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Electronic structure and prediction of atomization energy of naked homoleptic uranium hexacarbonyl $U(CO)_6$

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Our *ab initio* all-electron fully relativistic Dirac-Fock and nonrelativistic Hartree-Fock self-consistent field (SCF) calculations predict the octahedral (O_h) uranium hexacarbonyl $U(CO)_6$ to be *bound* with the calculated atomization energy of 49.84 and 48.76 eV at the predicted U–C bond lengths (assuming the C–O bond distance fixed at 1.17 Å) of 2.53 and 2.63 Å, respectively. Moreover, our all-electron fully relativistic Dirac-Fock SCF calculations predict $U(CO)_6$ to be lower in energy by 3.90 eV with respect to dissociation into U plus six CO ligands. We predict $U(CO)_6$ (O_h) to be very stable in view of our predicted large atomization energy (~49 eV) and stability (~4 eV) with respect to dissociation into U plus six CO molecules. Innovative techniques should be devised for the synthesis of uranium hexacarbonyl since the usual synthetic methods have failed so far for this naked actinide hexacarbonyl. © *2006 American Institute of Physics*.
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There has been an enormous activity in the study of the actinides,[1–3] especially uranium which has played a key role in nuclear technology. It is well established[4–7] that relativistic effects are very significant for the description of the electronic structure and bonding of systems containing heavy elements such as the actinides. Uranium compounds have become prototypes for testing the theoretical and computational[8–15] methodology for investigating the effects of relativity on the electronic structure and bonding of actinide compounds. Most metal carbonyls[16,17] are very stable and fairly volatile and are used in separation of metals. Uranium carbonyls were of crucial importance in the early days of Manhattan Project[18] because of the possible separation of uranium via its supposedly volatile carbonyl. There is an interesting account[18] of the numerous attempts which failed to synthesize uranium hexacarbonyl. Thirty years ago, using the matrix isolation technique of DeKock[19] for the preparation of particularly unstable or metastable metal carbonyl species, Slater *et al.*[20] claimed the synthesis of uranium carbonyls. Recently, Zhou *et al.*[21] have also reported to detect uranium carbonyls in the reaction of laser-ablated U atoms with CO. However, unlike the well-known hexacarbonyls of transition metals, naked actinide hexacarbonyls still elude the experimentalists.

In this communication, I report the *first ab initio all-electron* fully relativistic Dirac-Fock (DF) and the nonrelativistic (NR) limit Hartree-Fock (HF) calculations for the yet unknown octahedral $U(CO)_6$ and discuss its electronic structure and calculation of its atomization energy. We refer the reader to our extensive accounts for details of our Dirac-Fock (DF) SCF formalism for molecules and its applications to various molecular systems, especially those of the actinides and superheavy transactinides.[11,13–15] We have used our universal Gaussian basis set[22–24] (UGBS) in our Dirac-Fock (DF) and NR HF calculations on U, C, and O and $U(CO)_6$ (O_h) with the MOLFDIR package[7] (hereafter referred as package) assuming the Gaussian nuclear model. We refer the reader to earlier papers[11,13–15] for further theoretical and computational details. The 30s30p18d13f, 18s12p, and 18s12p UGBS were used for the large (L) component wave function (WF) of the U, C, and O atoms, respectively. The L component basis for the U, C, and O atoms were contracted to 10s12p10d6f (U), 4s3p (C), and 4s3p (O), respectively using the general contraction scheme along with the atomic balance procedure as implemented in the package.[7] The UGBS of the small (S) component wave function of U, C, and O were obtained from the UGBS of their corresponding L component WF, so that the L and S component WF of each atom satisfy the kinetic balance constraint.[25] The S component basis of U, C, and O were contracted to 14s22p22d13f8g, 4s5p5d, and 4s5p5d, respectively. The speed of light used in our DF SCF calculations was 137.03602 a.u., and the total energies calculated with our contracted relativistic UGBS described above for the U, C, and O atoms are −28052.7587, −37.6760, and −74.8248 a.u., respectively. In the nonrelativistic (NR) limit Hartree-Fock (HF) calculations which were also performed with the package,[7] however, only the L components of the contracted UGBS were used. The calculated total NR HF average of configuration energies with the contracted NR UGBS described above for the U, C, and O atoms (using the Gaussian nuclear model) are −25662.7099, −37.6596, and −74.7691 a.u., respectively. Dirac-Fock (DF) self-consistent field (SCF) calculations for $U(CO)_6$ (O_h) were performed assuming Gaussian nuclear model for U, C, and O at four different U–C internuclear distances keeping the C–O bond distance at 1.17 Å. The results were fitted to a polynomial obtaining thereby the optimum energy and the corresponding

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U–C bond distance for the $U(CO)_6$ (O_h). A Dirac-Fock calculation at one internuclear U–C distance for an octahedral geometry for $U(CO)_6$, takes about 20 hours of CPU on our Cray SV1 supercomputer. In order to economize the disk space required in an all-electron relativistic molecular calculation, we used the thresholds given in parentheses for the various two-electron integrals involving the large (L) and small (S) component basis sets: $[LL|LL](10^{-12})$, $[LL|SS]\times(10^{-10})$ and $[SS|SS](10^{-08}]$. The nonrelativistic (NR) limit Hartree-Fock (HF) SCF calculations were also performed (assuming Gaussian nuclear model for U, C, and O) for $U(CO)_6$ (O_h) at four different U–C internuclear distances (assuming also a fixed C–O bond distance of 1.17 Å) with our contracted NR UGBS for the U, C, and O atoms, discussed above, and the results were fitted to a polynomial obtaining thereby the minimum HF energy and the corresponding NR U–C bond distance for the $U(CO)_6$ (O_h). The Dirac-Fock ground state electron configuration of $U(CO)_6$ is given here for the *first* time as:

$$(1e_{1g})^2\ldots(12e_{1g})^2\ldots(1e_{1u})^2\ldots(12e_{1u})^2\ldots(1e_{2g})^2\ldots$$
$$(4e_{2g})^2\ldots(1e_{2u})^2\ldots(4e_{2u})^2\ldots(1f_g)^4\ldots$$
$$(14f_g)^4\ldots(1f_u)^4\ldots(14f_u)^4,$$

where we have designated the four *two-dimensional* extra irreducible representations (EIR) as e_{1g}, e_{1u}, e_{2g}, and e_{2u} and the two *four-dimensional* EIR of the octahedral double group (O_h^*) as f_g and f_u, respectively, as in our earlier work on octahedral UF_6 (Ref. 11) and UCl_6.[15] The calculated spinor energies of the inner *molecular spinors* or relativistic MOs (RMOs) $1e_{1g}$, $2e_{1g}$, $1e_{1u}$, $1f_u$, and $3e_{1g}$ of $U(CO)_6$ are *significantly* lower than those of the corresponding NR MOs, as expected due to *pronounced* relativistic effects in the inner orbitals of U atom, since these RMOs consist of almost pure inner (core) 4-component *atomic spinors* or relativistic AOs (RAOs) of U. The contraction of inner orbitals due to *direct* relativistic effects leads to a better screening of electrons in outer orbitals resulting thereby in the increase of their orbital energies and destabilization. Mulliken's population analysis was employed to calculate the total gross population on the U, C, and O atoms, and the charge distribution $U^{-0.16}(C^{+0.97}O^{-0.94})_6$ is obtained with our relativistic DF calculations for $U(CO)_6$ (O_h). However, the results of this analysis should be treated with caution.[26,27]

The calculated highest occupied molecular spinor (HOMS) or relativistic MO (HORMO) of $U(CO)_6$ (O_h) in our calculations is $14f_g$ with a spinor energy of −0.2338 a.u. and consists of 0.89 U(d), 0.19 C(p) and 0.12 O(p) RAO of U, C, and O, respectively. The lowest unoccupied molecular spinor (LUMS) $5e_{2g}$ with energy of −0.0236 a.u., on the other hand consists of 0.55 U(d), 0.33 C(p), and 0.11 O(p) RAOs, leading to the HOMS-LUMS gap of 5.72 eV. In addition to the HUMS and LUMS, the RAOs of U are significantly involved only in the $4e_{2u}(-0.4227)$ and $10f_u(-1.0638)$ molecular spinors with energies (in a.u.) given in parenthesis. The former MS consists purely of U(f) RAO while the latter comprises of 0.94 U(p) with 0.08 of C(s) RAO. The calculated total relativistic Dirac-Fock (DF) and NR HF energies for U (omitting the energies of C and O which are given in the text) and $U(CO)_6$ (O_h), the predicted U–C bond distance and atomization energy (A_e) with our relativistic DF and NR HF wavefunctions for $U(CO)_6$ (O_h), are presented in Table I. The HOMO calculated in our NR calculations is also $14f_g$ (we use the double group notation also for molecular orbitals) with an orbital energy of −0.2404 a.u. and like the HOMS ($14f_g$) consists of 0.678 U(d), 0.23 C(p) and 0.10 O(p) AOs. Therefore the HOMS and HOMO are almost identical with very similar energy. The lowest unoccupied MO (LUMO), however is calculated to be $15f_u$ with energy of −0.0275 a.u. consisting of 0.74 U(f), 0.49 O(s), 0.29 C(p), and 0.08 O(p) AOs with the calculated HOMO-LUMO gap of 5.79 eV. Moreover, in contrast to the very few valence MS which have contributions from U RAOs, the MO's $11e_{1u}$(0.49U(p) , $9e_{1u}$(0.63U(p)), $3e_{2u}$(0.84U(f)), $13f_u$(0.39U(p) , $10f_u$(0.60U(p)) have fairly significant contributions from U AOs and the contribution of the U AO to a particular MO is given in parenthesis. Finally, there are no *ab initio* all-electron calculations of atomization energy (A_e) of $U(CO)_6$ (O_h); however, our *all-electron* Hartree-Fock (HF) and relativistic Dirac-Fock (DF) wave functions predict $U(CO)_6$ (O_h) to be *bound* with the predicted atomization energy of 48.76 and 49.84 eV, respectively as given in Table I. Our Dirac-Fock and HF calculations for the $U(CO)_6$ (O_h) predict (assuming a fixed C–O bond distance of 1.17 Å) the U–C bond length of 2.53 and 2.63 Å, respectively.

TABLE I. Calculated total energy E (in a.u.), predicted atomization energy A_e (in eV) and U–C bond length R (in Å) for octahedral U $(CO)_6$ with our NR HF and relativistic DF wave functions.[a]

	$U(CO)_6$	U
E^{NR}	−26339.0741	−25662.7099
E^{DF}	−28729.5952	−28052.7587
A_e^{NR}	48.76	
A_e^{DF}	49.84	
R^{DF}	2.53	
R^{NR}	2.63	

[a]The E^{NR} and E^{DF} are the total NR HF and relativistic DF electronic energies at the predicted R^{NR} and R^{DF} U–C bond distances (for fixed C–O distance of 1.17 Å) with the corresponding atomization energies A_e^{NR} and A_e^{DF}, respectively for the octahedral $U(CO)_6$.

We have performed the *first ab initio all-electron fully relativistic* Dirac-Fock and NR HF calculations which predict the ground state $U(CO)_6$ to be *bound* with the very large atomization energy of 49.84 and 48.76 eV, respectively. Moreover, our all-electron fully relativistic Dirac-Fock calculations predict $U(CO)_6$ to be stable by 3.90 eV with respect to dissociation into one U plus six COs. In view of large atomization energy (~49 eV) and substantial stability (~4.0 eV) of $U(CO)_6$ as predicted from our relativistic DF calculations, efforts should be directed towards novel methods for synthesis of $U(CO)_6$. I would like to add that inclusion of electron correlation effects would lead to even larger atomization energy and possibly greater stability of $U(CO)_6$

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in view of our recent coupled-cluster calculations.[28,29] which predict an extra contribution of ~4 eV to the atomization energy of PbH_4 due to electron correlation effects.

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