

## ARTICLE

Spin Polarization Effect for Molecule Fe<sub>2</sub>Zheng-xin Yan<sup>a,b</sup>, An-dong Xie<sup>a,c</sup>, Shi-ying Yan<sup>a</sup>, Jin-he Wu<sup>a,b</sup>, Dong Hu<sup>b</sup>, Xiang-dong Yang<sup>a\*</sup>*a. Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, China; b. Laboratory for Shock Wave and Detonation Physics Research, Institute of Fluid Physics, CAEP, Mianyang 621900, China; c. Department of Physics, College of Jinggangshan, Ji'an 343009, China*

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Density functional method (B3p86) was used to optimize the structure of the molecule Fe<sub>2</sub>. The result showed that the ground electronic state for the molecule Fe<sub>2</sub> is nonet state instead of septet state, which indicates that there is a spin polarization effect in the molecule Fe<sub>2</sub>, i.e., in which there are 8 parallel spin electrons. In this case, the number of the unpaired d-orbit electrons is the largest, and these electrons occupy different spatial orbitals so that the energy of the molecule Fe<sub>2</sub> is minimized. Meanwhile, the spin pollution was not found because the wave functions of the ground state do not mix with those of the higher energy states. In addition, the Murrell-Sorbie potential functions with the parameters for the ground electronic state and other excited electronic states of the molecule Fe<sub>2</sub> were derived. The dissociation energy, equilibrium bond length and the vibration frequency for the ground electronic state of the molecule Fe<sub>2</sub> are 3.5522 eV, 0.2137 nm and 292.914 cm<sup>-1</sup>, respectively. Its force constants  $f_2$ ,  $f_3$  and  $f_4$  are  $1.4115 \times 10^2$  aJ/nm<sup>2</sup>,  $-37.1751 \times 10^3$  aJ/nm<sup>3</sup> and  $98.7596 \times 10^4$  aJ/nm<sup>4</sup>, respectively. The other spectroscopic parameters  $\omega_e X_e$ ,  $B_e$  and  $\alpha_e$  for the ground electronic state of Fe<sub>2</sub> are 0.3522, 0.0345 and  $0.4963 \times 10^{-4}$  cm<sup>-1</sup>, respectively.

**Key words:** Fe<sub>2</sub>, Spin polarization, Density functional theory, Potential function

## I. INTRODUCTION

Much attention has been given, experimentally as well as theoretically, to the analysis of the molecular structures composed of transition elements, especially those of transition elements in the fourth and eighth periods [1-5]. But up to now, the structure of the molecular Fe<sub>2</sub> is not yet understood completely. Theoretical and experimental estimates of the bond dissociation energy,  $D_e(\text{Fe}_2)$ , reported are  $6.30 \pm 0.01$  eV [6,7],  $5.9 \pm 0.2$  eV [8], and 4.0 eV [9]. The dissociation energy of the ground state of the molecule Fe<sub>2</sub> is 3.5522 eV in this work, which is in good agreement with the value of 4.0 eV obtained by Anzelm *et al.* [9].

Our previous papers have shown that there are spin polarization effects in molecules Ti<sub>2</sub>, Tc<sub>2</sub> and Ni<sub>2</sub> [10-12]. We focus on the molecules Fe<sub>2</sub> and other diatomic molecules composed of transition metal elements in this work, in spite of the fact that there are some difficulties in determining the ground state of the molecule Fe<sub>2</sub> owing to its delocalization effect of the d-electron of 3d<sup>6</sup>4s<sup>2</sup>. Using the density functional method (DFT, B3p86), we optimized the molecular structure and obtained the potential energy function of the molecule Fe<sub>2</sub>. The results showed that the ground electronic state of the molecule Fe<sub>2</sub> is nonet state instead of septet state, in spite of the fact that the energies of the other multiplet states of the molecule Fe<sub>2</sub> are very close to each other. This indicates

that there is a spin polarization effect in the molecule Fe<sub>2</sub>.

## II. THEORETICAL CALCULATIONS

The electronic configuration of the Fe atom is 3d<sup>6</sup>4s<sup>2</sup> with 4s<sup>2</sup> fully occupied. For 3d<sup>6</sup>, we can infer that the ground electronic configuration of the Fe atom is <sup>5</sup>D. The possible states of the molecule Fe composed of <sup>5</sup>D+<sup>5</sup>D might be singlet, triplet, quintet, septet, or nonet states. As showed in the calculated results, the ground state of the molecule Fe<sub>2</sub> is <sup>9</sup>Σ<sub>g</sub><sup>+</sup> with eight parallel spin electrons, which shows that there is a spin polarization effect in the Fe<sub>2</sub> molecule.

According to Ref.[13], the molecule Fe<sub>2</sub> belongs to the D<sub>∞h</sub> molecule group, and the electronic configuration is <sup>5</sup>D. From the group theory in Ref.[11], the atom group can be dissolved into the direct summation of the molecule group D<sub>∞h</sub> when two atoms form a linear molecule. That is,

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

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

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

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

where  ${}^1\Sigma_g$ ,  ${}^3\Sigma_g$ ,  ${}^5\Sigma_g$ ,  ${}^7\Delta_u$  and  ${}^9\Sigma_g$  are the possible electronic states of the molecule  $\text{Fe}_2$ . By employing the DFT (B3p86), we have optimized all the possible molecule states (see Table I, the theoretical bond lengths in nm, the lowest energies of the molecules in hartree, and the expected values and the calculated values of the total spin). Spin pollution is the main error in the unrestricted *ab initio* calculation. It often appears in the total energy because the wave function of the ground state mixed with that of the higher-energetic states. High spin pollution will have influences on the determination of the molecular structure and the analysis of distributed electron numbers of molecules, especially the densities of spin, moreover, it also affects the constringency, especially the  $\text{MP}_n$  assignment. The spin pollution can be validated by comparing the expected value of total spin  $S_1$  and the calculated  $S_2$ , if the error is not beyond 10%, the result is generally considered to be acceptable.

TABLE I Optimum results of molecule  $\text{Fe}_2$

Multiplicity	State	$R_e/\text{pm}$	$E/\text{hartree}$	$S_1$	$S_2$
1	${}^1\Sigma_g^+$	170.73	-247.2900	-	0.0
3	${}^3\Sigma_g^-$	182.20	-247.3621	2.0	2.0
5	${}^5\Sigma_g^+$	194.69	-247.4240	6.0	6.0
7	${}^7\Delta_u$	199.62	-247.4735	12.0	12.0
9	${}^9\Sigma_g^+$	213.68	-247.4785	20.0	20.0

From Table I, we find that the energy of  ${}^9\Sigma_g^+$  for the molecule  $\text{Fe}_2$  is the lowest, so  ${}^9\Sigma_g^+$  is the ground state of the molecule  $\text{Fe}_2$ , besides, the number of unpaired electrons goes high gradually as the multiplicity increases. That is to say, the loarger the number of the unpaired electrons in the molecule  $\text{Fe}_2$ , the lower its energy, which is known as the spin polarization effect. Meanwhile, we find that the minimal energy of the other multiplet states of the molecule  $\text{Fe}_2$  are very close to each other. According to our calculated results, the ground state of the molecule  $\text{Fe}_2$  is  ${}^9\Sigma_g^+$ , which shows that there is a spin polarization effect in the molecule  $\text{Fe}_2$ . The dissociation energy of the ground state of the molecule  $\text{Fe}_2$  ( ${}^9\Sigma_g^+$ ) is  $D_e = 3.5522$  eV. It is also noted that in Table I the expected values and the calculated values of the total spin for the other multiplet states are exactly the same except the singlet, owing to the expected values is not available for comparison. Since the errors between  $S_1$  and  $S_2$  in Table I are within 10%, we can draw a conclusion that there is no spin pollution in the DFT calculations for the molecule  $\text{Fe}_2$ , and that the wave functions of the ground state do not mix with those of the higher energy states.

### III. POTENTIAL FUNCTION AND SPECTRAL DATA

By using density functional method (DFT, B3p86), we calculated the energies of the singlet, triplet, quartet, septet, and nonet states of the molecule  $\text{Fe}_2$  and obtained a series of the values of the potential function. Using the least square fitting, we obtained the Murrell-Sorbie potential function [13,14], which can be expressed as

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

where  $\rho = R - R_e$ ,  $R$  is the inter-atomic distance and  $R_e$  is equilibrium value,  $D_e$  is the dissociation energy of the molecular,  $a_1$ ,  $a_2$ ,  $a_3$  are the modulus of the first, the second and the third orders, respectively. The results are shown in Table II.

According to the Murrell-Sorbie potential function above, we can achieve the corresponding potential curves and scan results of the multiple states, as shown in Fig.1: each state includes two curves, one for the scan value, and the other for the fitted value, the two curves are precisely accordant with each other, it means that the fitting process is successful.

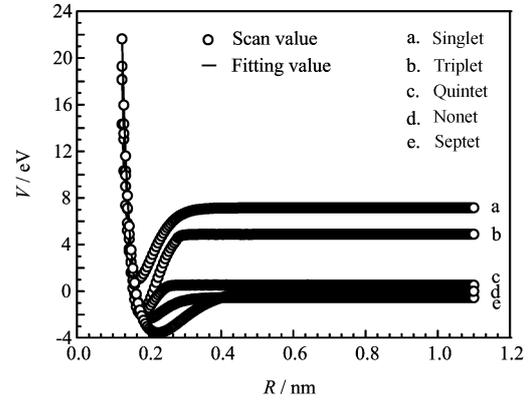


FIG. 1 The potential curve for the  $\text{Fe}_2$  molecule.

According to the relationship between the parameters  $a_1$ ,  $a_2$ ,  $a_3$  of the Murrell-Sorbie potential function, the force constants  $f_2$ ,  $f_3$ ,  $f_4$  and the spectroscopic data  $\omega_e$ ,  $\omega_e\chi_e$ ,  $B_e$ ,  $\alpha_e$  [15,16], we can obtain the relations between the spectroscopic data and the force constants of the molecule  $\text{Fe}_2$  as follows

$$f_2 = D_e(a_1^2 - 2a_2) \quad (2)$$

$$f_3 = 6D_e \left( a_1a_2 - a_3 - \frac{a_1^3}{3} \right) \quad (3)$$

$$f_4 = D_e a_1^4 - 6f_2 a_1^2 - 4f_3 a_1 \quad (4)$$

$$f_2 = 4\pi^2 m \omega_e^2 c^2 \quad (5)$$

$$f_3 = -\frac{3f_2}{R_e} \left( 1 + \frac{\alpha_e \omega_e}{6B_e^3} \right) \quad (6)$$

$$f_4 = \frac{f_2}{R_e^2} \left[ 15 - \left( 1 + \frac{\alpha_e \omega_e}{6B_e^2} \right)^2 - \frac{8\omega_e \chi_e}{B_e} \right] \quad (7)$$

TABLE II Parameters of Murrell-Sorbie potential function for molecule Fe<sub>2</sub>

Multiplicity	$D_e/\text{eV}$	$R_e/\text{nm}$	$a_1/10\text{nm}^{-1}$	$a_2/100\text{nm}^{-2}$	$a_3/1000\text{nm}^{-3}$
9	3.5522	0.2136	2.779	2.6239	1.2218
7	1.7746	1.9962	4.6036	5.6107	2.4572
5	3.9035	0.1947	1.7731	5.4672	1.7466
3	2.7245	0.1822	1.3193	5.1231	2.8828
1	6.1094	0.1707	4.4471	5.6112	3.2250

TABLE III The mechanical parameters and spectral data for the Fe<sub>2</sub> molecule

Multiplicity	$f_2/(\text{aJ}/10\text{nm}^2)$	$f_3/(\text{aJ}/100\text{nm}^3)$	$f_4/(\text{aJ}/1000\text{nm}^4)$	$\omega_e/\text{cm}^{-1}$	$\omega_e\chi_e/\text{cm}^{-1}$	$B_e/\text{cm}^{-1}$	$\alpha_e/10^{-4}\text{cm}^{-1}$
9	1.4116	-3.71751	98.75955	292.91	3.4436	0.1322	3.1363
7	2.8354	-15.609	54.60910	315.14	1.3586	0.1514	8.8348
5	6.8388	-42.9324	175.4923	644.73	3.0202	0.1593	7.2566
3	9.5975	-44.5347	136.1115	763.78	1.6378	0.18185	4.7233
1	8.3731	-44.5614	181.9618	713.40	1.92233	0.20890	7.3981

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

$$B_e = \frac{h}{8\pi^2 cm R_e^2} = \frac{h}{8\pi^2 c I_e} \quad (8)$$

The similar method is also used to calculate the Ni<sub>2</sub>, Tc<sub>2</sub> and Ti<sub>2</sub> molecules and molecules composed of other transition metal element. The results showed that the spin-polarization effect exists in these molecules. So we used the similar method to deal with the molecule Fe<sub>2</sub> and it was believed that our calculation method and the corresponding results were reasonable and acceptable.

#### IV. CONCLUSION

By using the DFT (B3p86) method, we calculated the singlet, triplet, quintet, septet, and nonet states of the molecule Fe<sub>2</sub> and the spin pollution was not found. The result showed that the ground state of the molecule Fe<sub>2</sub> should be nonet state instead of septet state [1]. Their minimal energies are very close to each other. Meanwhile, we found there is a spin polarization effect in the molecule Fe<sub>2</sub>, and the wave functions of the ground state do not mix with those of the higher energy states. The 8 parallel spin electrons occupy different spatial orbitals, and hence the energy of the molecule Fe<sub>2</sub> is minimal. The dissociation energy  $D_e$  of the  ${}^9\Sigma_g^+$  state of the molecule Fe<sub>2</sub> is 3.5522 eV, which is in good agreement with the value of 4.0 eV [9], and the equilibrium bond length is 0.1996 nm. We obtained the Murrell-Sorbie potential function of the molecule Fe<sub>2</sub>, in which the vibration frequency is 292.914 cm<sup>-1</sup>, the force constants  $f_2$ ,  $f_3$  and  $f_4$  are  $1.4115 \times 10^2$  aJ/nm<sup>2</sup>,  $-37.1751 \times 10^3$  aJ/nm<sup>3</sup> and  $98.7596 \times 10^4$  aJ/nm<sup>4</sup>, respectively. This result is very helpful to understanding the molecular structures composed of the transition metal.

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- [1] I. Shim and K. A. Gingerich, *J. Chem. Phys.* **77**, 2490 (1982).
- [2] W. Q. Jiang, C. L. Zhu and Z. Y. Chen, *Chin. J. Chem. Phys.* **14**, 629 (2001).
- [3] G. F. He, Y. X. Ke and S. M. Lu, *Chin. J. Chem. Phys.* **15**, 307 (2002).
- [4] H. R. Cong, X. F. Bian and H. Li, *Chin. J. Chem. Phys.* **15**, 288 (2002).
- [5] H. Zhang, R. Qi and L. Liu, *Chin. J. Chem. Phys.* **16**, 45 (2003).
- [6] E. A. Rohlfing, D. M. Cox, A. Kaldor and K. H. Johnson, *J. Chem. Phys. Lett.* **99**, 161 (1983).
- [7] E. A. Rohlfing, D. M. Cox, A. Kaldor and K. H. Johnson, *J. Chem. Phys.* **81**, 3846 (1984).
- [8] S. S. Lin and A. Kant, *J. Phys. Chem.* **73**, 2450 (1969).
- [9] J. Anzelm, E. Radzio and D. R. Salahub, *J. Am. Chem. Soc.* **100**, 5659 (1978).
- [10] S. Y. Yan, Z. H. Zhu and H. Y. Wang, *J. Sichuan Univ.* **41**, 574 (2004).
- [11] Z. H. Zhu, *Atomic and Molecular Reaction Statics*, Beijing: Science Press (1996).
- [12] S. Y. Yan and Zhu Z H, *Chin. Phys.* **13**, 2053 (2004).
- [13] Z. H. Zhu and H. G. Yu, *Molecular Structure and Molecular Potential Energy Function*, Beijing: Science Press (1997).
- [14] J. N. Murrell, S. Carter, S. C. Farantos, P. Huxley and A. J. C. Varandas, *Molecular Potential Energy Function*, New York: John Wiley Sons Ltd. M (1984).
- [15] J. L. Dunham, *Phys. Rev.* **41**, 721 (1932).
- [16] I. M. Mills, *Theoretical Chemistry*, London: The Chemical Society Press 110 (1974).