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Citation: *The Journal of Chemical Physics* **142**, 064311 (2015); doi: 10.1063/1.4907595

View online: <http://dx.doi.org/10.1063/1.4907595>

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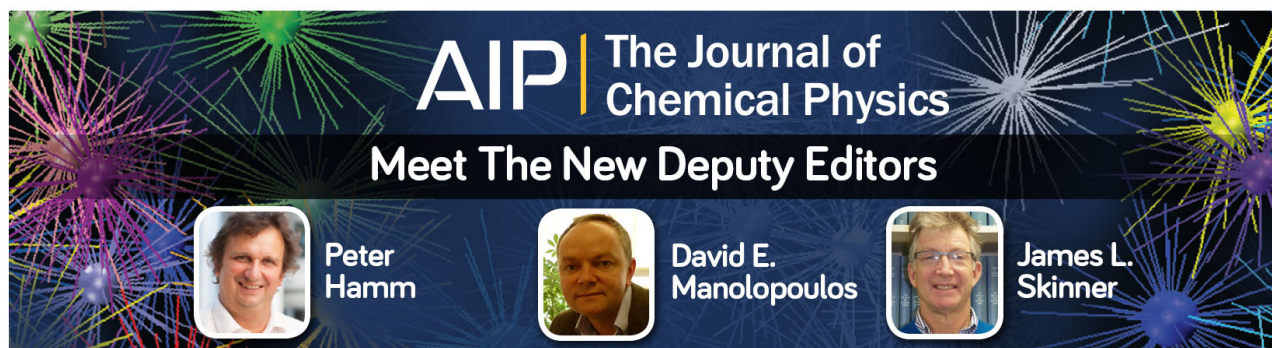
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Relativistic effects for the reaction $\text{Sg} + 6 \text{CO} \rightarrow \text{Sg}(\text{CO})_6$: Prediction of the mean bond energy, atomization energy, and existence of the first organometallic transactinide superheavy hexacarbonyl $\text{Sg}(\text{CO})_6$

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(Received 22 August 2014; accepted 26 January 2015; published online 11 February 2015)

Our *ab initio* all-electron fully relativistic Dirac–Fock (DF) and nonrelativistic (NR) Hartree–Fock calculations predict the DF relativistic and NR energies for the reaction: $\text{Sg} + 6 \text{CO} \rightarrow \text{Sg}(\text{CO})_6$ as -7.39 and -6.96 eV, respectively, i.e., our calculated ground state total DF relativistic and NR energies for the reaction product $\text{Sg}(\text{CO})_6$ are *lower* by 7.39 and 6.96 eV than the total DF and NR ground state energies of the reactants, viz., one Sg atom plus six CO molecules, respectively. Our calculated DF relativistic and NR atomization energies (Ae) are 65.23 and 64.82 eV, respectively, and so the contribution of relativistic effects to the Ae of ~ 0.40 eV is marginal. The Sg–C and C–O optimized bond distances for the octahedral geometry as calculated in our DF (NR) calculations are 2.151 (2.318 Å) and 1.119 (1.114 Å), respectively. The BSSE correction calculated using the DIRAC code ~ 14 kcal/mol. The relativistic DF and NR mean energies predicted by us are 118.8 and 111.9 kJ/mol, respectively, and the contribution of ~ 7 kJ/mol due to relativistic effects to the mean energy of $\text{Sg}(\text{CO})_6$ is negligible. Ours are the *first* calculations of the relativistic effects for the atomization energy, mean bond energy, and energy of the reaction for possible formation of $\text{Sg}(\text{CO})_6$, and both our relativistic DF and the NR treatments clearly predict for the first time the existence of hexacarbonyl of the transactinide superheavy element seaborgium Sg. In conclusion, *relativistic effects are not significant* for $\text{Sg}(\text{CO})_6$. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4907595>]

I. INTRODUCTION

Superheavy elements (SHEs) have been the subject of numerous^{1–8} experimental and theoretical investigations during the last many decades. The discovery of element 106 was announced in 1974 by the Dubna research group led by Flerov¹ and the Lawrence Berkeley Livermore group headed by Ghiorso.² The confirmation of the discovery of element 106 by Gregorich *et al.*,³ however, came about two decades later, and after a period of controversy, the IUPAC in 1997 named the element 106 as seaborgium (Sg) in honor of the living American chemist Seaborg. Schaedel *et al.*⁴ from the isothermal gas chromatography (IC) and liquid chromatographic separation studies have concluded that seaborgium is similar to its lighter homologues molybdenum (Mo) and tungsten (W) and its behavior is typical for a group 6 element in the periodic table. Since a very few atoms with a very short lifetime can be synthesized of SHE, it is not 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 experimental investigations of SHE and can be the preferred methodology for investigating the nature of bonding, chemical, and physical properties of the SHE. There is, however, a major hurdle in

treating theoretically the systems of SHE because it is well recognized^{11–17} 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 Sg. The usual Schrodinger's nonrelativistic (NR) 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 may be more appropriate for such systems.

In 1975, we⁹ developed the relativistic 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. Seaborgium compounds are eminently suitable for testing the theoretical and computational methodology for investigating the effects of relativity on their electronic structure and bonding.^{10–17} During the last three decades, we have reported *ab initio* Dirac–Fock (DF) and Dirac–Fock–Breit (Brown) calculations for numerous actinides and transactinides including seaborgium hexahalides^{11,13,14} (SgF_6 , SgCl_6 , and SgBr_6) and seaborgium oxychlorides,^{11,14} SgO_2Cl_2 and SgOCl_4 . In this paper, we report the *first ab initio* relativistic DF (and the corresponding NR) calculations (without electron correlation) for the reaction: $\text{Sg} + 6 \text{CO}$

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→ $\text{Sg}(\text{CO})_6$ and predict the possible existence of the first organometallic transactinide $\text{Sg}(\text{CO})_6$. We refer the reader to our extensive accounts for details of our DF SCF formalism for molecules and its applications to various molecular systems, especially those of superheavy transactinides.^{11–17}

In 1999⁸ using the shape-consistent relativistic effective core potentials (RECPs), the bond lengths and vibrational frequencies at various levels of theory as well as the first carbonyl dissociation energy (FCDE) for the octahedral $\text{Sg}(\text{CO})_6$ were reported; the FCDE for $\text{Sg}(\text{CO})_6$ was, however, obtained by extrapolation of their results for the hexacarbonyls of Mo and W, the lighter congeners of Sg. It should be pointed out that extrapolation of properties of $\text{Sg}(\text{CO})_6$ from those of $\text{W}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ is not expected to be very reliable and trustworthy. Recent relativistic density functional calculations¹⁷ have reported the bond distances Sg–C and C–O, ionization potential, and adsorption enthalpies *assuming an octahedral geometry* for $\text{Sg}(\text{CO})_6$. However, from the results of their calculations of the adsorption enthalpies of the hexacarbonyls of group 6 on a quartz surface, the authors have remarked¹⁷ that “in future gas-phase chromatography experiments, it will be *almost impossible* to distinguish between the W and Sg hexacarbonyls by their deposition on quartz.” One should bear in mind that IC and thermo chromatography (TC) are the two most popular methods for gas-phase studies of SHE and these results virtually rule out the use of IC for future studies of hexacarbonyl of Sg. However, most recently, a critical perspective¹⁸ discusses the experimental identification of the “seaborgium carbonyl” by a team of international nuclear scientists after many years of extensive research.

II. CALCULATIONS

A. Calculations for $\text{Sg}(\text{CO})_6$ using DIRAC

There are neither *ab initio* all-electron 4-component relativistic DF nor the corresponding NR Hartree-Fock (HF) calculations available for the superheavy $\text{Sg}(\text{CO})_6$. We report, here, the *first* DF and NR HF calculations (without correlation effects) for the superheavy seaborgium hexacarbonyl. All of our calculations with the Dirac code¹⁹ are performed using the D_{2h}^* double group for $\text{Sg}(\text{CO})_6$ and we use for Sg the Gaussian dyall.v2z basis while the aug-cc-pVDZ basis was used for both C and O, and all the basis used here for Sg, C, and O are available from the Dirac website.¹⁹ We only mention, here, briefly salient features of our DF (HF) calculations and refer the reader to Dirac’s website¹⁹ and the various papers appended therein for further theoretical and computational details on the selection of basis set, performance of calculations at various levels of theory, etc. There are in total 2546 primitive Gaussians with 755 large (L) and 1791 small (S) components for our relativistic DF $\text{Sg}(\text{CO})_6$ calculation using the above mentioned basis for Sg, C, and O. Geometry optimizations for the octahedral $\text{Sg}(\text{CO})_6$ and the diatomic CO were carried out automatically using the Dirac code¹⁹ with the basis sets described above using the kinetic balance²⁰ constraint and assuming Gaussian nuclear model for the constituent atoms as implemented in the DIRAC11 code. As a test of our calculations, our calculated total relativistic

DF energies with the Dirac11 code for the atoms C, O, and Sg are in very good agreement with those reported by the benchmark calculations of Visscher and Dyall.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.

B. Calculations for $\text{Sg}(\text{CO})_6$ using MOLFDIR

DF SCF calculations for $\text{Sg}(\text{CO})_6$ were also performed assuming octahedral double group (O_h^*) symmetry with the MOLFDIR code²² using our universal Gaussian basis set (UGBS).^{23,24} The relativistic [30s 30p 18d 13f], [18s 12p], and [18s 12p] uncontracted UGBS for the large (L) component wavefunction (WF) of Sg, C, and O were contracted to Sg [L: 12s 14p 11d 6f], C [L: 4s 3p], and O [L: 4s 3p], respectively. The UGBS of the small (S) component wavefunctions (to be used in DF calculations) for Sg, C, and O, however, was obtained from the UGBS of their corresponding L component WF, so that the L and S component WFs of each atom satisfies the kinetic balance constraint²⁰ as implemented in the code.²² The uncontracted NR UGBS was contracted to Sg [L: 12s, 14p, 11d, 6f], C [L: 4s, 3p], and O [L: 4s, 3p], respectively, where L stands for the large component and only large component WF was used for NR calculations. The total NR Hartree Fock and Dirac-Fock atomic energies calculated with our contracted UGBS for Sg, C, and O are in fairly good agreement with those calculated with the Dirac code assuming a Gaussian nuclear model, and so our DF (HF) UGBS for the Sg, C, and O atoms used in our DF (NR HF) calculations for $\text{Sg}(\text{CO})_6$ is of near DF (HF) accuracy. In the DF calculations, in particular, even the use of contracted basis sets mentioned above leads to billions of molecular integrals and storage and calculation of which requires huge amount of computer time and very large disk space. Therefore to reduce the number of integrals to be stored (and evaluated using pre-screening, etc.), we have used thresholds of 10^{-11} , 10^{-9} , and 10^{-5} for the [LL | LL], [LL | SS], and [SS | SS] integrals, respectively. The theoretical formalism⁹ and the technical details of our NR Hartree-Fock and relativistic Dirac-Fock calculations carried out with the MOLFDIR code²² have been presented in great details in our earlier publications^{10–16} and we refer the interested reader to these papers for further information. The DF and NR SCF calculations for the ground state of CO were similarly performed using the contracted basis sets for C and O mentioned above with the code²² at four different bond distances; the results were fitted to a polynomial obtaining, thereby, the optimized value of the DF(NR) and optimized DF(NR) bond distance for CO. The relativistic Dirac-Fock SCF calculations for $\text{Sg}(\text{CO})_6$ (O_h^*) were performed with the MOLFDIR code using the contracted DF UGBS for Sg, C, and O at the optimized bond distances Sg–C (2.138 Å) and C–O (1.11 Å) assuming octahedral geometry. The optimization of the bond distances Sg–C and C–O for $\text{Sg}(\text{CO})_6$ (O_h^*) was done manually. Both the DF and NR HF calculations were performed at four Sg–C distances, and the results were fitted to a polynomial obtaining thereby an optimum value (DF and NR) for Sg–C, $\text{Ropt}^{\text{DF}}(\text{Sg–C})$, and $\text{Ropt}^{\text{NR}}(\text{Sg–C})$. Four more calculations were performed for $\text{Sg}(\text{CO})_6$ at four C–O

distances (DF and NR) with the fixed value of Ropt^{DF} (Sg–C) or Ropt^{NR} (Sg–C) obtained earlier. These four results (for each DF and NR C–O distances) are fitted to a polynomial obtaining, thereby, Ropt^{DF} (C–O) and Ropt^{NR} (Sg–C), and the corresponding optimized total energy, respectively. Hence, *at least* eight DF and eight NR calculations are performed for the $\text{Sg}(\text{CO})_6$ molecule in order to optimize two bond distances. It should be pointed out that the manual optimization is not as accurate as the automatic optimization available in the relativistic molecular code DIRAC but it can yield results fairly close to those obtained by using the automatic optimization available in the DIRAC code.

III. RESULTS AND DISCUSSION

A. Dirac-Fock and NR Hartree-Fock prediction of the mean bond energy and atomization energy for $\text{Sg}(\text{CO})_6$

There are no calculations for the atomization energy as well as the mean bond energy for the superheavy $\text{Sg}(\text{CO})_6$. We report, here, the results of our relativistic DF and the NR HF calculations for the atomization and mean bond energies for $\text{Sg}(\text{CO})_6$. The total relativistic DF energy calculated for the ground state of $\text{Sg}(\text{CO})_6$ with the MOLFDIR code using the contracted UGBS for Sg, C, and O mentioned under Sec. II at the optimized DF octahedral bond distances of Sg–C (2.138 Å) and C–O (1.11 Å) is $-41\,402.0760$ au (1 au = 27.211 eV). The total NR HF energy calculated for the ground state of $\text{Sg}(\text{CO})_6$ with the MOLFDIR code using the contracted NR UGBS for Sg, C, and O mentioned under Sec. II at the optimized NR octahedral bond distances of Sg–C (2.28 Å) and C–O (1.139) is $-36\,598.6862$ au. The relativistic correction to the total electronic energy of $\text{Sg}(\text{CO})_6$ is calculated to be ~ -4800 au. The calculated optimized bond distances for the ground state of CO using our relativistic and nonrelativistic UGBS's for C and O described under Sec. II are 1.128 Å and 1.138 Å, with the corresponding total energies of -112.7822 and -112.6959 au, respectively. Our calculated relativistic DF and NR mean bond energies for the ground state configuration of $\text{Sg}(\text{CO})_6$ are 118.8 and 111.9 kJ/mol, respectively, and it is clear that relativistic effects are very marginal for the mean bond energy and atomization energy of $\text{Sg}(\text{CO})_6$. The relativistic DF and NR HF atomization energies (A_e^{DF} and A_e^{NR}) calculated for $\text{Sg}(\text{CO})_6$ in our calculations with the DIRAC code are 65.23 and 64.82 eV, respectively, and the calculated A_e^{DF} is larger only by 0.41 eV than the corresponding A_e^{NR} . It appears that the breakage of the Sg–CO bonds requires almost the same energy in both the DF relativistic and NR cases, as does the breakage of C–O bonds. It is reasonable to expect this behavior in the case of C–O bond as it involves very light atoms for which relativistic effects are negligible, but further investigation is necessary in the case of the Sg–CO bond.

B. Relativistic effects for the energy of the reaction $\text{Sg} + 6 \text{CO} \rightarrow \text{Sg}(\text{CO})_6$

No calculations have been reported so far either for the energy of the reaction $\text{Sg} + 6 \text{CO} \rightarrow \text{Sg}(\text{CO})_6$ or for the effects

TABLE I. Calculated total DF relativistic and NR energies E (in au), the predicted bond distance (R) in Å, and predicted atomization energy (A_e) in eV by using results obtained with the DIRAC code^a for $\text{Sg}(\text{CO})_6$ (O_h). The ΔE^X (in eV) is the energy for the reaction $\text{Sg} + 6 \text{CO} \rightarrow \text{Sg}(\text{CO})_6$, where $X = \text{NR}$ or DF. The $E_{\text{DF}}^{\text{mean}}$ and $E_{\text{NR}}^{\text{mean}}$ (in kJ/mol) are the relativistic DF and NR mean bond energies predicted by using results obtained with the DIRAC code^a for $\text{Sg}(\text{CO})_6$ (O_h).

$\text{Sg}(\text{CO})_6$	
E^{NR}	$-36\,599.1298^a$
E^{DF}	$-41\,402.5012$
A_e^{NR}	64.82
A_e^{DF}	65.23
$R_{\text{C-O}}^{\text{NR}}$	1.114
$R_{\text{C-O}}^{\text{DF}}$	1.119
$R_{\text{Sg-C}}^{\text{NR}}$	2.318
$R_{\text{Sg-C}}^{\text{DF}}$	2.151
ΔE^{NR}	-6.96
ΔE^{DF}	-7.39
$E_{\text{NR}}^{\text{mean}}$	111.9
$E_{\text{DF}}^{\text{mean}}$	118.8

^aAll the quantities (with values given under second column) were calculated with the DIRAC code (Ref. 19) using the dyall. v2z basis for Sg and the aug-cc-pvDZ basis set for both C and O as described in the text.

of relativity on this reaction involving an atom of SHE Sg. Our all-electron fully relativistic DF and NR HF calculations predict the DF relativistic and NR energies for the reaction: $\text{Sg} + 6 \text{CO} \rightarrow \text{Sg}(\text{CO})_6$ as -7.39 and -6.96 eV, respectively, i.e., our calculated ground state total DF relativistic and NR energies for the reaction product $\text{Sg}(\text{CO})_6$ are *lower* by 7.39 and 6.96 eV than the total DF and NR ground state energies of the reactants, viz., one Sg atom plus six CO molecules, respectively. The results of our relativistic DF and the corresponding NR calculations for the optimized bond lengths, mean bond energy, atomization energy (for $\text{Sg}(\text{CO})_6$), and energy for the reaction: $\text{Sg} + 6 \text{CO} \rightarrow \text{Sg}(\text{CO})_6$, etc., are collected in Table I.

IV. RELATIVISTIC ELECTRONIC STRUCTURE, BONDING, AND MOLECULAR SPINOR ENERGY LEVELS OF $\text{Sg}(\text{CO})_6$

As a prelude to the electronic structure and bonding for $\text{Sg}(\text{CO})_6$, we shall very briefly mention, here, the methods used for electronic structure and bonding for the TM hexacarbonyls because of their possible relevance to bonding, etc., in the hexacarbonyl of the SHE Sg (with ...6d4 configuration) which is the higher congener of the TM W (with... 5d4 configuration). This topic has been discussed very extensively in numerous publications^{25–38} which should be consulted for further details. However, I should warn that although for W ($Z = 74$), the valence 6s level (-0.2667) lies above the 5d+ (-0.3239) and 5d– (-0.3480) levels; however, due to very pronounced relativistic effects for Sg (with $Z = 106$), the order of valence levels is reversed as 6d+ (-0.2570), 6d– (-0.2972), and 7s (-0.3188), where the spinor energy (in au) of each level is given in parenthesis. This reversal of nd and $(n + 1)s$ levels for Sg (vs. W) may reflect in the difference and resemblance if any of the chemistry of Sg and W.

It is well-known that bonding in TM hexacarbonyls can be understood via ligand field theory²⁶ (LFT), which can be

looked upon as a simplified MO theory that takes into account mainly the valence d orbitals of the TM and the frontier orbitals of the ligands. A theoretical MO model originally introduced by Dewar³⁹ and by Chatt and Duncanson⁴⁰ (DCD) has also been exploited in order to investigate the TM compounds. We shall not discuss the details of the methods used in this vast area of research but refer the interested reader to the critical reviews by Davidson *et al.*^{31,32} and Frenking.³⁶ The TM–ligand (L) interactions are considered in terms of $L \rightarrow TM$ donation and $TM \rightarrow L$ back donation. The synergistic bonding model is extended to metal–ligand bonds where the high-lying occupied orbitals of the ligand are considered as donor orbitals. The back donation, then, occurs between occupied orbitals of the metal (usually of π symmetry) with the low lying empty π^* orbitals of the ligand.^{32–36} During the last decade, there has been much progress in quantum mechanical (QM) methods for high accuracy calculations^{41–44} on TM compounds and other heavy atom molecules. This has mostly become possible because of the application of the gradient-corrected DFT, ECP, MP2, coupled-cluster singles doubles (CCSD), etc., methods³⁶ which seem to give accurate geometries, energies, and other important properties of TM molecules.

The relativistic ground state closed-shell electron configuration for the 190-electron $Sg(CO)_6$ under the octahedral double symmetry group (O_h^*) is written here for the first time: $(1e_{1g})^2 \dots (12e_{1g})^2 \dots (1e_{1u})^2 \dots (13e_{1u})^2 \dots (1e_{2g})^2 \dots (5e_{2g})^2 \dots (1e_{2u})^2 \dots (5e_{2u})^2 \dots (1f_g)^4 \dots (14f_g)^4 \dots (1f_u)^4 \dots (16f_u)^4$, where we have designated as, in our earlier work,^{12–14} the four *two-dimensional* extra irreducible representations (EIRs) as e_{1g} , e_{1u} , e_{2g} , e_{2u} and the two *four-dimensional* EIR as f_g and f_u of the double octahedral group (O_h^*). There are for $Sg(CO)_6$ (O_h^*), $12e_{1g}$, $13e_{1u}$, $5e_{2g}$, $5e_{2u}$, $14f_g$, and $16f_u$ occupied molecular spinors (MS's) in the ground state. It should be pointed out that the s, p, d, and f orbitals of the central atom (Sg) in an octahedral molecule ($Sg(CO)_6$) transform as follows: $s \leftrightarrow a_{1g}$, $p \leftrightarrow t_{1u}$, $d \leftrightarrow e_g + t_{2g}$, $f \leftrightarrow (a_{2u} + t_{1u} + t_{2u})$, whereas the ns and np atomic orbitals (AOs) of the six ligands (C and O) transform as $(a_{1g} + e_g + t_{1u})$ and $(a_{1g} + e_g + t_{1g} + t_{2g} + 2t_{1u} + t_{2u})$, respectively. Therefore, considering only the energy of the valence orbitals of Sg, C, and O, it is the a_{1g} and $e_g + t_{2g}$ combination of the six valence 2s and 2p AOs of both the C and O atoms which may combine (depending upon the energy of the a_{1g} , e_g , t_{2g} combination arising from the 2s and 2p relativistic atomic orbitals (RAO's) of the six C and six O ligands) with the corresponding octahedrally transformed s (a_{1g}) and d ($e_g + t_{2g}$) valence orbitals of the central Sg atom to yield molecular orbitals of $Sg(CO)_6$. Therefore, we can expect mixing of the valence AO's of Sg with the linear combination of the valence 2s and 2p (and 3d carbon) AO's of the six C and O ligands. There are 66 electrons in valence and 124 electrons in core out of a total of 190 electrons of $Sg(CO)_6$. The calculated spinor energies of the inner MS's or relativistic MO's (RMOs) $1e_{1g}$, $2e_{1g}$, $1e_{1u}$, $1f_u$, and $3e_{1g}$ of $Sg(CO)_6$ are significantly lower in energy than the corresponding MO's as expected due to very pronounced relativistic effects for the inner orbitals of the Sg atom as these MS's consist of almost pure inner (core) four component atomic spinors (AS's) or RAOs. The lowering in orbital energy for the inner $1a_{1g}$, $2a_{1g}$, and $3a_{1g}$ MOs (which

arise from the 1s, 2s, and 3s AOs of Sg, respectively) is ~ 1121 , 319, and 84 au, whereas the energy lowering for the $1e_{1u}$ spinor of $Sg(CO)_6$ arising from the $2p_{1/2}$ atomic spinor of Sg is ~ 306 au. Moreover, our calculated spin-orbit splitting of the 2p energy level of Sg is ~ 293 au, and this is reflected in the spinor energy of the two molecular spinors of $Sg(CO)_6$ arising from the $2p_{1/2}$ and $2p_{3/2}$ atomic spinors of Sg. It should be pointed out that the increased stability (lowering of energy) of the inner MOs is due to the fact that all $s_{1/2}$ and $p_{1/2}$ AOs are stabilized due to the *direct* relativistic effects, and the stability is greater for the AOs closer to the nucleus, i.e., inner (core) orbitals of the superheavy Sg atom. The d and f orbitals (and to a lesser extent $p_{3/2}$ orbitals), however, are *destabilized* due to the *indirect* relativistic effects, viz., contraction of inner orbitals due to *direct* relativistic effects leads to a better screening of electrons in outer orbitals resulting, thereby, in *destabilization* and an increase of their orbital energies, e.g., the nd and nf AOs of Sg are *destabilized* and this is reflected also in the energies of the MS's arising from the nd and nf atomic spinors of Sg. Relativistic effects, however, lead to a decrease of 0.14 Å for the predicted bond length of Sg–C while these effects are very marginal for the C–O bond length in $Sg(CO)_6$ as expected.

The highest occupied relativistic molecular orbital (HORMO) or molecular spinor (HOMS) $5e_{2g}$ lies at -0.3111 au (-8.45 eV) in our $Sg(CO)_6$ (O_h^*) calculations performed with MOLFDIR code and arises from the combination of the $Sg6d$ (0.67), $O2p$ (0.20), and $C2p$ (0.12) atomic spinors with the coefficients of atomic spinors given in parenthesis. The HOMO ($45e_{1g}$) in our NR calculations (with the DIRAC code) for $Sg(CO)_6$ lies at -0.2939 au and consists of $0.74 Sg(6d) + 0.11 C(2p) + 0.07 C(3d) + 0.07 O(2p)$, where the coefficient of each atomic orbital is given in front of the AO. Since the d orbitals are destabilized due to relativistic effects, the spinor energy of (HOMS) ($45e_{1g}$) is slightly higher than that of the NR HOMO ($45e_{1g}$). Almost all our calculated MS levels for $Sg(CO)_6$ using the MOLFDIR and DIRAC codes are fairly close in energy except for a few levels like the case cited above for HOMS, and it shows that both the codes can be used for relativistic and NR calculations for molecules even of superheavy elements. DIRAC, however, is the nearest to state of the art code that has been developed and is being improved continually by an international team of dedicated quantum scientists and is used by most researchers at present. Therefore, we will, hereafter, discuss only our results obtained for $Sg(CO)_6$ (D_{2h}^*) with the DIRAC code. It should be mentioned, however, that calculations with the DIRAC code are performed under the D_{2h}^* double group symmetry, and in the ground state configuration of $Sg(CO)_6$, there are 45 MS's of e_{1g} and 50 MS of e_{1u} (*two-dimensional* additional or EIRs, respectively).

A. Relativistic electronic structure, bonding, and molecular spinor energy levels of e_{1g} symmetry of $Sg(CO)_6$

Since bonding is expected mostly due to valence molecular spinors, we shall discuss our calculated molecular spinor (orbital) energy levels first of the 45 e_{1g} MS's starting

with the HORMO or HOMS of e_{1g} symmetry of $\text{Sg}(\text{CO})_6$ to the lowest energy molecular spinor (orbital) levels of the e_{1g} symmetry.

The HOMS ($45e_{1g}$) is antibonding with respect to the symmetry combinations of the 2s and 2p RAO's of the C and O ligands but bonding with respect to the Sg 6d (RAO) and in our $\text{Sg}(\text{CO})_6$ (D_{2h}^*) calculations (with the DIRAC code) lies at -0.2846 au and consists of the Sg 6d (0.55), C 2p (0.20), O 2p (0.15), and C 3d (0.10) atomic spinors and can be regarded overall as very slightly bonding. The small contribution of the C 3d to the HOMS ($45e_{1g}$) for calculations carried out with DIRAC code stems from the fact that the C and O basis used with DIRAC include the d basis. The lowest unoccupied relativistic molecular orbital (LURMO) or molecular spinor (LUMS) lies at 0.0439 au, and the HORMO-LURMO (HOMS-LUMS) gap is calculated as 0.3285 au or 8.94 eV. The doubly degenerate MS ($44e_{1g} - 43e_{1g}$) is also very slightly bonding and lies at -0.3054 au and consists of the orbitals with coefficients very similar to those of the HOMS. The triply degenerate MS ($42e_{1g} - 40e_{1g}$) lies at -0.6507 au and consists of 0.78 O(2p) and 0.21 C(2p) and is the $2p\pi$ bonding combination of $2p\pi$ RAO's of C and O. The MS ($39e_{1g} - 37e_{1g}$) is triply degenerate with a spinor energy of -0.6668 au and consists of 0.32 O(2p), 0.30 C(2p), 0.23 C(2s), 0.07 O(2s), and 0.08 Sg(6d). This is a bonding spinor as the symmetry orbitals ($e_g + t_{2g}$) arising from combination of six C 2s, six C 2p (with orbital energy of 0.71 and 0.40 au, respectively), and six O 2p (with orbital energy of ~ 0.62 au) may combine with the symmetry orbitals ($e_g + t_{2g}$) arising from the Sg 6d (with orbital energy of ~ 0.28 au) so as to yield molecular spinors ($39e_{1g} - 37e_{1g}$) of $\text{Sg}(\text{CO})_6$. The doubly degenerate ($36e_{1g} - 35e_{1g}$) bonding MS with spinor energy of -0.6700 au consists of 0.50 O(2p) and 0.31 of C(2p) plus 0.08 C(2s) and minor amount (0.03) of the Sg(6d) and C(3d). The next $34e_{1g}$ MS with spinor energy of -0.7410 au is a bonding nondegenerate MS which consists of 0.38 O(2p), 0.30 C(2p), 0.13 O(2s), 0.10 C(2s), and 0.07 Sg(7s). The Sg(7s) which transforms as a_{1g} in O_h with a spinor energy of ~ 0.32 au can mix with the a_{1g} symmetry orbital arising from the combination of six C(2p) RAO's each with an energy of ~ 0.40 au. It would be more difficult for it to combine, however, with the corresponding a_{1g} symmetry spinor arising from the combination of six O(2p) RAO's each with an energy of ~ 0.62 au. The doubly degenerate bonding MS ($33e_{1g} - 32e_{1g}$) with a spinor energy of -0.8189 au consists of 0.45 O(2p), 0.30 C(2p), and 0.25 O(2s) AS's. The next MS $31e_{1g}$ is a bonding spinor of energy -0.8564 au and comprises of 0.63 C(2s), 0.18 O(2p), 0.15 C(2p), and 0.14 O(2s) AS's. The triply degenerate bonding MS ($30e_{1g} - 28e_{1g}$) with energy of -1.5425 au arises from the combination 0.75 O(2s), 0.22 C(2s), and 0.03 O(2p). The next MS is nonbonding and consists of the pure Sg(6s) with an energy of -3.8689 au which is identical with the energy of the AS Sg(6s). The triply degenerate ($30e_{1g} - 28e_{1g}$) MS and the lower lying molecular spinors consist of pure atomic spinors lying below the Sg(6s) and the spinors arising from the combination of six C(1s) and six O(1s) atomic spinors. The triply degenerate spinor ($21e_{1g} - 19e_{1g}$), for example, arising from a combination of the six C(1s) RAO's lies at -11.4006

au, which is identical with the energy of the atomic spinor C(1s). Similarly, the triply degenerate ($18e_{1g} - 16e_{1g}$) MS with spinor energy of -20.6954 au, arises from combination of six O(1s) atomic spinors, and all these pure "atomic spinors" lead to nonbonding molecular spinors. This trend continues all the way to the lowest energy Sg(1s) AS which yields a nonbonding MS of energy of -6104.4441 au. I should point out, however, that the innermost AS's of Sg like 1s, 2s, and 3s have contributions from small components of ~ 0.18 , 0.04 , and 0.02 , respectively. This has not been pointed out before for DF relativistic calculations for any system of SHE.

B. Relativistic electronic structure, bonding, and molecular spinor energy levels of e_{1u} symmetry of $\text{Sg}(\text{CO})_6$

A bonding analysis similar to that given above for the e_{1g} symmetry can be carried out for the 50 molecular spinors of the e_{1u} symmetry for $\text{Sg}(\text{CO})_6$. We shall not go into details but point out, here, the salient features of bonding for the e_{1u} symmetry. The lowest MS $1e_{1u}$ of the e_{1u} symmetry arises from the $2p_{1/2}$ AS of Sg, and the MS arising from this AS lies at -1178.4400 au and is a pure atomic spinor and is nonbonding. The nonbonding $2e_{1u}, \dots, 9e_{1u}$ MS's arise from the $2p_{3/2}, 3p_{1/2}, 3p_{3/2}, 4p_{1/2},$ and $4p_{3/2}$ AS's of Sg with spinor energies of $-885.2741, -306, -236.1793, -83.0590,$ and -63.2174 au, respectively. It should be mentioned that the MS's $2e_{1u}$ and $3e_{1u}$ arising from $2p_{3/2}$ are degenerate as are also the MS's arising from $3p_{3/2}$ and $4p_{3/2}$ AS's of Sg. The next MS ($10e_{1u} - 12e_{1u}$) with energy of -29.9922 au is triply degenerate and nonbonding and consists of $4f_{5/2}$ AS of Sg. The next set of quadruple degenerate ($13e_{1u} - 16e_{1u}$) nonbonding MS's with spinor energy of -29.0283 au consists of pure $4f_{7/2}$ AS of Sg. The next triply degenerate nonbonding ($17e_{1u} - 19e_{1u}$) MS with energy of -20.6954 au arise from combination of O(1s) AS of the six O ligands. The next MS $20e_{1u}$ is nonbonding with energy of -19.2530 au and is the pure $5p_{1/2}$ AS of Sg. The doubly degenerate ($21e_{1u} - 22e_{1u}$) nonbonding MS with energy of -13.9016 arises from the $5p_{3/2}$ AS of Sg. The triply degenerate nonbonding MS ($23e_{1u} - 25e_{1u}$) with spinor energy of -11.4001 au arises from a combination of C(1s) AS's of the six C ligands. The next nonbonding MS $26e_{1u}$ with energy of -2.6132 au consists of pure $6p_{1/2}$ AS of Sg and below it lies the doubly degenerate ($27e_{1u} - 28e_{1u}$) nonbonding MS with energy of -1.6254 au and consists of 0.95 $6p_{3/2}$ AS of Sg and 0.03 2s AS of C. The triply degenerate nonbonding ($29e_{1u} - 31e_{1u}$) MS lies at -1.5714 au and comprises of the $5f_{5/2}$ AS of Sg, while the triply degenerate ($32e_{1u} - 34e_{1u}$) MS with energy of -1.5420 au consists of 0.66 O(2s), 0.20 C(2s), 0.05 C(2p), and 0.04 O(2p) AS and is definitely a bonding spinor. The quadruply degenerate ($35e_{1u} - 38e_{1u}$) MS with energy of -1.4274 au consists of the $5f_{7/2}$ AS of Sg and is nonbonding. Thus, out of the 38 MS's ($1e_{1u} - 38e_{1u}$) of e_{1u} symmetry of $\text{Sg}(\text{CO})_6$, all except the triply degenerate MS ($32e_{1u} - 34e_{1u}$) with energy of -1.5420 au are nonbonding pure AS's of the Sg, C, and O atoms. The 3-fold degenerate MS ($39e_{1u} - 41e_{1u}$) with spinor energy of -0.8191 au is a bonding MS and consists of 0.50

O(2p), 0.28 O(2s), and 0.22 C(2s) AS's. Most of the valence AS's of the Sg, O, and C atoms lie in the energy range of ~ -1.25 to -0.25 au and one would expect the mixing of valence AS's to yield the various molecular spinors and hopefully some of which may be bonding. The $42e_{1u}$ MS with energy of -0.6737 au consisting of 0.45 O(p), 0.30 C(p), 0.18 Sg(p), and 0.04 Sg(f) AS's is a bonding MS. The doubly degenerate bonding MS ($43e_{1u} - 44e_{1u}$) lies at -0.6597 au and consists of 0.71 O(p), 0.24 C(p), and 0.05 Sg(6p) atomic spinors. The triply degenerate bonding MS ($45e_{1u} - 47e_{1u}$) with energy of -0.6551 au consists of 0.75 O(p) and 0.24 C(p) atomic spinors, while the bonding $48e_{1u}$ MS is composed of 0.39 O(p), 0.29 C(p), 0.15 C(s), 0.10 Sg(6p), and 0.04 O(s) atomic spinors. The doubly degenerate ($49e_{1u} - 50e_{1u}$) MS contains 0.34 C(2p), 0.26 C(2s), 0.16 Sg(6p), 0.10 O(2p), 0.05 O(2s), and 0.02 Sg($5f_{7/2}$) atomic spinors with energy of -0.6310 au and is slightly bonding. This completes the bonding analysis of 45 MS's of e_{1g} symmetry and 50 MS's of e_{1u} symmetry of Sg(CO)₆.

C. Nonrelativistic electronic structure, bonding, and molecular orbital energy levels of the e_{1g} and e_{1u} symmetries of Sg(CO)₆

The bonding and molecular orbital energy level structure calculated in our NR HF calculations are quite similar to that discussed in Sec. III for DF relativistic calculations for Sg(CO)₆ (both the e_{1g} and e_{1u} symmetries). In our discussion in this section, we shall also use the double group symmetry notation although single group is appropriate for NR HF calculations. The NR molecular orbitals (MO) $1e_{1g}$ to $14e_{1g}$ (taking into account the degeneracy of each level, if any) are almost like the 1s, 2s, 3s, 3d, 4s, and 4d AOs of Sg with energies of -4982.4255 , -896.8386 , -239.8737 , -202.7867 , -66.8258 , and -48.5510 au, respectively. The ($15e_{1g} - 17e_{1g}$) MO with energy of -20.6789 au is nonbonding 3-fold degenerate and it arises from the combination of the six O(1s) AO's. The next MO $18e_{1g}$ with energy of -16.0484 au is also nonbonding and is alike 5s AO of Sg. The 3-fold degenerate ($19e_{1g} - 21e_{1g}$) nonbonding MO with energy of -11.3827 au arises from the combination of six C(1s) AO's. The next is the five-fold degenerate ($22e_{1g} - 26e_{1g}$) nonbonding MO which is the 4d AO of Sg with energy of -8.2823 au. The $27e_{1g}$ MO with energy of -2.4392 au is nonbonding and is the 6s AO of Sg. The next MO's ($28e_{1g} - 45e_{1g}$), however, unlike being the pure AO's of Sg or the combination of six O(ns), O(np), C(ns), and C(2p) AO's, are linear combinations of the AO's of the C, O, and Sg atoms. These are the MO's (in addition to similar MOs of the e_{1u} symmetry) which are involved in the so-called NR bonding (and antibonding) of Sg(CO)₆. The next MO 3-fold degenerate ($28e_{1g} - 30e_{1g}$) with energy of -1.5431 au is bonding and consists of 0.75 O(2s), 0.17 C(2s), and 0.07 O(2p). It should be borne in mind that hereafter, whenever for a MO (in LCAO form), the AO's C(ns), C(np), O(ns), and O(np) are mentioned, one actually uses the MO's of the proper symmetry by combining various AO's of the six C and O ligands using group theory. The next MO ($31e_{1g} - 33e_{1g}$) with an energy of -0.8201 au is bonding 3-fold degenerate and consists of 0.50 O(2p), 0.24 C(2s), and 0.26 O(2s) AO's.

The next MO ($34e_{1g} - 36e_{1g}$) is bonding, triply degenerate with energy of -0.6618 au, and comprises of 0.72 O(2p) and 0.26 C(2p) AO's. The MO $37e_{1g}$ is bonding with energy of -0.6558 au and consists of 0.44 C(2p), 0.47 C(2s), and 0.07 O(2p) AS's, while the MO ($38e_{1g} - 40e_{1g}$) is bonding, triply degenerate with energy of -0.6618 au and comprises of 0.72 O(2p) and 0.26 C(2p) AO's. The MO ($41e_{1g} - 42e_{1g}$) is bonding, doubly degenerate with energy of -0.6317 au and consists of 0.40 C(2s), 0.36 C(2p), 0.10 O(2p), and 0.08 Sg(6d) AS's. It is, here, that we notice the presence of Sg(6d) AO for the first time in MOs of e_{1g} symmetry (although with a very small coefficient). The last 3-fold degenerate MO ($43e_{1g} - 45e_{1g}$) (in the e_{1g} symmetry) is antibonding, triply degenerate with an energy of -0.2939 au, and consists of 0.74 Sg(6d), 0.11 C(2p), 0.07 O(2p), and 0.07 C(3d).

The NR bonding analysis of the MO's of the e_{1u} symmetry of Sg(CO)₆ can be carried out similarly and the MO's ($1e_{1u} - 3e_{1u}$), ($4e_{1u} - 6e_{1u}$), ($7e_{1u} - 9e_{1u}$) all triply degenerate and the 7-fold degenerate ($10e_{1u} - 16e_{1u}$) MO are all nonbonding and consist of the 2p, 3p, 4p, and 4f AO's of Sg, respectively. The triply degenerate nonbonding MO ($17e_{1u} - 19e_{1u}$) with an energy of -20.6789 au arises from the combination of the 1s AO's of the six O ligands. The next triply degenerate nonbonding MO ($20e_{1u} - 22e_{1u}$) with an energy of -13.2781 au consists of the 5p AO of Sg, while the nonbonding triply degenerate MO ($23e_{1u} - 25e_{1u}$) with an energy of -11.3827 au consists of the combination of 1s AO's of the six C ligands. The next MO ($26e_{1u} - 32e_{1u}$) with an energy of -2.0028 au is nonbonding 7-fold degenerate and comprises of the 5f AO of Sg. The two triply degenerate MO's ($33e_{1u} - 35e_{1u}$) and ($36e_{1u} - 38e_{1u}$) with energies of -1.5481 and -1.5366 au consist of the 0.54 Sg(6p), 0.34 O(2s), 0.06 C(2s), 0.03 O(2p), and 0.03 C(2p) AO's, respectively. These two MO's have major contributions from the Sg(6p) and O(2s) AO's but only a minor contribution from the C(2s) and C(2p) AO's and are weakly bonding. The next MO ($39e_{1u} - 41e_{1u}$) with energy of -0.8120 au is triply degenerate and bonding and consists of 0.52 O(2p), 0.27 O(2s), and 0.20 C(2s) AO's. The next two 3-fold degenerate bonding MO's ($42e_{1u} - 44e_{1u}$) and ($45e_{1u} - 47e_{1u}$) with energies -0.6564 and -0.6541 au consist of 0.76 O(2p) and 0.23 C(2p) AO's, respectively. It should be pointed out that combination of O(2p) and C(2p) AO's of the six O and six C ligands results in two t_{1u} MO's, and the two MO's ($42e_{1u} - 44e_{1u}$) and ($45e_{1u} - 47e_{1u}$) arise from a combination of these two t_{1u} MO's. Finally, the triply degenerate MO ($45e_{1u} - 47e_{1u}$) with energy -0.5764 au consists of 0.35 C(2p), 0.34 C(2s), 0.12 Sg(6p), 0.09 O(2p), 0.04 O(2s), and 0.03 Sg(5f) AO's and is bonding though weakly. This is the HOMO of the e_{1u} symmetry and has contribution (although small) from the much lower energy 6p (energy -1.6475 au) and 5f (energy -2.1400 au) AO's of Sg. The resulting MO as a combination of these AO's is a MO of much higher energy of -0.5764 au. Although the combination of the 2p AO (with energy of -0.4066 au) of the six C ligands yields bonding MO's, the combination of the 2s AO (with energy of -0.7126 au) of the six C ligands as well as the combinations of the 2s and 2p AO's of the six O ligands (with energy of -1.2524 and 0.6168 au)

leads to antibonding MO's, as does the MO resulting from the 6p and 5f AO's of Sg. Thus, I have discussed in great detail the bonding and molecular energy levels calculated in our all electron *ab initio* DF and NR HF calculations for $\text{Sg}(\text{CO})_6$.

V. CONCLUSION

We have performed the first *ab initio* all-electron fully relativistic Dirac-Fock and NR HF SCF calculations for the ground state of the octahedral $\text{Sg}(\text{CO})_6$. A summary of our major conclusions is as follows.

- (1) Our relativistic DF SCF and NR HF wavefunctions predict the octahedral $\text{Sg}(\text{CO})_6$ to be *bound*, with the calculated atomization energies of 65.23 and 64.82 eV, respectively, at the optimized Sg-C and C-O bond distances given in Table I. Relativistic effects are not significant in binding and lead to only 0.41 eV increment in the predicted atomization energy for $\text{Sg}(\text{CO})_6$.
- (2) Our *ab initio* all-electron fully relativistic DF and NR Hartree-Fock calculations *predict* the DF relativistic and NR HF energies for the formation of $\text{Sg}(\text{CO})_6$ via the reaction: $\text{Sg} + 6 \text{CO} \rightarrow \text{Sg}(\text{CO})_6$ as -7.39 and -6.96 eV, respectively. It appears that relativistic effects are not significant for the reaction energy for formation of $\text{Sg}(\text{CO})_6$. However, both our relativistic DF and the NR treatments clearly predict for the *first time* the existence of the hexacarbonyl of the superheavy element Sg.
- (3) Our predicted relativistic DF and NR HF mean bond energies for $\text{Sg}(\text{CO})_6$ are 118.8 and 111.9 kJ/mol, respectively, and it is clear that relativistic effects are not significant at all for the calculation of the mean bond energy.
- (4) There are very large relativistic corrections to the binding energies of the MOs, especially, the inner core orbitals of $\text{Sg}(\text{CO})_6$. In addition, very large S-O splitting is calculated for the core MOs that consist of the inner (core) p, d, and f AOs of Sg, as expected.
- (5) The 1s...6s RAOs of the Sg atom as well as the 1s RAOs of the six O and C ligands, and their associated electrons are not involved in bonding in $\text{Sg}(\text{CO})_6$, since they remain as if in pure RAOs or core. Therefore, these core electrons could be treated in molecular calculations on compounds of the SHE Sg, using appropriate frozen core or pseudopotential approximations with tremendous savings in computational cost.
- (6) The valence 6d RAOs are not only major constituents of a few valence molecular spinors but also make minor (<10%) contributions to some of the MS. The 7s RAO of Sg, although, is a minor contributor but leads to the bonding $31e_{1g}$ MS. Minor contributions of the nonvalence 6p and 5f RAO's of Sg have been noted in a few MS's.
- (7) The relativistic and nonrelativistic optimized Sg-C bond distances are 2.151 and 2.318 Å, however, the corresponding optimized C-O distances are almost identical as expected since CO consists of light atoms C and O, and relativistic effects are negligible for such light systems.

In conclusion, *ab initio fully relativistic all-electron* Dirac-Fock SCF calculations for molecular systems of super-

heavy elements are no longer the *bottlenecks* of relativistic quantum chemistry.

ACKNOWLEDGMENTS

This research used in part resources of the National Energy Research Scientific Computing Center (NERSC), which is supported by the Office of Science of the U.S. Department of Energy (DOE) under Contract No. DE-AC03-76SF00098. I am most grateful to Professor Walter D. Loveland for making available to me the state of the art supercomputing facility at NERSC through his Research grant from the Division of Nuclear Physics of DOE of the U.S. This supercomputing facility was *sine quo non* for my massive computations reported herein.

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