The structure and the potential energy function of AlSO (C_S, X^2A'')*

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By using the B3P86/aug-cc-pvtz method, the accurate equilibrium geometry of the AlSO (C_S, X^2A'') molecule has been calculated and compared with available theoretical values. The obtained results show that the AlSO molecule has a most stable structure with bond lengths of $R_{\rm OAl} = 0.1864$ nm, $R_{\rm OS} = 0.1623$ nm, $R_{\rm AlS} = 0.2450$ nm, together with a dissociation energy of 13.88 eV. The possible electronic states and their reasonable dissociation limits for the ground state of the AlSO molecule were determined based on the principle of atomic and molecular reaction statics. The analytic potential energy function of the AlSO molecule was derived by the many-body expansion theory and the contour lines were constructed for the first time, which show the internal information of the AlSO molecule, including the equilibrium structure and stable point. The analysis demonstrates that the obtained potential energy function of AlSO is reasonable and successful and the present investigations provide important insights for further study on molecular reaction dynamics.

Keywords: AlSO, analytic potential energy function, many-body expansion theory

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1. Introduction

A theoretical study on the chemical reaction mechanism of triatomic molecule is required to build an accurate potential energy surface for a deeper understanding of the dissociation processes at different reaction channels. It has been possible to construct a reliable analytical function, which is capable of covering the whole potential surface of triatomic molecule and giving a quantitative interpretations of kinetic and spectroscopic data since 1975.[1] Understanding the structure and the potential function of interstellar molecule is required to confirm these molecules and to further explore their reaction mechanisms from a dynamic point of view. Meanwhile, it is very important to comprehensively understand the formation and the dissociation processes of the astrophysical species in interstellar chemistry and molecule astronomy. Investigations on the collision processes among these atoms and molecules in astronautical science could reveal the complicated excitation and ionization interaction mechanism.

Aluminum-containing compounds have received increasing attention recently because of their wide applications in solid propellants and explosives. The chemical reactivity of small metal clusters has also been a hot topic owing to the metals' rich behaviours, varied chemical characters and crucial roles in numerous chemical systems, such as aluminium-containing

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compounds AlO, AlS. It is urgent to clearly clarify the interaction mechanism between small interstellar molecules, as some of these compounds exhibite confusing stoichiometric diversity, such as structural isomers.[2] Meanwhile, reactions of aluminum species often play a central role in the flame[3] and the combustion chemistry,[4,5] thus more attention should be paid to aluminum species. It is particularly worth mentioning that the basic chemistry of short-lived species, radical groups and many metastable molecular intermediates has been an active research area over the years. Despite considerable work being done, many questions currently remain unresolved, such as the individual channel dissociation kinetics of the concerned AlSO molecule. As we all know that the SO molecule is an important reactive intermediate produced in the oxidization process of the sulfides with reducibility, which is closely related to the interstellar chemistry processes as well. Accordingly, the study on the compound AlSO, which is synthesized by small radicals such as AlO and SO molecules, will be helpful to understand the chemical properties of the fragments AlO and SO. However, the experimental reports on the AlSO triatomic species are still unavailable, the obtained theoretical reports only focus on basic geometry and energy information.[6,7] Based on above discussion, more efforts for fully understanding the interaction mechanism of the fragments of AlSO are indeed required. To the best of our knowledge, there has been no report related with accurate potential energy surface of AlSO molecule to date. Thus we carried out extensive calculations for the AlSO molecule and gave the first report.

In this work, the equilibrium geometry, dissociation energy, spectroscopic constants and force constants of AlSO were calculated by the B3P86/aug-cc-pvtz method. The possible electronic states and their reasonable dissociation limits for the ground state of the AlSO molecule were determined based on the principle of atomic and molecular reaction statics. The analytical potential energy function of AlSO was derived from the many-body expansion theory. The detailed structures and the bonding mechanisms in the AlSO systems were examined by the B3P86/aug-cc-pvtz methods.

2. Optimization calculation for AlSO

Density functional theory (DFT) based on hybrid B3P86 functional with Dunning's augmented correlation corrected triple zeta plus polarization Gaussian basis set, i.e., B3P86/aug-cc-pVTZ, has been used to optimize the ground state geometries for the AlSO molecule. The selected function is a very successful computational model for optimizing molecular stable structures.[8−11] To derive the analytical potential energy function of AlSO, the stable structure of AlSO should be optimized first by using the B3P86/aug-cc-pvtz method. The dissociation energy ($D_{\rm e}$ = 13.88 eV) and the force constants ($f_{\rm R_1R_1}$ = 0.1018 a.u., $f_{\rm R_1R_2}$ = 0.0254 a.u., $f_{\rm R_2R_2}$ = 0.3141 a.u., $f_{\theta\theta}$ = 0.0481 a.u., $f_{\rm R_1R_3}$ = 0.00575 a.u., $f_{\rm R_2R_3}$ = −0.018 a.u.) could then be obtained simultaneously. The calculated results listed in Table 1 are compared with the available theoretical values, which show that the ground state of AlSO has a C_S configuration.

Table 1. The equilibrium geometry, dissociation energy and force constants of AlSO.

	$R_{\rm OAl}$/nm	$R_{\rm OS}$/nm	$R_{\rm AlS}$/nm
This work	0.1864	0.1623	0.2450
Ref. [5]	0.18611	0.16137	0.24395
Ref. [6]	0.18698	0.16380	0.24848

3. The analytical potential energy function based on many-body expansion for the ground state of AlSO

To derive a correct analytical potential energy function for AlSO, the correct dissociation limits should be determined first. Based on the basic principle of atom and molecular reaction statics,[13] the AlSO has three possible dissociation limits,

$$\mathrm{AlO}\left(X^2\Sigma^+\right) \rightarrow \mathrm{Al}\left(^2P_u\right) + \mathrm{O}\left(^3P_g\right), \quad (1)$$

$$\mathrm{SO}\left(X^3\Sigma^-\right) \rightarrow \mathrm{S}\left(^3P_g\right) + \mathrm{O}\left(^3P_g\right), \quad (2)$$

$$\mathrm{AlS}\left(X^2\Sigma^+\right) \rightarrow \mathrm{Al}\left(^2P_u\right) + \mathrm{S}\left(^3P_g\right). \quad (3)$$

Suppose that the atomic ground state is defined as the energy zero point and R_1, R_2 and R_3 are the SO, AlS and AlO distances, respectively. The analytical potential energy function, satisfied the above three dissociation limits (1), (2) and (3), obtained through the many-body expansion theory can then be expressed as[14]

$$V = V_{\rm SO}^{(2)}(R_1) + V_{\rm AlO}^{(2)}(R_2) + V_{\rm AlS}^{(2)}(R_3) + V_{\rm AlSO}^{(3)}(R_1, R_2, R_3), \quad (4)$$

where $V_{\rm SO}^{(2)}(R_1)$, $V_{\rm AlS}^{(2)}(R_2)$ and $V_{\rm AlO}^{(2)}(R_3)$ are the two-body terms corresponding to SO, AlS and AlO, re-

spectively and the $V^{(3)}_{\rm AlSO}(R_1, R_2, R_3)$ is the three-body term for AlSO, which will be zero if any one of the atoms is moved to infinity. The two- and three-body terms will be described in detail as follows.

3.1. Two-body terms

The potential energy functions of diatomic molecules, SO, AlS and AlO, can be written as the extended Rydberg functions as developed by Murrell and Sorbie,[14]

$$V(\rho) = -D_{\rm e}(1 + a_1\rho + a_2\rho^2 + a_3\rho^3)\exp(-a_1\rho), \quad (5)$$

where $\rho = r - R_{\rm e}$, with r and$R_{\rm e}$ being the diatomic distance and the equilibrium geometry value, respectively. The $D_{\rm e}$ is the ground state dissociation energy. The parameters a_1, a_2 and a_3, fitted using the Murrell–Sorbie function are listed in Table 2, based on which the calculated spectroscopic constants and force constants for SO, AlS and AlO are presented in Table 3.

3.2. Three-body term

The stable C_S structure is taken as a reference coordinate system in the three-body calculations. The internal coordinates are $\rho_i = R_i - R_i^{\rm e}$ $(i = 1, 2, 3)$ and the symmetric internal coordinates are given by[15−17]

$$\begin{pmatrix} S_1 \\ S_2 \\ S_3 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1/\sqrt{2} & 1/\sqrt{2} \\ 0 & 1/\sqrt{2} & -1/\sqrt{2} \end{pmatrix} \begin{pmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \end{pmatrix}. \quad (6)$$

Then, the three-body term in Eq. (4) can be written in the symmetric internal coordinates form as $V^{(3)} = P \cdot T$, where P is a polynomial and T is a range function. The P and T are given by[17−19]

$$\begin{aligned} P =\ & C_1 + C_2S_1 + C_3S_2 + C_4S_1^2 \\ & + C_5S_2^2 + C_6S_3^2 + C_7S_1S_2 + C_8S_2S_3^2 \\ & + C_9S_1(S_2^2 + S_3^2) + C_{10}S_3^4, \quad (7) \\ T =\ & [1 - \tanh(\gamma_1 S_1/2)][1 - \tanh(\gamma_2 S_2/2)] \\ & \times [1 - \tanh(\gamma_3 S_3/2)]. \quad (8) \end{aligned}$$

All the ten coefficients C_i in the polynomial P can be derived in terms of the data in Table 1. The nonlinear coefficients γ_1, γ_2, γ_3 in the range function T can be determined using an optimization method. Table 4 gives all the coefficients of the three-body term of AlSO.

Table 2. The Murrell–Sorbie function parameters for SO, AlS and AlO.

	$R_{\rm e}$/Å	$D_{\rm e}$/eV	a_1/nm^{-1}	a_2/nm^{-2}	a_3/nm^{-3}
SO	1.481	5.43	47.48	650.4	5228
AlO	1.618	5.33	24.09	–41.8	1106
AlS	2.029	3.878	26.34	82.7	466

Table 3. The spectroscopic constants and force constants for SO, AlS and AlO.

	$\omega_{\rm e}$/cm^{-1}	$\omega_{\rm e}\chi_{\rm e}$/cm^{-1}	$B_{\rm e}$/cm^{-1}	$\alpha_{\rm e}$/cm^{-1}	f_2/fJ·nm^{-2}	f_3/fJ·nm^{-3}	f_4/fJ·nm^{-4}
SO	1149.21	5.6295	0.721	0.005737	829.58	–52334.3	3139742
AlO	978.9192	6.9683	0.6413	0.0058	566.97	–34703.5	1657447
AlS	617.0945	3.0728	0.2798	0.00179	328.31	–16325.5	652471

Table 4. The three-body term potential energy function parameters for AlSO.

γ_1	γ_2	γ_3	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
2.0	3.0	0.0	–1.343	–6.161	–15.370	–2.998	–8.673	–0.223	–11.992	23.174	2.338	1.719

4. Results and discussion

The contours of the potential energy surface of AlSO are presented in Figs. 1–3, which clearly reproduce the characters of the ground state of the AlSO molecule in its equilibrium structure. Figure 1 shows the stretching contours of the Al–S and the S–O bonds at the fixed angle of the equilibrium structure ($R_{\rm OAl}$ = 0.1864 nm, $R_{\rm OS}$ = 0.1623 nm, $R_{\rm AlS}$ = 0.2450 nm). We can see that there is a potential well (–13.88 eV) at the equilibrium structure, which is also consistent with the calculated dissociation energy (–13.88 eV) of the sta-

ble geometry. It is of great interest to find that there is no saddle points on the reaction channels O+AlS and S+AlO. This means that the Al atom can easily attack the SO bond from both sideways. Moreover, the absence of evident potential barrier during the reaction indicates that this could be a non-threshold energy reaction and can easily occur.

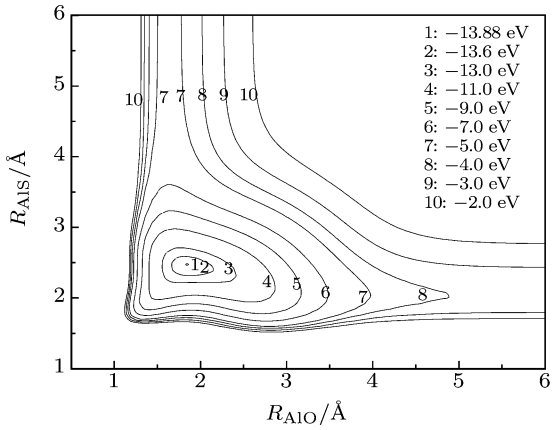


Fig. 1. Contours of the AlSO potential for stretch vibration.

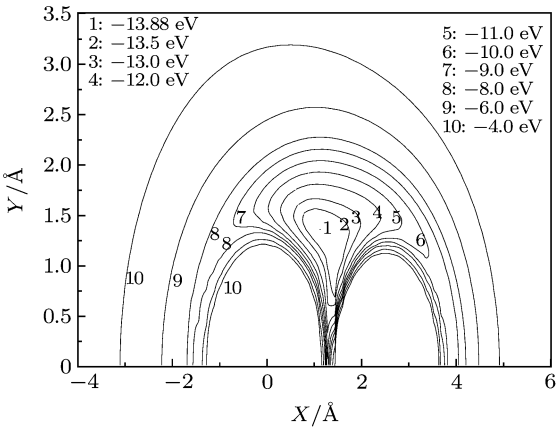


Fig. 2. Rotational contours of the AlSO potential energy function for O moving around Al–S.

Figure 2 shows the contours for O atom moving around the fixed Al–S bond. The contours reproduce the C_S symmetrical structure of AlSO. The AlSO molecule could be formed easily if the Al atom attacks the S–O bond from the O atom sideway. The corresponding angle is about 90°, which is also in accord with the optimized structure and agrees well with the result of Fig. 1.

Figure 3 shows the contours for the S atom moving around the Al–O bond, which is fixed at $R_{\mathrm{OAl}} = 0.1864$ nm on the X axis. Analysis shows that the obtained ground state AlSO analytical potential energy function successfully reflects the equilibrium structure characters and the dissociation limit features.

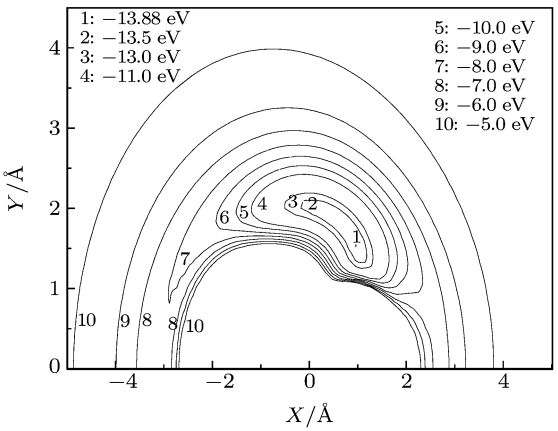


Fig. 3. Rotational contours of the AlSO potential energy function for S moving around Al–O.

5. Conclusions

The equilibrium geometry and the force constants of the AlSO molecule have been calculated with the B3P86/aug-cc-pvtz method. We scan the potential energy curves for the ground state of SO, AlS, AlO molecules by the same method and obtain the spectroscopic constants and the force constants for SO, AlS and AlO molecules. Based on the principle of atomic and molecular reaction statics, the dissociation limits of AlSO have been determined. For the first time, we computed the potential energy function of AlSO by the many-body expansion theory. The contours of the potential energy surface clearly reproduce the characters of the ground state AlSO. The obtained results are important and provide valuable information for molecular reaction dynamic studies and spectroscopic studies of AlSO.

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