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Electronic Spectrum of the NpO_2^{2+} and NpO_2^+ Ions

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The ground and excited states of the linear NpO_2^{2+} and NpO_2^+ ions have been calculated using relativistic spin−orbit configuration interaction methods based on effective core potentials. The f → f transitions and some charge-transfer transitions have been calculated for both ions and compared with experiment wherever possible. Various types of analysis are used to gain a better understanding of the types and patterns of electronic states.

Introduction

The chemistry of actinides is of particular interest because of their radioactivity and involvement in the production of nuclear energy. After World War II there was a great effort to understand actinide chemistry; in recent years this has been revived in an attempt to find efficient ways to treat nuclear waste.[1] Scientists are interested in the behavior of actinides in the environment, how they complex and migrate, and how they can be separated. Theoretical studies can be helpful in understanding this chemistry since calculations on radioactive material, although difficult, can be done without the restrictive experimental conditions. The actinides, being at the bottom of the periodic table, have many and fast-moving electrons, thus increasing the size of the calculations significantly and requiring that relativistic effects be included in any accurate calculations. Recently the progress of relativistic quantum chemistry has made these calculations feasible.

Neptunium is the first transuranium element in the periodic table and was the first to be identified.[2] It exists in oxidation states from III to VII, with V being the most common.[3] In oxidation states V and VI Np does not exist as a free ion but is coordinated with two oxygens, forming the linear ions NpO_2^+ and NpO_2^{2+}. Under most environmental conditions Np will be present as NpO_2^+.[4] Since the nomenclature is not universal, we clarify here that in this work we refer to AnO_2^{2+} as an actinyl ion and AnO_2^+ as a dioxoactinide(1+) ion, where An is an actinide. Actinyl ions are very stable units, present in many of the early actinides, and have very strong actinide−oxygen bonds. They are the species in which the actinides are found in high oxidation states in aqueous solutions, which makes them extremely important. Their small size makes their analysis and theoretical calculations easier. Of all the actinyl ions, uranyl has received the most attention, with many experimental and theoretical studies. Two reviews, which mostly discuss the uranyl ion, also discuss the other actinyl ions briefly, especially the neptunyl ion.[5,6] One of the reasons why the neptunyl ion attracted attention is that it is the actinyl ion with only one f electron, so it should be easier to analyze its spectrum, thus providing help in the interpretation of the spectra of the other, more complicated, actinyl ions.[6]

There are almost no experimental results for actinyl and dioxoactinide(1+) ions in the gas phase, only for solutions and crystals. Although different equatorial ligands affect the properties of these ions, the basic characteristics remain the same and the ions can be studied without detailed consideration of the ligands in most cases.

Since the 1950s, infrared and Raman experiments have recorded the vibrational frequencies of the AnO_2^+ and AnO_2^{2+} ions and how these vary with atomic number.[7−10] More recent studies, in different crystals, give bond lengths and frequencies that vary depending on the atomic number, the oxidation state, and the surrounding ligands.[11,12]

Magnetic susceptibility and EPR data have been reported for the neptunyl ion.[13−15] These data provided the first direct evidence that the unpaired electron in NpO_2^{2+} is in an f orbital and helped in the identification of the ground state, although the values of the g factors are strongly influenced by the equatorial ligands. NpO_2^{2+} is linear, and the f orbitals in linear symmetry split into σ_u, π_u, δ_u, and ϕ_u orbitals. The $5f\delta_u$, and $5f\phi_u$ orbitals are nonbonding since due to symmetry they do not mix with any oxygen orbitals, but the $5f\sigma_u$, and $5f\pi_u$ mix with the oxygen 2p orbitals. This occurs in a bonding manner for the occupied (primarily O 2p) σ_u and π_u orbitals and in an antibonding manner for the unoccupied (primarily 5f) σ_u and π_u orbitals; thus raising the energy of the latter. The single f electron, then, in the ground state should give a δ_u^1 or ϕ_u^1 configuration. The states arising from the δ_u^1 configuration are $^2\Delta_{3/2u}$ and $^2\Delta_{5/2u}$, and the ones from the ϕ_u^1 are $^2\Phi_{5/2u}$ and $^2\Phi_{7/2u}$. Important questions then are the order of the δ_u and ϕ_u orbitals and the identification of the ground state.

The electronic spectra for both ions have been reported in solutions[16−19] and crystals.[20−23] The earlier experiments did not give enough information to assign the peaks. A theoretical attempt to assign the spectra of both ions was made by Eisenstein and Pryce more than 30 years ago.[24,25] They calculated the spectrum of NpO_2^{2+} using parameters for the spin−orbit interaction and the ligand field and fitted them to experimental data. They used optical absorption measurements along with magnetic properties (paramagnetic resonance, susceptibilities). At that time, arguments had been made that the ϕ_u orbital should have a lower energy than the δ_u orbital,[26,27] and they obtained a fit and assignment of the NpO_2^{2+} spectrum consistent with these arguments. When they considered their similar analysis on plutonyl and the similarity in the intensity of certain lines, they found inconsistencies in the comparison and decided that the neptunyl assignment and fit should be

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redone. Both the plutonyl results and the revised neptunyl results gave the δ_u orbital lower than the ϕ_u orbital.

The ground states of all these ions had been established earlier from EPR experiments,[27] $\phi_u^1\ {}^2\Phi_{5/2u}$ for NpO_2^{2+} and $\delta_u^1\phi_u^1\ {}^3H_{4g}$ for both NpO_2^{+} and PuO_2^{2+}. The data, assignments, and parameter fitting[25] for NpO_2^{+} were less well established than those for PuO_2^{2+}, and some more questions were left open about its electronic states.

The spectrum of NpO_2^{2+} has been assigned in the very detailed work of Denning et al.,[22,23] who measured the polarized, single-crystal absorption spectra of the neptunyl ion doped into $Cs_2UO_2Cl_4$ and $CsUO_2(NO_3)_3$ crystals. They observed ten transitions in the former crystal and nine in the latter, five of which are of the charge-transfer type. They also reported g factors for several states. Finally they used a perturbation method to calculate parameters characterizing the f orbital energies, the spin−orbit interaction, and the equatorial ligand field. In their work they were able to address several properties of this ion. They again found the ground state to have $\Omega = 5/2$ and the δ_u orbital to be lower than the ϕ_u orbital.

Nonempirical theoretical calculations on these ions are even more limited. Pershina and co-workers did scattered-wave X_α calculations for all the actinyl and dioxoactinide(1+) ions, including NpO_2^{+}, NpO_2^{2+}, and $NpO_2Cl_4^{2-}$.[28−31] Makhyoun[32] reported quasi-relativistic multiple-scattering X_α (MS-X_α) calculations for two neptunyl complexes, $NpO_2Cl_4^{2-}$ and $NpO_2(NO_3)_3^{-}$. These calculations were of modest accuracy, and the spin−orbit interaction was included only as a perturbation.

Calculations on NpO_2^{2+} and NpO_2^{+} have focused on the ground-state properties, and very little has been done about the electronic spectrum. In this work we calculate the electronic spectra of both ions using ab initio methods in an attempt to assign the transitions and explore the character of each electronic state.

Methods

In systems which include heavy elements such as neptunium, relativistic effects are very important and must be taken into account. An additional difficulty with heavy elements is the large number of electrons. Many methods have been developed over the years for the inclusion of relativistic effects in electronic structure calculations. A way to take care of the relativistic effects and also reduce the number of electrons that need to be treated explicitly is by using relativistic effective core potentials (RECPs). In this method, the core electrons are replaced by a potential derived from Dirac−Fock atomic calculations and only the valence electrons are treated explicitly. Spin−orbit operators are generated simultaneously from the atomic calculations. In our calculations we have used the RECPs developed by Christiansen and co-workers.[33] The neptunium core consists of the 78 1s through 5d electrons, and the oxygen core consists of the 2 1s electrons.

The basis sets are contracted Gaussian basis sets which have been developed in our group.[34] Traditionally, the basis sets for effective core potentials have been contracted the same way as the all-electron basis sets, by freeing some diffuse primitive functions. However, basis sets for RECPs describe pseudoorbitals, which are small in the core region. Freeing the most diffuse primitive does not give contracted orbitals that are small in the core region, especially for s orbitals. Alternative ways to do the contractions have been investigated,[34] and it was found that the most efficient way is by using natural orbitals from correlated atomic calculations. For Np we optimized the (sd, p, f) exponents at the HF level for the Np^{2+} ($5f^36d^2$) average of configurations. Trying to use 1s primitives led to multiple exponent collapses, so 3s primitives were used constrained to have the same exponents as the d primitives. The g polarization set was obtained by optimizing the exponent of a single g primitive in CISD calculations of the lowest state of the $5f^36d^2$ configuration, allowing for correlation of the 5f shell only. The resulting basis set is (4sd4p4f1g)/[3sd2p2f1g].

TABLE 1: Ground-State Neptunyl SCF Mulliken Population Analysis

	gross atomic populations					
atom	s	p	d	f	g	total
Np	2.040	5.567	1.454	3.593	0.000	12.655
O	3.861	8.419	0.062	0.000	0.000	12.341

We obtained the molecular orbitals from average-of-states SCF calculations of the states we were interested in. The SCF calculations do not include the spin−orbit interaction. We performed multireference spin−orbit configuration interaction (SOCI) calculations using a SOCI program based on the graphical unitary group approach (GUGA) formalism. This approach has been recently extended[35] and is expected to be in the next release of the COLUMBUS suite of programs, which was used for all the present calculations.[36]

For the ground-state calculations on both ions, all electrons were correlated. The references used were the $1\delta_u^1$ and $1\phi_u^1$ configurations for NpO_2^{2+} since both of them are essential for the ground state, as will be discussed later, and the $1\delta_u^1 1\phi_u^1$, $1\delta_u^2$, and $1\phi_u^2$ configurations for NpO_2^{+}. We calculated the potential energy surfaces close to the minima and fitted them to get the symmetric-stretch vibrational frequencies (ν_1). The resulting size of the calculations for NpO_2^{2+} was about 4 million double group functions (dgf) and for NpO_2^{+} about 6.5 million dgf. For the excited states many references needed to be included so the size of the calculations increased, and we had to freeze some of the electrons. For both ions the $1\sigma_g^2 2\sigma_g^2 1\sigma_u^2 1\pi_g^4$ electrons were frozen (uncorrelated). It was found that these orbitals were the least important in correlating the states of interest. The reference space consisted of all the states arising from the configurations $1\delta_u^1$, $1\phi_u^1$, $3\pi_u^1$, $3\sigma_u^1 1\delta_u^1 1\phi_u^1$, $3\sigma_u^1 1\delta_u^2$, and $3\sigma_u^1 1\phi_u^2$ for NpO_2^{2+} and $1\delta_u^1 1\phi_u^1$, $1\delta_u^2$, $1\phi_u^2$, $3\sigma_u^1 1\delta_u^3$, $3\sigma_u^1 1\delta_u^2 1\phi_u^1$, $3\sigma_u^1 1\delta_u^1 1\phi_u^2$, and $3\sigma_u^1 1\phi_u^3$ for NpO_2^{+}. We calculated the vertical transitions for 15 states in NpO_2^{2+} and 19 states in NpO_2^{+}. Even with a reduced number of correlated electrons, the size of the calculations approached 10 million dgf.

Results and Discussion

Np in NpO_2^{2+} is in the VI oxidation state and is an f^1 system. The bonding in neptunyl is very similar to that of uranyl, which has one less electron and is a closed-shell system.[37] The $3\sigma_g$, $3\sigma_u$, $1\pi_g$, and $2\pi_u$ occupied MOs are approximately degenerate and higher in energy than the other MOs. They have a considerable mixing of Np 6d and 5f atomic orbitals, with the $3\sigma_u$ having the largest Np 5f mixing; the population of Np 5f in $3\sigma_u$ is 1.285 (or 64.3% f character). The overall Mulliken population analysis is shown in Table 1. The "hole" observed in the U 6p shell[37−39] is also observed here, proving the participation of Np 6p electrons in the bonding. Np has a partial charge of +2.34, slightly lower than that of U in uranyl,[37] and each oxygen has a partial charge of −0.17.

As we discussed earlier, among the f orbitals in $D_{\infty h}$ symmetry, the $4\sigma_u$ and $3\pi_u$ are antibonding and are higher in energy than the $1\delta_u$ and $1\phi_u$ orbitals. The $4\sigma_u$ orbital proved to be much higher than the others and beyond the range of energies of interest, so we did not consider it further.

At the SCF level, where there is no spin−orbit coupling in our calculations, the $^2\Delta_u$ state was lower than $^2\Phi_u$ by a small amount, indicating that the δ_u orbital is lower than ϕ_u. Spin−orbit coupling splits both states, but splits $^2\Phi_u$ more than $^2\Delta_u$. If we assume an atomic ion model, then the splitting of $^2\Phi_u$ is 3/2 that of $^2\Delta_u$. Thus, the $^2\Phi_{5/2u}$ component can go lower than the $^2\Delta_{3/2u}$ component. Furthermore, second-order spin−orbit coupling will mix the states with the same Ω value, $^2\Delta_{5/2u}$ and $^2\Phi_{5/2u}$. The result will be a ground state with both ϕ and δ character, with the ϕ dominating. In an alternative way, in the atomic ion limit an f^1 configuration gives the terms $^2F_{5/2}$ and $^2F_{7/2}$, with $^2F_{5/2}$ being lower in energy.[26] In linear symmetry $^2F_{5/2}$ splits into $\Omega = 1/2$, 3/2, and 5/2 while $^2F_{7/2}$ splits into $\Omega = 1/2$, 3/2, 5/2, and 7/2. Only the $\Omega = 5/2$ and 7/2 wave functions are composed exclusively of the (low-energy) δ and ϕ orbitals; the first one, $\Omega = 5/2$, corresponds to the ground state, and the second, $\Omega = 5/2$, and third, $\Omega = 7/2$, correspond to the second and third excited states. The two wave functions with $\Omega = 3/2$ are composed of the π and δ orbitals; by mixing extensively to remove the (high-energy) π orbitals, they form one low-energy state which corresponds to the first excited state, but it is no longer an approximate eigenfunction of J^2. The $\Omega = 5/2$ component of $^2F_{5/2}$ will consist of δ and ϕ in a ratio of 1:6 according to Clebsch−Gordan coefficients. In our calculations the ground state is found to have $\Omega = 5/2$, and there is a strong mixing of $^2\Delta_{5/2u}$ and $^2\Phi_{5/2u}$ character, with 17% δ and 68% ϕ, the ratio being 1:4. The deviation from the atomic ion ratio of 1:6 is due to the different energies of the δ and ϕ orbitals. The δ orbital is lower and thus contributes more to the ground state than if the energies were equal.

Which one is the ground state proved to be sensitive to the $^2\Delta_u$−$^2\Phi_u$ splitting prior to spin−orbit coupling. If there is not enough correlation, this splitting is large and the spin−orbit interaction does not succeed in bringing the 5/2 state lower than the 3/2 state. If enough correlation is included, however, the splitting decreases and the $\Omega = 5/2$ state becomes the ground state. The electrons in the $3\sigma_u$ orbital are strongly correlated by the δ_u and ϕ_u orbitals, which are unoccupied or partially occupied in the excited states, since all three orbitals have substantial 5f character. The δ_u orbital is more efficient than the ϕ_u orbital in this regard because it is lower in energy and because its exchange integral with $3\sigma_u$ is larger. (Exchange integrals have the form of electrostatic self-interaction integrals of charge distributions equal to the product of the orbitals involved. The self-interaction of the δ_g charge distribution from $\sigma_u\delta_u$ is larger than that of the ϕ_g charge distribution from $\sigma_u\phi_u$ if their spatial extents are otherwise similar.) Thus, the correlation energy obtained by double excitations from the $3\sigma_u$ orbital for the $^2\Phi_u$ state was found to be almost double that obtained for the $^2\Delta_u$ state. Although the $3\sigma_u$ orbital contributes the largest amount to the differential correlation of these states, other excitations also contribute and their total contributions are significant.

The equilibrium bond distance r_e is found to be 1.66 Å, and the symmetric stretch vibrational frequency ν_1 is found to be 1059 cm^{-1}. There are no experimental values for the free ion. The values of r_e in different environments[11] vary from 1.71 to 1.77 Å, and the frequency varies from 800 to 863 cm^{-1}, making clear that the equatorial ligands affect these values significantly.

TABLE 2: Np−O Bond Distances, r_e, and Symmetric-Stretch Vibrational Frequencies, ν_1, for all the f^1 States and the First Charge-Transfer State of the Neptunyl Ion

state	Λ−*S* contributions	r_e (Å)	ν_1 (cm^{-1})
$5/2_u$	70% $^2\Phi_{5/2u}$ + 20% $^2\Delta_{5/2u}$	1.65	1054
$3/2_u$	$^2\Delta_{3/2u}$	1.64	1058
$5/2_u$	70% $^2\Delta_{5/2u}$ + 20% $^2\Phi_{5/2u}$	1.64	1069
$7/2_u$	$^2\Phi_{7/2u}$	1.65	1037
$1/2_u$	$^2\Pi_{1/2u}$	1.68	1005
$3/2_u$	$^2\Pi_{3/2u}$	1.68	1012
$7/2_u$	$^4H_{7/2u}$	1.70	874

There are two types of transitions in the spectrum of the neptunyl ion. First, the f → f transitions correspond to excitation of the single f electron in the ground state to another f orbital. Second, there are transitions similar to the ones observed in the uranyl ion, where an electron is excited from a filled MO to one of the f orbitals. These are ligand-to-metal charge-transfer transitions since the electron originally is in an orbital with substantial oxygen character, and then moves to a predominantly neptunium orbital. Which one of the (nearly degenerate) highest filled MOs, $3\sigma_g$, $3\sigma_u$, $1\pi_g$, $2\pi_u$, is the MO from which the excitations occur has been discussed for a long time.[5,6] It has been established experimentally that $3\sigma_u$ is the one that is responsible for these excitations in both uranyl and neptunyl ions.[6] In the Hartree−Fock approximation, the excitation energy from a closed-shell state, such as the ground state of UO_2^{2+}, to an excited state triplet, is $\epsilon_a - \epsilon_i - J_{ai}$ where a is a virtual orbital and i is a closed-shell orbital and J_{ai} is the coulomb integral between them;[40] the expression for excitation from a doublet ground state is similar. Thus, the closed-shell orbital involved in the lowest energy excitations will be the one with the largest coulomb integral with the virtual orbital. Since $3\sigma_g$, $3\sigma_u$, $1\pi_g$, and $2\pi_u$ are the high-lying orbitals and $3\sigma_u$ is the one which is the most concentrated on the Np atom, excitations from this orbital should give the largest coulomb integral and therefore the lowest energy excited states. We carried out singles-only CI calculations (CIS) and found that the lowest energy transitions are from the $3\sigma_u$ orbital and excitations from the other orbitals have much higher energies. For the uranyl ion the states arising from excitations from the $3\sigma_g$ orbital have been measured[41] as well as calculated,[37] and they were found to start at 37 100 cm^{-1}.

An important difference between these two kinds of states is the shift of the Np−O equilibrium distance and the vibrational frequencies. Excitation of a bonding electron to a nonbonding orbital decreases the strength of the bond, with a subsequent lengthening of the bond and lowering of ν_1. This difference enables one to distinguish the different states in the spectrum, since whenever there is a shift in r_e, there is a progression in the spectrum and the bands are broad. We have investigated this feature by finding the equilibrium distance r_e and symmetric stretch vibrational frequency ν_1 for each state. These calculations were done with less correlation than the ones for calculating the vertical transitions in the spectrum, since we were only interested in the relative trends and correlating more electrons would be prohibitably expensive for calculating many points on the potential surface. So, in addition to the $1\sigma_g^2 2\sigma_g^2 1\sigma_u^2 1\pi_g^4$ electrons, the $1\pi_u^4 2\sigma_u^2 3\sigma_g^2$ electrons were also frozen, leaving only seven active electrons. The results for all the f states and the first charge-transfer state are reported in Table 2. It is seen that the first four states, which are mostly δ_u, and ϕ_u, have very similar r_e and ν_1, the states with mostly π_u character (antibonding) have increased r_e and decreased ν_1, and the charge-transfer states have even longer r_e and smaller ν_1.

The vertical transitions for all the states calculated are shown in Table 3 along with the experimental transitions for the neptunyl ion doped into $Cs_2UO_2Cl_4$ and $CsUO_2(NO_3)_3$.[22,23] The calculations were done at $r_e = 1.66$ Å, which is the minimum of the ground state at this level of calculation. The agreement

TABLE 3: Spectrum of Neptunyl[a]

state	$\Lambda-S$ term (configuration)	T_e (cm^{-1})	$Cs_2NpO_2Cl_4$[22,23] (cm^{-1})	$CsNpO_2(NO_3)_3$[22,23] (cm^{-1})
$5/2_u$	68% $^2\Phi_{5/2u}$ + 17% $^2\Delta_{s/2u}$	0	0	0
$3/2_u$	85% $^2\Delta_{3/2u}$	447	1000	
$5/2_u$	69% $^2\Delta_{5/2u}$ + 17% $^2\Phi_{5/2u}$	5 515	6 880.4	6 459.0
$7/2_u$	85% $^2\Phi_{7/2u}$	6 565	7 990	9 420.2
$7/2_u$	85% $^4H_{7/2u}$ $(\sigma_u\delta_u\phi_u)^b$	12 622	13 264.9	13 918.1
$9/2_u$	83% $^4H_{9/2u}$ $(\sigma_u\delta_u\phi_u)^b$	15 418	15 683	16 092.6
$1/2_u$	60% $^4\Sigma^-_{1/2u}$ $(\sigma_u\delta_u^2)^b$	15 668	15 406.4	16 072.5
$3/2_u$	65% $^4\Sigma^-_{3/2u}$ $(\sigma_u\delta_u^2)^b$	16 664	16 799.8	17 967.7
$11/2_u$	85% $^4H_{11/2u}$ $(\sigma_u\delta_u\phi_u)^b$	18 676		
$1/2_u$	52% $^4\Pi_{1/2u}$ + 24% $^4\Pi_{-1/2u}$ $(\sigma_u\delta_u\phi_u)^b$	21 580	19 375.2	19 510.2
$13/2_u$	86% $^4H_{13/2u}$ $(\sigma_u\delta_u\phi_u)^b$	21 925		
$3/2_u$	60% $^4\Pi_{3/2u}$ $(\sigma_u\delta_u\phi_u)^b$	22 230		
$1/2_u$	55% $^4\Pi_{-1/2u}$ + 16% $^4\Pi_{1/2u}$ $(\sigma_u\delta_u\phi_u)^b$	22 469		
$5/2_u$	86% $^4\Pi_{5/2u}$ $(\sigma_u\delta_u\phi_u)^b$	23 882		
$1/2_u$	85% $^2\Pi_{1/2u}$	25 844	17 241.4	17 843.6
$3/2_u$	84% $^2\Pi_{3/2u}$	28 909	20 080.8	20 816.3

[a] Vertical transitions at $r_e = 1.66$ Å. [b] Charge-transfer state.

TABLE 4: Np−O Bond Distance, r_e, and Symmetric-Stretch Vibrational Frequency, ν_1, of the NpO_2^{2+} and NpO_2^+ Ions

	r_e (Å)	ν_1 (cm^{-1})
NpO_2^{2+}	1.66 (1.72−1.77[11])	1059 (800−863[22])
NpO_2^+	1.73 (1.83−1.86[11,12])	913 (767[9])

TABLE 5: Ground-State NpO_2^+ SCF Mulliken Population Analysis

	gross atomic populations					
atom	s	p	d	f	g	total
Np	2.044	5.669	1.353	3.981	0.000	13.047
O	3.866	9.041	0.043	0.000	0.000	12.950

with experiment is satisfactory in all but the Π states. The first charge-transfer state is at 12 622 cm^{-1}, much lower than the corresponding transition in the uranyl ion (near 20 000 cm^{-1}). This is a $^4H_{7/2u}$ state, the lowest state of a $\sigma_u^1\,\delta_u^1\,\phi_u^1$ configuration according to Hund's rules. All the charge-transfer states that we calculated up to 24 000 cm^{-1} are predominantly quartets, from either a $\sigma_u^1\,\delta_u^1\,\phi_u^1$ or a $\sigma_u^1\,\delta_u^2$ configuration showing that the exchange part of the energy is dominant in determining the order of the states.

One of the charge-transfer excited states is $\sigma_u^1\,\delta_u^1\,\phi_u^1\ {}^4\Pi_u$, which in isolation would have components, in energy order, of $^4\Pi_{-1/2u}$, $^4\Pi_{1/2u}$, $^4\Pi_{3/2u}$, and $^4\Pi_{5/2u}$. The −1/2 and 1/2 components do not mix directly but do mix indirectly through the states $^2\Sigma^+_{1/2u}$, $^2\Sigma^-_{1/2u}$, and $^4\Sigma^-_{1/2u}$ arising from the $\sigma_u\delta_u^2$ and $\sigma_u\phi_u^2$ configurations. This mixing is extensive and results in a lowest state with majority 1/2 character.

In NpO_2^+ the two f electrons can occupy either one or two of the nonbonding orbitals. We have found the ground state to come from the $\delta_u^1\,\phi_u^1$ configuration. This configuration gives rise to states $^3H_{4,5,6}$, $^3\Pi_{0^+,0^-,1,2}$, $^1H_5$, and $^1\Pi_1$ in $\Lambda-S$ coupling. The ground state has $\Omega = 4$. The same has been observed experimentally and theoretically for the isoelectronic PuO_2^{2+}.[25,27,42] In agreement with experiment, the bond distance in this case is longer than for the 2+ ion, and ν_1 is smaller, demonstrating the weakening of the bond. Table 4 shows these properties for both ions.

The Mulliken population analysis in shown in Table 5. Notice that the partial charge in Np here is +1.9 and the reduction from the Np charge in neptunyl is less than a whole unit.

With two f orbitals occupied in the ground state, there are many more f → f transitions. We have calculated 15 excited states of this type from the $\delta_u^1\,\phi_u^1$, δ_u^2, and ϕ_u^2 configurations. In addition there are charge-transfer transitions, similar to the ones for the neptunyl ion. Due to its lower charge, Np here is less oxidizing and the charge-transfer transitions are expected to be at higher energies. We have calculated the lowest transition of this type to be at 23 079 cm^{-1}, indeed much higher than the first transition of this type in NpO_2^{2+}. Experimentally it has also been observed at approximately the same energy.[43] This state and all the other charge-transfer states that we calculated have predominantly $\sigma_u^1\,\delta_u^2\,\phi_u^1\ {}^5\Phi_g$ character. All the states calculated are shown in Table 6, along with the most important $\Lambda-S$ contributions and configurations.

TABLE 6: Spectrum of NpO_2^+ [a]

state	$\Lambda-S$ term (configuration)	T_e (cm^{-1})
4_g	84% $^3H_{4g}$ $(\delta_u\phi_u)$	0
0_g^+	42% $^3\Sigma^-_{0^+g}$ $(\delta_u\delta_u)$ + 17% $^3\Sigma^-_{0^+g}$ $(\phi_u\phi_u)$ + 15% $^3\Pi_{0^+g}$ $(\delta_u\phi_u)$	3 366
5_g	86% $^3H_{5g}$ $(\delta_u\phi_u)$	4 721
1_g	40% $^3\Sigma^-_{1g}$ $(\delta_u\delta_u)$ + 26% $^3\Pi_{lg}$ $(\delta_u\phi_u)$	4 938
6_g	84% $^3H_{6g}$ $(\delta_u\phi_u)$	8 867
1_g	30% $^3\Pi_{1g}$ $(\delta_u\phi_u)$ + 24% $^3\Sigma^-_{1g}$ $(\delta_u\delta_u)$ + 20% $^1\Pi_{1g}$ $(\delta_u\phi_u)$	9 076
0_g^-	85% $^3\Pi_{0^-g}$ $(\delta_u\phi_u)$	9 537
0_g^+	61% $^3\Pi_{0^+g}$ $(\delta_u\phi_u)$ + 17% + $^1\Sigma^+{}_{0+g}$ $(\delta_u\delta_u)$	9 708
2_g	85% $^3\Pi_{2g}$ $(\delta_u\phi_u)$	11 187
0_g^+	53% $^1\Sigma^+_{0^+g}$ $(\delta_u\delta_u)$ + 28% $^3\Sigma^-_{0^+g}$ $(\delta_u\delta_u)$	14 415
4_g	84% $^1\Gamma_{4g}$ $(\delta_u\delta_u)$	15 249
1_g	47% $^1\Pi_{1g}$ $(\delta_u\phi_u)$ + 26% $^3\Pi_{1g}$ $(\delta_u\phi_u)$	16 156
0_g^+	59% $^3\Sigma^-_{0^+g}$ $(\phi_u\phi_u)$ + 12% $^1\Sigma^+_{0^+g}$ $(\delta_u\delta_u)$	19 647
1_g	57% $^3\Sigma^-_{1g}$ $(\phi_u\phi_u)$ + 16% $^3\Sigma^-_{1g}$ $(\delta_u\delta_u)$	21 672
5_g	85% $^1H_{5g}$ $(\delta_u\phi_u)$	22 031
1_g	83% $^5\Phi_{1g}$ $(\sigma_u\delta_u^2\phi_u)^b$	23 079
6_g	84% $^1I_{6g}$ $(\phi_u\phi_u)$	23 327
2_g	79% $^5\Phi_{2g}$ $(\sigma_u\delta_u^2\phi_u)^b$	23 649
3_g	78% $^5\Phi_{3g}$ $(\sigma_u\delta_u^2\phi_u)^b$	24 834
4_g	82% $^5\Phi_{4g}$ $(\sigma_u\delta_u^2\phi_u)^b$	26 592

[a] Vertical transitions calculated at $r_e = 1.72$ Å. [b] Charge-transfer state. The contribution of a $\Lambda-S$ term in the wave function was cut off at 12%.

One of the most important characteristics of the absorption spectrum of NpO_2^+ is an intense peak at about 10 200 cm^{-1}.[19] A similar transition is present in the plutonyl ion.[19] This high intensity has raised questions as to its nature. In $D_{\infty h}$ symmetry all transitions are g → g and therefore electric dipole forbidden, so a mechanism that would allow these transitions to occur would be a magnetic dipole or electric quadrupole transition. A magnetic dipole mechanism allows transitions with $\Delta\Omega = 0$

and ±1, while an electric quadrupole mechanism allows $\Delta\Omega = 0, \pm1$, and ±2. In our calculated spectrum the state that seems closest to these requirements is the 2_g ($^3\Pi_{2g}$) at 11 187 cm^{-1}. An alternative explanation that has been suggested[44] uses the fact that the ion in all experimental spectra is surrounded by ligands. These ligands may induce an electric dipole mechanism if they destroy the center of inversion. To be able to give a definite answer to this problem, we need to be able to calculate the electric dipole, magnetic dipole, and electric quadrupole transition moments. Currently we are developing the necessary programs for these calculations.

A question that arises often in the study of these systems is how important the spin−orbit coupling is, especially for ground-state properties. For the spectrum, it is clear that it can affect the transitions dramatically and should always be included. But for some properties of the ground state there is less of an effect. We performed the same calculations with and without spin−orbit coupling, for the neptunyl ion, to determine its importance. The equilibrium Np−O bond distance decreased by 0.01 Å and ν_1 increased by about 30 cm^{-1}, not a very large effect. But the character of the ground state was different. As explained earlier, the ground state of neptunyl has a very strong mixing of both δ_u and ϕ_u character, due to spin−orbit coupling. When the coupling is not there, the ground state is $^2\Delta_u$, which is not correct. So, the spin−orbit interaction is not so important for the ground-state potential curve but is very important for other things. For uranyl, which is a closed-shell system, the spin−orbit interaction affects the character of the ground state even less.

Conclusions

The most important species of Np in aqueous solution, NpO_2^{2+} and NpO_2^{+}, have been studied in this work. The Np−O bond distance, r_e, for both ions is about 0.1 Å smaller than experimental values, and the symmetric-stretch vibrational frequencies, ν_1, about 150 cm^{-1} larger, but most of this difference is believed to be due to the environment of the ions in the different experiments. The vertical transition energies for 15 excited states for NpO_2^{2+} and 19 for NpO_2^{+} have been calculated, as well as the character of the wave function for each state.

Future work includes taking into account the crystalline environment where most of the experimental studies have been done. We have already started an effort to place NpO_2^{2+} in the crystal $Cs_2UO_2Cl_4$ and repeat the calculations to observe the effect of this environment. Additionally, to better understand the spectrum of NpO_2^{+} and to assign the states with confidence, we are developing a program to calculate the transition moments of various types and thus calculate the intensities.

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