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Relativistic $X\alpha$–scattered-wave calculations for the uranyl ion

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Relativistic $X\alpha$–scattered-wave molecular orbital calculations have been carried out on the uranyl ion UO_2^{2+}. The calculated orbital eigenvalues are in good agreement with the results of a recent x-ray photoelectron spectroscopy study of uranyl compounds. An interpretation of the optical spectrum of the uranyl ion in terms of a Hund's case (c) (ω, ω) coupling scheme is given.

INTRODUCTION

There have been a number of attempts to describe the electronic structure and bonding of the uranyl ion UO_2^{++} within the framework of molecular orbital theory. Most recently, self-consistent-field molecular orbital calculations have been carried out by the $X\alpha$–scattered-wave method ($X\alpha$–SW)[1] and the $X\alpha$ discrete variational method (DVM).[2,3] Using the discrete variational method both nonrelativistic[2] and relativistic Dirac–Slater[3] molecular orbital calculations have been carried out. The $X\alpha$–SW calculations of Boring and Moskowitz,[1] however, did not include relativistic effects. Recently, one of us (C. Y. Y.) has developed a relativistic scattered-wave formalism based on the one-electron Dirac equation and the muffin-tin potential,[4] which has been successfully applied to the diatomic molecules C_2 and I_2[5] and clusters of lead selenides.[6] We report here the results of calculations performed on the UO_2^{++} ion using this method. The calculations are used to interpret the x-ray photoemission and optical spectra of UO_2^{++}.

COMPUTATIONAL METHOD

The electronic structure calculations presented here for the uranyl ion were performed using the nonrelativistic[7] and relativistic[4] versions of the $X\alpha$–scattered-wave ($X\alpha$–SW) method. The overlapping sphere model[8,9] was employed for the linear UO_2^{++} ion (point group $D_{\infty h}$) and the sphere radii were chosen with the criteria suggested by Norman.[10] The U–O separation was chosen to be 1.73 Å (3.269 a.u.), which roughly corresponds to the primary U–O bond lengths in the compounds UO_2CO_3 and $UO_2(NO_3)_2 \cdot 6H_2O$.[11] The exchange parameter α was chosen to be 2/3 for uranium and the value given by Schwarz[12] for oxygen. In the intersphere region and outside the outer sphere α was taken to be a simple average of the two. The sphere radii used were $R_U = 2.3631$ a.u., $R_O = 1.5597$ a.u., $R_{out} = 4.8287$ a.u.

Fully relativistic (Dirac) scattered-wave calculations have been performed on a number of systems ranging from the diatomic molecule I_2[5] to sizable (over 10 atoms) defect-containing clusters of the lead salts.[6] For I_2[5] the calculated valence orbital ionization potentials were all within 0.7 eV of the experimental values obtained from photoemission spectroscopy, and the calculated transition energies to the lowest unoccupied orbitals were all within 0.25 eV of the values obtained from the optical spectrum. Although the calculation has not been made fully self-consistent, the results for I_2 show that a non-self-consistent relativistic calculation using the self-consistent nonrelativistic potential can give satisfactory agreement with experimental I. P.'s and transition energies. The lack of *relativistic* self-consistency has the effect of not allowing the redistribution of relativistic valence electrons, but this redistribution of charges often only results in almost uniform shifts of all levels, which is physically inconsequential.

Atomic $X\alpha$ calculations for U^{++} and O were performed using the computer program developed by Herman and Skillman[13] for the nonrelativistic case, and the program developed by Liberman, Cromer, and Waber[14] for the relativistic case.

RESULTS AND COMPARISON WITH EXPERIMENTAL XPS SPECTRUM

The one-electron energies of U^{++}, O, and UO_2^{++} are shown in Tables I and II and plotted in Fig. 1. The nonrelativistic results are basically the same as the $X\alpha$–SW results obtained by Boring *et al.*[1] with our U–O separation. The discrepancies between the two calculations are primarily due to the different choices of sphere radii. The valence levels of the uranyl ion form three distinct groups. The $1\sigma_g$ orbital is predominantly U 6*s* in character. The $1\sigma_u$ and $2\sigma_u$ levels are mixtures of U 6*p* and O 2*s*. $1\pi_u$ is predominantly U 6*p* and $2\sigma_g$ is predominantly O 2*s*. The origins of the last four bonding orbitals are not as simple, but they are largely O 2*p*, with some U 5*f* and U 6*d* contributions. The low-lying unoccupied orbitals $1\delta_u$, $1\phi_u$, and $3\pi_u$ constitute the bulk of the "U 5*f* band."

The relativistic results shown in the next column exhibit the expected shifts and splittings. The notations used to label the orbitals are based on the usual convention: The letter gives the degeneracy of the irreducible representation for the one-electron wavefunc-

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TABLE I. Nonrelativistic $X\alpha$–SW eigenvalues (in Rydberg).

Atoms		UO_2^{++}	
Orbital	Eigenvalue	Orbital	Eigenvalue
U^{++} $6s$	−3.905	$1\sigma_g$	−3.693
U^{++} $6p$	−2.852	$1\sigma_u$	−3.277
O $2s$	−1.892	$2\sigma_g$	−2.784
U^{++} $5f$	−2.093	$1\pi_u$	−2.498
U^{++} $6d$	−1.350	$2\sigma_u$	−2.338
U^{++} $7s$	−0.953	$3\sigma_g$	−1.853
O $2p$	−0.837	$2\pi_u$	−1.828
		$3\sigma_u$	−1.791
		$1\pi_g$ [a]	−1.790
		$1\delta_u$	−1.623
		$1\phi_u$	−1.623
		$3\pi_u$	−1.461

[a]Highest occupied level.

tion, e.g., e for a two-dimensional irreducible representation, while the half-integral subscript denotes the quantum number $\omega = |m_j|$, the magnitude of the component of the total angular momentum along the internuclear axis. The $1\sigma_g$ (U $6s$) orbital becomes $1e_{1/2g}$ and its energy is shifted down by about 1.6 Rydberg. This shifting is more than 50% larger than that in the U^{++} ion, and is probably due to ligand field effects. The next lowest level $1e_{1/2u}$ is primarily U $6p_{1/2}$ in character, but the two levels $2e_{1/2u}$ and $3e_{1/2u}$ have mixed U $6p$–O $2s$ character. Both the $2e_{1/2u}$ and $3e_{1/2u}$ orbitals contain significant amounts of O $2s$; hence, the separation between $3e_{1/2u}$ and $1e_{3/2u}$ cannot strictly be classified as a "U $6p_{3/2}$ ligand-field splitting."[11] The same conclusion was reached by Walch and Ellis from their DVM calculations.[3] The highest valence "band" is not shifted much by relativistic effects, and since the mixings between the two $e_{1/2g}$ orbitals and between the two $e_{1/2u}$ orbitals are not very strong, the six relativistic orbitals can be matched against their approximate nonrelativistic counterparts in this manner

$$4e_{1/2u}2e_{3/2u}(2\pi_u)3e_{1/2g}(3\sigma_g)5e_{1/2u}(3\sigma_u)4e_{1/2g}1e_{3/2g}(1\pi_g) .$$

The unoccupied "f band" is shifted down somewhat and its separation from the top valence band is reduced to about 0.2 eV. This energy separation will be discussed in more detail in the section dealing with the absorption spectrum.

The agreement between our SW results and the DVM results of Walch and Ellis[3] for the isolated UO_2^{++} ion is fairly good. The ordering of the energy levels in the valence band is different in the two calculations, however. The highest occupied orbitals in the SW calculations correspond to the two components of the $1\pi_g$ orbital of the nonrelativistic calculation, while the highest occupied orbitals in the DVM calculation correspond to the $3\sigma_u$ and $3\sigma_g$ orbitals of the nonrelativistic calculation. However, the levels in the valence band are all very

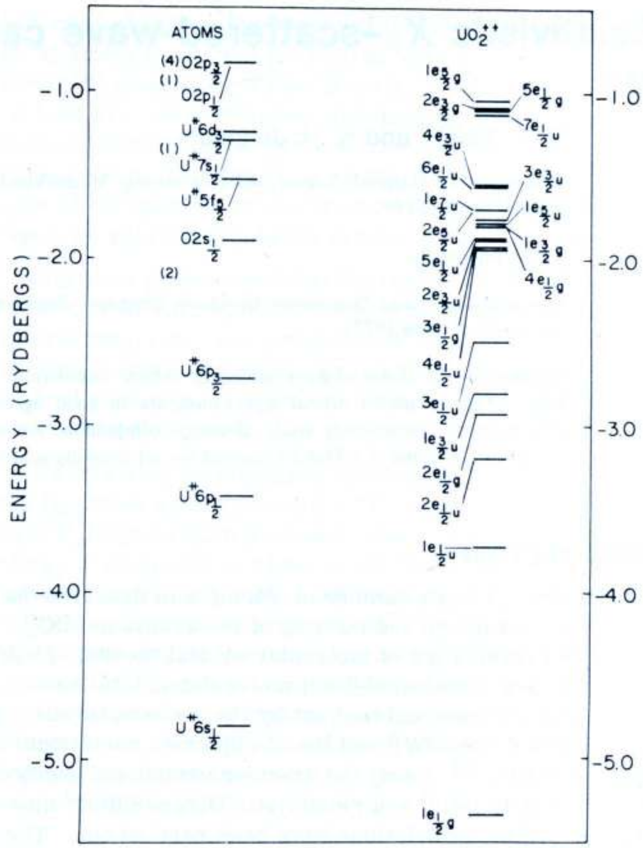

FIG. 1. Relativistic $X\alpha$–SW orbital energies for UO_2^{++}, U^{++}, and O.

TABLE II. Relativistic $X\alpha$–SW eigenvalues (in Rydberg).

Atoms		UO_2^{++}	
Orbital	Eigenvalue	Orbital	Eigenvalue
U^{++} $6s_{1/2}$	−4.806	$1e_{1/2g}$	−5.333
U^{++} $6p_{1/2}$	−3.424	$1e_{1/2u}$	−3.728
U^{++} $6p_{3/2}$	−2.719	$2e_{1/2g}$	−2.929
O $2s_{1/2}$	−1.896	$2e_{1/2u}$	−3.195
U^{++} $5f_{5/2}$	−1.532	$1e_{3/2u}$	−2.802
U^{++} $6d_{3/2}$	−1.248	$3e_{1/2u}$	−2.496
U^{++} $7s_{1/2}$	−1.299	$4e_{1/2u}$	−1.945
O $2p_{1/2}$	−0.838	$3e_{1/2g}$	−1.932
O $2p_{3/2}$	−0.836	$2e_{3/2u}$	−1.885
		$5e_{1/2u}$	−1.875
		$4e_{1/2g}$	−1.809
		$1e_{3/2g}$ [a]	−1.805
		$1e_{5/2u}$	−1.788
		$3e_{3/2u}$	−1.761
		$2e_{5/2u}$	−1.701
		$1e_{7/2u}$	−1.700
		$6e_{1/2u}$	−1.562
		$4e_{3/2u}$	−1.550

[a]Highest occupied level.

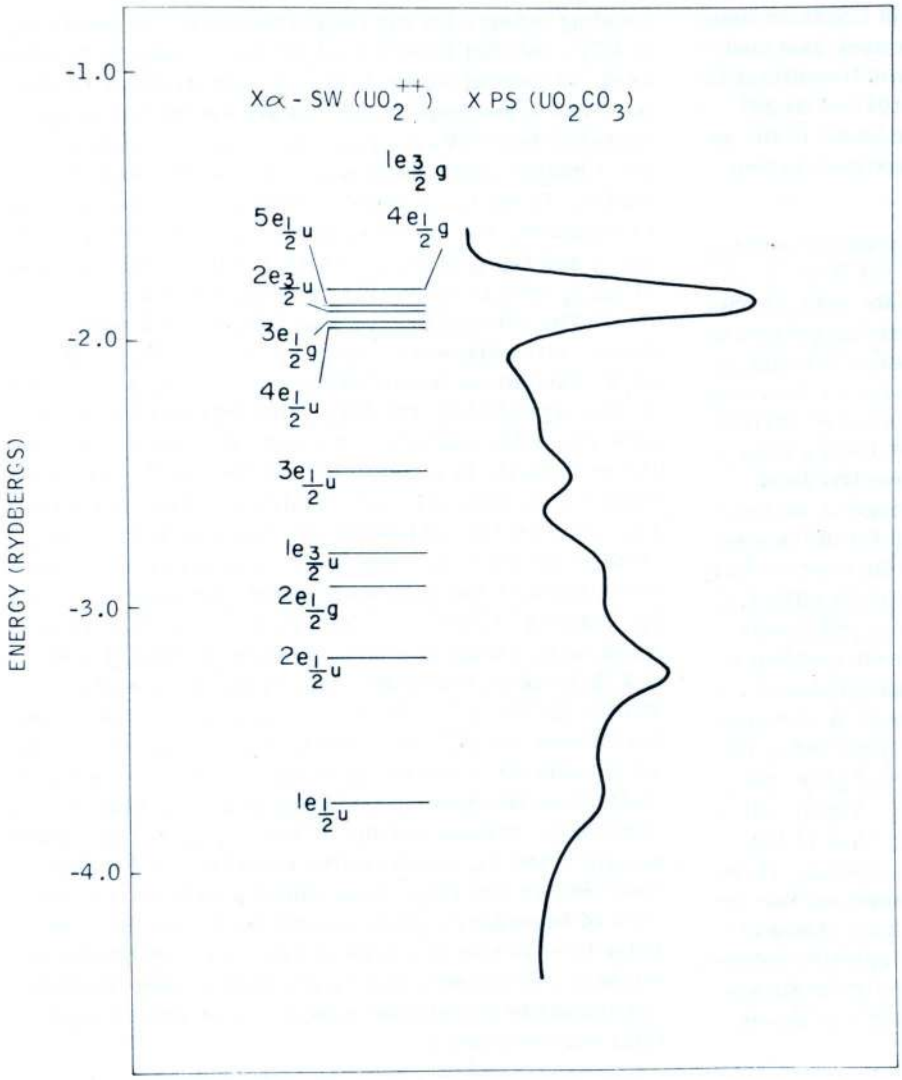

FIG. 2. Comparison of the relativistic $X\alpha$–SW orbital energies of UO_2^{++} with the XPS spectrum of UO_2CO_3 obtained by Veal *et al.* (Ref. 11).

close so that the change of ordering corresponds to only small differences in the energy levels between the two calculations. The only other significant difference is that the $3e_{1/2u}$ orbital, immediately below the valence band, is shifted down by about 0.2 Rydberg in the SW calculation compared to the DVM calculation. In both calculations the energy gap between the highest occupied and lowest unoccupied orbital is much smaller than the absorption spectrum would indicate, and the lowest unoccupied orbital is a $e_{5/2u}$ orbital.

Figure 2 gives a comparison of our relativistic results with the x-ray photoemission spectrum (XPS) for UO_2CO_3 obtained by Veal *et al.*,[11] which is sketched alongside the calculated orbital energies by aligning the center of gravity of the top valence band with the first peak of the XPS spectrum.

According to Veal *et al.*[11] the electronic structure of the uranyl ion as observed in various crystalline environments is principally a function of the primary U–O separation. Based on this finding, one could use the calculated electronic structure of a single UO_2^{++} ion for a given U–O separation. The U–O primary separations in UO_2CO_3 measured by x-ray diffraction and calculated from infrared data are ~1.70 and 1.73 Å, respectively.[11] Hence, it is not unreasonable to compare our results for UO_2^{++} with the U–O separation 1.73 Å to the XPS of UO_2CO_3. Apart from the major feature corresponding to the top valence band, each of the other features can be identified with levels in the calculated energy spectrum. The three peaks in the middle fall directly on top of the region of the mixed U $6p_{3/2}$–O $2s$ orbitals, with the first corresponding to $3e_{1/2u}$, the second to $1e_{3/2u}$, and $2e_{1/2g}$, and the third to $2e_{1/2u}$. As we pointed out before the mixings in the $e_{1/2u}$ orbitals are sufficiently strong that one cannot truly identify the corresponding XPS peaks with a purely atomic origin. The last peak in the spectrum, which lines up with $1e_{1/2u}$, can quite safely be identified as almost atomic in character, since $1e_{1/2u}$ is predominantly U $6p_{1/2}$.

INTERPRETATION OF THE ABSORPTION SPECTRUM OF UO_2^{++}

The absorption spectrum of UO_2^{++} in solution consists of a series of weak bands between 20 000 and 30 000 cm^{-1} followed by stronger continuous absorption in the uv which increases in intensity towards shorter wavelengths. Bell and Biggers[15] were able to resolve the visible and uv spectrum into a series of 24 bands by fitting the observed spectrum to a series of Gaussian functions by least squares. Nineteen bands were assigned to vibronic progressions in two electronic transitions in the visible and near uv, centered at 24 101 and 31 367 cm^{-1}, respectively. The remaining five bands in the uv are broad and structureless and were assigned to five separate electronic transitions.

A number of interpretations of the absorption spectrum of UO_2^{++} have been put forward[16–20] but there is no agreement as to which interpretation is the correct one. Even the fundamental question of the coupling scheme in the excited states of UO_2^{++} is controversial. In order to interpret the spectrum it is first necessary to determine whether the appropriate coupling scheme in the excited states corresponds to Hund's case (a) or Hund's case (c).[21] In Hund's case (a) a large axial electric field strongly couples the electronic orbital angular momentum to the internuclear axis, the component of the electronic orbital angular momentum along the internuclear axis having the quantum number Λ. States of different Λ are widely separated compared with the spin–orbit splitting. In Hund's case (c) the spin–orbit splitting becomes greater than or equal to the splitting between states of different Λ. The quantum number Λ is therefore no longer well defined. Only the component of the total electronic angular momentum, orbital plus spin, is well defined, with quantum number Ω. Nearly all the interpretations of the absorption spectrum of UO_2^{++} are based on a Hund's case (a) coupling scheme. However, Jorgensen and Reisfeld[19] have pointed out that the spin–orbit splitting in some of the low-lying states of UO_2^{++} will be very much greater than the splitting between states of different Λ, so that Hund's case (c) is the appropriate coupling scheme for at least some of the excited states.

In principle, one could attempt to interpret the observed spectrum of UO_2^{++} by comparing the calculated relativistic SW–$X\alpha$ energy differences between pairs of occupied and unoccupied orbitals with the observed transitions. However, the calculated energy gap between the highest occupied ($1e_{3/2g}$) orbital and the lowest unoccupied ($1e_{5/2u}$) orbital is only 0.02 Rydberg (0.3 eV). A transition state calculation with half an electron placed in each of these orbitals would undoubtedly increase this gap somewhat, but it still appears to be far too small compared with the first observed feature in the spectrum, which begins around 5000 Å (2.5 eV). The error in the calculations probably arises at least in part from the neglect of secondary ligands, as Walch and Ellis found that inclusion of secondary ligands in the form of point charges increased the gap between the occupied and unoccupied orbitals by about 0.7 eV. The lack of self-consistency in our calculation may also be responsible for part of the error. In view of this we will not attempt to make a quantitative comparison of our results with the observed spectrum, but we will limit ourselves to a purely qualitative interpretation based on the set of orbitals which we have calculated and a recent experimental study of the UO_2^{++} spectrum.

One conclusion which may be drawn immediately for our calculations is that Λ–Σ coupling is not the correct coupling scheme for the interpretation of the spectrum of UO_2^{++}, but that Hund's case (c) (ω, ω) coupling must be used, as pointed out by Jorgensen and Reisfeld. In fact, the δ and ϕ unoccupied orbitals are degenerate in the nonrelativistic SW–$X\alpha$ calculation, so the quantum number λ has no significance when spin–orbit coupling is included. In the (ω, ω) coupling scheme, according to our calculations, the lowest energy excitations are from the $1e_{3/2g}$ and $4e_{1/2g}$ orbitals, which are the two components of the π_g orbital obtained in the nonrelativistic calculation. The orbital is largely localized on the oxygen atoms so the spin–orbit splitting is very small. However, excitations from these orbitals to the lowest unoccupied orbitals $1e_{5u}$ and $3e_{3/2u}$ give rise to electric-dipole allowed transitions. It seems very improbable that the weak bands in the region 20–30 000 cm^{-1} correspond to electric-dipole allowed transitions. They are more likely to correspond to electric-dipole forbidden g–g transitions which become weakly allowed through vibronic mixing with the secondary ligand vibrations. Recently, Denning *et al.*[20] in a high resolution study of the absorption spectrum of single crystals of $Cs_2UO_2Cl_4$ at 4.2 °K found 12 electronic transitions in the region 20 000–29 000 cm^{-1}, all g–g in character. If the lowest transitions in UO_2^{++} are g–g transitions, then the calculated ordering of the occupied orbitals is incorrect and the highest occupied orbital should be an orbital of u symmetry, presumably the oribtal $5e_{1/2u}$, which corresponds to the $3\sigma_u$ orbital in the nonrelativistic calculation. Walch and Ellis[3] have indeed found that the presence of secondary ligands around the uranyl ion does raise the orbitals of u symmetry with respect to the orbitals of g symmetry and, in particular, they found that the highest occupied orbital is a $e_{1/2u}$ orbital ($S_{1/2u}$ in their nomenclature).

The effective symmetry of the $UO_2Cl_4^{2-}$ ion is D_{2h}, obtained by a slight distortion from a D_{4h} structure. Denning *et al.* were able to determine the symmetries (in the D_{2h} point group) of the excited states in the 12 electronic transitions observed by them. If it is assumed that the Cl^- ions simply act as a perturbation on the UO_2^{++} ion, then these 12 states can be regarded as stemming from six parent states of the UO_2^{++} ion with $D_{\infty h}$ symmetry. The symmetries of these six $D_{\infty h}$ states are, according to Denning *et al.*, Π_g, $\Delta_g(2)$, $\Phi_g(2)$, and Γ_g.

Let us now consider the excited states that can be obtained by excitation from the $5e_{1/2u}$ orbital to the lowest unoccupied orbitals. The lowest unoccupied orbitals are obtained from the spin–orbit and ligand field splitting of the nonbonding uranium $5f$ orbital. This gives one orbital of symmetry $e_{3/2u}$, two orbitals of symmetry $e_{5/2u}$, and one of symmetry $e_{7/2u}$ (Table I). We can therefore obtain the following electronic states by excitation to these orbitals:

$$\cdots(e_{1/2u})(e_{3/2u}), \qquad \Omega = 1, 2,$$

$$\cdots(e_{1/2u})(e_{5/2u}) \text{ (twice)}, \qquad \Omega = 2, 3,$$

$$\cdots(e_{1/2u})(e_{7/2u}), \qquad \Omega = 3, 4.$$

These excitations are shown schematically in Fig. 3. In

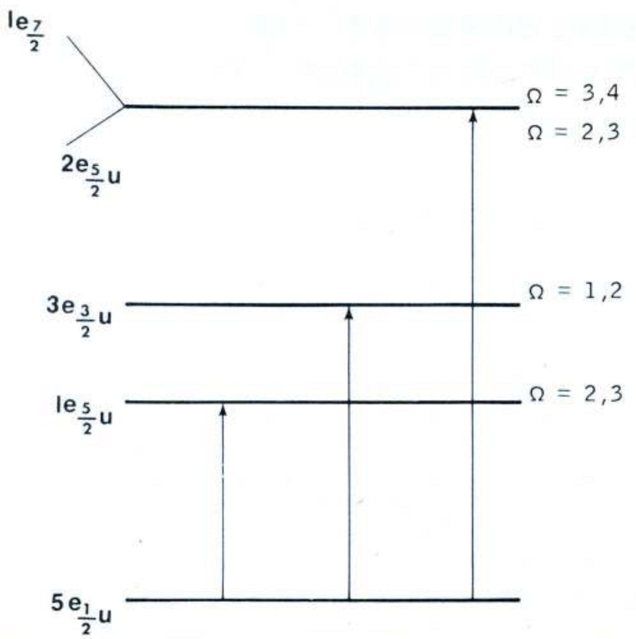

FIG. 3. Schematic representation of the electronic transitions from the highest occupied orbital of UO_2^{++} to the lowest unoccupied orbitals.

the nomenclature of Denning *et al.* states with $\Omega = 1$, 2, 3, and 4 are Π, Δ, Φ, and Γ states, respectively. The $X\alpha$–SW calculations indicate that the $3e_{3/2u}$ and $1e_{5/2u}$ orbitals are almost degenerate in energy and are separated by ~0.5 eV from the $2e_{5/2u}$ and $1e_{7/2u}$ orbitals, which are also almost degenerate. This agrees with the results of Denning *et al.* who assign states stemming from a Π_g state, two Δ_g states, and one Φ_g state in the region 20100–22750 cm^{-1}, and assign states stemming from a Φ_g state and a Γ_g state in the region 26200 and 27750 cm^{-1}. This leaves one Δ_g and one Φ_g state predicted by theory but not observed by Denning *et al.* However, all of the assigned states can be accounted for terms of the (ω, ω) coupling molecular orbital scheme outlined above.

The weak visible and near uv absorption system of the uranyl ion in solution can therefore be interpreted in terms of electric-dipole forbidden transitions from an $e_{1/2u}$ (σ_u) orbital to unoccupied $e_{3/2u}$, $e_{5/2u}$, and $e_{7/2u}$ orbitals of UO_2^{++}. The upper states have $\Omega = 1$, 2, 3, and 4 but no well defined Λ. The transitions derive their intensity from vibronic mixing with the secondary ligand vibrations. The stronger absorption at wavelengths below 3600 Å can probably be assigned to electric dipole allowed transitions from the $e_{1/2g}$ and $e_{3/2g}$ (π_g) orbitals to the unoccupied $e_{3/2u}$, $e_{5/2u}$, and $e_{7/2u}$ orbitals.

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