Dirac-Fock-Breit-Gaunt calculations for the reaction $\text{Og}^+ + 6 \text{CO} \rightarrow \text{Og} \,(\text{CO})_6$ or $\text{Og} \,(\text{OC})_6$: Prediction of the isomer $\text{Og} \,(\text{OC})_6$ as the ground state geometry and its atomization energy.

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**Abstract:** Our *ab initio* all-electron relativistic Dirac-Fock-Breit-Gaunt (DFBG), relativistic Dirac–Fock (DF), and nonrelativistic Hartree-Fock (NR) calculations predict the energies for the reaction: \( \text{Og} + 6\text{CO} \rightarrow \text{Og} (\text{CO})_6 \) as 9.79, 7.66 and 17.51 eV, respectively. However, our relativistic DFBG, DF and NR calculations predict the energies of the reaction \( \text{Og} + 6\text{CO} \rightarrow \text{Og} (\text{OC})_6 \) as 5.89, 5.87, and 5.21, eV respectively. The contribution of relativistic effects to the Ae of ~2.50 eV for \( \text{Og} (\text{CO})_6 \) is significant. Our relativistic DF and the NR calculations for the isomer \( \text{Og} (\text{OC})_6 \), however, predict Ae of 55.64 and 53.57, eV respectively and there are significant relativistic effects of ~2.0 eV for the Ae of the isomer \( \text{Og} (\text{OC})_6 \). Our prediction for the isomerization energy \( (E_{\text{iso}}) \) of \( \text{Og} (\text{OC})_6 \rightarrow \text{Og} (\text{CO})_6 \) at the DF and NR levels of the theory is 2.05 and 2.3 eV, respectively. Both the isomers are predicted to be stable enough. However, it is most surprising that the isomer \( \text{Og} (\text{OC})_6 \) is predicted to be more stable at the NR, DF, and DFBG levels of theory. Such a prediction has not been proposed in the literature before and it is relevant for Og.
I. INTRODUCTION

The discovery and investigation of the superheavy elements (SHE) has been one of the most active areas of research during the last decades. Recently four new SHE were discovered and placed in the periodic table completing the 7th row of the periodic table. Since very few SHE atoms with a very short life can be synthesized, it may not be possible to study the chemistry of the SHE routinely. However, theoretical investigation of the chemistry and physics of the SHE does not suffer from the enormous difficulties associated with the experimental investigation of SHE and can be the preferred methodology for investigating the nature of bonding, chemical, and physical properties, etc. of the SHE. There is, however, a major hurdle in treating theoretically the systems of SHE, because it is well recognized that relativistic effects, as well as correlation effects would be very significant for the description of the electronic structure and bonding of systems containing SHE such as the transactinide Og with Z=118. The usual Schrodinger's nonrelativistic treatment is not expected to be suitable for systems of SHE, but instead, a generalization of Dirac's relativistic treatment for an electron to many-electron atomic and molecular systems would be more appropriate for such systems.

In 1975 we developed the relativistic Dirac-Fock (DF) SCF theory for closed-shell molecules in which the many-electron relativistic Hamiltonian was taken to be what is called Dirac-Coulomb, and, in addition, the relativistic correction to the inter-electron interaction was taken as magnetic part of the Breit interaction (which we have called the Breit-Brown interaction) to be treated perturbationally. However, quantum electrodynamical (QED) and electron correlation effects were neglected. Oganesson compounds are eminently suitable for testing the theoretical and computational methodology for investigating the effects of relativity on their electronic structure and bonding. During the last three decades we have reported \textit{ab initio} Dirac-Fock (DF) and Dirac-Fock-Breit (Brown) calculations for numerous
actinides and transactinides including the superheavy seaborgium hexahalides[^11-13][18] (SgF₆, SgCl₆, and SgBr₆) and seaborgium oxychlorides[^11,14] SgO₂Cl₂ and SgOC₄. In this paper, we report the first ab initio relativistic DF (and the corresponding NR) calculations (without electron correlation) for the reaction Og+6CO → Og (CO)₆ or Og(OC), and predict the existence of the first organometallic isomers Og(CO)₆ and Og(OC)₆. We refer the reader to extensive accounts for details of our Dirac-Fock (DF) SCF formalism for molecules and its applications to various molecular systems, especially those of superheavy transactinides.[^11-17]

II. CALCULATIONS
A. Calculations for Og (CO)₆ and Og (OC)₆ using DIRAC

There are neither ab initio all-electron 4-component relativistic Dirac-Fock (DF) nor the corresponding nonrelativistic (NR) Hartree-Fock (HF) calculations available for the superheavy Og (CO)₆ and its isomer Og(OC)₆. We report here the first DF and NR HF calculations (without correlation effects) for the isomers of the superheavy oganesson hexacarbonyl. All of our calculations with the Dirac code[^19] are performed using the D₂h* double group for Og (CO)₆ and we use for Og the gaussian dyall.v3z basis while the aug-cc-pVTZ basis was used for both C and O, and all the basis sets used here for Og, C, and O are available from the Dirac website[^19]. We mention here briefly the salient features of our DF (HF) calculations and refer the reader to Dirac's website[^19] and the various papers appended therein for further theoretical and computational details on the selection of basis set, the performance of calculations at various levels of theory, etc. There are in total 3869 primitive gaussians with 1171 large (L) and 2698 small (S) components for our relativistic DF calculation for Og(CO)₆ and Og(OC)₆ using the above-mentioned basis for Og, C, and O. Geometry optimizations for the octahedral Og(CO)₆ and Og(OC)₆ and the diatomic CO were carried out.
automatically using the Dirac code \(^{19}\) with the basis sets described above using the kinetic balance \(^{20}\) constraints, and assuming Gaussian nuclear model for the constituent atoms as implemented in the DIRAC code. As a test of our calculations, our calculated total relativistic DF energies with the Dirac code for the atoms C, O, and Og are in very good agreement with those reported in literature \(^{21}\). Both the DF and NR calculations for the ground state of CO were performed obtaining thereby the optimized bond distance and the corresponding total energy of CO.

III. RESULTS AND DISCUSSION

A. Dirac-Fock and NR Hartree-Fock prediction of the atomization energy for Og (CO)\(_6\) and Og (OC)\(_6\)

There are neither calculations for the atomization energy nor the energy for the titled reaction Og +6 CO → Og (CO)\(_6\) or (OC)\(_6\). We report here the results of our first relativistic DF and the NR HF calculations for the atomization energy, energy of the titled reaction, and isomerization energy for Og (CO)\(_6\) and Og (OC)\(_6\). The total relativistic DF energy calculated for the ground state of Og(CO)\(_6\) with the Dirac code (using the basis mentioned above for Og, C, and O) at the optimized bond distances of Og-C (2.941Å) and C-O (1.103) Å is -55484.7793 au. However, the calculated total DF energy of the isomer Og (OC)\(_6\) (at the optimized bond distance of Og -O (2.777) and C-O (1.098) Å is -55484.8453 au. The DF and NR HF atomization energies (\(A_e^{DF}\) and \(A_e^{NR}\)) calculated for Og(CO)\(_6\) in our
calculations are 53.84 and 51.27 eV, while for the isomer Og(OC)_6 the calculated DF and NR energies are 55.64 and 53.57 eV respectively.

B. **Dirac-Fock and NR Hartree-Fock prediction of the energy of reaction for**

Og + 6 CO → Og (CO)_6 and Og (OC)_6

Our all-electron fully relativistic Dirac–Fock (DF) and NR Hartree-Fock (HF) calculations predict the DF relativistic and NR energies for the reaction: Og+6CO → Og (CO)_6 as 7.66 and 17.51 eV, respectively. However, the DF and NR energies of reaction for the isomer reaction Og+6CO → Og (OC)_6 are predicted to be 5.87 and 5.21 eV, respectively. The results of our relativistic DF and the NR HF calculations are collected in Table 1.

**IV. ELECTRONIC STRUCTURE, BONDING, AND MOLECULAR ENERGY LEVELS OF Og (OC)_6.**

The relativistic ground state closed-shell electron configuration for the 202-electron Og (OC)_6 or Og (CO)_6 under the octahedral double symmetry group (Oh*) is written here for the first time: (1 e_{1g})^2 .... (13 e_{1g})^2 ...(1 e_{1u})^2 ...(14 e_{1u})^2 ...(1 e_{2g})^2 ...(5 e_{2g})^2 ..

It should be mentioned, however, that calculations with the Dirac code are performed under the D_{2h}* double group symmetry, and (using the double group
symmetry notation also for the single group), the ground state configuration of Og (OC)\textsubscript{6} has 48 \(e_{1g}\) molecular orbitals (MO) and 53 \(e_{1u}\) MO's.

The doubly degenerate nonbonding HOMO \((53 \; e_{1u} - 52 \; e_{1u})\) in our NR calculations for Og (OC)\textsubscript{6} lies at -0.2861 au and consists of 1.00 Og (7p) AO, where the coefficient of each atomic orbital is given in front of the atomic orbital (AO). The triply degenerate non-bonding MO \((51 \; e_{1u} - 49 \; e_{1u})\) with the energy of -0.5505 au, consists of 0.63 C(2s) and 0.36 C(2p).

The 7-fold degenerate bonding MO \((48 \; e_{1u} - 42 \; e_{1u})\) has an energy of -0.6505 au and consists of 0.73 O(2p) and 0.22 C(2p). The degenerate bonding MO's \((41 \; e_{1u} - 40 \; e_{1u})\) with the energy of -0.8246 au consisting of 0.57 O(2p), 0.24 O(2s), 0.15 C(2s), and 0.02 Og(7p) are bonding. The next bonding MO \((39 \; e_{1u})\) with the orbital energy of -0.84 au consists of 0.50 O(2p), 0.21 O(2s), 0.12 C(2s), and 0.15 Og(7p).

\textbf{V. CONCLUSION} We have performed the first \textit{ab initio} all-electron \textit{fully} relativistic Dirac–Fock and NR HF SCF calculations for the ground state of the octahedral isomers Og (OC)\textsubscript{6} and Og (CO)\textsubscript{6}, and a summary of our major conclusions is as follows:

(1) Our all-electron NR HF, relativistic DF, and DFBG calculations predict for the \textit{first time} the existence of both the hexacarbonyl isomers of the superheavy element Og.
Our relativistic DF SCF and NR HF wavefunctions predict both the isomers Og (OC)₆ and Og (CO)₆ to be bound, with the calculated DF atomization energies of 55.64 and 53.84, eV, respectively at the optimized Og-C, Og-O, and C-O bond distances collected in Table I.

Relativistic effects are significant in binding and lead to ~ 2 eV increment for the predicted atomization energy for Og (OC)₆ and Og (CO)₆, respectively.

Our all-electron fully relativistic Dirac–Fock (DF) and NR HF energies for the titled reaction: Og+6CO → Og(OC)₆ are 5.87 and 5.21 eV, whereas the DF and NR HF energies for the isomeric reaction Og+6CO → Og(CO)₆ are 7.66 and 17.51 eV, respectively. However, the relativistic effects are not significant for the reaction energy for the formation of Og (OC)₆.

There are very large relativistic corrections to the binding energies of the MOs, especially, the inner core orbitals of both the isomers. Moreover, very large S–O splitting is calculated for the core MOs that consist of the inner (core) p, d, and f AOs of Og, as expected.

The 1s...7s AS's of the Og atom as well as the 1s AS's of the six O and C ligands, and their associated electrons are not involved in bonding in Og(CO)₆ and Og(OC)₆ since they remain as if in pure AS's or core. Therefore, these core electrons could be treated in molecular calculations on compounds of the
superheavy element (SHE) Og, using appropriate frozen core or pseudopotential approximations with tremendous savings in computational cost.

In conclusion, *ab initio fully relativistic all-electron* DFBG and Dirac-Fock SCF calculations for molecular systems of superheavy elements are no longer the *bottlenecks* of relativistic quantum chemistry of SHE.

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**TABLE I** Calculated total DFBG, DF relativistic, and NR energies $E$ (in au), the predicted atomization energy ($A_e$) in eV for Og (CO)$_6$ ($O_h$) and Og (OC)$_6$ ($O_h$).

The $\Delta E^X$ (in eV) is the energy for the reaction $\text{Og}+6\text{CO} \rightarrow \text{Og (CO)}_6$, and $\text{Og}+6\text{CO} \rightarrow \text{Og (OC)}_6$. The $\Delta E_{iso}^X$ is the predicted isomerization energy (in eV) for $\text{Og (OC)}_6 \rightarrow \text{Og (CO)}_6$ at the X level of theory.

|                  | Og(CO)$_6$     | Og(OC)$_6$     |
|------------------|----------------|----------------|
| $E^{NR}$         | -46996.7517    | -46996.8361    |
| $E^{DF}$         | -55484.7793    | -55484.8453    |
| $E^{DFBG}$       | -55375.0155    | -55375.1591    |
| $A_e^{NR}$       | 51.27          | 53.57          |
| $A_e^{DFBG}$     | 52.22          | 56.12          |
| $A_e^{DF}$       | 53.84          | 55.64          |
| $\Delta E^{NR}$ | 17.51          | 5.21           |
| $\Delta E^{DF}$ | 7.66           | 5.87           |
| $\Delta E^{DFBG}$ | 9.79          | 5.89           |
| $\Delta E_{iso}^{NR}$ |             | 2.05           |
| $\Delta E_{iso}^{DF}$ |             | 2.30           |
| $\Delta E_{iso}^{DFBG}$ |             | 3.91           |
