

Relativistic Effects Break Periodicity in Group 6 Diatomic Molecules

Yi-Lei Wang, Han-Shi Hu,* Wan-Lu Li, Fan Wei, and Jun Li*

Department of Chemistry & Key Laboratory of Organic Optoelectronics and Molecular Engineering of Ministry of Education, Tsinghua University, Beijing 100084, China

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 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 Hs_2 .

The Periodic Table (PT) of chemical elements is one of the most profound discoveries in chemistry.¹ The inherent periodic law is fundamental for chemical properties and has continuously been explored beyond the currently known element of Uuo ($Z = 118$).^{2,3} 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.^{4,5} The chemical property of the heaviest elements is challenging to obtain and requires the development of theoretical methods to predict it.⁶ Elements such as Sg are now available only one atom at a time. Experimental^{7,8} and theoretical⁹ 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 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.¹⁰ So far the maximum bond order between two atoms of the same element is six,¹¹ as in W_2 and its lighter analogues Cr_2 and Mo_2 .^{11,12} Although the bonds are weak in Cr_2 and natural orbital-based effective bond order (EBO) is only 4.8, the maximum formal bond order (MBO) is six with two σ -, two π -, and two δ -bonds formed by the $(n - 1)d$ and ns atomic orbitals, as in the case of Mo_2 and W_2 .¹¹

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.¹³ 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 orders¹⁴ are around 6 for $\text{Cr}_2, \text{Mo}_2, \text{W}_2$ and about 4 for Sg_2 . The MO energy levels calculated using the PBE functional¹⁵ with the scalar relativistic (SR) ZORA (zeroth-order regular approximation) Hamiltonian¹⁶ are shown in Figure 1 for $\text{Cr}_2, \text{Mo}_2, \text{W}_2,$ and Sg_2 , where the spin–orbit (SO) coupled levels are also shown for the 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 W_2 and 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 σ_g bonds from s - and d -orbitals and two π_u and two δ_g bonds from d -orbitals. The EBO in Cr_2 is 4.8, much less than 6, due to the radially contracted 3d orbitals and thus rather weak δ_g bonds.¹¹ Despite the small bond strength in Cr_2 , the bond types and orders of the chemical bonds are consistent in $\text{Cr}_2, \text{Mo}_2,$ and W_2 . In contrast, the electron configuration in Sg_2 is quite different. The 7s valence shell is drastically stabilized and becomes fully occupied in Sg_2 ,^{2,23} 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.²⁴ Accordingly the bond dissociation energies decrease significantly from W_2 (5.3 eV) to Sg_2 (4.6 eV) (Table S1). The dissociation energy for Cr_2 computed here is much lower than the reported results since CCSD(T) does not account for the static correlation effects.^{11,25}

Theoretical analysis indicates that the difference of the bond multiplicities of M_2 ($M = \text{Cr, Mo, W}$) and 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

Received: November 10, 2015

Published: January 19, 2016

Table 1. Bond Lengths and Bond Orders of Cr₂, Mo₂, W₂, and Sg₂

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

^aMOLPRO calculations with Gaussian-type basis sets. ^bADF calculations with Slater basis sets. ^cNalewajski–Mrozek bond orders. ^dCASSCF calculations based on CCSD(T) optimized geometries.

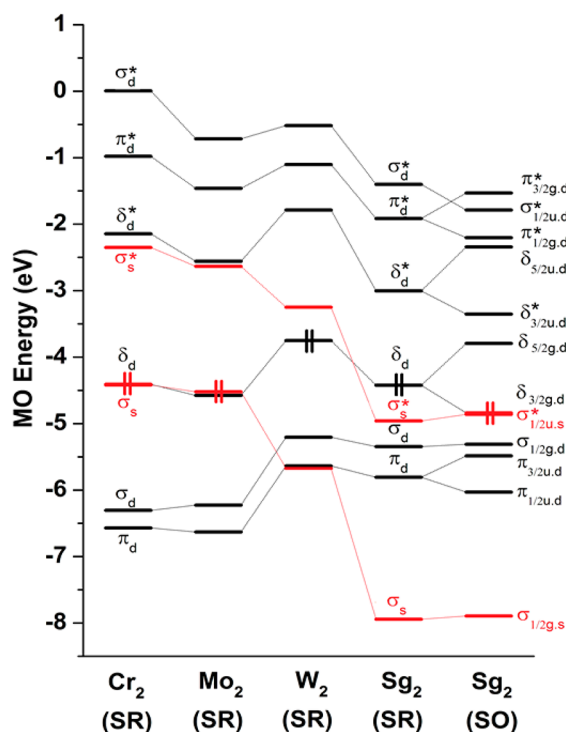


Figure 1. Scalar relativistic MO energy levels of Cr₂, Mo₂, W₂, and Sg₂ with the highest occupied orbitals showing with two vertical bars.

2.8 eV. Thus, the fully occupied 7s² tends to become an energetically inert electron pair and has little contribution in bonding,²⁶ 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.²⁷

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 Sg₂ from its analogs also results in marked changes in their geometries. In Sg₂, 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 M₂ (X = Cr, Mo, W). To illustrate individual orbital contribution to chemical bonding, we performed EDA-NOCV analyses²⁸ for all the group 6 diatomics (Table S3). It is interesting to find that the d- π orbitals show more bonding effect than the d- σ orbitals in the metal diatomics here, which is different from the scenario of classical ethylene, where the s- σ bonding is stronger than the p- π bonding.

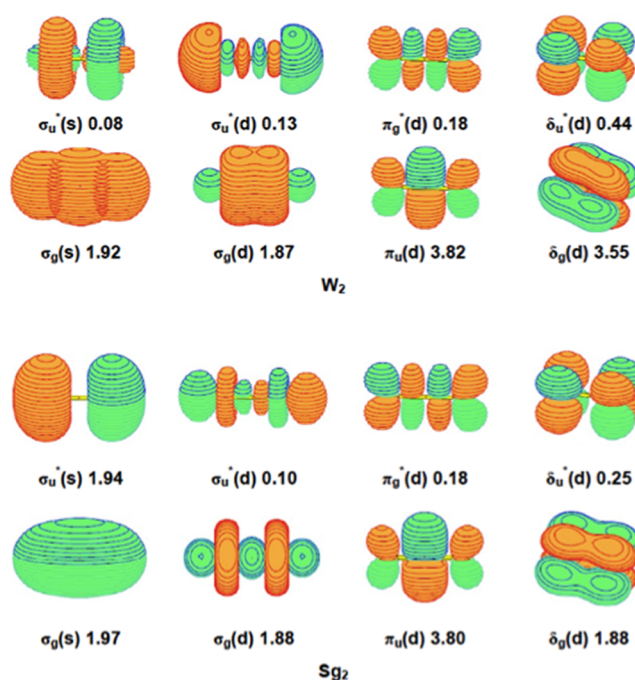


Figure 2. Valence natural molecular orbitals and the natural orbital occupation numbers of W₂ and Sg₂ from CASSCF calculations.

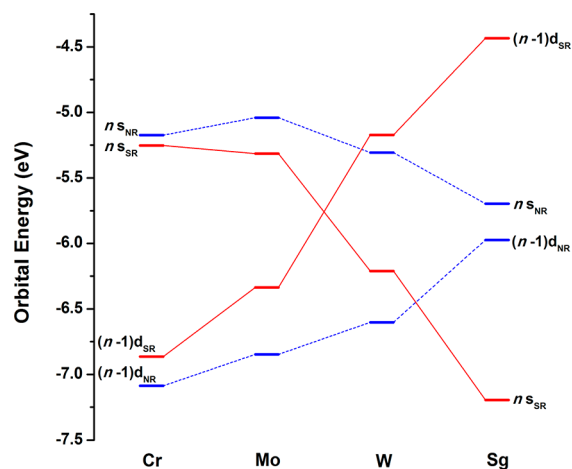


Figure 3. NR (blue) and SR (red) energy levels of the (n – 1)d and ns orbitals of Cr(3d⁴s²), Mo(4d⁴s²), W(5d⁴s²), and Sg(6d⁴s²) calculated using PBE method. The same electron configuration is used for comparison.

Remarkably relativistic spin–orbit (SO) coupling effects are also important for the geometry of Sg₂. In general, SO effects mainly affect the energy levels of heavy-element compounds

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

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

^aMOLPRO calculations with Gaussian-type basis sets.¹³ ^bThe details of the active spaces for CASPT2 optimizations are described in Tables S2 and S4. ^cADF calculations with Slater basis sets. ^dThe 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 Sg₂. 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 Sg₂, 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 Rf₂, Db₂, Bh₂, and Hs₂, 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 Cr₂, Mo₂, and W₂ to four in Sg₂. 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 (Rf₂, Db₂, Bh₂, and Hs₂) 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)

■ AUTHOR INFORMATION

Corresponding Authors

*huhanshi12@gmail.com

*junli@mail.tsinghua.edu.cn

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are indebted to Prof. Pekka Pyykkö and Prof. W. H. Eugen Schwarz for helpful discussions. This work was supported by the National Natural Science Foundation of China (Grants 21433005, 21590792, and 91426302). The calculations were performed using the Supercomputer Center of the Computer Network Information Center, Chinese Academy of Sciences, and Tsinghua National Laboratory for Information Science and Technology.

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- (13) The geometries were optimized at the DFT level using the PBE functional¹⁵ 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 2008.1¹⁸ with the $(8s7p6d2f1g)/[6s5p3d2f1g]$ basis sets for Cr,¹⁹ cc-pVTZ-PP for Mo and W,²⁰ and $(18s19p18d15f)/[3s5p3d3f]$ for Sg,²¹ 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 2009.1.²² For other computational details, see the [Supporting Information](#).

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