Application of Relativistic Quantum Chemistry to the Electronic Energy Levels of the Uranyl Ion

Zhiyong Zhang[†] **and Russell M. Pitzer***

Department of Chemistry, The Ohio State University, 100 W. 18th Ave., Columbus, Ohio 43210

Received: June 8, 1999

The ground and excited electronic states of the uranyl ion UO_2^{2+} are computed using relativistic core and spin−orbit potentials and multireference graphical unitary group approach configuration interaction as implemented in the COLUMBUS suite of programs. Excitation energies, symmetric stretch vibrational frequencies, and angular momentum coupling properties are compared to the extent possible with spectroscopic data from $Cs_2UO_2Cl_4$ and $CsUO_2(NO_3)_3$.

1 Introduction

The visible spectrum of the uranyl ion (UO_2^{2+}) is quite distinctive, and few spectroscopic or electronic structure problems have as long or as extensive a history. The tendency of a uranium atom to bond two oxygen atoms tightly and closely has played a central role in uranium chemistry from its beginning. Thus, approximately half of the uranium compounds listed in the Handbook of Chemistry and Physics[1] contain uranium in the form of the uranyl ion, and the most common uranium salts and minerals are uranyl compounds.

Although uranium compounds have been used since Roman times,[2−4] the first recognition that they contained a new element was by Klaproth[5] in 1789; the substance he named "uranium" was actually UO_2, and the "uranium" compounds he prepared, such as the chloride, nitrate, and sulfate, were actually uranyl salts. Elemental uranium was first obtained in 1841, by Péligot,[6] who also proposed the name "uranyl" for the UO_2^{2+} ion.[7]

Structure. As shown in a survey of 180 crystal structures,[8] uranyl ions are fundamentally linear, rarely deviating from linearity by more than a few degrees even in low-symmetry environments. Uranyl ions are coordinated with various ligands at larger distances in the equatorial plane, with common equatorial coordination numbers being[8] four, five, and six. The UO bond distances, in carbonate complexes for example,[9] are in the range 1.7 to 1.9 Å for axial distances and 2.4 to 2.6 Å for equatorial distances. Among transition metals, the most closely analogous case of very tight metal−oxygen binding occurs[10] in the vanadyl ion VO^{2+}.

Early Optical Work. Prior to 1940, when mining for nuclear weapons and power began, uranium had only been used on a minor scale as a coloring agent (such as in canary glass, a light-yellow Bohemian glass used for decorative and glass-blowing purposes) and for catalysis.[11] In the 1840s, Brewster[12] began the study of the optical properties of uranium compounds. His study of canary glass showed that it absorbs light in the blue, transmits light in the yellow, and has luminescence ("internal dispersion" or "dispersive reflexion") in the green.

In 1852, Stokes[13] studied the optical properties of many solids and solutions using a candle, sunlight, and prisms. The best data came from samples containing uranium: canary glass, several U minerals, and several UO_2^{2+} salts. These showed several absorption bands in the blue and several emission bands in the yellow with a green band in common. Stokes coined the term "fluorescence" (from fluorspar and opalescence) for this phenomenon. From his data he drew several conclusions, one of which described the shift between the wavelengths of absorbed and emitted light: "The refrangibility of the incident light is a superior limit to the refrangibility of the components of the dispersed light." This came to be known as "Stokes' Law" and has been restated[14] as: "The emitted radiation is displaced to longer wavelengths compared to the absorbed radiation", which we now know is a result of transitions to different excited vibrational levels. It is perhaps most commonly referred to in connection with Raman spectroscopy.

Becquerel Family. The fluorescence of the uranyl ion was studied by several generations of the Becquerel family. C. Becquerel (grand-père) established the family scientific tradition in the early 1800s and contributed to the new science of electrochemistry.[15] E. Becquerel (père) did much to develop methods for studying fluorescence and phosphorescence and in 1872 published photographically recorded fluorescence spectra of several uranyl salts.[16] More studies of uranyl fluorescence by H. Becquerel (fils) appeared[17] in 1885. A consequence of these fluorescence studies was the discovery of radioactivity when a sample of $K_2UO_2(SO_4)_2$ was placed next to a covered photographic plate and the image of the sample was observed on the developed plate.[18] J. Becquerel (petit-fils) collaborated with Kamerlingh Onnes in observing uranyl fluorescence spectra down to liquid hydrogen temperature.[19]

Up to 1940. From the 1870s on, many different research groups studied the spectroscopy of uranyl salts. The work up to 1919 was summarized by Nichols and Howes[20] in a (first) book on uranyl spectroscopy. They included much analysis of the properties of the spectra, but noted that "... no satisfactory theory has as yet been evolved, ...". Almost all uranyl salts absorb light beyond 20 000 cm^{-1} (blue, violet, and ultraviolet) and fluoresce brightly from 20 000 to 15 000 cm^{-1} (blue, green, yellow, and orange) with some overlap between the two spectra. The absorption in the blue region gives the salts a yellow color, and they have a green color when viewed by fluorescence. The absorption spectra contain many weak but sharp features.[21]

---

* Corresponding author. E-mail: pitzer.3@osu.edu.

[†] Present address: Pacific Northwest National Laboratory, P. O. Box 999, Richland, WA 99352.

10.1021/jp991867q CCC: $18.00

Approaching 30,000 cm^{-1} the absorption becomes stronger but with few features.[22]

In 1925, Dieke and Van Heel[23] described the absorption and fluorescence spectra as being progressions in a vibration that has a lower frequency in the excited electronic state than in the ground electronic state. In 1930, Freed and Kasper[24] found that the uranyl ion has temperature-independent paramagnetism. In 1935, Fankuchen[25] published a crystal structure of a uranyl salt with sufficient data to show that the uranyl ion is linear. In 1939 Moerman and Kraak[26] noted that (1) the 0-1 band is always the most intense band in fluorescence, (2) the 1-0 band is always the most intense band in absorption, and (3) the excited-state vibrational frequency is lower than the ground-state vibrational frequency; accordingly, the excited state must have a weaker bond and a longer bond distance.

1940−1950. During World War II, as part of the Manhattan Project, much work on the spectroscopy of uranyl compounds was carried out to investigate any possible optical methods of isotope separation. This work was summarized by Dieke and Duncan[27] in 1949 in a (second) book on uranyl spectroscopy. They noted that the fluorescence spectra are independent of the wavelength of the exciting radiation, showing that it is entirely due to the first excited electronic state. Of the three vibrations of UO_2^{2+}, the symmetric stretch (typical frequencies: 830 cm^{-1} in the ground state, 710 cm^{-1} in the excited state) plays a dominant role in the form of the spectra, but the bend (typical frequency: 210 cm^{-1}) and asymmetric stretch (typical frequency: 930 cm^{-1}) can also be found from the spectra as well as from infrared and Raman spectra. All of the spectroscopic parameters vary a few percent with changes in the other ions and molecules in the salts. The fluorescence lifetimes are typically in the range 10^{-4} to 10^{-3} s. The fluorescence oscillator strength is in the range 10^{-7} to 10^{-8}, "... expected for quadrupole radiation" (rather than dipole radiation). In 1949, Kasha[28] noted that the maximum value of the fluorescence extinction coefficient in solution is 8.5 L mol^{-1} cm^{-1} (0.85 m^2 mol^{-1}), indicating an (electric-dipole) forbidden transition.

Electronic Assignment Progress. Working out the electronic structure of the uranyl ion has been a slow process, especially establishing the angular momentum quantum numbers and orbital excitations of the excited states, for which a 1971 statement[29] was "Several mutually exclusive hypotheses have been proposed." The summary here will concentrate on the work that has stood the test of time, while more complete references and discussion are available from review articles.[10,30] In 1952, Connick and Hugus[31] argued that the unusually strong UO bonding implies participation of U 5f orbitals in the bonding, especially the σ bonds. In 1955, Eisenstein and Pryce[32] described the molecular orbitals (MOs) involved in the ground and low-lying excited states.

A brief summary of the MOs is obtained by starting with the uranyl in its extreme ionic form as described by the oxidation numbers, $[O^{2-}U^{6+}O^{2-}]^{2+}$. The U 5f and 6d orbitals are empty and the O2p orbitals are full and form the highest-lying MOs, σ_g, σ_u, π_g, π_u. These MOs are formed in the same way in simple diatomics such as N_2, O_2, and F_2, (as used, for example, to explain the triplet ground state of O_2), but in UO_2^{2+} the O atoms are farther apart, and the empty orbitals on the U atom are available to mix with the O2p orbitals: 5fσ in σ_u, 5fπ in π_u, 6dσ in σ_g, 6dπ in π_g. The extent of this mixing is a key question. The lowest lying empty MOs are the 5fδ and 5fϕ, since they are of the wrong symmetry to mix into any occupied MOs.

In 1957, Jørgensen[33] ascribed the low intensities of the fluorescent transition and the low-lying transitions in absorption as being due to the parity selection rule. Since the excited orbital is either δ_u or ϕ_u, this means that the excitation must come from either σ_u or π_u. The work up to 1964 was described in a (third) book on uranyl spectroscopy by Rabinowitch and Belford,[34] which also described the photochemistry and early theory work on uranyl compounds. Uranyl photochemistry work has also been extensive, starting in 1805 with the observation[35] of sunlight-induced reactions in solutions of uranyl salts and ethanol. The most extensively studied reaction has been that of uranyl oxalate.[34,36] In 1968, Bell and Biggers[37] published a deconvoluted spectrum of uranyl ion in $HClO_4$ solution where the low complexing tendency of the perchlorate ions would mean that the spectrum was primarily that of hydrated uranyl ions. They found 24 bands between 20 000 and 55 710 cm^{-1}; the higher-energy bands had oscillator strengths typical of electric-dipole-allowed transitions.

In 1972, Görller-Walrand and Vanquickenbourne,[38] in examining uranyl absorption spectra, pointed out cases of sufficiently large splittings due to equatorial ligands that the values for such splittings should be given by first-order perturbation theory. Their analysis showed that this can occur only if the excitation comes from a σ (therefore σ_u) orbital and if the dominant angular momentum coupling is $\Lambda-S$.

Denning Group. The most detailed spectroscopic studies have been of crystalline[39] $Cs_2\,UO_2\,Cl_4$ for which the ionic units are Cs^+ and $UO_2Cl_4^{2-}$; the UO distance is 1.774 Å and the UCl distance is 2.671 Å. The site symmetry of the U atoms is C_{2h}, very close to D_{2h} and moderately close to D_{4h}. In 1976, Denning, Snellgrove, and Woodwark[40] published polarized, single-crystal absorption spectra of $Cs_2UO_2Cl_4$ taken at 4.2 K. They compared vibrational frequencies (cm^{-1}) of 831, 252, 916 in the ground state to 715, 234, 731 in the fluorescent (first excited) state and assigned 12 excited states in D_{2h} symmetry, which correspond to the first six excited states in $D_{\infty h}$ UO_2^{2+} having Ω values of 1, 2, 3, 2, 3, 4. They measured magnetic moments and found the very small value of (0.16 ± 0.07) μ_B for the fluorescent state. To obtain this low value, the electron orbital and spin contributions must almost entirely cancel, which can only occur for two electrons in singly occupied MOs if the state is $^3\Delta_{g1}$. The orbital excitation must then be from σ_u to δ_u. They assigned some of the higher states to excitations from σ_u to ϕ_u, particularly the sixth excited state to $^3\Phi_{g4}$. The excited states were assigned as either magnetic-dipole or electric-quadrupole allowed. In 1979, they argued[41] that the magnetic moments of the excited states with Ω values of 2 and 3 did not correspond to single $\Lambda-S$ states so that there must be spin−orbit mixing between the states resulting from excitations to δ_u and ϕ_u. They also calculated a UO bond length increase of 0.07 Å due to excitation from the ground state to the fluorescent state.

In 1987, Barker, Denning, and Thorne[22] reported two-photon spectra for the same system and added another $D_{\infty h}$ state; its Ω value is 2. In 1991, Denning and Morrison[42] obtained polarized excited-state absorption spectra from the fluorescent state. The new state found was at 37 100 cm^{-1} above the ground state and has a symmetric stretch vibrational frequency of 585 cm^{-1}. The intensity is large so the transition is electric-dipole allowed. The assignment is for a σ_g-to-δ_u excitation from the ground state and an Ω value of 1. The UO distance in this state is calculated to be 0.18 Å longer than the ground-state value. In 1992, Barker et al.[43] reported two-photon spectra of $CsUO_2(NO_3)_3$ corresponding to the first seven excited states of UO_2^{2+}.

Previous Electronic Theory. In previous theoretical calculations on the uranyl ion, both nonrelativistic and relativistic methods have been used, including MS−X_α,[44−48] discrete variational,[49−51] effective core potential,[52−55] extended Hückel,[56−59] local approximation for relativistic scalar operators,[60] density functional,[61] and four-component.[62,63] Actual calculations have been confined to the ground state, primarily to test new methods and to understand the bonding and bond angle, but discussion and approximations for excited states were included in a number of cases.[44,45,47,48,50,51]

2 Theoretical and Computational Methods

Basics. The theoretical and computational difficulties in treating systems such as the uranyl ion are the need to include relativistic effects and to treat large numbers of electrons. We address these difficulties by the use of the relativistic effective core potential (RECP) approximation[64−66] and spin−orbit configuration interaction (CI) implemented by the graphical unitary group approach (GUGA).[67,68]

Core Potentials. The RECPs used in this work are those developed by Christiansen and co-workers.[69,70] Their procedure[71,72] starts with Dirac−Fock (DF) relativistic atomic calculations and converts the valence orbitals to valence pseudo-orbitals, which are unchanged in the valence region and go smoothly and nodelessly to zero in the core region and are used to define core potentials and spin−orbit operators simultaneously. These operators include the effects of the core electrons as well as the relativistic effects of the valence electrons in the core region.[73] With explicit treatment of the core electrons removed from the problem, the Hamiltonian to be considered thus includes the usual nonrelativistic kinetic energy and Coulomb terms for the valence electrons plus the core potentials and spin−orbit operators. The core potentials represent, for the valence electrons, the repulsion of the core electrons, and the spin−orbit operators include the (large) spin−orbit interactions of the valence electrons with the nucleus and with the core electrons as well as an approximation[74] to the (small) spin−orbit interaction between the valence electrons. The oxygen core[69] is the 1s shell (2 electrons), and the uranium core is the 1s through 5d shells (78 electrons). Thus in UO_2^{2+}, 82 electrons (core) are not treated explicitly and 24 electrons (valence) are treated explicitly.

Spin−Orbit and Correlation. The simultaneous treatment of electron correlation and the spin−orbit interaction is most efficiently done by the use of the multireference CI method of treating electron correlation.[68] Other workers have treated spin−orbit and correlation in separate steps in the overall calculation.[65] The spin−orbit interaction for the valence electrons of heavy atoms, even though they are not moving especially close to the speed of light, is sufficiently large that $\Lambda-S$ coupling is often not a good approximation and yet neither is $\omega-\omega$ coupling. Thus, an adequate treatment can easily require including all of the intermediate coupling space[75] within the reference configuration space, which is usually larger in relativistic calculations than in nonrelativistic calculations. The GUGA methodology,[76] as implemented in the COLUMBUS system of quantum chemistry computer programs,[77] is the basis for the programs used here for direct spin−orbit CI[68] calculations. These programs are expected to be available in the upcoming release,[68,77,78] COLUMBUS 5.5.

Computational. Integrals over (symmetrized) atomic orbitals (AOs) are generated by the ARGOS program. The CNVRT program then converts these integrals into supermatrix form for use in the SCFPQ program for self-consistent-field (SCF) calculations. MO coefficients generated from SCFPQ may be used as the initial guess in multiconfiguration SCF (MCSCF) calculations, which may be for an average of electronic states. Either SCFPQ or MCSCF MO coefficients can be used by the TRAN program to transform the AO integrals to MO integrals. Spin−orbit CI singles (CIS) and singles and doubles (CISD) calculations may be carried out. The CIS calculations were done using the (older non-GUGA) CGDBG and CIDBG programs, and the CISD calculations were done using the CIDRT, CISRT, CIUFT, and CIUDG spin−orbit GUGA programs.

TABLE 1: Timing Data for Example CI Calculations

size of CI (million)	wall-clock time (hours)
9.16	5.74
4.16	2.00
1.77	0.76
0.25	0.083

TABLE 2: O cc-pVDZ Basis Set: (4s4p1d)/[2s2p1d]

orbital	primitives	contraction	contraction
s	41.04	−0.0097241	0.0222003
	7.161	−0.1318703	0.1265661
	0.9074	0.5903463	−1.6261307
	0.2807	0.5169632	1.5531546
p	17.72	0.0433004	−0.0559967
	3.857	0.2330835	−0.4246360
	1.046	0.5017961	−0.5598365
	0.2752	0.4652332	0.9990806
d	1.213	1.0	

In Table 1 we list sample timing data (diagonalization step only; other steps require negligible time) for several calculations on the uranyl ion done on a Sun Ultra 1 model 200E Workstation. Only one root was converged, and the convergence criterion was approximately 10^{-8} E_h.

AO Basis Sets. We have developed our own (contracted Gaussian) AO basis sets.[79] Basis sets for effective core potential calculations describe (valence) pseudo-orbitals, which are small in the core region. Choosing correlating orbitals by freeing the most diffusive primitives, as is usually and successfully done for all-electron basis sets, does not necessarily produce orbitals which are small in the core region, especially for s orbitals. This implies that all contraction coefficients should be obtained by energy-related methods. The best results are obtained by using natural orbitals from correlated atomic calculations.

The basis sets were derived in the correlation-consistent (cc) manner.[80,81] The oxygen polarized double-ζ (Table 2) and triple-ζ (cc-pVDZ and cc-pVTZ) sets were obtained by optimizing the *s* and *p* primitives in atomic SCF calculations[82] on the ^3P ground state. Next, an uncontracted CISD calculation was done to obtain the natural-orbital contraction coefficients. Finally, the polarization function was optimized in contracted CISD calculations. Optimizing a basis set for O^- gave poorer results at the UO_2^{2+} SCF level and was not used further.

For uranium, we first generated a U^{2+} (4sd4p4f1g)/[3sd2p2f1g] cc-pVDZ basis set (Table 3). Then, to be able to allow for 7s and 7p character, we also developed a U basis set by adding some primitives to the U^{2+} basis set, obtaining a (5sd6p4f1g)/[4sd4p2f1g] cc-pVDZ set. The sd (shared exponents), p, and f primitives were optimized in atomic SCF calculations[82] on the $6d^2$ $5f^2$ average of configurations for U^{2+}, and on the $6d^2$ $5f^2$ $7s^2$ and $6d^2$ $5f^2$ $7s^1$ $7p^1$ averages for U, since these choices would give the reasonably compact 5f description needed for U(VI) complexes. The s and d exponents were constrained to be the same to prevent exponent collapse and to improve molecular integral computation efficiency. Since no 1s primitive functions were used, the contraction coefficients were obtained (1) from the atomic SCF calculations and (2) by freeing the most diffuse

TABLE 3: U cc-pVDZ Basis Set: (4sd4p4f1g)/[3sd2p2f1g]

orbital	primitives	contraction	contraction	contraction
sd	2.168	−0.1289505	−0.0195499	0.0
	1.009	0.7955080	−0.0090364	0.0
	0.4025	0.3649706	0.5279641	0.0
	0.1398	0.0020985	0.5899125	1.0
p	6.728	−0.0033035	0.0	
	1.419	−0.3142991	0.0	
	0.6199	0.7755420	0.0	
	0.2445	0.4902717	1.0	
f	4.436	0.1957684	0.0	
	1.860	0.4559656	0.0	
	0.7552	0.4265113	0.0	
	0.2770	0.1970811	1.0	
g	1.690	1.0		

TABLE 4: Ground-state Uranyl SCF Population Analysis

	gross atomic populations					
atom	s	p	d	f	g	total
U	2.034	5.546	1.469	2.524	0.005	11.577
O	3.863	8.499	0.062	0.000	0.000	12.423

primitive functions. The *g* polarization function was then optimized in CISD calculations in which only the 5f shell was correlated. The U^{2+} basis set was used in the uranyl CISD calculations.

Ground-State SCF. The (closed-shell) ground-state SCF energy of UO$_2^{2+}$ was computed as a function of UO distance using the U and O cc-pVDZ basis sets. The minimum energy was found at 1.699 Å. The $3\sigma_g$, $3\sigma_u$, $1\pi_g$, $2\pi_u$ occupied MOs are considerably separated from the other occupied MOs. The ordering within this top group depends on the basis set and the UO distance.[52,62] All of these MOs show extensive mixing by uranium AOs, with the largest amount being the 5f character in the $3\sigma_u$ MO (54% by population analysis). The group of low unoccupied MOs contains, in addition to the expected $1\delta_u$ (5f) and $1\phi_u$ (5f), the $4\sigma_g$ (largely 7s), $1\delta_g$ (6d), and $3\pi_u$ (5f, antibonding with O2p). The orbital energies for these MOs, in hartrees, are −1.062, −1.071, −1.097, −1.069, −0.406, −0.387, −0.403, −0.396, −0.346, respectively.

The overall population analysis is given in Table 4 and shows that the oxygen charge is only −0.21 by this measure. The U 6p shell, not ordinarily involved in bonding, has a "hole" of 0.45 electrons,[58,62] showing that the short UO distance does cause it to mix with oxygen orbitals.

DF calculations have been carried out with larger basis sets.[62,63] Reference 62 has an oxygen charge of −0.66 with, in particular, a larger O *p* population and smaller U *d* and U *f* populations. Since population analyses are known to be particularly sensitive to basis set choice, particularly when diffuse basis functions are involved, the actual MOs and charge distribution may be more similar than the populations suggest.

CIS Survey of Excited States. To gather preliminary information on excited states, we performed a CIS calculation, using ground-state MOs, including excitations from all occupied MOs to all unoccupied MOs. The first six excited-state Ω values agreed with the experimental assignments from the single-crystal spectra.[30] Despite the close spacing of the high group of occupied MOs, the principal excitations for the first eight excited states (Table 5) were only from the $3\sigma_u$ MO. Despite the proximity of the $4\sigma_g$, $1\delta_g$, and $3\pi_u$ MOs to the $1\delta_u$ and $1\phi_u$ MOs, only the latter pair participated significantly in the excited states. When the $4\sigma_g$ (7s) and 7p-based MOs also did not contribute significantly to preliminary CICI calculations, we decided to use the U^{2+} basis set (Table 3) for further work rather than the U basis set. With this smaller basis, the minimum SCF energy occurs at 1.646 Å (vs 1.699 Å for our larger basis set and 1.650 Å for DF[62]).

TABLE 5: Lower Excited States from CIS Calculation at 1.699 Å

energy (cm^{-1})	state	Λ−*S* term	configuration
0	0_g^+	$^1\Sigma_g^+$	$3\sigma_u^2$
28,600	1_g	$^3\Delta_g$	$3\sigma_u^1 1\delta_u^1$
29,634	2_g		
31,269	3_g		
33,147	2_g	$^3\Phi_g$	$3\sigma_u^1 1\phi_u^1$
35,205	3_g		
37,275	4_g		
42,612	3_g	$^1\Phi_g$	$3\sigma_u^1 1\phi_u^1$
45,909	2_g	$^1\Delta_g$	$3\sigma_u^1 1\delta_u^1$

For all of these excited states, the largest terms were excitations from $3\sigma_u$ to either $1\delta_u$ or $1\phi_u$. In all cases, the second-largest term differed from the principal term in that the excitation came from $2\sigma_u$ rather than $3\sigma_u$. The corresponding CI coefficients were all close to 0.39. Since the $3\sigma_u$ and $2\sigma_u$ terms are single excitations with respect to each other, they can be combined by mixing (rotating) the two MOs in the ratio of their CI coefficients. With the rotated σ_u MOs, the CI coefficient of the principal term was substantially increased and all the excited-state wave functions were in single-reference form, making the CISD description simpler and more efficient.

Another consequence of mixing the $2\sigma_u$ and $3\sigma_u$ MOs is the amount of "charge-transfer" nature[83,84] in the excitations. Even with the unrotated σ_u MOs, the excitation is from an approximately 50% U MO ($3\sigma_u$) to MOs almost entirely on U ($1\delta_u$ and $1\phi_u$). When the σ_u MOs are rotated, $3\sigma_u$ contains even more 5fσ character and $2\sigma_u$ increases its O2pσ character. Thus the rotation of the σ_u MOs reduces the amount of charge "transferred". The population analysis of an excited-state SCF calculation on $3\sigma_u{}^1 1\phi_u{}^1\,{}^3\Phi_g$ gave essentially the same charge on the oxygen atoms as did the ground-state SCF calculation. Thus, the simplest description of the excitations is from 5$f\sigma$ (bonding) to 5fδ or 5fϕ (both nonbonding).

Refined MOs. CISD calculations on the ground state, using the ground-state SCF MOs, showed some single excitations with CI coefficients of moderate magnitude. Some of these were for configurations with different spatial symmetry than the reference configuration (largest coefficient ≈ 0.03) and are therefore due to spin−orbit mixing[68] (principally from the 6p shell), and are little affected by the choice of MOs. The only larger coefficient (≈0.05) was for excitation from $2\pi_u$ to $3\pi_u$; it is an indication that the ground-state SCF $2\pi_u$ MOs are somewhat less than optimum for a correlated description of the UO π bonding. Improving the $2\pi_u$ MO increases the magnitude of the reference CI coefficient and of some of the double-excitation coefficients, which improves the overall correlation description.

Finding an optimum set of MOs for both the ground state and the excited states is quite desirable in terms of computational simplification, particularly in future calculations of transition moments. For uranyl, the two improvements needed, ($2\sigma_u$, $3\sigma_u$) and ($2\pi_u$, $3\pi_u$) rotations, are independent and can be accomplished simultaneously. The ($2\sigma_u$, $3\sigma_u$) rotation has no effect on the ground state, since both MOs are full; the ($2\pi_u$, $3\pi_u$) rotation has approximately the same effect on both the ground and excited states. Thus, we carried out energy-averaged MCSCF calculations in which the energy expressions for the wave functions for the ground and six excited states were averaged. Each wave function included a complete CI in the ($2\pi_u$, $3\pi_u$) space. The resulting natural orbitals from these

TABLE 6: Composition of Multireference Wave Functions at 1.733 Å (Single Reference for the Ground State)

state	${}^1\Sigma_g^+$	${}^3\Delta_g$	${}^3\Phi_g$	${}^1\Delta_g$	${}^1\Phi_g$	tot ref
0_g^+	0.833					0.833
1_g		0.839				0.839
2_g		0.617	0.221			0.839
3_g		0.551	0.233		0.055	0.839
2_g		0.209	0.599	0.030		0.838
3_g		0.283	0.513		0.043	0.839
4_g			0.838			0.838

MCSCF calculations were used in the final CISD calculations. The ($2\pi_u$, $3\pi_u$) improvement was modest in magnitude, while the ($2\sigma_u$, $3\sigma_u$) improvement was quite important for the excited states.

Single-Reference CISD Results. Using the MCSCF MOs, single-reference CISD calculations were done for the ground-state and first six excited-state potential curves. The ground-state equilibrium internuclear distance and vibrational frequency were 1.668 Å (vs 1.697 Å for RECP coupled cluster[55] and 1.710 Å for 4-component coupled cluster[62]) and 1104 cm^{-1}, respectively. The $1\delta_u$ potential curves all had minima very close to 1.735 Å, and the $1\phi_u$ curves all had minima near 1.752 Å. The first 3_g curve crossed the second 2_g curve and approached the second 3_g curve closely at the last point computed, 1.80 Å, despite there being little mixing of $3\sigma_u{}^1$ $1\delta_u{}^1$ wave functions with $3\sigma_u{}^1$ $1\phi_u{}^1$ wave functions for any of the 2_g or 3_g states. Nevertheless, the pattern of excited-state curves suggested that multireference calculations should be done.

The mixing of singlet character into the first 2_g wave function was only 1.3%, but in the second 3_g wave function it was 11.8%, suggesting that the $1\phi_u$ spin−orbit integral is larger and the $3\sigma_u$, $1\phi_u$ exchange integral is smaller than the corresponding $1\delta_u$ integrals, as expected from the CIS results.

The single-reference calculations were repeated using the O cc-pVTZ basis set. The spacing between the excited-state energies changed very little, but all of the excitation energies from the ground state increased by ca. 2300 cm^{-1}. Presumably the ground state, having one more doubly occupied MO than the excited states, was lowered significantly more by the improved correlation treatment afforded by the larger basis set. The ground-state internuclear distance and vibrational frequency changed to 1.645 Å and 1204 cm^{-1}, respectively.

Multireference CISD Results. The CISD excited-state calculations were repeated using both $3\sigma_u{}^1$ $1\delta_u{}^1$ and $3\sigma_u{}^1$ $1\phi_u{}^1$ as reference configurations (triplet and singlet). The fluorescent state equilibrium internuclear distance and vibrational frequency were 1.733 Å (0.065 Å longer than for the ground state vs 0.07 Å experimentally[41]) and 867 cm^{-1}. The composition of all of the wave functions at this distance is described in Table 6. The 2_g and 3_g states show substantial mixing of the δ_u and ϕ_u terms, as anticipated from their magnetic moment values;[41] the mixing increases at longer distances. The potential curves are shown in Figure 1 and have no crossings or near-crossings.

The R_e values, symmetric stretch vibrational frequencies, and excitation energies are given in Table 7. Since there are no gas-phase experimental values to compare to, we include the experimental crystalline results[30,43] for $Cs_2UO_2Cl_4$ and $CsUO_2(NO_3)_3$, with splittings averaged out. The ground-state vibrational frequency of 1103 cm^{-1} is 272 cm^{-1} more than the observed crystal value of 831 cm^{-1} for $Cs_2UO_2Cl_4$. The equatorial ligands presumably elongate the UO bonds and decrease the vibrational frequency. The calculated fluorescent-state vibrational frequency of 867 cm^{-1} is similarly higher than the $Cs_2UO_2Cl_4$ value of 715 cm^{-1}. The excitation energies correspond reasonably to the crystalline values; the calculated values are known to be sensitive to further basis set improvements. For the seventh excited-state we find a 3_g state (mostly ${}^1\Phi_{g3}$), while the crystalline assignment is 2_g. We have not studied this state in as much detail as the lower excited states.

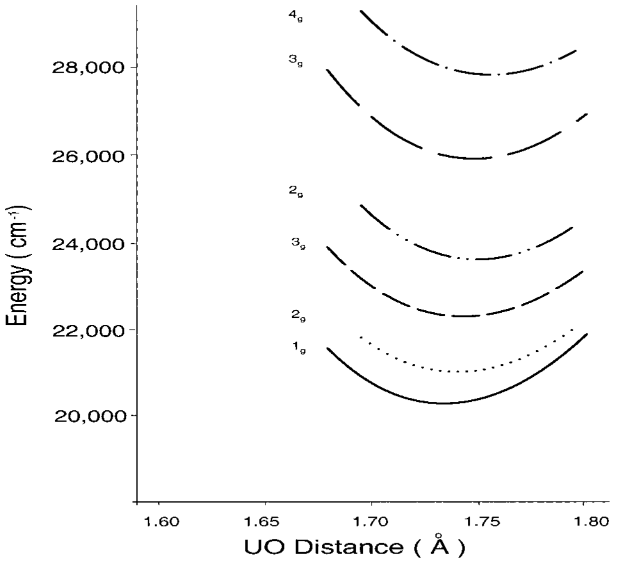

Figure 1. Excited-State Curves From Multireference Calculations.

TABLE 7: Multireference Calculations with cc-pVDZ Basis Sets (Single Reference for the Ground State)

state	R_e (Å)	ν_e (cm^{-1})	T_e	$Cs_2UO_2Cl_4$	$CsUO_2(NO_3)_3$
0_g^+ (ground)	1.668	1103	0	0	0
1_g (fluorescent)	1.733	845	21,421	20,861	21,694
3_g	1.742	847	22,628	22,051	22,786
2_g	1.749	900	23,902	22,578	23,474
3_g	1.747	898	26,118	26,222	27,062
4_g	1.755	880	27,983	27,738	29,618
3_g			31,710	29,412	31,262

TABLE 8: Higher Excited States

energy (cm^{-1})	state	configuration
0	${}^3\Delta_u$	$3\sigma_g^1 1\delta_u^1$
652	${}^1\Delta_u$	$3\sigma_g^1 1\delta_u^1$
3,976	${}^3\Phi_u$	$3\sigma_g^1 1\phi_u^1$
5,703	${}^1\Phi_u$	$3\sigma_g^1 1\phi_u^1$
15,160	${}^1\Phi_u$	$1\pi_g^3 1\delta_u^1$
15,318	${}^3\Pi_u$	$1\pi_g^3 1\delta_u^1$
15,441	${}^3\Phi_u$	$1\pi_g^3 1\delta_u^1$
16,771	${}^1\Pi_u$	$1\pi_g^3 1\delta_u^1$

The excited states are all subject to Renner−Teller splitting; we investigated this for the fluorescent state. Bending the molecule to 160° raises the energy by 1600 cm^{-1}, but the splitting between the two Renner−Teller components is only 0.31 cm^{-1}.

Odd-Parity States. To survey the lowest energy states of odd parity, we performed MCSCF calculations which included all odd-parity single excitations from the occupied to the unoccupied MOs discussed above. The orbitals were optimized for the lowest state. The UO distance used was 1.736 Å and the results for the eight lowest states are given in Table 8. Since no spin−orbit coupling was included, Λ−S notation is used.

The lowest odd-parity states come from the $3\sigma_g{}^1$ $1\delta_u{}^1$ configuration, as concluded experimentally.[30,42] The observed transition from the first excited state is $3\sigma_u \leftarrow 3\sigma_g$; the unobserved transition from the ground state would be $1\delta_u \leftarrow 3\sigma_g$. The next higher states have the configuration $3\sigma_g{}^1 1\phi_u{}^1$.

TABLE 9: Low Odd-Parity Excited States (CISD Calculations at 1.736 Å)

energy (cm^{-1})	state	configuration
34 588	1_u	
34,603	2_u	$3\sigma^1_{g1/2}1\delta^1_{u3/2}$
37,668	3_u	
37,688	2_u	$3\sigma^1_{g1/2}1\delta^1_{u5/2}$

The results of spin−orbit single-reference CISD calculations on the $3\sigma_g{}^1 1\delta_u{}^1$ states at 1.736 Å are shown in Table 9. The pattern of two pairs of states with appreciable separation between them suggests $\omega-\omega$ coupling. The $1_u \leftarrow 1_g$ transition is observed at 17 000 cm^{-1}, which corresponds to 37 100 cm^{-1} from the ground state.[42] Our computed results are 13 869 cm^{-1} above the first excited state and 34 588 cm^{-1} above the ground state. We have not investigated the potential curve or other properties of this state. Our initial calculations with cc-pVTZ basis sets indicate that they would increase the calculated excitation energy for this state.

3 Conclusions

The uranyl ion has been studied since uranium compounds were first isolated, and among its most-studied properties has been the visible spectrum. We have studied the ground and six lowest excited states of this ion using relativistic effective core potentials, spin−orbit operators, and spin−orbit GUGA CI wave functions. Our results agree well with experimental results in terms of orbital excitations and angular momentum quantum numbers, but we provide some additional information about spin coupling and configuration mixing. The agreement in terms of excitation energies and symmetric stretch vibrational frequencies is quite reasonable in view of the fact that the best comparison available is from crystalline data rather than gas-phase data. Our results for the seventh excited state give a different Ω value, and our result for the lowest odd-parity state agrees in assignment but is low in excitation energy; we have not investigated either of these states as thoroughly as we have the lower states.

Future work includes calculations on crystalline $Cs_2UO_2Cl_4$ for better comparisons with experiment and the calculation of magnetic moments and transition moments of all applicable types. The primary example, the magnetic moment of the fluorescent state and its transition magnetic dipole moment with the ground state, will require a close examination of the $3\sigma_u{}^1 3\pi_u{}^1$ terms in the wave functions. At present there are already efforts underway to set up the crystalline model, to refine the uranium core potential and spin−orbit operators, to develop a larger uranium basis set, and to develop a parallel version of the spin−orbit GUGA CI program. Together, these projects should lead to substantially improved and extended results; much of this work is being done by people listed below.

Acknowledgment. We thank J. Beitz, J. Blaudeau, S. Brozell, P. Christiansen, L. Curtiss, R. Denning, W. A. de Jong, S. Matsika, D. Reed, I. Shavitt, R. Shepard, and S. Yabushita for helpful discussions. We thank Argonne National Laboratory (ANL) for support from their Actinide Synchrotron Studies project, and Pacific Northwest National Laboratory (PNNL) for support through Contract 200210, U. S. Department of Energy, the Mathematical, Information, and Computational Science Division, High-Performance Computing and Communications Program of the Office of Computational and Technology Research. PNNL is operated by Battelle Memorial Institute under contract DE-AC06-76RLO 1830. We acknowledge the use of computational facilities at the Ohio Supercomputer Center, ANL, and Ohio State University (largely provided by the PNNL grant).

References and Notes

(1) *Handbook of Chemistry and Physics*; CRC: Boca Raton, annual editions.

(2) Günther, R. T. *Archaeologia* **1912**, *63*, 99−105.

(3) Manley, J. J. *Archaeologia* **1912**, *63*, 106−108.

(4) Caley, E. R. *Isis* **1948**, *38*, 190−193.

(5) Klaproth, M. H. *Chem. Ann. Freunde Naturl.* **1789**, No. 2, 387−403.

(6) Péligot, E. *J. Pharm. Sci. Accessoires* **1841**, *27*, 525−535.

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

(8) Denning, R. G. Properties of $UO_2{}^{n+}$ (n = 1, 2). In *General Properties. Criticality*; *Gmelin Handbook of Inorganic Chemistry*, Uranium A6; Buschbeck, K.-C., Keller, C., Eds.; Springer: Berlin, 1983; pp 31−79.

(9) Clark, D. L.; Keough, D. W.; Neu, M. P.; Runde, W. Uranium and Uranium Compounds. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; Howe-Grant, M., Ed.; Wiley: New York, 1997; pp 638−694.

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

(11) Weigel, F. Uranium. 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 169−442.

(12) Brewster, D. *Trans. R. Soc. Edinburgh* **1849**, *16*, 111−121.

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

(14) Curie, D. *Luminescence in Crystals*; G. F. J. Garlick, Translator; Methuen: London, 1963; p 31; *Luminescence Cristalline*; Dunod: Paris, 1960; p 37.

(15) Knight, D. M. Antoine-César Becquerel. In *Dictionary of Scientific Biography*; Gillispie, C. C., Ed.; Scribner: New York, 1981; pp 557−558.

(16) Becquerel, E. *C. R. Hebd. Seances Acad. Sci.* **1872**, *75*, 296−303.

(17) Becquerel, H. *C. R. Hebd. Seances Acad. Sci.* **1885**, *101*, 1252−1256.

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

(19) Becquerel, H.; Becquerel, J.; Kamerlingh-Onnes, H. *Versl. Gewone Vergad. Afd. Natuurkd., K. Ned. Akad. Wet.* **1909**, *12*, 76−88.

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

(21) Denning, R. G.; Snellgrove, T. R.; Woodwark, D. R. *Mol. Phys.* **1975**, *30*, 1819−1828.

(22) Barker, T. J.; Denning, R. G.; Thorne, R. G. *Inorg. Chem.* **1987**, *26*, 1721−1732.

(23) Dieke, G. H.; Van Heel, A. C. S. *Versl. Gewone Vergad. Afd. Natuurkd., K. Ned. Akad. Wet.* **1925**, *28*, 953−954.

(24) Freed, S.; Kasper, C. *J. Am. Chem. Soc.* **1930**, *52*, 4671−4679.

(25) Fankuchen, I. *Z. Krystallogr.* **1935**, *91*, 473−479.

(26) Moerman, N. F.; Kraak, H. H. *Recl. Trav. Chim. Pays-Bas* **1939**, *58*, 34−38.

(27) 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.

(28) Kasha, M. *J. Chem. Phys.* **1949**, *17*, 349−349.

(29) Görller-Walrand, C.; Vanquickenbourne, L. G. *J. Chem. Phys.* **1971**, *54*, 4178−4186.

(30) Denning, R. G. *Struct. Bonding (Berlin)* **1992**, *79*, 215−277.

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

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

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

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

(35) Bucholz, C. F. *Neues Allg. J. Chem.* **1805**, *4*, 134−160.

(36) Ebelmen *Ann. Chim. Phys.* **1842**, *5*, 189−223.

(37) Bell, J. T.; Biggers, R. E. *J. Mol. Spectrosc.* **1968**, *25*, 312−329.

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

(39) Watkin, D. J.; Denning, R. G.; Prout, K. *Acta Crystallogr.* **1991**, *C47*, 2517−2519.

(40) Denning, R. G.; Snellgrove, T. R.; Woodwark, D. R. *Mol. Phys.* **1976**, *32*, 419−442.

(41) Denning, R. G.; Snellgrove, T. R.; Woodwark, D. R. *Mol. Phys.* **1979**, *37*, 1109−1143.

(42) Denning, R. G.; Morrison, I. D. *Chem. Phys. Lett.* **1991**, *180*, 101−104.

(43) Barker, T. J.; Denning, R. G.; Thorne, R. G. *Inorg. Chem.* **1992**, *31*, 1344−1353.

(44) Boring, M.; Wood, J. H.; Moskowitz, J. W. *J. Chem. Phys.* **1975**, *63*, 638−642.

(45) Yang, C. Y.; Johnson, K. H.; Horsley, J. A. *J. Chem. Phys.* **1978**, *68*, 1001−1005.

(46) Boring, M.; Wood, J. H. *J. Chem. Phys.* **1979**, *71*, 392−399.

(47) Wood, J. H.; Boring, M.; Woodruff, S. B. *J. Chem. Phys.* **1981**, *74*, 5225−5233.

(48) Pershina, V. G.; Ionova, G. V.; Suraeva, N. I. *Sov. Radiochem.* **1990**, *31*, 386−391.

(49) Ellis, D. E.; Rosén, A.; Walch, P. F. *Int. J. Quantum Chem., Symp.* **1975**, *9*, 351−358.

(50) Walch, P. F.; Ellis, D. E. *J. Chem. Phys.* **1976**, *65*, 2387−2392.

(51) DeKock, R. L.; Baerends, E. J.; Boerrigter, P. M.; Snijders, J. G. *Chem. Phys. Lett.* **1984**, *105*, 308−316.

(52) Wadt, W. R. *J. Am. Chem. Soc.* **1981**, *103*, 6053−6057.

(53) Pyykkö, P.; Li, J.; Runeberg, N. *J. Phys. Chem.* **1994**, *98*, 4809−4813.

(54) Craw, J. S.; Vincent, M. A.; Hillier, I. H.; Wallwork, A. L. *J. Phys. Chem.* **1995**, *99*, 10181−10185.

(55) Cornehl, H. H.; Heinemann, C.; Marçalo, J.; Pires de Matos, A.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 891−894.

(56) Tatsumi, K.; Hoffmann, R. *Inorg. Chem.* **1980**, *19*, 2656−2658.

(57) Pyykkö, P.; Lohr, L. L. *Inorg. Chem.* **1981**, *20*, 1950−1959.

(58) Pyykkö, P.; Laaksonen, L. *J. Phys. Chem.* **1984**, *88*, 4892−4895.

(59) Pyykkö, P.; Laakkonen, L. J.; Tatsumi, K. *Inorg. Chem.* **1989**, *28*, 1801−1805.

(60) Wahlgren, U.: Schimmelpfennig, B.; Jusuf, S.; Stromsnes, H.; Gropen, O.; Maron, L. *Chem. Phys. Lett.* **1998**, *287*, 525−530.

(61) Ismail, N.; Heully, J.-L.; Saue, T.; Daudey, J.-P.; Marsden, C. J. *Chem. Phys. Lett.* **1999**, *300*, 296−302.

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

(63) Dyall, K. G. *Mol. Phys.* **1999**, *96*, 511−518.

(64) Ermler, W. C.; Ross, R. B.; Christiansen, P. A. *Adv. Quantum Chem.* **1988**, *19*, 139−182.

(65) Dolg, M.; Stoll, H. Electronic Structure Calculations for Molecules containing Lanthanide Atoms. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneider, K. A., Eyring, L., Eds.; Elsevier: Amsterdam, 1995; Vol. 22, pp 607−729.

(66) Balasubramanian, K. *Relativistic Effects in Chemistry: Part A, Theory and Techniques*; Wiley: New York, 1997.

(67) Morokuma, K.; Yamashita, K.; Yabushita, S. Potential Energy Surfaces of Several Elementary Chemical Reactions. In *Supercomputer Algorithms for Reactivity, Dynamics and Kinetics of Small Molecules*; Laganà, A., Ed.; Kluwer: Dordrecht, 1989; pp 37−56.

(68) Yabushita, S.; Zhang, Z.; Pitzer, R. M. *J. Phys. Chem. A* **1999**, *103*, 5791−5800.

(69) See www.clarkson.edu/∼pac/reps.html for complete references and a library of potentials.

(70) Ermler, W. C.; Ross, R. B.; Christiansen, P. A. *Int. J. Quantum Chem.* **1991**, *40*, 829−846.

(71) Lee, Y. S.; Ermler, W. C.; Pitzer, K. S. *J. Chem. Phys.* **1977**, *67*, 5861−5876.

(72) Christiansen, P. A.; Lee, Y. S.; Pitzer, K. S. *J. Chem. Phys.* **1979**, *71*, 4445−4450.

(73) Christiansen, P. A.; Ermler, W. C.; Pitzer, K. S. *Annu. Rev. Phys. Chem.* **1985**, *36*, 407−432.

(74) Ross, R. B.; Ermler, W. C.; Christiansen, P. A. *J. Chem. Phys.* **1986**, *84*, 3297−3300.

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

(76) Shavitt, I. Unitary Group Approach to Configuration Interaction Calculations of the Electronic Structure of Atoms and Molecules. In *Mathematical Frontiers in Computational Chemical Physics*; Truhlar, D. G., Ed.; Springer: Berlin, 1988; pp 300−349.

(77) See www.itc.univie.ac.at/∼hans/Columbus/Columbus.html for information and references on the COLUMBUS programs.

(78) See Chang, A. H. H.; Pitzer, R. M. *J. Am. Chem. Soc.* **1989**, *111*, 2500−2507 and ref 47 therein.

(79) Blaudeau, J.; Brozell, S.; Matsika, S.; Zhang, Z.; Pitzer, R. M. Atomic Orbital Basis Sets for Use with Effective Core Potentials. *Int. J. Quantum Chem.*, submitted for publication.

(80) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007−1023.

(81) Wallace, N. M.; Blaudeau, J. P.; Pitzer, R. M. *Int. J. Quantum Chem.* **1991**, *40*, 789−796.

(82) Pitzer, R. M. *QCPE* **1987**, 587.

(83) Jørgensen, C. K. *Adv. Chem. Phys.* **1963**, *5*, 33−146.

(84) Jørgensen, C. K. *Prog. Inorg. Chem.* **1970**, *12*, 101−158.