

## Relativistic Effects Break Periodicity in Group 6 Diatomic Molecules

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## S Supporting Information

**ABSTRACT:** The finding of the periodic law is a milestone in chemical science. The periodicity of light elements in the Periodic Table is fully accounted for by quantum mechanics. Here we report that relativistic effects change the bond multiplicity of the group 6 diatomic molecules  $M_2$  ( $M = \text{Cr, Mo, W, Sg}$ ) from hexuple bonds for  $\text{Cr}_2$ ,  $\text{Mo}_2$ ,  $\text{W}_2$  to quadruple bonds for  $\text{Sg}_2$ , thus breaking the periodicity in the nonrelativistic domain. The same trend is also found for other superheavy-element diatomics  $\text{Rf}_2$ ,  $\text{Db}_2$ ,  $\text{Bh}_2$ , and  $\text{Hs}_2$ .

The Periodic Table (PT) of chemical elements is one of the most profound discoveries in chemistry.<sup>1</sup> The inherent periodic law is fundamental for chemical properties and has continuously been explored beyond the currently known element of Uuo ( $Z = 118$ ).<sup>2,3</sup> The earlier PT reveals the periodicity of light elements. Each period row of the PT corresponds to filling up the quantized shells with electrons. Elements in the same group column have similar properties due to the analogous valence-shell electron configurations. While quantum mechanics alone accounts for all the periodicities of the lighter elements, the case becomes more complicated for the heavier elements, roughly beginning with the so-called  $6s^2$  inert electron pairs of the main-group elements in the sixth row. Relativistic effects start to play a more significant role by stabilizing the  $s$ - and  $p_{1/2}$ -shells (dominating *direct relativistic effects*) and destabilizing the  $d$ - and  $f$ -shells (dominating *indirect relativistic effects*), thus bringing novel and sometimes unexpected properties into the heavier elements (e.g., gold) and their compounds.<sup>4,5</sup> The chemical property of the heaviest elements is challenging to obtain and requires the development of theoretical methods to predict it.<sup>6</sup> Elements such as Sg are now available only one atom at a time. Experimental<sup>7,8</sup> and theoretical<sup>9</sup> studies suggest that the mononuclear chemistry of Sg is rather similar to that of Mo or W. Outside the immediate experimental availability, we here show a striking counterexample. The simplest dinuclear system, the diatomic  $\text{Sg}_2$  molecule, is drastically different from its lighter congeners.

For a given atom, the maximum bond multiplicity is related to the formed molecular orbitals (MO) and available valence electrons.<sup>10</sup> So far the maximum bond order between two atoms of the same element is six,<sup>11</sup> as in  $\text{W}_2$  and its lighter analogues  $\text{Cr}_2$  and  $\text{Mo}_2$ .<sup>11,12</sup> Although the bonds are weak in  $\text{Cr}_2$  and natural orbital-based effective bond order (EBO) is only 4.8, the maximum formal bond order (MBO) is six with two  $\sigma$ -, two  $\pi$ -, and two  $\delta$ -bonds formed by the  $(n-1)d$  and  $ns$  atomic orbitals, as in the case of  $\text{Mo}_2$  and  $\text{W}_2$ .<sup>11</sup>

Quantum chemical calculations using wave function theory (WFT) and density functional theory (DFT) were hereby carried out to optimize the geometries and analyze the chemical bonding and properties of group 6 diatomic molecules.<sup>13</sup> The PBE and CCSD(T) optimized bond lengths with the same basis sets for  $M_2$  ( $X = \text{Cr, Mo, W, Sg}$ ) are within 0.03 Å and have the same trend from Cr to Sg (Tables 1 and S1). The calculated Nalewajski–Mrozek bond orders<sup>14</sup> are around 6 for  $\text{Cr}_2$ ,  $\text{Mo}_2$ ,  $\text{W}_2$  and about 4 for  $\text{Sg}_2$ . The MO energy levels calculated using the PBE functional<sup>15</sup> with the scalar relativistic (SR) ZORA (zeroth-order regular approximation) Hamiltonian<sup>16</sup> are shown in Figure 1 for  $\text{Cr}_2$ ,  $\text{Mo}_2$ ,  $\text{W}_2$ , and  $\text{Sg}_2$ , where the spin–orbit (SO) coupled levels are also shown for the  $\text{Sg}_2$ . The natural orbitals and their occupation numbers of the multiple bonds obtained by the CASSCF method are listed in Table S2 and are compared in Figure 2 for  $\text{W}_2$  and  $\text{Sg}_2$ .

From Figure 1, each  $M$  ( $M = \text{Cr, Mo, W}$ ) atom provides five  $(n-1)d$  and one  $ns$  electrons and form two  $\sigma_g$  bonds from  $s$ - and  $d$ -orbitals and two  $\pi_u$  and two  $\delta_g$  bonds from  $d$ -orbitals. The EBO in  $\text{Cr}_2$  is 4.8, much less than 6, due to the radially contracted 3d orbitals and thus rather weak  $\delta_g$  bonds.<sup>11</sup> Despite the small bond strength in  $\text{Cr}_2$ , the bond types and orders of the chemical bonds are consistent in  $\text{Cr}_2$ ,  $\text{Mo}_2$ , and  $\text{W}_2$ . In contrast, the electron configuration in  $\text{Sg}_2$  is quite different. The 7s valence shell is drastically stabilized and becomes fully occupied in  $\text{Sg}_2$ ,<sup>2,23</sup> thus forming one bonding  $\sigma_g(s)$  orbital and one antibonding  $\sigma_u^*(s)$  orbital that cancel the bonding effect of each other. Only the four 6d electrons are left for one  $\sigma_g(d)$ , two  $\pi_u(d)$ , and one  $\delta_g(d)$  bond, leading to a bond order of 4, instead of 6 in its lighter congeners. Because of this reduction of bond order, the calculated  $M$ – $M$  distance increases by 0.3 Å even though the covalent radii of Sg is only 0.06 Å larger than that of W.<sup>24</sup> Accordingly the bond dissociation energies decrease significantly from  $\text{W}_2$  (5.3 eV) to  $\text{Sg}_2$  (4.6 eV) (Table S1). The dissociation energy for  $\text{Cr}_2$  computed here is much lower than the reported results since CCSD(T) does not account for the static correlation effects.<sup>11,25</sup>

Theoretical analysis indicates that the difference of the bond multiplicities of  $M_2$  ( $M = \text{Cr, Mo, W}$ ) and  $\text{Sg}_2$  arises from relativistic effects. The nonrelativistic (NR, blue) and scalar relativistic (SR, red) energy levels of the  $(n-1)d$  and  $ns$  orbitals of Cr, Mo, W, and Sg are compared in Figure 3. The direct relativistic effects stabilize the  $ns$  orbitals, and the indirect relativistic effect destabilizes the  $(n-1)d$  orbitals steadily from Cr to Sg. In the Sg atom, the 7s orbital is relativistically stabilized and lies energetically lower than the 6d ones by some

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Table 1. Bond Lengths and Bond Orders of Cr<sub>2</sub>, Mo<sub>2</sub>, W<sub>2</sub>, and Sg<sub>2</sub>

	M–M/Å					Bond Order			
	CCSD(T) <sup>a</sup>	PBE <sup>a</sup>	PBE <sup>b</sup>			NR <sup>b,c</sup>	SR <sup>b,c</sup>	SO <sup>b,c</sup>	EBO <sup>a,d</sup>
			NR	SR	SO				
Cr <sub>2</sub>	1.593	1.589	1.595	1.599	1.596	6.11	6.11	6.11	4.84
Mo <sub>2</sub>	1.932	1.925	1.906	1.936	1.936	6.15	6.13	6.13	5.13
W <sub>2</sub>	2.020	2.002	1.999	2.026	2.028	6.11	6.08	6.10	5.17
Sg <sub>2</sub>	2.349	2.377	2.203	2.306	2.338	6.12	4.24	4.06	3.53

<sup>a</sup>MOLPRO calculations with Gaussian-type basis sets.<sup>13</sup> <sup>b</sup>ADF calculations with Slater basis sets. <sup>c</sup>Nalewajski–Mrozek bond orders. <sup>d</sup>CASSCF calculations based on CCSD(T) optimized geometries.

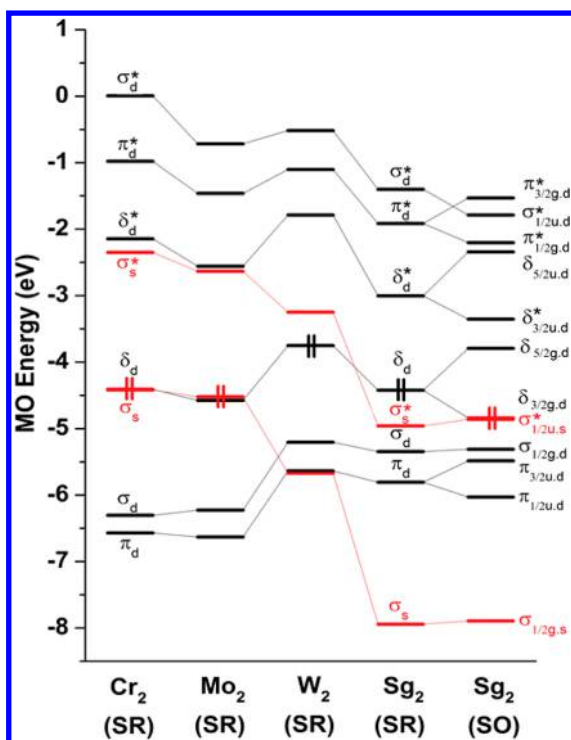


Figure 1. Scalar relativistic MO energy levels of Cr<sub>2</sub>, Mo<sub>2</sub>, W<sub>2</sub>, and Sg<sub>2</sub> with the highest occupied orbitals showing with two vertical bars.

2.8 eV. Thus, the fully occupied 7s<sup>2</sup> tends to become an energetically inert electron pair and has little contribution in bonding,<sup>26</sup> which is reminiscent of the 2s-orbitals in the second row being increasingly inactive across N, O, and F. As a result, Sg tends to have a lower oxidation state than those of Cr, Mo, and W in metal complexes.<sup>27</sup>

Our calculations show that without relativistic effects the half-occupied 7s orbitals would form one  $\sigma_g(s)$  bonding orbital and the remaining ten electrons in 6d orbitals form one  $\sigma_g(d)$ , two  $\pi_u(d)$ , and two  $\delta_g(d)$  bonds, just like its lighter analogs. The difference caused by SR effects in the bonding feature of Sg<sub>2</sub> from its analogs also results in marked changes in their geometries. In Sg<sub>2</sub>, the bond distance increases by 0.10 Å due to the SR effects, much larger than those of no more than 0.03 Å in M<sub>2</sub> (X = Cr, Mo, W). To illustrate individual orbital contribution to chemical bonding, we performed EDA-NOCV analyses<sup>28</sup> for all the group 6 diatomics (Table S3). It is interesting to find that the d- $\pi$  orbitals show more bonding effect than the d- $\sigma$  orbitals in the metal diatomics here, which is different from the scenario of classical ethylene, where the s- $\sigma$  bonding is stronger than the p- $\pi$  bonding.

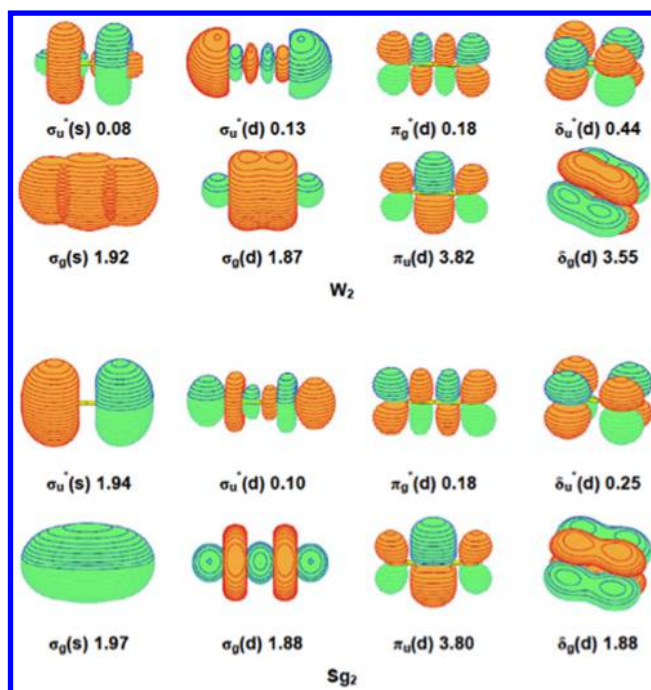


Figure 2. Valence natural molecular orbitals and the natural orbital occupation numbers of W<sub>2</sub> and Sg<sub>2</sub> from CASSCF calculations.

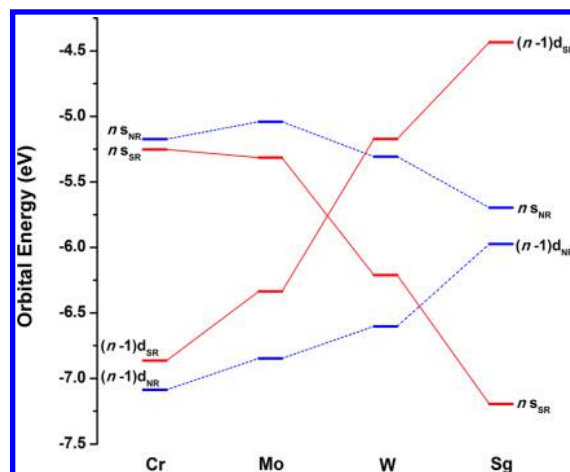


Figure 3. NR (blue) and SR (red) energy levels of the (n – 1)d and ns orbitals of Cr(3d<sup>4</sup>4s<sup>2</sup>), Mo(4d<sup>4</sup>5s<sup>2</sup>), W(5d<sup>4</sup>6s<sup>2</sup>), and Sg(6d<sup>4</sup>7s<sup>2</sup>) calculated using PBE method. The same electron configuration is used for comparison.

Remarkably relativistic spin–orbit (SO) coupling effects are also important for the geometry of Sg<sub>2</sub>. In general, SO effects mainly affect the energy levels of heavy-element compounds

**Table 2. Bond Lengths (*R*), Force Constant (*k*), Vibrational Frequencies ( $\nu$ ), Electron Configurations, and Bond Orders of  $M_2$  ( $M = \text{Rf, Db, Sg, Bh, and Hs}$ )**

	$R_{(M-M)}/\text{\AA}$			$k/\text{N cm}^{-1c}$	$\nu/\text{cm}^{-1c}$	Configuration <sup>c</sup>	Formal BO <sup>c</sup>	EBO <sup>d</sup>
	CCSD(T) <sup>a</sup>	CASPT2 <sup>a,b</sup>	PBE <sup>c</sup>					
Rf <sub>2</sub>	2.72	2.76	2.69	1.89	156.3	$\sigma_s^2\sigma_s^{*2}\pi_d^4$	2	1.88
Db <sub>2</sub>	2.50	2.52	2.46	4.07	228.8	$\sigma_s^2\sigma_s^{*2}\pi_d^4\sigma_d^2$	3	2.74
Sg <sub>2</sub>	2.35	2.36	2.32	5.83	273.2	$\sigma_s^2\pi_d^4\sigma_d^2\sigma_s^{*2}\delta_d^2$	4	3.53
Bh <sub>2</sub>	2.24	2.29	2.21	7.97	319.1	$\sigma_s^2\pi_d^4\sigma_d^2\sigma_s^{*2}\delta_d^4$	5	4.30
Hs <sub>2</sub>	2.25	2.27	2.23	7.55	209.8	$\sigma_s^2\pi_d^4\sigma_d^2\delta_d^4\sigma_s^{*2}\delta_d^{*2}$	4	3.49

<sup>a</sup>MOLPRO calculations with Gaussian-type basis sets.<sup>13</sup> <sup>b</sup>The details of the active spaces for CASPT2 optimizations are described in Tables S2 and S4. <sup>c</sup>ADF calculations with Slater basis sets. <sup>d</sup>The details are given in Table S2.

and have little influence on the geometries. However, when SO effects are large enough to change electron configurations, the geometries will be affected considerably. At the SR level, the highest occupied orbitals are degenerate  $\delta_g(d)$  with two electrons, implying an open-shell triplet ground state for Sg<sub>2</sub>. However, the SO effects split the two  $\delta_g(d)$  orbitals by about 1 eV, leading to a closed-shell ground state. The bond length is expanded by 0.03 Å due to the SO effects in Sg<sub>2</sub>, much larger than the expansion (0.003 Å) in its lighter analogs (Table 1).

Our preliminary DFT, CCSD(T), and CASPT2 calculations reveal that the diatomic molecules composed from the seventh-row neighbors of Sg, such as Rf<sub>2</sub>, Db<sub>2</sub>, Bh<sub>2</sub>, and Hs<sub>2</sub>, all follow this relativistically deduced new periodicity, where the  $7s^2$  inert electron pair does not significantly participate in direct chemical bonding in these zerovalent molecules (Tables 2 and S1, S2, S4), thus preventing the formation of a high bond order as in its respective lighter congeners. These results show that this periodicity breakdown is a general rule for the seventh-row elements and beyond because of the strong relativistic effects.

In conclusion, both SR and SO effects are important for the diatomic molecules of the superheavy group 6 element with the M–M bond multiplicity being reduced from six in Cr<sub>2</sub>, Mo<sub>2</sub>, and W<sub>2</sub> to four in Sg<sub>2</sub>. This reduction of bond order causes significant changes in the bond distances, vibrational frequencies, force constants, and dissociation energies. The same trend applies to the diatomics (Rf<sub>2</sub>, Db<sub>2</sub>, Bh<sub>2</sub>, and Hs<sub>2</sub>) of other seventh-row superheavy elements. Our work thus provides a rare example where relativistic effects break the periodicity in the nonrelativistic domain derived from light-element chemistry, and novel properties are expected for chemical compounds of superheavy elements.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b11793.

Natural orbital occupation numbers; PBE-DFT, CCSD(T), and CASPT2 bond lengths; EDA-NOCV energies; force constants and vibrational frequencies (PDF)

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### Notes

The authors declare no competing financial interest.

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- (13) The geometries were optimized at the DFT level using the PBE functional<sup>15</sup> and wave function-based CCSD(T). The (12,12) active spaces in the CASSCF calculations included all the orbitals and

electrons from the  $ns$  and  $(n-1)d$  derived molecular orbitals. The PBE, CCSD(T), and CASSCF calculations were performed using MOLPRO 2008.1<sup>18</sup> with the  $(8s7p6d2f1g)/[6s5p3d2f1g]$  basis sets for Cr,<sup>19</sup> cc-pVTZ-PP for Mo and W,<sup>20</sup> and  $(18s19p18d15f)/[3s5p3d3f]$  for Sg,<sup>21</sup> respectively, and effective core potentials with 10, 28, 60, and 78 core electrons for Cr, Mo, W, Sg, respectively. The PBE calculations were performed using the nonrelativistic, SR- and SO-ZORA Hamiltonian with the TZ2P basis sets with the frozen cores of Cr.2p, Mo.3d, W.4d, and Sg.5d using ADF 2009.1.<sup>22</sup> For other computational details, see the [Supporting Information](#).

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