Numerical Calculation of Three-Dimensional Ground State Potential Energy Function of Na$_2$F System

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1. Introduction

Because the alkali atoms are small electron affinity, the excess electron in the alkali anion is loosely bound in space. Recently, alkali metal diatomic molecules are found to form stoichiometric system with various new elements. On the contrary, sodium fluoride phosphate is the core of the electrolyte material NaF, and other electronic injection material introductions of organic optoelectronic devices have become a good luminescent material [1–4]. Na$_2$F system belongs to super valence optical properties, so the scientists study on super molecular structure of alkali metal fluoride which has always maintained a strong interest in Na$_2$F system [5–7].

The first thing we should do is to build precise PES when we studied reaction kinetics characteristics. In the past ten years, some studies on polarization molecular science of the system offer Na$_2$F system structure and the dynamic response process [8–14]. Through investigation, we learned that most of the potential energy surface of Na$_2$F system before is studied using semiempirical fitting.

In our calculations, there were 1460 adiabatic energy points chosen from previous 3D diabatic PES. In this paper, our calculations covered a wide range of interaction energy of the potential energy surface including the peak area, the well area, and the long-range area. We considered this system is vibrational weakly bound van der Waals complexes and the good performance on similar optimization, then we used the CCSD (T) calculation method for single point of interaction energy. By fitting, we gave the algebraic analytic function of the Na$_2$F system. Finally, we analyzed the three-dimensional characteristics of the potential energy surface.

2. Methodology

The electronic related functions must be considered when we do calculation, because the single-point energy calculation and geometric optimization (including optimization to transition states) are the most common types of tasks. The sensitivity of geometric optimization to the basis group is much lower than the calculation of single point energy, and the time of geometric optimization is ten times, dozens of times, or even hundreds of times of the single point calculation, so the geometric optimization absolutely does not need large basis group; using medium basis group is enough.
In consideration of computational efficiency, we have chosen the basis sets of aug-cc-pCVQZ for the sodium atom and the basis sets of aug-cc-pCVQZ for the fluorine atom. In order to improve the convergence of basis set, we added an additional (3s3p2d) set of midbond functions (mf) at the midpoint of \( R \). We used quantum analysis framework in the process of computing the Jacobi coordinates system \((r, R, \theta)\). As shown in Figure 1, \( r \) is the distance of Na-Na, \( R \) is the length of the vector connecting the Na-Na center of mass and the F atom, and \( \theta \) is the angle between \( R \) and the \( x \)-axis. For a given value of \( R \), the angle \( \theta \) changes from 0° to 360° in steps of 10°. We calculated 1460 geometries for the whole interaction energy, and the ground state of the spacing is \( r_s = 3.228a_0 \) [15].

The whole ab initio calculations have been calculated with Gaussian 09 W perform packet [16]. We considered all electronic correlation calculation processes. When we calculated the interaction between alkali metal pairs to the atom fluoride for the supramolecular systems described here, they are only weakly adsorbed on a substrate, so the method of supramolecular was used.

In order to avoid the fluorine atom to be too close to the geometric center of Na-Na set, in the process of calculation, we added diffuse augmentation functions to ensure that the basis permits polarization by Na-Na. In the peak area (the short range) \( 0a_0 < R < 4a_0 \) and \( \theta = -60° \sim 60° \) and \( 120° \sim 240° \), we used the interval equal step way \( \Delta R = 0.1a_0 \). In the well area \( 4a_0 < R < 12a_0 \) and \( \theta = -70° \sim 110° \) and \( 250° \sim 290° \), we used the interval equal step way \( \Delta R = 0.2a_0 \). In the long-range area \( 4a_0 < R < 12a_0 \) and \( \theta = -0° \sim 360° \), we used the interval equal step way \( \Delta R = 1a_0 \). The aim is to hope that it describes the characteristics of the peak value and potential well more clearly.

We calculated the freeze the nuclear energy \( E \) as follows:

\[
E(r, R, \theta) = E_p(r, R, \theta) + E_w(r, R, \theta) + E_l(r, R, \theta)
\]  

where \( E(\ldots) \) represents the total electronic energy of respective species including zero point correction. The function contains the location of the potential peak range \( E_p \), the well area \( E_w \), and the long range \( E_l \). The peak range and the well range include a damped dispersion expansion.

The exponential functional form is as follows:

\[
E(r, R, \theta) = \sum_{n=4}^{9} \sum_{l=0,2,\cdots} \int f_n(A(\theta)R) \times \frac{B(\theta)}{R^l} L_l^2(I) \cos(\theta),
\]

where the term \( f_n(x) \) is defined by

\[
f_n(x) = 1 - e^{-x} \sum_{k=0}^{n} \frac{x^k}{k!}.
\]

\( A(r, \theta) \) and \( B(r, \theta) \) denote expansions in Legendre polynomials \( P_l(\cos \theta) \):

\[
A(r, \theta) = \sum_{I=0}^{L} a_i(r) P_i(\cos \theta),
\]

\[
B(r, \theta) = \sum_{I=0}^{L} b_i(r) P_i(\cos \theta).
\]

We present all the fitting parameters for the analytic PES in Table 1; the 1460 ab initio points on the PES are fitted to a 10-parameter algebraic form. The maximum error is 0.0565%, and the average absolute error is less than 0.00483%.

### Table 1: Parameters for the analytic PES of the Na₂F system.

| \( l \) | \( a_l \) | \( b_l \) |
|---|---|---|
| 0 | \( 5.272 \times 10^{-3} \) | \( 4.011 \times 10^{-6} \) |
| 2 | \( 1.411 \times 10^{-5} \) | \( 8.643 \times 10^{-7} \) |
| 4 | \( 9.565 \times 10^{-5} \) | \( 6.153 \times 10^{-7} \) |
| 6 | \( 3.099 \times 10^{-8} \) | \( 2.225 \times 10^{-7} \) |
| 8 | \( 5.057 \times 10^{-6} \) | \( 2.457 \times 10^{-5} \) |

3. **Results and Discussion**

We show the behavior of the potential energy surface from ten different anglers as we can see in Figure 2. From the picture, we can analyze that the peak appears in the region of \( 0a_0 < R < 3a_0 \), with the increase of \( R \) ten different points of view of potential energy are gradually increasing. An obvious the potential barrier appears at \( \theta = 0° \). After reaching different peaks, the potential energy reduces with the increase of \( R \). In the scope of \( R > 5a_0 \), the potential energy changes flatten. Potential energy curve appearing in the overall trend is consistent; there are differences between the local
phenomena. The calculation results show that the highest peak to linearity of Na-Na-F angle of 0° the height of the barrier is 721 eV at $R = 2.6a_0$.

Figure 3 shows the details of Figure 2 when we discuss $R$ in the potential well area. In Figure 3, we can clearly see that an obvious potential well appears at $\theta = 90°$. When the angle changes from 70 to 90 degrees by the interval equal step way $\Delta \theta = 10°$, the position of the potential well also decreases with the increase of $R$ coordinates, 90 degrees at the minimum, that is, the potential energy surface potential well position. The shallow potential well appears as the Na-F-Na configuration angle of 90°; the depth of potential well is -5.3061 eV at $R = 3a_0$.

In Figure 4, we can see clearly that as the $R$ increases in the large area of the long range, the interaction converges to the same asymptotic value. The shape of a “T” backwards (Na-F-Na) is the lowest energy configuration of -5.3061 eV at $R = 3a_0$ which is close to that obtained from the experiment [17].

In Figure 5, we show the 3D-PES for angles $\theta = -90° \sim 360°$. The figure shows that the potential energy changes the present strong anisotropy. The highest peak to linearity of Na-Na-F angle of 0° is very clear. Also we can see that a shallow well appears at $\theta = 90°$.

There are two obvious peaks on the ground state potential energy surface in Figure 5. The peak corresponds to the
left Na$_2$F, and the right peak corresponds to the Na-F-Na reactants. We can easily see that the whole potential energy changes in large angle are anisotropic. By analytic potential energy function, we can know that whether there are two symmetric saddle points on the static potential energy surface, reaction for the threshold. Such features, reflected the alkali metal diatomic molecules interact with the fluorine atoms, in short range has the strong exclusive but in the long-range attract each other.

In Table 2, we compared the calculation results with the experimental data and analyzed the previous calculation results of others. Because the basis group used in our calculation is appropriate, there is not much difference with the experimental results, so our model is reasonable and the calculation is reliable.

### 4. Conclusion

We adopted ab initio calculation method to calculate the ground state potential energy of Na$_2$F system and $r_e$ fixed at 3.228a$_0$. We draw out the potential energy surface in the whole process of the three-dimensional space, by the continental scientific drilling CCSD (T) method and aug-cc-pCVQZ/aug-cc-pCVDZ+332 basis set for the sodium atom and the fluorine atom, respectively. Compared with previous experience and semiempirical potential curves earlier, our theoretical results agree well with the experimental data.
Data Availability
The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Conflicts of Interest
The authors declare that they have no conflicts of interest.

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