Noble-Gas Complexes

Significant Interactions between Uranium and Noble-Gas Atoms: Coordination of the UO_2^+ Cation by Ne, Ar, Kr, and Xe Atoms[**]

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We recently reported the existence of direct bonding interactions between uranium atoms and noble-gas (Ng) atoms[1] in the matrix-isolated neutral CUO molecule from the reaction of laser-ablated U atoms with CO and isolated in solid noble-gas matrices.[2] We have since demonstrated that CUO forms complexes with four or more noble-gas atoms bonded to the uranium atom of CUO.[3,4] The discovery of U–Ng bonding depended on the remarkable energetic closeness of two very different electronic states of CUO with distinct vibrational frequencies, and we have demonstrated that the binding of three or four Ar, Kr, or Xe atoms to CUO causes a changeover in the electronic ground state of the $CUO(Ng)_n$ complexes.[5,6]

The discovery of actinide–noble-gas bonding adds to the recent renaissance in noble-gas chemistry,[7,8] including the HArF molecule of Räsänen and co-workers,[9] which is kinetically stable in solid argon, and the $[AuXe_4]^{2+}$ ion of Seidel and Seppelt,[10] which is stable enough to be characterized by X-ray crystallography. The U–Ng bonds in the $CUO(Ng)_n$ complexes are weak: The U–Ng binding energy ranges from about 4 kcal mol^{-1} for Ar to about 7 kcal mol^{-1} for Xe, values that are at the threshold of what can be called a bond. In contrast, the Au–Xe bonds in $[AuXe_4]^{2+}$ are strong: Calculations estimate the Au–Xe binding energy in $[AuXe_4]^{2+}$ as 57 kcal mol^{-1} per bond.[11,12]

The U–Ng bonds in our systems and the Au–Xe bonds in $[AuXe_4]^{2+}$ are formed from Lewis acid–base interactions in which electron density in the Ng lone pairs is donated into vacant orbitals on the metal center. We anticipated that part of the strong interaction between the Au and Xe atoms is due to charge polarization effects facilitated by the positive charge of Au^{2+}, and we predicted that the positively charged UO_2^{2+} ion, which is isoelectronic with CUO, might form stronger U–Ng bonds.[1] Herein we report that U^V monocation, UO_2^+, forms a variety of noble-gas complexes in solid noble-gas matrices, and our calculations indicate that the U–Ng bonding in these complexes is stronger than the U–Ng bonds that involve neutral CUO. The UO_2^+ ion has previously been isolated and characterized by a 980.1 cm^{-1} antisymmetric U–O stretching frequency in solid neon.[13]

The laser-ablation matrix-isolation method used to prepare uranium dioxide molecules has been described previously.[13–15] Laser-ablated uranium atoms insert into dioxygen to form UO_2 during condensation with excess noble gas at 4 K. Other product molecules include UO and UO_3. In addition laser-ablation produces U^+ cations, which react in a similar fashion to form the linear, centrosymmetric UO_2^+ cation.[13] These uranium-bearing species are identified and characterized from matrix-infrared spectra by using $^{16}O_2$, $^{18}O_2$, and $^{16}O_2$, $^{16}O^{18}O$, $^{18}O_2$ mixtures, from comparison to frequencies observed by trapping uranium-oxide vapor species in solid argon,[16] and to frequencies calculated by using relativistic density functional theory (DFT).

The UO_2^+ cation exhibits a strong, sharp U–O stretching mode absorption at 980.1 cm^{-1} in solid neon, at 952.3 cm^{-1} in solid argon, at 940.6 cm^{-1} in solid krypton, and at 929.0 cm^{-1} in solid xenon.[13,14,17] These bands reveal the 1.0527 ± 0.0001 $^{16}O/^{18}O$ isotopic frequency ratio characteristic of the antisymmetric stretching mode of a linear O-U-O linkage. Our calculated antisymmetric stretching frequency of isolated UO_2^+ is 1007 cm^{-1} at the CCSD(T) level. The matrix shifts from this yet-to-be-observed gas-phase frequency are caused by progressively stronger bonding interactions and ion-induced dipole interactions between U and the heavier, more polarizable noble gas (Ng) atoms. How can we determine the number of Ng atoms that bind intimately to UO_2^+ in the first coordination sphere? We prepare these $[(UO_2)(Ng)_n]^+$ complexes by using mixtures of a lighter noble gas host (Ng) doped with heavier noble-gas guest (Ng′) atoms and determine the number of mixed $[(UO_2)(Ng)_n(Ng')_m]^+$ complexes prepared from their perturbations on the UO_2^+ infrared spectrum. Here we warm the solid samples to allow successive substitution of heavier Ng′ for lighter Ng in the first coordination sphere and to determine the number of new absorption bands formed.

The infrared spectra for UO_2^+ in pure neon, argon, and xenon, and in mixtures of the noble gases are compared in Figure 1. Spectrum A shows the characteristic 980.1 cm^{-1} UO_2^+ absorption in pure neon. The weaker O_4^- band[18] decreases on annealing while the UO_2^+ absorption increases. Experiments were done with 0.1, 0.3, and 3 % Ar added to 0.01 % O_2/neon samples and spectra B, C, and D evolve for successive annealing cycles into the 10–15 K range. Note the appearance of just five new absorptions at 975.1, 970.3, 965.5, 961.0 and 957.1 cm^{-1}, marked with arrows, that approach the

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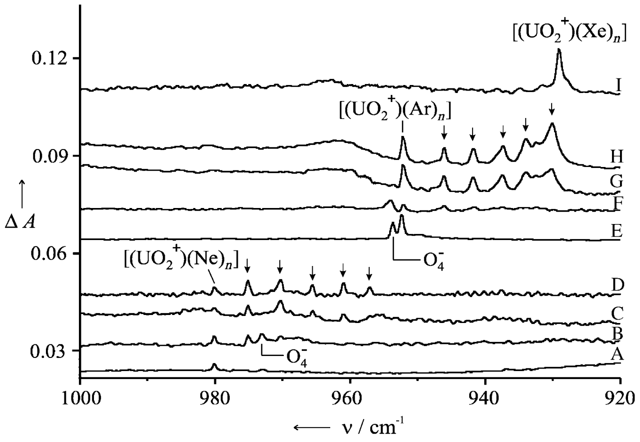

Figure 1. Infrared spectra in the 1000–900 cm^{-1} region for UO_2^+ in various solid noble-gas environments at 4 K. Samples were co-deposited with laser-ablated uranium. A) Neon with 0.01% O_2 after annealing to 10 K. B) Neon with 0.1% O_2 and 0.3% Ar. C) After annealing to 14 K. D) After annealing to 14.5 K. E) Argon with 0.4% O_2 after annealing to 20 K. F) Argon with 0.1% and 6% Xe. G) After annealing to 40 K. H) After annealing to 45 K. I) Xenon with 0.2% O_2 after annealing to 40 K. Arrows denote new product absorptions.

952.3 cm^{-1} absorption of UO_2^+ in pure argon[13] illustrated in spectrum E.

Xenon was allowed to interact with UO_2^+ in excess argon. The 952.3 cm^{-1} $[(UO_2)(Ar)_n]^+$ band was observed as before, and the O_4^- band shifted to 953.7 cm^{-1}.[19] Annealing and increasing the Xe concentration evolved a set of five new absorptions at 946.1, 941.5, 937.2, 933.8 and 930.6 cm^{-1}, spectra F, G, and H, which terminate before the pure xenon absorption at 929.0 cm^{-1} shown in spectrum I. A similar experiment with $^{18}O_2$ gave five new analogous bands shifted to lower frequencies with $^{16}O/^{18}O$ ratios of 1.0528 ± 0.0001.

Infrared spectra were recorded for UO_2^+ in neon doped with Kr and with Xe and in argon doped with Kr, and the spectra are similar to those shown in Figure 1. Infrared absorptions for UO_2^+ in various noble gas environments are presented in Table 1.

Relativistic DFT calculations were performed for $[(UO_2)(Ng)_n]^+$ (Ng = Ne, Ar, Kr, Xe; n = 0–7), $[(UO_2)(Ne)_4(Ng')]^+$ and $[(UO_2)(Ne)(Ng')_4]^+$ (Ng' = Ar, Kr, Xe) complexes by using the Amsterdam Density Functional (ADF) program[20] with the ZORA Hamiltonian,[21] the PW91 functional,[22,23] and triple-zeta plus two polarization functions (TZ2P) basis sets for U and Ng.[24] To calibrate these results additional ab initio CCSD(T) calculations were carried out for UO_2^+ and the model complexes $[(UO_2)(Ng)]^+$ (Ng = Ne, Ar, Kr, Xe) by using the MOLPRO program[25] with the Hay–Martin effective core potentials and basis sets for U[26] and the Stuttgart pseudopotentials and basis sets for the O and Ng atoms.[27] UO_2^+ is an f^1 complex with a $^2\Phi_u$ ground state in the absence of spin–orbit coupling. The ground states of all the noble-gas complexes of UO_2^+ are derived from this same state; unlike CUO, there is no significant change in the ground state upon coordination of Ng atoms. The calculated ground-state geometries, total binding energies ($-\Delta E$ for $UO_2^+ + n\,Ng \rightarrow [UO_2(Ng)_n]^+$), and vibrational frequencies are listed in Table 2. Note that the optimized U–O and U–Ng (NG = Ne, Ar, Kr, Xe) distances and binding energies of UO_2^+ and $[UO_2(Ng)]^+$ from the PW91 DFT calculations are in reasonably good agreement with those from the CCSD(T) calculations, and the calculated frequencies also agree well with the experiments.

Table 1: Infrared absorptions for UO_2^+ in various solid noble-gas environments.

Host	ν[cm^{-1}]	Guest	ν[cm^{-1}]
Ne	980.1	Ar[a]	975.1, 970.3, 965.5, 961.0, 957.1
Ne	980.1	Kr[b]	972.6, 967.3, 964.6, 959.8
Ne	980.1	Xe[c]	970.0, 960.0, 952.5, 940.0
Ar	952.3	Kr[d]	949.4, 947.3, 945.5, 943.3, 941.6
Ar	952.3	Xe[e]	946.0, 914.5, 937.5, 933.8, 930.6[f]

[a] Ar (0.1, 0.3, 3%). [b] Kr (0.3, 1, 2%). [c] Xe (0.3, 1, 3%). [d] Kr (5, 8, 12%). [e] Xe (2, 3, 6, 8%). [f] Frequencies, ±0.2 cm^{-1}.

Table 2: Predicted geometry parameters, binding energies, and stretching vibrational frequencies of UO_2^+, $[UO_2(Ng)]^+$, and $[UO_2(Ng)_n]^+$ (Ng = Ne, Ar, Kr, Xe).[a,b]

	U-O	U-Ng	E_B	ν_s	ν_{as}	ν_{as} (exp)
UO_2^+	1.773 (1.789)	–	0.0	911	987	–
$UO_2(Ne)^+$	1.773 (1.790)	3.08 (2.83)	2.6 (3.4)	909	986	–
$UO_2(Ar)^+$	1.778 (1.792)	3.04 (3.06)	7.0 (7.9)	902	979	–
$UO_2(Kr)^+$	1.778 (1.793)	3.14 (3.18)	9.5 (9.2)	900	976	–
$UO_2(Xe)^+$	1.781 (1.794)	3.28 (3.36)	12.7 (12.1)	895	971	–
$UO_2(Ne)_6^+$	1.776	3.24	13.5	906	985	980.1
$UO_2(Ar)_5^+$	1.788	3.15	28.2	884	958	952.3
$UO_2(Kr)_5^+$	1.791	3.29	35.4	878	953	940.6
$UO_2(Xe)_5^+$	1.794	3.49	42.9	869	943	929.0

[a] The bond lengths are in Å, binding energies in kcal mol^{-1}, and frequencies in cm^{-1}. [b] The optimized CCSD(T) U–O bond lengths and binding energies are listed in parenthesis for comparison.

The total DFT binding energies for four series of Ng complexes are shown Figure 2. We see that the n = 6 complex is most stable for Ne, while the n = 5 complexes appear to be

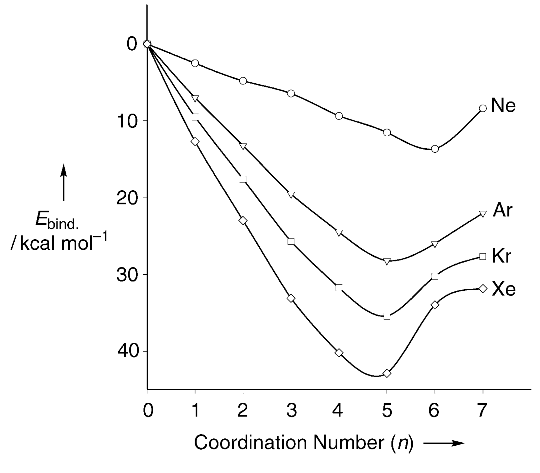

Figure 2. Total binding energy curves calculated for $[UO_2(Ng)_n]^+$ (Ng = Ne, Ar, Kr, Xe) complexes by using relativistic density functional theory.

the most stable for Ar, Kr, and Xe. Our calculations indicate that all the ground states of these $[(UO_2)(Ng)_n]^+$ species are derived from the UO_2^+ $^2\Phi_u$ state. Even though the states derived from the $^2\Delta_u$ state of UO_2^+ are only ≈ 2 kcal mol^{-1} higher in energy, spin–orbit coupling will favor $^2\Phi_u$ as the ground state. Note also that at the scalar-relativistic DFT level, replacement of six Ne atoms with five Ar atoms lowers the energy by 15 kcal mol^{-1}, replacement of Ar with Kr lowers the energy by another 7 kcal mol^{-1}, and replacement of Kr with Xe lowers the energy by an additional 7 kcal mol^{-1}. The calculated binding energies of $[(UO_2)(Ne)_4(Ng')]^+$ (Ng′ = Ar, Kr, Xe) are larger than the binding energy of $[(UO_2)(Ne)_6]^+$, thus indicating that replacing two Ne atoms in the first coordination sphere with one heavier Ng atom is energetically beneficial. This observation explains why only 0.3 % Ar (or Kr or Xe) in neon leads to the formation of complexes with heavier Ng′ atoms. Furthermore, as shown by the calculations on the $[(UO_2)(Ne)_4(Ng')]^+$ and $[(UO_2)(Ne)(Ng')_4]^+$ complexes, substitution of Ne atoms in $[(UO_2)(Ne)_6]^+$ by heavier Ng′ atom(s) is energetically favorable. The theoretically optimized structure for the $[(UO_2)(Ne)_4(Ar)]^+$ complex is illustrated in Figure 3.

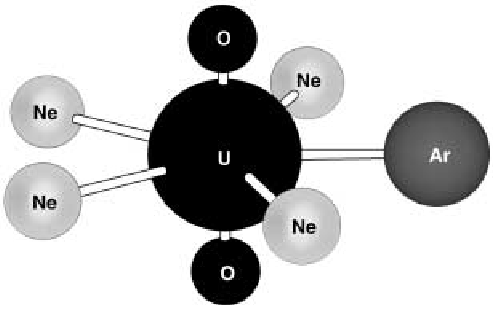

Figure 3. Structure optimized for the $[(UO_2)(Ne)_4(Ar)]^+$ cation complex by using relativistic density functional theory.

Several chemical comparisons can be made for the observed and calculated frequencies. First, the predicted strong infrared active antisymmetric stretching frequencies shift from 987 cm^{-1} for $^2\Phi_u$ UO_2^+ to 985 cm^{-1} for $[(UO_2)(Ne)_6]^+$, and to 958, 953, and 943 cm^{-1} for $[(UO_2)(Ng)_5]^+$ (Ng = Ar, Kr, Xe), in good agreement with experimental data. The calculated frequency shifts for substituting two Ne atoms with one Ar, Kr, and Xe atom in the first coordination shell of UO_2^+ are 8, 13, and 14 cm^{-1}, in accord with the experimentally determined shifts of 5.0, 7.4, and 10.1 cm^{-1}. Shifts of 5.6, 7.8, and 10.7 cm^{-1} in the U–O stretching mode have been observed for the analogous $(CUO)(Ne)_{n-1}(Ng')$ complexes.[5,6] On the other hand, smaller 2.9 and 6.3 cm^{-1} shifts are found for $[(UO_2)(Ar)_{n-1}(Ng')]^+$ with Kr and Xe substitution, similar to what is observed for $(CUO)(Ar)_{n-1}(Ng')$.[3,4]

The combination of experimental and theoretical results presented here provide strong evidence that UO_2^+ coordinates five heavy noble-gas atoms in forming complexes. In each of the mixed noble-gas experiments, five new IR bands are observed, which we propose are due to the stepwise formation of $[(UO_2)(Ng)_{5-n}(Ng')_n]^+$ ($n = 1, 2, 3, 4, 5$) complexes.[28] The calculations predict maximum stability for UO_2^+ coordinated by five heavy Ng atoms, and the calculated frequency shifts for the five-coordinate complexes are in very good agreement with the observed shifts.

Based on a comparison of the binding energies, the U–Ng bonds in the Ng complexes of UO_2^+ are about twice as strong as those we reported for CUO, largely because of the combination of electron-donation and ion-induced dipole interactions. The calculated binding energies are also much larger than those for neutral $[(UO_2)(Ng)_n]$.[29] The interactions of noble-gas atoms with the uranyl ion, UO_2^{2+}, may be strong enough to form stable and isolable complexes by analogy to $[AuXe_4]^{2+}$.

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