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A Fock space coupled cluster study on the electronic structure of the UO_2, UO_2^+, U^{4+}, and U^{5+} species

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The ground and excited states of the UO_2 molecule have been studied using a Dirac-Coulomb intermediate Hamiltonian Fock-space coupled cluster approach (DC-IHFSCC). This method is unique in describing dynamic and nondynamic correlation energies at relatively low computational cost. Spin-orbit coupling effects have been fully included by utilizing the four-component Dirac-Coulomb Hamiltonian from the outset. Complementary calculations on the ionized systems UO_2^+ and UO_2^{2+} as well as on the ions U^{4+} and U^{5+} were performed to assess the accuracy of this method. The latter calculations improve upon previously published theoretical work. Our calculations confirm the assignment of the ground state of the UO_2 molecule as a $^3\Phi_{2u}$ state that arises from the $5f^1 7s^1$ configuration. The first state from the $5f^2$ configuration is found above 10 000 cm^{-1}, whereas the first state from the $5f^1 6d^1$ configuration is found at 5 047 cm^{-1}.
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I. INTRODUCTION

The study of small actinide molecules presents a challenge for experimental and theoretical chemists.[1] The nearly degenerate $5f$, $6d$, $7s$, and $7p$ orbitals give rise to a multitude of possible configuration interactions and a dense manifold of low-lying states, which complicates computations and renders assignment of experimental spectra difficult. A joint effort of experimentalists and theoreticians is therefore needed to resolve the electronic structure of these systems. An example is the ionization potential (IP) of the UO_2 molecule, measured as 5.4 eV by Capone *et al.*,[2] using the electron impact technique. Theoretical calculations[3] consistently gave a higher value. Gagliardi *et al.*,[4] who had done accurate complete active space second order perturbation theory (CASPT2) calculations that gave an IP of 6.27 eV, proposed that the experimental data were in error. A new measurement by Han *et al.*[5] using resonantly enhanced multiphoton ionization (REMPI), gave a value of 6.13 eV, in very good agreement with the theoretical values.

Other aspects of these small actinide molecules are, however, less well understood, as different theoretical and experimental techniques give conflicting information. A particularly interesting aspect is the interaction of small actinide molecules with noble gas matrices. Laser ablation spectroscopy has been used by Andrews and co-workers to trap UO, UO_2, and CUO in noble gas matrices[3,6–15] and measure vibrational frequencies as a function of the matrix composition (Ne, Ar, Kr, Xe, or mixtures thereof). An intriguing feature of both CUO and UO_2 is the large redshift (about 130 cm^{-1}) in the antisymmetric stretch found when replacing a neon matrix by an argon matrix. Li *et al.* suggested that this is due to a change in the electronic ground state, and presented density functional theory (DFT) calculations indicating that a weak bond arises by donation of electron density of the noble gas into the empty uranium $6d$ orbitals in CUO and UO_2.[9,15] In argon and heavier noble gas matrices, this bonding interaction is strong enough to change the ordering of the ground and first excited states, leading to the observed strong redshifts. A convincing argument was the very good agreement between the calculated and observed asymmetric stretch frequencies. Since in these initial DFT calculations the effect of spin-orbit coupling (SOC) was neglected, theoreticians nevertheless questioned the validity of the simple picture presented. This spurred extensive theoretical work, notably by Gagliardi and co-workers,[4,16–18] who applied the more sophisticated CASPT2 method and also studied the effect of SOC.

In CUO, the two competing states are the uranyl-like closed shell state, with two formal triple bonds between uranium, carbon, and oxygen, and a triplet in which the C–U bonding orbital and the uranium $5f_\phi$ orbital are singly occupied. The latter state has a longer CU bond length, allowing for a more effective interaction with a matrix than the singlet state. In argon, this interaction should then be sufficiently strong to reverse the order of the two states, while in the more weakly interacting neon matrix, the ordering is the same as in the gas phase. This explanation of the large matrix effect is currently generally accepted for CUO, even though the CASPT2 calculations of Roos *et al.*[17] gave the triplet $^3\Phi$ at slightly lower energy in the gas phase. Our previous work[19] using the Dirac-Coulomb coupled cluster method, DC-CCSD(T), gives the closed shell state as ground state in the gas phase, in agreement with the original picture. More important is that all methods predict small energy differences between the two states in the gas phase and do not contradict the explanation given by Andrews and co-workers.

The situation is more complicated for the UO_2 molecule. Likely candidates for the ground state are the $5f^1 7s^1\,^3\Phi_u$ and $5f^2\,^3H_g$ states. These states differ in occupation of the $5f_\delta$ orbital (the ^3H_g state) versus the $7s$ orbital (the $^3\Phi_u$ state). Both orbitals are nonbonding but the $7s$ orbital is more diffuse, leading to stronger and shorter bonds in the $^3\Phi_u$ state. Vibrational spectroscopy gives an asymmetric stretch in the Ne matrix of 915 cm^{-1} versus 776 cm^{-1} in the Ar matrix,[3,14] which suggests that the ordering of states in UO_2 also depends on the matrix. Bonding of the noble gas atoms to the ^3H_g state would not only be favored by the longer bond length of that state but also by the lack of repulsive interaction with the electron in the $7s$ orbital. This picture is corroborated by DFT calculations[15] of vibrational frequencies for gas phase UO_2. The $5f^1 7s^1\,^3\Phi_u$ and $5f^2\,^3H_g$ states do indeed match the experimental frequencies in the neon and argon matrices, respectively. In this case there are, however, also complementary experimental data available. Heaven and co-workers carried out electron spectroscopy in gas phase[5,20] and in Ar matrices.[21] These experiments, using the REMPI technique in the gas phase and electronic emission spectroscopy in the matrix, do not indicate a reordering of the states. Both the gas phase and matrix spectra can only be rationalized by assuming that the first excited state lies slightly above the ground state (360 cm^{-1} in the gas phase, 408 cm^{-1} in the argon matrix) and is of the same parity. This fits well with the assignment of the ground state as the lower components of the spin-orbit split $^3\Phi_u$ state. SOC is rather large, leading to significant admixture of $^3\Delta_u$ character in both the $2u$ ground state and the $3u$ first excited state (better described in a *jj*-coupling picture as pure $5f^1_{5/2} 7s^1_{1/2}$ states). Actual calculations on gas phase UO_2 by Chang,[22] Gagliardi *et al.*[4,18] and Fleig *et al.*[23] reproduce this splitting well. The manifold of SOC-split grade states does not have two so closely spaced states at low energy. If the ^3H_g state would be the lowest state in the argon matrix, the next gerade state is expected to lie several thousands of cm^{-1} higher. Han *et al.*[5] and later Gagliardi *et al.*[4] discussed the difficulties in ex-

plaining both experimental findings but could not present definite theoretical or experimental data to settle the issue of matrix-induced ground state swapping.

A survey of the theoretical and experimental data that is available leads to more questions. For example, the third and fourth excited states in the argon matrix[21] lie, experimentally, at 1094 and 1401 cm^{-1}, whereas the CASPT2 values[18] are, respectively, at 2567 and 2908 cm^{-1}, about 1500 cm^{-1} off. Is this large discrepancy caused by the differences induced by the argon matrix, by deficiencies in the calculation, such as limits on the size of the active space used, or by both? The generalized active space configuration interaction (GASCI) results by Fleig *et al.*[23] agree better with experiment and with older spin-orbit configuration interaction calculations of Chang[22] but both calculations were done in rather modest basis sets and could suffer from basis set incompleteness errors. It is therefore clear that more theoretical work is desirable.

Accurate calculations of the quasidegenerate states of UO_2 and similar actinide systems, where d and f orbitals belong to the valence space, are extremely difficult. First principles methods aimed at such systems should not only be based on size-extensive, size-consistent, and balanced treatment of the dynamic and nondynamic correlation effects, but also include the relativistic effects from the outset. The aim of our paper is to reanalyze the UO_2 molecule with the relativistic Fock space coupled cluster (FSCC) method that satisfies all these requirements. The FSCC method has been applied to a large number of atoms and molecules, including transition and heavy elements, with experimentally known spectroscopic properties. Examples are atomic gold,[24,25] Fr,[26] the lanthanides La,[27] Pr,[28] Yb, and Lu,[29] the actinides Ac,[30] Th,[31] and U,[28] as well as Hg,[31] Tl,[30,32] Pb,[33] and Bi.[34] Good agreement with experimental transition energies (within a few hundreds of wave numbers) was obtained. To quote one example, the average error for the f^2 levels of Pr^{3+} was 222 cm^{-1}, four times smaller than that of an extensive multiconfigurational Dirac-Fock calculation.[25] The quality of results was sufficient to allow reliable predictions for the nature of the ground states and spectra of a number of superheavy elements. Molecules calculated by the method include AuH,[35] Au_2,[36] HgH,[37] and TlF.[38] The FSCC approach has recently been extended by the intermediate Hamiltonian (IH) scheme,[39,40] which allows the use of much larger P spaces and improves results considerably [see, e.g., the electron affinity of Bi (Ref. 41)]. The new, more accurate IH-FSCC method is applied on the electronic spectrum of neptunyl and plutonyl ions,[42] and is also used in the present work.

An advantage of this approach is its relatively low computational cost, allowing us to use adequate basis sets and active spaces that include all relevant orbitals. The largest calculation performed in the current work had 41 Kramer pairs in the P part of the active space. The method scales, like regular CCSD, as N^6 in the number of correlated electrons, N. This scaling is sufficiently low to make calculations on UO_2 surrounded by one or more argon atoms feasible in the near future. Such calculations were, however, not possible with the computers currently available to us.

II. METHODOLOGY

Benchmark calculations on the U(IV) ion were done using the radial relativistic Fock space CC code of Eliav *et al.*[24] and the multi-reference Møller-Plesset (MR-MP) code of Vilkas *et al.*[43–45] for the CASPT2 calculations. All-electron single- and multireference correlated calculations on the UO$_2$ molecule were carried out utilizing a locally modified version of the DIRAC04 program.[46]

We considered two types of basis sets, the universal basis set (UBS) of Malli *et al.*,[47] consisting of 37s32p24d21f12g10h9i uncontracted Gaussians, which provides nearly basis-set-free results in the atomic case, and the more economical 33s29p21d15f3g1h even-tempered basis set provided by Faegri.[48] The difference between the atomic results calculated in both sets gives an indication of basis set incompleteness errors, this was furthermore checked by adding additional diffuse functions to the Faegri basis in some of the molecular calculations. The basis set on the oxygen atoms is the uncontracted cc-pVTZ (Refs. 49–51) basis that can be considered sufficient for the accuracy that is targeted. In all cases, the relativistic four-component Dirac-Coulomb (DC) or Dirac-Coulomb-Breit (DCB) Hamiltonians[52,53] include SOC from the outset, so that mixing of orbitals with different orbital angular momenta occurs already at the Hartree-Fock (HF) level. To facilitate analysis, and for comparison with more conventional approaches, we also used the spin-free modified DC (SFDC) Hamiltonian,[54] in which SOC is projected out, leaving only the scalar relativistic effects in a four-component framework.

In the atomic calculations, the number of correlated electrons was taken as 51 for U^{5+} and 52 for U^{4+}. The active virtual space was limited from above by the orbital energy value of +100.0 a.u. The model space P used in the Fock space coupled cluster calculations consisted of all determinants built from the 7−11s, 7−11p, 6−10d, 5−9f, 7−9g, 8−9h, and 9i orbitals and was subdivided in a primary (P_m) space that included determinants constructed from 7s, 7p, 6d, and 5f orbitals and a secundary (P_i) space that contained the remaining P determinants.

For the molecular correlated calculations we included 12 electrons from the 5f, 7s, 6d, and 6p orbitals of the uranium atom. The 2s and 2p orbitals of the oxygen atoms, six electrons each, were always taken active given a minimum of 24 electrons that is correlated. The stability of the results with number of electrons correlated was tested by also including the U 6s and 5d shells in some calculations. We used two coupled cluster methods that differ in the way the outermost valence electrons are treated. In a conventional single-reference relativistic coupled cluster with explicit inclusion of single and double excitations and perturbative treatment of triples [DC-CCSD(T)] (Refs. 55 and 56) approach, open shell orbitals are generated by a restricted Hartree-Fock method that averages the energy expression of the lowest 5f7s or 5f^2 open shell singlet and triplet (borrowing the nomenclature from nonrelativistic work; a more accurate description is that we place one electron in each of the two highest occupied Kramers spinor pairs). The CC calculation is then carried out starting from a $|5f_{5/2}7s_{\pm1/2}|$ reference determinant. A single-reference approach can be used since, in contrast to approaches in which SOC is added *a posteriori*; the determinants $|5f_{5/2}7s_{\pm1/2}|$ and $|5f_{5/2}5f_{3/2}|$ provide good first approximations to the 2$_u$, 3$_u$, and 4$_g$ states. This method is complemented by the genuine multireference FSCC approach[57] in which we start from a common closed shell reference determinant of the UO$_2^{2+}$ molecule, or the U^{6+} ion, then add two electrons successively in sectors (0,1) and (0,2). A full CI (P-space diagonalization) is performed in the selected Fock space valence sectors, in order to obtain the nondynamic correlation energy and the multireference wave-function characteristics of each excited state. The choice of the model space P is nontrivial, the largest P_m space for which the FSCC scheme was found to converge, comprising the 7s, two of the five 6d, and six of the seven 5f spinors, excluding the higher lying $5f_{\sigma_{1/2}}$. Further increase of the model space was not possible, because it leads to intruder states, in particular, in sector (0,2). The CASPT2 approach[43–45] used in some of the atomic reference calculations is similar, but not identical to the method used by Gagliardi *et al.* in calculations of the UO$_2$ molecule.[18] The main difference is in construction of one-electronic orbital space. We have used common set of radial average-state self-consistent field (SCF) canonical spinors for the ground and all excited states, while in the Roos-Gagliardi CASSCF/CASPT2 approach a common set of orbitals is used only for states with the same spin and same wave-function symmetry.

To determine the equilibrium geometry of the ground state, we performed FSCC calculations using an evenly spaced (0.005 Å) grid of U–O bond distances, spanning the range from 1.680 to 1.840 Å. Since DC-IHFSCCSD provides the energy of all states in one calculation, we could obtain the equilibrium geometry of the ground state and that of many excited states. The equilibrium bond distances, found by energy minimization, were 1.739 Å for UO$_2^+$ and 1.770 Å for UO$_2$. These distances are used to compute adiabatic excitation and ionization energies.

III. RESULTS AND DISCUSSION

A. The spectrum of the atomic ions

The FSCC method was first applied by Eliav *et al.*[28] for the 5f^2 states of U^{4+}. Here, we employ a larger basis set and extend the analysis of the excited states to the U^{5+} ion. We include transitions to 5f7s and 5f6d states of U^{4+}, because these excitations are important in the electronic spectrum of the neutral UO$_2$ molecule. To compare accuracies of method applied in the molecular case, we report also the atomic CASPT2 energies in Table I.

Comparing the different methods with the experimental data of Kaufman and Radziemski,[58] the excitation energies of the U^{5+} ion appear to be best described by the XIHF-SCCSD scheme (extrapolated intermediate Hamiltonian Fock space coupled cluster with single and double excitations), which within the large UBS basis set gives a mean absolute error (MAE) relative to the experimental data of

TABLE I. The excitation energies (cm⁻¹) and mean absolute errors (MAE) relative to the experimental data of U⁵⁺ and U⁴⁺ ions computed at different levels of theory. For the ground state of U (IV) and U (V) we list the ionization potential (cm⁻¹).

Symmetry	Type	Expt.[c]	Universal basis set[a]				Faegri basis set[b]			
			DCB-CASPT2 ($5f6d7s$)	DCB-XIH FSCC	DC-CASPT2 ($5f6d7s$)	DC-XIH FSCC	DC-XIH FSCC	DC-CASPT2 ($5f7s$)	DC-CASPT2 ($5f6d7s$)	DC-CASPT2 ($5f6d7s7p$)
					U⁵⁺ states					
$6p^65f_{5/2u}$	$5f$	⋯	⋯	508 183	⋯	507 326	505 260			⋯
$^2F_{7/2}$	$5f$	7 609	8 226	7 598	8 384	7 833	7 784	8 228	8 228	8 228
$^2D_{3/2}$	$6d$	91 000	95 309	90 562	92 989	89 564	88 930	⋯	88 772	88 772
$^2D_{5/2}$	$6d$	100 511	105 871	100 107	103 619	99 245	98 586	⋯	99 271	99 271
$^2S_{1/2}$	$7s$	141 448	144 946	140 211	142 206	139 062	137 660	135 660	135 811	135 811
$^2P_{1/2}$	$7p$	193 340	⋯	192 351	⋯	190 993	194 402	⋯	⋯	188 322
$^2P_{3/2}$	$7p$	215 886	⋯	215 112	⋯	213 698	216 531	⋯	⋯	212 988
	MAE		⋯	651	⋯	1 650	1 603	⋯	⋯	2 948
					U⁴⁺ states					
$^3H_4$	$5f^2$	⋯	402 654	381 074	401 337	380 220	378 222	⋯	⋯	⋯
$^3F_2$	$5f^2$	4 161	3 773	4 202	3 742	4 190	4 202	3 822	3 815	3 815
$^3H_5$	$5f^2$	6 137	6 631	6 070	6 746	6 275	6 223	6 198	6 593	6 596
$^3F_3$	$5f^2$	8 983	8 897	8 974	8 986	9 147	9 118	8 614	8 907	8 922
$^3F_4$	$5f^2$	9 434	9 779	9 404	9 892	9 586	9 574	9 598	9 575	9 930
$^3H_6$	$5f^2$	11 514	12 486	11 420	12 676	11 780	11 713	11 759	12 463	12 466
$^1D_2$	$5f^2$	16 465	15 106	16 554	15 196	16 785	16 709	15 723	15 479	17 476
$^1G_4$	$5f^2$	16 656	17 391	16 630	17 599	16 937	16 870	16 755	17 473	17 464
$^3P_0$	$5f^2$	17 128	15 556	17 837	15 546	17 840	17 941	16 728	16 014	16 014
$^3P_1$	$5f^2$	19 819	18 426	20 441	18 500	20 570	20 638	19 356	18 844	18 845
$^1I_6$	$5f^2$	22 276	21 089	22 534	21 306	22 812	23 067	22 950	22 182	22 185
$^3P_2$	$5f^2$	24 652	23 539	24 991	23 753	25 315	25 300	24 077	23 937	23 923
$^1S_0$	$5f^2$	43 614	43 361	45 611	43 483	45 765	45 571	45 340	44 454	44 443
$^3H_4$	$5f6d$	59 183	65 821	57 161	63 221	56 289	55 501	⋯	58 609	58 612
$^3F_2$	$5f6d$	59 640	65 172	57 324	62 542	56 475	55 667	⋯	58 003	58 067
$^3G_3$	$5f6d$	63 053	68 182	61 331	65 353	60 510	59 739	⋯	60 941	60 983
$^1G_4$	$5f6d$	65 538	72 154	63 336	69 659	62 641	61 791	⋯	65 173	65 176
$^3F_3$	$5f6d$	67 033	71 826	64 485	69 537	64 141	63 334	⋯	65 153	65 146
$^3H_5$	$5f6d$	67 606	75 044	65 755	72 542	65 052	64 282	⋯	67 828	67 831
$^3F_2$	$5f7s$	94 070	97 573	91 410	94 548	90 411	88 841	81 073	89 132	89 673
$^3F_3$	$5f7s$	94 614	98 083	91 941	95 059	90 965	89 402	81 578	89 727	90 134
$^3F_4$	$5f7s$	101 612	105 500	98 921	102 614	98 168	96 512	88 572	97 080	97 437
$^1F_3$	$5f7s$	102 407	105 987	99 713	103 108	98 967	97 492	89 312	97 774	98 302
$^3G_3$	$5f7p$	139 141	⋯	138 614	⋯	137 582	138 904	⋯	⋯	135 528
$^3F_2$	$5f7p$	140 642	⋯	139 502	⋯	138 380	138 990	⋯	⋯	133 929
$^3G_4$	$5f7p$	146 926	⋯	145 150	⋯	143 970	147 671	⋯	⋯	143 111
$^3D_3$	$5f7p$	147 170	⋯	146 413	⋯	145 613	146 180	⋯	⋯	141 555
$^3F_3$	$5f7p$	156 493	⋯	156 024	⋯	155 028	155 402	⋯	⋯	154 659
	MAE $5f^2$		825	357	814	514	507	488	626	654
	MAE $5f6d$		6 024	2 110	3 467	2 824	3 623	⋯	1 132	1 115
	MAE $5f7s$		3 610	2 680	657	3 548	5 114	13 042	4 784	4 289
	MAE $5f7p$		⋯	898	⋯	1 924	907	⋯	⋯	4 282
	MAE		⋯	1 191	⋯	1 738	1 956	⋯	⋯	1.967

[a]Reference 47.
[b]Reference 48.
[c]References 58 and 59.

1650 cm⁻¹ without and 651 cm⁻¹ with the Breit interaction. One possible drawback of the Fock space approach is that the starting orbitals to compute the U⁵⁺ and U⁴⁺ energies are optimized for the highly ionized U⁶⁺ ion. Thus, the method must include the full orbital relaxation when computing the excitation energies of the less charged ions. The major part of the orbital relaxation effects in the present FSCCSD calculations is taken into account by single-electronic excitation amplitudes and two-electronic diagrams with a pair of so-called "spectator" lines (correspond to identical valence orbitals). To account for the rest of the orbital relaxation, which could still be substantial, one must include the contribution
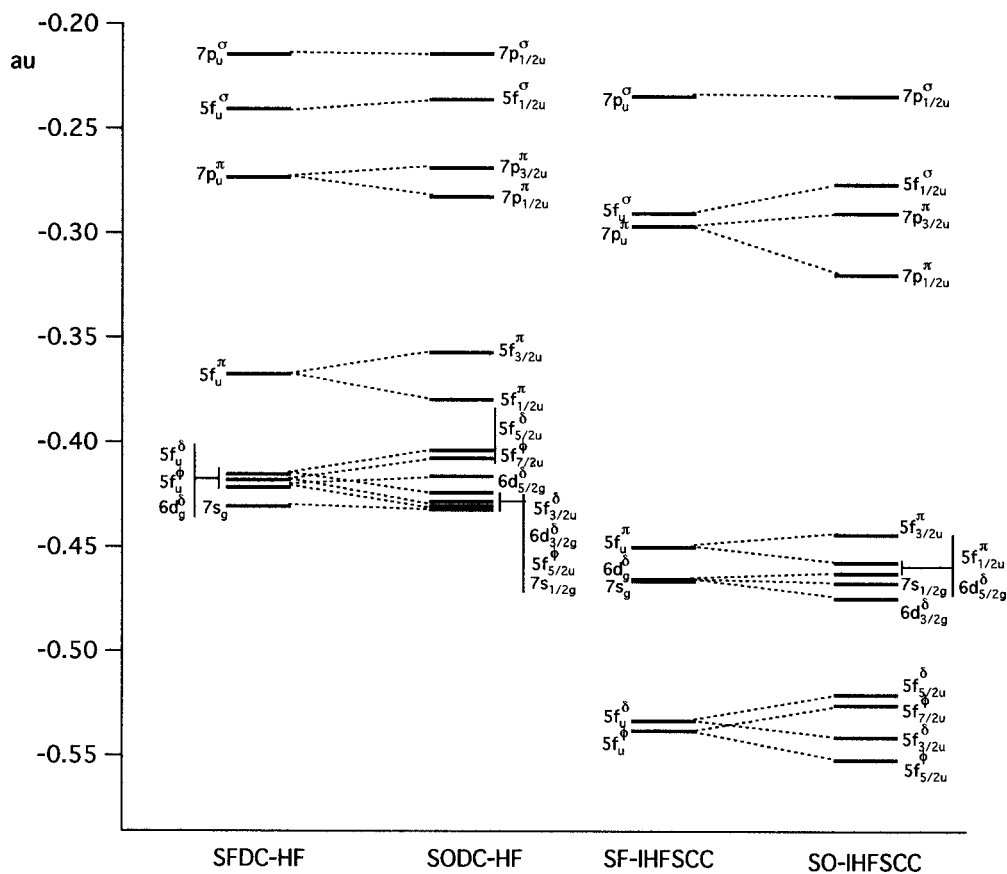
FIG. 1. The electron affinities of UO$_2^{2+}$ molecule for the $5f$, $7s$, $6d$, and $7p$ orbitals. On the left, the spin-free and spin-orbit coupling contributions calculated at DC-HF level. On the right, the correlated values from sector (0,1) of the DC-IHFSCCSD calculations. The correlation space was ($24e/6$ a.u.), with a ($17g$, $20u$) P model space that includes the $7p$ orbitals in P_m. All calculations were performed with the Faegri basis set. The bond distance is 1.770 Å.

of higher excitations amplitudes with the appropriate spectator lines [e.g., triples with two pairs of spectators in the case of (0,2) sector] and use a large active space.

For the U^{5+} ion, the errors are larger for the more diffuse orbitals, like the $6d$, $7s$, and $7p$ shells that show discrepancies from experiment of about 500–1000 cm^{-1}, while the $5f$ states have errors in the range of 100–200 cm^{-1}. Errors that can be related to incomplete orbital relaxation are also visible in the U^{4+} ion. The errors relative to the experimental data of Wyart *et al.*[59] we obtain with DCB-XIHFSCCSD are small for energy differences among the $5f^2$ states, a MAE of 357 cm^{-1}, but are significant, with a MAE of 2110 cm^{-1} for transitions to $5f^16d^1$ states, and for transitions to the $5f^17s^1$ states, a MAE of 2680 cm^{-1}. Despite the fact that these errors are larger than the ones found for the U^{5+} ion, the overall MAE is still rather low, 1191 cm^{-1}. For comparison, we may look at the CASPT2 method, which does not improve or worsen much, compared to the U^{5+} ion, and shows errors that are about twice as large as the XIHFSCC values if the largest basis and most accurate Hamiltonian (DCB) are used. It is interesting to note that XIHFSCC and CASPT2 give a qualitatively different error in the calculation of the energy of the $5f^16d^1$ manifold relative to the $5f^2$ states: the XIHFSCC values are 2000 cm^{-1} too low whereas the CASPT2 values are 6000 cm^{-1} too high.

Table I shows that the effect of the Breit interaction is

much larger in CASPT2 than in the all-order FSCC calculation. Similar large effects are observed in the results of the first FSCC iteration, equivalent to a second order perturbation calculation. The MAEs of atomic excitation energies calculated by CASPT2 increase strongly upon inclusion of the Breit interaction, indicating that the relatively good performance of the CASPT2 method based on the DC Hamiltonian may be due to cancellation of errors. We also investigated the convergence of the CASPT2 energies with the systematic enlargement of the CAS as they may be relevant in discussing the molecular results. It is clear from the table that inclusion of the $6d$ orbital into the CAS is very important for the quantitatively correct description of the intrashell excitations, while the effect of the $7p$ orbital is much less pronounced. This points towards the inclusion of the $6d$ orbital of uranium in the CAS, a procedure that is usually not followed as it leads to prohibitively large CAS spaces in molecular calculations.

The atomic calculations indicate that the FSCC approach is a systematic and precise method to describe the excitation energies of the actinide ions. Inclusion of the Breit term in the Hamiltonian significantly improves the quality of the results, as it should, giving a mean absolute error of 1191 cm^{-1} for U^{+4} with all levels coming out in the correct order. It is likely that this accuracy is representative for the errors made when computing the excited states of the UO$_2$ molecule as

TABLE II. The excitation energies at IHFSCC level are given at our best level of approximation for the UO_2^+ ion using the Faegri basis set with 24 electrons correlated and 6 a.u. as the threshold for the virtual space. The bond distance for our calculation is 1.739 Å. The P model space is $(17g, 20u)$ with the $7p$ orbitals included in the P_m. The full manifold of excited states up to 20 000 cm^{-1} is shown.

Symmetry	This work	$[UO_2(dbm)_2DMSO]^{-a}$ (Ref. [60])	$[UO_2(saloph)_2DMSO]^{-b}$ (Ref. [60])	$[UO_2(CO_3)_3]^{5-}$ (Ref. [60])	UO_2^+ aqueous (Refs. [65] and [66])
$5f_{5/2u}^{\phi}$	0	0	0	0	0
$5f_{3/2u}^{\delta}$	2 736	⋯	⋯	⋯	⋯
$5f_{7/2u}^{\phi}$	5 751	5 290	5 330	5 560	⋯
$5f_{5/2u}^{\delta}$	6 567	6 800	7 140	6 250	⋯
$6d_{3/2g}^{\delta}$	15 999	11 600	11 100	8 770	10 638
$7s_{1/2g}^{\sigma}$	17 635	13 500	13 300	10 100	13 550
$6d_{5/2g}^{\delta}$	19 774	15 600	15 400	13 200	⋯

[a]dmb=dibenzoylmethanate, DMSO=dimethyl sulfoxide.
[b]saloph=N,N′-disalicylidene-o-phenylenediaminate, DMSO=dimethyl sulfoxide.

these are composed by orbitals that are nonbonding with the oxygen atoms. In the next sections, we will show whether this is the case.

B. Orbital composition of uranyl and the UO_2^+ excitation energies

In Fig. 1, we sketch the orbital energy and electron affinity diagrams of UO_2^{2+} in the spin-free (SFDC) and full (DC) Dirac-Coulomb approximations. We chose the uranyl, UO_2^{2+}, orbital energies, because these present the first step in the Fock space calculation and give a conceptually simple interpretation of the spectrum of singly ionized UO_2. In uranyl, the unoccupied metal orbitals are split induced by the oxo ligands to the extent that $5f$ and $6d$ manifolds overlap. The $7s$, that was found at high energy in the U(IV) ion, lies slightly below $5f$ and becomes the lowest unoccupied molecular orbital. This crude Koopmans picture is improved by the DC-IHFSCCSD method which provides correlated electron affinities. These energies are listed in Fig. 1, where we see a lowering of the $5f$ manifold that fits with experimental evidence that the unpaired electron resides in the $5f_\phi$ orbital. Inclusion of SOC is important, because it produces a splitting of the same order as the crystal field splitting. This strong SOC effect is also reflected in the composition of the $5f$ orbitals. The lower $5f_{5/2}$ orbital can be described as 87% $5f_\phi$ and 13% $5f_\delta$, while the upper $5f_{5/2}$ orbital is 13% $5f_\phi$ and 87% $5f_\delta$. Given these rather large admixtures, it is clear that a jj-coupling picture is appropriate.

We computed the UO_2^+ energies as electron affinities of uranyl but may of course also take the $5f_{\phi,5/2u}$ ground state energy as reference and list the electron affinities of the remaining states as excitation energies. There is no experimental data of the UO_2^+ molecule *in vacuo* but one may consider data from this ion bound to different types of ligands. These experimental spectra show five characteristic bands, which are listed in Table II. The first two low-lying peaks are in line with the computed excitation energies and can be assigned to $5f_{\phi,5/2u} \rightarrow 5f_{\phi,7/2u}$ and $5f_{\phi,5/2u} \rightarrow 5f_{\delta,5/2u}$ transitions. These excitations are Laporte forbidden *in vacuo* but are allowed if ligands break the inversion symmetry.

The remaining three bands are found experimentally at different energies, depending of the type of equatorial ligand bound to the uranium atom. These transitions have been assigned previously by Mizuoka *et al.*[60] as $5f \rightarrow 5f$ type. Our calculation suggests that these three peaks are related to $5f \rightarrow 6d$ and $5f \rightarrow 7s$ transitions. This justifies the more intense bands because the transitions are already dipole allowed ($u \rightarrow g$) in the bare ion. Our values are systematically higher in energy by about 3000 cm^{-1} which is perhaps not so surprising given the fact that the more diffuse $6d$ and $7s$ orbitals will interact stronger with the surrounding ligands in the equatorial region than the $5f$ orbitals, leading to a larger environmental shift.

The ionization energy of UO_2 (calculated in the FSCC approach as the second electron affinity of uranyl) can be readily obtained by subtracting the energy of the lowest UO_2^+ state from that of the lowest UO_2 state. This procedure gives a vertical excitation energy of 5.95 eV and an adiabatic value of 5.92 eV. These values are significantly below the experimental value of 6.13 eV.[5] A possible reason could be the fact that both states are described using the orbitals from the dication, thus biasing the cation, for which orbital relaxation effects should be smaller than the neutral. To test the influence of this common orbital approximation we compared the multireference approach with the single-reference CCSD approach in which both the cation and the neutral system are treated with optimized orbitals. These DC-CCSD calculations give a vertical ionization energy of 6.00 eV, while DC-CCSD(T) result is 6.04 eV. A calculation with a common set of orbitals (to mimic the FSCC approach) gives indeed a smaller value of 5.95 eV (see also Table III), suggesting that the orbital relaxation effect is present but also indicating that CC-type methods may underestimate the ionization energy of UO_2. This is in agreement with earlier work by Majumdar *et al.*[61] who reported a ECP-CCD value of 6.01 eV, in good agreement with our DC-CCSD value of 6.00 eV.

The DC-IHFSCCSD second ionization energy is 14.63 eV, which lies within the interval of 12.8–18.0 eV that was estimated by Cornehl *et al.*[62] on basis of thermochemical data. Cornehl *et al.* also performed pseudopotential coupled cluster calculations that gave an ionization energy of 15.0 eV but argued that this value is probably smaller than the exact value. Our calculations as well as the CASPT2

TABLE III. The first and second ionization potentials (IPs) of the UO$_2$ molecule, calculated at different levels of approximation are given using the Faegri basis set with 24 electrons correlated and 6 a.u. as the threshold for the virtual space. The bond distances used for computing the adiabatic IP values are 1.680 Å for UO$_2^{2+}$, 1.739 Å for UO$_2^+$, and 1.770 Å for UO$_2$. The vertical IPs are computed at 1.770 Å. The P model space is $(17g, 20u)$ with the $7p$ orbitals included in the P_m. The values in parentheses are IPs evaluated using the orbitals of the uranyl dication.

IP	IH-FSCC adiabatic	IH-FSCC vertical	DC-CCSD vertical	DC-CCSD(T) vertical	CCD vertical[a]	CASPT2 adiabatic[b]	Expt.[c]
UO$_2 \rightarrow$ UO$_2^+$	5.92	5.97	6.00 (5.95)	6.04 (6.06)	6.01	6.17	6.13
UO$_2 \rightarrow$ UO$_2^{2+}$	14.63	21.00	20.86 (17.53)	22.21 (19.25)	$\cdots$	14.36	12.8–18.0

[a]Reference 61.
[b]Reference 18.
[c]Reference 5.

calculations (14.36 eV, see Ref. 18) give a value considerably below 15 eV and do not support that assumption.

C. The excited states of UO$_2$: Scalar relativistic results

Results from the SFDC can be directly compared to scalar relativistic results obtained by the Douglas-Kroll-Hess and effective core potential (ECP) approaches. In Table IV, we show the values of the excitation energies up to 35 000 cm^{-1} in the SFDC-FSCC model. Configurations of interest for the interpretation of the experimental spectroscopic data are $5f^17s^1$, $5f^2$, $5f^16d^1$, and $5f^17p^1$. The $7s^2$ $^1\Sigma_g^+$ state appears also at low energy, but cannot be easily reached from the ground state and should have a strongly repulsive interaction with noble gas atoms in a matrix. When analyzing the eigenvectors of the effective Hamiltonian, we observe significant configurational mixing in many of the states. Comparison with the CASPT2 relative energies given by Gagliardi et al.[18] shows close agreement between the two methods with respect to singlet-triplet splittings and, in general, all differences between states that arise from the same configuration. The striking difference in the $^3\Phi_u-{}^3\Delta_u$ vertical excitation energy can be explained by considering the large difference in bond distances used in the two calculations. The CASPT2 calculations were done at 1.827 Å, while the Fock space calculations were done at 1.770 Å. Recalculating the vertical excitation energy at 1.827 Å gives 1219 cm^{-1}, in much better agreement with the CASPT2 value.

From Table IV it is, however, also clear that there are large discrepancies between the methods for energy differences between states that come from different configurations. The FSCC energy of the $5f^2$ ^3H_g state relative to the $5f^17s^1$ $^3\Phi_u$ ground state is again smaller (11 989 cm^{-1}) at the longer CASPT2 bond length, but remains much higher than the CASPT2 excitation energy of 5954 cm^{-1}. In general, we find states with primarily $5f^2$ character at rather high energies, sometimes heavily mixed with low-lying $5f^17p^1$ and $6d^2$ states. The first state with significant $5f^17p^1$ character, the $^1\Delta_g$, appears at 14 865 cm^{-1} above the ground state.

The ^3H_g excitation was considered important for the reasons we have outlined in Sec. I. Li et al.[15] have shown that at the ECP-CCSD(T) level of theory on UO$_2$(Ar), the ^3H_g is sufficiently low in energy that the effect of spin-orbit coupling could be strong enough to change the ground state. Gagliardi et al.[18] do not disregard this possibility, but point out that this would make it very difficult to interpret the fluorescence and REMPI data of Heaven and co-workers.[5,21] The relative energy of the $5f^2$ ^3H_g state, as calculated by the SFDC-IHFSCCSD is in qualitative disagreement with these results, as the energy gap with the ground state is so large that matrix-induced ground state switching is improbable.

Our calculations include, however, the $5f^16d^1$ states that have not been studied so far. These states could also be of importance to explain the experimental findings. We find the lowest state from that manifold, the ^3H_u state, just 6000 cm^{-1} above the ground state. This small energy difference makes it likely that the ^3H_u state plays a role in the chemistry of UO$_2$. What important is, furthermore, that transition to the ground state is parity forbidden so that the state might have a sufficiently long lifetime to present an alternative for the suggestion of Gagliardi et al.[18] that the older experimental value of the ionization potential (5.4 eV) could be due to ionization from a metastable excited state. They proposed that this state would be the ^3H_g state, which would be thermally populated in the production of UO$_2$ in a laser ablation process. Our results indicate a similar possibility, but now based on thermal population of the ^3H_u state, followed by ionization from the $6d_\delta$ orbital.

A more detailed analysis of all aspects of the available spectroscopic data requires, of course, the introduction of SOC, which will perturb the relatively simple scalar relativistic picture sketched above. We will discuss this aspect in the next section.

D. Analysis of the excited states: Inclusion of spin-orbit coupling

Adding SOC, or rather, not switching it off in our calculations, leads to a more crowded manifold of states below 35 000 cm^{-1} (see Table V). To reduce the number of entries in the table we use dipole selection rules and consider only the allowed $u \rightarrow g$ and $\Delta\Omega = 0, \pm 1$ excitations, with the exception of the higher components of the SO-split ^3H_g and ^3H_u states that are relevant in the discussion of spectroscopic data. From the analysis of the eigenvectors of the effective Hamiltonian we may distinguish between single, double, and

TABLE IV. Vertical excitation energies (cm^{-1}) for the UO$_2$ molecule at SFDC-IHFSCC level of theory using the Faegri basis set with 24 electrons correlated and 6 a.u. as the threshold for the virtual space. The UO bond distance was taken as 1.770 Å. The P model space is (17g, 20u) with the 7p orbitals included in the P_m. CASPT2 values (Ref. 18) refer to calculations done at a bond length of 1.827 Å. The full manifold of excited states up to 32 000 cm^{-1} is shown.

	Excited states		
Symmetry	CASPT2[a]	IHFSCC 24e Faegri	Composition
$^3\Phi_u$	0	0	97% $(5f_\phi 7s)$
$^3\Delta_u$	1 990	575	97% $(5f_\delta 7s)$
$^1\Phi_u$	991	826	100% $(5f_\phi 7s)$
$^1\Delta_u$	2 852	1 300	100% $(5f_\delta 7s)$
$^1\Sigma_u^+$		5 544	100% $(5f_\delta 6d_\delta)$
^3H_u		6 038	100% $(5f_\phi 6d_\delta)$
$^3\Gamma_u$		7 250	100% $(5f_\delta 6d_\delta)$
$^3\Sigma_u^-$		7 508	100% $(5f_\delta 6d_\delta)$
$^1\Sigma_g^+$	22 119	7 549	83 $(7s7s)$, 14% $(6d_\delta 6d_\delta)$
$^3\Pi_u$		9 193	97% $(5f_\phi 6d_\delta)$
$^3\Delta_g$		9 760	91% $(7s6d_\delta)$
^1H_u		9 910	94% $(5f_\phi 6d_\delta)$
$^3\Sigma_u^+$		10 244	97% $(5f_\delta 6d_\delta)$
$^1\Gamma_u$		11 101	100% $(5f_\delta 6d_\delta)$
^3H_g	5 954	12 863	97% $(5f_\phi 5f_\delta)$
$^1\Sigma_u^-$		13 815	100% $(5f_\delta 6d_\delta)$
$^1\Gamma_g$	11 921	13 865	32% $(5f_\delta 5f_\delta)$+30% $(5f_\delta 5f_\pi)$+28% $(6d_\delta 6d_\delta)$
$^3\Sigma_g^-$	7 271	13 926	50% $(5f_\delta 5f_\phi)$+30% $(5f_\delta 5f_\delta)$+18% $(6d_\delta 6d_\delta)$
$^3\Pi_u$	12 645	14 789	97% $(7s5f_\pi)$
$^1\Delta_g$		14 865	52% $(7s6d_\delta)$+20% $(5f_\phi 5f_\pi)$+20% $(5f_\phi 7p_\pi)$
$^1\Pi_u$		15 459	100% $(5f_\phi 6d_\delta)$
$^3\Sigma_g^-$	15 549	15 526	55% $(5f_\delta 5f_\delta)$+42% $(6d_\delta 6d_\delta)$
$^3\Pi_g$	9 076	15 574	88% $(5f_\phi 5f_\delta)$+8% $(5f_\pi 5f_\delta)$
$^1\Sigma_g^+$	12 164	16 331	58% $(5f_\delta 5f_\phi)$+20% $(5f_\delta 5f_\delta)$+11% $(6d_\delta 6d_\delta)$
$^1\Pi_u$	14 320	16 824	87% $(7s5f_\pi)$+8% $(5f_\pi 6d_\delta)$
$^1\Pi_g$	13 106	17 410	80% $(5f_\phi 5f_\delta)$+8% $(5f_\delta 5f_\pi)$+8% $(5f_\delta 7p_\pi)$
$^3\Gamma_g$	14 262	18 529	54% $(5f_\delta 5f_\pi)$+44% $(5f_\phi 7p_\pi)$
$^3\Phi_g$	17 625	19 373	52% $(5f_\delta 5f_\pi)$+44% $(5f_\delta 7p_\pi)$
$^3\Delta_g$	14 472	19 418	49% $(5f_\delta 5f_\pi)$+43% $(5f_\phi 7p_\pi)$
$^1\Sigma_g^+$		20 237	66% $(5f_\delta 5f_\delta)$+24% $(6d_\delta 6d_\delta)$
$^3\Pi_g$	20 676	20 518	52% $(5f_\delta 7p_\pi)$+37% $(5f_\delta 5f_\pi)$
$^3\Phi_u$		21 486	100% $(5f_\pi 6d_\delta)$
$^1\Phi_g$	23 117	21 551	65% $(5f_\delta 6p_\pi)$+30% $(5f_\delta 5f_\pi)$
$^1\Pi_g$	22 081	21 709	52% $(5f_\delta 7p_\pi)$+24% $(5f_\delta 5f_\pi)$+16% $(5f_\delta 5f_\delta)$
$^1\Delta_g$	17 816	22 015	34% $(5f_\delta 7p_\pi)$+30% $(6d_\delta 7s)$+28% $(5f_\phi 5f_\pi)$
$^1\Gamma_g$		22 440	44% $(5f_\phi 5f_\pi)$+44% $(5f_\delta 5f_\delta)$
$^3\Pi_u$		22 598	100% $(5f_\pi 6d_\delta)$
^1I_g	22 337	23 931	97% $(5f_\phi 5f_\phi)$
^1H_g	20 949	24 396	50% $(5f_\phi 5f_\delta)$
$^1\Phi_u$		24 564	83% $(5f_\pi 6d_\delta)$
$^1\Pi_u$		24 587	92% $(5f_\pi 6d_\delta)$
$^1\Gamma_g$		25 109	56% $(6d_\delta 6d_\delta)$+34% $(5f_\delta 5f_\delta)$
$^3\Sigma_g^+$		26 246	52% $(5f_\phi 5f_\phi)$+25% $(6d_\delta 6d_\delta)$+17% $(5f_\delta 5f_\delta)$
$^1\Sigma_g^+$	30 157	31 858	40% $(5f_\phi 5f_\phi)$+18% $(5f_\pi 5f_\pi)$+16% $(6d_\delta 6d_\delta)$
$^3\Phi_g$	36 917	32 089	90% $(5f_\phi 7p_\sigma)$
$^1\Phi_g$	37 518	32 277	90% $(5f_\phi 7p_\sigma)$

[a]Reference 18.

mixed single-double excitations relative to the ground state. We assume that double excitations have a negligible intensity and can be discarded in the comparison with experimental data. For convenience, we discuss Table V in different sections according to the main parentage of the states.

1. Region 0–3 000 cm^{-1}: 5$f^1$7s^1 states

As discussed in Sec. I, the first two states are best described in a *jj*-coupling picture as pure $5f^1_{\phi,5/2u}7s^1_{\sigma,1/2g}$ states. The computed energy differences are consistent with the ear-

TABLE V. Vertical excitation energies (cm^{-1}) for the UO$_2$ molecule at DC-IHFSCC level of theory using the Faegri basis set with with the Fægri2+ basis, 40 electrons correlated and 45 a.u. as the threshold for the virtual space. The P model space is (17g, 20u) with the 7p orbitals included in the P_m. The bond distance is 1.770 Å. The composition of each state is given as a percentage. Single reference CCSD and CCSD(T) transition energies are computed with 24 electrons in the active space and a threshold of 6 a.u. Only the excited states that satisfy the selection rule $\Delta\Omega=0, \pm1$ have been selected, with the exception of the first 5$_g$, 6$_g$, 5$_u$, and 6$_u$ states. All states composed by double excitations were also removed. Experimental values for which the assignment is not clear are listed in parentheses.

								Excited states		
Symmetry	Expt.[a]	GASCI[b]	CASPT2[c]	CCSD 24e Fægri	CCSD(T) 24e Fægri	IHFSCC 24e Fægri	IHFSCC 40e Fægri2+ +spdl	$f(2u)$	$f(3u)$	Composition
2$_u$	0	0	0	0	0	0	0			97%$\|5f_{\phi,5/2u}7s_{\sigma,-1/2g}\|$
3$_u$	360	427	378	417	384	348	368			96%$\|5f_{\phi,5/2u}7s_{\sigma,1/2g}\|$
1$_u$	1 094[d]	1 089	2 567	1 841	2 052	1 877	2 231	0	0	98%$\|5f_{\delta,3/2u}7s_{\sigma,-1/2g}\|$
2$_u$	1 401[d]	1 542	2 908	2 224	2 421	2 224	2 588	0	0	96%$\|5f_{\delta,3/2u}7s_{\sigma,-1/2g}\|$
4$_u$				3 079	3 521	4 975	5 047	0	0	98%$\|5f_{\phi,5/2u}6d_{\delta,3/2g}\|$
4$_u$						5 706	6 148	0	0	97%$\|5f_{\phi,7/2u}7s_{\sigma,1/2g}\|$
3$_u$						6 028	6 501	0	0	85%$\|5f_{\phi,7/2u}7s_{\sigma,-1/2g}\|$, 10%$\|5f_{\delta,5/2u}7s_{\sigma,1/2g}\|$
0$_u$						6 470	7 081	0	0	48%$\|5f_{\delta,3/2u}6d_{\delta,-3/2g}\|$, 48%$\|5f_{\delta,3/2u}6d_{\delta,-3/2g}\|$
3$_u$						6 725	7 152	0	0	86%$\|5f_{\delta,5/2u}7s_{\sigma,1/2g}\|$, 9%$\|5f_{\phi,7/2u}7s_{\delta,-1/2g}\|$
2$_u$						6 460	7 431	0	0	97%$\|5f_{\delta,5/2u}7s_{\sigma,-1/2g}\|$
3$_u$						7 291	7 867	0	0	95%$\|5f_{\delta,3/2u}6d_{\delta,3/2g}\|$
5$_u$						8 532	8 746	0	0	70%$\|5f_{\phi,5/2u}6d_{\delta,5/2g}\|$, 14%$\|5f_{\phi,7/2u}6d_{\delta,3/2g}\|$
6$_u$						12 970	13 458	0	0	98%$\|5f_{\phi,7/2u}6d_{\delta,5/2g}\|$
4$_g$				5 545	6 991	12 103	10 914	0.0004	0	95%$\|5f_{\phi,5/2u}5f_{\delta,3/2u}\|$
0$_g$				12 012	8 970	10 065	11 436	0	0	73%$\|7s_{\sigma,1/2g}7s_{\sigma,-1/2g}\|$, 15%$\|6d_{\delta,3/2g}6d_{\delta,-3/2g}\|$
1$_g$						11 017	12 564	0	0.0273	92%$\|7s_{\sigma,-1/2g}6d_{\delta,3/2g}\|$
2$_g$						11 667	12 958	0.0192	0	62%$\|7s_{\sigma,1/2g}6d_{\delta,3/2g}\|$, 17%$\|7s_{\sigma,-1/2g}6d_{\delta,5/2g}\|$
1$_g$						15 024	13 919	0	0.0004	79%$\|5f_{\phi,5/2u}5f_{\delta,-3/2u}\|$
5$_g$						16 335	15 408	0	0	54%$\|5f_{\phi,5/2u}5f_{\delta,5/2u}\|$, 46%$\|5f_{\phi,7/2u}5f_{\delta,3/2u}\|$
3$_g$						13 926	15 502	0	0	88%$\|7s_{\sigma,1/2g}6d_{\delta,5/2g}\|$
3$_g$	(18 159)					16 753	16 625	0	0.1004	63%$\|5f_{\phi,5/2u}5f_{\pi,-1/2u}\|$ 29%$\|5f_{\phi,5/2u}7p_{\pi,1/2u}\|$
1$_g$						17 345	16 949	0	0	48%$\|5f_{\phi,-5/2u}5f_{\phi,7/2u}\|$, 36%$\|6d_{\delta,5/2g}6d_{\delta,-3/2g}\|$
2$_g$	(18 573)					16 703	17 340	0	0.0680	38%$\|5f_{\phi,5/2u}5f_{\pi,-1/2u}\|$, 20%$\|5f_{\phi,5/2u}7p_{\pi,1/2u}\|$
4$_g$	17 859					17 120	17 516	0	0.0276	32%$\|5f_{\delta,5/2u}5f_{\delta,3/2u}\|$, 27%$\|6d_{\delta,5/2g}6d_{\delta,3/2g}\|$
6$_g$						19 756	18 913	0	0	69%$\|5f_{\phi,5/2u}5f_{\phi,7/2u}\|$, 31%$\|5f_{\delta,5/2u}5f_{\phi,7/2u}\|$
1$_g$						20 778	20 801	0	0	40%$\|5f_{\delta,3/2u}5f_{\pi,-1/2u}\|$, 34%$\|5f_{\delta,3/2u}7p_{\pi,-1/2u}\|$
1$_g$	(27 259)					21 180	21 247	0	0.1686	51%$\|5f_{\phi,5/2u}7p_{\pi,-3/2u}\|$, 40%$\|5f_{\phi,5/2u}5f_{\pi,-3/2u}\|$
2$_g$						21 443	22 307	0.0116	0	22%$\|7s_{\sigma,1/2g}6d_{\delta,3/2g}\|$, 22%$\|7s_{\sigma,-1/2g}6d_{\delta,5/2g}\|$
3$_g$						32 644	30 853	0.1281	0	34%$\|5f_{\phi,5/2u}7p_{\pi,1/2u}\|$, 27%$\|5f_{\phi,5/2u}5f_{\pi,1/2u}\|$
2$_g$	31 838					32 378	31 125	0	0.1021	81%$\|5f_{\phi,5/2u}7p_{\sigma,-1/2u}\|$, 15%$\|5f_{\phi,5/2u}5f_{\sigma,-1/2u}\|$
3$_g$	31 838					32 444	31 203	0.1013	0	80%$\|5f_{\phi,5/2u}7p_{\sigma,1/2u}\|$, 15%$\|5f_{\phi,5/2u}5f_{\sigma,1/2u}\|$
2$_g$	(29 700)					33 841	32 071	0	0.1499	31%$\|5f_{\phi,5/2u}7p_{\pi,-1/2u}\|$, 27%$\|5f_{\phi,5/2u}5f_{\pi,-1/2u}\|$
1$_g$						35 007	33 189	0	0.1671	47%$\|5f_{\phi,5/2u}5f_{\pi,-3/2u}\|$, 28%$\|5f_{\phi,5/2u}7p_{\pi,-3/2u}\|$
4$_g$						35 530	33 832	0.1267	0	39%$\|5f_{\phi,5/2u}5f_{\pi,3/2u}\|$, 20%$\|5f_{\phi,5/2u}7p_{\pi,3/2u}\|$

[a]References 5 and 21.
[b]Reference 23.
[c]Reference 18.
[d]In Ar matrix.

lier CASPT2 calculations, but the GASCI calculation of Fleig *et al.*[23] and also the multireference configuration interaction (MRCI) calculations of Tyagi[63] give a significantly smaller value for the excitation from $5f_{\phi,5/2u}$ to $5f_{\delta,3/2u}$. This is probably due to the fact that fewer electrons were correlated in these CI calculations; if we correlate only 14 electrons we also obtain smaller energy differences of 1621 and 1911 cm^{-1}. The experimental data for the transition to the $5f^1_{3/2}7s^1_{1/2}$ states is based on the measurements in the argon matrix.[21] Also, with SOC, the discrepancy between these data and the theoretical values (that were all done in the gas

phase) (Refs. 3, 4, 18, 22, and 23) remains much larger than would be expected from a matrix effect on energy differences between four rather similar states. It is curious that almost the same vibrational frequency (776 cm^{-1}) in the argon matrix that was assigned by Andrews and co-workers[3,14] to the asymmetric stretch of the ^3H_g (4$_g$) is also seen as a vibrational band (771 cm^{-1}) in the fluorescence spectra. Lue *et al.*[21] assign this band to a symmetric stretch of 776 cm^{-1} that they deduced from the observation of a 728 cm^{-1} band of ^{18}OU ^{16}O by Gabelnick *et al.*[64] This value is, however, much lower than the $^3\Phi_u$ symmetric stretch frequency com-

puted by DFT (856 cm^{-1}),[15] large basis set CASPT2 (948 cm^{-1}),[18] and DC-FSCC (961 cm^{-1}). In the paper of Li *et al.*[15] the symmetric stretch of the 4_g state is reported at 779 cm^{-1}, which does fit the experimental band found in the fluorescence experiment. This interpretation is, however, not corroborated by our calculations, as we compute a symmetric stretch vibration of 911 cm^{-1} for this state.

2. Region 3 000–9 000 cm^{-1}: $5f^1 7s^1$ and $5f^1 6d^1$ ungerade states

These states have the same parity as the ground state and are therefore difficult to observe directly. The fluorescence data, that were already discussed above, give some bands in the range of 470–600 nm. From these experiments of Lue *et al.*,[21] it could not be deduced whether these peaks were caused by direct or indirect emission. If the emission occurs from the state excited by the 380.5 nm (26 281 cm^{-1}) laser, there should be accessible states that have energies in the range of 5000–9600 cm^{-1}. Our calculations give both $5f^1 7s^1$ states and $5f^1 6d^1$ states in this range that could be reached by an emission from a $5f^1 7p^1$ state. To check the value of 5047 cm^{-1} calculated for the $5f^1 6d^1\ ^3H_u$ state, we also performed a single reference DC-CCSD(T) calculation on this state. This gives a value of 3521 cm^{-1} that is comparable to the DC-FSCCSD result and reinforcing the conclusion that the lower $5f^1 6d^1$ states should not be disregarded in the analysis of experimental observations.

3. Region 10 000–22 000 cm^{-1}: $5f^2$ gerade states

The second interpretation of the fluorescence bands that was given is that they are caused by an indirect process, in which an upper level is populated by nonradiative transfer before exhibiting radiative decay to the ground state. This should correspond to a strong emission from a state at 21 280 cm^{-1} to the ground state. In our calculations, we find a $1g$ state at 21 247 cm^{-1} with a large contribution of the $5f^1 7p^1$ configuration and therefore a large oscillator strength, 0.1686, the most intense found in our calculations. Other states that could contribute to this fluorescence band are the $3g$ at 16 625 cm^{-1} and the $2g$ at 17 840 cm^{-1}. Since these fluorescence measurements were done in the argon matrix, it is hard to compare directly, but the predicted bands at 470, 577, and 602 nm are not incompatible with the observed fluorescence.

For this region of the spectrum one may, however, also consider the much more precise gas phase REMPI data of Han *et al.*[5] On the basis of theoretical data available at that time,[22] they assigned a state at 17 859 cm^{-1} to a $4g$ state and two states at 18 159 and 18 423 cm^{-1} to $1g$ states. This assignment is supported by Tyagi[63] but contested by Gagliardi *et al.*[18] who proposed a reassignment of the first transition to $2g$. Our calculations place a $4g$ state at 17 516 cm^{-1} which agrees well with the original assignment of this transition as $3u \rightarrow 4g$. For the other two transitions, agreement is less good. The most likely candidates are both the $3g$ at 16 625 cm^{-1} and the $2g$ at 17 340 cm^{-1} states that have a significant intensity for excitation from the $2u$ ground state.

Like in the spin-free case, we find significant differences with the CASPT2 results. We find the lowest $5f^2$ state at 10 914 cm^{-1}, whereas with CASPT2 this state is only 3330 cm^{-1} above the ground state. Also the $5f^1 7p^1$ states come out somewhat higher than with CASPT2-SO. As discussed in the previous section, part of the cause for the discrepancy is the difference in bond length used to compute these vertical excitation energies, but this is only a relatively small effect. The same holds for the way in which relatively is treated, such differences usually give rather small deviations for valence properties. This leads us to conclude that differences should be primarily due to the completely different approach to electron correlation that is chosen in both methods. This was already pointed out in the atomic calculations in which case the two methods did also differ from each other by an amount of 6000 cm^{-1}. As the Fock space approach is less well tested in such demanding molecular applications as the one studied here, we decided to also perform some calculations with the more established DC-CCSD(T) method. The two states of interest, the $5f^1 7s^1\ 2u$ and the $5f^2\ 4g$ states, are both well described by a single determinant reference, which makes it possible to compute the $2u \rightarrow 4g$ excitation energy directly. The DC-CCSD calculation gives a rather small excitation energy of 5545 cm^{-1} that increases to 6991 cm^{-1} if triple excitations are included with the DC-CCSD(T) approach. This is significantly higher than the CASPT2 value, but also significantly lower than the DC-FSCC value. The discrepancy between the two CC approaches can be due to two factors: the CCSD(T) approach has a large T_1 diagnostic value of 0.040 in the $4g$ calculation which, together with the large effect of the (T) correction, could be indicative of a breakdown in the single-reference approach. On the other hand, as already discussed for the calculation of the ionization energy, we base the Fock space approach on orbitals that are obtained in a HF calculation of the dication. This will make the orbitals used in the Fock space calculation tighter, possibly favoring the $5f^1 7s^1$ configuration above the $5f^2$. To assess this effect, we repeated the CCSD calculation using the same orbitals (from the dication, uranyl) as employed in the DC-IHFSCCSD calculation. This resulted in a CCSD excitation energy of 5247 cm^{-1}, indicating that the difference in orbitals is again only marginally important.

4. Region 30 000–50 000 cm^{-1}: $5f^1 7p^1$ gerade states

This region includes mainly $5f^1 7p^1$ states. Experimentally, both the absorption REMPI spectrum[5] and the fluorescence spectrum in Ar matrix[21] give an intense band at about 27 000 cm^{-1}. This is regarded as evidence for the suggestion that the ground state does not change in an argon matrix. In both cases, the transitions should then be due to an intense $7s \rightarrow 7p$ transition. Our calculations are in qualitative agreement with this assignment, but give transitions to the $5f^1 7p^1$ states starting around 30 000 cm^{-1} with all excitations in the region between 22 000 and 30 000 corresponding to double excitations, which should have too little intensity. The difference of 3000 cm^{-1} could be due to a flaw in the calculations, possibly a remaining basis set deficiency. The $7p$ orbitals are very diffuse and may require more diffuse functions than the

single shell that we added. We do not expect that the method itself does give large errors in this case, since the ground and excited states are composed of states that have the same main quantum number. In the atomic calculation the errors for such transitions were of the order of few hundreds of wave numbers.

IV. CONCLUSIONS

We applied the relativistic Fock space coupled cluster method and its intermediate Hamiltonian modifications to analyze the electronic spectrum of the UO$_2$ molecule. The method is size extensive and provides an accurate treatment of dynamic and nondynamic correlation effects, which is crucial for correct calculation and interpretation of the complicated UO$_2$ spectrum. The ease with which a full manifold of excited states is computed in a single run is an important asset of the method. The IHFSCC approach scales as N^6, but this can be ameliorated by applying linear scaling techniques, because all computationally intensive terms are similar to those that occur in regular CC algorithms.

For the first time, the $6d$ shell has been included explicitly in the correlated calculation. A 4_u state arising from the $5f^1 6d^1$ configuration is found at about 5000 cm^{-1}, which makes it an interesting alternative for explaining the low values found in older IP measurements.[2] The first gerade state, 4_g, is found at more than 10 000 cm^{-1}, which is much higher than that predicted by all previous theoretical calculations. This value could be overestimated, but it appears unlikely that this state is the lowest when the UO$_2$ molecule is trapped in an Ar matrix. We propose that it is more likely that the $5f^1 6d^1$ $4u$ state is of importance in the heavier noble gas matrices. Like previous calculations, the present work cannot fully explain all experimental observations, but they add more pieces to the complex puzzle that nature has posed.

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