Relativistic and magnetic Breit effects for the isomerization of Sg(CO)₆ = Sg(OC)₆:
Prediction of the existence and atomization energies of the isomers Sg(CO)₆ and Sg(OC)₆

Gulzari L. Malli
Department of Chemistry
Simon Fraser University
Burnaby BC: Canada V5A 1S6

Walter Loveland
Department of Chemistry
Oregon State University
Corvallis, OR 97331 USA

a email: malli@sfu.ca
b email: lovelanw@onid.orst.edu
Abstract  Our *ab initio* all-electron relativistic Dirac–Fock (DF) calculations for seaborgium hexacarbonyl Sg(CO)\(_6\) and seaborgium hexaisocarbonyl Sg(OC)\(_6\) predict atomization energies (Ae) of 68.80 and 64.30 eV. Our Dirac-Fock-Breit-Gaunt (DFBG) calculations for Sg(CO)\(_6\) and Sg(OC)\(_6\) yield atomization energies (Ae) of 69.18 and 64.77 eV. However, our calculated non-relativistic (NR) Ae for Sg(CO)\(_6\) and Sg(OC)\(_6\) are 68.46 and 62.62 eV. The calculated isomerization energies (E\(_{\text{iso}}\)) at the DFBG, DF, and NR levels are 4.41, 4.50, and 5.83 eV. The contribution of relativity to the E\(_{\text{iso}}\) is ~1.33 eV. The optimized bond distances Sg-C and C-O for octahedral Sg(CO)\(_6\) using our DF (NR) calculations are 2.151 (2.318 Å) and 1.119 (1.114 Å). The optimized six Sg-O and C-O bond distances for octahedral Sg(OC)\(_6\) at the DF level are equal to 4.897 and 1.108 Å. However, the optimized four Sg-O bond distances for the octahedral Sg(OC)\(_6\) at the NR level are 5.160 Å each, and two Sg-O bonds of 2.721 Å each, but all six C-O bonds are 1.108 Å each. The energies at the DF level of theory (ΔE\(_{\text{DF}}\)) for the reaction Sg+6CO to yield Sg(CO)\(_6\) and Sg(OC)\(_6\) are calculated as -7.30 and -2.80 eV. Moreover, the energies of the reaction at the DFBG level (ΔE\(_{\text{DFBG}}\)) to yield Sg(CO)\(_6\) and Sg(OC)\(_6\) are very close to those predicted at the DF level of theory of -7.17 and -2.76 eV. However, the NR energies of the above-mentioned reaction (ΔE\(_{\text{NR}}\)) are -6.99 and -1.15 eV. The mean bond energies predicted for Sg(CO)\(_6\) with our DF, DFBG, and NR calculations are 117.40, 115.31, and 112.41 kJ/mol, whereas the mean bond energies calculated for the isomer Sg(OC)\(_6\) at DF, DFBG and NR levels are 45.03, 44.39, and 18.49 kJ/mol. The predicted existence of both the isomers with E\(_{\text{iso}}\) of ~4.50 and ~5.80 eV, may cause problems for experimental identification of seaborgium hexacarbonyl.
I. Introduction

There has been enormous activity in the experimental investigation of the superheavy elements (SHE) and it is well-recognized that because of the very large Z of the SHE, the relativistic effects would be significant for the description of the electronic structure and bonding of systems containing transactinide superheavy elements (SHE). Seaborgium compounds are eminently suitable for testing the theoretical and computational methodology for investigating the effects of relativity on the electronic structure and bonding of compounds of SHE. In this paper, we report ab initio all-electron relativistic Dirac–Fock (DF), Dirac-Fock-Breit-Gaunt (DFBG) and the corresponding nonrelativistic (NR) Hartree–Fock (HF) calculations for the mean bond energy and atomization energies of octahedral (O_h) Sg(OC)_6. Moreover, we report at the DF, DFBG and NR levels of theory the heat of reactions for Sg+6CO \rightarrow Sg(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 and especially our recent paper on Sg(CO)_6.

2. Theoretical Remarks

We present here only a brief outline of the Dirac-Fock treatment for molecules and refer the reader to earlier accounts for details. The approximate relativistic Dirac-Fock-Coulomb Hamiltonian (H_DC) for an N-electron molecular system containing n nuclei, under the Born-Oppenheimer approximation (omitting the nuclear repulsion terms which are constant for a given molecular configuration) can be written (in atomic units):

$$H_{DC} = \sum_{i=1}^{N} H_D(i) + \sum_{i<j}^{N} \frac{1}{r_{ij}}$$

In eq. (1), the $H_D(i)$ consists of the Dirac's kinetic energy operator, mass energy and nuclear attraction of the i-th electron and has the well-known expression, viz.;

$$H_D(i) = c\alpha_i \cdot p_i + (\beta_i - 1)c^2 + V_{\text{nuc}}$$
The rest mass energy of an electron has been subtracted in eq. (2), to get its binding energy, and the potential $V_{\text{nuc}}$ due to n \textit{finite nuclei} of the molecular system is taken to be the sum of their nuclear potentials viz.: $V_{\text{nuc}} = \sum_n V_n$, and for molecular systems involving heavy atoms (with $Z > 70$), a finite nuclear model is invariably used. We shall use the Gaussian nuclear model \textsuperscript{20} in which a single Gaussian function is used for each nuclear charge distribution. The instantaneous Coulomb repulsion between the electrons is treated \textit{nonrelativistically} in the Dirac-Coulomb Hamiltonian and the magnetic and retardation corrections to it are generally included perturbationaly.

The N-electron wavefunction $\Phi$ for the closed-shell molecular system is taken as a single Slater determinant (SD), also called an antisymmetrized product (AP) of one-electron 4-component molecular spinors (MS) \textsuperscript{7} viz.:

$$\Phi = (N!)^{1/2} | \phi_1(1) \phi_2(2) \phi_3(3) \ldots \phi_N(N) |. \quad (4)$$

The molecular spinors (MS) $\phi_i$ are generally taken to form an orthonormal set and can be constructed to transform like the extra or \textit{additional irreducible representations} (EIR) of the double symmetry group of the molecule under investigation.

The energy expectation value $E$ can then be written as:

$$E = \langle \Phi | H | \Phi \rangle / \langle \Phi | \Phi \rangle \quad (5)$$

The molecular spinors $\phi_i$ are expressed in terms of the large and small components

$$\phi_i^X = \sum_{q=1}^{n} C_{iq}^X \chi_q^X, \quad X = L \text{ or } S. \quad (6)$$

The $\chi_q^L$ and $\phi_i$ can be symmetry adapted; however, we shall ignore the double group symmetry labels. for the molecular spinors. The basis spinors $\chi_q^X$ will be constrained to obey the kinetic balance relation, viz.,

$$\chi_q^S = (\sigma \cdot p) \chi_q^L. \quad (7)$$

Then following Malli and Oreg \textsuperscript{8}, the Dirac-Hartree-Fock- Roothaan (DHFR) or relativistic Hartree-Fock-Roothaan (RHFR) SCF equations for closed-shell molecules can be written as:

$$Fc_i = \varepsilon_i sc_i. \quad (8)$$
where in eq. (8), F is the Dirac-Fock matrix operator, the $e_i$ is the orbital energy of the molecular spinor (MS) $\phi_i$ and S is the overlap matrix.

### 3. Dirac–Fock and Hartree-Fock calculations for Sg(CO)$_6$ and Sg(OC)$_6$

All of our DF and NR calculations for Sg (CO)$_6$ and Sg(OC)$_6$ are performed with the Dirac code$^{17}$ using the D$_{2h}^*$ double group. We use the dyall.v3z for Sg and aug-cc-pVTZ basis sets for, C and O and all the basis sets are available from the Dirac website$^{17}$. We use the gaussian nuclear model for Sg, C and O and the kinetic balance$^{18}$ constraint implemented in the code.

We only mention here briefly salient features of our DF (HF) calculations and refer the reader to the Dirac website$^{18}$ 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. Geometry optimizations for the octahedral Sg(OC)$_6$, Sg(OC)$_6$ and the diatomic CO were carried out automatically using the Dirac code$^{17}$ with the basis sets described above. As a test of our calculations, our calculated total relativistic DF energies with the Dirac code for the atoms C, O and Sg are in very good agreement with the benchmark calculations of Visscher and Dyall$^{19}$. 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.

### 4. RESULTS AND DISCUSSION

#### A. Dirac-Fock and NR Hartree-Fock prediction of the mean bond energy and atomization energy for Sg (OC)$_6$

The relativistic DF, DFBG and the NR HF atomization energies ($A_{e}^{DF}$, $A_{e}^{DFBG}$ and $A_{e}^{NR}$) calculated for Sg(OC)$_6$ in our calculations with the DIRAC code are 60.65, 64.77 and 58.33 eV, respectively. The contribution of $\sim 2.32$ eV to the $A_e$ of Sg (OC)$_6$ is quite significant.

#### B. Relativistic effects for the energy of the reaction Sg+ 6 CO → Sg(OC)$_6$
We have recently reported ab initio all-electron relativistic DF and the corresponding NR calculations for the effects of relativity on the energy of the reaction Sg+ 6 CO \rightarrow Sg(CO)\textsubscript{6}. Our all-electron relativistic Dirac-Fock (DF) and NR Hartree-Fock (HF) calculations predict the DF relativistic and NR energies for the reaction: Sg+6CO \rightarrow Sg (CO)\textsubscript{6} as –7.39 and –6.96 eV, respectively. Our calculated ground state total DF relativistic and NR energies for the reaction product Sg (CO)\textsubscript{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, DFBG and the corresponding NR calculations for the optimized bond lengths, mean bond energy, atomization energy (for Sg(CO)\textsubscript{6}), and energy for the reaction: Sg+ 6CO \rightarrow Sg (CO)\textsubscript{6}, etc. are collected in Table 1. The corresponding results of our relativistic DF, DFBG, and NR Hartree-Fock (HF) calculations for the reaction leading to the isomer Sg (OC)\textsubscript{6}: Sg+6CO \rightarrow Sg (OC)\textsubscript{6} as obtained here using the Dirac code are also presented for the first time in Table I in order to compare results for the two hexacarbonyl isomers of a superheavy element (SHE). No such calculations have been reported for the hexacarbonyl isomers of any superheavy elements (SHE).

5. RELATIVISTIC ELECTRONIC STRUCTURE OF Sg(OC)\textsubscript{6}.

The relativistic ground state closed-shell electron configuration for the 190-electron Sg (CO)\textsubscript{6} and Sg(OC)\textsubscript{6} under the octahedral double symmetry group (O\textsubscript{h*}) is written here for the first time:

\((1\,e\textsubscript{1g})^2\,\ldots\,(12e\text sub{1g})^2\,(1e\textsub{1u})^2\,(13e\textsub{1u})^2\,(1e\textsub{2g})^2\,(5e\textsub{2g})^2\ldots\,(1e\textsub{2u})^2\,(5e\textsub{2u})^2\,(1f\textsub{g})^4\,(14f\textsub{g})^4\,(1f\textsub{u})^4\,(16f\textsub{u})^4\), where we have designated, as in our earlier work \textsuperscript{12-16}, the four two-dimensional extra irreducible representations (EIR) as \(e\textsub{1g},\ e\textsub{1u},\ e\textsub{2g},\ e\textsub{2u}\) and the two four-dimensional EIR as \(f\textsub{g}\) and \(f\textsub{u}\) of the double octahedral group (O\textsub{h*}).There are
for both Sg (CO)$_6$ ($O_h^*$) and Sg(OC)$_6$ ($O_h^*$) 12 e$_{1g}$, 13 e$_{1u}$, 5 e$_{2g}$, 5 e$_{2u}$, 14 f$_g$ and 16 f$_u$ occupied molecular spinors (MS) 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 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 AOs of the six ligands (C and O) transform as $(a_{1g} + e_g + t_{1u})$ and $(a_{1g} + e_g + t_{1g} + t_{2g} + 2 t_{1u} + t_{2u})$, 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 atomic spinors 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 both the isomers. 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 the valence and 124 electrons in core atomic spinors (AS) or relativistic atomic orbitals (RAO) out of a total of 190 electrons of both Sg(CO)$_6$ and Sg(OC)$_6$. The calculated spinor energies of the inner molecular spinors (MS) or relativistic MO's (RMO) $1e_{1g}$, $2e_{1g}$, $1e_{1u}$, $1f_u$ and $3e_{1g}$ of both the isomers 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) or relativistic atomic orbitals (RAO). We have discussed in great detail the bonding and molecular energy levels calculated using our all electron ab initio DF and NR HF calculations for Sg (CO)$_6$ and shall not repeat here the details.
6. **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 Sg (OC)$_6$

the hexaisocarbonyl of the superheavy element seaborgium Sg. A summary of our major conclusions is as follows:

(1) Our relativistic DF SCF and NR HF calculations predict the octahedral *seaborgium hexaisocarbonyl* Sg (OC)$_6$ to be *bound*, with the calculated atomization energy of 64.30 and 62.62 eV, respectively at the optimized geometry. The relevant results are collected in Table I. Relativistic effects are significant and lead to increase of $\sim$ 1.68 eV to the the predicted atomization energy ($A_e$) for Sg (OC)$_6$.

(2) Our *ab initio* all-electron fully relativistic Dirac-Fock (DF) and nonrelativistic Hartree-Fock (NR) calculations predict the DF relativistic and NR HF energy for the formation of Sg (OC)$_6$ via the reaction: Sg+6CO $\rightarrow$ Sg (OC)$_6$ as $-7.30$ and $-6.99$ eV, respectively. Therefore, both our relativistic DF and the NR calculations clearly predict for the first time the existence of the hexaisocarbonyl of the superheavy element Sg.

(3) Our predicted relativistic DF and NR HF mean bond energies for Sg (OC)$_6$ are 12.70 and 45.03 kJ/mol, respectively. It is clear that relativistic effects are significant for the calculation of the mean bond energy.

(4) Our calculated DF and NR energies for the reaction Sg+6CO $\rightarrow$ Sg (OC)$_6$ are $-2.80$ and $-2.15$ eV, respectively. The relativistic effects make significant contribution to the energy of this reaction and predict it to be much more *exothermic* as compared to the nonrelativistic treatment.
(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 Sg(OC)₆, since they remain as if in pure atomic spinors or core. Therefore, these core electrons could be treated in molecular calculations on compounds of the superheavy element by means of effective core methodology.

In conclusion, \textit{ab initio fully relativistic all-electron} Dirac-Fock SCF calculations for organometallics of superheavy elements are no longer the \textit{bottlenecks} of relativistic quantum chemistry.

**ACKNOWLEDGEMENTS**  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 US Department of Energy (DOE) under Contract No. DE-AC03-76SF00098. This supercomputing facility was \textit{sine qua non} for the massive computations reported herein.

**REFERENCES**

1. Yu.Ts.Oganessian, Yu.P.Tretyakov, A.S.Ilinov, A.G.Demin, A.A.Pleve, S.P.Yretyakova, V.M.Plofko, M.P.Ivanov, N.A.Danilov, Yu.S.Korotkin, and G.N.Flerov, Journal of Experimental and Theoretical Physics (JETP) Letters, \textbf{20}, 580(1974)

2. A.Ghiorsos, J.M.Nitschke, J.R.Alonso, C.T.Alonso, M.Nurmia, G.T.Seaborg, E.K.Hulet, and R.W.Lougheed, Phys.Rev.Lett.\textbf{33}, 1490(1974).

3. M.Schädel, W.Bruchle, R.Dresser, B.Eichler, H.W.Gaggeler, R.Gunther, K.E.Gregorich, D.C.Hoffman, S.Hubner, D.T.Jost, J.V.Kratz, W.Paulus, D.Schumann, S.Timokhin, N.Trautmann, A.Turler, G.Wirth and A.Yakuschev, Nature, \textbf{388}, 55 (1997).

4. G.T. Seaborg and W.Loveland, \textit{The elements beyond uranium}, Wiley, 1990.
5. Yu.Ts.Oganessian, Phys.Rev.Letters.\textbf{104}, 142502 (2010)

6. Matthias Schädel and Dawn Shaughnessy (eds.), The Chemistry of Superheavy Elements, Springer-Verlag, Berlin, 2014

7. G.Malli and J.Oreg, J.Chem.Phys. \textbf{63},830 (1975).

8. G.L.Malli, in \textit{Relativistic and Electron Correlation Effects in Molecules and Solids}, G.L.Malli (ed), NATO ASI SERIES B, Vol \textbf{318}, 1-15, Plenum Press, New York, 1994

9. G.L.Malli, in \textit{Proceedings of the Robert A. Welch Foundation, 41st Conference on Chemical Research THE TRANSACTINIDE ELEMENTS}, pp 197-228, Houston Texas, October 27-28, 1997.

10. G.L.Malli and J.Styszynski, J.Chem.Phys. \textbf{109}, 4448 (1998).

11. G.L.Malli, J.Chem.Phys. \textbf{116}, 5476 (2002).

12. G.L.Malli in \textit{Fundamental World of Quantum Chemistry, Volume III}, Erkki J. Brandas and Eugene S. Kryachko (eds), pp 323-364, Kluwer Academic Publishers, Dordrecht, The Netherlands, 2004.

13. G.L.Malli, J.Chem.Phys. \textbf{124}, 071102 (2006).

14. G.L.Malli, Theor.chem.Acc, \textbf{118},473 (2007)

15. G L Malli, J.Chem.Phys. \textbf{142}, 064311 (2015).

16. G L Malli, J.Chem.Phys. \textbf{144}, 194301 (2016).

17. DIRAC, a relativistic ab initio electronic structure program, Release DIRAC12 (2012), written by

H. J. Aa. Jensen, R. Bast, T. Saue, and L. Visscher,

with contributions from V. Bakken, K. G. Dyall, S. Dubillard,

U. Ekstroem, E. Eliav, T. Enevoldsen, T. Fleig, O. Fossgaard,

A. S. P. Gomes, T. Helgaker, J. K. Laerdahl, Y. S. Lee, J. Henriksson,
TABLE I. Calculated total DF relativistic and NR energies $E_X$ (in au), predicted atomization energy ($A_e$) in eV and $E_{NR}^{iso}$ or $E_{DF}^{iso}$ is the isomerization energy (in eV) at the NR or DF level of theory for $\text{Sg (CO)}_6 \rightarrow \text{Sg (OC)}_6$. The $\Delta E_X$ (in eV) is the energy for the reaction $\text{Sg+6CO} \rightarrow \text{Sg (CO)}_6$ or $\text{Sg (OC)}_6$ ($O_h$). The $E_{DF}^{mean}$ or $E_{NR}^{mean}$ (in kJ/mol) is the relativistic DF or NR mean bond energy for the isomers.

|          | $\text{Sg(CO)}_6$ | $\text{Sg(OC)}_6$ |
|----------|-------------------|-------------------|
| $E_{NR}$ | -36599.3009       | -36599.0865       |
| $E_{DF}$ | -41402.6833       | -41402.5181       |
| $E_{DFBG}$ | -41331.3242   | -41331.1622       |
| $A_e^{NR}$ | 68.46            | 62.62             |
| $A_e^{DF}$ | 68.80            | 64.30             |
| $A_e^{DFBG}$ | 69.18            | 64.77             |
|                  |   ΔE<sub>NR</sub> |   ΔE<sub>DF</sub> |   ΔE<sub>DFBG</sub> |   E<sub>NR</sub><sub>mean</sub> |   E<sub>DF</sub><sub>mean</sub> |   E<sub>DFBG</sub><sub>mean</sub> |
|-----------------|------------------|------------------|---------------------|---------------------------|---------------------------|---------------------------|
| ΔE              | -6.99            | -7.30            | -7.17               | 112.41                    | 117.40                    | 115.31                    |
| NR              |                  |                  |                     |                           |                           |                           |
| DF              |                  |                  |                     |                           |                           |                           |
| DFBG            |                  |                  |                     |                           |                           |                           |
| mean            |                  |                  |                     | 18.49                     | 45.03                     | 44.39                     |

<sup>a</sup> The results for Sg(CO)<sub>6</sub> and Sg(OC)<sub>6</sub> tabulated here were recalculated using the the basis dyall.v3z for Sg and aug-cc-pVTZ basis for both C and O and differ from those reported earlier [see Ref. 16.] using the basis dyall.v2z for Sg and aug- cc-pVDZ for both C and O.