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A theoretical study of the ground state and lowest excited states of $PuO^{0/+/+2}$ and $PuO_2^{0/+/+2}$

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ABSTRACT: The ground and excited states of neutral and cationic PuO and PuO_2 have been studied with multiconfigurational quantum chemical methods followed by second order perturbation theory, the CASSCF/CASPT2 method. Scalar relativistic effects and spin-orbit coupling have been included in the treatment. As literature values for the ionization energy of PuO_2 are in the wide range of ~6.6 eV to ~10.1 eV, a central goal of the computations was to resolve these discrepancies; the theoretical results indicate that the ionization energy is near the lower end of this range. The calculated ionization energies for PuO, PuO^+ and PuO_2^+ are in good agreement with the experimental values.

KEYWORDS Plutonium oxides; multiconfigurational quantum chemical methods; spin-orbit coupling; electronic spectroscopy; ionization energies.

INTRODUCTION

The spectroscopy and thermodynamics of actinide containing molecules pose great challenges to both experimentalists and computational chemists. Among actinides, uranium and thorium species are certainly widely studied. Plutonium systems have also been the subject of extended research. In particular, thermodynamics of elementary plutonium oxide molecules PuO_x (x=1,2) have been studied experimentally by one of us (JKG and co-workers[1-4,]), and also recently by F. Capone and co-workers.[5,6]

The value of the first ionization energy (IE) of PuO_2 has recently become an issue of particular controversy. An early Knudsen effusion electron impact (EI) study[7] provided IE(PuO_2) = 9.4±0.5 eV; a more recent EI study[5] yielded IE(PuO_2) = 10.1±0.1 eV. These two values are remarkably some 3-4 eV higher than the spectroscopically measured IE(UO_2) = 6.128±0.003 eV.[8] Also, they are in discord with the recently determined bond energy of PuO_2^+, D(OPu^+-O).[1] In view of the anomalously high literature values resulting from EI experiments, Santos et al.[1] employed an electron-transfer bracketing approach to establish that IE(PuO_2) is in the range 6.91-7.14 eV, and thus assigned IE(PuO_2) = 7.03±0.12 eV; this latter value is in full accord with the thermodynamics of neutral and ionized plutonium oxides. Given the reduced propensity for transneptunium actinides to exist in oxidation states above IV, particularly as compared with uranium, and that plutonium is in the IV oxidation state in PuO_2, it seems reasonable that IE(PuO_2) should be somewhat higher than both IE(PuO) = 6.1±0.2 eV[2,4] and IE(UO_2) = 6.13 eV.[8] Furthermore, the following trend for the ionization energies across the series of actinide dioxides, IE(AnO_2)/eV, appears entirely reasonable, where the cited values (ranges), except that for IE(UO_2), were obtained by Santos and co-workers using the electron-transfer bracketing method:

UO_2 / 6.13 eV[8] < NpO_2 / 6.33±0.18eV[4] < PuO_2 / 7.03±0.12 eV[1] < AmO_2 / 7.23±0.15 eV[2]

Considering the substantial discrepancy between the value for IE(PuO_2) determined from their EI measurements, 10.1 eV, and the range for IE(PuO_2) subsequently established by electron-transfer bracketing, Capone et al. carried out additional high-temperature Knudsen effusion experiments.[6] To arrive at IE(PuO_2), approximate values for D(Pu-O) = 7.1 eV and IE(PuO) = 6.2 eV were assumed;[6] this latter value for IE(PuO) is close to the experimental value of 6.1±0.2 eV determined by Santos et al.[2,4] A value for IE(PuO_2) was then derived by presuming that equilibrium was achieved between PuO^+ and PuO_2^+ ions at high temperature in a Knudsen cell, and further that their equilibrium concentrations in the cell could be measured by monitoring with a mass spectrometer the ions which were purported to be effusing from the cell.[6] From this so-called "new type of experiment"[6] it was ultimately inferred that IE(PuO_2) = (IE(PuO) + 0.42±0.005 eV) ≈ (6.2 eV + 0.42 eV) ≈ 6.6 eV, which is only 0.3 eV below the lower limit of the previously established range of 6.91-7.14 eV.[1] The validity of the experiment performed by Capone et al.,[6] and particularly the evaluation by which IE(PuO_2) = 6.6 eV was obtained, has been a matter of discussion.[9] Of particular concern is the necessary and novel assumption that thermodynamic equilibrium between PuO^+ and PuO_2^+ was achieved and measured under the conditions of the high-temperature Knudsen effusion experiments[6,9,]. In view of the uncertainties associated with the assignment of IE(PuO_2) = 6.6 eV, the somewhat higher experimental range, 6.91-7.14 eV, as obtained from the well-established and demonstrated technique of electron-transfer bracketing[1] should be considered the more reliable. A direct spectroscopic determination of IE(PuO_2) would definitively resolve this issue. The accuracy of most current computational methods may not be fully adequate to definitively resolve the 0.3 eV discrepancy between the two low-range experimental values for IE(PuO_2), 7.03±0.12 eV[1] and ~6.6 eV[6], but their accuracy is certainly adequate to resolve the ~3-4 eV discrepancy between this lower range and the much higher values obtained from the earlier EI experiments, 9.4 eV[1] and 10.1 eV[5].

Computationally, Archibong and Ray[10] have performed a study of the ground state and some excited states of PuO_2 and PuN_2 using the Coupled Cluster method CCSD(T) and the complete active space second-order perturbation theory method (CASPT2). They have predicted the ground state of PuO_2 to be a $^5\Sigma_g^+$, the ground state of PuN_2 to be a $^3\Pi_g$, and computed a vertical ionization energy of 9.92 eV for PuO_2 at the CCSD(T) level of theory; they did not report an adiabatic ionization energy, but implied that it should not be significantly lower than the vertical value. Clavaguéra-Sarrio et al.[11] have perfomed Density Functional Theory (DFT) and CASPT2 calculations on PuO_2^{2+} and PuN_2 and they have predicted a ^3H_g ground state for PuN_2, in disagreement with the ground state predicted by Archibong and Ray[10].

It thus seems that many unresolved questions still exist for Pu-containing small molecules, particularly the elementary monoxide and dioxide molecules. We have thus decided to perform accurate quantum chemical calculations on PuO and PuO_2 in order to explore the nature of their ground and lowest excited states, and determine their first and second ionization energies.

COMPUTATIONAL METHODS

All the calculations were performed using the MOLCAS 7.1 package.[12] Basis sets of atomic natural type (ANO)[13,14] including relativistic corrections were employed. They were contracted to 9s8p6d5f2g1h and 4s3p2d1f on plutonium and oxygen, respectively. We performed density functional theory (DFT) based calculations using the B3LYP functional and also multiconfigurational calculations followed by second order perturbation theory, CASSCF/CASPT2. The complete active space CASSCF method[15] is used to generate wave functions for a predetermined set of electronic states. Dynamic correlation is added using second-order perturbation theory, CASPT2.[16] Scalar relativistic effects were included using a Douglas-Kroll-Hess Hamiltonian. Spin-orbit coupling effects were estimated using the Complete Active Space State Interaction (CASSI) method,[17] in which an effective one-electron spin-orbit (SO) Hamiltonian, based on the atomic mean field approximation of the two-electron part, is employed. All CASSCF wave functions of the appropriate symmetries are used as basis functions to set up the SO Hamiltonian, and CASPT2 energies are used in the diagonal elements. This approach has been shown to work successfully in a number of earlier applications.[18-31] In the CASSCF calculations the complete active space for PuO, PuO^+ and PuO^{2+} contains 12, 11 and 10 electrons, respectively, distributed into 16 orbitals, which are linear combinations of the thirteen orbitals coming from the 5f, 6d and 7s shells of Plutonium, and the three 2p orbitals of Oxygen. In the PuO_2, PuO_2^+, PuO_2^{2+} cases the ideal active space would contain again thirteen Pu orbitals and six 2p orbitals from the two oxygen atoms. This would yield a complete active space of 19 orbitals with 16 electrons (in case of PuO_2): 8

electrons from plutonium and the other 8 from the oxygen atoms. Such an active space is too big, and we thus decided to truncate the space by removing two π_g bonding orbitals and the corresponding antibonding orbitals, and one σ^* antibonding orbital. This gives a complete active space that contains 12, 11 and 10 electrons for PuO_2, PuO_2^+, PuO_2^{2+}, respectively, distributed into 14 orbitals (see the discussion below of the nature of the orbitals in details). In all subsequent CASPT2 calculations the orbitals up to and including the 5d on plutonium and 1s on oxygen have been kept frozen, while the remaining valence orbitals have been correlated. In order to be more definitive on the value of the ionization energy of PuO_2, we have also performed a series of CASSCF/CASPT2 calculations on PuO_2 with active spaces of increasing size: 4/10, 8/12, 12,14, 12,15 and 12/17 and 16/17. The last three active spaces represent increasing size truncations of the full valence 16/19 active space (all the linear combinations of U 5f, 6d and 7s with O 2p), which is unaffordable.

RESULTS

In Table 1 the spectroscopic constants of the ground states of neutral and cationic PuO and PuO_2 are reported. PuO has a $^7\Pi$ ($\Omega = 0$) ground state with bond distance of 1.82-1.83 Å according to CASPT2 and B3LYP, respectively; PuO^+ has a $^6\Pi$ ($\Omega = 0.5$) ground state with a bond distance of 1.79 Å, according to CASPT2 and B3LYP, respectively. PuO_2 has a $^5\Sigma^+_g$ ($\Omega = 1g$) ground state. The molecule is linear and the Pu-O bond distance is, according to our best estimate, 1.74 Å. This compares with 1.77 Å previously obtained for the U-O distance in UO_2,[22,27] and with previous but less accurate calculations which predicted the Pu-O bond distance to be longer than 1.85 Å.[10] PuO_2^+ has a $^4\Phi_u$ $\Omega = 1.5u$ ground state and a Pu-O bond distance of 1.70 Å. PuO_2^{2+} has a ^3H_g $\Omega = 4g$ ground state and a Pu-O bond distance of 1.68 Å. In Table 2 and 3 the spin-orbit (SO) and spin-free (SF) excitation energies of the lowest electronic states of PuO and PuO^+ are reported, respectively. The ground state, Ω=0, is mainly composed by the $^7\Pi$ spin-free state, which is dominated by the electronic configuration $(7s)^1(5f\pi)^1(5f\delta)^2(5f\varphi)^2$. The spectrum is very dense and in Table 2 we report only the excitations up to 3800 cm^{-1}. The ground state of PuO^+, Ω=0.5, is mainly composed by the $^6\Pi$ spin-free state, which is dominated by the electronic configuration $(5f\pi)^1(5f\delta)^2(5f\varphi)^2$. In Table 4 and 5 the SO and SF excitations, respectively, of PuO_2, PuO_2^+ and PuO_2^{2+} are reported. The ground state of PuO_2, $\Omega=1_u$, is mainly composed by the $^5\Phi_u$ spin-free state, which is dominated by the electronic configuration $(7s)^1(5f\delta)^2(5f\varphi)^1$. This state is not the ground state in the spin-free spectrum. The ground state of PuO_2^+, $\Omega=1.5_u$, is mainly composed by the $^4\Phi_u$ spin-free state, which is dominated by the electronic configuration $(5f\pi)^2$ $(5f\varphi)^1$. The ground state of PuO_2^{2+}, $\Omega=4_g$, is mainly composed by the ^3H_g spin-free state, which is dominated by the electronic configuration $(5f\delta)^1(5f\varphi)^1$. In Table 6 the vertical excitation energies (cm-1) for PuO_2^{2+} calculated at the CASPT2 level including the spin-orbit coupling are reported, together with values obtained by previous theoretical studies and experimentally. We notice the overall better agreement of the present values with experiment, compared to previous theoretical studies. Table 7 shows the calculated values for the first and second ionization energies for PuO and PuO_2. Comparisons with available experimental values and previous theoretical estimations are also presented there.

DISCUSSION

PuO, PuO^+ and PuO^{2+}

To our knowledge this is the first theoretical work that studies the plutonium monoxide species. The first IE of PuO from CASPT2+SO, 6.11 eV, in good agreement with the experimental value of 6.1±0.2 eV obtained by Santos et al.[2,4], who employed a reactivity method developed and demonstrated by Schwarz and co-workers for lanthanide oxide ions.[32] The ground state of PuO, $\Omega=0$, is mainly composed by two dominant spin-free electronic states, 44% of $^7\Pi$ and 26% of $^7\Sigma$. The $^7\Pi$ state is characterized by two electronic configurations: $(7s)^1(5f\pi)^1(5f\delta)^2(5f\varphi)^2$ and $(7s)^1(5f\sigma)^1(5f\delta)^1(5f\pi)^1(5f\varphi)^2$. The electron removed in the process of ionization in order to form PuO^+ belongs to the Pu 7s orbital, which has only little SO coupling. For this reason, the IE of PuO does not change very much if one includes spin-orbit coupling in the calculation: the CASPT2-SF value is 6.17 eV and the CASPT2-SO value is 6.11 eV. The ground state of PuO^+, $\Omega=0.5$, has a composition that resembles the neutral species, $^7\Pi$ (44%) and $^7\Sigma$

(32%), with the only absence of the 7s electron. The Pu-O bond distance is similar in the neutral and ionic species, 1.820 Å in PuO and 1.790 Å in PuO^+. The IE of PuO computed at the SF-DFT/B3LYP is equal to 6.31 eV, a value which is very close to the multi-reference SF-CASPT2 result and well inside the experimental uncertainty range, 5.9-6.3 eV.[2,4]

The second ionization energy of PuO (or first ionization energy of PuO^+), computed at the SO-CASPT2 level, is equal to 14.51 eV, which should be compared to the experimental mean value, 13.7(+/-0.8) eV, based on a thermodynamic evaluation.[3] In that evaluation, the Pu^{2+}-O bond energy, and thereby $\Delta H_f(PuO^{2+})$, were estimated from oxidation reactions of the Pu^{2+} ion. The value for $IE(PuO^+)$ was then obtained as the difference between $\Delta H_f(PuO^+)$ and $\Delta H_f(PuO^{2+})$. In the ionization of PuO^+, an electron is removed from a $5f_\phi$ orbital, which has a larger orbital angular momentum compared to the 7s, from which the ionization of PuO occurs. This gives a different spin-orbit coupling of the valence electrons for the ground state of PuO^{2+}, $\Omega=2$. One would thus imagine that the SO effect is larger in PuO^{2+} than in PuO and PuO^+. On the other hand, SO-CASPT2 predicts a IE of PuO^+ of 14.51 eV, which is only 0.06 eV lower than the value predicted by SF-CASPT2, 14.57 eV, apparently indicating a small SO contribution. To address this apparent inconsistency, one should consider the Pu-O bond distance in the three species, 1.820 Å in PuO, 1.790 Å in PuO^+ and 1.727 Å in PuO^{2+}. While the distance does not change much upon ionization from PuO to PuO^+, it undergoes a significant shortening in going from PuO^+ to PuO^{2+}. The vertical SF and SO IE of PuO^+ (at the PuO^+ bond distance), is equal to 14.64 eV and 14.52 eV, respectively. The SO effect, 0.12 eV, is indeed quite large, but the geometrical relaxation of the dication reduces these values to 14.57 and 14.51 eV, respectively, giving the impression of a small SO contribution.

The ground state of PuO^{2+}, $\Omega=2$, is mainly composed by the spin-free states $^5\Gamma$ and $^5\Phi$. The $^5\Gamma$ state has a strong single-reference character and is dominated by the configuration $(5f\delta)^2(5f\varphi)^1(5f\pi)^1$. It thus seems appropriate to compute also the second IE of PuO at the SF-DFT/B3LYP level of theory. We obtain a value of 14.52 eV, which is in agreement with the SF-CASPT2 value.

PuO_2, PuO_2^+ and PuO_2^{2+}

Our most accurate value, CASPT2-SO, for the first ionization energy for PuO_2 is equal to 6.36 eV, and we are thus confident that the Knudsen effusion electron impact experimental values in the ~9-10 eV range[5,7] must be significantly too high; the actual value is almost certainly in the region of the more recent experimental values, 7.03±0.12 eV[1] and ~6.6 eV.[6] It would also appear that the vertical ionization energies previously calculated by CCSD and CCSD(T), 9.7 and 9.9 eV,[10] are substantially higher than the actual (adiabatic) value. The IE(PuO_2) = 6.36 eV computed by CASPT2+SO is in reasonably good agreement with the value of about 6.6 eV estimated by Capone et al.[6] It is notable that the higher of the two values obtained with B3LYP, 6.70 eV, is rather close to the range of 6.91-7.14 eV established by Santos et al.[1] The value for IE(PuO_2) computed by CASPT2+SO is 0.2 eV below the Capone et al. value, [6] and 0.5 eV below the lower end of the range established by the electron-transfer bracketing technique.[1] We have verified that the CASPT2+SO method did not substantially underestimate IE(PuO_2) by performing a series of calculations with an increasing active space. The results are summarized in Figure 1. The spin-free first IE of two different electronic states of PuO_2, namely $^5\Sigma_g^+$ and $^5\Phi_u$, is reported as a function of the active space. The IE for the $^5\Sigma_g^+$ state converges to the asymptotic limit of 6.5 eV without SO coupling, while the IE of the $^5\Phi_u$ state converges to the asymptotic limit of 6.4 eV. We can state that our calculations are converged with the active spaces of increasing size and we have no reason to believe that the value predicted by the CASPT2+SO method of 6.4 eV represents a significant underestimation of the IE of PuO_2.

The computed value of IE(PuO_2) = 6.4 eV is not in full agreement with the range of 6.91-7.14 eV previously established by electron transfer bracketing experiments.[1] A crucial requirement for such “bracketing” experiments is that the reactant ion, in this case PuO_2^+, be thermalized prior to electron transfer reactions. The presence of excited state PuO_2^+ ions could result in otherwise endothermic abstraction of an electron from a neutral molecule, which would give an apparent ionization energy higher than the actual value. Although the validity of the “bracketing” experiments was carefully confirmed by accurately determining IE[Mo^+],[1] it is feasible that molecular PuO_2^+ ions, in contrast to atomic Mo^+ ions, were not completely thermalized under the conditions of the electron transfer experiments. This possibility was explicitly acknowledged by Santos et al.[1]: "Doubts could arise concerning the possibility of an ineffective thermalization of the PuO_2^+ ions in the charge-transfer reactions, but, if this was the case, it would mean that IE(PuO_2^+) was even lower than the 'bracketed' value." The key point made by Santos et al.[1] was that IE(PuO_2) is approximately 2-3 eV lower than the previously reported values, which are in the range of 9-10 eV.[5,7] This conclusion is clearly validated by the present theoretical results. It should be noted that the discrepancy of 0.5 eV between the computed value of 6.4 eV and the lower limit of 6.9 eV[1] determined from the electron transfer reactions is minor relative to the large correction, >2 eV, to previously reported experimental[5,7] and theoretical[10] values.

Another aspect that requires some consideration is the large difference, about 0.30 eV, between the SF and SO values of the IE of PuO_2. This difference is almost ten times larger than the one found for PuO. Like in the PuO case, also for PuO_2 the electron released in the ionization process belongs to the 7s shell, but in this case the SO effect seems to be considerably more significant. In order to understand this feature, we have to analyze the ground state of PuO_2, $\Omega = 1u$, which is mainly formed by the $^5\Phi_u$ spin-free state, $(7s)^1(5f\delta)^2(5f\varphi)^1$. This state is not the ground state, according to the spin-free calculation, but the second state, lying about 0.3 eV above the ground-state, $^5\Sigma_g$, composed by $(5f\delta)^2(5f\varphi)^2$. When we compute the spin-free ionization energy, we are thus not considering the ionization from the true ground state of the neutral species, $^5\Phi_u$, but the ionization from the $^5\Sigma_g$ state of PuO_2 to the ground state of PuO_2^+, a $^4\Phi_u$ state, mainly composed of $(5f\delta)^2(5f\varphi)^1$. This happens because $^5\Sigma_g$ state does not couple with spin-orbit terms and remains substantially unaffected, while the $^5\Phi_u$ mixes with other states and is further stabilized by SO. This analysis is confirmed by considering that the energy difference between the PuO_2 $^5\Phi_u$ state and the PuO_2^+ $^4\Phi_u$ state is equal to 6.36 eV. Such a value is very close to the SO IE of 6.36 eV, indicating that the actual loss of a 7s electrons leads to a SO effect on IE of 0.03 eV, very close to the one computed for PuO.

The SF-DFT/B3LYP method predicts a vertical IE(PuO_2) of 6.28 eV for the $^5\Phi_u$ to $^4\Phi_u$ ionization, a value just 0.08 eV different from the one obtained at the SF-CASPT2 level of theory. The agreement between the two methods is not surprising because both the $^5\Phi_u$ (PuO_2) and $^4\Phi_u$ (PuO_2^+) ground states have a strong single reference character.

Inspection of Table 7 shows that the CASPT2+SO value for the IE of PuO_2^+, 15.17 eV, is in very good agreement with the experimental value, 15.1±0.4 eV. The SO effect on the IE, 0.3 eV, is rather large. In this case the difference between the SF and the SO values is due to the fact that the ionized electron belongs to a $5f_\delta$ orbital. The ground state of PuO_2^{2+} has indeed a large total angular moment, $\Omega=4$, as compared to $\Omega=1.5$ for PuO_2^+. This alters the result when the IE is computed including the SO coupling and is also one of the reasons why the SF-DFT/B3LYP overestimates the IE(PuO_2^+).

The PuO_2^{2+} ion has been the subject of earlier theoretical studies due to the availability of experimental absorption spectra measured in water solution and for which the first excited states seem unaffected by the presence of the environment. Our study represents a drastic improvement not only in detection of the correct ordering of the experimental bands, but also in the evaluation of the transition energies. If we compare our data to the values obtained with the IHFSCC method,[33] we notice that CASPT2-SO performs very well with differences of the order of only 100-200 cm^{-1}.

CONCLUSIONS

The results of the present computational study confirm that IE(PuO_2) is in the general region of the recent experimental values, ~6.6-7.0 eV, and not in the ~9-10 eV range previously reported. While the B3LYP value for IE(PuO_2) is in good agreement with the currently most reliable experimental value, 7.03±0.12 eV, the corresponding CASPT2+SO value of 6.4 eV is evidently lower. For the other three calculated ionization energies, IE(PuO), IE(PuO^+), and IE(PuO_2^+), the CASPT2+SO method gives good agreement with available experimental values. The CASPT2+SO method employed here provides ionization energies for small actinide molecules which are typically accurate to within ~0.2 eV. The discrepancy of ~0.5 eV between the currently best available experimental[1] and theoretical values for

IE(PuO_2) (present work) remains unresolved. Refinement of both experiment and theory for such elementary molecules, as well as application to additional types of species, should remain a key focus of actinide science.

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SUPPORTING INFORMATION PARAGRAPH

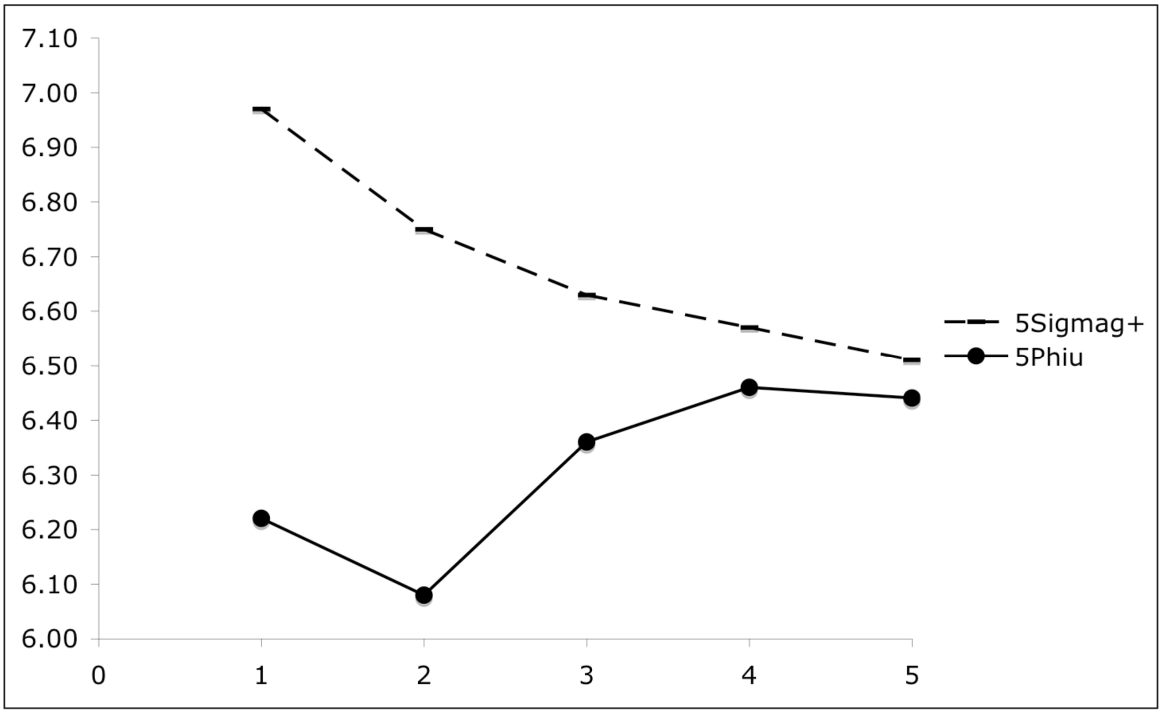

Figure1: The spin-free first IE of PuO2 (in eV) as a function of the size of the active space for the ${}^5\Sigma_g^+$ and ${}^5\Phi_u$ states. The five points 1to 5 represents the following active spaces: 4/10, 8/12, 12/14, 12/15, 12/17, respectively.

Table 1. Pu-O bond distance (Å) and harmonic vibrational frequency (cm^{-1}) for the ground state of neutral and cationic PuO and PuO_2 calculated with different methods.

Species	**State**	**Method**	**R(Pu-O)**	**ω**
PuO	$^7\Pi$; $\Omega = 0$	B3LYP	1.834	820
		CASPT2(12,16)	1.818	767
		CASPT2-SO	1.820	858
PuO^+	$^6\Pi$ $\Omega = 0.5$	B3LYP	1.788	899
		CASPT2(11,16)	1.791	1352
		CASPT2-SO	1.790	1180
PuO^{2+}	$^6\Gamma$ $\Omega = 0.5$	B3LYP	1.720	961
		CASPT2(10,16)	1.724	872
		CASPT2-SO	1.727	899
PuO_2	$^5\Sigma^+_g$ $\Omega = 1g$	HF[10]	1.883	-
		B3LYP	1.818/1.751	773/997
		CCSD[10]	1.866	769
		CCSD(T)[10]	1.870	792
		CASSCF(8,8) [10]	1.866	751
		CASPT2(8,8)[10]	1.846	-
		CASPT2(12,14)	1.792	812
		CASPT2-SO	1.744	837
PuO_2^+	$^4\Phi_u$ $\Omega =$ 1.5u	B3LYP	1.718	949
		CASPT2(11,14)	1.703	957
		CASPT2-SO	1.704	962
PuO_2^{2+}	^3H_g $\Omega = 4g$	B3LYP	1.678	1004
		CASSCF(2,4)[34]	1.6084	-
		CASSCF(8,10)[34 []	1.6394	1110
		CASPT2(2,4)[35] [c]	1.6849	-
		CASPT2(2,4)[11] [d]	1.697	1074
		CASPT2-SO[11]	1.699	1065
		IHFSCC [23]	1.644	1144
		CASPT2(10,14)	1.675	1017
		CASPT2-SO	1.675	1019

Table 2. Spin-orbit vertical excitation energies (cm^{-1}) for PuO, PuO^{+} and PuO^{2+}, and composition of each spin-state in terms of spin-free states. The analysis has been performed at the equilibrium bond distance (in parentheses) of the ground state for each species.

PuO (1.820 Å)			**PuO^{+} (1.790 Å)**			**PuO^{2+} (1.727 Å)**		
Ω	**Composition (%)**	**ΔE**	**Ω**	**Composition (%)**	**ΔE**	**Ω**	**Composition (%)**	**ΔE**
0	$^{7}\Pi(44),^{7}\Sigma(26),^{7}\Delta(12),^{7}\Delta(10)$	0	0.5	$^{6}\Pi(44),^{6}\Sigma(32),^{6}\Delta(8),^{6}\Delta(7)$	0	2	$^{5}\Gamma(25),^{5}\Gamma(25),^{5}\Phi(32),^{5}\Delta(14)$	0
1	$^{7}\Pi(41),^{7}\Sigma(23),^{7}\Delta(12),^{7}\Delta(9)$	209	1.5	$^{6}\Pi(32),^{6}\Sigma(18),^{6}\Delta(11),^{6}\Delta(10)$	694	3	$^{5}\Gamma(25),^{5}\Gamma(24),^{5}\Phi(21),^{5}H(22)$	665
2	$^{7}\Pi(30),^{7}\Delta(25),^{7}\Sigma(15),^{7}\Phi(9)$	868	2.5	$^{6}\Phi(32),^{6}\Delta(13),^{6}\Delta(12),^{6}\Pi(9)$	1939	1	$^{5}\Pi(26),^{5}\Delta(18),^{5}\Delta(17),^{5}\Phi(25)$	819
0	$^{7}\Phi(36),^{7}\Delta(21),^{7}\Delta(16),^{7}\Pi(9)$	1264	0.5	$^{6}\Phi(36),^{6}\Delta(19),^{6}\Delta(16),^{6}\Pi(12)$	2284	0	$^{5}\Sigma(30),^{5}\Pi(26),^{5}\Delta(12),^{5}\Delta(12)$	1092
1	$^{7}\Phi(28),^{7}\Delta(12),^{7}\Pi(10),^{7}\Gamma(10)$	1474	1.5	$^{6}\Phi(24),^{6}\Sigma(21),^{6}\Gamma(14),^{6}\Gamma(14)$	2349	4	$^{5}\Gamma(43),^{5}H(28),^{5}\Phi(16)$	2653
3	$^{7}\Phi(26),^{7}\Delta(14),^{7}\Delta(12),^{7}\Pi(21)$	2029	3.5	$^{6}\Phi(38),^{6}\Delta(13),^{6}\Delta(12),^{6}\Gamma(10)$	3709	2	$^{5}\Delta(27),^{5}\Gamma(16),^{5}\Gamma(16),^{5}\Pi(26)$	3220
2	$^{7}\Sigma(19),^{7}\Gamma(13),^{7}\Gamma(11),^{7}\Phi(20)$	2276	2.5	$^{6}\Pi(30),^{6}\Sigma(16),^{6}\Gamma(14),^{6}\Gamma(14)$	4220	0	$^{5}\Delta(34),^{5}\Delta(32),^{5}\Pi(32)$	3658
0	$^{7}\Phi(60),^{7}\Sigma(13),^{7}\Delta(6),^{7}\Delta(4)$	2622	0.5	$^{6}\Phi(34),^{6}\Delta(16),^{6}\Delta(14),^{6}\Pi(14)$	4356	1	$^{5}\Sigma(31),^{5}\Phi(34),^{5}\Pi(30)$	3774

Table 3. Spin-free vertical excitation energies (cm^{-1}) for PuO, PuO^{+} and PuO^{2+}, and dominating electronic configuration for each spin-free state. The analysis has been performed at the equilibrium bond distance (in parentheses) of the ground state for each species.

Spin-Free								
PuO (1.818 Å)			**PuO^{+} (1.791 Å)**			**PuO^{2+} (1.724 Å)**		
$^{7}\Pi$	$(7s)^1(5f\pi)^1(5f\delta)^2(5f\varphi)^2$	0	$^{6}\Pi$	$(5f\pi)^1(5f\delta)^2(5f\varphi)^2$	0	$^{5}\Gamma$	$(5f\pi)^1(5f\delta)^2(5f\varphi)^1$	0
$^{7}\Sigma$	$(7s)^1(5f\sigma)^1(5f\delta)^2(5f\varphi)^2$	67	$^{6}\Sigma$	$(5f\sigma)^1(5f\delta)^2(5f\varphi)^2$	940	$^{5}\Gamma$	$(5f\pi)^1(5f\delta)^2(5f\varphi)^1$	86
$^{7}\Delta$	$(7s)^1(5f\pi)^2(5f\delta)^1(5f\varphi)^2$	715	$^{6}\Phi$	$(5f\pi)^2(5f\delta)^2(5f\varphi)^1$	1097	$^{5}\Delta$	$(5f\sigma)^1(5f\delta)^1(5f\varphi)^2 + (5f\pi)^1(5f\delta)^2(5f\varphi)^1$	1234
$^{7}\Phi$	$(7s)^1(5f\pi)^2(5f\delta)^2(5f\varphi)^1$	885	$^{6}\Delta$	$(5f\pi)^2(5f\delta)^1(5f\varphi)^2$	1171	$^{5}\Phi$	$(5f\sigma)^1(5f\delta)^2(5f\varphi)1 + (5f\pi)^1(5f\delta)^1(5f\varphi)^2$	1273
$^{7}\Delta$	$(7s)^1(5f\pi)^2(5f\delta)^1(5f\varphi)^2$	1467	$^{6}\Delta$	$(5f\pi)^2(5f\delta)^1(5f\varphi)^2$	1767	$^{5}\Delta$	$(5f\sigma)^1(5f\delta)^1(5f\varphi)^2 + (5f\pi)^1(5f\delta)^2(5f\varphi)^1$	1284
$^{7}\Gamma$	$(7s)^1(5f\sigma)^1(5f\pi)^1(5f\delta)^2(5f\varphi)^1$	1890	$^{6}\Phi$	$(5f\pi)^2(5f\delta)^2(5f\varphi)^1 + (5f\sigma)^1(5f\pi)^1(5f\delta)^1(5f\varphi)^2$	2870	$^{5}\Sigma$	$(5f\pi)^2(5f\varphi)^2 + (5f\delta)^2(5f\varphi)^2$	1620
$^{7}\Gamma$	$(7s)^1(5f\sigma)^1(5f\pi)^1(5f\delta)^2(5f\varphi)^1$	2922	$^{6}\Gamma$	$(5f\sigma)^1(5f\pi)^1(5f\delta)^2(5f\varphi)^1$	2996	$^{5}\Pi$	$(5f\pi)^1(5f\delta)^1(5f\varphi)^2$	2007
$^{5}\Sigma$	$(7s)^1(5f\sigma)^1(5f\delta)^2(5f\varphi)^2$	2954	$^{6}\Gamma$	$(5f\sigma)^1(5f\pi)^1(5f\delta)^2(5f\varphi)^1$	3431	^{5}H	$(5f\pi)^2(5f\delta)^1(5f\varphi)^1$	3373

Table 4. Spin-orbit vertical excitation energies (cm^{-1}) for PuO_2, PuO_2^+ and PuO_2^{2+}, and composition of each spin-state in terms of spin-free states. The analysis has been performed at the equilibrium bond distance (in parentheses) of the ground state for each species.

PuO_2 (1.744 Å)			**PuO_2^+ (1.704 Å)**			**PuO_2^{2+} (1.675 Å)**		
Ω value	**Composition (%)**	**ΔE**	**Ω**	**Composition (%)**	**ΔE**	**Ω**	**Composition (%)**	**ΔE**
1_u	$^5\Phi_u(96)$,$^5\Delta_u(2)$,$^5\Delta_u(2)$	0	1.6_u	$^4\Phi_u(86)$,$^4\Sigma_u(11)$,$^2\Delta_u(2)$	0	4_g	$^3H_g(98)$, $^1\Gamma_g(2)$	0
2_u	$^5\Phi_u(88)$,$^5\Delta_u(5)$,$^3\Phi_u(7)$	447	2.3_u	$^4\Phi_u(89)$,$^2\Pi_u(5)$,$^4\Sigma_u(4)$	1708	0_g	$^3\Sigma_g(58)$, $^1\Sigma_g(16)$,$^3\Pi_g(26)$	3177
2_u	$^5\Phi_u(89)$,$^5\Delta_u(3)$,$^3\Phi_u(8)$	623	3_u	$^4\Phi_u(69)$,$^4\Sigma_u(27)$,$^2\Pi_u(1)$	4531	1_g	$^3\Pi_g(50)$,$^3\Sigma_g(31)$, $^1\Pi_g(18)$	5251
0_g	$^5\Sigma_g(86)$,$^3\Delta_u(13)$	1794	1.2_u	$^4\Sigma_u(71)$, $^4\Phi_u(15)$,$^2\Delta_u(9)$,$^2\Pi_u(2)$	6252	5_g	$^3H_g(99)$	6920
3_u	$^5\Phi_u(85)$,$^3\Phi_u(7)$,$^3\Phi_u(2)$,$^5\Delta_u(3)$,$^5\Delta_u(2)$	2133	2.2_u	$^4\Sigma_u(70)$, $^4\Phi_u(24)$,$^2\Pi_u(2)$	7241	0_g	$^3\Pi_g(99)$	10390
1_g	$^5\Sigma_g(88)$,$^3\Delta_u(11)$	2315	4.3_u	$^4\Phi_u(94)$,$^4\Sigma_u(2)$,$^4\Sigma_u(1)$, $^2\Delta_u(1)$	8216	1_g	$^3\Sigma_g(65)$, $^1\Pi_g(21)$,$^3\Pi_g(11)$,$^3\Sigma_g(2)$	11100
2_g	$^5\Sigma_g(100)$	4131	3.7_u	$^2\Gamma_u(38)$,$^2\Phi_u(23)$,$^4\Sigma_u(11)$,$^2\Delta_u(9)$,$^2\Pi_u(6)$	14325	0_g	$^3\Pi_g(66)$,$^1\Sigma_g(26)$,$^3\Sigma_g(7)$	12052
4_u	$^5\Phi_u(86)$,$^3\Phi_u(5)$,$^5\Delta_u(5)$	4491	3.2_u	$^2\Phi_u(58)$,$^2\Gamma_u(24)$,$^4\Sigma_u(9)$,$^2\Delta_u(3)$,$^4\Sigma_u(2)$	15771	6_g	$^3H_g(92)$,$^1\Sigma_g(7)$	12450

Table 5. Spin-free vertical excitation energies (cm^{-1}) for PuO_2, PuO_2^+ and PuO_2^{2+}, and dominating electronic configuration for each spin-free state. The analysis has been performed at the equilibrium bond distance (in parentheses) of the ground for each species.

PuO_2 (1.792 Å)			**PuO_2^+ (1.703 Å)**			**PuO_2^{2+} (1.675 Å)**		
$^5\Sigma_g$	$(5f\delta)^2(5f\varphi)^2$	0	$^4\Phi_u$	$(5f\delta)^2(5f\varphi)^1$	0	^3H_g	$(5f\delta)^1(5f\varphi)^1$	0
$^5\Phi_u$	$(7s)^1(5f\delta)^2(5f\varphi)^1$	1800	$^4\Phi_u$	$(5f\delta)^2(5f\varphi)^1$	1368	$^3\Sigma_g$	$(5f\delta)^2+(5f\varphi)^2$	1830
$^5\Delta_u$	$(7s)^1(5f\delta)^1(5f\varphi)^2$	4797	$^4\Sigma_u$	$(5f\pi)^1(5f\delta)^1(5f\varphi)^1$	2663	$^3\Pi_g$	$(5f\delta)^1(5f\varphi)^1$	4879
$^5\Delta_u$	$(7s)^1(5f\delta)^1(5f\varphi)^2$	8548	$^2\Phi_u$	$(5f\delta)^2(5f\varphi)^1$	11733	$^1\Sigma_g$	$(5f\delta)^2+(5f\varphi)^2$	6069
$^3\Phi_u$	$(7s)^1(5f\delta)^2(5f\varphi)^1$	8843	$^2\Gamma_u$	$(5f\delta)^2(5f\varphi)^1$	11765	$^1\Pi_g$	$(5f\delta)^1(5f\varphi)^1$	9465
^5H_u	$(6d\delta)^1(5f\delta)^2(5f\varphi)^1$	10919	$^2\Delta_u$	$(5f\delta)^1(5f\varphi)^2$	13117	$^3\Sigma_g$	$(5f\delta)^2+(5f\varphi)^2$	12511
$^3\Delta_u$	$(7s)^1(5f\delta)^1(5f\varphi)^2$	11699	$^2\Delta_u$	$(5f\delta)^1(5f\varphi)^2$	13208	$^1\Gamma_g$	$(5f\delta)^2$	13332
$^5\Pi_u$	$(6d\delta)^1(5f\delta)^2(5f\varphi)^1$	12670	$^4\Sigma_u$	$(5f\pi)^1(5f\delta)^1(5f\varphi)^1$	13538	$^1\Gamma_g$	$(5f\delta)^2$	13888

Table 6. Vertical excitation energies(cm^{-1}) for PuO_2^{2+} calculated at the CASPT2 level including the spin-orbit coupling. The computed energies are evaluated at 1.675 Å (equilibrium bond length). For comparison, results obtained at different level of theory as well as experimental data have been included.

SDCI+Q+SO **Maron et al.**[35]		**CASPT2+SO** **Clavaguera-Sarrio et al.**[11]		**IHFSCC** **Infante et al.** [3323]		**This work**		**Experiment**[24]	
State	**E (cm^{-1})**	**State**	**E (cm^{-1})**	**State**	**E (cm^{-1})**	**State**	**E (cm^{-1})**	**State**	**E (cm^{-1})**
4_g	0	4_g	0	4_g	0	4_g	0	4_g	0
0_g	4295	0_g	4190	0_g	2530	0_g	3177	0_g	---
5_g	6593	1_g	6065	1_g	4870	1_g	5251	1_g	---
1_g	7044	5_g	8034	5_g	6700	5_g	6920	5_g	---
0_g	7393	0_g	12874	0_g	10334	0_g	10390	0_g	10185
6_g	7848	1_g	12906	1_g	10983	1_g	1110	1_g	10500
0_g	9415	6_g	14326	0_g	11225	0_g	12052	0_g	10700
1_g	12874	0_g	14606	6_g	11651	6_g	12450	6_g	---

Table 7. Vertical Ionization energies (eV): this work unless otherwise specified.

Species	IE (eV)	Method
PuO	6.6±0.1[5]	Knudsen effusion / Electron impact
	5.8±0.5[7]	Knudsen effusion / Electron impact
	6.1±0.2[2,3]	FTICR-MS / "Schwarz method"
	6.31	DFT(B3LYP)
	6.17	CASPT2(12,16)
	6.11	CASPT2(12,16)+SO
PuO^+	13.7±0.8[3]	Thermodynamic evaluation
	14.52	DFT(B3LYP)
	14.57	CASPT2(11,16)
	14.51	CASPT2(11,16)+SO
PuO_2	9.4[7]	Knudsen effusion / Electron impact
	10.1±0.1[5]	Knudsen effusion / Electron impact
	7.03±0.12[1]	FTICR-MS / Electron transfer bracketing
	6.6	Knudsen effusion / Ion equilibrium
	6.70 6.28	B3LYP ($^5\Sigma_g^+$ to $^4\Phi_u$) B3LYP ($^5\Phi_u$ to $^4\Phi_u$)
	9.72[10]	CCSD
	9.92[10]	CCSD(T)
	6.63 6.36	CASPT2(12,14) ($^5\Sigma_g^+$ to $^4\Phi_u$) CASPT2(12,14) ($^5\Phi_u$ to $^4\Phi_u$)
	6.36	CASPT2(12,14)+SO
PuO_2^+	15.1±0.4[3]	FTICR-MS / Electron transfer kinetics
	16.3	B3LYP
	15.47	CASPT2(11,14)
	15.17	CASPT2(11,14)+SO

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