On the Electronic Structure of Molecular UO$_2$ in the Presence of Ar Atoms: Evidence for Direct U−Ar Bonding

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We have recently proposed that the CUO molecule forms direct, albeit weak, U−Ng (Ng = Ar, Kr, Xe) bonds when isolated in solid noble-gas matrices.[1,2] The direct CUO−Ng bonding was a surprising outcome that was observed only because of the energetic closeness of two distinct electronic states of CUO, which led to very different vibrational stretching frequencies for CUO when isolated in solid argon[3,4] than in solid neon.[5]

Molecular UO$_2$ is another actinide triatomic molecule that has received a great deal of recent attention, in part because of unusual behavior of the matrix-isolated molecule as the noble-gas host is changed. In 1993, Andrews and Hunt reported that UO$_2$ in solid argon exhibits an infrared band at 776.0 cm^{-1}.[6] This value is in close agreement with earlier Knudsen effusion studies.[7] In 2000, Andrews et al. reported that UO$_2$ in solid neon exhibits a stretch at 914.8 cm^{-1}, i.e., 139 cm^{-1} higher than that in solid argon.[8] The large shift in frequency from argon to neon is unlikely to be due to typical polarizability-based matrix effects, which tend to cause shifts on the order of 5−20 cm^{-1} in vibrational frequencies.[9]

UO$_2$ is a linear U(IV) complex with two metal-localized electrons. Andrews et al. used DFT calculations to predict that UO$_2$ has a $^3\Phi_u$ ground state arising from a 5f^{1}7s^1 configuration.[8] Those calculations also predicted the antisymmetric stretch at 931 cm^{-1}, in good agreement with the experimental value in solid neon. Gagliardi et al. performed CASPT2/SO calculations on molecular UO$_2$ with the explicit inclusion of spin−orbit coupling.[10] They also concluded that UO$_2$ has a $^3\Phi_u$ ($\Omega = 2$) ground state and found that the lowest state derived from the U(IV) 5f^2 configuration was the ^{3}H$_g$ ($\Omega = 4$) state, which was 0.52 eV above the $^3\Phi_u$ ground state. Chang and Pitzer performed spin−orbit configuration interaction (SOCI) calculations on UO$_2$.[11] Their calculations also led to a $^3\Phi_u$ ($\Omega = 2$) ground state, with the ^{3}H$_g$ ($\Omega = 4$) state only 0.20 eV higher adiabatically in energy. Recent experimental studies by Heaven et al. provide strong support for the theoretical calculations discussed above.[12] There is clearly good agreement that isolated UO$_2$ has a $^3\Phi_u$ ($\Omega = 2$) ground state.

The results on isolated UO$_2$ could not reconcile the difference in the vibrational frequencies of UO$_2$ in solid Ne and Ar hosts, however. Given that the electronic state of CUO undergoes a change from neon to argon,[1] and that UO$_2$ has a low-lying ^{3}H$_g$ state that is derived from a different configuration than the $^3\Phi_u$ ground state, we were intrigued by the possibility that UO$_2$ exhibits a noble-gas-induced ground-state reversal like that for CUO. We have therefore performed scalar-relativistic DFT calculations on UO$_2$-(Ar)$_n$ ($n = 1−6$) complexes and coupled-cluster [CCSD(T)] calculations on UO$_2$ and UO$_2$(Ar)$_n$ ($n = 1, 5$).[13] We present here

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Table 1. Calculated DFT and CCSD(T) Bond Lengths (Å) and U−O Stretching Frequencies (cm^{-1}) for the $^3\Phi_u$- and ^{3}H$_g$-Derived States of UO$_2$ (D_{4h}), UO$_2$(Ar) (C_{2v}), and UO$_2$(Ar)$_5$ (D_{5h})^a

molecule	state	U–O	U–Ar	$\nu_s{}^b$	$\nu_{as}{}^b$
UO$_2$	$^3\Phi_u$	1.807 (1.835)	−	856	919
	^{3}H$_g$	1.851 (1.893)	−	779	824
UO$_2$(Ar)	"$^3\Phi_u$"	1.808 (1.834)	4.30 (4.006)	855	918
	"^{3}H$_g$"	1.851 (1.895)	3.28 (3.192)	765	806
UO$_2$(Ar)$_5$	"$^3\Phi_u$"	1.808 (1.833)	4.31 (4.097)	851	917
	"^{3}H$_g$"	1.856 (1.901)	3.37 (3.216)	755	805

^{a} CCSD(T) values are listed in parentheses when available. ^{b} ν_s and ν_{as} are the symmetric and antisymmetric U−O stretching frequencies, respectively. Only the antisymmetric stretches are infrared active.

results for UO$_2$(Ar) and UO$_2$(Ar)$_5$; binding energy studies indicate that the latter is the likely coordination number.

Table 1 presents the optimized geometries and frequencies for UO$_2$, UO$_2$(Ar), and UO$_2$(Ar)$_5$ in the two electronic states. The U−Ar bond lengths in UO$_2$(Ar) and UO$_2$(Ar)$_5$ are quite different in the two states: U−Ar = 4.31 and 3.37 Å in UO$_2$(Ar)$_5$ for the $^3\Phi_u$ and ^{3}H$_g$ states, respectively. Upon coordination of Ar atom(s), the U−O distance is hardly changed in the $^3\Phi_u$ state, but it markedly increases in the ^{3}H$_g$ state. The DFT results for UO$_2$ and UO$_2$(Ar)$_n$ are corroborated by the more accurate CCSD(T) calculations.

The UO$_2$−Ar interactions are far less attractive for the 5f^{1}7s^1 configuration of UO$_2$, largely because of repulsive interactions between the Ar atoms and the 7s-localized electron. That repulsion is alleviated when the metal-based electrons in UO$_2$ occupy the 5f orbitals; the calculated U−Ar bond distance for 5f^2 UO$_2$(Ar)$_n$ is comparable to that for CUO(Ar)$_4$ (3.185 Å).[2b] In essence, the 7s electron of the $^3\Phi_u$ state of UO$_2$ is destabilized in the presence of equatorial ligands, much as the (n + 1)s orbital of transition metals is destabilized upon the coordination of ligands.

A comparison of the calculated DFT vibrational frequencies to those observed in neon and argon matrices suggests that the large change is very likely due to a change in electronic state. The calculated antisymmetric stretching frequency for isolated $^3\Phi_u$ UO$_2$, 919 cm^{-1}, is in excellent agreement with that observed in solid neon, 915 cm^{-1}.[8] This value is essentially unchanged upon the coordination of five Ar atoms. The calculated antisymmetric stretching frequency for the ^{3}H$_g$ state of UO$_2$ is red-shifted by 95 cm^{-1} relative to the $^3\Phi_u$ state, and the coordination of five Ar atoms leads to an additional 19 cm^{-1} red-shift. The calculated frequency and ^{16}O/^{18}O isotopic frequency ratio for the pseudo-^{3}H$_g$ UO$_2$(Ar)$_5$, 805 cm^{-1} and 1.0530, agree well with the values observed in solid argon, 776 cm^{-1} and 1.0529, respectively.[8]
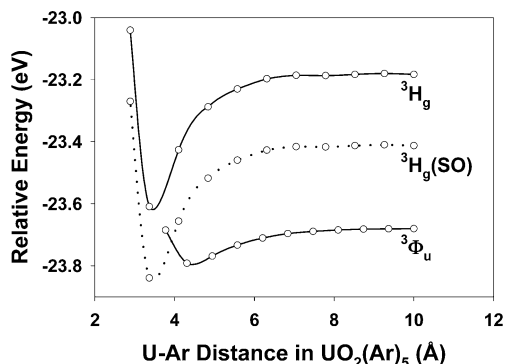
Our calculations suggest that the ^{3}H$_g$ state of UO$_2$ can be sufficiently stabilized upon the coordination of Ar atoms to cause a noble-gas-induced reversal of the ground state of the molecule. Figure 1 shows the scalar-relativistic DFT linear-transit potential

Figure 1. Calculated linear-transit potential energy curves for D_{5h} UO$_2$-(Ar)$_5$ for the $^3\Phi_u$ and ^3H_g electronic states of UO$_2$. The dotted line represents a lowering of the curve for the ^3H_g state by a constant 0.23 eV to account for differential spin−orbit stabilization of the ^3H_g state.

energy curves for D_{5h} UO$_2$(Ar)$_5$ in states that correspond to the $^3\Phi_u$ (5f^{1}7s^1) ground state and ^3H_g (5f^2) excited state of isolated UO$_2$. The U−O bond length was reoptimized at each step in the transit for the two different electronic states. One can see the greater relative stabilization of the ^3H_g state upon interaction with the Ar atoms. The minimum energy of ^3H_g UO$_2$(Ar)$_5$ is still 0.18 eV above the minimum of the $^3\Phi_u$ state at the scalar relativistic level. However, the effects of spin−orbit coupling will further stabilize the ^3H_g state relative to the $^3\Phi_u$ state. Gagliardi et al. found that the ^3H_g state of UO$_2$ was differentially stabilized relative to the $^3\Phi_u$ state by 0.23 eV.[10] Similar differential stabilization was found by Maron et al. in their SOCI calculations on PuO$_2^{2+}$, which is isoelectronic with UO$_2$.[14] The dotted line in Figure 1 represents the lowering of the ^3H_g curve by the 0.23 eV differential stabilization found by Gagliardi et al. Applying this empirical correction lowers the energy of the ^3H_g state below that of the $^3\Phi_u$ state at the optimized U−Ar bonding distances.

The more accurate CCSD(T) calculations further affirm the direct bonding between Ar and the ^3H_g state of UO$_2$. The CCSD(T)-optimized U−Ar distance in UO$_2$(Ar) (3.192 Å) is very close to that in CUO(Ar) (3.189 Å).[15] At the scalar-relativistic CCSD(T) level, the $^3\Phi_u$ state of UO$_2$ is 0.59 eV below the ^3H_g state, but the latter is stabilized relative to the former by 0.11 eV (2.5 kcal/mol) upon coordination of a single Ar atom. The coordination of five Ar atoms will bring the ^3H_g state much closer to the $^3\Phi_u$ state. Indeed, CCSD(T) calculations at the DFT-optimized structure of UO$_2$(Ar)$_5$ find that the $^3\Phi_u$ state is favored by only 2.1 kcal/mol (0.09 eV). The spin−orbit stabilization of the ^3H_g state is therefore expected to change the ground state in the presence of Ar atoms.

Recent results by Heaven et al. provide more intrigue into the electronic structure of UO$_2$.[16] They have obtained dispersed fluorescence spectra for molecular UO$_2$ in an argon matrix, which suggest that UO$_2$ in solid argon exists in the $^3\Phi_u$ (5f^{1}7s^1) state, but

do not address the changes in the vibrational frequencies when the noble-gas matrix host is changed. Our results suggest a different conclusion than that of Heaven et al. The consistency of the calculated vibrational frequencies and isotopic ratios with those observed for UO$_2$ in solid noble-gas matrices, coupled with the calculated potential energy curves, strongly suggest that the electronic state of UO$_2$ changes when the matrix changes from neon to argon. Our studies also suggest that significant U−Ar bonding interactions occur when UO$_2$ is in an argon matrix, similar to the U−Ng bonding found for CUO in Ar, Kr, and Xe matrices. We are left with somewhat of a conundrum in which the two different experimental techniques seem to lead to different conclusions. Definitive answers to the questions of whether the electronic state of UO$_2$ undergoes a noble-gas-induced change will await further experimental and theoretical scrutiny.

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