Vol 15 No 2, February 2006
1009-1963/2006/15(02)/0324-05

Chinese Physics

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Spin polarization effect for molecule Ta_2*

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(Received 10 July 2005; revised manuscript received 10 October 2005)

Density functional theory (DFT) (B3p86) has been used to optimize the structure of the molecule Ta_2. The result shows that the ground state of molecule Ta_2 is a 7-multiple state and its electronic configuration is $^7\Sigma_u^+$, which shows the spin polarization effect for molecule Ta_2 of transition metal elements for the first time. Meanwhile, spin pollution has not been found because the wavefunction of the ground state does not mix with those of higher states. So, the fact that the ground state of molecule Ta_2 is a 7-multiple state indicates a spin polarization effect of molecule Ta_2 of the transition metal elements, i.e. there exist 6 parallel spin electrons and the non-conjugated electrons are greatest in number. These electrons occupy different space orbitals so that the energy of molecule Ta_2 is minimized. It can be concluded that the effect of parallel spin of the molecule Ta_2 is larger than the effect of the conjugated molecule, which is obviously related to the effect of d-electron delocalization. In addition, the Murrell–Sorbie potential functions with parameters for the ground state $^7\Sigma_u^+$ and other states of the molecule Ta_2 are derived. The dissociation energy D_e, equilibrium bond length R_e and vibration frequency ω_e for the ground state of molecule Ta_2 are 4.5513eV, 0.2433 nm and 173.06 cm^{-1}, respectively. Its force constants f_2, f_3 and f_4 are 1.5965×10^2aJ·nm^{-2}, -6.4722×10^3aJ·nm^{-3} and 29.4851×10^4aJ·nm^{-4}, respectively. Other spectroscopic data $\omega_e\chi_e$, B_e and α_e for the ground state of Ta_2 are 0.2078 cm^{-1}, 0.0315 cm^{-1} and 0.7858×10^{-4} cm^{-1}, respectively.

Keywords: Ta_2, spin polarization, density functional theory, potential function
PACC: 3420, 3520G

1. Introduction

Currently it is a major research subject to determine the molecular structures of the transition elements, especially those transition elements in the fifth and sixth periods. But there still lack experimental and theoretical researches for ditantalum, Ta_2. Empirical estimates of D_e of Ta_2 are 4.09±0.06,[1] 5.09±1.02,[2] 4.09,[3] 3.62±0.52 eV,[4] and 5.2±0.2eV.[5] On the basis of these results, an estimated D_e (Ta_2) of 4±1 eV is chosen. Binuclear tantalum compounds containing several ligated bond, such as Ta_2CI_6(tetrahydrothiophene)$_3$ (Ta–Ta bond distance 0.2681nm), Ta_2Br_6 (tetrahydrothiophene)$_3$ (Ta–Ta bond distance 0.2710nm), Ta_2CI_6 (di-tert-butylacetylene) (tetrahydrothio-phene)$_2$ (Ta–Ta bond distance 0.2677nm), $Ta_2CI_6(S(CH_3)_2)_3$ (Ta–Ta bond distance 0.2691nm), and $Ta_2CI_6(P(CH_3)_3)_4$ (Ta–Ta bond distance 0.2721nm) are now well known, demonstrating the potential of multiple 5d bonding between tantalum atoms.[6] So far there is no other useful information about the tantalum dimer except for the results of Cotton and Walton.[6]

We have shown that there exist spin polarization effects in molecules Ti_2, Ni_2, Tc_2 and Os_2.[7–10] We are researching the diatomic molecules of the other transition metal elements and their clusters. But it is difficult to determine the ground state of the molecule Ta_2 as it may be related to the delocalization effect of the d-electron of $5d^36s^2$. By using the density functional theory (DFT,B3p86) of Gaussian03, we have optimized the structure and obtained the potential energy function of molecule Ta_2. The result shows that the 7-multiple state is the ground state although the energies of 1-, 3-, 5-, 7-multiple states are very close to each other. This indicates that there exists a spin polarization effect in the molecule Ta_2.

2. Theoretical techniques and calculation

The electronic configuration of the Ta atom is

*Project supported by the National Natural Science Foundation of China (Grant No 10376022), by the Scientific Project of Jiangxi Eduction Departments of China, and by the Research Funds of College of Jinggangshan.

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$5d^36s^2$ with $6s^2$ fully occupied. From $5d^3$, we can infer that the ground electronic configuration of the Ta atom is ^4F. The possible states of molecule Ta_2 composed of $^4F+^4F$ can be 1-, 3-, 5- or 7-multiple states. From the calculations, the ground state of the molecule Ta_2 is 7-multiple state with six parallel spin electrons, which shows the spin polarization effect of the electron in the molecule.

According to atomic and molecular reaction statics in Ref.[11], molecule Ta_2 belongs to $D_{\infty h}$ group, and the electronic configuration of atom Ta is ^4F. From the group-theory derivation of molecular electronic states in Ref.[12], 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,

$$^4F_g \rightarrow {}^4\Sigma_g^- \oplus {}^4\Pi_g \oplus {}^4\Delta_g \oplus {}^4\Phi_g.$$

The direct product of two Ta atoms with spherical symmetry is

$$\begin{aligned}
&({}^4\Sigma_g^- \oplus {}^4\Pi_g \oplus {}^4\Delta_g \oplus {}^4\Phi_g) \otimes ({}^4\Sigma_g^- \oplus {}^4\Pi_g \oplus {}^4\Delta_g \oplus {}^4\Phi_g) \rightarrow \\
&{}^{1,3,5,7}\Sigma_g^+ \oplus {}^{1,3,5,7}\Pi_g \oplus {}^{1,3,5,7}\Delta_g \oplus {}^{1,3,5,7}\Phi_g \oplus {}^{1,3,5,7}\Pi_g \oplus {}^{1,3,5,7}\Sigma_g^+ \oplus {}^{1,3,5,7}\Sigma_g^- \oplus {}^{1,3,5,7}\Delta_g \oplus {}^{1,3,5,7}\Pi_g \\
&\oplus {}^{1,3,5,7}\Sigma_g^+ \oplus {}^{1,3,5,7}\Pi_g \oplus {}^{1,3,5,7}\Delta_g \oplus {}^{1,3,5,7}\Phi_g \oplus {}^{1,3,5,7}\Pi_g \oplus {}^{1,3,5,7}\Sigma_g^+ \oplus {}^{1,3,5,7}\Sigma_g^- \oplus {}^{1,3,5,7}\Delta_g \oplus {}^{1,3,5,7}\Pi_g \\
&\oplus {}^{1,3,5,7}\Phi_g \oplus {}^{1,3,5,7}\Delta_g \oplus {}^{1,3,5,7}\Gamma_g \oplus {}^{1,3,5,7}\Delta_g \oplus {}^{1,3,5,7}\Pi_g \oplus {}^{1,3,5,7}\Phi_g \oplus {}^{1,3,5,7}\Sigma_g^+ \oplus {}^{1,3,5,7}\Sigma_g^- \oplus {}^{1,3,5,7}\Gamma_g \oplus {}^{1,3,5,7}\Pi_g \\
&\oplus {}^{1,3,5,7}\mathrm{H}_g \oplus {}^{1,3,5,7}\Phi_g \oplus {}^{1,3,5,7}\Delta_g \oplus {}^{1,3,5,7}\Gamma_g \oplus {}^{1,3,5,7}\Pi_g \oplus {}^{1,3,5,7}\mathrm{H}_g \oplus {}^{1,3,5,7}\Sigma_g^+ \oplus {}^{1,3,5,7}\Sigma_g^- \oplus {}^{1,3,5,7}\mathrm{I}_g \\
=&{}^{1,3,5,7}\Sigma_g^+(6) \oplus {}^{1,3,5,7}\Sigma_g^-(4) \oplus {}^{1,3,5,7}\Pi_g(9) \oplus {}^{1,3,5,7}\Delta_g(7) \oplus {}^{1,3,5,7}\Phi_g(5) \oplus {}^{1,3,5,7}\Gamma_g(3) \oplus {}^{1,3,5,7}\mathrm{H}_g(2) \oplus {}^{1,3,5,7}\mathrm{I}_g
\end{aligned}$$

where $^1\Sigma^+$, $^3\Sigma^+$, $^5\Sigma^+$ or $^7\Sigma^+$ are the possible electronic configurations of molecule Ta_2. Making use of the DFT (B3p86) of Gaussian03, we have optimized all the possible molecule states (see Table 1 for the theoretical bond lengths in nm, the lowest energy levels of the molecules in a.u., and the total s expectance values and calculation values of spin).

Spin pollution is the main error in the unrestricted *ab initio* calculation. It often appears 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 determination of 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 expectation value S_1 of total spin and the value of calculation S_2. S_1 should equal $s(s+1)$, where the s is the total spin of molecule Ta_2. In general, the result is acceptable if the error is not beyond 10%.

Table 1. Optimum results of molecule Ta_2.

multiplicity	state R_e/nm	E/a.u.	Expectance of spin S_1	Calculation of spin S_2	
1	$^1\Sigma_g^+$	0.21466	–115.9459		0.0
3	$^3\Sigma_u^+$	0.21457	–115.9581	2.0	2.0
5	$^5\Sigma_g^+$	0.22486	–115.9635	6.0	6.0
7	$^7\Sigma_u^+$	0.24329	–115.9710	12.0	12.0

From Table 1, we can find that the energy of the 7-multiple state of the molecule Ta_2 is the lowest, i.e. the 7-multiple state is the ground state of the molecule Ta_2. As the multiplicity increases, the number of unpaired electrons increases gradually. That is, in the molecule Ta_2, the greater the number of the unpaired electrons is, the lower its energy will be; the state with the lowest energy is the most stable. This effect is known as spin polarization effect. Pairing of electrons may reduce the energy of the system. However, the interchange integral of spin parallel electrons is positive, which also leads to the reduction of energy of the transition element molecule system. This shows that the effect of spin parallel is larger than the effect of paired electrons. This is obviously related to the delocalization of d-electron. Meanwhile,

we find that the minimal energy values of 1-, 3-, 5-, 7-multiple states of molecule Ta_2 are very close to each other. According to our calculations, the ground state of the molecule Ta_2 is the 7-multiple state. This fact shows that there exists the spin polarization effect in the diatomic molecule Ta_2 of the transition metal elements. The dissociation energy of the ground state of molecule Ta_2 (7-multiple state) is D_e=4.5514eV. From Table 1, we can find that expectation values and the calculation values of total spin of 3-, 5-, 7-multiple states are exactly the same respectively except that 1-multiple state does not come up in the optimum result. This shows that there is no spin pollution in the DFT calculations for molecule Ta_2, and that the wavefunction of the ground state does not mingle with the wavefunctions of higher energy states.

3. Potential function and spectral data

Making use of the DFT (B3p86) of Gaussian03 program, we calculated the 1-multiple state, 3-multiple state, 5-multiple state, 7-multiple state of molecule Ta_2 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,[12] 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 inter-atomic distance and R_e its equilibrium value, D_e is the molecular energy of the dissociation, a_1, a_2, a_3 are the moduli of first, second and third order, respectively. They can be obtained through fitting. See Table 2 for the result.

Table 2. Parameters for Murrell–Sorbie potential function about molecule Ta_2.

multiplicity	D_e/eV	R_e/nm	$a_1/10\text{nm}^{-1}$	$a_2/100\text{nm}^{-2}$	$a_3/1000\text{nm}^{-3}$
7	4.5514	0.2433	2.3122	1.5779	1.0079
5	6.7331	0.2249	2.6954	1.7124	0.8468
3	3.8122	0.2146	3.5233	2.2540	0.7351
1	7.4873	0.2147	2.8301	1.8647	0.9962

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.1–5). Each state includes two curves, one for the scan value and the other for fitting value. They are in accordance with each other precisely. It means that the process of fitting is successful. The 7-multiple state is the ground state of the molecule Ta_2.

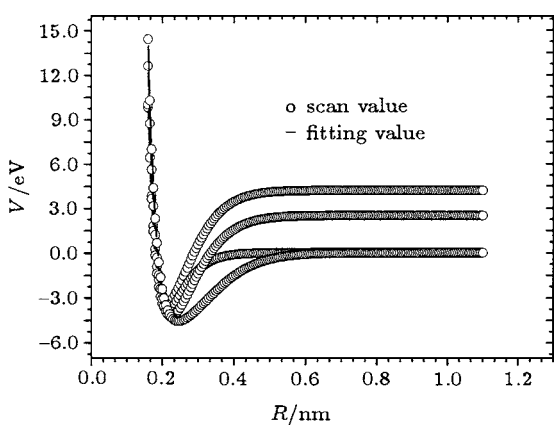


Fig.1. The potential curve for the molecule Ta_2.

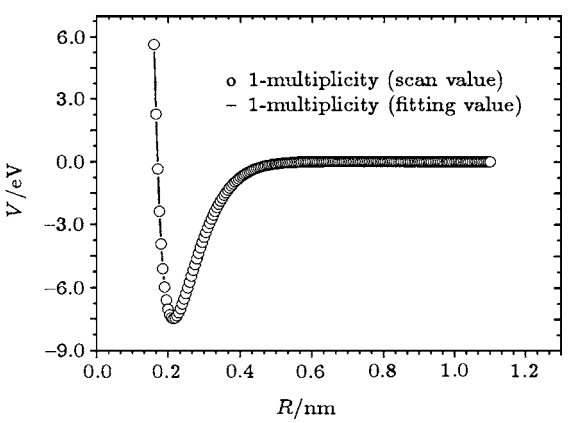


Fig.2. The potential curve of molecule Ta_2 for 1-multiplicity.

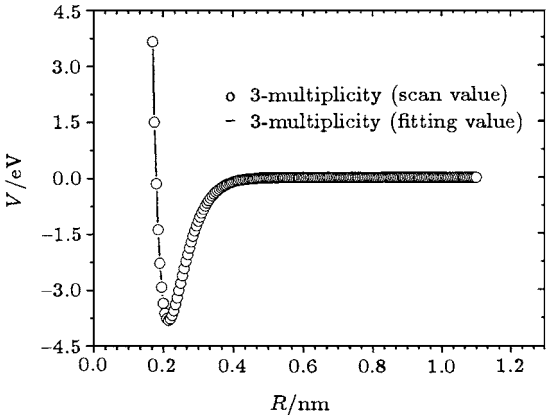


Fig.3. The potential curve of molecule Ta_2 for 3-multiplicity.

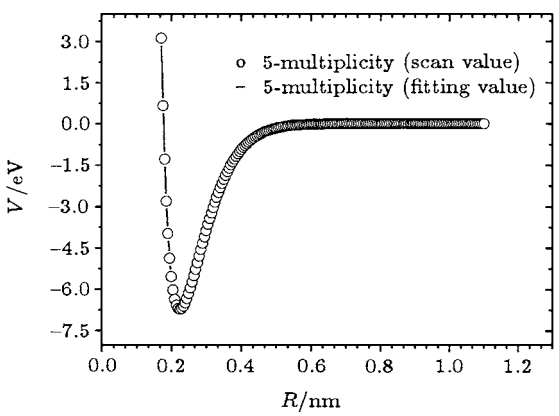


Fig.4. The potential curve of molecule Ta_2 for 5-multiplicity.

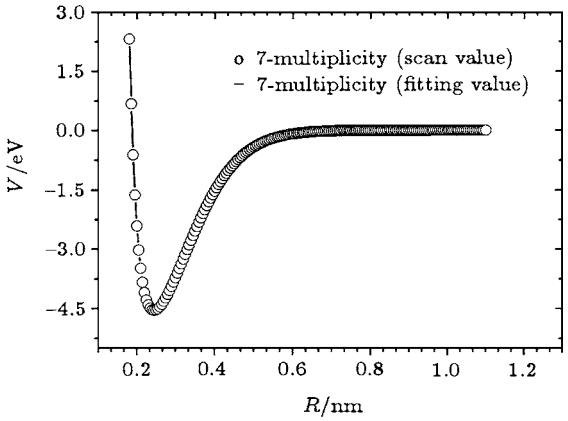


Fig.5. The potential curve of molecule Ta_2 for 7-multiplicity.

According to the relations between the parameters a_1, a_2, a_3 of the Murrell–Sorbie potential function and the spectroscopic data ω_e, $\omega_e\,\chi_e$, B_e, α_e, and the force constants f_2, f_3, f_4 and the spectroscopic data ω_e, $\omega_e\,\chi_e$, B_e, α_e,[12–17] we can obtain the relations between spectroscopic data and force constants of the molecule Ta_2 as follows:

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

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 molecule Ta_2.

multiplicity	$f_2/(\mathrm{aJ/0.1^{-2}nm^2})$	$f_3/(\mathrm{aJ/0.1^{-3}nm^3})$	$f_4/(\mathrm{aJ/0.1^{-4}nm^4})$	$\omega_e/\mathrm{cm^{-1}}$	$\omega_e\chi_e/\mathrm{cm^{-1}}$	$B_e/\mathrm{cm^{-1}}$	$\alpha_e/10^{-4}\mathrm{cm^{-1}}$
7	1.5965	–6.4722	29.4851	173.06	0.2078	0.0315	0.7858
5	4.1437	–17.8628	68.9004	278.81	0.3341	0.0369	0.6520
3	4.8271	–27.0057	115.1749	300.92	0.6592	0.0405	0.9801
1	5.1328	–23.5593	96.9852	310.30	0.3777	0.0404	0.7218

We have used a similar method to calculate Ni_2, Ti_2, Tc_2 and Os_2 molecules and that of other transition metal elements. The results show that spin-polarization effect exists in them. So we use the similar method to deal with the molecule Ta_2.

4. Conclusion

Making use of the DFT (B3p86) of Gaussian03 program we have calculated the 1-, 3-, 5- and 7-multiple states of molecule Ta_2. The result shows that the ground state of the molecule Ta_2 should be the 7-multiple state. The minimal energy values of 1-, 3-, 5- and 7-multiple states of molecule Ta_2 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 wavefunctions of higher energy states. The result shows that the ground state for molecule Ta_2 is the 7-multiple state, which shows

the spin polarization effect of molecule Ta_2 of transition metal elements, and is indicative of the fact that there exist 6 parallel spin electrons in the molecule Ta_2, where the non-conjugated electrons are the greatest in number. These electrons occupy different space orbitals, and hence the energy of molecule Ta_2 is minimal. This shows that the effect of parallel spin of molecule Ta_2 is larger than the conjugated effect of the electrons in the molecule, which is obviously related to the effect of the delocalization of the d-electron. Dissociation energy D_e of 7-multiple state (ground state) of molecule Ta_2 is 4.5514eV, and the equilibrium bond length is 0.2433nm. We have obtained the Murrell–Sorbie potential function of molecule Ta_2, for which the vibration frequency is $173.06 cm^{-1}$, the force constants f_2, f_3, and f_4 are $1.5965\times10^2 aJ\cdot nm^{-2}$, $-6.4722\times10^3 aJ\cdot nm^{-3}$, $29.4851\times10^4 aJ\cdot nm^{-4}$, respectively. The ground state of molecule Ta_2 is $^7\Sigma_u^+$. This result is very helpful to understanding the structure of the transition metal molecules.

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