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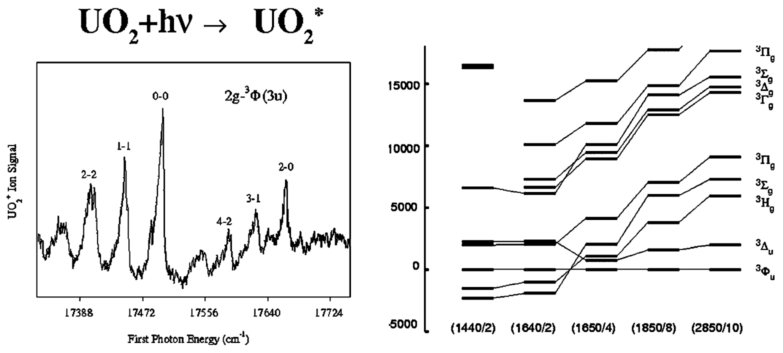

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The Electronic Spectrum of the UO_2 Molecule

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Abstract: The electronic spectrum of the UO_2 molecule has been determined using multiconfigurational wave functions together with the inclusion spin−orbit coupling. The molecule has been found to have a (5fϕ)(7s), $^3\Phi_{2u}$, ground state. The lowest state of gerade symmetry, $^3H_{4g}$, corresponding to the electronic configuration $(5f)^2$ was found 3330 cm^{-1} above the ground state. The computed energy levels and oscillator strengths were used for the assignment of the experimental spectrum in the energy range 17 000−19 000 and 27 000−32 000 cm^{-1}.

1. Introduction

The calculation of excited-state properties for heavy element compounds poses a formidable theoretical challenge. This is particularly true for actinide compounds, where the large number of electrons, open f- and d-shells, and strong relativistic effects must be taken into account. Development of the necessary theoretical tools is hampered by the fact that there are few spectroscopic observations for actinide compounds that are suitable for direct comparison with properties calculated for isolated molecules. Ideally, gas phase data are required for such comparisons. It has been found that even the data for molecules isolated in cryogenic rare gas matrixes, a medium usually considered to be minimally perturbing, can be influenced by the host to a degree that seriously complicates the relationship between the matrix data and calculations for free molecules. As a convenient model compound, molecular UO_2 has been the subject of several recent theoretical and experimental studies. High-level theoretical calculations have been carried out for the ground and low-lying excited states. In parallel with these efforts, gas phase electronic spectra have been recorded and partially analyzed. Additional motivation for the studies of UO_2 was provided by reports of anomalously large interactions between UO_2 and the heavier rare gas atoms in matrixes.

Andrews and co-workers[1−4] have studied the UO, UO_2, and CUO molecules trapped in rare gas matrixes. The antisymmetric stretch of UO_2 was observed at 914 cm^{-1} in a Ne matrix and 776 cm^{-1} in an Ar matrix.[1,4] Density functional theory (DFT) calculations by Zhou et al.[1] indicated that UO_2 has a $^3\Phi_u$ ground state derived from the U(5f7s) configuration. They also found that the calculated vibrational frequencies for the $^3\Phi_u$ state corresponded to the Ne matrix result, while the frequency for the ^3H_g state, derived from the U(5f^5) configuration, corresponded to the Ar matrix data. Consequently, they proposed that guest−host interaction in Ar reversed the energy ordering of the $^3\Phi_u$ and ^3H_g states. Similarly, Andrews, Bursten, and co-workers[5,6] have suggested that the interaction between CUO and Ar reorders the low-lying electronic states of CUO, and they concluded that the rare gas atoms Ar, Kr, and Xe form weak chemical bonds with CUO. More recently, they have also studied UO_2 in the presence of Ar atoms[7] at the DFT and coupled-cluster CCSD(T) level of theory, providing direct evidence of a significant U−Ar bonding interaction when UO_2 is in an argon matrix.

Han et al. have investigated the electronic spectroscopy of UO_2 in the gas phase by using resonantly enhanced multiphoton ionization (REMPI) with mass-selected ion detection.[8] The observed transitions were found to originate from the ground state and an electronically excited state that was just 360 cm^{-1} above the latter. This result was in agreement with the most recent theoretical calculations[9,10] that predict a X $^3\Phi_{2u}$ ground state with the first excited state (formally $^3\Phi_{3u}$) lying about 400 cm^{-1} higher. Lue et al.[11] subsequently have examined the electronic emission spectrum of UO_2 trapped in solid Ar and characterized the low-lying electronic states. They have obtained the same ordering of the lowest energy UO_2 states as in the gas

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phase study, in contrast to the results of the vibrational analysis by Andrews et al. and supported by DFT calculations.[1]

Among the theoretical studies, the thesis by Chang[10] and our previous work[9] are the most extensive studies of the low-lying electronic states of UO_2 to date. They both predict a $^3\Phi_{2u}$ ground state.

Han et al.[8] used the results from the calculation of Chang to propose assignments for the more intense features of the electronic spectrum. The correlation between the observed and calculated energies was not sufficient to permit the unambiguous determination of assignments. Chang[10] has also calculated oscillator strengths for transitions from the X $^3\Phi_{2u}$ state, and this information was used to restrict the possible range of assignments. Further refinement was achieved by considering the $\Delta\Omega = 0, \pm1$ selection rule. Most upper levels were accessed from either the 2_u or the 3_u lower levels. If the second transition was excluded because of the $\Delta\Omega$-selection rule, this information could be used to fix the Ω-value of the upper state. For example, the state at 17 499 cm^{-1} that could only be accessed from the 3_u level was assigned as $\Omega = 4_g$. As oscillator strengths for the transitions originating from 3_u were not available, the assignments were guided by applying the Ω-selection rule. The obvious limitation for this approach is that transitions that obey the selection rule may still not be observed because of low oscillator strengths.

In an attempt to place the assignment of the UO_2 spectrum on a firmer footing, we have calculated excited-state energies using high-level theoretical methods. This study is more comprehensive than our previous work,[9] since a larger number of excited states have been considered. Oscillator strengths for transitions from both the 3_u and 2_u states have been calculated.

2. Method and Details of the Calculations

All calculations were carried out with the software MOLCAS-6.0.[12] The complete active space (CAS) SCF method[13] was used to generate molecular orbitals and reference functions for subsequent multiconfigurational second-order perturbation calculations of the dynamic correlation energy (CASPT2).[14−16]

Scalar relativistic effects were included using a Douglas−Kroll (DK) Hamiltonian.[17,18] We shall refer to results obtained including only the scalar relativistic effect, as spin−orbit free (SOF). The effects of spin−orbit coupling (SOC) were introduced using a newly developed method based on the CASSCF state interaction approach (CASSI).[19,20] Here, the CASSCF wave functions generated for a number of electronic states are allowed to mix under the influence of a spin−orbit Hamiltonian, CASSI−SOC.[21] For a more detailed discussion of the theoretical model and the computational approach used, we refer to the recent article cited in ref 22 and articles cited in there.

ANO-type basis sets were used for U and O. The U exponents were optimized using the DK Hamiltonian. The primitive set 26s23p17d13f5g2h was contracted to 9s8p7d5f2g,[23] and this was combined with the ANO-L basis of the MOLCAS library for O,[24] contracted to 4s3p2d1f.

All calculations were performed at the ground-state equilibrium geometry of UO_2 previously optimized[9] at the CASPT2 level of theory, which corresponds to a linear molecule with a uranium−oxygen bond distance of 1.8268 Å. The C_{2h} point group was used in the calculations to be able to average between the components of degenerate representations (angular momentum larger than zero), thus keeping the linear symmetry intact. This is especially important when SOC is included.

In our previous studies of the U(IV), U(V), and U(VI) systems XUY (X,Y = C,N,O),[9,25] we found that it was important to include in the active space the oxygen 2p orbitals and the corresponding UO antibonding orbitals of σ- and π-type. They are hybrid orbitals mixing 5f and 6d orbitals of uranium with the 2p orbitals of oxygen. This gives an active space of 12 electrons in 12 orbitals (12/12). For the ground state of UO_2 one needs to add to these orbitals the 5fϕ and 7s orbitals of uranium and two more electrons. If also the electronic spectrum is to be studied, one should add at least the uranium 5fδ and 7p orbitals. We now have 14 electrons in 20 orbitals, currently an impossible calculation. This illustrates the difficulty in performing excited-state calculations on actinide compounds where the active space requirements easily become excessive. A more simplified approach is necessary, which means that the results may be less accurate than one normally expects from a CASSCF/CASPT2 calculation. The need to include spin−orbit coupling also adds to the complexity both in the choice of the active space and the number of electronic states to be included in the calculation.

We have performed five sets of calculations of increasing complexity with the hope that computed excitation energies would converge to values that would be at least of semiquantitative value. The first attempt starts with an essentially Hartree−Fock (HF)-like ground state. The six occupied UO bonding orbitals are thus left inactive. The active space then comprises the orbitals that contribute to the ground-state open shell and to the most intense excited states corresponding to excitations from the 7s to the 7p orbitals. Thus, we need the active orbitals 5fϕ, 5fδ, 7s, and 7p, which give two electrons in eight orbitals (labeled 1430/2, meaning 1 orbital (7sσ_g) in irrep 1 of C_{2h}, 4 in irrep 2 (5fϕ_u and 7pπ_u), and 3 in irrep 3 (5fδ_u and 7pσ_u). As it turns out, in the calculation, the 7pσ_u orbital is replaced by 5fσ_u, and thus this orbital has to be added to the active space: (1440/2). Fifty-two states were studied with this active space (24 triplets and 28 singlets). As we shall see in the next section, the results are not very impressive, yielding among other things the incorrect ground state.

The active space was first extended with two orbitals of π_u symmetry, of mainly 5fπ character, still with two active electrons, (1640/2) (both components of the π_u orbitals are in irrep 2). More states were also added (now 35 triplets). Singlets were not included with this active space. The SOF results changed considerably. All orbitals with 5f, 7s, and 7p character now had been included in the active space. We then started to add occupied orbitals. They were selected according to their orbital energies, which are for the six UO bonding orbitals (in au): −0.55 (σ_g), −0.54 (π_g), −0.50 (π_u), and −0.47 (σ_u). The energies are similar, and it would be preferable to include all of them, but this is impossible. Instead, we start with the highest occupied orbital, of σ_u

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symmetry, yielding the active space (1650/4). Again 35 triplet states were computed. Now only moderate changes were observed with respect to the 1640/2 calculation. The pair of π_u orbitals were then added, leading to the active space (1850/8). This calculation is satisfactory in many respects, but the excitation energies are not yet stable even if the changes from the 1640/4 active space are smaller. The next extension would be to include the two π_g orbitals leading to the active space (1852/12), but this calculation becomes unfeasible, especially because a large number of excited states are needed. Instead, we have added the occupied σ_u orbital with two more active electrons resulting in the active space (2850/10). This is thus the final calculation. It included 38 triplet and 37 singlet states with CASPT2 energies ranging from 0 to above 40 000 cm^{-1}. CASSI–SOC calculations were performed in this basis, yielding 151 levels (counting Kramers pairs as 2) with energies up to 50 000 cm^{-1}. To summarize, we have performed calculations with the five active spaces: (1440/2), (1640/2), (1650/4), (1850/8), and (2850/10). In the Results section, we report the excitation energies and oscillator strengths obtained with the largest active space.

There is one set of orbitals that was not discussed above: the 6d orbitals. They could be of interest because excited states of character (5f)(6d) have ungerade character and are thus allowed from a gerade ground state. Some of our earlier exploratory studies included these orbitals, but no transitions carrying any intensity were found in the relevant energy regions. It should, however, be emphasized that the chosen active space will not cover all possible transitions in the energy region studied, but all triplet and singlet states of (5f)^2, (5f)(7s), and (5f)(7p) character are included.

3. Results

3.1. Analysis of the Spin–Orbit Free States. We present in Figure 1 the SOF energy levels (with respect to an assumed (5f)(7s) $^3\Phi_u$ ground state) for the five different calculations that were performed. At first glance, this picture may give a rather pessimistic impression of the possibility of obtaining quantitative results. It is clear that the energies are not converged with respect to the size of the active space. There are, however, a number of positive observations to be made. First of all, we note that the addition of more active orbitals after the (1640/2) space does not change the number and characteristics of the electronic states. It is not likely that the addition of more orbitals with lower energies will change this feature. We also note that the order of the states below 40 000 cm^{-1} does not change after the (1650/4) active space. The only exception is the $^3\Sigma_g^-$ state in the energy region around 25 000 cm^{-1}. The SOC results in Table 2 show, however, that this state will not contribute to the spectrum because of the low intensity for excitation to the 1_g component. Transitions to the $\Omega = 0$ levels are forbidden from the two lowest levels (2_u and 3_u; see below).

Another satisfactory feature of the 2850/10 energies is the ordering of the lowest states. The two smallest active spaces give the wrong ground state ($^3\Sigma_g^-$ instead of $^3\Phi_u$). The relative energies of the low-lying SO levels are also in good agreement with experiment as we shall show below. Thus, even if Figure 1 does not show any convergence of the relative energies, there is good evidence that further enlargement of the active space will not lead to drastic modifications of the results. The band of energies in the region 12 000–17 000 cm^{-1} increases constantly with the active space, and therefore these energies are more uncertain than those of the band around 25 000 cm^{-1}.

The energies and the main characteristics in terms of orbital occupancy for the open shells are presented in Table 1 for the triplet and singlet states obtained in the (2850/10) calculation.

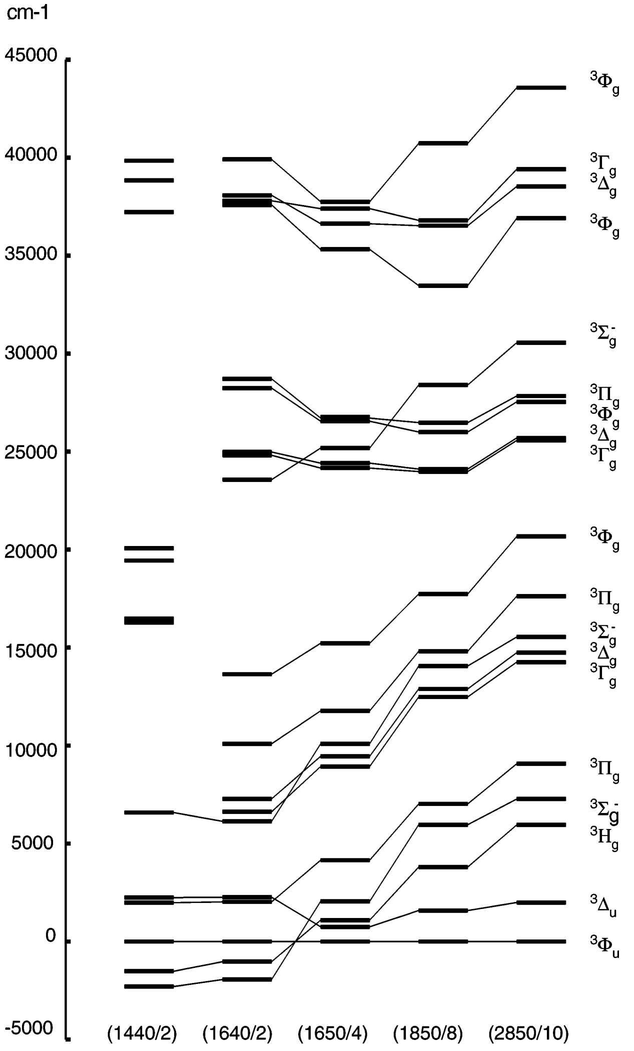

Figure 1. SOF energy levels computed with five different active spaces (CASPT2 results). See text for explanation of the active spaces used.

We notice that there are no (5f)(7p) states below 17 600 cm^{-1}. States of the type (5f)(7s) appear at low energies with $^3\Phi_u$ as the ground state. The first even (5f)^2 state, ^3H_g, appears at 5954 cm^{-1} (0.74 eV), which is the same result as obtained in our earlier study of the lowest electronic states of UO_2, 0.75 eV.[9] This calculation used a smaller active space (two electrons in eight orbitals). Recent studies by Li et al.[7] indicate that the ground state changes from $^3\Phi_u$ to ^3H_g when the molecule is immersed in an Ar matrix. The evidence for this state reordering was deduced from substantial changes in the vibrational frequencies, and the findings were supported by DFT calculations. We shall return to this crucial issue when discussing the SOC results. At this point, we note that the relative energy of the ^3H_g state strongly depends on the active space (cf., Figure 1). We can therefore not claim that our results are converged, even if the evidence presented below seems to indicate that the error is not large.

Singlet and triplet states appear in the same energy region and will, as a result, mix strongly under the influence of SOC. A more detailed discussion of the energies of the SOF spectrum is therefore not meaningful.

3.2. The Electronic Energy Levels of UO_2 with Spin–Orbit Coupling. Table 2 presents the excited states computed with SOC. It is not possible to present all computed levels. In

Table 1. Analysis of the (2850/10) Spin−Orbit Free Wave Functions for the Triplet and Singlet States in Terms of Main Configurations[a]

type[b]	state	Δ*E*	osc. str.	type[b]	state	Δ*E*
(5f)(7s)	$^3\Phi_u$	0		(5f)(7s)	$^1\Phi_u$	991
(5f)(7s)	$^3\Delta_u$	1990	0	(5f)(7s)	$^1\Delta_u$	2852
$(5f)^2$	^3H_g	5954	0	$(5f)^2$	$^1\Sigma_g^+$	12164
$(5f)^2$	$^3\Sigma_g^-$	7271	0	$(7s)^2$	$^1\Sigma_g^+$	22119
$(5f)^2$	$^3\Pi_g$	9076	0	$(5f)^2$	$^1\Gamma_g$	11921
$(5f)^2$	$^3\Gamma_g$	14262	0.0637	$(5f)^2$	$^1\Pi_g$	13106
(5f)(7s)	$^3\Pi_u$	12645	0	(5f)(7s)	$^1\Pi_u$	14320
$(5f)^2$	$^3\Delta_g$	14472	0.0748	(5f)(7p)	$^1\Delta_g$	17816
$(5f)^2$	$^3\Sigma_g^-$	15549	0	(5f)(7p)	$^1\Gamma_g$	20456
(5f)(7p)	$^3\Phi_g$	17625	0.0000	$(5f)^2$	^1H_g	20949
(5f)(7p)	$^3\Pi_g$	20676	0	$(5f)^2$	^1I_g	22337
(5f)(7s)	$^3\Sigma_u^-$	21695	0	$(5f)^2$	$^1\Sigma_g^+$	30157
(5f)(7p)	$^3\Gamma_g$	25575	0.1417	(5f)(7p)	$^1\Pi_g$	22081
(5f)(7p)	$^3\Delta_g$	25701	0.1248	(5f)(7p)	$^1\Phi_g$	23117
(5f)(7p)	$^3\Phi_g$	27546	0.0003	(5f)(7p)	$^1\Delta_g$	28638
(5f)(7p)	$^3\Pi_g$	27846	0	(5f)(7p)	$^1\Gamma_g$	33688
(5f)(7p)	$^3\Sigma_g^-$	30561	0	(5f)(7p)	$^1\Pi_g$	29905
(5f)(7p)	$^3\Phi_g$	36917	0.0282	(5f)(7p)	$^1\Phi_g$	32119
(5f)(7p)	$^3\Delta_g$	38533	0.0028	(5f)(7p)	$^1\Phi_g$	37518
(5f)(7p)	$^3\Delta_g$	39416	0.0000	$(5f)^2$	$^1\Phi_g$	52611
(5f)(7p)	$^3\Sigma_g^-$	39578	0			
$(5f)^2$	$^3\Phi_g$	43574	0.0000			

[a] Excitation energies in cm^{-1} and oscillator strengths. [b] The type indicates the major occupation of the open shell.

this table we have restricted the presentation to states with energies below 37 000 cm^{-1} and oscillator strengths (*f*) larger than 0.0001 with respect to excitations from one of the two lowest levels, 2_u or 3_u. Transitions from the 3_u level can be called *electronically hot bands*. They are quite uncommon compared to vibrationally hot bands but are observed for molecules with low-lying electronically excited states (e.g., metal compounds with open f and/or d shells; see ref 26 and references therein). The spectra for UO_2 were obtained by using pulsed laser vaporization to generate gas phase samples. The vapor was cooled by supersonic expansion, but this process does not always equilibrate the electronic, vibrational, and rotational degrees of freedom. It is not unusual to observe a very cold rotational distribution while a significant fraction of the population remains in electronically and/or vibrationally excited levels. This was the case for UO_2, where the supersonic expansion was unable to relax the population trapped in the 3_u excited state.

The ground state has been found to be $^3\Phi_{2u}$, which is in agreement with earlier findings and is by now the established ground state for the isolated molecule. The corresponding 3_u state is found 378 cm^{-1} above the lowest level, which can be compared with the experimental excitation energy of 360 cm^{-1}.[8] This agreement is important for the judging of the quality of the SOF energies. The amount of spin−orbit splitting is crucially dependent on the mixing between the $^3\Phi_u$, $^1\Phi_u$, and $^3\Delta_u$ states as seen in the last column of Table 2. The mixing depends strongly on the relative energy for the three interacting states. Thus, we can conclude that the energy difference between these states is correctly reproduced by the calculations. The experimental study of UO_2 in a solid Ar matrix locates the 1_u and 2_u components of $^3\Delta_u$ at 1094 and 1401 cm^{-1}, respectively (it should be noted that the labels 1_u and 2_u in Table 1 of ref 11 have been reversed). The present results are 2567 and 2908 cm^{-1}, respectively. The splitting is again correctly reproduced. A direct comparison of the energies is difficult because of the effect of the matrix.

The lowest level, 4_g, of the ^3H_g state is found 3330 cm^{-1} (0.41 eV) above the ground level. This energy is not inconsistent with the suggestion that the ground state changes from $^3\Phi_u$ to ^3H_g when going from the gas phase to the matrix.[7] The spectroscopic measurements in Ar give, however, strong evidence that $^3\Phi_u$ is still the ground state. One argument is the distribution of the low-lying odd states that fits well with the experimental emission spectrum. If ^3H_g was the ground state, one would expect to see emission to the different levels of this state. The calculation gives the following splitting: $4_g - 5_g$: 5357, $5_g - 6_g$: 4562 cm^{-1}, which does not fit the spectrum at all. The only other gerade states at energies below 9000 cm^{-1} are a $0_g(^3\Sigma_g^+)$ and $1_g(^3\Pi_g)$ at 5572 and 6823 cm^{-1}, respectively, none of which is suitable. We shall return to this issue later in a more detailed comparison between experiment and theory.

Turning now to the higher excited states, we find a first set of allowed transitions between 12 000 and 17 000 cm^{-1}. This region has not yet been studied experimentally. A number of allowed transitions of the (5f)(7p) type are found in the energy range up to 36 000 cm^{-1}. We shall discuss possible assignments in the next section.

4. Comparison with the Experimental Spectrum

The present calculation predicts that there are very few intense transitions from UO_2 $X^3\Phi(2_u)$ and 3_u, which would appear in the visible and near-UV spectral range. In principle, excited states of 2_g or 3_g type could be accessed from both lower states. However, inspection of the oscillator strengths in Table 2 shows that states that are optically connected to 2_u have negligible oscillator strengths for 3_u, and vice versa. These results indicate that both 2_u and 3_u must be considered as the lower state. In agreement with the results of Chang,[10] we find that the most intense transitions correspond to the 5f7p ← 5f7s electron promotion. Furthermore, the calculations are in agreement concerning the molecular upper states that are accessed. For transitions from 2_u the leading eigenvectors of the upper states are $^3\Gamma_{3g}$, $^3\Delta_{1g}$, and $^3\Phi_{2g}$. Here we consider the correlation between transitions that are predicted to have large oscillator strengths and the dominant features of the spectrum. To facilitate comparison with the experimental data, we list the states that have oscillator strengths >0.01 for transitions originating from 2_u or 3_u in Table 3. Proposed assignments for the observed transitions are also indicated.

Transitions observed at 31 838 and 31 478 cm^{-1} were previously assigned to a common upper level because the ionization energy of the excited state was the same for both bands (note that the energy of the 31 478 band is also 31 838 cm^{-1} when related to the 2_u zero level). However, as the ionization thresholds were determined with an uncertainty of 20 cm^{-1}, it is also possible that the transitions accessed two nearby excited states. The present calculations support the latter interpretation. On the basis of Chang's calculations,[10] the transition at 31 838 cm^{-1} was previously attributed to $2_g(^3\Phi) - 2_u$. This assignment is supported by the present calculation, which yields an excitation energy of 36 783 cm^{-1}. The transition at 31 478 cm^{-1} was previously attributed to $2_g(^3\Phi) - 3_u$. The present calculations predict that the oscillator strength for the $2_g(^3\Phi) - 3_u$ band is 2 orders of magnitude smaller that that of

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Table 2. Analysis of the Spin−Orbit Wave Functions in Terms of Contributing SOF States[a] with the 2850/10 Active Space[b]

state	type[c]	Δ*E*	*f*(2u)	*f*(3u)	composition(weight in %)
2_u	(5f)(7s)	0			$^3\Phi_u(91)$, $^3\Delta_u(05)$, $^1\Delta_u(03)$
3_u	(5f)(7s)	378	0.0000		$^3\Phi_u(53)$, $^1\Phi_u(37)$, $^3\Delta_u(10)$
1_u	(5f)(7s)	2567	0.0000	0.0000	$^3\Delta_u(96)$, $^3\Pi_u(02)$, $^1\Pi_u(02)$
2_u	(5f)(7s)	2908	0.0000	0.0000	$^3\Delta_u(54)$, $^1\Delta_u(42)$, $^3\Pi_u(04)$
4_g	$(5f)^2$	3330	0.0000	0.0001	$^3H_g(91)$, $^1\Gamma_g(06)$, $^3\Gamma_g(02)$
1_g	$(5f)^2$	6823	0.0007	0.0003	$^3\Sigma_g^-(32)$, $^3\Pi_g(48)$, $^1\Pi_g(12)$, $^3\Delta_g(02)$
1_g	$(5f)^2$	11390	0.0012	0.0000	$^3\Sigma_g^-(64)$, $^1\Pi_g(17)$, $^3\Pi_g(12)$, $^3\Delta_g(02)$
2_g	$(5f)^2$	12073	0.0000	0.0095	$^3\Pi_g(84)$, $^3\Delta_g(14)$
3_g	(5f)(7p)	13182	0.0595	0.0000	$^3\Gamma_g(96)$, $^3\Phi_g(03)$
4_g	$(5f)^2$	14790	0.0000	0.0194	$^1\Gamma_g(79)$, $^3\Gamma_g(05)$, $^3H_g(07)$, $^3\Phi_g(04)$
2_g	(5f)(7p)	15452	0.0000	0.0681	$^3\Delta_g(49)$, $^1\Delta_g(35)$, $^3\Pi_g(13)$
1_g	(5f)(7p)	16725	0.0777	0.0000	$^3\Delta_g(75)$, $^1\Pi_g(14)$, $^3\Sigma_g^-(08)$, $^1\Pi_g(02)$
4_g	(5f)(7p)	17274	0.0000	0.0466	$^3\Gamma_g(87)$, $^1\Gamma_g(08)$, $^1\Gamma_g(02)$
2_g	(5f)(7p)	17625	0.0001	0.0014	$^3\Phi_g(98)$
1_g	(5f)(7p)	17645	0.0102	0.0000	$^3\Sigma_g^-(55)$, $^3\Pi_g(20)$, $^1\Pi_g(07)$, $^3\Delta_g(06)$
1_g	$(5f)^2$	19948	0.0006	0.0000	$^1\Pi_g(37)$, $^3\Sigma_g^-(27)$, $^3\Pi_g(29)$
3_g	(5f)(7p)	20610	0.0010	0.0000	$^3\Phi_g(92)$, $^1\Phi_g(04)$, $^3\Gamma_g(02)$
1_g	(5f)(7p)	21290	0.0048	0.0000	$^3\Pi_g(47)$, $^1\Pi_g(34)$, $^1\Pi_g(06)$, $^3\Sigma_g^-(08)$
2_g	(5f)(7p)	23073	0.0000	0.0091	$^1\Delta_g(39)$, $^3\Delta_g(34)$, $^3\Pi_g(24)$
4_g	(5f)(7p)	23277	0.0000	0.0687	$^1\Gamma_g(85)$, $^3\Gamma_g(07)$, $^3\Phi_g(04)$
4_g	(5f)(7p)	24600	0.0000	0.0004	$^3\Phi_g(86)$, $^1\Gamma_g(12)$
3_g	(5f)(7p)	24859	0.1298	0.0002	$^3\Gamma_g(81)$, $^1\Phi_g(11)$, $^3\Phi_g(03)$, $^1\Phi_g(021)$
2_g	(5f)(7p)	24964	0.0000	0.0338	$^3\Pi_g(54)$, $^1\Delta_g(26)$, $^3\Delta_g(15)$
1_g	(5f)(7p)	26349	0.1026	0.0000	$^3\Delta_g(70)$, $^1\Pi_g(16)$, $^3\Pi_g(07)$
2_g	(5f)(7p)	26617	0.0000	0.0762	$^3\Delta_g(44)$, $^1\Delta_g(23)$, $^3\Pi_g(22)$
3_g	(5f)(7p)	26622	0.0066	0.0000	$^1\Phi_g(76)$, $^3\Phi_g(07)$, $^3\Gamma_g(10)$
4_g	(5f)(7p)	28121	0.0000	0.0740	$^3\Gamma_g(85)$, $^1\Gamma_g(09)$, $^3\Phi_g(06)$
1_g	(5f)(7p)	28124	0.0108	0.0000	$^1\Pi_g(40)$, $^3\Pi_g(33)$, $^3\Delta_g(21)$
1_g	(5f)(7p)	29098	0.0001	0.0000	$^3\Pi_g(61)$, $^1\Pi_g(35)$, $^3\Sigma_g^-(02)$
3_g	(5f)(7p)	30540	0.0000	0.0005	$^3\Delta_g(93)$, $^3\Phi_g(05)$
3_g	(5f)(7p)	30677	0.0001	0.0001	$^3\Phi_g(77)$, $^1\Phi_g(09)$, $^3\Delta_g(06)$
2_g	(5f)(7p)	32412	0.0003	0.0000	$^3\Pi_g(70)$, $^3\Delta_g(24)$, $^1\Delta_g(05)$
4_g	(5f)(7p)	33840	0.0000	0.0006	$^3\Phi_g(87)$, $^3\Gamma_g(09)$, $^1\Gamma_g(03)$
2_g	(5f)(7p)	34027	0.0001	0.0024	$^1\Delta_g(63)$, $^3\Delta_g(13)$, $^3\Pi_g(18)$, $^3\Sigma_g^-(05)$
3_g	$(5f)^2$	35727	0.0000	0.0004	$^1\Phi_g(88)$, $^3\Phi_g(06)$, $^3\Gamma_g(03)$
3_g	(5f)(7p)	36770	0.0009	0.1676	$^3\Phi_g(48)$, $^1\Phi_g(41)$, $^3\Delta_g(10)$
2_g	(5f)(7p)	36783	0.1816	0.0014	$^3\Phi_g(90)$, $^3\Delta_g(09)$

[a] Only states with an oscillator strength larger than 0.0001 from either the $^3\Phi_u(2_u)$ or the $^3\Phi_u(3_u)$ state, and energies <37 000 cm^{-1} are included. [b] Excitation energies in cm^{-1}. Oscillator strengths, *f*, are given for excitations from the lowest 2_u and 3_u levels. [c] The type indicates the major occupation of the open shell.

Table 3. Possible Assignment of the Electronic Spectrum of UO_2[a]

state	calcd	exptl	*f*(2_u)[b]	*f*(3_u)[b]	composition(weight in %)
2_u	0	0			$^3\Phi_u(91)$, $^3\Delta_u(05)$, $^1\Delta_u(03)$
3_u	378	360	0.0000		$^3\Phi_u(53)$, $^1\Phi_u(37)$, $^3\Delta_u(10)$
1_u	2567	1094[c]	0.0000	0.0000	$^3\Delta_u(96)$, $^3\Pi_u(02)$, $^1\Pi_u(02)$
2_u	2908	1401[c]	0.0000	0.0000	$^3\Delta_u(54)$, $^1\Delta_u(42)$, $^3\Pi_u(04)$
2_g	15452	17859[d]	0.0000	0.0681	$^3\Delta_g(49)$, $^1\Delta_g(35)$, $^3\Pi_g(13)$
1_g	16725	18159	0.0777	0.0000	$^3\Delta_g(75)$, $^1\Pi_g(14)$, $^3\Sigma_g^-(08)$, $^1\Pi_g(02)$
4_g	17274	18587[d]	0.0000	0.0466	$^3\Gamma_g(87)$, $^1\Gamma_g(08)$, $^1\Gamma_g(02)$
1_g	17645	18423	0.0102	0.0000	$^3\Sigma_g^-(55)$, $^3\Pi_g(20)$, $^1\Pi_g(07)$, $^3\Delta_g(06)$
4_g	23277		0.0000	0.0687	$^1\Gamma_g(85)$, $^3\Gamma_g(07)$, $^3\Phi_g(04)$
3_g	24859		0.1298	0.0002	$^3\Gamma_g(81)$, $^1\Phi_g(11)$, $^3\Phi_g(03)$, $^1\Phi_g(021)$
2_g	24964		0.0000	0.0338	$^3\Pi_g(54)$, $^1\Delta_g(26)$, $^3\Delta_g(15)$
1_g	26349	27259[d]	0.1026	0.0000	$^3\Delta_g(70)$, $^1\Pi_g(16)$, $^3\Pi_g(07)$
2_g	26617	28700	0.0000	0.0762	$^3\Delta_g(44)$, $^1\Delta_g(23)$, $^3\Pi_g(22)$
4_g	28121		0.0000	0.0740	$^3\Gamma_g(85)$, $^1\Gamma_g(09)$, $^3\Phi_g(06)$
1_g	28124	29700[d]	0.0108	0.0000	$^1\Pi_g(40)$, $^3\Pi_g(33)$, $^3\Delta_g(21)$
3_g	36770	31838[d]	0.0009	0.1676	$^3\Phi_g(48)$, $^1\Phi_g(41)$, $^3\Delta_g(10)$
2_g	36783	31838	0.1816	0.0014	$^3\Phi_g(90)$, $^3\Delta_g(09)$

[a] Energies in cm^{-1} relative to the 2_u zero energy level. [b] Only states with an oscillator strength larger than 0.01 from either the $^3\Phi_u(2_u)$ or the $^3\Phi_u(3_u)$ state, and energies <37 000 cm^{-1} are included. [c] Results obtained in an Ar matrix; ref 11. [d] Assignment differs from that proposed in ref 8.

$2_g(^3\Phi) - 2_u$, whereas the observed intensities indicate comparable oscillator strengths. The results in Table 3 suggest that the 31 478 cm^{-1} band should be assigned to the $3_g(^3\Phi) - 3_u$, which has a calculated transition energy of 36 770 − 378 = 36 392 cm^{-1}. As the calculated spacing between $2_g(^3\Phi)$ and $3_g(^3\Phi)$ is only 13 cm^{-1}, this assignment is compatible with the experimental results.

The transition at 29 700 cm^{-1} was previously assigned to $2_g(^1\Delta_g) - 2_u$, but the present calculations yield very poor agreement for the energy and relative intensity with this choice. Reassignment to the $1_g(^1\Pi_g)$ upper state is indicated (cf., Table 3).

The dominant transition in the visible range terminated on a level at 18 159 cm^{-1}. This was previously assigned to a $1_g(^3\Delta)$

excited state, despite the fact that Chang's calculation did not predict this $1_g - 2_u$ transition to be the strongest feature near this energy. The transition to the $3_g(^3\Gamma)$ state was predicted to be a better fit in terms of both energy and intensity. However, as a transition from 3_u was not observed, this assignment was rejected (Ω-selection rule). The 3_g state in question has an energy of 24 859 cm^{-1} in Table 3. Here it can be seen that the oscillator strength of the $3_g - 3_u$ transition is predicted to be lower than that of $3_g - 2_u$ by several orders of magnitude. Consequently, reassignment of the state at 18 159 cm^{-1} to $3_g(^3\Gamma)$ is possible, although this would imply an error of 6700 cm^{-1} in the calculated energy. Alternatively, the next most intense transition in this energy range is $1_g(^3\Delta) - 2_u$, predicted to occur at 16 725 cm^{-1}. This assignment yields a more acceptable error of 1434 cm^{-1}. Given that we expect the energies to be predicted more reliably than the oscillator strengths, we favor the latter assignment.

A transition from 2_u to a state at 18 423 cm^{-1} was another prominent feature in the visible spectrum. Chang's[10] calculation indicated that the upper level was $1_g(^3\Delta)$, but, as this state had already been assigned, the next best choice of $1_g(^3\Sigma^-)$ was proposed. The present calculation confirms this assignment.

Below 20 000 cm^{-1}, the calculations predict two relatively strong transitions that originate from the 3_u level. The upper levels for these transitions are $2_g(^3\Delta)$ at 15 452 and $4_g(^3\Gamma)$ at 17 274 cm^{-1}. The upper states observed via transition from 3_u have term energies of 17 859 and 18 587 cm^{-1}, and it seems reasonable to correlate these with $2_g(^3\Delta)$ and $4_g(^3\Gamma)$. Previously, the 17 859 cm^{-1} level had been assigned to a 4_g state on the basis of the Ω-selection rule. Reassignment to the $2_g(^3\Delta)$ state does not cause a problem as the oscillator strength for the $2_g(^3\Delta) - 2_u$ transition is predicted to be insignificant.

The calculations predict that there should be additional transitions from 3_u with observable intensities at 23 277, 24 964, and 28 121 cm^{-1}. The spectrum shows a congested group of bands in the 28 660−28 810 cm^{-1} range, and these transitions may well be contained in this cluster (unfortunately, the lower states were not identified). The $1_g(^1\Pi) - 2_u$ transition, predicted to occur at 28 124 cm^{-1}, may also be in this group.

5. Conclusions

The electronic spectrum of the UO_2 molecule up to ca. 40 000 cm^{-1} has been calculated, and excitation energies and oscillator strengths have been used to assign the experimental spectrum. The results show that the most intense transitions from the two lowest levels, 2_u and 3_u states, correspond to excitations from the U 7s to U 7p orbitals. The lowest 4_g level of the ^3H_g state is found 3330 cm^{-1} (0.41 eV) above the ground level. This energy is not inconsistent with the suggestion that the ground state changes from $^3\Phi_u$ to ^3H_g when going for the gas phase to the matrix, as previously suggested,[7] although the electronic spectrum measured in an Ar matrix is very difficult to understand with a ^3H_g ground state. The present study gives, however, a consistent assignment of the lowest electronic levels based on the assumption of a $^3\Phi_u$ ground state and thus does not confirm the change of ground state when the molecule is dispersed in an Ar matrix. At present, we have no explanation for the different results.

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