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Spin polarization effect for Os_2 molecule*

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Density functional Theory (DFT) (B3p86) of Gaussian03 has been used to optimize the structure of Os_2 molecule. The result shows that the ground state for Os_2 molecule is 9-multiple state and its electronic configuration is $^9\Sigma_g^+$, which shows spin polarization effect of Os_2 molecule of transition metal elements for the first time. Meanwhile, we have not found any spin pollution because the wavefunction of the ground state does not mingle with wavefunctions with higher energy states. So, the fact that the ground state for Os_2 molecule is a 9-multiple state is indicative of spin polarization effect of Os_2 molecule of transition metal elements. That is, there exist 8 parallel spin electrons. The non-conjugated electron is greatest in number. These electrons occupy different spacious tracks, so that the energy of Os_2 molecule is minimized. It can be concluded that the effect of parallel spin of Os_2 molecule is larger than the effect of the conjugated molecule, which is obviously related to the effect of electron d delocalization. In addition, the Murrell–Sorbie potential functions with the parameters for the ground state $^9\Sigma_g^+$ and other states of Os_2 molecule are derived. Dissociation energy D_e for the ground state of Os_2 molecule is 3.3971eV, equilibrium bond length Re is 0.2403nm, vibration frequency ω_e is 235.32cm^{-1}. Its force constants f_2, f_3, and f_4 are 3.1032×10^2aJ·nm^{-2}, -14.3425×10^3aJ·nm^{-3} and 50.5792×10^4aJ·nm^{-4} respectively. The other spectroscopic data for the ground state of Os_2 molecule $\omega_e\chi_e$, B_e and α_e are 0.4277cm^{-1}, 0.0307cm^{-1} and 0.6491×10^{-4}cm^{-1} respectively.

Keywords: Os_2, spin polarization, density functional theory, potential function
PACC: 3420, 3520G

1. Introduction

Currently it is a major research subject to analyse the molecular structures of the transition elements, especially those transition elements in the 5th and 6th periods. But up to now, as for molecular structure of Os_2, no research has been done: neither experimental nor theoretical results are available for diosmium, Os_2. Empirical estimates of the bond dissociation energy, $D_e(Os_2)$, have been provided, however, as 4.20±0.26,[1] 5.13±1.07,[2] 4.20,[3] and 3.79±0.52eV.[4] On the basis of these values, an estimated D_e (Os_2) of 4.3±0.8eV is selected. Binuclear osmium compounds containing a triple bond, such as Os_2 (2-hydroxypyridine)$_4CI_2\cdot(C_2H_5)_2O$(Os–Os bond distance 0.2344nm), are now well-known and demonstrate the potential of multiple 5d bonding between osmium atoms.[5] So far, there is no other useful information about the osmium dimer except for the results of Cotton and Walton.[5]

It is difficult to confirm the ground state $^9\Sigma_g^+$ of Os_2 molecule. It might be related to the delocalization effect of the electron d of $5d^66s^2$. By making use of the density functional theory (DFT) (B3p86) of Gaussian03, we optimized the structure of Os_2 molecule and obtained the potential energy function of this molecule. The result shows that the corresponding minimal energies of 1-, 3-, 5-, 7-, 9-multiple states of Os_2 molecule are very close to each other, but even so, the 9-multiple state is the ground state of Os_2. It follows that in Os_2 molecule there exists the spin polarization effect. Besides, we have confirmed that there exist the spin polarization effects in Ti_2, Ni_2 and Tc_2 molecules after we studied the structures of Ti_2, Ni_2 and Tc_2 molecules.[6–8] We are making research into the diatomic molecules of the other transition metal elements and their clusters.

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2. Theoretical techniques and calculation

The electronic configuration of Os atom is $5d^66s^2$ where $6s^2$ is fully occupied. From $5d^6$, we can infer that the ground electronic configuration of Os atom is ^{5}D. The Os_2 molecule composed of $^5D+^5D$ might have 1-, 3-, 5-, 7-, or 9-multiple states. According to the calculations, the ground state of Os_2 molecule is 9-multiple state of the parallel spin of 8 electrons, which shows the spin polarization effect of the electron in the molecule.

According to atomic and molecular reaction statics in Ref.[9] Os_2 molecule belongs to $D_{\infty h}$ molecule group, and the electronic configuration of Os atom is ^{5}D. Also, according to the group theoretical derivation of molecular electronic states in Ref.[9], the atom group can be dissolved into the direct summation of molecule group $D_{\infty h}$ when two atoms form a linear molecule. That is,

$$^5D_g \to {}^5\Sigma_g \oplus {}^5\Pi_g \oplus {}^5\Delta_g$$

So the direct product of two Os atoms with spherical symmetry is

$$\begin{aligned}&({}^5\Sigma_g \oplus {}^5\Pi_g \oplus {}^5\Delta_g) \otimes ({}^5\Sigma_g \oplus {}^5\Pi_g \oplus {}^5\Delta_g) \to \\ &{}^{1,3,5,7,9}\Sigma_g^+ \oplus {}^{1,3,5,7,9}\Pi_g \oplus {}^{1,3,5,7,9}\Delta_g \oplus {}^{1,3,5,7,9}\Pi_g \oplus {}^{1,3,5,7,9}\Sigma_g^+ \oplus {}^{1,3,5,7,9}\Sigma_g^- \oplus {}^{1,3,5,7,9}\Delta_g \oplus {}^{1,3,5,7,9}\Pi_g \\ &{}^{1,3,5,7,9}\Phi_g \oplus {}^{1,3,5,7,9}\Delta_g \oplus {}^{1,3,5,7,9}\Pi_g \oplus {}^{1,3,5,7,9}\Phi_g \oplus {}^{1,3,5,7,9}\Sigma_g^+ \oplus {}^{1,3,5,7,9}\Sigma_g^- \oplus {}^{1,3,5,7,9}\Gamma_g = {}^{1,3,5,7,9}\Sigma_g^+(3) \\ &{}^{1,3,5,7,9}\Sigma_g^-(2) \oplus {}^{1,3,5,7,9}\Pi_g(4) \oplus {}^{1,3,5,7,9}\Delta_g(3) \oplus {}^{1,3,5,7,9}\Phi_g(2) \oplus {}^{1,3,5,7,9}\Gamma_g\end{aligned}$$

where $^1\Sigma_g$, $^3\Sigma_g$, $^5\Sigma_g$, $^7\Sigma_g$, or $^9\Sigma_g$ are the possible electronic configuration of Os_2 molecule. Making use of DFT (B3p86) of Gaussian03, we have optimized all the possible molecular states (See Table 1 for the theoretical bond lengths in nm, the lowest energy levels of the molecules in H.a.u., and the total s expectance values and calculation values of spin).

Spin pollution is the error in the unlimited *ab initio* calculation. It often comes about in the total energy because the wavefunction of the ground state mingles with the wavefunction in higher-energetic states. High spin pollution will influence the molecular structure and the analysis of distributed numbers of molecules, especially the densities of spin. It also influences the constringency, especially the MP_n assignment. The spin pollution can be validated by comparing the total S_1 prospective value of spin and the value of calculation S_2. S_1 should equal $s(s+1)$, where the s is the total spin value of Os_2 molecule. In general, the result is acceptable if the error is not beyond 10%.

Table 1. Optimum results of Os_2 molecule.

Multiplicity	State	R_e/nm	E/H.a.u.	Expectance of spin S_1	Calculation of spin S_2
1	$^1\Sigma_g^+$	0.21046	−182.5951		0.0
3		0.21074	−182.6252	2.0	2.0
5		0.21469	−182.6397	6.0	6.0
7		0.22652	−182.6536	12.0	12.0
9	$^9\Sigma_g^+$	0.24033	−182.6715	20.0	20.0

From Table 1, we can find that the energy of 9-multiple state of Os_2 molecule is the lowest, so 9-multiple state is the ground state of Os_2 molecule. As the multiplicity increases, the unpaired electrons increase gradually. That is, in Os_2 molecule, the greater the number of the unpaired electrons is, the lower its energy will be—the state with the lowest energy is stablest. This condition is known as spin polarization effect. Pairing of electrons may reduce the energy of the system. However, the commutative integral of spin parallel electrons is positive, which also leads to reduction of the energy of the system. It shows that, in the transition element molecules, the effect of spin parallel is larger than the effect of paired electrons. It

is obviously related to the delocalization of electron d. Meanwhile, we find that the minimal energy values of 1-, 3-, 5-, 7-, 9-multiple states of Os_2 molecule are very close to each other. According to our thorough calculations, the ground state of Os_2 molecule is 9-multiple state. The fact that the ground state of Os_2 molecule is 9-multiple state shows that there exists spin polarization effect in Os_2 molecule, the diatomic molecule of transition metal elements. The dissociation energy of the ground state of Os_2 molecule (9-multiple state) is D_e=3.3971eV. From Table 1, we can find that the prospective values and the calculation values of total spin about 3-, 5-, 7-, 9-multiple states are absolutely the same except that 1-multiple state does not come up in the optimum result. It shows that there is no spin pollution in the DFT calculations for Os_2 molecule, and that the wavefunction of the ground state does not mingle with the wavefunction of higher energy state.

3. Potential function and spectral data

Making use of DFT (B3p86) of Gaussian03 program, we calculated the 1-multiple state, 3-multiple state, 5-multiple state, 7-multiple state, 9-multiple state of Os_2 molecule and attained a series of spot values of potential function. Using the least square fitting, we obtained the function form of Murrell–Sorbie potential function,[10,11] which can be expressed as

$$E(\rho) = -D_e(1 + a_1\rho + a_2\rho^2 + a_3\rho^3)\exp(-a_1\rho)$$

In the above formula, $\rho = R - R_e$, R is the interatomic distance and R_e is its equilibrium value, D_e is the molecular energy of the dissociation, a_1, a_2, a_3 are the modulus of one, two and three order respectively. They can be conducted through fitting. See Table 2 for the result.

Table 2. Parameters for Murrell–Sorbie potential function about Os_2 molecule.

Multiplicity	D_e/eV	R_e/nm	$a_1/10\text{nm}^{-1}$	$a_2/100\text{nm}^{-2}$	$a_3/1000\text{nm}^{-3}$
9	3.3971	0.2403	3.2560	2.4697	0.8631
7	6.9921	0.2265	3.2065	2.6643	1.0314
5	5.4574	0.2147	3.5760	2.7783	1.0239
3	5.8246	0.2107	3.6669	2.7309	0.9590
1	9.2486	0.2105	2.9873	1.8272	0.9384

According to the Murrell–Sorbie potential function from the above fitting data, we can see the relevant potential curve and the corresponding scan results of the multiple states (from Figs.1–6). Every state includes two curves, one for the scan value, and the other for fitting value. They accord with each other precisely. It means that the process of fitting is successful. 9-multiple state is the ground state of Os_2 molecule.

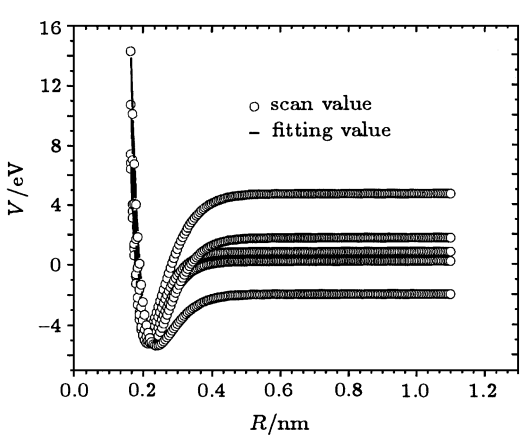


Fig.1. The potential curve for Os_2 molecule.

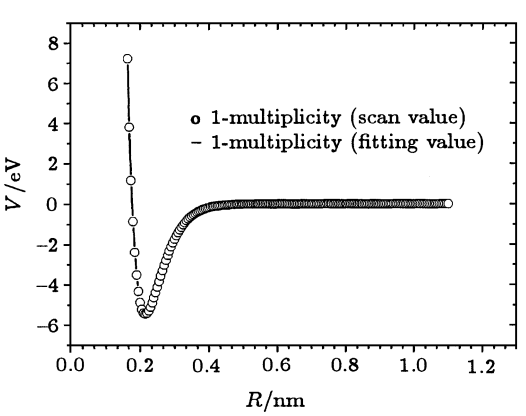


Fig.2. The potential curve of Os_2 molecule for 1-multiplicity.

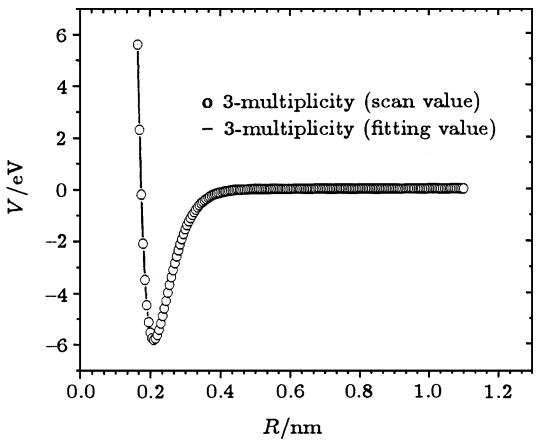


Fig.3. The potential curve of Os_2 molecule for 3-multiplicity.

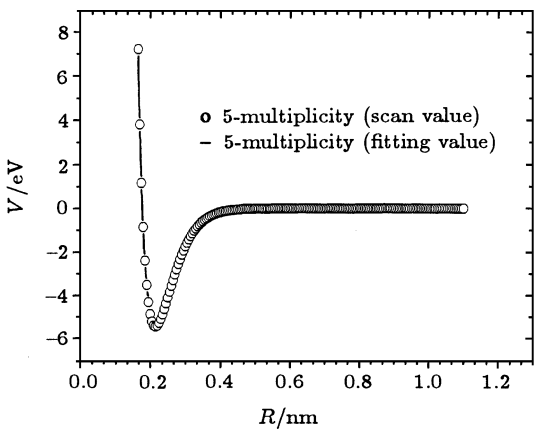


Fig.4. The potential curve of Os_2 molecule for 5-multiplicity.

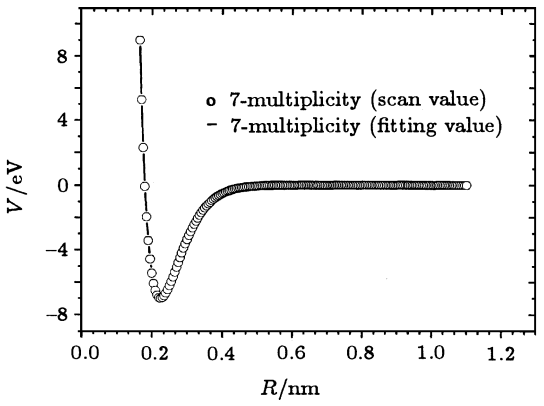


Fig.5. The potential curve of Os_2 molecule for 7-multiplicity.

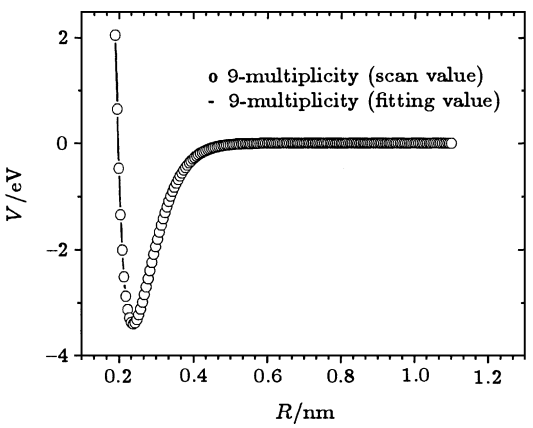


Fig.6. The potential curve of Os_2 molecule for 9-multiplicity.

According to the relationship between the parameters a_1, a_2, a_3 of Murrell–Sorbie potential function and the spectroscopic data ω_e, $\omega_e\chi_e$, B_e, α_e, and that between the force constants f_2, f_3, f_4 and the spectroscopic data ω_e, $\omega_e\chi_e$, B_e, α_e,[12–15] we can conclude that the relationships between spectroscopic data and force constants of Os_2 molecule are as follows:

$$f_2 = D_e(a_1^2 - 2a_2),$$
$$f_3 = 6D_e(a_1a_2 - a_3 - a_1^3/3),$$
$$f_4 = D_e a_1^4 - 6f_2a_1^2 - 4f_3a_1,$$
$$f_2 = 4\pi^2 m\omega_e^2 c^2,$$
$$f_3 = -3f_2/R_e(1 + \alpha_e\omega_e/6B_e^3),$$
$$f_4 = f_2/R_e^2[15 - (1 + \alpha_e\omega_e/6B_e^2)^2 - 8\omega_e\chi_e/B_e],$$

where c is the velocity of light, m is the reduced mass of individual atoms, and the value of B_e is given by

$$B_e = (h/8\pi^2)cmR_e^2 = h/8\pi^2 cI_e.$$

Table 3. The mechanical parameters and spectral data for Os_2 molecule.

Multiplicity	$f_2/(aJ/0.1^{-2}nm^2)$	$f_3/(aJ/0.1^{-3}nm^3)$	$f_4/(aJ/0.1^{-4}nm^4)$	ω_e/cm^{-1}	$\omega_e\chi_e/cm^{-1}$	B_e/cm^{-1}	$\alpha_e/10^{-4}cm^{-1}$
9	3.1032	–14.3425	50.5792	235.32	0.4277	0.0307	0.6491
7	5.5494	–23.3819	75.9819	314.68	0.3522	0.0345	0.4963
5	6.3234	–33.2241	133.0532	335.91	0.5532	0.0384	0.7289
3	7.4511	–41.3245	173.7216	364.64	0.6192	0.0399	0.7593
1	7.8086	–38.8191	163.7665	373.28	0.4479	0.0400	0.6402

We used a similar method to calculate Ni_2 molecule and Ti_2 molecule and other transition metal element molecules. The results show that spin-polarization effect exists in them. So we use the similar method to deal with Os_2 molecule.

4. Conclusion

Making use of the DFT (B3p86) of the Gaussian03 program, we have calculated the 1-, 3-, 5-, 7- and 9-multiple states of Os_2 molecule one by one. The result shows that the ground state of Os_2 molecule should be 9-multiple state. The minimal energy values of 1-, 3-, 5-, 7- and 9-multiple states of Os_2 molecule are very close to each other. Meanwhile, we have not found any spin pollution, and the wavefunction of the ground state does not mingle with wavefunction with higher energy states. The result shows that the ground state for Os_2 molecule is the 9-multiple state, which shows spin polarization effect of Os_2 molecule of transition metal elements, and is indicative of the fact that there exist 8 parallel spin electrons in Os_2 molecule, where the non-conjugated electron is greatest in number. These electrons occupy different spacious tracks, and in this case, the energy of Os_2 molecule is minimal. It shows that the effect of parallel spin of Os_2 molecule is larger than the conjugated effect of the electrons of the molecule, which is obviously related to the effect of the delocalization of the electron d. Dissociation energy D_e of 9-multiple state (ground state) of Os_2 molecule is 3.3971eV, and the equilibrium bond length is 0.2403nm. We have obtained the Murrell–Sorbie potential function of Os_2 molecule, of which the vibration frequency is 235.31cm^{-1}, the force constants f_2, f_3, and f_4 are 3.1032×10^2aJ·nm^{-2}, -14.3425×10^3 aJ·nm^{-3}, 50.5792×10^4 aJ·nm^{-4} respectively. The electronic configuration of Os_2 molecule ground state is $^9\Sigma_g^+$. This result is very helpful for us to understand the structural characteristics of the transition metal molecules. We used a similar method to calculate Ni_2 molecule and Ti_2 molecule and other transition metal element molecules. The results show spin-polarization effect exists in them. So we use the similar method to deal with the Os_2 molecule.

References

[1] Miedema A R and Gingerich K A 1979 *J. Phys.* B **12** 2081
[2] Krasnov K S 1975 *Teplofiz Vys. Temp.* **13** 441
[3] Miedema A R 1980 *Faraday Symp. Chem. Soc.* **14** 136
[4] Brewer L and Winn J S 1980*Faraday Symp. Chem. Soc.* **14** 126
[5] Cotton F A and Walton R A 1982 *Multiple Bonds Between Metal Atoms* (New York: Wiley)
[6] Yan S Y, Zhu Z H and Wang H Y 2004 *J. Sichuan University* (Natural Science Edition) **41** 574 (in Chinese)
[7] Yan S Y and Zhu Z H 2004 *Chin. J. Chem. Phys.* **17** 249 (in Chinese)
[8] Yan S Y and Zhu Z H 2004 *Chin. Phys.* **13** 2053
[9] Zhu Z H 1996 *Atomic and Molecular Reaction Statics* (Beijing: Science Press)
[10] Zhu Z H and Yu H G 1997 *Molecular Structure and Molecular Potential Energy Function* (Beijing: Science Press)
[11] Murrell J N, Carter S, Farantos S C, Huxley P and Varandas A J C 1984 *Molecular Potential Energy Function* (New York: Wiley)
[12] Dunham J L 1932 *Phys. Rev.* **41** 721
[13] Mills I M 1974 *Theoretical Chemistry* (London: The Chemical Society) p110
[14] Yan S Y, Ma M Z and Zhu Z H 2005 *Acta Phys. Sin.* **54** 3106 (in Chinese)
[15] Fang Y T and Luo C L 2000 *Chin. Phys.* **9** 581