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Electronic Structure and Spectra of Actinyl Ions

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Actinyl complexes are shown, on the basis of known theoretical and experimental results, to be weak-field complexes in 4/7 of the 5f orbital space, the other 3/7 of this space being strongly affected by bonding to the -yl oxygens. The interactions present in these complexes are placed in order of size so that a coupling scheme (Λ-S), including the choice of quantum numbers of varying quality, can be specified. Electronic spectra in the near-infrared and visible regions are discussed in general terms, including different choices of both the lower and upper orbitals (or spin−orbitals) involved in the excitations. For the isolated ions, all transitions in this region are forbidden by electric-dipole selection rules, but the interactions with equatorial ligands can make such transitions allowed.

Introduction

The early actinide elements differ from the early lanthanide elements in having larger numbers and ranges of oxidation states.[1] Perhaps the most important example of this behavior is the formation of actinyl ions AnO_2^{n+}, where An represents the actinide elements U, Np, Pu, and Am. In the strictest sense, actinyl ions are the AnO_2^{2+} ions formed from the actinides in their VI oxidation state, but the name is often extended to the AnO_2^{+} and AnO_2^{3+} ions as well,[2] designating them as actinyl(V) and actinyl(VII) ions, respectively. The actinyl name stems from Péligot's designation[3] of the UO_2 (actually UO_2^{2+}) moiety in many uranium compounds as the uranyl group. The most stable oxidation numbers under common chemical conditions are[1] VI for U, V for Np, IV for Pu, and III for Am. Thus[4] many U compounds contain UO_2^{2+} and many Np compounds contain NpO_2^{+}. Actinyl ions are all linear ($D_{\infty h}$ symmetry) or have slight deviations from linearity in some crystalline environments.[1] Simple ligands interacting directly with the actinyl ions are located in the plane perpendicular to the axis of the actinyl ion and contain the An atom (equatorial plane).

The study of the spectroscopy of actinyl ions began in 1846 with Brewster's description[5] of the optical properties of canary (uranium) glass, for which the species absorbing and emitting visible light is the uranyl ion. The study of uranyl spectroscopy has thus been of very long duration[4,6−11] and has played a role in the coining of the word fluorescence,[12] the formulation of the Stokes law,[12] and the discovery of radioactivity.[13]

To obtain a description of the overall pattern of the electronic states of the actinyl ions, we apply crystal field theory. The fundamental information needed is the nature of the orbitals involved and the relative sizes of all of the interactions of the electrons occupying these orbitals. Putting the interactions in decreasing order then defines the good quantum numbers, coupling scheme, and pattern of electronic states.

Orbitals

In 1955 Eisenstein and Pryce[14] described the orbitals involved in forming the bonds in actinyl ions. Strong σ bonds are formed from the An 5fσ and 6dσ orbitals and the O 2s and 2pσ orbitals. Two weaker π bonds are formed from the O 2pπ orbitals with some participation of An 5fπ and 6dπ orbitals. It had been argued earlier[15] that the most important metal orbital participating in the bonding is 5fσ.

The molecular orbital (MO) configuration for these bonding orbitals[16] is $\sigma_g^2\,\sigma_u^2\,\pi_g^4\,\pi_u^4$, all at approximately the same energy since they are all based heavily on O 2p orbitals. The corresponding antibonding MOs, based heavily on An 5f and 6d orbitals are therefore 5fπ, 5fσ, 6dπ, 6dσ, with the 5fπ being the lowest in energy.[14] This leaves, as the lowest unoccupied orbitals, the 5fδ and 5fϕ; these are nonbonding because their symmetries are different from those of the available valence orbitals on O atoms. At higher energy are 5fπ (somewhat antibonding) and 6dδ (nonbonding). Thus, taking orbital degeneracies into account, four of the seven 5f orbitals (δ and ϕ) are nearly degenerate at low energy compared to the other three 5f orbitals (σ and π), which have acquired enough antibonding character to raise their energies significantly.

Eisenstein and Pryce expected the 5fϕ to be moderately lower than the 5fδ (separated by more than the spin−orbit splitting), but in a later crystal-field calculation[17] of the PuO_2^{2+} infrared electronic spectrum, they found that the two levels are separated by less than the spin−orbit splitting with the 5fδ lower. This small difference in energy could have been due to interactions with the equatorial ligands, which are much weaker than the bonding interactions with the axial (-yl) oxygen atoms, but a number of calculations[11,18−20] on the bare actinyl ions show that the 5fδ is lower even without the presence of equatorial ligands.

The energy order of the highest occupied MOs (σ_g, σ_u, π_g, π_u) has been of considerable interest[4,10] since, in the simplest MO theories, an excitation energy is given by

$$\Delta E = \epsilon_a - \epsilon_i$$

where i denotes the MO from which an electron is excited (σ_g, σ_u, π_g, π_u) and a denotes the MO into which it is excited (5fδ_u, 5fϕ_u). Thus the higher the ϵ_i value, the lower the excitation

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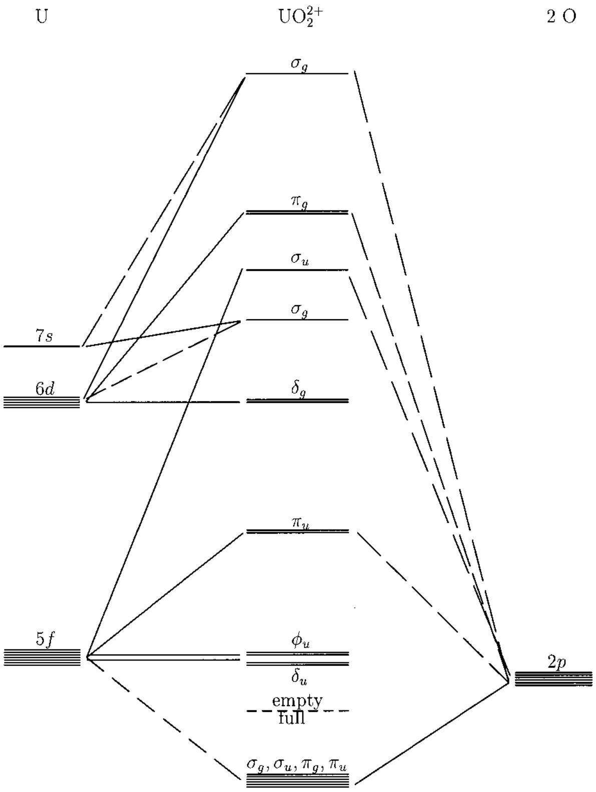

Figure 1. UO_2^{2+} MO diagram.

energy. The order of the occupied MOs is difficult to establish, even in the most accurate calculations.[21] The focus changes somewhat at an improved, but still simple, level of theory.[18] Using ground-state Hartree–Fock orbitals for a closed-shell system such as UO_2^{2+}, the excitation energy to the lowest excited state, a triplet state, is[22]

$$\Delta E = \epsilon_{a} - \epsilon_{i} - J_{ai}$$

where J_{ai} is the coulomb integral between orbitals a and i. Since the a MO is localized on the metal atom (5fδ or 5fϕ), J_{ai} will be the largest for the i orbital with the largest amplitude on the metal. As the 5fσ_u orbital is the An orbital expected to participate the most in the occupied (i) MOs,[15] this suggests that, given nearly equal ϵ_i values, the σ_u MO will give the lowest excitation energy.[18] This result was originally established experimentally from (1) Jørgensen's conclusion[23] that the low intensity of the lowest uranyl excitation required it to be forbidden by parity, (2) Görller-Walrand and Vanquickenbourne's analysis[24] that large crystal-field splittings in the uranyl absorption spectrum required that the electron be excited from a σ_u orbital, and (3) Denning et al.'s measurement of the magnetic moment of the first uranyl excited state[25] as nearly zero, implying that it is a $^3\Delta_1$ state, and thus $\sigma_u^1\,\delta_u^1$, $^3\Delta_{1g}$.

Interactions and Coupling Schemes

It was recognized early by Eisenstein and Pryce[14] that the axial oxygens provide a strong ligand interaction, splitting the 5fσ and 5fπ to considerably higher energy than 5fδ and 5fϕ, and the 6dπ and 6dσ to higher energy than 6dδ. This axial ligand interaction does not split the 5fδ and 5fϕ appreciably, however. A typical MO diagram[26] for the MOs based on the actinide 5f, 6d, and 7s and axial oxygen 2p orbitals is shown in Figure 1. The addition of equatorial ligands raises the 7s orbital even higher in energy.

The next question is the size of the electron repulsion interaction relative to that of the spin–orbit interaction; both are smaller than the axial splittings that do occur. Although the actinides are very heavy elements, the spin–orbit effects, for the lower states at least, are due to electrons in 5f orbitals. Comparing approximate An electron repulsion parameters with An ζ_{5f} values led to the conclusion[14] that the spin–orbit effects are smaller than the electron repulsion effects and that Λ–S coupling should be the best approximation. Görller-Walrand and Vanquickenbourne, in their analysis[24] of crystal-field splittings in uranyl spectra, also came to the conclusion that Λ–S is the best coupling scheme to use. Recent calculations on uranyl excited states[11] also give this result, although spin–orbit mixing of Λ–S states is substantial in some cases. Intermediate coupling is a better description, but it is closer to the Λ–S limit than to the ω–ω limit.

The final general statement, based on a number of the calculations now available,[11,18–20] is that the δ_u and ϕ_u orbitals are close enough in energy that weak-field coupling prevails in this space of four MOs and eight spin–orbitals. The splitting between these orbitals, with or without additional equatorial ligand splittings, must be smaller than the electron-repulsion effects for this to remain true. This splitting is usually smaller than the spin–orbit effects as well.

The order of interactions is then

$$\text{ax. field } (\sigma,\pi) > \text{el. rep.} > \text{spin–orbit} > \text{ax. field } (\delta,\phi) + \text{eq. field}$$

The good quantum numbers are, in order of how much of the Hamiltonian their operators commute with:

first quality:	Ω, parity
second quality:	Λ, S
third quality:	electron configuration shell occupancies for σ_u (bonding) $\delta_u + \phi_u$ (nonbonding) π_u (antibonding)

Note that, in general, the occupancies of the δ_u and ϕ_u MOs are not good quantum numbers,[27] but their total is, although exceptions to this statement are common. Only the σ_u, δ_u, ϕ_u, and π_u MOs need be considered at this point because they are the only ones involved in electronic excitations in the infrared and visible regions.

The general procedure, by successive application of first-order degenerate perturbation theory, is (1) diagonalize the electron repulsion operator over the many-electron functions from the electron configuration, giving the Λ–S eigenfunctions and electron-repulsion splittings, (2) diagonalize the spin–orbit operator over each set of Λ–S eigenfunctions, giving the Λ–S–Ω eigenfunctions and the spin–orbit splittings, and (3) account for the effect of the intrinsic δ_u, ϕ_u energy difference and for the interactions with equatorial ligands. Such calculations are principally for use in understanding the general pattern of energy levels rather than being of quantitative use, since more accurate calculations are already feasible.[11,18–20] Hund's Rules, adapted to Λ–S coupling for linear molecules, usually apply.

Exceptions to this general scheme are already known, such as (1) intermediate coupling for uranyl excited states with Ω = 2,3 requiring simultaneous consideration of electron repulsion and spin–orbit[11] and (2) sufficient equatorial splitting in $NpO_2Cl_4^{2-}$ requiring simultaneous consideration of spin–orbit and equatorial ligand interactions.[28–30]

Electronic States

The known actinyl ions have the σ_u MO doubly occupied in the ground state and numbers of electrons from zero to four in the low (δ_u, ϕ_u) 5f-based MOs. Thus we can label these electron configurations $\sigma_u{}^2(\delta_u, \phi_u)^n$. The lowest energy excitations are within this $(\delta_u, \phi_u)^n$ shell, if $n > 0$, and are therefore f → f in nature. Higher energy f → f excitations are (δ_u, ϕ_u) to π_u, giving the $\sigma_u^2(\delta_u, \phi_u)^{n-1}\,\pi_u^1$ electron configuration if $n > 0$. These excitations are from a nonbonding orbital to a somewhat antibonding orbital, so the An−O bond distance increases. In the same general energy range are $\sigma_u \rightarrow (\delta_u, \phi_u)$ excitations giving the $\sigma_u^1(\delta_u, \phi_u)^{n+1}$ electron configuration. Because the latter excitations are from a bonding MO (composed of both An and O orbitals) to a nonbonding MO (localized on An), they are often called charge-transfer transitions. For these transitions the An−O distance increases even more and the absorption bands are wider than those for f → f transitions.

The simplest example of a $(\delta_u, \phi_u)^n$ configuration is $(\delta_u, \phi_u)^1$, as in UO_2^+, NpO_2^{2+}, and PuO_2^{3+}. With only one electron there is no electron repulsion, so the most important interaction to consider is the spin−orbit interaction. If we neglect the higher energy of the ϕ_u orbital even without equatorial ligands, the problem becomes a diagonalization of the spin−orbit operator in the $\Omega = 7/2$ space, the $\Omega = 5/2$ space, both of which are the same as for atomic ions, and for a single $\Omega = 3/2$ function. Determining the $\Omega = 7/2$ and 5/2 wave functions and energies can be done using standard angular momentum algebra,[31] because the wave functions are only on the An atom. In energy order, the states and wave functions are $\Omega = 5/2$ (86% ${}^2\Phi_{5/2u}$, 14% ${}^2\Delta_{5/2u}$, corresponding to the atomic ${}^2F_{5/2}$ with $M_J = 5/2$); $\Omega = 3/2$ (${}^2\Delta_{3/2u}$, corresponding to a mixture of atomic ${}^2F_{5/2}$ and ${}^2F_{7/2}$ wave functions, both with $M_J = 3/2$); and two wave functions corresponding to atomic ${}^2F_{7/2}$, the first with $\Omega = 5/2$ (86% ${}^2\Delta_{5/2u}$, 14% ${}^2\Phi_{5/2u}$, corresponding to $M_J = 5/2$), and the second with $\Omega = 7/2$ (${}^2\Phi_{7/2u}$, corresponding to $M_J = 7/2$). Allowing for the energy difference between the δ_u and ϕ_u orbitals[18] puts more ${}^2\Delta_{5/2u}$ character into the ground state and splits the ${}^2F_{7/2}$ energy level into a lower state with $\Omega = 5/2$ and an upper state with $\Omega = 7/2$.

The $(\delta_u, \phi_u)^2$ case at the electron repulsion level gives ${}^3\Sigma_g^-$, ${}^3\Sigma_g^-$, ${}^3\Pi_g$, ${}^3H_g$ and several singlets. The two ${}^3\Sigma_g^-$ wave functions (originating from δ_u^2 and ϕ_u^2) must be found from a 2 × 2 secular equation. The (molecular) ${}^3H_g$ wave function corresponds to an (atomic) ${}^3H$ wave function, while the three other molecular wave functions correspond to linear combinations of atomic ${}^3H$, ${}^3F$, and ${}^3P$ wave functions and are therefore higher in energy. These energies can be approximated by carrying out a calculation in terms of atomic parameters. Assuming as before, that δ_u and ϕ_u are degenerate, and evaluating the integrals in terms of Slater−Condon parameters[31] for atoms gives a particularly simple form because the off-diagonal element is equal to the difference of the diagonal elements (most simply given in terms of the Racah parameter[32] E^3). The energies and wave functions can be expressed in terms of the Greek golden ratio.[33] Comparing the energies in terms of the Slater−Condon parameter[34] F^2 gives ${}^3H_g$ ($-0.111\ F^2$, 50% δ_u, 50% ϕ_u), 1 ${}^3\Sigma_g^-$($-0.069\ F^2$, 72% δ_u, 28% ϕ_u), ${}^3\Pi_g$ ($0.000\ F^2$, 50% δ_u, 50% ϕ_u), and 2 ${}^3\Sigma_g^-$ ($0.180\ F^2$, 28% δ_u, 72% ϕ_u). Including the spin−orbit interaction lowers ${}^3H_{4g}$ considerably and lowers the 1 ${}^3\Sigma_g^-$ states modestly by mixing with ${}^3\Pi_g$. Allowing for an energy difference between δ_u and ϕ_u favors the 1 ${}^3\Sigma_g^-$ states over the ${}^3H_g$ states, but should be the smallest of these effects. Thus the ground state is ${}^3H_{4g}$, as given by magnetic resonance data,[35−37] initial theoretical estimates,[14] and current theoretical treatments.[18,19,38]

TABLE 1: Lowest Energy Electronic States for Electron Configurations[41]

el. config.	$n = 0$	$n = 1$	$n = 2$	$n = 3$	$n = 4$
	UO_2^{2+} NpO_2^{3+}	UO_2^+ NpO_2^{2+} PuO_2^{3+}	NpO_2^+ PuO_2^{2+}	PuO_2^+ AmO_2^{2+}	AmO_2^+
$\sigma_u^2(\delta_u, \phi_u)^n$	${}^1\Sigma_{0^+g}^+$	${}^2\Phi_{5/2u}({}^2F_{5/2})$	${}^3H_{4g}$	${}^4\Phi_{3/2u}$	${}^5\Sigma_{0^+g}^+$
$\sigma_u^2(\delta_u, \phi_u)^{n-1}\pi_u^1$		${}^2\Pi_{1/2u}$	${}^3\Gamma_{3g}$	${}^4I_{9/2u}$	${}^5\Gamma_{2g}$
$\sigma_u^1(\delta_u, \phi_u)^{n+1}$	${}^3\Delta_{1g}$	${}^4H_{7/2u}$	${}^5\Phi_{1g}$	${}^6\Sigma_{1/2u}^+$	${}^5\Delta_{4g}$

The lowest energy terms from all of the electron configurations are given in Table 1. Several cases are of particular interest: (1) For $\sigma_u^1(\delta_u, \phi_u)^1$ the excited states are in the order ${}^3\Delta_g$,${}^3\Phi_g$,${}^1\Phi_g$,${}^1\Delta_g$ because the exchange integral between σ_u and δ_u is larger[9,18] than the exchange integral between σ_u and ϕ_u, contrary to what Hund's Rule would suggest if extended to excited electron configurations. With Ω values, the states are ${}^3\Delta_{1g}$,${}^3\Delta_{2g}$,${}^3\Delta_{3g}$,${}^3\Phi_{2g}$,${}^3\Phi_{3g}$, ${}^3\Phi_{4g}$, ${}^1\Phi_{3g}$, ${}^1\Delta_{2g}$ and are the much-studied[10,11] excited states of UO_2^{2+}. States with the same Ω value are mixed appreciably by the spin−orbit interaction.[11] (2) The case most susceptible to ligand influence[28,29] is $\sigma_u^2(\delta_u, \phi_u)^1$ because there is no electron repulsion in the δ_u, ϕ_u shell. The ligand interactions must only overcome the spin−orbit interaction, rather than the larger electron repulsion interaction, to change the order of states. (3) The energy order with respect to Ω values for $(\delta_u, \phi_u)^4$ and $\sigma_u^1(\delta_u,\phi_u)^4$ are not given by Hund's Rules because these are half-filled shells. The values given are the results of calculations.[20] (4) The lowest state involving a σ_u excitation for AmO_2^+ is calculated[20] to be $\sigma_u^1(\delta_u,\phi_u)^4\pi_u^1$, ${}^7\Pi_{0+g}$ rather than $\sigma_u^1(\delta_u, \phi_u)$,[5] ${}^5\Delta_{4g}$. (5) A combined density functional and spin−orbit CI calculation[39] has given $\delta_u^1\,\phi_u^1\,\pi_u^1$, ${}^4I_{9/2u}$ as the ground state of PuO_2^+ in contrast to our result[40] of $\delta_u^2\,\phi_u^1$, ${}^4\Phi_{3/2u}$. The two calculations differ in their manner of calculating MOs and incorporating electron correlation. With sufficient basis sets and electron correlation descriptions, both methods should calculate both states in the same order.

Electronic Spectra

Actinyl solution spectra for the infrared and visible regions are collected in the book by Keller.[42] Crystal spectra are known very extensively.[4,6−8,10,43] A central question for all of them is the source of the intensities. All of the MOs involved, (σ_u, δ_u, ϕ_u, π_u) have ungerade symmetry. Thus, transitions between them are electric-dipole forbidden as long as a center of inversion is present.

In crystal spectra for uranyl with approximately D_{4h} coordination, the intensities have been determined to be due to magnetic dipole and electric quadrupole mechanisms.[25]

Only recently have intensity calculations for solution spectra been carried out.[28] The spectra[42] in $HClO_4$ are presumably of hydrated actinyl complexes. It has been pointed out that the equatorial ligands must remove the inversion symmetry for there to be electric-dipole intensities,[44] and this is in agreement with a number of known spectra. Mixing of gerade orbitals into ungerade orbitals is required for electric-dipole intensity. Because the 6dδ orbitals are the lowest energy gerade orbitals, mixing them with the 5fδ or 5fϕ (both ungerade) is the most efficient way to obtain such intensities. Mixing of 6dδ ($\lambda = \pm 2$) with 5fδ ($\lambda = \pm 2$) requires an equatorial field with ungerade Fourier components of 4 or 0, which do not exist.[28] Mixing of 6dδ with 5fϕ ($\lambda = \pm 3$) requires an equatorial field with ungerade Fourier components (and therefore coordination numbers) of 5 or 1, which do exist.[28] The value of 5 has been found to be the most effective in the cases examined so far.[28]

Conclusions

The ground states and low-lying excited states of actinyl ions (and complexes) are weak-field states in the (δ_u, ϕ_u) subspace of the 5f orbital space. Other excited states involve excitations from this space to (5f) π_u or excitations to this space from a filled (bonding) MO. Criteria for the latter are given.

Electronic spectra in the near-infrared region come from excitations within the (δ_u, ϕ_u) space, whereas excitations of the other two types extend through the visible region. Electric-dipole intensity depends on the interactions with the equatorial ligands. Five-fold coordination gives the highest intensities.

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References and Notes

(1) Katz, J. J.; Morss, L. R.; Seaborg, G. T. Summary and Comparative Aspects of the Actinide Elements. In *The Chemistry of the Actinide Elements*, 2nd ed.; Katz, J. J., Seaborg, G. T., Morss, L. R., Eds.; Chapman and Hall: London, 1986; pp 1137−1140.

(2) *The Chemistry of the Actinide Elements*, 2nd ed.; Katz, J. J., Seaborg, G. T., Morss, L. R.; Eds; Chapman and Hall: London, 1986; Chs. 14, 21.

(3) Péligot, E. *Ann. Chim. Phys.* **1842**, *5*, 5−47. See p 35.

(4) Jørgensen, C. K.; Reisfeld, R. *Struct. Bonding (Berlin)* **1982**, *50*, 121−171.

(5) Paper read in 1846; published as Brewster, D. *Trans. R. Soc. Edinburgh* **1849**, *16*, 111−121.

(6) Nichols, E. L.; Howes, H. L. *Fluorescence of the Uranyl Salts*; Carnegie Institute of Washington: Washington, D.C., 1919.

(7) Dieke, G. H.; Duncan, A. B. F. *Spectroscopic Properties of Uranium Compounds*; National Nuclear Energy Series, Division III, Vol. 2; McGraw-Hill: New York, 1949.

(8) Rabinowitch, E.; Belford, R. L. *Spectroscopy and Photochemistry of Uranium Compounds*; Pergamon: New York, 1964.

(9) Denning, R. G.; Norris, J. O. W.; Short, I. G.; Snellgrove, T. R.; Woodwark, D. R. Electronic Structure of Actinyl Ions. In *Lanthanide and Actinide Chemistry and Spectroscopy;* Edelstein, N. M., Ed.; ACS Symposium Series 131; American Chemical Society: Washington, D.C., 1980; pp 313−330.

(10) Denning, R. G. *Struct. Bonding (Berlin)* **1992**, *79*, 215−271.

(11) Zhang, Z.; Pitzer, R. M. *J. Phys. Chem. A* **1999**, *103*, 6880−6886. The second line of Table 7 in this paper should be replaced by two lines:

1_g (fluorescent)	1.733	867	20,719	20,096	21,090
2_g	1.739	845	21,421	20,861	21,694

(12) Stokes, G. G. *Philos. Trans. R. Soc. London* **1852**, 463−562.

(13) Becquerel, H. *C. R. Hebd. Seances Acad. Sci.* **1896**, *122*, 420−421.

(14) Eisenstein, J. C.; Pryce, M. H. L. *Proc. R. Soc. London* **1955**, *A229*, 20−38.

(15) Connick, R. E.; Hugus, Z. Z. *J. Am Chem. Soc.* **1952**, *74*, 6012−6015.

(16) McGlynn, S. P.; Smith, J. K. *J. Mol. Spectrosc.* **1961**, *6*, 164−187.

(17) Eisenstein, J. C.; Pryce, M. H. L. *J. Res. Natl. Bur. Stand.* **1966**, *70A*, 165−173.

(18) Matsika, S.; Pitzer, R. M. *J. Phys. Chem. A* **2000**, *104*, 4064−4068. A version of this paper with some subsequent improvements is Ch. 3 in Matsika, S. Ph.D. Dissertation, The Ohio State University, Columbus, OH, 2000.

(19) Blaudeau, J.-P.; Bursten, B. E.; Pitzer, R. M. *Book of Abstracts, 217th ACS National Meeting,* Anaheim, CA, March 21−25, 1999; American Chemical Society; Washington, D.C., 1999; NUCL-179.

(20) Brozell, S. R. Ph.D. Dissertation, The Ohio State University, Columbus, OH, 1999.

(21) de Jong, W. A.; Visscher, L.; Nieuwpoort, W. C. *THEOCHEM* **1999**, *458*, 41−52.

(22) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69−89.

(23) Jørgensen, C. K. *Acta Chem. Scand.* **1957**, *11*, 166−178.

(24) Görller-Walrand, C.; Vanquickenbourne, L. G. *J. Chem. Phys.* **1972**, *57*, 1436−1440.

(25) Denning, R. G.; Snellgrove, T. R.; Woodwark, D. R. *Mol. Phys.* **1976**, *32*, 419−442. See also ref 10.

(26) Previous versions of such diagrams are Figures 3 and 14 in ref 9 and Figures 2 and 17 in ref 10.

(27) Ballhausen, C. J. *Introduction to Ligand Field Theory*; McGraw-Hill: New York, 1962; see p 74.

(28) Matsika, S.; Pitzer, R. M.; Reed, D. T. *J. Phys. Chem. A* **2000**, *104*, 11983−11992.

(29) Matsika, S.; Pitzer, R. M. *J. Phys. Chem. A*, **2001**, *105*, 637−645.

(30) Denning, R. G.; Norris, J. O. W.; Brown, D. *Mol. Phys.* **1982**, *46*, 287−323.

(31) Condon, E. U.; Shortley, G. H. *The Theory of Atomic Spectra*; Cambridge University Press: Cambridge, 1935.

(32) Racah, G. H. *Phys. Rev.* **1949**, *76*, 1352−1365.

(33) Gardner, M. *Sci. Am.* **1959**, *201*, No. 2, 128−134; the earliest reference is Euclid *Elements*; Book II, Proposition 11.

(34) Jørgensen, C. K. *Modern Aspects of Ligand Field Theory*; North-Holland: Amsterdam, 1971; p 255.

(35) Bleaney, B.; Llewellyn, P. M.; Pryce, M. H. L.; Hall, G. R. *Philos. Mag.* **1954**, *45*, 773−774.

(36) Hutchinson, C. A.; Lewis, W. B. *Phys. Rev.* **1954**, *95*, 1096−1096.

(37) Bleaney, B. *Discuss. Faraday Soc.* **1955**, *19*, 112−118.

(38) Maron, L.; Leininger, T.; Schimmelpfennig, B.; Vallet, V.; Heully, J.-L.; Teichteil, C.; Gropen, O.; Wahlgren, U. *Chem. Phys.* **1999**, *244*, 195−201.

(39) Hay, P. J.; Martin, R. L.; Schreckenbach, G. *J. Phys. Chem. A* **2000**, *104*, 6259−6270. The $^4I_{15/2u}$ and $^4\Phi_{9/2u}$ states referred to in this paper should have been labeled as $^4I_{9/2u}$ and $^4\Phi_{3/2u}$, respectively (Hay, P. J., private communication, 2001).

(40) Blaudeau, J.-P. To be submitted for publication, 2001. The calculations in this work have been carried out in the same manner as those in ref 11, 18, 19, and 20.

(41) Actinyl ion electronic states use a wider range of Λ values than lighter molecules so we include a table of Greek spectroscopic notation.

$\|\lambda\|$ or $\|\Lambda\|$	0	1	2	3	4	5	6	7	8	9	10	11
code for $\|\lambda\|$	σ	π	δ	ϕ	γ	η	ι	κ	λ	μ	ν	o
code for $\|\Lambda\|$	Σ	Π	Δ	Φ	Γ	Η	Ι	Κ	Λ	Μ	Ν	Ο

The large number of identical upper case Greek and Latin letters is a potential source of confusion. The above list is limited by finding a Greek equivalent of Q. The corresponding atomic notation goes up to 20 and is given by Meggers, W. F.; Moore, C. E. *J. Opt. Soc. Am.* **1953**, *43*, 422−425. We thank P. Bernath for a useful discussion of this subject.

(42) Keller, C. *The Chemistry of the Transuranium Elements*; Verlag Chemie: Weinheim/Bergstr., 1971.

(43) Ryan, J. L. Absorption Spectra of Actinide Compounds. In *Lanthanides and Actinides*; Bagnall, K. W., Ed.; Inorganic Chemistry Series One, Vol. 7, MTP International Review of Science; Butterworth: London, 1972, 323−367.

(44) Garnov, A. Yu.; Krot, N. N.; Bessonov, A. A.; Perminov, V. P. *Radiochemistry* **1996**, *38*, 402−406.