

Research Article

Numerical Calculation of Three-Dimensional Ground State Potential Energy Function of Na_2F System

Yue Wang , Yu Liu, BiLv Fang, Gan Gao, Chengwen Zhang, and Dezhi Dong

Department of Electrical Engineering, Tongling University, Tongling, 244000 Anhui, China

Correspondence should be addressed to Yue Wang; wangyue@tlu.edu.cn

Received 18 May 2022; Revised 6 June 2022; Accepted 24 June 2022; Published 20 July 2022

Academic Editor: Meraj Ali Khan

Copyright © 2022 Yue Wang et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

We present a new three-dimensional global potential energy surface (PES) for the ground state of Na_2F system. A total of about 1460 points were generated for the PES. All of the points have been carried out by using the coupled-cluster single-, double-, and perturbative triple-excitations [CCSD(T)]. Two Jacobi coordinates, R and θ , and the frozen molecular equilibrium geometries were used. We mixed the basis sets of aug-cc-pCVQZ for the sodium atom and the basis sets of aug-cc-pCVDZ for the fluorine atom with an additional (3s3p2d) set of midbond functions; the energies obtained were extrapolated to the complete basis set limit. The whole calculation adopted supramolecular approximation approach. We divided the potential energy surface into three regions, the peak region, the well region, and the long range region, and calculate the single point energy, respectively. Our ab initio calculations will be useful for future studies of the collision-induced absorption for the $\text{Na}_2\text{-F}$ dimer, and it can be used for modeling the dynamical behavior in Na_2F system too.

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 be 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_2F system belongs to super valence compounds containing odd electronic; it has good nonlinear optical properties, so the scientists study on super molecular structure of alkali metal fluoride which has always maintained a strong interest in Na_2F 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_2F system structure and the dynamic response process [8–14]. Through investigation, we learned that most of the potential energy surface of Na_2F 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_2F 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-pCVDZ 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, θ) . 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 θ is the angle between R and the x -axis. For a given value of R , the angle θ 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 $r_e = 3.228a_0$ [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 $\theta = -60^\circ \sim 60^\circ$ and $120^\circ \sim 240^\circ$, we used the interval equal step way $\Delta R = 0.1a_0$. In the well area $0a_0 < R < 4a_0$ and $\theta = -70^\circ \sim 110^\circ$ and $250^\circ \sim 290^\circ$, we used the interval equal step way $\Delta R = 0.2a_0$. In the long-range area $4a_0 < R < 12a_0$ and $\theta = -0^\circ \sim 360^\circ$, 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:

$$E(r, R, \theta) = E_p(r, R, \theta) + E_w(r, R, \theta) + E_l(r, R, \theta) \quad (1)$$

where $E(\dots)$ 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:

$$E(r, R, \theta) = \sum_{n=4}^8 \sum_{l=0,2,\dots} f_n(A(\theta)R) \times \frac{B(\theta)}{R^n} P_l^0(\cos \theta), \quad (2)$$

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

$$f_n(x) = 1 - e^{-x} \sum_{k=0}^n \frac{x^k}{k!}. \quad (3)$$

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

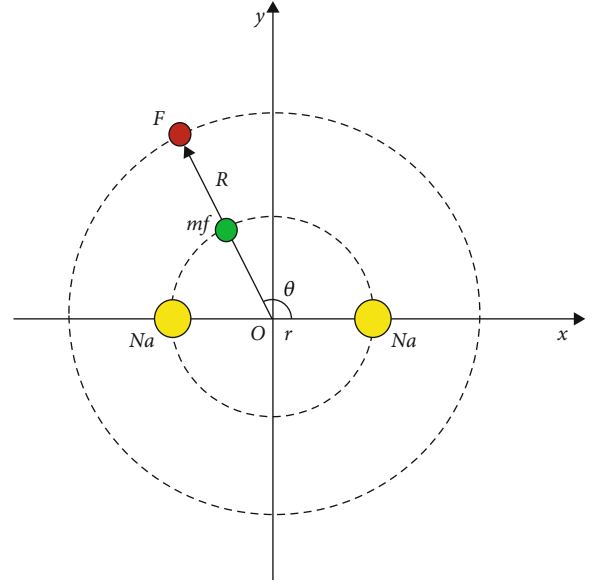


FIGURE 1: The coordinate system for calculation.

TABLE 1: Parameters for the analytic PES of the Na_2F system.

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

$$A(r, \theta) = \sum_{l=0}^{L_1} a^l(r) P_l(\cos \theta), \quad (4)$$

$$B(r, \theta) = \sum_{l=0}^{L_1} b^l(r) P_l(\cos \theta).$$

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%.

3. Results and Discussion

We show the behavior of the potential energy surface from ten different angles 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 $\theta = 0^\circ$. 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

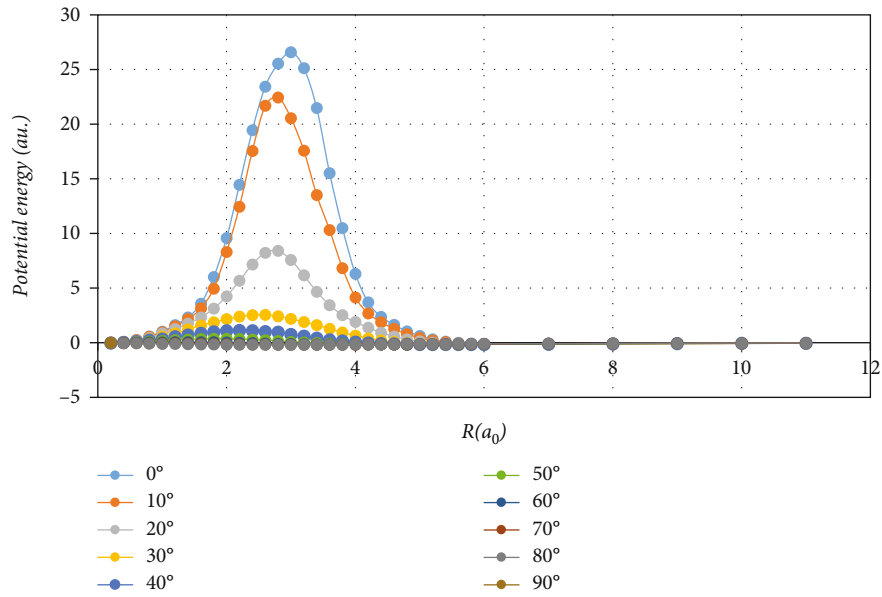


FIGURE 2: The analysis of the peak from 0 to 90 degrees for the potential curve.

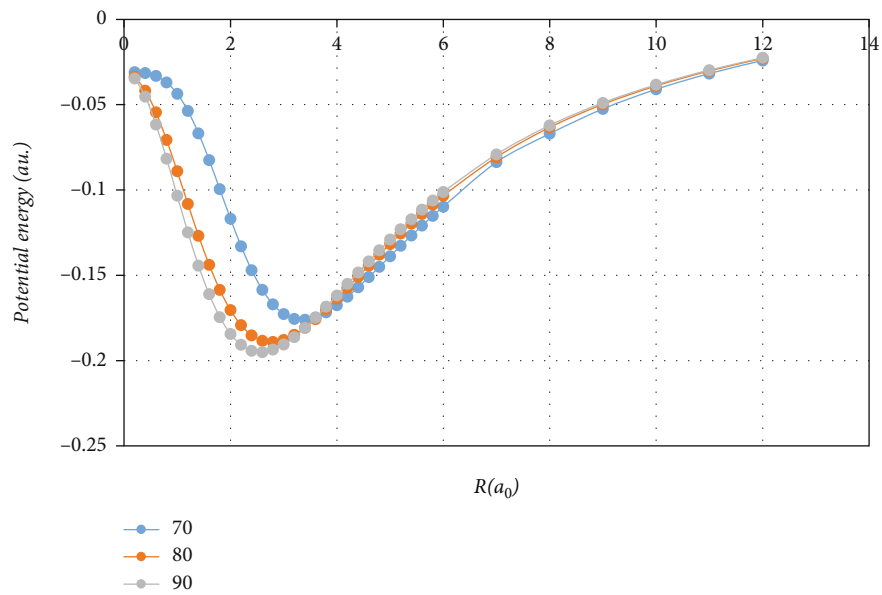


FIGURE 3: The analysis of the potential well from 70, 80, and 90 degrees for the potential curve.

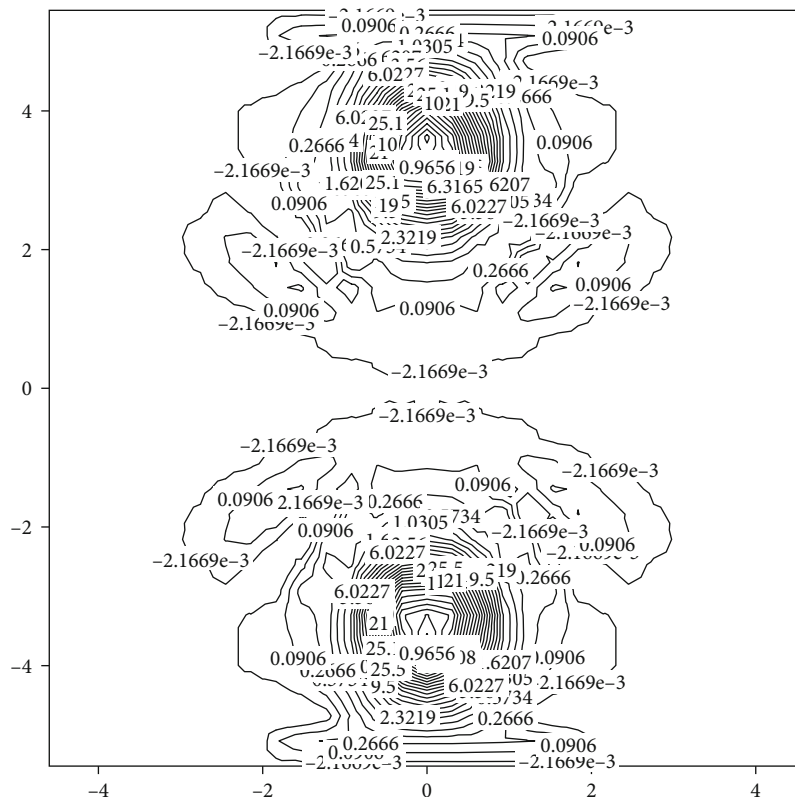
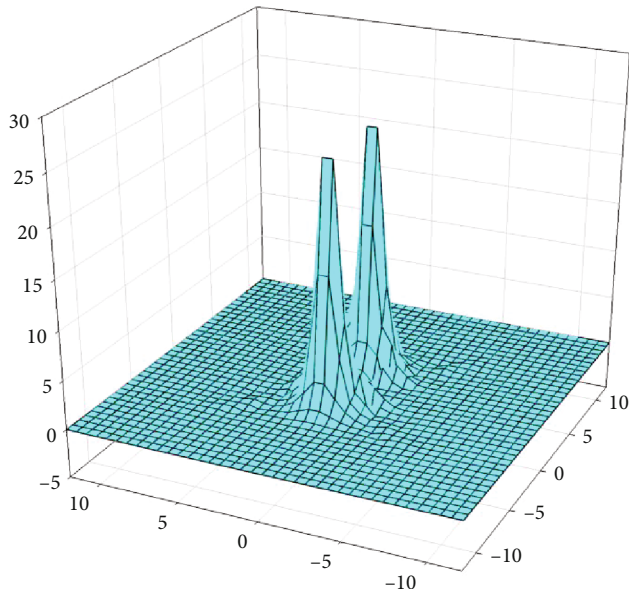
phenomena. The calculation results show that the highest peak to linearity of Na-Na-F angle of 0° the height of the barrier is 721 eV at $R = 2.6a_0$.

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 $\theta = 90^\circ$. When the angle changes from 70 to 90 degrees by the interval equal step way $\Delta\theta = 10^\circ$, 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 $\theta = -0^\circ \sim 360^\circ$. 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 $\theta = 90^\circ$.

There are two obvious peaks on the ground state potential energy surface in Figure 5. The peak corresponds to the

FIGURE 4: Contours of the V00 PES for Na_2F system.3D potential energy (au.) for Na_2F FIGURE 5: PES for the Na-Na-F (angle $\theta = -0^\circ \sim 360^\circ$).

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 sur-

TABLE 2: Comparison of the barriers with experimental values.

| Parameters | Experimental data (Ref. [17]) | Ref. [12] | Relative error | Ours | Relative error |
|-------------------------|----------------------------------|--------------|-------------------|-------|-------------------|
| $R_{\text{Na-Na}}(a_0)$ | 3.30 | 3.224 | 2.3% | 3.228 | 2.18% |
| $D(\text{eV})$ | 5.3 | 5.72 | 7.9% | 5.306 | 0.1% |

face, reaction for the threshold. Such features, reflects 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_2F 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.

Acknowledgments

The authors acknowledge the key projects of science research in the University of Anhui Province (Grants: KJ2020A0695, KJ2021A1059, and KJ2020A0699); the Teaching Demonstration Class Project in Anhui Province (Grant: 2020SJJXSFK2400); the Innovation Project of Excellent Talents Training in Anhui Province (Grant: 2020zyrc153); Tongling University grassroots party construction model branch project; the Key Teaching Research Projects in Anhui Province (2021jyxm154); the College Students' Innovative Training Program (Grants: tlxy2022103830001 and tlxy2022103830004).

References

- [1] F. A. Fernandez-Lima, O. P. VilelaNeto, A. S. Pimentel et al., "A theoretical and experimental study of positive and neutral LiF clusters produced by fast ion impact on a polycrystalline LiF target," *The Journal of Physical Chemistry*, vol. 113, no. 9, pp. 1813–1821, 2009.
- [2] J. E. Del Bene, I. Alkorta, and J. Elguero, "Characterizing complexes with F–Li⁺–F lithium bonds: structures, binding energies, and spin–spin coupling constants," *The Journal of Physical Chemistry A*, vol. 113, no. 29, pp. 8359–8365, 2009.
- [3] B.-Q. Wang, Z.-R. Li, D. Wu, and F.-F. Wang, "Structures and static electric properties of novel alkalide anions F⁻Li⁺Li⁻ and F⁻Li₃⁺Li₃⁻," *The Journal of Physical Chemistry A*, vol. 111, no. 28, pp. 6378–6382, 2007.
- [4] A. A. Redkin and O. Y. Tkacheva, "Electrical conductivity of molten fluoride–oxide melts," *Journal of Chemical & Engineering Data*, vol. 55, no. 5, pp. 1930–1939, 2010.
- [5] J. Cheng, R. Li, Q. Li et al., "Prominent effect of alkali metals in halogen-bonded complex of MCCBr–NCM⁺ (M and M⁺ = H, Li, Na, F, NH₂, and CH₃)," *The Journal of Physical Chemistry A*, vol. 114, no. 37, pp. 10320–10325, 2010.
- [6] H. Wan, Z. Liu, G. Liu et al., "A strategy to improve the electrochemical performance of Ni-rich positive electrodes: Na/F-co-doped LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂," *Chinese Physics B*, vol. 30, no. 7, pp. 073101–073151, 2021.
- [7] Z. Z. Hao, S. L. Wu, Y. C. Wang, G. P. Luo, H.-I. Wu, and X.-g. Duan, "Acting mechanism of F, K, and Na in the solid phase sintering reaction of the Baiyunebo iron ore," *International Journal of Minerals, Metallurgy, and Materials*, vol. 17, no. 2, pp. 137–142, 2010.
- [8] A. W. S. Antunes, W. F. Da Cunha, G. M. E. Silva, J. B. L. Martins, and R. Gargano, "Dynamical properties and thermal rate coefficients for the Na + HF reaction using genetic algorithm," *International Journal of Quantum Chemistry*, vol. 110, no. 5, pp. 1070–1079, 2010.
- [9] L. Xiao-jun, H. Xian-li, and S. Rui-juan, "Theoretical study of structures, stabilities, and infrared spectra of the alkali-metal (Li₂F)_nM (M=Li, Na, K; n=1, 2) clusters," *Spectroscopy and Spectral Analysis*, vol. 7, pp. 2064–2069, 2018.
- [10] W. Chen, Z. R. Li, D. Wu et al., "Nonlinear optical properties of alkalides Li⁺(calix[4]pyrrole)_nM⁻ (M = Li, Na, and K): alkali anion atomic number dependence," *Journal of the American Chemical Society*, vol. 128, no. 4, pp. 1072–1073, 2006.
- [11] S. V. Abramov, N. S. Chilingarov, A. Y. Borshchevsky, and L. N. Sidorov, "Mass spectrometric determination of partial pressures of ions in the saturated vapor over the NaF–Na₃AlF₆ system," *International Journal of Mass Spectrometry*, vol. 231, no. 1, pp. 31–35, 2004.
- [12] A. K. Srivastava and N. Misra, "Structures, stability, and electronic properties of novel superalkali-halogen clusters," *Journal of Molecular Modeling*, vol. 21, no. 6, p. 147, 2015.
- [13] E. Cochran, G. Muller, and G. Meloni, "Stability and bonding of new superalkali phosphide species," *Dalton Transactions*, vol. 44, no. 33, pp. 14753–14762, 2015.
- [14] Z. J. Li, Z. R. Li, F. F. Wang et al., "Cis–trans isomerization and spin multiplicity dependences on the static first hyperpolarizability for the two-alkali-metal-doped saddle[4]pyrrole compounds," *Theoretical Chemistry Accounts*, vol. 122, no. 5–6, pp. 305–311, 2009.
- [15] A. K. Srivastava and N. Misra, "M₂X (M= Li, Na; X= F, Cl): the smallest superalkali clusters with significant NLO responses and electride characteristics," *Molecular Simulation*, vol. 42, no. 12, pp. 981–985, 2016.
- [16] "Gaussian 09W is a package of ab initio programs written by M J Frisch, G W Trucks with contributions from others; for more information," <http://gaussian.com/glossary/g09/>.
- [17] M.-C. Heitz, G. Durand, F. Spiegelman, and C. Meier, "Time-resolved photoelectron spectra as probe of excited state dynamics: a full quantum study of the Na₂F cluster," *Journal of Chemical Physics*, vol. 118, no. 3, pp. 1282–1291, 2003.