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Spin polarization effect for Tc_2 molecule

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Density functional method (DFT) (B3p86) of Gaussian98 has been used to optimize the structure of the Tc_2 molecule. The result shows that the ground state for Tc_2 molecule is an 11-multiple state and its electronic configuration is $^{11}\Sigma_g^-$, which shows the spin polarization effect of Tc_2 molecule of a transition metal element for the first time. Meanwhile, we have not found any spin pollution because the wavefunction of the ground state does not mingle with wavefunctions of higher energy states. So, that the ground state for Tc_2 molecule is an 11-multiple state is indicative of the spin polarization effect of Tc_2 molecule of a transition metal element: that is, there exist 10 parallel spin electrons. The non-conjugated electron is greatest in number. These electrons occupy different spacious tracks, so that the energy of Tc_2 molecule is minimized. It can be concluded that the effect of parallel spin of the Tc_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 $^{11}\Sigma_g^-$ and other states of Tc_2 molecule are derived. Dissociation energy D_e for the ground state of T_{c2} molecule is 2.266eV, equilibrium bond length R_e is 0.2841nm, vibration frequency ω_e is 178.52cm^{-1}. Its force constants f_2, f_3, and f_4 are 0.9200aJ·nm^{-2}, −3.5700aJ·nm^{-3}, 11.2748aJ·nm^{-4} respectively. The other spectroscopic data for the ground state of Tc_2 molecule $\omega_e\chi_e$, B_e, α_e are 0.5523cm^{-1}, 0.0426cm^{-1}, 1.6331× 10^{-4}cm^{-1} respectively.

Keywords: Tc_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 4th and 5th periods. But up to now, for the molecular structure of Tc_2, no research has been conducted: neither experimental data on ditechnetium Tc_2 nor theoretical calculation on the technetium dimer are available at present. Nevertheless, several ligated Tc_2 species have been synthesized, which display multiple 4d bonding between the metal atoms.[1] Known chemical species are $Tc_2\ Cl_8^{3-}$ (Tc–Tc bond distance 0.2117nm),[2] $Tc_2\ (O_2CC(CH_3)_3)_4Cl_2$ (Tc–Tc bond distance 0.2192nm),[3] and Tc_2 (2-hydroxypyridine)$_4$ Cl (Tc–Tc bond distance 0.2095nm).[4] These compounds are in marked contrast with what is found for manganese, which does not form multiply bonded dimeric compounds.[1] The nearly comparable sizes of the 4d and 5s orbitals in technetium, as compared to the 3d and 4s orbitals in manganese, probably contribute to the increased stability of the multiply bonded Tc_2 moiety as the Mn_2. This factor, along with the low 5s–4d promotion energy in Tc (0.41eV) as compared to the 4s–3d promotion energy in Mn (2.14eV), suggests that Tc_2 is likely to possess a bonded ground state with a short internuclear distance. In agreement with this model, Miedema and Gingerich predict D_e=3.42eV by using an empirical correlation of bond strength with the heat of vaporization and surface energy of the bulk metal.[5,6]

So far, there is no other useful information about the technetium dimer except for the results of Cotton *et al.*

It is difficult to confirm the ground state of the Tc_2 molecule. This might be related to the delocalization effect of the electron d of $4d^55s^2$. By making use of the density functional method (DFT) (B3p86) of Gaussian98, we optimized the structure of Tc_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- and 11-multiple states of Tc_2 molecule are very close to one another, but even so, the 11-multiple state is the ground state of Tc_2. It follows that in the Tc_2 molecule there ex-

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ists the spin polarization effect. Also, we confirmed that there exist the spin polarization effects in Ti_2 and Ni_2 molecules after we studied the structures of Ti_2 and Ni_2molecules.[7,8] We are currently conducting research into the diatomic molecules of the other transition metal elements and their clusters.

It is generally known that the multiplicity of the ground state of diatomics for light elements is usually comparatively low, for example $2s+1=1\sim4$, which is because of the interaction of electronic configuration, particularly the effect of electron pairing. However, recent work[9] indicates that this is not the case for heavy elements. For example, for molecules Pu_n (n=2, 3, 4), the ground state of plutonium Pu is ^7F_g with 6 unpaired electrons; the unpaired electrons for Pu_2, Pu_3 and Pu_4 will be 12, 18 and 24 in number, respectively; the possible multiplicities will be $2s+1=1$, 3, 5, 7, 9, 11, and 13 for Pu_2, $2s+1=1$, 3, 5, 7, 9, 11, 13, 15, 17, and 19 for Pu_3, $2s+1=1$, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, and 25 for Pu_4. The energy will decrease with multiplicity, and the most stable configurations are of the multiplicities of 13, 19, 25 for Pu_2, Pu_3 and Pu_4, respectively. This is similar to the cases for U clusters. What are the implications of this situation? It means that the electrons prefer parallel spin in Pu_n and U clusters. This sort of non-equilibrium for electron spin is called spin-polarization effect. One of the major current research subjects is the spin-polarization for the actinide element molecules. The potential functions of compounds involving heavy elements are also one of many scientific workers' interests.[10,11]

2. Theoretical techniques and calculation

The electronic configuration of the Tc atom is $4d^55s^2$, where $5s^2$ is fully occupied. From $4d^5$, we can infer that the ground electronic configuration of the Tc atom is ^6S. The Tc_2 molecule composed of $^6S+^6S$ might have 1-, 3-, 5-, 7-, 9- or 11-multiple states. According to the calculations, the ground state of the Tc_2 molecule is 11-multiple state of the parallel spin of 10 electrons, which shows the spin polarization effect of the electron in the molecule.

According to Atomic and Molecular Reaction Statics,[12] the Tc_2 molecule belongs to the $D_{\infty h}$ molecule group, and the electronic configuration of the Tc atom is ^6S. According to the Group Theoretical Derivation of Molecular Electronic States,[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

$$^6S = {}^6\Sigma_g.$$

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

$$\begin{aligned} {}^6S \times {}^6S &= {}^6\Sigma_g \times {}^6\Sigma_g \\ &= {}^1\Sigma_g + {}^3\Sigma_g + {}^5\Sigma_g + {}^7\Sigma_g + {}^9\Sigma_g + {}^{11}\Sigma_g, \end{aligned}$$

where $^1\Sigma_g$, $^3\Sigma_g$, $^5\Sigma_g$, $^7\Sigma_g$, $^9\Sigma_g$ or $^{11}\Sigma_g$ are the possible electronic configurations of Tc_2 molecule. Making use of density functional method (DFT) (B3p86)of Gaussian98, all the possible molecule states have been optimized (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 wavefunctions of higher-energetic states. High spin pollution will influence the molecular structure and the analysis of distributed numbers of molecules, especially the density 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_1 should equal $s(s+1)$, where the s is the total spin value of Tc_2 molecule. In general, the result is acceptable if the error is not beyond 10%.

From Table 1, we can find that the energy of the 11-multiple state of the Tc_2 molecule is lowest, so the 11-multiple state is the ground state of the Tc_2 molecule. As the multiplicity increases, the unpaired electrons increase gradually, that is, in the Tc_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 the spin polarization effect. The pairing of electrons may reduce the energy of the system. However, the commutative integral of spin-parallel electrons is positive, which also leads to a reduction of the energy of the system. This shows that, in the transition element molecules, the effect of spin parallel is larger than the effect of paired electrons. This is obviously related to the delocalization of electron d. Meanwhile, we find that the minimal energy values of 1-, 3-, 5-, 7-, 9-, 11-multiple states of the Tc_2 molecule are very close to

one another. According to our thorough calculations, the ground state of the Tc_2 molecule is the 11-multiple state. That the ground state of the Tc_2 molecule is the 11-multiple state shows that there exists the spin polarization effect in the Tc_2 molecule, the diatomic molecule of transition metal elements. The dissociation energy of the ground state of the Tc_2 molecule (11-multiple state) is D_e=2.266eV. From Table 1, we can find that prospective values and the calculation values of total spin about 3-, 5-, 7-, 9-, 11-multiple states are absolutely the same respectively except that the 1-multiple state does not come up in the optimum result. This shows that there is no spin pollution in the DFT calculations for Tc_2 molecule, and that the wavefunction of the ground state does not mingle with the wavefunctions of higher energy states.

Table 1. Optimum results of Tc_2 molecule.

Multiplicity	State	R_e/nm	E/H.a.u.	Expectance value S_1 of spin	Calculation value S_1 of spin
1		0.20915	–8376.5654		0
3	$^3\Sigma_u^-$	0.19893	–8376.6334	2	2
5		0.21300	–8376.6243	6	6
7		0.24163	–8376.5881	12	12
9		0.26345	–8376.6352	20	20
11	$^{11}\Sigma_g^-$	0.28414	–8376.6493	30	30

3. Potential function and spectral data

Making use of the DFT method (B3p86) of the Gaussian98 program, we calculated the 1-multiple state, 3-multiple state, 5-multiple state, 7-multiple state, 9-multiple state, 11-multiple state of Tc_2 molecule and attained a series of spot values of potential function. Using the least square fitting, we obtained the function form of the Murrell–Sorbie potential function,[13,14] 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 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 the Tc_2 molecule.

Multiplicity	D_e/eV	R_e/nm	$a_1/0.1\text{nm}^{-1}$	$a_2/0.1\text{nm}^{-2}$	$a_3/0.1\text{nm}^{-3}$
11	2.266	0.2841	1.669	0.126	0.299
9	4.081	0.2635	1.334	–0.381	0.278
7	5.344	0.2416	1.333	–0.561	0.328
5	9.277	0.2130	1.476	–0.629	0.340
3	12.233	0.1989	1.731	–0.632	0.589
1	9.576	0.2092	1.309	–1.094	0.338

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. Every state includes two curves: one for the scan value, and the other for fitting value. They accord with each other precisely. This means that the process of fitting is successful. The 11-multiple state is the ground state of the Tc_2 molecule.

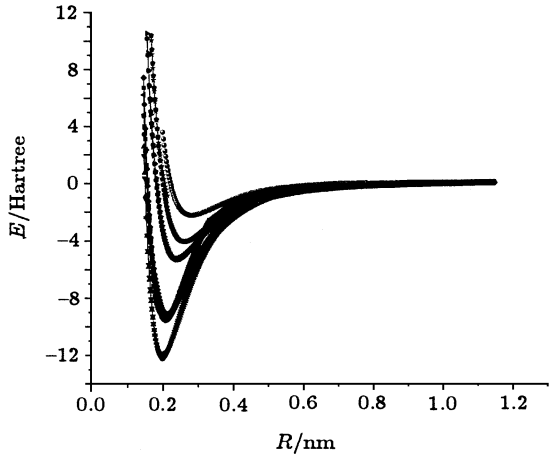


Fig.1. The potential curve for the Tc_2 molecule.

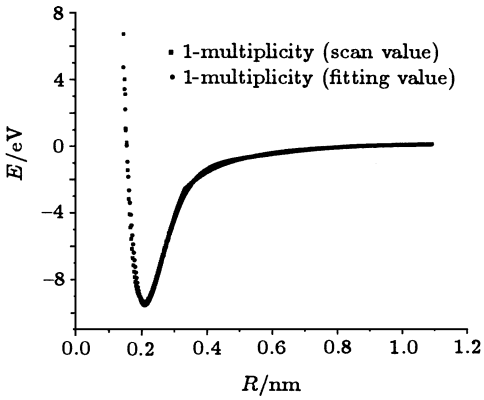


Fig.2. The potential curve of the Tc_2 molecule for 1-multiplicity.

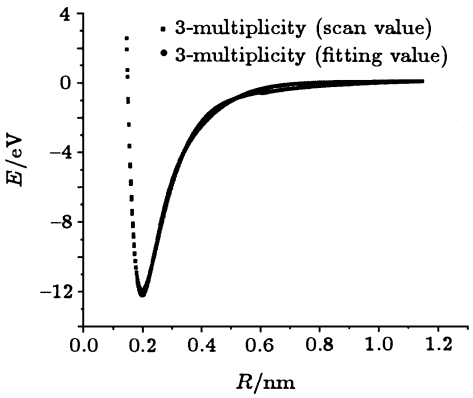


Fig.3. The potential curve of the Tc_2 molecule for 3-multiplicity.

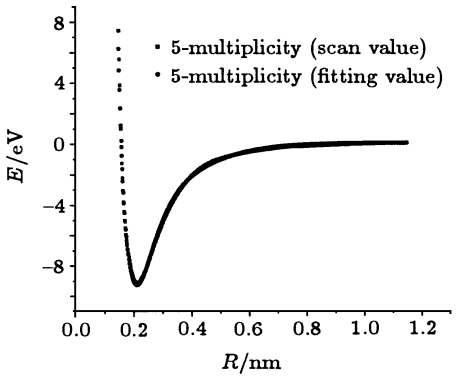


Fig.4. The potential curve of the Tc_2 molecule for 5-multiplicity.

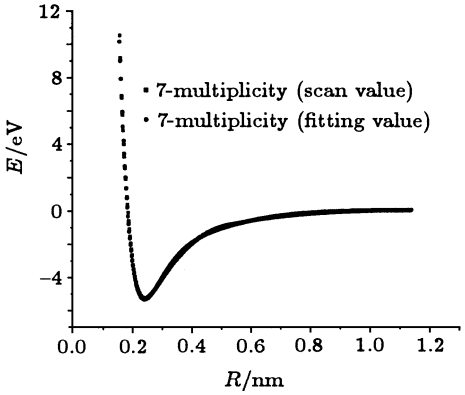


Fig.5. The potential curve of the Tc_2 molecule for 7-multiplicity.

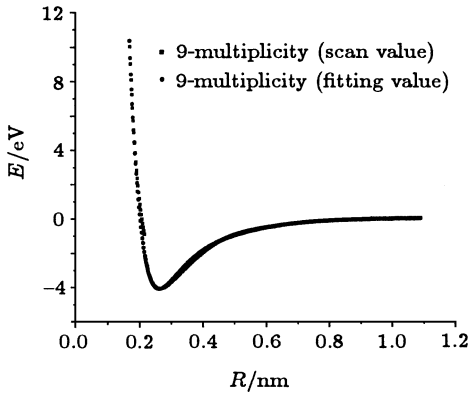


Fig.6. The potential curve of the Tc_2 molecule for 9-multiplicity.

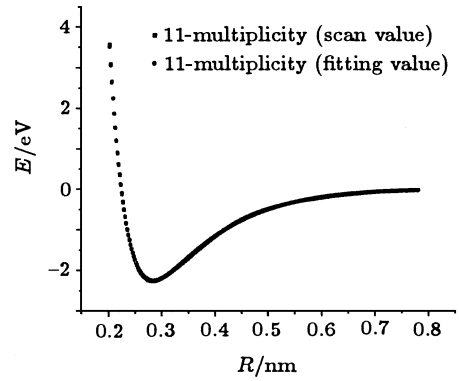


Fig.7. The potential curve of the Tc_2 molecule for 11-multiplicity.

According to the relationship 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 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,[15,16] we can obtained the spectroscopic data and force constants Tc_2 molecule 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 the Tc_2 molecule.

Multiplicity	$f_2/(aJ/nm^2)$	$f_3/(aJ/nm^3)$	$f_4/(aJ/nm^4)$	$\alpha_e/10^{-4}cm^{-1}$	$\omega_e\chi_e/cm^{-1}$	B_e/cm^{-1}	ω_e/cm^{-1}
11	0.9200	–3.5700	11.2748	1.6331	0.5523	0.0426	178.52
9	1.6608	–6.1827	17.3259	1.3949	0.5447	0.0496	239.86
7	2.4819	–9.5791	27.3166	1.4985	0.5944	0.0589	293.22
5	5.1085	–20.8771	63.5385	1.5599	0.6623	0.0758	420.67
3	8.3468	–40.1011	145.1864	1.8437	0.9065	0.0869	537.72
1	5.9865	–23.1757	64.3052	1.3849	0.6123	0.0787	455.39

We used a similar method to calculate for the Ni_2 molecule and the Ti_2 molecule and other transition metal element molecules. The results show that spin-polarization effects exist in them. So we use a similar method to deal with the Tc_2 molecule.

4. Conclusion

Making use of the DFT (B3p86) of the Gaussian98 program, we have calculated the 1-, 3-, 5-, 7-, 9- and 11-multiple states of the Tc_2 molecule one by one. The result shows that the ground state of the Tc_2 molecule should be the 11-multiple state. The minimal energy values of 1-, 3-, 5-, 7-, 9- and 11-multiple states of the Tc_2 molecule are very close to one another. 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 the Tc_2 molecule is the 11-multiple state, which shows the spin polarization effect of the Tc_2 molecule of transition metal elements, and is indicative of the fact that there exist 10 parallel spin electrons in the Tc_2 molecule, where the non-conjugated electron is greatest in number. These electrons occupy different spacious tracks, and in this case, the energy of the Tc_2 molecule is minimal. This shows that the effect of parallel spin of Tc_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 the 11-multiple state (ground state) of the Tc_2 molecule is 2.266eV, and the equilibrium bond length is 0.2841nm. We have obtained the Murrell–Sorbie potential function of the Tc_2 molecule; the vibration frequency is $178.52cm^{-1}$, and the force constants f_2, f_3, and f_4 are $0.9200aJ{\cdot}nm^{-2}$, $-3.5700aJ{\cdot}nm^{-3}$, $11.2748aJ{\cdot}nm^{-4}$ respectively. The electronic configuration of the Tc_2 molecule is $^{11}\Sigma_g^-$. This result is very helpful for us to understand the structural characteristics of the transition metal molecules. We used a similar method to calculate for the Ni_2 molecule and Ti_2 molecule and other transition metal element molecules. The results show spin-polarization effects exist in them. So we use a similar method to deal with the Tc_2 molecule.

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