Vol 16 No 8, August 2007
1009-1963/2007/16(08)/2356-05
Chinese Physics
© 2007 Chin. Phys. Soc.
and IOP Publishing Ltd

The molecular structure and the analytical potential energy function of S_2^- and S_3^-*

Liu Yu-Fang(刘玉芳)[a], Li Jun-Yu(李俊玉)[a)b)],
Han Xiao-Qin(韩晓琴)[a], and Sun Jin-Feng(孙金锋)[a]

[a] *Department of Physics, Henan Normal University, Xinxiang* 453007, *China*

[b] *Department of Technology and Physics, Zhengzhou University of Light Industry, Zhengzhou* 450002, *China*

(Received 20 November 2006; revised manuscript received 23 December 2006)

In this paper, the equilibrium geometry, harmonic frequency and dissociation energy of S_2^- and S_3^- have been calculated at QCISD/6-311++G(3d2f) and B3P86/6-311++G(3d2f) level. The S_2^- ground state is of $^2\Pi_g$, the S_3^- ground state is of $^2B_1$ and S_3^- has a bent (C_{2V}) structure with an angle of 115.65° The results are in good agreement with these reported in other literature. For S_3^- ion, the vibration frequencies and the force constants have also been calculated. Base on the general principles of microscopic reversibility, the dissociation limits has been deduced. The Murrell–Sorbie potential energy function for S_2^- has been derived according to the ab initio data through the least-squares fitting. The force constants and spectroscopic data for S_2^- have been calculated, then compared with other theoretical data. The analytical potential energy function of S_3^- have been obtained based on the many-body expansion theory. The structure and energy can correctly reappear on the potential surface.

Keywords: S_2^-, S_3^-, molecular structure, potential energy function
PACC: 3120, 3130, 3520D

1. Introduction

Sulfur and its compounds are of widespread importance in chemistry and biology.[1] In recent years there has been increasing interest in pure sulfur molecules and ions.[2−5] S_2 molecule has been studied by many authors,[6,7] but its singly charged ions S_2^+ and S_2^- are rarely studied. In 1991, Li *et al*[3] determined the structure and dissociation limit of S_3 molecule. As we know, potential energy surface (PES) plays a very important role in molecular structure or chemical dynamics study, but constructing a PES even for a simple system is a demanding task. Many-body expansions of the PES are still widely applied in statistical mechanics and molecular dynamics. John *et al*[8] have computed the PES of O_3. For S_2^- and S_3^-, experimental information is very scarce. On the theoretical side, there have been some studies.[9,10] However, most authors focused their work on optimizing equilibrium geometries and electronic states. The sulfur anions S_n^- have also been the subject of many studies, S^-, S_2^- and S_3^- have been identified in single crystals and their electron affinities in the gas phase have been determined by photoelectron spectroscopy to be 2.077 eV, 1.66 eV and 2.09 eV[1] respectively. Some papers have researched into the potential energy function (PEF) of S_2 and S_3, but the analytical potential energy functions (APEF) of S_2^- and S_3^- have not been reported up to now.

2. Computational results of S_3^-

The equilibrium geometries, force constants and vibration frequencies of S_3^- have been calculated by using the B3P86/6-311++G(3d2f) method. All calculations are performed by using the Gaussian 03 program package. The ground-state symmetry of $S_3^-(\tilde{X}^2B_1)$ is of point group C_{2V}, the ground state is of $^2B_1$, the bond structure of S_3^- is 0.19911 nm, the bond angle is 115.6567°. At this time, the total energy is −1193.304 a.u. In addition, the harmonic force constants are determined. See Table 1.

*Project supported by the National Natural Science Foundation of China (Grant No 10574039),the Key Program of Science and Technology Research of Education Ministry, China (Grant No 206084), Innovation Talents of Institution of Higher Education of Henan Province, China (Grant No 2006KYCX002), the Natural Science Foundation of Education Bureau of Henan Province, China (Grant No 200510476004).
†Corresponding author. E-mail: yf-liu@henannu.edu.cn

Table 1. Computational results of S_3^-.

Equilibrium geometries	Harmonic frequencies	Force constants
$R_{SS-} = 0.19911$ nm (0.210 nm)	$\omega_1 = 228.2$ cm^{-1} (232 cm^{-1})	$f_{RR} = 0.19189$ a.u.
$\angle SSS = 115.6567°$	$\omega_2 = 558.8$ cm^{-1} (535 cm^{-1})	$f_{Rr} = 0.02414$ a.u.
$D_e = 12.186$ eV	$\omega_2 = 580.8$ cm^{-1} (585 cm^{-1})	$f_{Ra} = 0.00791$ a.u.
		$f_{aa} = 0.24235$ a.u.

3. Theory—many-body expansion theory

The many-body expression of a triatomic system can be written as[11]

$$V = \sum V_A{}^{(1)} + \sum V_{AB}{}^{(2)} + \sum V_{ABC}{}^{(3)}(R_{AB}, R_{BC}, R_{CA}). \quad (1)$$

If we choose the energy of the ground state of atoms or ions as the reference energy, the $V_A = 0$, as for two-body terms, the Murrell–Sorbie PEF (MSPEF) seems to be a good choice. In general, the three-body term in Eq.(1) is

$$\sum V_{ABC}{}^{(3)}(R_{AB}, R_{BC}, R_{CA}) = PT, \quad (2)$$

where P is the expression of (R_{AB}, R_{BC}, R_{CA}), and should meet the requirement of symmetry; T is range function:

$$T = \prod\nolimits_i (1 - \tanh\gamma_i s_i/2) \quad (i = 1, 2, 3), \quad (3)$$

where γ_i are parameters, and S_i are symmetrical internal coordinates.

4. The dissociation limits and potential energy function of S_2, S_2^-

A number of functions have been proposed to fit APEF of diatomic molecule. Among them, MSPEF seems to be the best one. It can accurately reproduce the interaction potential energies of neutral and univalent diatomic molecules, and has been used to deduce APEFs for many molecules,[12−16] including the ground and excited states. Now, we try to use it to represent the ground states of S_2^-.

In this paper, using ab initio density function B3LYP, B3P86 and quadratic CI calculation QCISD method and on the many basis sets level, we optimized the bond of S_2^-, see Table 2.

Table 2. The bond length optimized result of S_2^-.

	6-311G	6-311G**	6-311G(3d2f)	6-311++G(3d2f)	6-311G(3df,3pd)	6-311++G(3df,3pd)	Ref.
B3LYP	0.22113	0.20606	0.20256	0.20201	0.20242	0.20192	0.20201[17]
QCISD	0.22398	0.20450	0.20160	0.20123	0.20129	0.20100	
B3P86	0.21882	0.20382	0.20066	0.20023	0.20052	0.20014	

First and foremost, we must determine the electronic states and their reasonable dissociation limits, for the analytical potential energy curve is certainly meaningless without indicating its electronic state and dissociation limit. Based on the group theory and the general principles of microscopic reversibility,[18] the reasonable dissociation limit of S_2^- is derived.

The optimum dissociation channel for S_2^- is $S_2^- \rightarrow S + S^-$, where if S and S^- are in their ground states ^3P_g and ^2P_u respectively, then the representations ^3P_g and ^2P_u of the atomic group are resolved into those of $D_{\infty h}(S_2^-)$,

$$^3P_g \rightarrow {}^3\Sigma_g^- \oplus \Pi_g, \qquad ^2P_u \rightarrow {}^2\Sigma_u^+ \oplus {}^2P_u,$$

its direct product:

$$\left({}^3\Sigma_g^- \oplus {}^3\Pi_g\right) \otimes \left({}^2\Sigma_u^+ \oplus {}^2\Pi_u\right) = {}^{2,4}\Sigma_u^-(2) \oplus {}^{2,4}\Pi_u \oplus {}^{2,4}\Pi_u + {}^{2,4}\Sigma_u^+ + {}^{2,4}\Delta_u\,.$$

S_2^- also has the exchange of the excited energy, so there are other possible electronic states: $^{2,4}\Sigma_g^-(2)$, $^{2,4}\Pi_g(2)$, $^{2,4}\Sigma_g^+$, $^{2,4}\Delta_g$, then we can obtain

$$S(^3P_g) + S^-(^2P_u) \rightarrow S_2^-\left(^{2,4}\Sigma_u^-(2),\ ^{2,4}\Pi_u(2),\ ^{2,4}\Sigma_u^+,\ ^{2,4}\Delta_u,\ ^{2,4}\Sigma_g^-(2),\ ^{2,4}\Pi_g(2),\ ^{2,4}\Sigma_g^+\ ^{2,4}\Delta_g\right).$$

The lowest energy level of electronic configuration and its ground state of S_2^- is $X^2\Pi_g$. So its reasonable dissociation limit is

$$S_2^-(X^2\Pi_g) \rightarrow S(^3P_g) + S^-(^2P_u). \quad (4)$$

In order to fit the APEF of $S_2^-(X^2\Pi_g)$, we compute the energies for 101 values of R at QCISD/6-311++G(3d2f) level in the range of the atomic distance R from 0.12 nm to 0.68 nm. By employing the MSPEF and least-squares fitting method, we can deduce the APEF of S_2^-. The MSPEF[19] is

$$V = -D_e(1 + \alpha_1\rho + \alpha_2\rho^2 + \alpha_3\rho^3)\exp(-\alpha_1\rho), \quad (5)$$

where $\rho = R - R_e$, R_e is the equilibrium value, D_e is the dissociation energy. The parameters a_1, a_2, a_3 and D_e are determined by fitting, the results are presented in Table 3.

Table 3. Parameters for MSPEF of S_2,[20] S_2^-.

	States	R_e/nm	D_e/eV	a_1/nm^{-1}	a_2 /nm^{-2}	a_3/ nm^{-3}
S_2	$X^3\Sigma_g^-$	0.18892	4.414	39.54	431.2	2332
S_2^-	$X^2\Pi_g$	0.20123	4.218	26.14	159.3	1007
Ref.[12]		0.3955				

Based on the relationship between the spectroscopic data and APEF, the spectroscopic data can be calculated. The precision and credibility of APEF can be examined by comparing the calculated spectroscopic data with experimental results. First of all, the force constants can be determined from the parameters of the MSPEF[21]

$$f_2 = D_e(\alpha_1^2 - 2\alpha_2), \quad (6)$$

$$f_3 = 6D_e\left(\alpha_1\alpha_2 - \alpha_3 - \frac{\alpha_1^3}{3}\right), \quad (7)$$

$$f_4 = D_e\alpha_1^4 - 6f_2\alpha_2^2 - 4f_3\alpha_1, \quad (8)$$

where f_2, f_3 and f_4 are quadratic, cubic and quartic force constants respectively. Then the spectroscopic data are

$$\omega_e = \sqrt{\frac{f_2}{4\pi^2 mc^2}}, \quad (9)$$

$$B_e = \frac{h}{8\pi c\mu R_e^2}, \quad (10)$$

$$\alpha_e = -\frac{6B_e^2}{\omega_e}\left(1 + \frac{f_3 R_e}{3f_2}\right), \quad (11)$$

$$\omega_e\chi_e = \frac{B_e}{8}\left[-\frac{f_4 R_e^2}{f_2} + 15\left(1 + \frac{\omega_e\alpha_e}{6B_e^2}\right)^2\right]. \quad (12)$$

All calculation results are collected in Table 4.

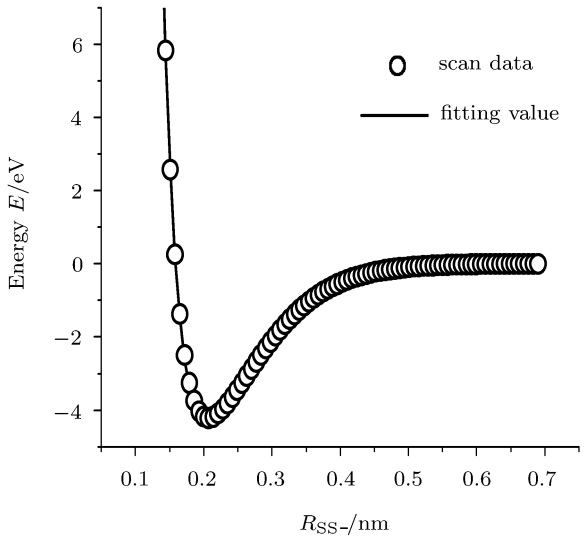


Fig.1. The potential energy curves of $S_2^-(X^2\Pi_g)$.

Table 4. Derived force constants and spectroscopic data of S_2, S_2^-.

	f_2/aJ·nm^{-2}	f_3/aJ·nm^{-3}	f_4/aJ·nm^{-4}	ω_e/cm^{-1}	a_e/cm^{-1}	$\omega_e\chi_e$/cm^{-1}	B_e/cm^{-1}
S_2	432.091	−19965.5	1201800	734.78	0.001498	1.93267	0.30974
S_2^-	246.13	−3561.09	195564	612.8	0.001443	2.8706	0.2735
Ref.[22]				600.8		3.01	

5. The APEF of S_3^-

Based on the selection rule for channels, the reasonable dissociation limit for the ground state of S_3^- is

$$S_3^-(X^2B_1) \rightarrow \begin{cases} S_2(X^3\Sigma_g^-) + S^-(^2P_u), \\ S_2^-(X^2\Pi_g) + S(^3P_g), \\ S(^3P_g) + S(^3P_g) + S^-(^2P_u). \end{cases} \quad (13)$$

The nuclear distances are defined as $R_{SS^-} = R_1 = R_2$, and $R_{SS} = R_3$, then, the PEF based on many-body expansion for $S_3^-(X^2B_1)$ is

$$V = V_{SS}(R_1) + V_{SS^-}(R_2) + V_{SS^-}(R_3) + V_{SSS^-}(R_1, R_2, R_3). \quad (14)$$

The parameters of two-body terms are given in the Table 3. Here, we mainly derived the three-body terms. It is convenient that three-body terms are shown as the functions of symmetrical internal coordinates. We choose C_{2V} symmetry ($R_1^0 = R_2^0 = R_{SS^-} = 0.19911$ nm, $R_3^0 = R_{SS} = 0.33708$ nm) as the reference structure; then the internal coordinates are

$$\rho_i = R_i - R_i^0, \quad (i = 1, 2, 3). \quad (15)$$

The corresponding symmetry internal coordinates are

$$\begin{bmatrix} S_1 \\ S_2 \\ S_3 \end{bmatrix} = \begin{bmatrix} 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 1/\sqrt{2} & -1/\sqrt{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \rho_1, \\ \rho_2, \\ \rho_3, \end{bmatrix}. \quad (16)$$

The three body term is

$$V^{(3)} = PT, \quad (17)$$

where

$$P = C_1 + C_2S_1 + C_3S_2^2 + C_4S_3 + C_5S_1S_2 + C_6S_1^2 + C_7S_3^2, \quad (18)$$

$$T = [1 - \tanh(\gamma_1 s_1/2)][1 - \tanh(\gamma_3 s_3/2)]. \quad (19)$$

S_2 is asymmetrical, when R_1 and R_2 interchange, but the molecule is the same after the interchange. So S_2 has even power. The seven linear parameters $C_1 - C_7$ can be determined by using the equilibrium structure and the force constants (in Table 1) and nonlinear ones γ_1 and γ_3 can be determined by optimizing the PES. The parameters are listed in Table 5.

Table 5. Parameters of three-body term of $S_3^-(X^2B_1)$.

C_1	C_2	C_3	C_4	C_5	C_6	C_7	λ_1	λ_2
−3.8894	−7.190	-406.12	35.092	804.29	166.75	233.95	1.00	1.208

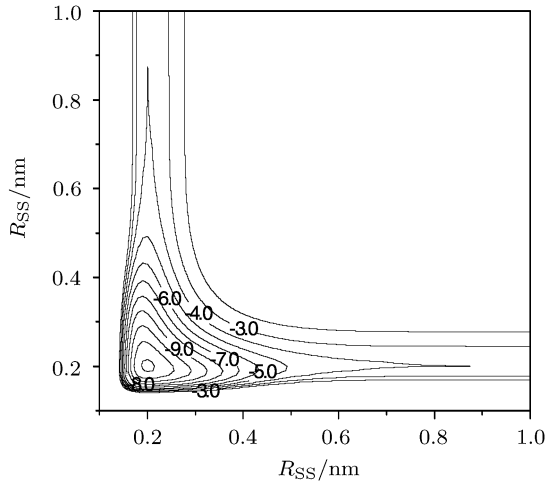


Fig.2. Stretch potential surface of S_3^- (the interval of inoline is 1 eV) ($S - S^-$ bond stretching contours for PES of the ground states $S_3^-(C_{2V}, X^2B_1)$ with a fixed angle 115.66°).

Figures 2–4 are the graphs of contours of the S_3^- PEF. These figures reproduce the equilibrium geometry and potential energy of S_3^-. Fig.2 is the $S - S^-$ bond stretching contours for a fixed angle $\angle SS^-S = 115.66°$. From this figure, we can see that there is a potential well (12.186 eV) at ($R_{SS^-} = R_{SS^-} = 0.19911$ nm) and no saddle point. The contours are symmetrical.[23,24]

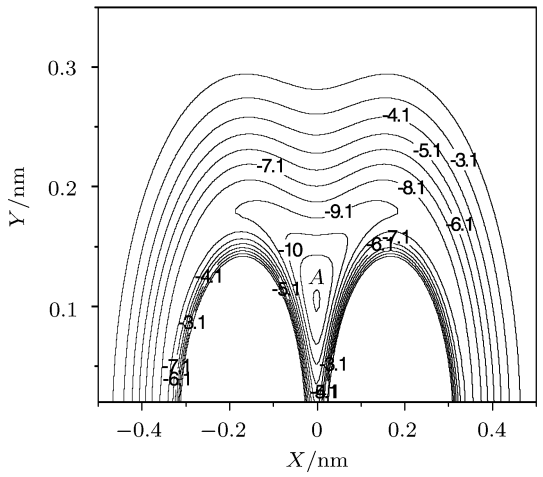


Fig.3. Rotation potential surface of S_3^- (the interval of inoline is 1 eV) (Contours lines of $S_3^-(C_{2V}, X^2B_1)$ for S^- ion moving around the fixed $S - S$ bond 0.33708 nm).

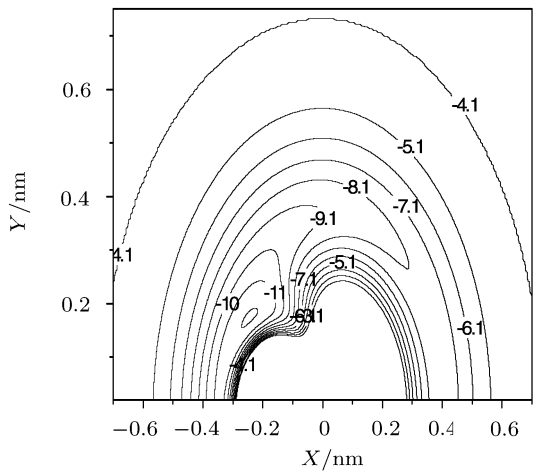


Fig.4. Rotation potential surface of S_3^- (the interval of inoline is 1 eV) (Contours lines of $S_3^-(C_{2V}, X^2B_1)$ for S ion moving around the fixed $S-S^-$ bond 0.1911 nm).

Figure 3 is the contour lines for S^- ion moving around S_2 with the fixed $S-S$ bond 0.33708 nm. The lowest energy is at point $A(-12.186$ eV). The counters reproduce C_{2V} symmetry of $S_3^-(X^2B_1)$. It shows that S_3^- could easily form if S^- attacks S_2 from the front side. Figure 4 is those for S atom moving around $S-S^-$ bond with the bond length 0.1911nm. It shows that S_3^- could easily form if S atom attacks S_2^- from the side. It is in agreement with the result of Fig.3.

6. Conclusions

The correct ground state of the S_2^- has been determined by ab initio calculation at the QCISD/6-311++G(3d2f) level. By employing the MSPEF and the least-squares fitting method, the APEF of the ground state of the S_2^- is deduced from the ab initio results. Based on the APEF, the spectroscopic data are calculated systematically.

The equilibrium geometry, force constants and vibration frequencies of S_3^- have been calculated by using the B3P86/6-311++G(3d2f) method. The geometry and vibration frequencies of them are in good agreement with those in the literature. Based on the group theory and the general principles of microscopic reversibility, the reasonable dissociation limit of $S_3^-(X^2B_1)$ is determined. For the first time, we extended the many-body expansion theory to negative triatomic ion S_3^-, and got satisfactory results. The structure and energy can correctly reappear on the potential surface. The above results are useful for dynamic study of S_2^- and S_3^- ions.

References

[1] Hunsicker S, Jones R O and Gantefor G 1995 *J. Chem. Phys.* **102** 5917

[2] Raghavachari K, Rohlfing C M and Binkley J S 1990 *J. Chem. Phys.* **93** 5862

[3] Li X M, Jiang G and Liu X Y 1999 *J. At. Mol. Phys.* **16** 482

[4] Wong M W and Steudel R 2003 *Chem. Phys. Lett.* **379** 162

[5] Bai Y L and Chen X R 2003 *Acta Phys. Chem. Sin.* **19** 1102

[6] Tang Y J, Zhao Y K and Zhu Z H 1998 *Chem. Phys. Soc.* **47** 1600

[7] Tang Y J, Gao T and Wang H Y 1998 *J. At. Mol. Phys.* **15** 159

[8] John D G, Chen X Q and Galina O 1999 *J. Phys. Chem.* A **103** 478

[9] Koch W, Natterer J and Heinemann C 1995 *J. Chem. Phys.* **102** 6159

[10] Nimlos M R and Ellion G B 1986 *J. Phys. Chem.* **90** 2574

[11] Sato S J 1955 *J. Chem. Phys.* **23** 2465

[12] Wang R, Zhu Z H and Yang C L 2001 *J. Mol. Struc.* (Theochem) **571** 133

[13] Zavitsas A A 2003 *J. Mol. Spectrosc.* **221** 67

[14] Chen L H and Shang R C 2003 *J. Mol. Struc.* (Theochem) **629** 37

[15] Yang C L, Zhang X and Han K L 2004 *J. Mol. Struc.* (Theochem) **678** 183

[16] Wang F H, Yang C L, Zhu Z H and Jing F Q 2005 *Chin. Phys.* **14** 0317

[17] Xu H J, 2004 *Paper for the Degree of Master* (Henan Normal University) (in Chinese)

[18] Shi D H, Liu Y F, Sun J F, Yang X D and Zhu Z L 2006 *Chin. Phys.* **15** 1015

[19] Murrell J N, Farantons S C and Huxeley P 1984 *Molecular Potential Energy Functions* (New York: Wiley)

[20] Zhu Z H, Yu H G 1997 *Molecular Structure and Potentical Energy Function* (Beijing: Science Press) (in Chinese)

[21] Geng Z D, Zhang Y S and Fan X W 2006 *Chin. Phys.* **15** 1257

[22] Hersberg 1979 *Molecular Spectra and Molecular Structure* (New York: Van Nostrand Reinhold)

[23] Yan S Y 2006 *Acta Phys. Sin.* **55** 3408 (in Chinese)

[24] Wang H Y, Zhu Z H, Meng D Q and Wang X L 2003 *Chin. Phys.* **12** 0154