Xe,[19] and aug-cc-pVTZ basis sets for C and O atoms[20] were employed. The scalar relativistic effects were taken into account by the SDB pseudopotentials: spin-orbit coupling effects were not included because of lack of appropriate methods for open-shell systems within the one-electron DFT formalism. Because the potential energy surfaces involving noble gas atoms are usually very flat, an ultra-fine grid was used for integrations and very tight criteria were used for energy and gradient convergence. All the computations were accomplished by using the NWChem program developed by the high-performance computational chemistry group at Pacific Northwest National Laboratory.[21]

Infrared spectra

New experiments aimed at understanding the argon and neon matrix spectra of CUO involved mixtures of noble gases. Binary rare gas mixtures were used to investigate HCl rotational hindering in different matrix environments.[22] Let us first consider 1 to 3% Xe in argon: the infrared spectra shown in Fig. 3 have been described in the past year.[14,15] The pure argon matrix CUO species absorbing at 852.5 and 804.3 cm^{-1} is denoted CUO(Ar)$_n$. With 1% Xe and 0.2% CO in excess argon and after annealing to 40 K to allow diffusion of Xe within the solid argon medium, two new bands were observed at 848.0, 843.6 cm^{-1} and at 801.3, 798.4 cm^{-1}. With 2% Xe new satellite features were found at 839.4 and 795.5 cm^{-1}, and with 3% Xe additional satellite absorptions appeared at 835.4 and 792.6 cm^{-1}. Final annealing to 50 K allowed the latter features to become the strongest in the spectrum. How do we explain the appearance of four new satellite absorptions below each CUO(Ar)$_n$ fundamental frequency? The straightforward explanation is that four Xe atoms replace Ar atoms in the intimate complexation shell around the central U atom in CUO.[14,15] It therefore follows that $n = 4$ is most likely, but 4 Xe atoms could replace 5 Ar atoms in the intimate complexation sphere around the metal center.

Similar experiments were performed for Xe in krypton and Kr in argon, and again four-band patterns emerged.[14,15] It appears that the intimate coordination sphere about the uranium center contains 4 complexing Ng atoms. Note that the upper band shifts from 852.5 to 835.4 cm^{-1} for CUO(Ar)$_4$ to

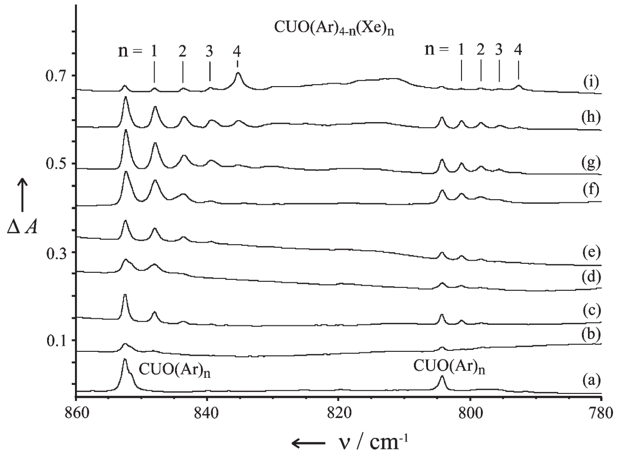

Fig. 3 Infrared spectra in the 860–780 cm^{-1} region for CUO formed by the reaction of laser-ablated U and CO in excess argon: (a) 0.3% CO in pure argon after sample deposition at 7 K, (b) 0.2% CO, 1% Xe in argon after deposition at 7 K, (c) after annealing to 40 K, (d) 0.2% CO, 2% Xe in argon after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

$CUO(Xe)_4$, or about 4.3 cm^{-1} per Xe atom, but that $CUO(Xe)_4$ in krypton is 2.8 cm^{-1} lower and $CUO(Xe)_4$ in xenon is another 2.8 cm^{-1} lower. Hence, the secondary solvent shell around the intimate shell offers much less interaction and perturbation.

Next we investigated Ar in neon with the CUO species formed by the same reaction of laser-ablated U with CO. Infrared spectra of laser-ablated U, 0.1% ^{12}CO, and 1% Ar in neon are illustrated in Fig. 4. The deposited sample reveals 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 in spectrum a, Fig. 4). In these experiments CUO absorptions appear unshifted within ±0.1 cm^{-1} from the pure neon values,[9] but CUO^- peaks are displaced by up to 1 cm^{-1}. Ultraviolet photolysis destroys CUO^- and produces $(C_2)UO_2$ and OUCCO absorptions at 914.6 and 835.7 cm^{-1} shifted 7.3 and 5.3 cm^{-1} from pure neon matrix values, 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} (spectrum b in Fig. 4). Annealing to 8 and 10 K (spectra c and d in Fig. 4) increased sharp new 1033.3, 866.6 cm^{-1} bands (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 species, $CUO(Ne)_x(Ar)_{n-1}$ and $CUO(Ne)_x(Ar)_n$ (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 4 relative to the 3 component, and produced a broad OUCCO absorption near 831 cm^{-1} (spectra e and f in Fig. 4). Final annealing to 13 K slightly increased the 4 band and decreased all other product bands (spectrum g, Fig. 4). Table 1 collects the product absorptions. The number labels represent the n value in the $CUO(Ne)_x(Ng)_n$ complexes proposed in this work. (We use the x subscript here because the number of coordinating Ne atoms is unknown, and we suspect that x has different values for Ng = Ar, Kr and Xe.).

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 1 bands at 1033.3 and 866.6 cm^{-1}, where the latter was almost equal to the 872.2 cm^{-1} CUO band and much stronger than the very weak bands at 861.9, 858.8, 857.2 and 854.3 cm^{-1}. Fig. 5 shows the spectrum using 0.5% Ar. 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 intensity of the 1 bands, particularly on annealing. With the lower 3 band intensity, the two bands labeled 2 at 861.9 and 858.8 cm^{-1}, can be observed more clearly. Again, higher annealing favored the 4 bands over the 3 features. With 3% Ar and 0.1% CO, the only CUO absorptions observed were the matched pair of $CUO(Ne)_x(Ar)_{n-1}$ and $CUO(Ne)_x(Ar)_n$

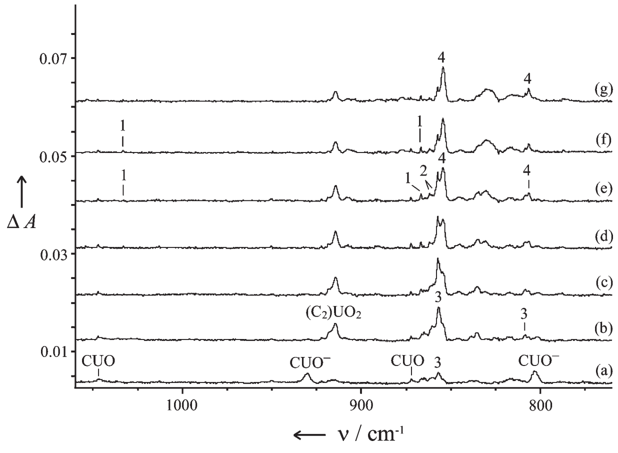

Fig. 4 Infrared spectra in the 1060–760 cm^{-1} region for laser-ablated U atoms, 0.1% CO, 1% Ar reaction products in excess neon at 3.5 K: (a) after sample deposition for 60 min, (b) after 240–700 nm photolysis for 15 min, and (c) after sample annealing to 8 K, (d) 10 K, (e) 11 K, (f) 12 K, and (g) 13 K.

Table 1 Comparisons of frequencies (cm^{-1}), shifts, and isotopic frequency ratios for $CUO(Ng)(Ne)_x$ complexes

Ne	Ne + Ar	Ne + Kr	Ne + Xe	Ar	Comments[a]
1047.3	1033.3	1029.6	1019.4		CUO(Ng)
	14.0	17.7	29.9		Shift from Ne
1.0361	1.0354	1.0342	1.0330		$^{12}C^{16}O/^{13}C^{16}O$ freq. ratio[b]
1.0010	1.0011	1.0012	–		$^{12}C^{16}O/^{12}C^{18}O$ freq. ratio[b]
872.2	866.6	864.4	861.5		CUO(Ng)
	5.6	7.8	10.7		Shift from Ne
1.0020	1.0023	1.0023	1.0023		$^{12}C^{16}O/^{13}C^{16}O$ freq. ratio
1.0554	1.0552	1.0552	1.0550		$^{12}C^{16}O/^{12}C^{18}O$ freq. ratio
	861.9	858.6	854.1		2a, $CUO(Ng)_2$
	858.8	855.7	851.8		2b, $CUO(Ng)_2$
	857.2	852.2	847.4		3, $CUO(Ng)_3$
	1.0172	1.0174	1.0032		$^{12}C^{16}O/^{13}C^{16}O$ freq. ratio
	1.0106	1.0106	1.0544		$^{12}C^{16}O/^{12}C^{18}O$ freq. ratio
	854.3	848.9	843.3	852.5	4, $CUO(Ng)_4$
	1.0174	1.0159	1.0165	1.0188	$^{12}C^{16}O/^{13}C^{16}O$ freq. ratio
	1.0106	1.0114	1.0131	1.0092	$^{12}C^{16}O/^{12}C^{18}O$ freq. ratio
	808.3	804.7			3, $CUO(Ng)_3$
	1.0455	1.0434			$^{12}C^{16}O/^{12}C^{18}O$ freq. ratio
	806.4	802.7	798.6	804.3	4, $CUO(Ng)_4$
	1.0455	1.0434	1.0445	1.0469	$^{12}C^{16}O/^{12}C^{18}O$ freq. ratio

[a] For simplicity $(Ne)_x$ in the intimate coordination sphere is omitted.
[b] Ratio for the immediately preceding frequency.

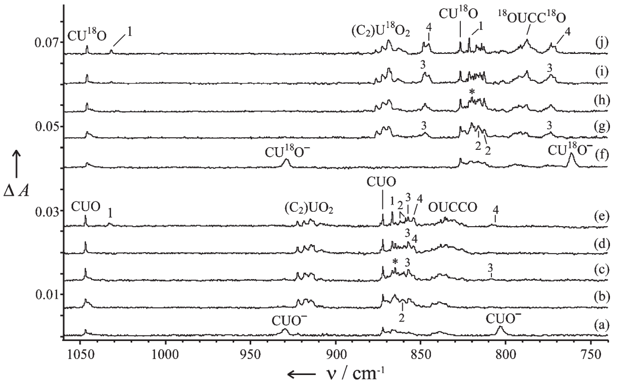

Fig. 5 Infrared spectra in the 1060–740 cm^{-1} region for laser-ablated U atom, 0.1% CO, 0.5% Ar reaction products in excess neon at 3.5 K: (a) after sample deposition with $^{12}C^{16}O$ for 60 min, (b) after 240–700 nm photolysis for 15 min, and (c) after sample annealing to 8 K, (d) 10 K, and (e) to 12 K, (f) after sample deposition with 0.1% $^{12}C^{18}O$ 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.

absorptions at 857.2, 854.3 cm^{-1} and at 808.3, 806.4 cm^{-1}, with the latter component of each pair increasing markedly on annealing.

Infrared spectra for CUO in pure neon and for CUO with dilute Ar, Kr and Xe in neon are compared in Fig. 6. The presence of Ng in the neon sample reduces the yield of isolated $CUO(Ne)_m$ as $CUO(Ne)_x(Ng)_n$ complexes are formed in preference.

Our NWChem calculation results are summarized in Table 2. We believe the calculated DFT energies for the triplet states are too low, possibly due to the incorrect asymptotical behavior of the functional used. However, the calculated frequencies and the isotopic frequency ratios are in good agreement with the experimental results presented here. Obviously, the U–Ng bond distances in the triplet CUO(Ng) are shorter than the corresponding distances in the singlet, implying that more coordination by the Ng atoms could eventually make the triplet more stable than the singlet state, particularly if the U–Ng binding is strong enough. Without basis set superposition error (BSSE) corrections, our NWChem calculations predict binding energies of 1.3, 2.2, 3.1, and 4.1 kcal mol^{-1}, respectively, for the singlet CUO(Ne), CUO(Ar), CUO(Kr), and CUO(Xe) complexes. Therefore, the intersystem crossover of the triplet and singlet states of CUO is feasible *via* multiple Ng coordination. The gradual bending of the CUO molecule upon coordination of the Ne, Ar, Kr, and Xe atom emphasizes the large size of the Xe atom compared with the Ne atom. The large size of the Xe atom, as shown by the optimized U–Xe distance, can reduce the U–Xe binding energy (per bond) when multiple Xe atoms are present. This might be one of the reasons that more Xe atoms are needed to obtain the intersystem crossover.

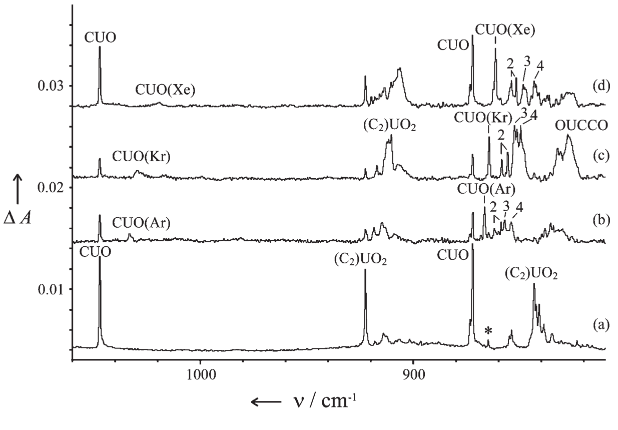

Fig. 6 Infrared spectra in the 1060–810 cm^{-1} region for laser-ablated U atom, 0.1% CO, Ng reaction products in excess neon at 3.5 K after sample deposition, photolysis and annealing to 12–13 K: (a) pure neon, (b) 1% Ar in neon, (c) 0.5% Kr in neon, and (d) 0.3% Xe in neon.

Discussion

In order to help the reader understand the evolution of product absorptions, we will first discuss the reaction mechanisms and then identify the complexes so-formed.

Reaction mechanisms

The novel CUO molecule is formed from the reaction of excited uranium atoms with CO. In our experiments excited U is produced by laser ablation and by near ultraviolet-visible photolysis. Since there are a plethora of excited U electronic-states in this energy region,[23] it is perhaps pointless to attempt to identify the reactive state. However, the insertion reaction of ^3P (6s6p) Hg with H_2 to form linear HHgH[24] suggests that U (5f^{3}6d7s7p) might be a reactive state here.

$$U^* \text{ (laser-ablation)} + CO \rightarrow [CUO]^* \xrightarrow[m\ \mathrm{Ne}]{\text{relax}} CUO(Ne)_m \qquad (1)$$

$$U + CO \xrightarrow{400\ \mathrm{nm}} U^* + CO \rightarrow [CUO]^* \xrightarrow[m\ \mathrm{Ne}]{\text{relax}} CUO(Ne)_m \qquad (2)$$

When Ar approaches the growing $CUO(Ne)_m$ complex during the relaxation/condensation process, excited $[CUO(Ne)_{m-n}(Ar)_n]^*$ complexes are produced as the excited triplet CUO molecule forms stronger bonds to Ng atoms than the $^1\Sigma^+$ ground state CUO,[12,13] as given in eqn. (3). If Ar is sufficiently dilute in the neon matrix then the "pure" $CUO(Ne)_m$ complex is trapped, as in eqn. (1). Subsequent annealing allows successive replacement of Ne in the intimate coordination sphere of the ground singlet state complex with more strongly bound Ar, eqn. (4), to form weak complexes with larger Ng atoms. These weaker singlet complexes appear to be formed by replacement eqn. (4) on annealing in the cold neon matrix after the CUO product is completely quenched.

$$U + CO + nAr \xrightarrow{\text{UV}} [CUO]^* + nAr \xrightarrow[m\ \mathrm{Ne}]{\text{relax}} CUO(Ne)_{m-n}(Ar)_n (n = 3, 4)[T] \qquad (3)$$

$$CUO(Ne)_m + nAr \rightarrow CUO(Ne)_{m-n}(Ar)_n\ (n = 1,\ 2)[S] + nNe \qquad (4)$$

Isotopic shifts for U–O and U–C modes

A 0.1% ^{13}CO experiment was done with 0.7% Ar in neon and the shifted bands behaved the same as the ^{12}CO counterparts. The effect of isotopic substitution is given by the isotopic frequency ratios in Table 1. Infrared spectra recorded for 0.07% ^{12}CO + 0.07% ^{13}CO and 0.7% Ar in neon are the sum of the ^{12}CO and ^{13}CO product spectra. The major products give doublet peaks containing ^{12}CO and ^{13}CO components, which show that one CO reagent molecule is involved. First, the bands labeled CUO(Ar) mimic isolated CUO in that the $^{12}C^{16}O$, $^{13}C^{16}O$ 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. Second, 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}; the weaker 3 band is observed only for ^{12}CO at 808.3 cm^{-1}, but

Table 2 Electronic states, total energies (hartree), bond lengths (Å), bond angles (deg), and vibrational frequencies (cm^{-1})[a]

Molecule	State	E	dU–C	dU–O	dU–Ng	∠C–U–O	∠C–U–Ng	$\nu_{U\text{–}Ng}$	ν_{Bend}	$\nu_{U\text{–}O}$	$\nu_{U\text{–}C}$
CUO	$^1\Sigma^+$	−590.344297	1.757	1.798	–	180	–	–	57i × 2	870	1089
CUO(Ne)	$^1A'$	−625.405810	1.764	1.802	3.181	162.2	102.5	49	12, 75	850	992
CUO(Ar)	$^1A'$	−611.487289	1.768	1.805	3.257	160.6	98.6	60	5, 97	849	987
CUO(Kr)	$^1A'$	−608.746326	1.769	1.806	3.317	159.9	97.6	53	6i, 105	847	987
CUO(Xe)	$^1A'$	−605.901319	1.772	1.807	3.430	158.4	95.4	52	5, 114	847	982
CUO	$^3\Phi$	−590.342459	1.857	1.825	–	180	–	–	57 × 2	828	893
CUO(Ne)	$^3A''$	−625.412016	1.859	1.827	3.074	176.9	91.5	59	56, 83	825	890
CUO(Ar)	$^3A''$	−611.493618	1.862	1.828	3.205	172.2	90.2	70	57, 106	823	884
CUO(Kr)	$^3A''$	−608.752555	1.863	1.829	3.280	170.8	89.6	60	58, 117	821	881
CUO(Xe)	$^3A''$	−605.907560	1.865	1.829	3.396	168.8	87.8	58	56, 123	820	877

[a] The small imaginary frequencies calculated for some of these molecules indicate that these systems indeed have very flat energy surfaces. Further calculations with even more stringent convergence criteria have not been pursued.

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 the 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 CUO (singlet state) and the 3 and 4 products with the pure argon isolated CUO (triplet state).

A similar experiment was done with $^{12}C^{18}O$ substitution; the spectra are compared in Fig. 5. The isotopic frequency ratios are also listed in Table 1. The most important observations are that the bands labeled 1 at 1032.2 and 821.3 cm^{-1} follow 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 1 bands show $^{12}C^{18}O$ shifts of 1.1 and 45.3 cm^{-1}, which are almost the same as those of CUO (1.0 and 45.8 cm^{-1}) whereas the 3 (9.0 and 34.8 cm^{-1}) and 4 (9.0 and 35.0 cm^{-1}) bands shift almost like those for $CUO(Ar)_n$ (7.8 and 36.0 cm^{-1}). The 820–810 cm^{-1} region in the $^{12}C^{18}O$ experiment is a good place to search for higher singlet state complexes as this U–O mode is lower than the U–C mode for triplet state complexes, which are represented by only the 848.2 and 845.3 cm^{-1} (3 and 4) bands.

Since the 872.2 cm^{-1} absorption for singlet CUO is primarily a U–O stretching mode (1.0554 $^{12}C^{16}O/^{12}C^{18}O$ isotopic frequency ratio) and the 852.5 cm^{-1} band for triplet $CUO(Ar)_4$ is primarily a U–C stretching mode (1.0092 $^{12}C^{16}O/^{12}C^{18}O$ isotopic frequency ratio), the $^{12}C^{16}O/^{12}C^{18}O$ isotopic frequency ratio can be used as a diagnostic of CUO electronic state multiplicity.

$CUO(Ne)_{m-1}(Ng)$ complexes

The new 866.6 and 1033.3 cm^{-1} bands persist on dilution of argon and are due to the first weak CUO(Ar) complex formed with singlet CUO. The 1.0552 $^{12}C^{16}O/^{12}C^{18}O$ ratio for the 866.6 cm^{-1} band characterizes the U–O stretching mode of a singlet complex. The low (1.0023) $^{12}C^{16}O/^{13}C^{16}O$ frequency ratio is in agreement with this. The associated 1033.3 cm^{-1} band has the large ^{13}C and small ^{18}O shifts of a U–C stretching mode. Accordingly, the slightly shifted 1033.3 and 866.6 cm^{-1} bands are assigned to the CUO(Ar) complex in the singlet state. Slightly shifted 1029.6, 864.4 cm^{-1} and 1019.4, 861.5 cm^{-1} pairs with Kr and Xe exhibit similar isotopic character and are due to the singlet CUO(Kr) and CUO(Xe) complexes. Hence, we have identified the singlet CUO(Ng) complexes and determined that one Ar, Kr, or Xe atom sharing the intimate coordination sphere with neon atoms does not affect crossover from the singlet to triplet ground state.

For the CUO(Ng) (Ng = Ar, Kr, Xe) complexes, the NWChem isotopic frequency calculations produce $^{12}C^{16}O/^{13}C^{16}O$ frequency ratios of 1.0330, 1.0330, and 1.0334 and $^{12}C^{16}O/^{12}C^{18}O$ frequency ratios of 1.0037, 1.0036, and 1.0034 for the higher frequency C–U mode and the analogous 1.0058, 1.0057, and 1.0056 and 1.0529, 1.0530, and 1.0533 frequency ratios for the lower frequency C–O mode for the CUO(Ng) complexes, respectively. These are in very good agreement with the experimental frequency ratios.

$CUO(Ne)_x(Ng)_2$ complexes

The next argon matrix absorptions at 861.9 and 858.8 cm^{-1} appear to be due to the $CUO(Ne)_x(Ar)_2$ complex. The isotopic shifts follow those of the 866.6 cm^{-1} absorption and suggest a singlet complex. Table 1 compares the corresponding bands for Kr and Xe. The two bands are probably due to matrix site effects as previous calculations show that cis and trans structures have the same frequencies.

$CUO(Ne)_x(Ng)_3$ and $CUO(Ne)_x(Ng)_4$ complexes

The next two absorptions for argon complexes at 857.2 and 854.3 cm^{-1} (labeled 3 and 4) approach the pure argon matrix 852.5 cm^{-1} absorption and their isotopic frequency ratios are comparable for this mostly U–C mode of a triplet state complex. Weaker associated 3 and 4 bands at 808.3 and 806.4 cm^{-1} approach the pure argon matrix 804.3 cm^{-1} absorption and isotopic frequency ratios for this mostly U–O mode of a triplet state complex. Thus, it appears that 3 and 4 complexing argon atoms in the neon coordination sphere are sufficient to stabilize the triplet complex and affect intersystem crossing. The same holds for 3 and 4 Kr Atoms in the neon coordination sphere; however, it appears that 3 Xe atoms are not sufficient but 4 Xe atoms are required for the triplet state complex. This apparent inconsistency is rationalized by the larger size of Xe, which requires the replacement of more Ne atoms. Hence, the $CUO(Ne)_x(Ar)_3$ complex likely contains more Ne atoms than the $CUO(Ne)_y(Xe)_3$ complex ($x > y$) and accordingly the latter coordination sphere is not sufficient to stabilize the triplet complex whereas the former coordination with more Ne atoms stabilizes the triplet CUO complex.

The CUO molecule is formed by reaction of excited U atoms with CO in these experiments, during laser ablation/deposition and during mercury arc photolysis, and the resulting CUO molecule is solvated by neon atoms, as in eqn. (1) and (2) described above. If Ar is present during the excited U* reaction with CO, then stronger triplet CUO complexes can be formed, as in eqn. (3). Annealing to foster diffusion of the heavier Ng atoms allows Ng to replace Ne in the intimate coordination sphere, as in eqn. (4), to form weaker singlet complexes with smaller numbers of Ng atoms.

Conclusions

Excited uranium atoms, formed by laser ablation or UV photolysis, insert into CO to form CUO. In solid neon the ground $^1\Sigma^+$ state is trapped as the CUO(Ne)$_m$ complex based on comparison of the observed 1047.3 and 872.2 cm^{-1} frequencies for ^{12}CU^{16}O and isotopic frequency ratios for ^{13}CU^{16}O and ^{12}CU^{18}O with the values calculated by ADF and NWChem. The replacement of 1 and 2 neon atoms by Ar, Kr, and Xe gives slightly shifted frequencies and similar isotopic frequency ratios: the CUO(Ne)$_x$(Ng)$_{1,2}$ complexes retain the singlet ground state. However, 3 and 4 complexing Ar atoms give lower frequencies at 857.2, 854.3 cm^{-1} and at 808.3, 806.4 cm^{-1} with isotopic frequency ratios comparable to those of triplet CUO(Ar)$_4$ in solid argon. Hence, 3 argon atoms in the neon coordination sphere for CUO(Ne)$_x$(Ar)$_3$ are sufficient to cause intersystem crossing of CUO to the triplet state. This is consistent with our very recent CCSD(T) calculations that predict the singlet is 15.8 and 14.4 kcal mol^{-1} below the triplet for CUO and CUO(Ar),[25]respectively, and also with the preliminary Dirac–Coulomb–CCSD calculations of Visscher *et al.*, which find the isolated singlet CUO state to lie 17 kcal mol^{-1} below the triplet.[26]

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