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Electronic properties of rhenium, osmium and iridium dimers by density functional methods

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Abstract

Bond distance, vibrational frequency and dissociation energy of Re_2, Os_2 and Ir_2 were studied by density functional methods B3LYP, BLYP, B3PW91, BHLYP, BP86, B3P86 and PBE1PBE. Spin multiplicity 7 is the ground state for Os_2, 5 for Ir_2. For Re_2, the ground state spin multiplicity is sensitive to the density functionals. Spin multiplicity 5 is the ground state for B3LYP, B3PW91, B3P86, and PBE1PBE, while triplet state is the ground state for BLYP, BP86, and BHLYP. The calculated bond distances are less sensitive to the methods used, while it is not true for vibrational frequencies and dissociation energies.

1. Introduction

In recent years, homonuclear transition metal dimers have been studied both experimentally and theoretically. A good summary of these studies can be found in [1,2]. The spectroscopic constants (bond distance, vibrational frequency and dissociation energy) of the homonuclear transition metal dimers were also predicted empirically [3]. For a systematic theoretical study, all homonuclear dimers of the 3d transition metals were conducted independently by Yanasigava et al. [4] and Barden et al. [5]. In both articles [4,5], diverse density functional methods were tested and their performance was compared with the available data. On the other hand, Gutsev and Bauschlicher [6] studied all the homonuclear 3d transition metal dimers both at neutral and charged species (cation and anion) by use of different density functional methods. For the 4d transition metal, the homonuclear dimers were examined by one of the present authors by use of diverse density functional methods [7]. However, systematic theoretical studies on the 5d transition metal dimers are not available. Good summary of experimental studies on La_2, Pr_2, Nd_2, Gd_2, Tb_2, Lu_2, Hf_2, Ta_2, W_2, Re_2, Pt_2, and Au_2 can be found in [1]. For theoretical studies, it includes La_2 [8,9], Pr_2 [10], Gd_2 [10], Yb_2 [8,9], Lu_2 [8,9], Hf_2 [11], W_2 [12], Pt_2 [13], and Au_2 [14]. To our knowledge, both experimental and theoretical studies are rare for Re_2, Os_2 and Ir_2. Experimental study in matrix isolation on Re_2 was carried out by Lombardi and co-workers [15] by use of mass-selected techniques. Raman and fluorescence data indicated that the ground state of Re_2 is most likely a 1_g ($^3\Delta_g$) with the vibrational frequency 337.9(49) cm^{-1} [15]. This is in agreement with the value of 340(20) cm^{-1} from photodetachment spectroscopy [16]. For the dissociation energy, Morse [2] recommended a value of 4(1) eV. For Os_2 and Ir_2, there is very little spectroscopic information available probably due to the high cost. The dissociation energy of Os_2 is 4.3(8) eV [2], while for Ir_2, a value of 3.50 eV was reported [17]. On the other hand, theoretical studies on Ir_2 are available either by use of density functional

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theory (DFT) on the system of oxametallacycles [18] or ab initio multiconfigurational self-consistent-field calculations (MC-SCF) with relativistic pseudopotentials on the system of hydrogen activation by iridium dimer [19]. It indicated that for Ir_2, spin multiplicity at 5 is the lowest state with the bond distance 2.433 Å [19].

DFT is currently widely used to determine the structures and reaction energy diagrams for a wide variety of molecules. Compared to high-level ab initio molecular orbital theories, DFT has the advantage of applicability anywhere in the Periodic table and inherent computational efficiency. This makes it particularly effective for those molecules involving heavy metal elements. On the other hand, till now, many density functional methods have been developed during the past decade. It is known that each density functional method is different from others on theoretical aspect. Therefore, it is necessary and meaningful to test these density functional methods when applied on different systems, especially for systems containing transition metals because different density functional methods may produce quite different properties for a given system as shown in previous studies [4–8,11,12]. In this Letter, rhenium, osmium and iridium dimers are studied by use of diverse density functional methods. Spectroscopic constants, i.e., bond distances, vibrational frequencies and dissociation energies are calculated and compared with available data. The performance of different functional methods is compared. Hopefully, this research could stimulate both experimental and theoretical researches on rhenium, osmium and iridium dimers and provide guidance for advanced computations.

2. Computational details

Geometry optimizations were performed using the GAUSSIAN 98 suite of programs [20]. Bond distances, vibrational frequencies and dissociation energies were determined for the studied clusters by using seven different exchange-correlation functionals, denoted as B3LYP, BLYP, B3PW91, BHLYP, BP86, B3P86, and PBE1PBE [21–27]. For these density functional methods, the correlation functional is from either Lee, Yang and Parr (LYP) [21], Perdew-Wang 1991 (PW91) [22], or Perdew 86 [23], while the exchange functional is from either Becke's three-parameter HF/DFT hybrid exchange functional (B3) [24], pure DFT exchange functional of 1988 (B) [25], a modification of the half-and-half HF/DFT hybrid method (BH) [26], or Perdew-Wang 1991 (PW91) [22]. PBE1PBE is the GGA exchange-correlation functionals of Perdew et al. [27]. The basis set used in this study is CEP-121G (relativistic compact effective potential) [28] in which the dependence of spin-orbit effects was averaged out. The CEP-121G basis set was derived from numerical Dirac–Fock atomic wavefunctions using shape-consistent valence pseudo-orbitals and an optimizing procedure based on an energy-overlap functional [28]. The valence electrons considered are $5s^2 5p^6 5d^5 6s^2$ for rhenium, $5s^2 5p^6 5d^6 6s^2$ for osmium and $5s^2 5p^6 5d^7 6s^2$ for iridium. To avoid trapping at local minima of the potential energy surface, different initial geometries (bond distance) are used. The calculated dissociation energies were corrected by the zero-point vibrational energies.

3. Results and discussion

The calculated results are listed in Tables 1 and 2. Various spin multiplicities have been considered at B3LYP level, that is, 1,3,5,7,9,11 for Re_2, 1,3,5,7,9 for Os_2, and 1,3,5,7 for Ir_2 as listed in Table 1. For the remaining density functional methods (BLYP, B3PW91, BHLYP, BP86, B3P86, and PBE1PBE), only the spin state corresponding to the ground state obtained at B3LYP level is considered, i.e., spin multiplicity 7 for osmium dimer and 5 for iridium dimer. For Re_2, since the second lowest conformer at triplet is only 0.14 eV higher than the ground state (spin multiplicity at 5), both triplet and spin multiplicity at 5 are considered for the remaining functionals (Table 2).

3.1. Rhenium dimer

For Re_2, it is seen from Table 1 that spin multiplicity at 5 is the most stable at B3LYP with bond distance 2.146 Å and vibrational frequency 315 cm^{-1}. While the

Table 1
Calculated bond distances R (Å), harmonic vibrational frequencies ω_e (cm^{-1}), and relative energies ΔE (eV) at various spin multiplicities S for Re_2, Os_2 and Ir_2 at B3LYP level

S	Re_2			Os_2			Ir_2		
	R	ω_e	ΔE	R	ω_e	ΔE	R	ω_e	ΔE
1	2.077	381.5	0.82	2.135	348.7	1.26	2.224	295.8	1.24
3	2.070	388.0	0.14	2.121	360.5	0.75	2.255	284.6	0.88
5	2.146	315.7	0.00	2.251	301.2	0.71	2.265	284.3	0.00
7	2.264	300.4	0.24	2.283	289.7	0.00	2.427	217.8	1.31
9	2.506	215.9	1.13	2.426	237.0	0.55			
11	2.884	129.9	1.38						

Table 2
Calculated bond distances R (Å), harmonic vibrational frequencies ω_e (cm^{-1}), and dissociation energies D_e (in eV) at ground state spin multiplicity S for diverse density functional methods

	Re$_2$						Os$_2$			Ir$_2$		
	$S = 3$		$S = 5$		ΔE	D_e	$S = 7$			$S = 5$		
	R	ω_e	R	ω_e			R	ω_e	D_e	R	ω_e	D_e
B3LYP	*2.070*	*388*	2.146	315	0.14	4.16	2.283	289	2.51	2.265	284	3.11
BLYP	2.099	364	*2.171*	*333*	−0.31	3.11	2.305	274	3.68	2.287	268	4.50
B3PW91	*2.060*	*396*	2.132	361	0.21	3.73	2.267	298	2.86	2.249	292	3.48
BHLYP	2.046	414	*2.140*	*345*	−1.00	1.29	2.306	277	−0.94	2.246	301	3.27
BP86	2.084	375	*2.155*	*343*	−0.28	3.35	2.285	285	4.17	2.265	280	4.81
B3P86	*2.058*	*397*	2.132	361	0.17	1.29	2.265	299	3.01	2.246	294	3.62
PBE1PBE	*2.053*	*402*	2.129	364	0.35	3.55	2.294	280	1.22	2.244	296	3.21
Expt.				337.9(49)[a] 340(20)[b]		4(1)[c]			4.3(8)[c]			3.50[d]
Others										2.433[e]		

For Re$_2$, numbers not in italics are ground state, and D_e is calculated only for the ground state. ΔE is the energy difference between $S = 3$ and 5 (triplet – quintet), negative sign means triplet is more stable.

[a] Ref. [15].

[b] Ref. [16].

[c] Ref. [2].

[d] Ref. [17].

[e] Ref. [19], theoretical study at MCSCF level.

conformer at triplet state is only 0.14 eV higher than the ground state, indicating that it is a competitive candidate for the ground state. For this reason, both triplet and spin multiplicity at 5 are considered for the remaining density functional methods (Table 2).

From Table 2, it is seen that the ground state spin multiplicity is sensitive to the density functional used. Spin multiplicity at 5 is the ground state for hybrid density functional methods B3LYP, B3PW91, B3P86 and GGA exchange-correlation functional PBE1PBE, while triplet state is found to be the ground state for pure density functional methods BLYP, BP86 and half and half HF/DFT hybrid method BHLYP. Among these conclusions, our results at BLYP, BHLYP and BP86 are in agreement with experimental result in which triplet state ($^3\Delta_g$) is the ground state for Re$_2$ [15]. For all the density functionals except BHLYP (414 cm^{-1}), the calculated vibrational frequency from 315 cm^{-1} at B3LYP to 375 cm^{-1} at BP86 is close to the experimental value 340(20) cm^{-1} [16] or 337.9(49) cm^{-1} [15]. The calculated bond distance is from 2.046 Å at BHLYP to 2.146 Å at B3LYP, in agreement with the bond distance derived from measured force constants (2.13 Å using Pauling's rule, 2.32 Å using Badger's rule and 2.18 Å using Guggenheimer's rule) [3]. Except at BHLYP and B3P86 levels (1.29 eV), the calculated dissociation energy is from 3.11 eV at BLYP to 4.16 eV at B3LYP, close to experimental value 4(1) eV [2].

3.2. Osmium dimer

From Table 1, it is seen that the high spin state is preferred for Os$_2$. The ground state is found at spin multiplicity 7 (indicating a triple bond), similar to its congeners Fe$_2$ and Ru$_2$ in which spin multiplicity 7 ($^7\Delta_u$) is the ground state [1]. At B3LYP level, the bond distance at ground state is 2.283 Å and vibrational frequency 289 cm^{-1}. The second lowest conformer is from spin multiplicity at 9, which is 0.55 eV higher than the ground state, but the bond distance is 0.143 Å longer than the ground state.

The calculated bond distance at diverse density functional methods (Table 2) is from 2.265 Å at B3P86 level to 2.305 Å at BLYP level. This is in agreement with Os–Os internuclear distance 2.344 Å found at Os$_2$(2-hydroxypyridine)$_4$Cl$_2$(C$_2$H$_5$)$_2$O [29]. In addition, it is also consistent with the bond distance derived from measured force constants (2.13 Å using Pauling's rule, 2.32 Å using Badger's rule and 2.18 Å using Guggenheimer's rule) [3]. The calculated vibrational frequency is from 274 cm^{-1} at BLYP to 299 cm^{-1} at B3P86 level, lower than the value 334 cm^{-1} obtained indirectly from a fit of force constants with dissociation energies [3]. On the other hand, the empirical estimated and suggested dissociation energy for Os$_2$ is 4.3(8) eV [2]. While the calculated dissociation energy in this work spread on a very large scale from −0.94 eV at BHLYP level to 4.17 eV at BP86 level. Only BP86 (4.17 eV) predicts good dissociation energy compared with the suggested value of 4.3(8) eV [2]. At BHLYP level, Os$_2$ is even unbound.

Since the calculated dissociation energy spreads in a wide range, we examined osmium dimer further by CCSD(T) (coupled-cluster singles and doubles approach including the effect of connected triples determined using perturbation theory) method. The calculated bond distance is 2.347 Å, slightly longer than those obtained by density functional methods (Table 2), but close to Os–Os internuclear distance 2.344 Å measured at Os_2 (2-hydroxypyridine)$_4Cl_2(C_2H_5)_2O$ [29]. The calculated vibrational frequency 257 cm^{-1} is lower than the results from DFT calculation. The dissociation energy is 3.10 eV at CCSD(T) level, lower than the suggested value 4.3(8) eV [2]. The above calculation based on both DFT and CCSD(T) indicates that the method with high accuracy is necessary to study the osmium dimer, especially in predicting the dissociation energy. On the other hand, since the dissociation energy of osmium dimer was estimated in a wide range from 3.79 to 5.13 eV [2], experimental work is also needed to solve the discrepancy.

3.3. Iridium dimer

For considered spin multiplicity, our calculation indicates that spin multiplicity at 5 gives the ground state (Table 1), indicating a double bond. This is similar to its congeners Co_2 and Rh_2 in which spin multiplicity 5 ($^5\Delta_g$) is the ground state [1]. This is also in agreement with previous theoretical study at MC-SCF level that spin multiplicity at 5 gives the ground state [19]. At B3LYP, the equilibrium bond distance at the ground state is 2.265 Å and the vibrational frequency 284 cm^{-1}. The triplet state is the second lowest conformer which is 0.88 eV higher than the ground state.

The calculated bond distance at diverse density functional methods (Table 2) is from 2.244 Å at PBE1PBE level to 2.287 Å at BLYP level, which oscillates in a very narrow range. They are in good agreement with the bond distance derived from measured force constants (2.23 Å using Pauling's rule, 2.35 Å using Badger's rule and 2.25 Å using Guggenheimer's rule) [3], but smaller than the results from MC-SCF calculation, 2.433 Å [19]. The calculated vibrational frequency is from 268 cm^{-1} at BLYP level to 301 cm^{-1} at BHLYP level, in agreement with the value 280 cm^{-1} obtained indirectly from a fit of force constants with dissociation energies [3]. Finally, the calculated dissociation energy is from 3.11 eV at B3LYP level to 4.81 eV at BP86 level, in comparision with the suggested results of 3.50 eV [17].

4. Conclusions

Spin multiplicity 7 is the ground state for Os_2 and spin multiplicity 5 for Ir_2. For Re_2, the ground state spin multiplicity is sensitive to the density functionals. Spin multiplicity 5 is the ground state for hybrid density functionals B3LYP, B3PW91, B3P86 and GGA exchange-correlation functional PBE1PBE, while triplet state is the ground state for pure density functionals BLYP, BP86 and half and half HF/DFT hybrid method BHLYP. For the three dimers, the calculated bond distances are less sensitive to the methods used and are in agreement with the bond distances derived from measured force constants, in particular for Ir_2. For Re_2, the calculated vibrational frequency (except at BHLYP) and dissociation energy (except at BHLYP and B3P86) are in agreement with experimental results. For the dissociation energy of Os_2, only BP86 has better performance in reproducing the experimental data. At BHLYP level, Os_2 is even unbound. For Ir_2, all the considered density functional methods have a reasonable performance in reproducing the dissociation energy.

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