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Noble Gas Matrices May Change the Electronic Structure of Trapped Molecules: The $UO_2(Ng)_4$ [Ng = Ne, Ar] Case

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In the last two decades matrix isolation techniques have achieved a notable success for several types of spectroscopy, ranging from infrared, optical absorption, laser-induced fluorescence and electron-spin resonance spectroscopy.[1] Their major accomplishment lies on the possibility of embedding a guest molecule inside a host that acts as spectator and is inert towards any type of chemical interaction at very low temperatures (4–12 K). The most successful isolations occur when the gas used to trap the guest molecule is a light noble gas, known for its reluctance to form any type of chemical bond.

The recent discoveries of stable noble gas complexes, such as HArF and NgAuF (Ng = Ar, Kr, Xe), have spurred new questions regarding the actual inertness of Ng hosts in matrix isolation,[2–6] especially when actinide molecules, capable of forming bonds possibly involving the close-lying 5f, 6d, and 7s orbitals, are trapped. In particular, the molecules CUO and UO_2 have challenged this paradigm, having shown in recent years a very probable noble-gas-induced ground state reversal going from Ne to Ar as the isolating gases.[7,8]

On investigating the UO_2 molecule in more detail, Andrews et al. in 2000 noticed a large frequency shift for the asymmetric stretching mode at $\tilde{\nu} = 776\ \mathrm{cm}^{-1}$ in solid Ar, as compared to solid Ne at $\tilde{\nu} = 915\ \mathrm{cm}^{-1}$.[8] Such a significant shift can only be explained with the help of highly accurate calculations by exploring several electronic states and matching the measured asymmetric U–O stretch vibration with the computed ones. Following this procedure, the two possible candidates to the ground-state reversal have been recognized in the $^3\Phi_{2u}$ (ground state in gas phase) and the $^3H_{4g}$ states, with their values being computed at $\tilde{\nu} = 919$ and $824\ \mathrm{cm}^{-1}$, respectively, by using density functional theory (DFT).[8]

Subsequently, Heaven et al. have recorded fluorescence spectra attributed to UO_2 in solid Ar[9] and concluded that the pattern of low-lying electronic excited states is consistent with their previous gas-phase measurements,[10] where they established the $^3\Phi_{2u}$ as the ground state and stated that reversal of the ground state in solid Ar is unlikely.

As a consequence of this contradicting situation, theoretical chemists carried out state-of-the-art calculations pinpointing the $^3\Phi_{2u}$ state as the ground state and describing with great precision the excitation spectrum of the UO_2 molecule.[11–13] However, the calculations have been done for the bare molecule, certainly a good approximation for the gas phase, but not for the matrix.

Now with improvement of computer architecture, we can use computationally intensive methods to study the electronic excited states of the UO_2 molecule with a shell of noble gas atoms. In this work, we decided to run CASSCF/CASPT2 calculations on the $UO_2(Ng)_4$ [Ng = Ne, Ar] complex, where the four noble gas atoms are displaced along the equatorial plane at a fixed equal U–Ng bond length, thus enforcing a D_{4h} symmetry (D_{2h} in the calculations). We decided to keep the inversion center to distinguish between the ungerade and gerade states and to allow maximum computational advantage. See the Supporting Information for more details.

In Figure 1, the SO-CASPT2 potential energy surface (PES) computed with MOLCAS[14] is depicted for the most

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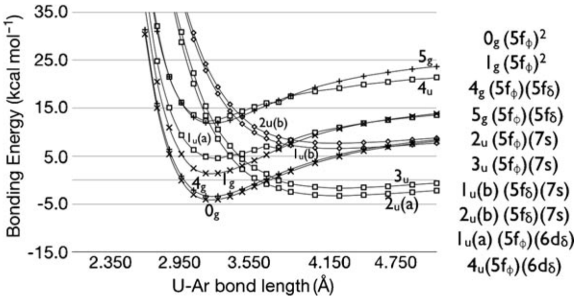

Figure 1. PES along the U−Ar bond for the $UO_2(Ar)_4$ complex computed at the SO-CASPT2 level of theory. The four Ar atoms move simultaneously at a fixed U−O bond length (1.827 Å) on the equatorial region of the UO_2 molecule.

important low-lying states. A summary of the excitation energies is given in Table 1. The eye-catching feature is the obvious difference between the energy profiles of the (5f)(7s) states and the $(5f)^2$ and (5f)(6d) states. The former present a shallow minimum, probably due to dispersion forces, at 4.2–4.3 Å and then become strongly repulsive at distances shorter than 3.8 Å. All other states behave differently and present attractive curves up to 3.1–3.3 Å and then become repulsive at shorter distances when the Pauli interaction kicks in.

Table 1. Excitation energies [cm^{-1}] obtained at two different minima on the PES, the first at U−Ar of 3.150 Å (minimum for the $^3\Sigma^-_{0g}$ state) and the second at 4.250 Å (minimum for the $^3\Phi_{2u}$ state). The U−O bond is fixed at 1.827 Å.

State	Type	Bare UO_2[a]	Minimum of $^3\Phi_{2u}$	Minimum of $^3\Sigma^-_{0g}$
$^3\Phi_{2u}$	(5f)(7s)	0	0	0
$^3\Phi_{3u}$	(5f)(7s)	548	557	700
$^3\Delta_{1u}$	(5f)(7s)	3435	3428	3307
$^3\Delta_{2u}$	(5f)(7s)	3830	3809	3783
$^3\Sigma^-_{0g}$	$(5f)^2$	3571	2873	−6092
$^3H_{4g}$	$(5f)^2$	3656	2987	−5821
$^3H_{4u}$	(5f)(6d)	5487	4957	−2964

[a] These excitation energies differ slightly from the ones reported in [11]. This occurs because of a different choice of the CAS. See the Supporting Information.

The total attraction of four Ar atoms for the most stable state at 3.150 Å is about 14 kcal mol^{-1}, which means about 3–4 kcal mol^{-1} per noble gas atom. Such an interaction can hardly be called a bond; however, the collective effect of several Ar atoms plays a major role in the stability of some states over others. Inspection of Table 1 shows that at a distance of 3.150 Å (the minimum for the $^3\Sigma^-_{0g}$ state), the $^3\Sigma^-_{0g}$ and the $^3H_{4g}$ are more stable than the $^3\Phi_{2u}$ by about 6000 cm^{-1}. Moreover, in going from the bare UO_2 molecule to the complex with Ar atoms these same two states decrease their energy of 9000–10 000 cm^{-1} (1.1–1.3 eV) as compared to the $^3\Phi_{2u}$. In such conditions, it is quite evident that when the matrix forms the possibility of a ground-state reversal is rather high.

To be more quantitative, we have carried out a fragment decomposition analysis[15] to study the interaction between the UO_2 molecule and the $(Ar)_4$ moiety (see the Supporting Information for more details on the meaning of each term). In Table 2, we have summarized the results computed at the spin-free DFT/PBE/TZ2P level of theory,[16] by using the ADF quantum chemistry program.[17] We chose the PBE exchange-correlation (xc) functional because it gave a qualitative correct description of the spin-free $^3\Phi_u$, found as the ground state (GS) for the bare UO_2 molecule (not all the xc functionals catch the correct GS) and the H_g state computed at $\tilde{\nu}=3826$ cm^{-1} above the GS (SF-CASPT2 gives it at $\tilde{\nu}=5792$ cm^{-1}).

Table 2. Energy decomposition [kcal mol^{-1}] of the interaction between the UO_2 fragment and the $(Ar)_4$ moiety at a fixed bond length for the U−O bond (1.827 Å) and the U−Ar bond (3.150 Å) for each given electronic state. SP = spin polarization.

	$^3\Phi_u$	$^3\Sigma_g$	^3H_g	^3H_u
$E[UO_2(Ar)_4]_{SP}$	13.1	16.8	19.7	18.1
$E[UO_2]_{SP}$	15.0	18.5	20.1	18.7
$E[(Ar)_4]_{SP}$	0.0	0.0	0.0	0.0
DE_{SP}	−1.9	−1.7	−0.4	−0.6
Pauli repulsion	136.2	22.4	26.0	32.9
electronic interaction	−61.8	−11.5	−13.0	−14.9
orbital interaction	−59.1	−19.2	−19.3	−26.2
ΔE_{int}	15.3	−8.3	−6.3	−8.2
ΔE_{bond}	13.4	−10.0	−6.7	−8.8

We notice immediately that the driving force for the destabilization of the $^3\Phi_u$ state at 3.150 Å (U−Ar) is the Pauli repulsion, that is, the 7s orbital, is so diffuse that at this distance this effect is as large as 136 kcal mol^{-1}, compared to the 20–30 kcal mol^{-1} for the other states. In contrast, the electrostatic interaction and the orbital interaction terms (i.e., charge transfer and polarization) of $^3\Phi_u$ are very much stabilizing, although not enough to overcome a total positive, that is, repulsive, bonding energy (+13 kcal mol^{-1}). As for the $(5f)^2$ and (5f)(6d) type of states, basically, a small charge transfer of about 0.05–0.07 e from the $(Ar)_4$ moiety to the UO_2 is responsible for about 19–26 kcal mol^{-1} of stabilization as compared to the smaller positive steric interaction term ranging at 11–18 kcal mol^{-1}.

For comparison, we computed the PES of the $UO_2(Ne)_4$ at the SF-CASPT2 level of theory. As it is clear from Figure 2, the Ne atoms act more as spectator and do not interact much with the UO_2 molecule. The $(5f)^2$ and (5f)(6d) energy curves are mostly flat and the (5f)(7s) curves are repulsive below 3.2 Å. The $^3\Phi_{2u}$ remains the most stable state throughout all the dissociation eventually forbidding any ground-state reversal in the Ne matrix.

New experiments have been done for laser-ablated U atom reactions with O_2 in mixed Ar/Ne to explore the effect of Ng coordination on the vibrational frequencies of the trapped UO_2 species (Figure 3 and Table 3). The first spectrum recorded in Ne (Figure 3 a,b) shows weak absorptions at $\tilde{\nu}=915$, 857, 799, and 797 cm^{-1}. The bands at $\tilde{\nu}=915$ cm^{-1}

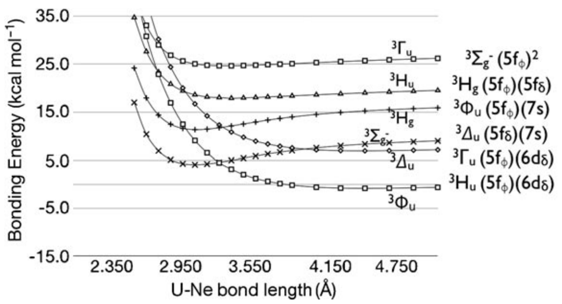

Figure 2. PES along the U–Ne bond for the $UO_2(Ne)_4$ complex computed at the SF-CASPT2 level of theory.

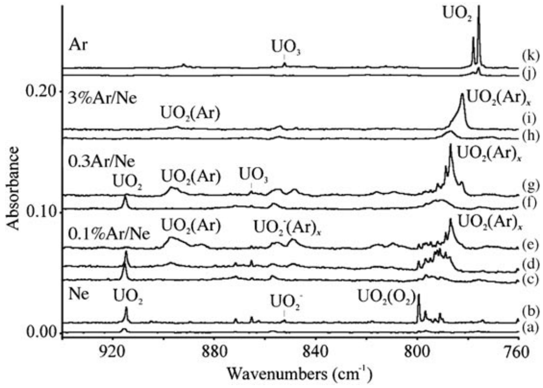

Figure 3. Infrared spectra in the $\tilde{\nu}=940$–$760\,cm^{-1}$ region for UO_2 in solid noble gas environments at 4 K. a,b) U co-deposited in Ne with 0.01 % O_2 and annealed to 10 K; c,d,e) U co-deposited in Ne with 0.01 % O_2 and 0.1 % Ar, and annealed to 11 and 14 K; f,g) U co-deposited in Ne with 0.01 % O_2 and 0.3 % Ar, and annealed to 14 K; h,i) U co-deposited in Ne with 0.01 % O_2 and 3 % Ar, and annealed to 14 K; j,k) U co-deposited in Ar with 0.04 % O_2, and annealed to 24 K.

in solid Ne and at $\tilde{\nu}=776\,cm^{-1}$ in solid Ar have been assigned to UO_2 in those solids, and the large shift of $139\,cm^{-1}$ was taken as evidence for a change in the UO_2 electronic state.[7] The weak bands at $\tilde{\nu}=799$ and $797\,cm^{-1}$ in Ne increase markedly on annealing to 11 K along with other bands at $\tilde{\nu}=795$ and $791\,cm^{-1}$, and they have been ascribed to UO_2 complexes with dioxygen in solid Ne. Note that these bands are getting close to the strong Ar matrix absorption for UO_2. The band at $\tilde{\nu}=857\,cm^{-1}$ in solid Ne has been assigned to the UO_2^- anion, and no Ar matrix counterpart has been identified.[4] Further annealing in the Ne/Ar experiments produced new bands at $\tilde{\nu}=894\,cm^{-1}$ and stronger bands at $\tilde{\nu}=789$, 787, and $782\,cm^{-1}$. The latter absorptions were enhanced relative to the band at $\tilde{\nu}=894\,cm^{-1}$ when the Ar concentration was increased from 0.1 to 0.3 to 3 %. These experiments were repeated by using statistically scrambled isotopic dioxygen (0.04 %) and Ar at higher temperatures.

The triplet isotopic patterns for the band at $\tilde{\nu}=915\,cm^{-1}$ has been reported and discussed earlier as this diagnostic information demonstrates the participation of two equivalent oxygen atoms in the OUO species.[4] Annealing with 1 % Ar reveals a triplet at $\tilde{\nu}=787$, 779, and $747\,cm^{-1}$ with a fourth weaker component at $\tilde{\nu}=731\,cm^{-1}$, and a new triplet appears at $\tilde{\nu}=894$, 882, and $849\,cm^{-1}$, whereas the band at $\tilde{\nu}=915\,cm^{-1}$ for isolated UO_2 decreases. These bands are better defined with 3 % Ar. A prominent, sharp triplet plus one additional band is observed at $\tilde{\nu}=782$, 775, 743, and $729\,cm^{-1}$, and a triplet pattern is observed at $\tilde{\nu}=894$, 882, and $850\,cm^{-1}$. Table S1 in the Supporting Information lists all of the frequencies observed here for the OUO species under the perturbing influences of Ne, O_2, and Ar.

All of these absorptions have ^{18}O counterparts that define 16/18 isotopic frequency ratios of 1.0525–1.0528 for the antisymmetric stretching mode of a linear OUO subunit and have the triplet-scrambled oxygen isotopic absorption pattern for two equivalent oxygen atoms. The fourth component is due to the symmetric stretching mode of the $^{16}OU^{18}O$ component, which gains intensity by interacting with the antisymmetric mode of the same symmetry. Table 3 summarizes the computed structural parameters and frequencies.

Table 3. Predicted geometry parameters [Å] and stretching vibrational frequencies [cm^{-1}] computed at DFT/PBE/TZ2P level of theory for the optimized $UO_2(Ar)_4$ molecule. nb = non bonded.

State	U–O	U–Ar	ν_s	ν_{as}
$^3\Phi_u$	1.800	nb	847	903
$^3\Sigma_g$	1.857	3.270	747	807
^3H_g	1.854	3.245	763	787
observed in excess Ar	–	–	–	915
observed in excess Ne	–	–	–	776

The band at $\tilde{\nu}=894\,cm^{-1}$ in solid Ne with Ar appears to be the red shifted OUO by $21\,cm^{-1}$ perhaps due to complexion by a single Ar atom. The final absorption at $\tilde{\nu}=782\,cm^{-1}$ on annealing by using 3 % Ar is $6\,cm^{-1}$ higher than for OUO in pure solid Ar and 4–$5\,cm^{-1}$ lower than found here with 1 % Ar in Ne. Clearly we are dealing with an OUO complex with Ar atoms in excess Ne starting at $\tilde{\nu}=789\,cm^{-1}$ with a smaller number of Ar atoms, $\tilde{\nu}=787\,cm^{-1}$ for more Ar, and $\tilde{\nu}=782\,cm^{-1}$ for the most coordinating argon atoms that we can still isolate for this species trapped in solid Ne. The evidence supports assignment of these bands to $(UO_2)(Ar)_x(Ne)_y$ species containing a linear OUO subunit.

Summarizing, the 800–$890\,cm^{-1}$ break in Table S1 in the Supporting Information corresponds to a change in the basic UO_2 electronic configuration from (5f)(7s) for the higher to $(5f)^2$ for the lower frequencies. The experimental spectra clearly show stepwise red shifts in the antisymmetric stretching fundamental of OUO when the number of complexing argon atoms is increased stepwise in a Ne matrix and support the ground-state change on going from solid Ne to Ar. This picture is confirmed by our highly accurate calculations in which the GS reversal is hindered in a Ne environment, whereas in an Ar host, four noble gas atoms are sufficient for this change to occur.

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Keywords: density functional calculations · laser spectroscopy · matrix isolation · noble gases · uranium

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