Ab Initio Study of the Two Iso-electronic Molecules NpO_4^- and UO_4^{2-}

Hélène Bolvin,*,† Ulf Wahlgren,‡ Odd Gropen,†,|| and Colin Marsden§

Institutt for kjemi, Universitetet i Tromsø, 9037 Tromsø, Norway, Fysikum, University of Stockholm, P.O. Box 6730, 11385 Stockholm, Sweden, and IRSAMC, Université Paul Sabatier, 31062 Toulouse Cedex 04, France

Received: April 2, 2001; In Final Form: July 17, 2001

The two iso-electronic molecules NpO_4^- and UO_4^{2-} have been investigated by means of different ab initio methods: Hartree−Fock, Møller−Plesset perturbation theory at the second order, complete active space perturbation theory at the second order (CASPT2), coupled pair functional, coupled cluster single double with perturbative contributions from triple excitations, and density functional theory with hybrid functionals. Relativistic effective core potentials have been used in all calculations. NpO_4^- is a square planar molecule, whereas UO_4^{2-} has a tetrahedral structure. The 5f orbitals, and, in particular, their lower energy in the neptunium compound that make them more available to form covalent bonds, play a crucial role in explaining the different structures of the two compounds.

1. Introduction

Applied relativistic quantum chemistry has made significant progress during the past decade.[1−3] The description of relativity is possible with high accuracy by using four-component methods, but these are still limited to small molecules. When one describes the valence properties in closed-shell molecules, the main relativistic effects are the scalar ones that can be well described by relativistic effective core potentials (RECPs). Thus, the usual methods of quantum chemistry can be applied with the relativistic density: Hartree−Fock (HF), complete active space self-consistent field (CASSCF), coupled cluster single double with perturbative contributions from triple excitations [CCSD(T)], density functional theory (DFT), with the usual gradient techniques to optimize the geometries. This approximation has given good results for geometry optimization, when compared with fully relativistic four-component methods at the same level of correlation.[4]

A lot of work has been done on the actinyl $(AnO_2)^{n+}$ series.[4−7] The molecule ThO_2 is bent, whereas the subsequent molecules in the series are linear. Recently, the bonding of the uranyl ion has been studied in alkaline solution[8,9] with some ligands forming $UO_2L_2^{2+}$ complexes, with water[10] and H_2S,[11] and its hydrolysis.[12] In all these studies, the uranyl keeps its own entity as a strongly bonded ion and forms weaker bonds with the other ligands.

In this article, we investigate the possibility that the uranium and the neptunium atoms form four oxo bonds by studying the two iso-electronic molecules, NpO_4^- and UO_4^{2-}. In these compounds, Np and U atoms are formally in oxidation states VII and VI, respectively, i.e., in the $[Rn]5f^06d^07s^0$ electronic configuration. The latter is highly negatively charged, but may be stabilized in solutions. Pyykkö and Zhao have shown that the calculation for geometries of anions in gas phase is meaningful.[13] The square planar molecules UO_4^{2-} and NpO_4^{2-} have been studied at the HF level by Pyykkö et al.[14−16]

These ions are known in the solid state as part of the deformed AnO_6 octahedron in various oxides of uranium and of neptunium. Many structures of hexavalent uranium oxides are known; in such crystals, there is a large variety of U−O distances. The UO_6 unit can be either of the uranyl type (two short and four long distances), as in Li_2UO_4 with distances of 1.89 Å (2 ×) and 1.98 Å (4 ×); or in Na_2UO_4 with distances of 1.93 Å (2 ×) and 2.08 Å (4 ×); or of an 'antiuranyl' type with four short and two long U−O distances, as for example in Li_4UO_5 with distances of 2.00 Å (4 ×) and 2.22 Å(2 ×).[17] On the other hand, there are very few experimental data concerning oxides of heptavalent neptunium. Crystals of $Na_3NpO_4(OH)_2\cdot nH_2O$[18] and $Co(NH_3)_6NpO_4(OH)_2\cdot 2H_2O$[19] display a tetragonal bipyramidal $NpO_4(OH)_2^{3-}$ central core. Other crystals like $LiCo(NH_3)_6Np_2O_8(OH)_2\cdot 2H_2O$[20] or $MNpO_4$ (M = Cs,K) contain a NpO_2^{3+} unit. This high oxidation state of neptunium exists only in alkaline solution; the presence of the NpO_4^- unit versus the NpO_2^{3+} one has been subject to controversy,[21,22] but we have argued in favor of the former thanks to a new extended X-ray absorption fine structure experiment and theoretical calculations in a recent study.[23] The UO_4^{2-} unit has never been observed in solution.

We will limit the study to the NpO_4^- and UO_4^{2-} ions alone, even if these molecules exist only coordinated with hydroxide ions, at least for the neptunate compound. The aim of this work is, on one hand, an analysis of these two iso-electronic molecules that, as we will see, are not iso-structural and, on the other hand, a comparison of correlated methods as a starting point for further chemical studies, as for example the study of the NpO_4^- ion in hydroxide solutions.[23] The bonding in uranyl and neptunyl involves the 5f orbitals of the actinide as well as the 7s, 6p, and 6d orbitals. This study will show how these orbitals are involved in these molecules with four oxo bonds, and the comparison between the two iso-electronic molecules will confirm that the 5f orbitals of the actinide atoms accept more electrons in the neptunium compound and give more covalent bonds.

After presenting some computational details in Section 2, this article studies extensively the two already-mentioned ions: NpO_4^- and UO_4^{2-}. The bond is analyzed at the HF level in Section 3.2; it is shown that the neptunate ion is square planar, whereas the uranate one is tetrahedral because of the role of 5f orbitals. In Section 3.3, correlated calculations are presented:

---

* Corresponding author. On leave from Université Paul Sabatier. E-mail: helene.bolvin@chem.uit.no.

† Universitetet i Tromsø.

‡ University of Stockholm.

§ Université Paul Sabatier.

|| Actual address: Laboratoire de Chimie Quantique, Université Louis Pasteur, 4 rue Blaise Pascal, 67000 Strasbourg, France.

10.1021/jp011240j CCC: $20.00

TABLE 1: Results of the HF Calculations for UO_2^{2+}, NpO_2^{2+}, and NpO_2^{3+} Ions; Equilibrium Distances, Frequency of the Totally Symmetrical Mode and Mulliken Charges for Atoms and Orbitals of the Actinide Atom

	formal oxidation state	R_e (Å)	frequency (cm^{-1})	atomic charges		An orbital occupation			
				Q_{An}	Q_O	s	p	d	f
UO_2^{2+}	VI	1.65	1300	3.08	−0.54	4.02	11.60	11.09	2.21
NpO_2^{2+} $^2\Phi_u$	VI	1.64	1314	3.04	−0.52	4.02	11.60	11.04	3.30
$^2\Delta_u$	VI	1.63	1290	3.02	−0.51	4.01	11.56	11.08	3.32
NpO_2^{3+}	VII	1.60	1441	3.66	−0.33	3.99	11.45	11.09	2.81

TABLE 2: Irreps of the Orbitals in the T_d Symmetry

metal	ligands
s → A_1	$p_\sigma \rightarrow A_1 \oplus T_2$
p → T_2	$p_\pi \rightarrow E \oplus T_1 \oplus T_2$
d → $E \oplus T_2$	
f → $A_1 \oplus T_1 \oplus T_2$	

TABLE 3: Irreps of the Orbitals in the D_{4h} Symmetry

metal	ligands
s → A_{1g}	$p_\sigma \rightarrow A_{1g} \oplus B_{2g} \oplus E_u$
p → $A_{2u} \oplus E_u$	$p_{\pi i} \rightarrow A_{2g} \oplus B_{1g} \oplus E_u$
d → $B_{1g} \oplus B_{2g} \oplus A_{1g} \oplus E_g$	$p_{\pi o} \rightarrow A_{2u} \oplus B_{1u} \oplus E_g$
f → $A_{1u} \oplus A_{2u} \oplus B_{2u} \oplus 2E_u$	

bond lengths calculated at the HF, Møller−Plesset perturbation theory at the second-order (MP2), CASSCF, complete active space perturbation theory at the second order (CASPT2), DFT, configuration interaction single double (CISD), coupled pair functional (CPF), and CCSD(T) levels will be compared for the constrained square planar and tetrahedral symmetries.

2. Computational Details

All the calculations have been performed with the energy-consistent small-core RECPs and their corresponding optimized basis sets of the group of Stuttgart.[24] For the uranium and neptunium atoms, the 1s−4s, 2p−4p, 3d−4d, and 4f atomic orbitals are in the core leaving 32 and 33 electrons, respectively, explicitly described by 12s11p10d8f basis contracted to 8s7p6d4f. No g-function has been added, because it does not play a major role on the geometry optimizations in such molecules.[25] For the oxygen atoms, the 1s orbital is in the core, and the 4s5p2d primitives are contracted to 2s3p2d.

Geometries of the species have been optimized at the HF (RASSCF) level with gradient techniques using the MOLCAS-4 program system.[26] As suggested by Hess, standard gradient programs are used with relativistic densities. Spin-free correlated calculations were done using MP2, CASPT2,[27] CISD, CPF,[28] CCSD(T)[29] levels of theory. The geometries were manually refined at the CI level. All DFT calculations were performed within the Gaussian 98 program.[30] Two hybrid functionals were used: B3LYP[31−33] and B3PW91.[34]

3. Results and Discussion

3.1. Preliminary Results: Uranyl and Neptunyl. Let us first compare properties of the two iso-electronic ions uranyl 2+ and neptunyl 3+. The results presented in Table 1 are at the HF level, because the goal is not to obtain the best description of the molecule, but only to achieve a comparison between UO_2^{2+} and NpO_2^{3+}, which are iso-electronic. Results concerning NpO_2^{2+} have been added; this ion is in formal oxidation VI, and the two states $^2\Phi_u$ and $^2\Delta_u$ are degenerate within 2 kJ·mol^{-1} and display very similar characteristics, the former being the ground state. We have not been able to find experimental information on neptunyl 3+ in gas phase. These results show that UO_2^{2+} has properties much closer to NpO_2^{2+} than to NpO_2^{3+} concerning equilibrium distance, vibrational frequency, and Mulliken charges. The only significant difference is the population of the f orbital; the two molecules seem to be very similar, and the extra electron of NpO_2^{2+} goes in an inactive f orbital, screening the larger charge of the Np nucleus, thus giving rise to the same behavior of the valence electrons. On the other hand, NpO_2^{3+} is a more bonding molecule than UO_2^{2+} with a much larger involvement of the f electrons in the bond (+0.6 electrons).

These first results show already that iso-electronicity is not a very helpful concept in the study of molecules containing actinide atoms.

3.2. Hartree−Fock Results and the Nature of the Bond. *3.2.1. NpO_4^- and UO_4^{2-}.* At the HF level, NpO_4^- is close to a square planar molecule, whereas UO_4^{2-} has a tetrahedral structure. In the neptunate ion, there is a small dihedral angle of 2° between the planes formed by the oxygens 1−2−3 and 2−3−4. All further discussion will assume that the point group of NpO_4^- is D_{4h}. The tetrahedral conformation is the one in which the ligands avoid each other the most, whereas in the square planar one, there must be some stabilizing interaction that compensates the greater repulsion between the ligands. The irreps of the different orbitals are summarized in Tables 2 and 3 for T_d and D_{4h} symmetries, respectively. In T_d symmetry, the p orbitals of the ligands split into two subgroups; the p_σ pointing toward the actinide center and the p_π perpendicular to the An−O bonds. As will be discussed later, the orbitals contributing most to the bond are the ones involving the f orbitals of the actinide and the p_σ orbitals of the ligands, namely the orbitals of irreps A_1 and T_2. These orbitals are plotted in Figures 1 and 2, respectively. The A_1 orbital is a pure mixture of a 5f orbital of the actinide with p_σ orbitals of the oxygens. The T_2 orbitals are lower in energy and have contribution of 6p, 6d, and 5f orbitals of the actinide, and the p_σ of the oxygens mix slightly with the p_π orbitals which allows an increase of the overlap. In the D_{4h} point group, the p orbitals of the four oxygen atoms split into three groups: the p_σ ones pointing toward the actinide; the $p_{\pi i}$ group, perpendicular to the An−O bonds and lying in the plane of the molecule; and finally, the $p_{\pi o}$ group, perpendicular to the plane of the molecule. Most bonding orbitals belong to the E_u irrep and involve the f, p_σ, and $p_{\pi i}$ orbitals. One of them is plotted Figure 3; it involves two p_σ orbitals on the top and bottom oxygen atoms and two $p_{\pi i}$ orbitals on the right and left atoms.

Results are summarized in Table 4. Results for the saddle points square planar UO_4^{2-} and tetrahedral NpO_4^- have been added. The highest occupied molecular orbital and lowest unoccupied molecular orbital energies are −0.02 and 0.13 au, respectively (−0.23 and 0.07 au) for tetrahedral UO_4^{2-} (square planar NpO_4^-). Although Mulliken charges do not have any absolute significance, they can be used in a comparative manner, as long as the same basis set is used. To quantify the covalency of the bond, the Mulliken charges of the oxygens can be taken as a criterion; a fully ionic bond would give a charge of −2 on the oxygens and the population of the actinides' s, p, d, and f orbitals would be 4, 12, 10, and 0, respectively, taking into

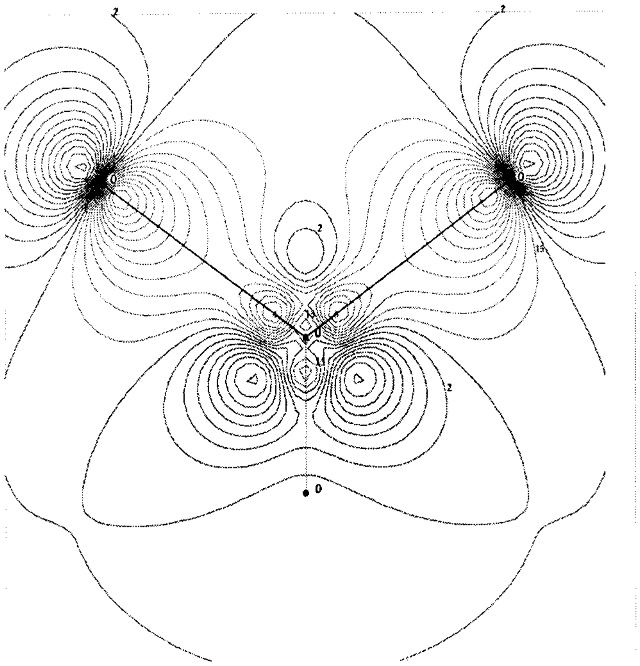

Figure 1. Molecular orbital of irrep A_1 of the tetrahedral UO_4^{2-} ion, drawn with MOLDEN.[39] The orbital is plotted in the plane of the uranium and two oxygens and represented by iso-value contours.

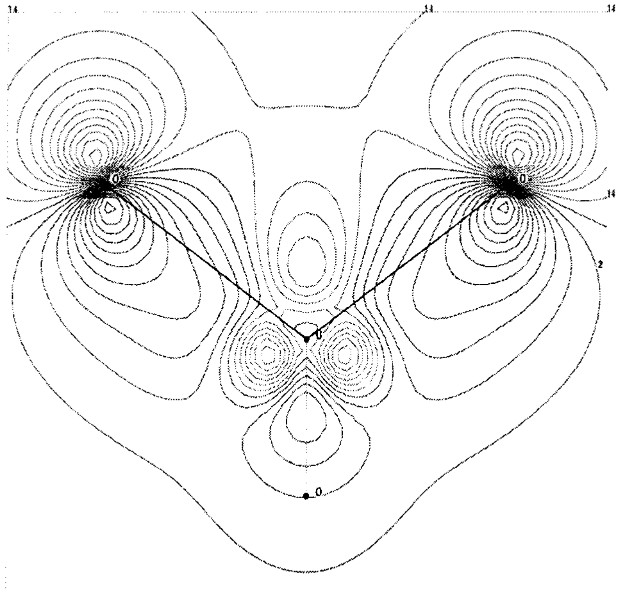

Figure 2. Molecular orbital of irrep T_2 of the tetrahedral UO_4^{2-} ion, drawn with MOLDEN.[39] The orbital is plotted in the plane of the uranium and two oxygens and represented the iso-value contours.

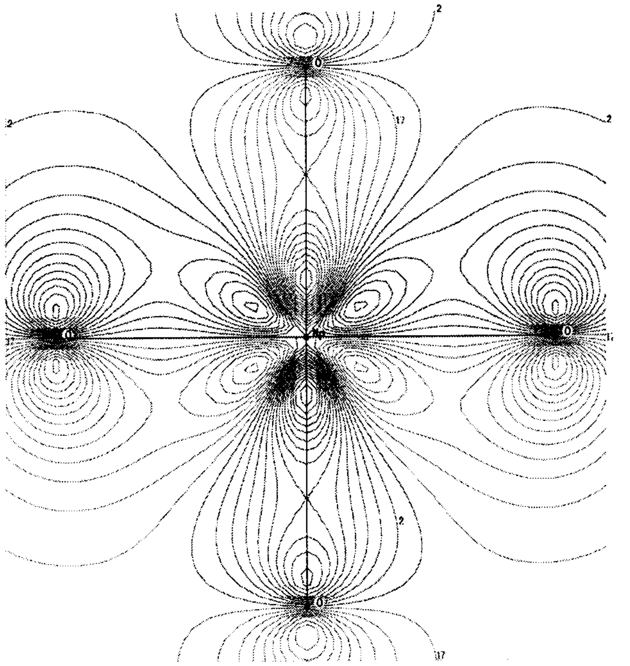

Figure 3. Molecular orbital of irreps E_u of the square planar NpO_4^- ion, drawn with MOLDEN.[39] The orbital is plotted in the plane of the molecule and represented by iso-value contours.

account the electrons described by the RECPs. Thus defined, the covalency increases when going down the table: the bond distance decreases and the net negative charge on the oxygen decreases from -1.22 in tetrahedral UO_4^{2-} to -0.90 in square planar NpO_4^-. The s-population is almost the same in the four systems, whereas the deficit in the p-population increases with the covalency of the bond. For example, it is 0.45 and 0.23 for the square planar NpO_4^- and UO_4^{2-}, respectively. This shows that there is a 6p hole as in the actinyl series (see for example ref 35 and references therein) and that the 6p electrons are more active in Np(VII) than in U(VI). The d-population depends more on the group symmetry than on the covalency; the 6d electrons participate more in the bond in the tetrahedral conformers than in the square planar ones, but in any case, this contribution is large. The 5f-population increases strongly with the covalency, from 1.46 to 3.27. Comparing the square planar molecules, there is a difference of 0.3 electron for the f orbitals belonging to the E_u irrep between the neptunate and the uranate in favor of the former. Comparing both the two tetrahedral molecules and the two square planar ones, the difference in the f-population is one in favor of the neptunate compounds.

However, it is not so obvious to decide whether the 5f orbitals contribute more or less than the 6d orbitals to the bond. When looking at the Mulliken charges or at the contribution of the atomic orbitals in the molecular ones, or finally at the plot of the orbitals, the d contribution to the bond seems to be as important as the f one. To discriminate between the two contributions, we have performed the following experiment. First, the geometry of the neptunate ion has been optimized without any f orbital in the basis set (remember that the 4f closed shell is described by the RECP): the basis set for neptunium was then (12s,11p,10d) contracted to [8s,7p,6d]. A tetrahedral molecule was obtained with a bond length of 1.94 Å. Then a similar procedure was adopted when deleting the atomic functions describing the 6 and higher d orbitals: the basis set was then (12s,11p,1d,8f) contracted to [8s,7p,1d,4f]. The energy of the occupied and almost pure 5d orbitals was shifted by only 0.04 au in a given geometry, which shows that only the 6 and higher d orbitals have been affected. The final geometry is square planar, with a bond length of 1.80 Å, which is slightly longer than with the complete basis set. In Table 5, Mulliken charges have been reported for the three basis sets in the same geometry (namely the geometry optimized with the full basis set). It is clear that both the 5f and the 6d orbitals contribute substantially to the covalency of the bond, but the effect of the 5f is much more dramatic: the effect of removing the 5f from the basis set raises the energy much more (about 3300 kJ/mol compared with 800) in a given geometry, and the optimized geometry is tetrahedral, which means that the covalency is no

TABLE 4: Results of the HF Calculations for UO_4^{2-} and NpO_4^- Ions in the Square Planar and Tetrahedral Conformations; Equilibrium Distances, Mulliken Charges for Atoms and Orbitals of the Actinide Atom, Difference of Energy between the Two Conformations

			atomic charges		An orbital occupation				
	symmetry	R_e (Å)	Q_{An}	Q_O	s	p	d	f	$E_{T_d} - E_{D_{4h}}$ (kJ·mol^{-1})
UO_4^{2-}	T_d	1.942	2.86	−1.22	4.09	11.84	11.75	1.46	
	D_{4h}	1.904	2.50	−1.12	4.07	11.77	11.47	2.20	−85.3
NpO_4^-	T_d	1.845	2.93	−0.98	4.08	11.76	11.81	2.42	
	D_{4h}	1.786	2.60	−0.90	4.08	11.55	11.50	3.27	+291.5

TABLE 5: HF Results for the NpO_4^- Ion with Three Different Basis Sets, in the D_{4h} Symmetry Group, with Np−O_{oxo} = 1.786 Å

		atomic charges		An orbital occupation			
	ΔE (kJ·mol^{-1})	Q_{An}	Q_O	s	p	d	f
total basis	0	2.60	−0.90	4.08	11.55	11.50	3.27
without 6d[a]	+910	3.82	−1.20	3.98	11.55	9.99	3.66
without 5f[a]	+3322	4.12	−1.28	4.10	11.87	12.91	0

[a] For an explanation of the basis sets, see the text.

longer able to compensate the higher repulsion between the ligands in the square planar structure.

To conclude, this computational experiment shows that the 5f orbitals seem to be more important in bonding than the 6d and are the cause of the square planar structure of the neptunate molecule. Furthermore, it seems that the 5f orbitals form more covalent bonds in neptunate than in uranate. Based on the previous Mulliken population analysis, a realistic starting point for a molecular orbital (MO) diagram seems to be Np^{3+} or U^{2+} surrounded by four O^-. Self-consistent field (SCF) calculations with four electrons evenly distributed among the 5f orbitals indicate that the 5f orbitals of Np^{3+} are energetically lower than those of U^{2+}, as could be expected. However, SCF calculations on O^- with five electrons evenly distributed among the 2p orbitals predict the 2p orbitals to lie *above* the 5f orbitals of either actinide atom. This result seems to contradict the previous observation that the 5f orbitals of neptunate form more covalent bonds than in uranate, because the 5f orbitals of the latter species are the less contracted and seem to lie energetically closer to the 2p orbitals of the oxygens. This apparent paradox can be resolved by an argument along the lines of ligand field theory. When Np^{3+} or U^{2+} is placed in the field of four negative charges, SCF calculations now indicate that the oxygen 2p orbitals lie *below* the 5f orbitals of either actinide atom, leading to the MO diagrams of Figures 4 and 5. In such a scheme the bonding orbitals of neptunate are more bonding and have greater actinide character than in uranate. And, in fact, in both T_d and D_{4h} symmetries, the equilibrium distances are shorter for neptunium and the bonds stronger. Finally, to discriminate between the tetrahedral and the square planar structures, we can use a simple picture; the neptunium accepts more electrons from the oxygens, actually one electron, and the resulting reduced repulsion between the latter favors the square planar structure.

3.2.2. Excited States, Ionization and Electron Affinity. Inspection of excited states sheds more light on the electronic structure of NpO_4^- and UO_4^{2-}. This section will be restricted to a qualitative overview. All the calculations have been done at the restricted open-shell Hartree−Fock (ROHF) level without inclusion of spin−orbit effects, which is a crude approximation for negative, open-shell actinide molecules. But we suppose that the main physics is contained at this level of description, and specifically the different behavior of the uranate and neptunate ions.

The first excited state of the square planar NpO_4^- is an excitation from the σ bond of symmetry E_u to the localized 5f of symmetry A_{2u}. There is no charge transfer compared with the ground state, because the transfer to the 5f orbital is compensated by a back-donation to the oxygens. The 5f-population in this state is 3.47, almost the same as in the ground state. This state is a bonding one, with a slightly larger equilibrium distance than in the ground state. The first ionized state lies well above; it has been obtained within a lower point group to permit a better localization of the electron on one oxygen atom. It consists of the removing of a p_π electron of one oxygen, and it is bonding. Finally, the NpO_4^{2-} does not exist at the ROHF level, the additional electron is found in the most diffuse f orbital which means that it is only restrained by the basis set from leaving the molecule. Even though the UO_2^{2+} and NpO_2^{2+} ions have very similar characteristics, the two UO_4^{2-} and NpO_4^{2-} anions are not similar. In NpO_2^{2+}, the additional f electron screens the larger nucleus charge of the neptunium atom, and the molecule becomes equivalent to the uranium one; its 5f-population is then 3.30 electrons (see Table 1). But, in NpO_4^-, the Mulliken 5f-population is already 3.27,

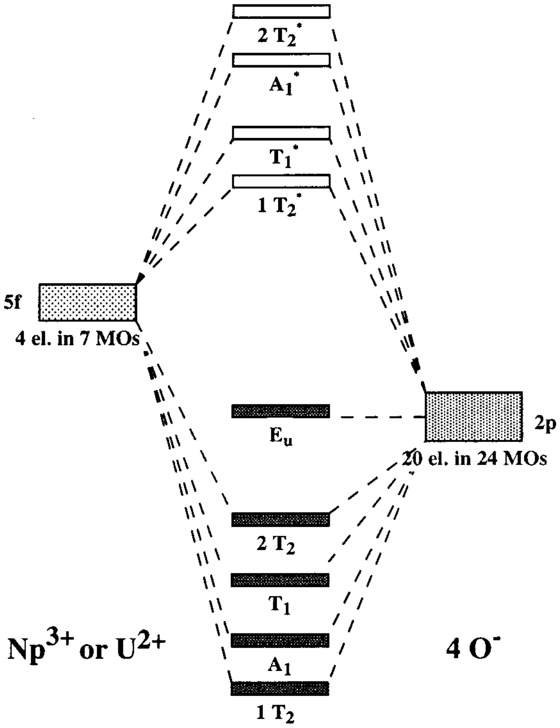

Figure 4. Simplified molecular orbital diagram in the T_d symmetry limited to the 5f orbitals of the actinide and the 2p orbitals of the oxygens.

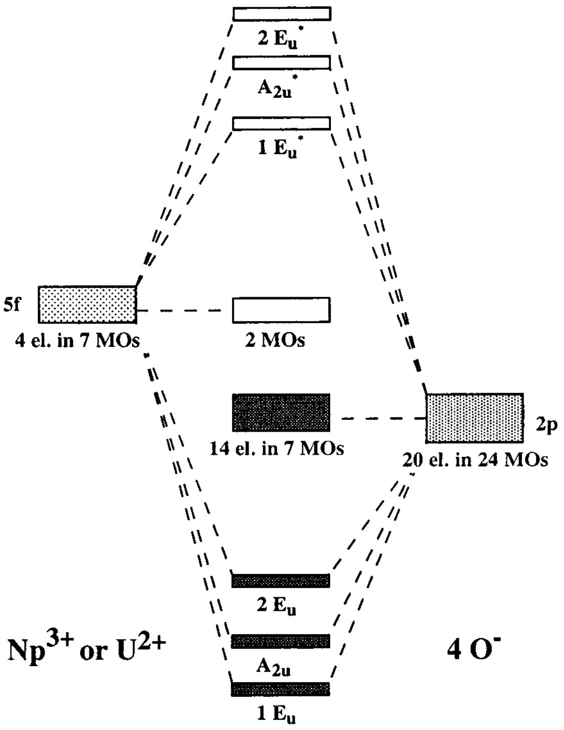

Figure 5. Simplified molecular orbital diagram in the D_{4h} symmetry limited to the 5f orbitals of the actinide and the 2p orbitals of the oxygens.

and it seems that the neptunium atom does not accept more than about 3.5 electrons in the 5f orbitals, perhaps because of the large repulsion in such contracted orbitals. It was already the case in the excited state where a back-donation to the oxygens compensates the transition of an electron in a 5f orbital.

For UO_4^{2-}, results are quite different. The ionized state, namely the UO_4^- anion with a hole on a p_π orbital of one oxygen, lies about 2.5 eV below the ground state of UO_4^{2-}, at least in the gas phase; it is no more the case when the molecule is embedded in a solvent with a conductor polarizable continuum model (CPCM)[36] model with parameters for water where it lies about 2.5 eV above the ground state. The excited state with an electron jumping from a bonding orbital to a 5f orbital is, on the contrary, very high in energy; it shows that the 5f orbitals on this atom lie much higher in energy than in the neptunium and it must be the reason the neptunium-molecule is more covalent than the uranium one.

3.3. Comparison of Correlated Methods. *3.3.1. Full Geometry Optimization.* Full geometry optimizations without any symmetry have only been possible with HF and DFT methods. With both B3PW91 and B3LYP, the neptunate remains almost square planar with a lengthening of the bond of 0.05 Å and 0.07 Å, respectively, compared with the HF results and a dihedral angle of 5 and 8°, respectively. Obtained vibrational wavenumbers are with B3LYP (irreps and IR intensities in km/mol are indicated in parentheses): 810 (a_{1g}), 620 (b_{1g}), 355 (b_{2g}), 217 (a_{2u}, 82), 798 (e_u, 1150), 328 (e_u, 18).

Things are more complicated for the uranate ion. The optimized geometry depends on the basis set and on the quality of the grid due to the flatness of the potential energy surface between the tetrahedral and the square planar structures; the difference of energies is 7 and 20 kJ·mol^{-1} with the B3LYP and the B3PW91 functionals, respectively. With the standard basis set as described in Section 2 and the default grid of Gaussian 98 (option grid = fine), an intermediate structure between the tetrahedral and the square planar ones of symmetry C_{2v} is obtained. It is no longer the case with a smaller basis set where the most diffuse s, p, d, and f functions (of exponent 0.005) of uranium have been deleted or with the standard basis set with a more accurate grid for the integration (option grid = ultrafine); in the former case, a tetrahedral structure is obtained, whereas in the latter the molecule is almost tetrahedral. Although it was too expensive to perform geometry optimizations with other correlated methods, it was possible to perform a single-point calculation on the C_{2v} structure obtained with DFT methods, and to compare it with the T_d energy. With all the investigated methods, the T_d structure was found to be more stable [by 84.7 kJ·mol^{-1} with MP2 and 67.5 kJ·mol^{-1} with CCSD(T)]; it confirms that the structure of the uranate ion is tetrahedral at the correlated level as well. In the tetrahedral structure, with the basis set without diffuse functions, vibrational wavenumbers are with B3LYP (irreps and IR intensities in km/mol are indicated in parentheses): 765 (a_1), 131 (e), 607 (t_2, 2022), 165 (t_2, 238).

3.3.2. Methodological Study in the Constrained D_{4h} and T_d Point Groups. The geometries of the two ions have been optimized in the D_{4h} and T_d symmetry with the aim of comparing different methods. For all methods, all the electrons outside the RECP have been correlated. Results are summarized in Table 6. Of the methods used in this study, it is widely believed that CCSD(T) is the most accurate method. Comparing CCSD and CCSD(T) results shows that the introduction of the triple excitations plays an substantial role in the determination of the equilibrium distance; it increases the distances by 0.03 Å and 0.02 Å in the tetrahedral and square planar structures, respectively. The T_1 diagnostic[37] is 0.030, 0.031, 0.039, and 0.041 for tetrahedral UO_4^{2-}, square planar UO_4^{2-}, tetrahedral NpO_4^-, and square planar NpO_4^-, respectively. These values are all above the 0.02 threshold, which shows that we are at the limit of validity of single-reference procedures; this T_1 diagnostic is

TABLE 6: Comparison of Methods for the Ions NpO_4^- and UO_4^{2-} in the Two Constrained Square Planar and Tetrahedral Conformations

	UO_4^{2-}			NpO_4^-		
method	Re_{T_d} (Å)	$Re_{D_{4h}}$ (Å)	$E_{D_{4h}} - E_{T_d}$ (kJ·mol^{-1})	Re_{T_d} (Å)	$Re_{D_{4h}}$ (Å)	$E_{D_{4h}} - E_{T_d}$ (kJ·mol^{-1})
HF	1.94	1.90	85.4	1.85	1.79	−283.7
MP2	2.01	1.99	83.7	2.04[a]	1.88	
CASSCF	1.95	1.92	38.9	1.98[a]	1.82	−87.4
CASPT2	2.00	1.97	114.2	1.87	1.89	−319.7
B3PW91	1.95	1.90	5.4	1.89	1.83	−172.0
B3LYP	1.97	1.92	24.7	1.91	1.85	−157.3
CISD	1.95	1.91	89.1	1.86	1.80	−191.7
CPF	2.00	1.98	96.7	1.93	>2.10[a]	
CCSD	1.96	1.94	90.0	1.89	1.84	−173.8
CCSD(T)	1.99	1.96	91.5	1.92	1.86	−105.0

[a] Nonconstant weight on the reference state.

also much larger for neptunium than for uranium compounds. Nevertheless, CCSD(T) calculations will be considered as the 'exact' solutions and will be used as a reference for the other methods. Comparison with experiment is not direct; NpO_4^- with two hydroxide ions shows a distance of 1.89 Å, and the effect of the two hydroxide molecules increases the distance by 0.04 Å at a correlated level with inclusion of solvent effects,[23] which shows that the obtained result of 1.86 Å is compatible with experiment. UO_4^{2-} with four short equivalent bonds is only known in crystalline Li_4UO_5[17] with a bond length of 2.00 Å. Again the difference with the 1.96 Å we find in this article can be attributed to the influence of the two oxygens in apical position. The comparison of HF and CCSD(T) results shows that the effect of correlation is 0.05 Å and 0.06 Å in the tetrahedral and square planar UO_4^{2-}, respectively, and 0.07 Å in the two conformations of NpO_4^-. The effect of correlation increases with the covalency of the bond and the compactness of the structure.

MP2 works well in three of the four cases; it tends to overestimate the equilibrium distances by 0.02 Å and gives a reasonable difference of energy in the UO_4^{2-}. In the tetrahedral NpO_4^-, the weight on the reference state is the lowest of the four molecules. It drops but then rises again if the distance is increased, giving unreliable values of the equilibrium distance and energy difference. Multireference methods CASSCF and CASPT2 have been used. The CAS comprises 8 electrons in 8 orbitals which correspond to a quadruple set of orbitals of symmetry E_u in the D_{4h} group, and a double set of orbitals of symmetry A_1 and T_2 in the T_d group. These 8 orbitals correspond to the more bonding orbitals of the complex involving f orbitals of the actinide and p_σ and $p_{\pi i}$ orbitals of the oxygens, and the set of the corresponding antibonding orbitals. This choice allows us to describe the correlation of the bonding orbitals in a variational manner. The weight of the reference determinant in the CASSCF function at the CASPT2 equilibrium geometry is 0.93, 0.90, 0.73, and 0.84 for tetrahedral UO_4^{2-}, square planar UO_4^{2-}, tetrahedral NpO_4^-, and square planar NpO_4^-, respectively. This weight is very small for tetrahedral NpO_4^- because of a large population in the antibonding T_2 orbital, which increases considerably with distance. This explains why the results for this molecule are poor at the CASSCF, CASPT2, and MP2 levels of theory. Except for the tetrahedral NpO_4^-, the CASSCF slightly improves the equilibrium distance, the effect being larger with a larger covalency in the bond. The CASPT2 results (neglecting the tetrahedral NpO_4^- again) give equilibrium distances slightly greater than the CCSD(T) ones, the results being of very good quality in the more ionic UO_4^{2-} systems. With these methods again, results for the tetrahedral NpO_4^{2-} are not reliable; the single-reference picture for the more covalent NpO_4^- is less adequate than for the more ionic UO_4^{2-}.

Within the DFT framework, the B3LYP functional gives good equilibrium distances that are slightly too small, the largest discrepancy of 0.04 Å being found for tetrahedral UO_4^{2-}. The discrepancy with the B3PW91 functional is slightly larger, distances always being 0.02 Å shorter than with B3LYP. The energy difference between the two conformations does not match the CCSD(T) results, the square planar structure being favored in the two cases by about 50 $kJ \cdot mol^{-1}$ and 70 $kJ \cdot mol^{-1}$ with B3LYP and B3PW91, respectively.

Finally, comparing CISD and CCSD(T) results, we see that the size-extensivity correction on the bond distances is large, about 0.05 Å in every case. CPF (ACPF gave similar results) gives accurate results in three cases, but no minimum was found for the square planar case of NpO_4^-; the weight on the reference state decreases with the distance. The SC2[38] method, which is similar to the CPF method, gives a good result, namely a distance of 1.87 Å.

To conclude, although the two conformations of the more ionic UO_4^{2-} are described well by either MP2, CASPT2, B3LYP (at least using an accurate grid for the integration), or CPF, these methods are less reliable for the more covalent NpO_4^-; this latter molecule is more compact and more covalent, correlation effects are larger, and thus single-reference methods are less adequate.

4. Conclusion

In this article, an extensive study of two iso-electronic molecules containing actinide atoms has been presented. The NpO_4^- ion has a square planar structure, whereas the UO_4^{2-} ion has a tetrahedral structure. In a given structure, equilibrium distances are shorter in the neptunate than in the uranate, and Mulliken population analysis shows that there is one more f electron in the former reducing the charge on the oxygens, whereas the 6p hole is greater. When one removes 5f orbitals from the basis set, NpO_4^- becomes tetrahedral, whereas the structure remains square planar when one removes the 6d orbitals. These observations show that the 5f orbitals are the key ingredient to explain the different molecular structures and the stronger bonds with oxygens formed by neptunium. The study of the excited states, namely a charge transfer from a bonding orbital to a nonbonding 5f orbital, confirms that the 5f orbitals are much lower in energy in neptunium than in uranium, which explains the greater availability of these orbitals to accept electrons from oxygen, although they are more contracted. The study of the excited states shows furthermore that the neptunium atom cannot accept more electrons in the 5f orbitals than in NpO_4^- (about 3.5 electrons as indicated by Mulliken analysis with our basis set). To conclude, the bond in the neptunate is more covalent, oxygens are less charged and thereby repel each other less; the square planar form structure is then favored.

The study of correlation shows that there is no perfect method. The T_1 diagnostic of the CCSD calculations shows that these molecules are at the limit of validity of single-reference methods, especially neptunate. MP2 and CASPT2 fail to describe tetrahedral NpO_4^-, whereas CPF fails for the description of its square planar isomer. DFT methods with hybrid functionals can lead to the wrong symmetry for the UO_4^{2-} ion because of the flatness of the potential energy curve, which is caused by the poor estimation of the differences in energy. Single-reference methods are of doubtful reliability for the description of such strongly correlated bonds. They generally give reasonable results, but there are cases of completely erroneous results. This work shows that B3LYP calculations give reasonable bond distances compared with more sophisticated methods for the description of such compounds, and we have used this method for geometry optimization of more complex molecules.[23]

Acknowledgment. H.B. thanks the CNRS for permitting her to work with her salary in Tromsø for one year and the Aurora program, which has given her the opportunity for journeys to Toulouse. We gratefully acknowledge fruitful discussions with Ingmar Grenthe and Trond Saue and the referees for very opportune remarks, and a grant of computing time from the Norwegian Supercomputing Committee (TRU).

References and Notes

(1) Pyykkö, P. *Chem. Rev.* **1988,** *88*, 563.
(2) Pepper, M.; Bursten, B. E. *Chem. Rev.* **1991,** *91*, 719.
(3) Schreckenbach, G.; Hay, P. J.; Martin, R. L. *J. Comput. Chem* **1999,** *20*, 70.

(4) Ismail, N.; Heully, J.-L.; Saue, T.; Daudey, J.-P.; Marsden, C. *J. Chem. Phys. Lett.* **1999,** *300*, 296.

(5) Pyykkö, P.; Laakkonen, L.; Tatsumi, K. *Inorg. Chem.* **1989,** *28*, 1801.

(6) Wadt, W. R. *J. Am. Chem. Soc.* **1981,** *103*, 6053.

(7) Dyall, K. G. *Mol. Phys.* **1999,** *96*, 511.

(8) Wahlgren, U.; Moll, H.; Grenthe, I.; Schimmelpfennig, B.; Maron, L.; Vallet, V.; Gropen, O. *J. Phys. Chem. A* **1999,** *103*, 8257.

(9) Schreckenbach, G.; Hay, P. J.; Martin, R. L. *Inorg. Chem.* **1998,** *37*, 4442.

(10) Spencer, S.; Gagliardi, L.; Handy, N. C.; Ioannou, A. G.; Skylaris, C.-K.; Willets, A. *J. Phys. Chem. A* **1999,** *103*, 1831.

(11) Ismail, N. Doctoral Dissertation, Université Paul Sabatier, Toulouse, France, 2000.

(12) Tsushima, S.; Yang, TX.; Suzuki, A. *Chem. Phys. Lett.* **2001,** *334*, 365.

(13) Pyykkö, P.; Zhao, Y.-F. *J. Phys. Chem.* **1990,** *94*, 7753.

(14) Pyykkö, P.; Zhao, Y *Inorg. Chem.* **1991,** *30*, 3787.

(15) Jové, J.; He, L.; Proust, J.; Pagès, M.; Pyykkö, P. *J. Alloys Comp.* **1991,** *177*, 285.

(16) Pyykkö, P.; Jové, J. *New J. Chem.* **1991,** *15*, 717.

(17) Keller, C. In *Inorganic Chemistry*; Bagnall, K. W., Ed.; MTP International Review of Science, Series 1, Vol. 7; Butterworths & Co Ltd.: Markham, ON, 1972.

(18) Tomilin, S. V.; Volkov, Y. F.; Kapshukov, I. J.; Rykov, A. G. *Radiokhimiya* (in English) **1981,** *23*, 695.

(19) Grigor'ev, M. S.; Gulev, B. F.; Krot, N.N. *Radiokhimiya* (in English) **1986,** *28*, 630.

(20) Burns, J. H.; Baldwin, W. H.; Stokely, J. R. *Inorg. Chem.* **1973,** *12*, 466.

(21) Shilov, V. P. *Radiokhimiya* (in English) **1998,** *40*, 12.

(22) Clark, D. L.; Conradson, S. D.; Neu, M. P.; Palmer, P. D.; Runde, W.; Tait, C. D. *J. Am. Chem. Soc.* **1997,** *119*, 5259.

(23) Bolvin, H.; Wahlgren, U.; Moll, H.; Reich, T.; Geipel, G.; Fanghänel, T.; Grenthe, I. *J. Chem. Phys. A*, in press.

(24) Küchle, W.; Dolg, M.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1994,** *100*, 7535.

(25) Vallet, V.; Schimmelpfennig, B.; Maron, L.; Teichtel, C.; Leininger, T.; Gropen, O.; Grenthe, I.; Wahlgren, U. *Chem. Phys.* **1999,** *244*, 185.

(26) Andersson, K.; Blomberg, M. R. A.; Fülscher, M. P.; Karlström, G.; Lindh, R.; Malmqvist, P.-Å.; Neogrády, P.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Schütz, A. J.; Seijo, L.; Serrano-Andrès, L.; Siegbahn, P. E. M.; Widmark, P.-O. *MOLCAS-4;* Lund University: Sweden, 1997.

(27) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O.; Sadlej, A. J.; Wolinski, K. *J. Phys. Chem.* **1990,** *94*, 5483.

(28) Ahlrichs, R.; Scharf, P.; Ehrhardt, C. *J. Chem. Phys.* **1985,** *82*, 890.

(29) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989,** *157*, 479.

(30) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

(31) Becke, A. D. *Phys. Rev. A* **1998,** *98*, 3098.

(32) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988,** *37*, 785.

(33) Stevens, P. J.; Devlin, J. F.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994,** *98*, 11623.

(34) Perdew, P.; Wang, Y. *Phys. Rev. B* **1992,** *45*, 13244.

(35) de Jong W. A.; Visscher, L.; Nieuwpoort, W. C. *THEOCHEM J. Mol. Struct.* **1999,** *458*, 41.

(36) Barone, V.; Cossi, M.; Tomasi, J. *J. Comput. Chem.* **1998,** *19*, 404.

(37) Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem. Quantum Chem. Symp.* **1989,** *23*, 199.

(38) Ben Amor, N; Maynau, D. *Chem. Phys. Lett.* **1998,** *286*, 211.

(39) Schaftenaar, G.; Noordik, J. H. *J. Comput.-Aided Mol. Des.* **2000,** *14*, 123−134.