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Edelstein, Norman M

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Reanalysis of the Aqueous Spectrum of the Neptunyl(V) [NpO₂⁺] Ion

Norman M. Edelstein

Chemical Sciences Division, MS 70A-1150, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

ABSTRACT: The actinyl ions, consisting of the dioxoactinide(VI) and dioxoactinide(V) ions, are unique in the periodic table. However, very few quantitative studies of the spectra of these ions have been performed. In this paper the analysis of the optical spectrum of the aqueous neptunyl(V) [NpO₂⁺] ion in 1 M HClO₄ is reexamined. The species in solution is assumed to be the linear NpO₂⁺ ion surrounded in the equatorial plane by five oxygen atoms from five H₂O molecules. The neptunyl(V) ion has the 5f² open-shell configuration, and the low-lying optical transitions (up to ~20 000 cm⁻¹) observed are primarily from the two 5f electrons occupying the 5f ϕ and 5f δ orbitals. The conventional parametric theory used for fⁿ systems is applied to these low-lying transitions utilizing the intensity calculations that Matsika et al.¹ have performed for this ion and the data reported by Eisenstein and Pryce.² Possible ratios for the Slater electrostatic repulsion parameters are obtained from the data for the isoelectronic ion U⁴⁺ (5f²) in various host crystals. The results are consistent with earlier crystal field analyses of the 5f¹ neptunyl(VI) [NpO₂²⁺] ion.

	A	B	C
$\epsilon_{\delta} - \epsilon_{\phi}$	-1994.5	253.	-1404
$\epsilon_{\pi} - \epsilon_{\phi}$	12626.0	12034	11787
$\epsilon_{\sigma} - \epsilon_{\phi}$	40000.0	48555	69179

Units - cm⁻¹A - Denning et al., 1982 Cs₂NpO₂Cl₄
diluted in Cs₂UO₂Cl₄B - Eisenstein and Pryce, 1966
NpO₂⁺ aqueousC - This work - NpO₂⁺ aqueous

■ INTRODUCTION

The actinyl ions, AnO₂ⁿ⁺ with $n = 1$ or 2 and $An = U, Np, Pu, Am$, have a unique structure and properties. The free U atom, which is the first member of the series, has the electronic configuration outside the closed radon shell, 5f⁶6d¹7s². These six electrons form covalent bonds with two oxygen atoms, one each on either side of the uranium atom, to create a linear molecular ion with a 2+ charge, [O=U=O]²⁺.^{3,4} In aqueous solution and in the gas phase much weaker bonds form with other ligands in the equatorial plane. The uranyl(VI) ion is stable in aqueous solution and difficult to reduce to the uranyl(V) state. For Np, the neptunyl(V) ion is the most stable species in aqueous solution. For the elements Pu and Am the most stable oxidation states in aqueous solution are the Pu⁴⁺ and Am³⁺ aquo ions, respectively, but the actinyl(V) and actinyl(VI) species can be formed for these elements. No actinyl structures have been observed for the trans-actinium elements.

Eisenstein and Pryce,^{2,5-7} in a series of classic publications, addressed the electronic structure of the actinyl ions [uranyl(VI) (UO₂²⁺), neptunyl(VI) (NpO₂²⁺), neptunyl(V) (NpO₂⁺), plutonyl(VI) (PuO₂²⁺)] and formulated methods to analyze their optical and magnetic properties. Denning and co-workers⁸⁻¹⁰ measured and analyzed the optical spectra of charge-transfer bands of the uranyl ion (from the primarily ligand-filled σ and π orbitals to the empty 5f and 6d orbitals). They also studied the 5f-to-5f transitions as well as the charge-transfer bands for the neptunyl(VI) ion (NpO₂²⁺, 5f¹)^{11,12} diluted in single crystals of Cs₂UO₂Cl₄ and CsUO₂(NO₃)₃. Gorshkov and co-workers^{13,14} also performed optical studies on the neptunyl(VI) and plutonyl(VI) ions diluted in Cs₂UO₂Cl₄. More recently, near-infrared fluorescence of the neptunyl(VI) ion in the solid state and solution¹⁵⁻¹⁷ and the plutonyl(VI) ion in the solid state¹⁸ has been reported.

The relative simplicity of the electronic configuration of the uranyl(VI), neptunyl(V), and plutonyl(VI) ions has made them

an attractive subject for ab initio calculations. These calculations have been published,^{1,19-25} and some utilized the assignments of Eisenstein and Pryce² for comparison with their theoretical results. One important study by Matsika et al.¹ calculated the intensities of the formally forbidden 5f-5f electric dipole transitions for the aqueous NpO₂⁺ ion using a crystal field configuration interaction model.

The aqueous actinyl ions, namely, neptunyl(V) (NpO₂⁺) and plutonyl(VI) (PuO₂²⁺), have the electronic configuration 5f² outside the closed shell. Unlike other lanthanide and actinide complexes with the 4f² or 5f² configuration, the strong axial bond of the actinyl complexes is on the order of the Coulomb repulsion (electrostatic interaction) between the two f electrons, which means the usual approximation for treating the electronic spectra of 4fⁿ and 5fⁿ complexes (the Coulombic interaction > spin-orbit interaction > crystal field interaction) is not applicable.

In this paper we will utilize the intensity calculations of Matsika et al.¹ and reassign the measured optical spectra of the aqueous neptunyl(V) (the NpO₂⁺ ion) using the parametric theory (effective Hamiltonian) that has been so successful in treating 4fⁿ and 5fⁿ ions in crystals and solution.²⁶

■ REVIEW OF THEORY

The uranyl ion has no 5f electrons, the neptunyl(VI) ion has one 5f electron, and neptunyl(V) ion has two 5f electrons outside the closed shells. Assuming no equatorial coordination, the symmetry of this molecular ion is axial ($D_{\infty h}$), so the f orbitals (for an f electron $l = 3$, and $m_l = 0, \pm 1, \pm 2, \pm 3$) will split into $\sigma_w, \pi_w, \delta_w$ and ϕ_w orbitals, corresponding to $m_l = 0, \pm 1, \pm 2, \pm 3$ orbitals. The 6d ($l = 2$) orbitals will split in a similar fashion. The 5f σ and π (and the 6d) orbitals will interact with

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the O 2p orbitals to form covalent bonds. The net result for the uranyl ion is that the nonbonding δ_u and φ_u orbitals (within the $5f^2$ configuration) will be the lowest unoccupied orbitals, and the $5f \sigma_u$ and π_u antibonding states will be significantly raised in energy. The $5f \sigma$ orbitals form the strongest covalent bond, and thus $5f\sigma_u$ will be higher in energy than the $5f\pi_u$ level. For the neptunyl(V) ion under consideration here, we have two $5f$ electrons outside the closed shell of the UO_2^{2+} ion, which we treat as an isolated $5f^2$ core similar to the calculations of Eisenstein and Pryce.² A succinct summary of the current knowledge of bonding in the actinyl ion is given in a recent review by Neidig, Clark, and Martin.²⁷

Aside from the transitions within the $5f^2$ configuration, there are relatively weak transitions that arise from the bonding levels of the actinyl ion and are assigned as charge-transfer transitions. Such transitions have been measured by Denning et al. for the UO_2^{2+} and the NpO_2^{2+} ions.^{10,12} For the UO_2^{2+} ion these transitions are observed above $20\,000\text{ cm}^{-1}$. However, for the NpO_2^{2+} ion diluted in $\text{Cs}_2\text{UO}_2\text{Cl}_4$, these transitions begin at $\sim 12\,300\text{ cm}^{-1}$.¹² Gorshkov et al.¹⁴ also observed these transitions for the PuO_2^{2+} ion (diluted in $\text{Cs}_2\text{UO}_2\text{Cl}_4$) above $15\,000\text{ cm}^{-1}$. For the NpO_2^+ ion, Matsika and Pitzer²³ calculate that these electron transfer transitions begin at $\sim 23\,000\text{ cm}^{-1}$. Thus, the assignment of the spectra of NpO_2^+ ion in aqueous solution below $20\,000\text{ cm}^{-1}$ can be attributed primarily to transitions within the $5f^2$ configuration.

■ PHENOMENOLOGICAL THEORY

For the analysis of an f^2 ion, the observed energy levels can be fitted to a phenomenological Hamiltonian $H = H_{\text{FI}} + H_{\text{CF}}$ by a simultaneous diagonalization of the free-ion Hamiltonian H_{FI} and the crystal field Hamiltonian H_{CF} . The free-ion Hamiltonian is given as follows:

$$H_{\text{FI}} = \sum_{k=0,2,4,6} F^k(nf, nf)f_k + \zeta_f\alpha_{so} \quad (1)$$

where $F^k(nf, nf)$ and ζ_f represent the radial parts of the electrostatic and spin-orbit interaction, respectively, between f electrons, and f_k and α_{so} are the angular parts of these interactions. For the different interactions the angular parts can be evaluated exactly; the radial parts, F^k and ζ_f , the Slater and spin-orbit coupling parameters, respectively, are evaluated empirically.^{28,29}

The crystal field Hamiltonian is expressed in terms of the phenomenological crystal field parameters B_q^k and the angular tensor operators C_q^k as follows:

$$H_{\text{CF}} = \sum_{k,q,i} B_q^k(C_q^k)_i \quad (2)$$

where the sum involving i is over all the f electrons. The values of k and q are limited by the point symmetry of the f^2 ion site. For states of the same parity, k will have only even values. The term for which $k = 0$ and $q = 0$ shifts all levels of an f^2 configuration equally and is not utilized in fitting levels within one configuration.³⁰ For the actinyl ions it is convenient to define the crystal field Hamiltonian as

$$H_{\text{CF}} = H_{\text{axialCF}} + H_{\text{equatCF}} \quad (3)$$

with the axial crystal field defined as

$$H_{\text{axialCF}} = B_0^2 + B_0^4 + B_0^6 \quad (4)$$

We will discuss the symmetry and magnitude of the H_{equatCF} in the next section.

Within an f^2 configuration, all f^i to f^i electric dipole transitions are formally forbidden as there must be change of parity for the transitions to be allowed. Non-centrosymmetric interactions, such as those caused by the odd vibrations of an f^2 complex and/or odd terms in the crystal field potential, induce non-centrosymmetric crystal fields, which can mix in states of electronic configurations of opposite parity to the f^2 configuration. These induced electric dipole transitions are much weaker than allowed electric dipole transitions. For the usual f^2 configurations, these transitions may be quantified by the use of the Judd–Ofelt theory.³¹ Matsika et al.¹ developed a five-coordinate equatorial crystal field model with both five chloride ions and five H_2O molecules to calculate theoretical transition intensities for the neptunyl(V) ion.

Eisenstein and Pryce² utilized as their basis set for the two $5f$ electrons the products of two one-electron wave functions that were antisymmetrized in accordance with the Pauli principle. Each of these one-electron wave functions correspond to $m_l = 0, \pm 1, \pm 2, \pm 3$ and $m_s = \pm 1/2$. For two equivalent f electrons, 91 states can be formed. Eisenstein and Pryce² calculated the angular matrix elements of the Hamiltonians of eq 1 and 2 in this basis set and fit the radial parameters (F^2, F^4, F^6, ζ_f) and the crystal field parameters (B_0^2, B_0^4 , and B_0^6) plus one equatorial crystal field parameter, B_6^6 , to the energy levels that they assigned in the experimental spectra. In 1966, when they published this work, the computing capability was extremely limited. We can easily perform these calculations with the complete basis set chosen by Eisenstein and Pryce² and in the more usual SLJz basis set where a number of computer programs are readily available.

For the neptunyl(V) ion, only the lower states, which primarily consist of $5f^2$ energy levels from the δ_u and φ_u orbitals, can be reliably fit using an f^2 effective Hamiltonian. As mentioned earlier, in the Eisenstein and Pryce model of strong σ bonding in the actinyl linear molecular ion, the σ electrons ($m_l = 0$) are utilized in bonding, and the antibonding $f\sigma$ orbitals are shifted much higher in energy. To a lesser extent, π bonding ($m_l = \pm 1$) also shifts the antibonding π orbitals to higher energies. The energy levels at lower energies are from the two nonbonding δ and φ orbitals ($m_l = \pm 2$ and/or $m_l = \pm 3$) and should be amenable to the parametric analysis given by Eisenstein and Pryce and extended in this paper. Thus, the primary terms in the wave functions for the lower states in this work will be built from these φ and δ orbitals with possible π orbital contributions to some higher-lying states.

■ DETAILS OF THE CALCULATIONS

Eisenstein and Pryce² assumed that the symmetry of the aqueous actinyl species was D_{6h} , that is in the coordination sphere of the equatorial plane of the actinyl species, there were six oxygen atoms from six coordinated water molecules perpendicular to the $\text{O}=\text{An}=\text{O}$ bond. More recent theoretical calculations and experimental evidence from EXAFS measurements and spectroscopic data^{32,33} strongly suggest that in this coordination sphere the number of H_2O molecules is five. Matsika et al.¹ used a model with five water molecules in the nearest neighbor equatorial plane in order to calculate the electric dipole intensities. In our work we have assumed the actinyl ion is surrounded by five H_2O molecules, therefore the symmetry of the crystal field is D_{5h} . The major components of the crystal field are from the axial terms, B_0^2, B_0^4 , and B_0^6 . Adding

a crystal field of D_{5h} symmetry would give one more crystal field parameter, B_5^6 . However, given the fact that the data we are analyzing are taken in solution at room temperature, are rather broad, and that B_5^6 is much smaller than the axial terms, we have neglected the B_5^6 term in the following energy analysis. In fact B_5^6 appears to be so small that no splittings are observed in the aqueous spectrum as shown by the assignments of all observed transitions (except for two very weak features) up to $\sim 17\,000\text{ cm}^{-1}$. Only the E_{5g} states will split in a crystal field with D_{5h} symmetry (see Table 1) and with our assignments there is only

Table 1. Group Theory Labeling of States for a Crystal Field of $D_{\infty h}$ and for a Descent in Symmetry to D_{5h} ^a

$D_{\infty h}$ ^b	D_{5h} ^b	$D_{\infty h}$ m_j value	$D_{\infty h}$ J_z value
A_{1g}	A_1'	0	0
A_{2g}	A_2'	0	0
E_{1g}	E_1''	± 1	± 1
E_{2g}	E_2'	± 2	± 2
E_{3g}	E_2''	± 3	± 3
E_{4g}	E_1'	± 4	± 4
E_{5g}	$A_1'' + A_2''$	± 5	± 5
E_{6g}	E_1'	± 6	± 6

^aThe corresponding values for m_j in the (m_1, m_s, m_2, m_3) basis set and J_z in the SLJz representations are given. ^bReference 39.

one $J = 5$ state observed. This is the rather sharp feature at 6100 cm^{-1} noted in Waggener's paper³⁴ with no evidence of any splitting. The B_5^6 term is essential for intensity calculations in providing the mechanism by which states of opposite parity can be mixed into the ground $5f^2$ state to allow nonzero electric dipole transitions.¹

We performed the calculations in two ways. First, following Eisenstein and Pryce,² we calculated the matrix elements of the electrostatic, the spin-orbit coupling, and the crystal field interactions, in the (m_1, m_s, m_2, m_3) basis set using the complete 91 basis states that can be formed. These matrix elements can be factored into smaller submatrices, but we just diagonalized the entire matrix as this is fast and easy. We also performed the same calculations (and did the parametric fitting) in the usual SLJz basis states utilizing the Reid set of programs³⁵ as well as the set of programs used in our earlier investigations. Our starting point was the set of parameters we obtained from Eisenstein and Pryce,² setting $B_5^6 = 0$. We then correlated the strongest features in the optical spectrum for the neptunyl(V) (NpO_2^+) ion with the calculated intensities from Matsika et al.¹ and allowed the free ion parameters and then the crystal field parameters to vary.

With a strong axial crystal field, $D_{\infty h}$, the "good" quantum number is m_j in the (m_1, m_s, m_2, m_3) basis set where $m_j = (m_1 + m_s + m_2 + m_3)$. In the SLJz representation J_z is the good quantum number. The only ambiguity in this representation is for $m_j = 0$ or for $J_z = 0$ as there are two possible assignments for this quantum number as shown in Table 1. For the states E_{ng} ($n = 1-6$) each of the states is doubly degenerate. For the E_{ng} states shown later, only one of the states is given. In the (m_1, m_s, m_2, m_3) basis, the second degenerate state may be obtained by changing the m_1 and m_2 to $-m_1$ and $-m_2$, and also changing m_s and m_3 to $-m_s$ and $-m_3$. For the E_{ng} states in the SLJz representation, the degenerate state can be obtained by changing J_z to $-J_z$.

The Ground Term. There are two reports of the electron paramagnetic resonance spectra (EPR) of the PuO_2^{2+} ion in

single crystals of $\text{NaPuO}_2(\text{C}_2\text{H}_3\text{O}_2)_3$ ³⁶ with $g_{\parallel} \approx 5.9$ and $g_{\perp} \approx 0$ and diluted into single crystals of $(\text{UO}_2)\text{Rb}(\text{NO}_3)_3$ ³⁷ with $g_{\parallel} \approx 5.32$ and $g_{\perp} \approx 0$. Here we follow the arguments of Eisenstein and Pryce⁶ and of Abragam and Bleaney.³⁸ For the $5f^2$ configuration outside the closed shell of the plutonyl(VI) ion, (the same arguments can be used for the isoelectronic ion neptunyl(V), NpO_2^+) there will be a strong exchange interaction, so the spins on each 5f electron will be parallel. Therefore, the ground state will be (in the (m_1, m_s, m_2, m_3) representation) $(+3- +2-)$ and its degenerate pair $(-3+ -2+)$. For this configuration $M_L = 5$ and $M_S = -1$ (or $M_L = -5$ and $M_S = +1$). g_{\parallel} can be calculated from the Zeeman operator as follows: $|g_{\parallel}| = 2 \times (L_z + 2S_z)$, where $L_z = M_L = m_1 + m_2 = 5$ (or -5) and $S_z = M_S = m_s + m_3 = -1$ (or $+1$) so $|g_{\parallel}| = 6$ and g_{\perp} is necessarily 0 as there are no states that differ by ± 1 . To obtain better agreement with the experimental values, an orbital reduction factor can be included in the Zeeman operator for the orbital moment so that this operator becomes $kL_z + 2S_z$. The experimental g values can be fit with values of $k = 0.99$ for the plutonyl sodium acetate and $k = 0.93$ for the plutonyl(VI) ion in $(\text{UO}_2)\text{Rb}(\text{NO}_3)_3$. These EPR measurements establish the ground term as the degenerate pair $M_L = 5$ and $M_S = -1$ (or $M_L = -5$ and $M_S = +1$), which in $D_{\infty h}$ symmetry is labeled as an E_{4g} state. We assume the ground state for the neptunyl(V) ion will be the same as found for the plutonyl(VI) ion.

The Neptunyl(V) Optical Spectrum. Figure 1 shows the optical spectrum of the neptunyl(V) ion in 1 M HClO_4 . The

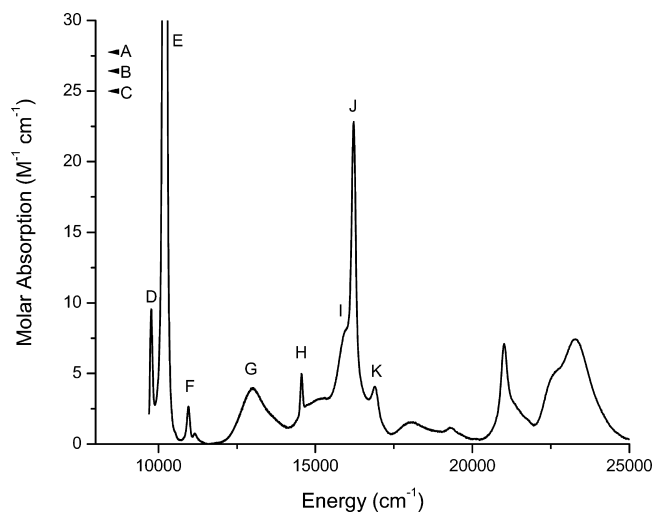


Figure 1. Optical spectrum of NpO_2^+ in 1 M HClO_4 (Courtesy of Dr. Linfeng Rao). The letters A–K in the figure represent the assignments shown in Table 4.

solution spectra are quite broad, and there are a number of overlapping lines. The spectrum and line list have been given in the work of Matsika et al.¹ and in Eisenstein and Pryce.² For most of our assigned levels, our list and that of Matsika et al. and of Eisenstein and Pryce² agree to better than 20 cm^{-1} . For one line which overlaps strongly with another, the agreement is on the order of 100 cm^{-1} , but because of the overlap there is a large uncertainty for this level. We chose to use the values given by Eisenstein and Pryce² in this paper. We include all their assigned levels up to $17\,000\text{ cm}^{-1}$ except for two very weak transitions at $11\,160$ and $13\,824\text{ cm}^{-1}$. Our assigned levels are indicated by letters in Figure 1. Note that we are fitting only a relatively small region of the $5f^2$ energy levels that extends to

Table 2. Slater, Spin–Orbit, and Crystal Field Parameters for Selected Actinyl Ions from Previous Studies and Present Results

parameters	Cs ₂ NpO ₂ Cl ₄ ^a	Cs ₂ NpO ₂ Cl ₄ ^a	CsNpO ₂ (NO ₃) ₃ ^a	CsNpO ₂ (NO ₃) ₃ ^a	NpO ₂ ²⁺ ^b	NpO ₂ ²⁺ ^c
	fit I (cm ⁻¹)	fit II (cm ⁻¹)	fit I (cm ⁻¹)	fit II (cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)
ζ_f	2196.1	2118.15	2212.0	2047.3	2090.	2069.1
F ²					49 387.5	46 801
F ⁴					44 877.7	44 823
F ⁶					34 430.4	29 869
B ₀ ²	95 360.8	42 099.3	96 265.	48 050	47 576	62 043
B ₀ ⁴	157 940.3	62 823.2	158 729	69 318	66 826	98 209
B ₀ ⁶	173 337.6	36 891	170 829	44 405.6	56 932	94 073
ϵ_φ	0	0	0	0	0	0
$\epsilon_\delta - \epsilon_\varphi$	-1932.0	-1994.5	-2074.5	-1366.0	253.	-1404
$\epsilon_\pi - \epsilon_\varphi$	13 003.45	12 626.0	13 847.0	14 179.8	12 034	11 787
$\epsilon_\sigma - \epsilon_\varphi$	114 000.0	40 000.0	114 000.0	46 000.0	48 555	69 179

^aReference: Denning et al.¹¹ We are not including the off-diagonal crystal field parameters given by Denning et al. as they give only small shifts and split the degeneracy of some energy levels. ^bParameters from the fit of optical spectra of the actinyl ions in aqueous solution by Eisenstein and Pryce.² ^cThis work. This is a compilation of the three fits given in Table 5. The estimated errors for the parameters from these fits are shown in Table 5.

Table 3. Free Ion Parameters for the U⁴⁺ Free Ion and for U⁴⁺ in Compounds^a

U ⁴⁺ parameters	[U(Br ₆) ²⁻	UCl ₄	UCl ₄	U(BD ₄) ₄ /	U ⁴⁺	U ⁴⁺ /	U ⁴⁺ /	U ⁴⁺ /	average
	cm ⁻¹	cm ⁻¹	cm ⁻¹	Hf(BD ₄) ₄	free ion	ThBr ₄	Ba ₂ YCl ₇	CsCdBr ₃	
F ²	40 290	42 561	42 632	41 280	51 938	42 253	44 078	45 601	43 829.
F ⁴	35 878	39 440	38 680	40 013	42 708	40 458	40 500	38 622	39 537.
F ⁶	23 657	24 174	23 320	22 554	27 748	25 881	27 605	28 423	25 420.
α	21.38	31	29	38	35.5	31	35.2	40.5	
β	-455	-576	-638	-648	-664	-644	-789	-1125	
γ	1573	1200	1617	1200	744	1200	800	800	
ζ	1772	1805	1819	1782	1968	1783	1802	1718	1806.
ref	40	41	42	43	44	45	46	47	
F ⁴ /F ²	0.890	0.927	0.907	0.969	0.822	0.958	0.919	0.847	0.905
F ⁶ /F ²	0.587	0.568	0.547	0.546	0.534	0.613	0.626	0.623	0.581

^aThe two-body configuration interaction parameters, namely, α , β , and γ^{30} , are given here but are not used in our analysis of the aqueous neptunyl(V) [NpO₂⁺] ion.

greater than 100 000 cm⁻¹. However, levels above ~18 000 cm⁻¹ will consist of increasing large admixtures of the $f\pi$ orbitals and will not be amenable to this analysis.

Initial Parameters For Fitting the Neptunyl(V) Solution Optical Spectrum and the Fitting Procedure.

As a first approximation we expect the axial crystal field to be similar but weaker in the neptunyl (V) (NpO₂⁺) ion than in the neptunyl(VI) (NpO₂²⁺) ion. However, the values found for the NpO₂²⁺ ion ($5f^1$ configuration) should give reasonable initial values for our fitting procedure. Denning et al.¹¹ have given a very detailed account of their analyses of the optical and Zeeman measurements of the NpO₂²⁺ ion diluted in two single crystals, CsUO₂(NO₃)₃ and Cs₂UO₂Cl₄. For each of these systems, they gave two sets of parameters, which fit their experimental results equally well. Most of their data were not sensitive to the value of $\epsilon_\sigma - \epsilon_\varphi$, so they chose two values for this parameter that straddled their measured g values of both the ground and one of the excited states. They then fit the remaining parameters to the experimental data. We used their values of the axial crystal field parameters, in their notation $\epsilon_\delta - \epsilon_\varphi$, $\epsilon_\pi - \epsilon_\varphi$, and $\epsilon_\sigma - \epsilon_\varphi$, in our notation B_0^2 , B_0^4 , and B_0^6 . There is a direct linear correlation between the Denning et al. notation

and B_0^2 , B_0^4 , and B_0^6 . The data of Denning et al.¹¹ are given in Table 2 along with their values given in the B_0^k notation. Values are also given in Table 2 for the spin–orbit coupling constant found for the neptunyl(VI) (NpO₂²⁺) ion in their work and also the results of the analysis for aquo neptunyl(V) ion by Eisenstein and Pryce.² We expect the value of the spin–orbit coupling constant for the neptunyl(V) ion to be smaller than the value for the NpO₂²⁺ ion because of its smaller charge.

Although Denning et al.¹¹ noted that for their NpO₂²⁺ data and analyses their two fits for each system were equally valid, we can immediately eliminate their Fit I for each of their systems as the use of their crystal field parameters with reasonable values for the Slater F^k and spin–orbit coupling constant parameters give completely unreasonable energy level diagrams for the NpO₂⁺ ion. Note also that the sets of crystal field parameters given for their Fit II for each NpO₂²⁺ system are of the same order of magnitude as that found in the analysis of Eisenstein and Pryce² for the aqueous $5f^2$ actinyl ions. The major difference between Fit I and Fit II in the Denning et al. data is that the energy of the ϵ_σ orbital is much too high in Fit I.

To determine reasonable starting values for the F^k parameters we surveyed the F^k parameters that were

Table 4. Calculated and Experimental Energies and Assignments for the NpO_2^+ Ion in Aqueous Solution

level (D_{Osh})	calculated energy cm^{-1}	exper energy ^b cm^{-1}	wave funct (m_1, m_{z1}, m_2, m_{z2}) %(m_1, m_{z1}, m_2, m_{z2}) + %(m_1, m_{z1}, m_2, m_{z2}) two largest terms	wave funct (SLJJz) % ($2S + 1$) $L(J, J_z)$ + % ($2S + 1$) $L(J, J_z)$ two largest terms	calc ^a f(10^7)	assign
E _{4g}	121	0	89% (2- 3-) + 4% (2- 2+)	91% 3H(4 4) + 8% 3H(5 4)		
A _{1g}	2174		43% (-2+ 2-) + 21% (-3+ 3-)	45% 3F(2 0) + 44% 3H(4 0)		
E _{1g}	3669		33% (-3+ 2-) + 23% (-2- 2-)	38% 3F(2 1) + 29% 3H(4 1)		
E _{2g}	6106	6173	55% (2+ 3-) + 44% (2- 3+)	91% 3H(5 5) + 9% 3H(6 5)	MD ^c	A
A _{2g}	9000	8953	47% (-3+ 2+) + 47% (-2- 3-)	63% 3F(3 0) + 29% 3H(5 0)		B
E _{1g}	9028	9146	26% (-2+ 2+) + 22% (-2+ 3-)	43% 3F(4 1) + 16% 3F(3 1)	103.8	C
A _{1g}	9620	9780	33% (-2+ 2-) + 32% (-2- 3-)	50% 3F(4 0) + 16% 3F(2 0)		D
E _{2g}	10 347	10 208	87% (-3- 2-) + 7% (-2- 1-)	36% 3F(3 2) + 18% 3F(4 2)	1246	E
E _{6g}	10 969	10 970	94% (2+ 3+) + 6% (3- 3+)	96% 3H(6 6) + 4% 1I(6 6)		F
E _{4g}	13 062	13 020	51% (-2- 2+) + 26% (2- 2+)	46% 3F(4 4) + 24% 1I(6 4)		G
A _{1g}	14 219		55% (-3+ 3-) + 37% (-2- 2+)	32% 1D(2 0) + 20% 3P(0 0)		
E _{3g}	14 500	14 577	89% (1- 3-) + 8% (1- 2+)	78% 3H(4 3) + 15% 3H(5 3)	MD ^c	H
E _{1g}	16 089	16 100	55% (-2- 3+) + 30% (-3+ 3+)	29% 3P(1 1) + 29% 1D(2 1)	94	I
E _{2g}	16 236	16 220	95% (1- 2-) + 2% (-1+ 3-)	41% 3F(2 2) + 27% 3H(4 2)	236.2	J
A _{1g}	16 975	16 906	32% (-2- 2+) + 26% (-3- 3+)	47% 1G(4 0) + 17% 3H(6 0)		K
E _{2g}	18 322		59% (-3+ 1-) + 21% (-1+ 3-)	41% 3F(4 2) + 17% 3F(2 2)		
E _{5g}	18 385		42% (-3- 2+) + 42% (-3+ 2-)	81% 1I(6 5) + 17% 3H(6 5)		
E _{4g}	18 996		54% (1+ 3-) + 32% (1- 3+)	66% 3H(5 4) + 14% 3H(6 4)		
E _{1g}	19 332		33% (-1+ 2-) + 25% (-3+ 3+)	26% 3P(1 1) + 22% 3H(4 1)		
E _{1g}	19 635		86% (-3+ 1+) + 4% (-3+ 2-)	25% 3F(4 1) + 24% 3F(3 1)		
E _{3g}	20 343		31% (1+ 2-) + 29% (-2+ 1-)	43% 3F(3 3) + 24% 3H(5 3)		
E _{6g}	21 436		59% (3- 3+) + 35% (-3- 3+)	96% 1I(6 6) + 4% 3H(6 6)		

^aCalculated intensities from ref 1. ^bExperimental energies from ref 2. ^cCalculated strong magnetic dipole transition.

Table 5. Values of the Parameters Found in Three Iterations by Fitting the Assigned Levels

parameters ^a	value cm^{-1}	estimated error ^b cm^{-1}	value cm^{-1}	estimated error ^b cm^{-1}	value cm^{-1}	estimated error ^b cm^{-1}
F^2	46 895		46 801	± 581	46 801	
F^4	44 925		44 835		44 823	± 1196
F^6	29 356		29 297		29 869	± 1760
ζ	2067.7		2067.6	± 22.4	2069.1	± 22.9
B_0^2	62 043	$\pm 13 677$	62 043		62 043	
B_0^4	98 209	$\pm 24 831$	98 209		98 209	
B_0^6	94 073	$\pm 36 332$	94 073		94 073	
std dev ^b	109		102		108	
F^4/F^2	0.958		0.958		0.958 ^c	
F^6/F^2	0.626		0.626		0.638 ^c	

^aThe parameters F^4 and F^6 are set by the ratios given in the rows below. ^bThe errors and standard deviation come from the statistical fitting of the assigned data and depend on the number of parameters fitted and the number of levels assigned. The parameters given without estimated errors were fixed for this iteration. ^cCalculated from above fit.

determined for isoelectronic U^{4+} compounds (Sf^2) in analyses of their optical spectra. A list of parametric data for U^{4+} compounds is given in Table 3. The number of $5f-5f$ transitions that Matsika et al.¹ calculated that were relatively intense was limited, so we utilized ratios of F^4/F^2 and F^6/F^2 in fitting this limited set of data. Preliminary calculations showed two magnetic dipole transitions that were of similar intensity and 2 orders of magnitude stronger than other magnetic dipole transitions. These transitions were included in the data set.

In our analysis we assigned 12 of the 14 levels listed by Eisenstein and Pryce² at energies up to $17\,500\text{ cm}^{-1}$. Bands with letters in the spectrum shown in Figure 1 were assigned. For the NpO_2^+ spectrum three reported bands were measured at energies less than $10\,000\text{ cm}^{-1}$ and are listed in Table 4. The first band A was reported only by Waggener³⁴ and was assigned

by Eisenstein and Pryce as a magnetic dipole transition. We also calculate a magnetic dipole transition in this energy range and agree with this assignment. A second strong magnetic dipole transition was calculated at $\sim 15\,000\text{ cm}^{-1}$, and we assign band H to this transition.

The selection rules for magnetic dipole transitions are as follows (in the SLJJz representation): $\Delta S = 0$, $\Delta L = 0$, $\Delta J = 0$, ± 1 , ($0 \rightarrow 0$ is forbidden), $\Delta J_z = 0, \pm 1$.³¹ The strong magnetic dipole transitions are from the ground state at 0 cm^{-1} (91% $3H(4\ 4)$) to the following excited states 6106 cm^{-1} (calc) 91% $3H(5\ 5)$ and to $14\,500\text{ cm}^{-1}$ (calc) 78% $3H(4\ 3)$ with notation as given in Table 4. For these transitions the largest components of the wave functions meet the criteria for the magnetic dipole transitions, which results in quite intense

transitions, comparable to the intensities of the induced electric dipole transitions.

In their calculation for the NpO_2^+ ion with five water molecules in the equatorial plane, Matsika et al. find the strongest transition to be to an E_{2g} state and a weaker transition at a lower energy to an E_{1g} state. We assign the band at E to the strong E_{2g} transition and the weaker transition to the band at C. (See Figure 1 in Matsika et al.¹ for the spectrum including these bands.) Two relatively strong transitions to E_{1g} and E_{2g} states calculated by Matsika et al., at $\sim 16\,000$ and $17\,000\text{ cm}^{-1}$, are assigned to features I and J. With these assignments, we did a preliminary fit to these energy levels and then assigned features B, D, F, and G as shown in Table 4. With these further assignments the parametric fit was refined, and the final parameters obtained are shown in Table 5 (and Table 2). The calculated energy levels and wave functions are given in Table 4. Six levels assigned up to and including the level at $10\,208\text{ cm}^{-1}$ agree with the assignments of Eisenstein and Pryce.² Our six assigned levels above $10\,208\text{ cm}^{-1}$ are different than the assignments of Eisenstein and Pryce.

We found the ratios for F^4/F^2 and F^6/F^2 shown in Table 5 gave the best fit using the Fit II crystal field parameters from Denning et al. Once these ratios were fixed, we allowed the parameters F^2 and ζ to vary to give the best fit, fixing the values of the crystal field parameters. We then fixed F^2 and ζ and allowed the crystal field parameters to vary. Finally we fixed the values of F^2 and the crystal field parameters and allowed F^4 , F^6 , and ζ to vary. The results of these various fits are shown in Table 5. As can be seen from Table 5, once the various sets of parameters converged, there were no major changes in the parameters. The parameter values given in Table 5 gave the best fit by this iterative method. The parameters from these fits (with errors) in Table 5 are summarized in Table 2 for comparative purposes.

DISCUSSION

The B_0^k parameters were poorly determined (as shown by the root-mean-square errors given in Table 5). When these B_0^k parameters are transformed to the one-electron $\varepsilon_\delta - \varepsilon_\varphi$, $\varepsilon_\pi - \varepsilon_\varphi$, and $\varepsilon_\sigma - \varepsilon_\varphi$ values as shown in Table 2, the values of $\varepsilon_\delta - \varepsilon_\varphi$ and $\varepsilon_\pi - \varepsilon_\varphi$ agree fairly well with the values found by Denning et al. for the neptunyl(VI) ion, but the value for $\varepsilon_\sigma - \varepsilon_\varphi$ is quite a bit larger than Denning's neptunyl(VI) Fit II value. Since all the B_0^k values are dependent on ε_σ , it is not surprising that the errors on these crystal field parameters are large as the data we are fitting are insensitive to $\varepsilon_\sigma - \varepsilon_\varphi$. This can be seen in the Denning et al. data for the crystalline neptunyl(VI) compounds as shown in Table 2, Fit I with very large values for $\varepsilon_\sigma - \varepsilon_\varphi$. For these compounds the B_0^k values are quite large. If we fix $\varepsilon_\sigma - \varepsilon_\varphi$ at the Denning value of $40\,000\text{ cm}^{-1}$ (Fit II), we find comparable B_0^k parameters.

Our free ion parameters are very similar to those obtained by Eisenstein and Pryce² for the aqueous neptunyl(V) ion as shown in Table 2. The spin-orbit coupling constant is slightly lower than that found by Denning et al.¹¹ for the neptunyl(VI) ion. We find the ground state (when the crystal field parameters are converted to one-electron energies) to be the δ state, consistent with that found for the NpO_2^{2+} ion but contrary to the work of Eisenstein and Pryce.²

In the formalism used in this work, the angular properties of the f^2 configuration are calculated exactly, but the radial integrals are treated as parameters. The radial parameters can incorporate a number of effects including electron correlation

when utilized in this manner. For $5f^n$ ions where considerably more levels can be assigned, additional terms are added to the Hamiltonian to take into account some of these effects.²⁹ From Table 4 column 4, we note that some states with calculated energies higher than $14\,450\text{ cm}^{-1}$ have an appreciable amount of states with $m_l = \pm 1$ in the calculated wave function. This means that states with π bonding are involved and should be treated with a different set of parameters than the nonbonding f states (δ or φ).⁶ We ignored this difference given the limited number of energy levels assigned. No σ states were found for the two largest eigenfunctions listed in Table 4 in this energy range, which is why ε_σ is poorly determined.

CONCLUSION

In this paper we have analyzed the optical spectrum for the neptunyl(V) ion in aqueous solution, assuming fivefold coordination by the water molecules in the horizontal plane perpendicular to the $\text{O}=\text{Np}=\text{O}$ bond. The crystal field symmetry for this ion, considering only the nearest neighbor atoms, is D_{5h} . The initial axial crystal field parameters were estimated from the data of Denning et al. for the $5f^1$ neptunyl(VI) ion. We also assumed the equatorial crystal field parameter B_5^6 is small compared to the axial crystal field parameters, and in the assignments of the transitions and the calculations of the energies we have set this parameter to zero. We utilized the data of Eisenstein and Pryce for the energies of the transitions, which agree (except for one overlapping line) with later data obtained in similar solutions to better than 20 cm^{-1} . The net result is that we have assigned 12 of the 14 levels listed by Eisenstein and Pryce² at energies up to $17\,500\text{ cm}^{-1}$, with the two unassigned bands due to very weak features just above background noise. Perhaps the most important simplification is the utilization of data only up to $\sim 17\,000\text{ cm}^{-1}$. The reasons for this approximation are twofold, first the theory we are applying is only accurate for levels that arise from the interactions within the manifold of the nonbonding $5f\delta$ and $5f\varphi$ electrons, which comprise the lowest-lying transitions. As the energies increase, these orbitals will be mixed more strongly by the spin-orbit and crystal field interactions with the higher-lying $5f\pi$ and $5f\sigma$ orbitals. Second, charge-transfer transitions (from the filled bonding orbitals) will appear at higher energies. It is unclear at what energies these transitions appear in the neptunyl(V) ion, so we have not attempted to assign transitions above $\sim 17\,000\text{ cm}^{-1}$.

Initially we utilized the calculated relative transition intensities given by Matsika et al.¹ Further assignments were made based on the levels obtained with the empirical parameters. The crystal field parameters, when converted to the one-electron parameters used by Denning et al.,¹¹ $\varepsilon_\delta - \varepsilon_\varphi$ and $\varepsilon_\pi - \varepsilon_\varphi$, are similar to the parameters found for the NpO_2^{2+} ion in various crystals, with the ground state as ε_δ . The value of the parameter $\varepsilon_\sigma - \varepsilon_\varphi$ is poorly determined resulting in large errors in the B_0^k parameters. The Slater parameters we found are not much different than those found by Eisenstein and Pryce,² but our assignments have a firm theoretical basis.

There are inherent limitations in analyzing room-temperature solution spectra of the actinyl ions due to their low resolution. To obtain a much better analysis for these systems what is needed is high-resolution low-temperature data for single-crystal samples as Denning et al.^{11,12} have provided for the neptunyl(VI) system. Gorshkov et al.¹⁴ have published the low-temperature spectra of the plutonyl(VI) (PuO_2^{2+}) diluted in $\text{Cs}_2\text{UO}_2\text{Cl}_4$ and assigned a number of the transitions. Their

published spectra are not of high enough quality to confirm their assignments. With higher quality data it should be possible to assign the lower-lying 5f levels and to analyze the unassigned transitions seen in the near-infrared fluorescence of the plutonyl(VI) ion.¹⁸

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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