



# Investigations of the reaction mechanism of sodium with hydrogen fluoride to form sodium fluoride and the adsorption of hydrogen fluoride on sodium fluoride monomer and tetramer

Qinwei Yu<sup>1</sup> · Jianming Yang<sup>1</sup> · Hai-Rong Zhang<sup>2</sup> · Peng-Yu Liang<sup>2</sup> · Ge Gao<sup>2</sup> · Yongna Yuan<sup>3</sup> · Wei Dou<sup>2</sup> · Pan-Pan Zhou<sup>2</sup>

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## Abstract

**Context** The reaction between Na and HF is a typical harpooning reaction which is of great interest due to its significance in understanding the elementary chemical reaction kinetics. This work aims to investigate the detailed reaction mechanisms of sodium with hydrogen fluoride and the adsorption of HF on the resultant NaF as well as the (NaF)<sub>4</sub> tetramer. The results suggest that the reaction between Na and HF leads to the formation of sodium fluoride salt NaF and hydrogen gas. Na interacts with HF to form a complex HF...Na, and then the approaching of F atom of HF to Na results in a transition state H...F...Na. Accompanied by the broken of H-F bond, the bond forms between F and Na atoms as NaF, then the product NaF is yielded due to the removal of H atom. The resultant NaF can further form (NaF)<sub>4</sub> tetramer. The interaction of NaF with HF leads to the complex NaF...HF; the form I as well as II of (NaF)<sub>4</sub> can interact with HF to produce two complexes (i.e., (NaF)<sub>4</sub>(I-1)...HF, (NaF)<sub>4</sub>(I-2)...HF, (NaF)<sub>4</sub>(II-1)...HF and (NaF)<sub>4</sub>(II-2)...HF), but the form III of (NaF)<sub>4</sub> can interact with HF to produce only one complex (NaF)<sub>4</sub>(III)...HF. These complexes were explored in terms of noncovalent interaction (NCI) and quantum theory of atoms in molecules (QTAIM) analyses. NCI analyses confirm the existences of attractive interactions in the complexes HF...Na, NaF...HF, (NaF)<sub>4</sub>(I-1)...HF, (NaF)<sub>4</sub>(I-2)...HF, (NaF)<sub>4</sub>(II-1)...HF and (NaF)<sub>4</sub>(II-2)...HF, and (NaF)<sub>4</sub>(III)...HF. QTAIM analyses suggest that the F...Na interaction forms in the HF...Na complex while the F...H hydrogen bonds form in NaF...HF, (NaF)<sub>4</sub>(I-1)...HF, (NaF)<sub>4</sub>(I-2)...HF, (NaF)<sub>4</sub>(II-1)...HF and (NaF)<sub>4</sub>(II-2)...HF, and (NaF)<sub>4</sub>(III)...HF complexes. Natural bond orbital (NBO) analyses were also applied to analyze the intermolecular donor-acceptor orbital interactions in these complexes. These results would provide valuable insight into the chemical reaction of Na and HF and the adsorption interaction between sodium fluoride salt and HF.

**Methods** The calculations were carried out at the M06-L/6-311++G(2d,2p) level of theory which were performed using the Gaussian16 program. Intrinsic reaction coordinate (IRC) calculations were carried out at the same level of theory to confirm that the obtained transition state was true. The molecular surface electrostatic potential (MSEP) was employed to understand how the complex forms. Quantum theory of atoms in molecules (QTAIM) and noncovalent interaction (NCI) analysis was used to know the topology parameters at bond critical points (BCPs) and intermolecular interactions in the complex and intermediate. The topology parameters and the BCP plots were obtained by the Multiwfn software.

**Keywords** Hydrogen fluoride · Sodium · Weak interaction · Reaction mechanism · Adsorption

## Introduction

Hydrogen fluoride (HF) and alkali metal M (M = alkali metal) have high reactivities which enable them to react with each other to form alkali metal fluoride salt MF and hydrogen gas (i.e.,  $2\text{HF} + 2\text{M} \rightarrow 2\text{MF} + \text{H}_2$ ), and these reactions

are of great interest due to their significance in understanding the elementary chemical reaction kinetics [1]. Especially, for the reaction between Na and HF, it is a typical harpooning reaction [2, 3] which has been extensively investigated by many experimental and theoretical work [1, 2, 4–28]. For instance, experimental studies focus on the characteristics of Na + HF reaction, including how the vibrational states of HF [5, 8, 9, 24] and HF(*j*) initial rotational excitations [6] affect the reaction. Düren and coworkers have done the

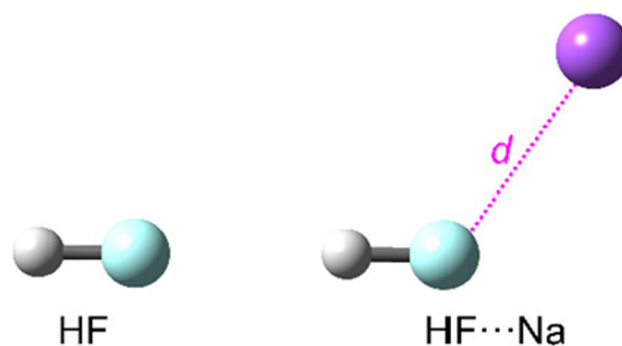
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scattering of Na from HF and suggested that the van der Waals wells exist and locate in the entrance channel of both ground and first excited potential energy surfaces [7–9]. A lot of theoretical work have been devoted to investigating the potential energy surface (PES) of Na + HF reaction system [1, 2, 4, 9, 11, 13, 16–19, 21–23, 25, 26, 29–32]. Different methods including semiempirical [19] and *ab initio* [2, 9, 16–18, 21, 30, 31] methods were used to explore the PES of the ground and excited electronic states of the Na + HF reaction. The investigations of ground state PES confirmed the existence of van der Waals well and late barrier etc. [1, 4, 10, 11, 13, 16, 22, 23, 25, 26, 30, 31] While the research on excited electronic state PES proved the harpooning process in the Na + HF reaction and the presence of a deep well in the first excited state. [18, 21, 30, 31]

The Na + HF reaction can lead to NaF monomer or larger cluster  $(\text{NaF})_n$  (in which  $n=4, 6, 9, 12, 15,$  and  $18.$ ), [33] and the resultant NaF monomer or  $(\text{NaF})_n$  tetramer might further adsorb HF. The interesting reaction processes from HF and Na to NaF and then  $\text{NaHF}_2$  or  $(\text{NaF})_n \bullet \text{HF}$  attract our attention, and the present work aims at exploring the detailed reaction mechanisms and the further adsorption processes. As a representative cluster, the  $(\text{NaF})_4$  tetramer can exist as cube (I), ladder (II), and ring (III) forms, [34–36] so it is selected in this study because the investigations of the adsorptions of HF on these three isomeric forms will be fascinating and thus provide insightful results. It can be expected that the Na + HF reaction might go through the processes including the interaction between Na and F atom of HF, the H-F bond breakage in the transition state  $\text{H}\cdots\text{F}\cdots\text{Na}$ , the Na-F bond formation in the intermediate  $\text{NaF}\cdots\text{H}$ , and the generation of the final product NaF, while the NaF molecule can assemble into larger cluster  $(\text{NaF})_4$ , and both of them can adsorb HF via hydrogen bond. Thereby, in the present work, quantum chemical calculations were carried out; the intermolecular interactions, the transition states, and intermediates formed in the reaction processes will be discussed; the reaction mechanism and the further adsorption processes will be elaborated.

## Computational methods

The structures of HF, Na, the complex formed via intermolecular interaction, transition state, intermediate and product, the  $(\text{NaF})_4 \bullet \text{HF}$  complexes were optimized at the M06-L [37, 38] /6-311++G(2d,2p) level of theory corrected with the Grimme's dispersion (D3) [39]. Vibrational frequency calculations at the same level of theory were carried out to make sure that the optimized reactants, intermediates, and product have no imaginary frequencies while the transition state has only one imaginary frequency. Intrinsic reaction coordinate (IRC) [40] calculations were carried out at the same level of theory



**Fig. 1** The optimized structures of HF and the complex HF...Na

to confirm that the obtained transition state was true. The calculations were performed using the Gaussian16 program [41].

To understand how the complex forms, the molecular surface electrostatic potential (MSEP) [29, 42–46] was employed to analyze the molecular electronic property. To know the topology parameters at bond critical points (BCPs) and intermolecular interactions in the complex and intermediate quantum theory of atoms in molecules (QTAIM [47–49]) and non-covalent interaction (NCI [50, 51]), analysis was used. The topology parameters and the BCP plots were obtained by the Multiwfn software [52]. The relative Gibbs free energy (i.e.,  $\Delta G$ ) is calculated as the difference between the Gibbs free energy of the complex (or the transition state or intermediate or product) and the sum of Gibbs free energies of the reactants. The interaction energy (i.e.,  $\Delta E$ ) of the complex is calculated as the energy difference between the total energy of the complex or the intermediate and the sum of energies of its components.

The reaction between HF and Na at 298 K leading to the formation of NaF, the formation of  $(\text{NaF})_4$ , and the adsorption of HF on NaF as well as  $(\text{NaF})_4$  was investigated (i.e., formulas 1, 2, 3 and 4 represent the generation of NaF, the adsorption of HF on NaF, the generation of  $(\text{NaF})_4$ , and the adsorption of HF on  $(\text{NaF})_4$ , respectively.):



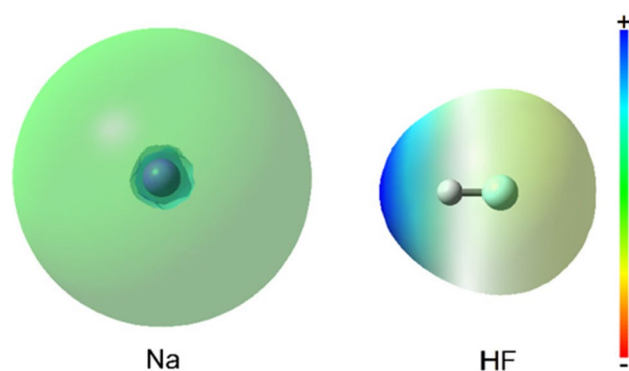
## Results and discussion

With regard to the reaction between HF and Na, the calculated results show that HF firstly interacts with Na to form a complex HF...Na, as shown in Fig. 1. The bond length

and stretching vibrational frequency of HF bond, the intermolecular distance, and interaction energy for the complex HF...Na are outlined in Table 1. It can be seen that the HF bond length in the complex HF...Na is elongated compared to that of HF, and the stretching vibrational frequency of HF bond in the complex HF...Na decreases relative to that of HF. The intermolecular distance for F...Na in the complex HF...Na is 2.4133 Å (Fig. 1 and Table 1). The interaction energy for the complex HF...Na is  $-1.07$  kcal/mol, meaning that it exists as an intermolecular interaction.

To understand how the complex HF...Na forms, the molecular surface electrostatic potential (MSEP) [29, 42–45] was employed to reveal the electronic properties of HF and Na, as depicted in Fig. 2. Evidently, the positive MSEP region is observed around Na atom which enables it to be an electron acceptor, while the negative MSEP region around the F atom of HF makes F atom donate electrons, so the F and Na atoms can interact with each other as F...Na interaction in the complex HF...Na.

Noncovalent interaction (NCI [50, 51]) analysis of the complex HF...Na is shown in Fig. 3a; it can be observed that a small green circle appears between F atom of HF and Na atom in the reduced density gradient (RDG) isosurface, indicating the existence of attractive interaction between them. Also, the intermolecular interaction in the complex HF...Na was assessed by QTAIM, the intermolecular BCP is depicted in Fig. 3b, and the topological parameters at the intermolecular BCP is summarized in Table 2. The appearance of intermolecular BCP between F atom of HF and Na atom in the complex HF...Na suggests the formation of F...Na interaction. The electron density (i.e.,  $\rho$ ) at the BCP of F...Na interaction is in the range of 0.01323 a.u., and its Laplacian (i.e.,  $\nabla^2\rho$ ) ranges from 0.07946 a.u. (Table 2). These values are within the ranges of the criteria for the existence of hydrogen bond (i.e.,  $\rho$  and  $\nabla^2\rho$  should be within the ranges 0.002–0.035 and 0.024–0.139 a.u., respectively [53]), indicating that the F...Na interaction in the complex HF...Na is an attractive intermolecular interaction. The electronic energy density (i.e.,  $H$ ) with positive or negative value at the BCP means that the interaction is electrostatic



**Fig. 2** The MSEP maps for Na and HF mapped on the surface of molecular electron density

or covalent dominant [54], respectively. It can be seen that the  $H$  value for F...Na interaction in the complex HF...Na is positive (Table 2), suggesting that the F...Na interaction is electrostatic dominant.

Natural bond orbital (NBO) [55, 56] analyses were applied to analyze the weak noncovalent interactions formed in the complex HF...Na, as depicted in Fig. 4. The intermolecular donor-acceptor orbital interaction (i.e.,  $E^{(2)}$ ) between the bonding orbital of HF and the lone pair orbital of Na atom is 0.96 kcal/mol, while that between the lone pair orbitals of F and Na atoms is 3.58 kcal/mol, meaning the strong electron transfer from HF to Na atom.

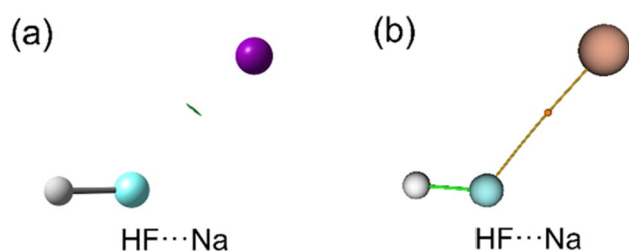
As displayed in Fig. 5, the initial step in the formation the complex HF...Na needs to absorb an energy of 3.4 kcal/mol. Then, the conversion from the complex HF...Na to the transition state H...F...Na needs to overcome an energy of 9.5 kcal/mol, as can be seen from the Gibbs free energy profile in Fig. 5. The optimized structures of the transition state H...F...Na, intermediate NaF...H, and NaF are shown in Fig. 6. The H...F distance in the transition state H...F...Na is 1.3899 Å which is even longer than the H-F bond length (ca. 0.92 Å), suggesting that the H-F bond is broken. The F...Na distance in the transition state H...F...Na is 2.0509 Å which is longer than the Na-F bond

**Table 1** The bond length ( $R_{\text{H-F}}$ , in Å) and stretching vibrational frequency ( $\nu_{\text{H-F}}$ , in  $\text{cm}^{-1}$ ) of HF bond, the F...Na distance ( $d$ , in Å), and interaction energy ( $\Delta E_{\text{int}}$ , in kcal/mol) for the complex HF...Na obtained at the M06-L/6-311++G(2d,2p) level of theory

	$R_{\text{H-F}}$	$\nu_{\text{H-F}}$	$d^a$	$\Delta E_{\text{int}}^b$
HF	0.9175	4154.8	–	–
HF...Na	0.9233	4032.3	2.4133	-1.07

<sup>a</sup> $d$  is the F...Na distance shown in Fig. 1

<sup>b</sup>The interaction energy  $\Delta E_{\text{int}}$  of the complex HF...Na is calculated as the energy difference between the total energy of the complex HF...Na and the sum of energies of HF and Na

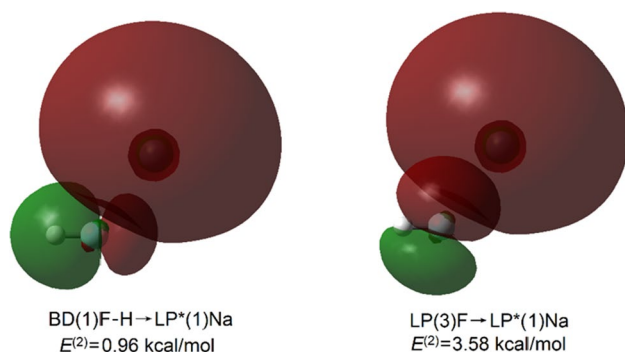
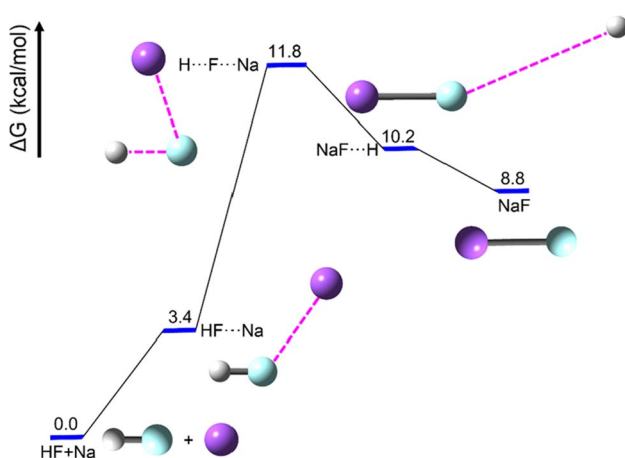
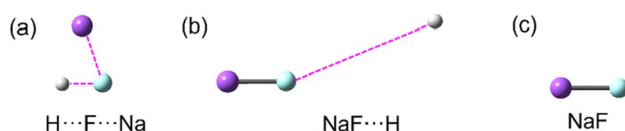


**Fig. 3** **a** The RDG isosurface for the complex HF...Na. The surfaces are colored on a blue-green-red scale. **b** The intermolecular BCP for the complex HF...Na

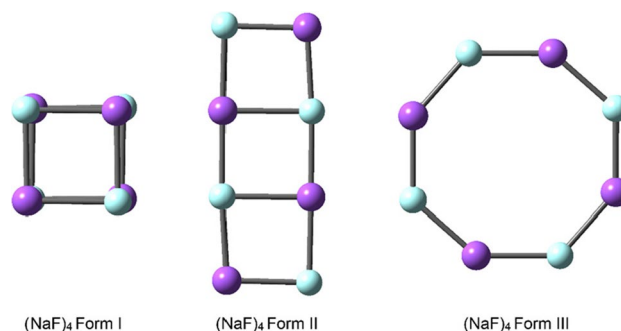
**Table 2** The electron density ( $\rho$ ) and Laplacian ( $\nabla^2\rho$ ), the electronic potential energy density ( $V$ ), the electronic kinetic energy density ( $G$ ), and the electronic energy density ( $H$ ) at the BCP for the complex HF...Na. Units are in a.u.<sup>a</sup>

Complex	BCP	$\rho$	$\nabla^2\rho$	$V$	$G$	$H$
HF...Na	BCP <sub>F...Na</sub>	0.01323	0.07946	-0.01371	0.01679	0.00308

<sup>a</sup>The intermolecular BCP for the complex HF...Na is shown in Fig. 3b

**Fig. 4** The intermolecular donor-acceptor orbital interactions for the complex HF...Na**Fig. 5** Gibbs free energy profile for the reaction of Na and HF in yielding NaF**Fig. 6** The optimized structures of a) the transition state H...F...Na, b) intermediate NaF...H, and c) NaF

length (ca. 1.93 Å). The approaching of F atom towards Na atom leads to the formation of intermediate NaF...H in which the NaF bond forms. After the removal of H atom, the final product NaF is yielded.

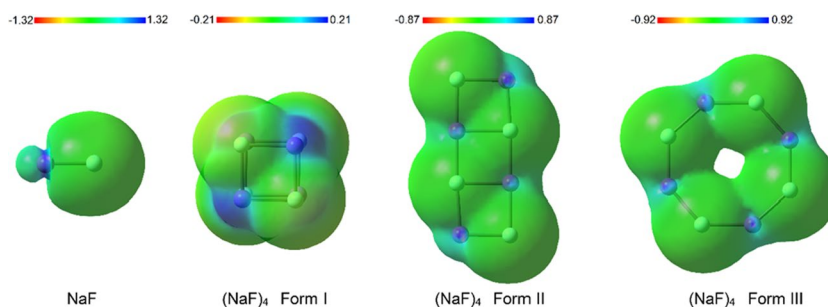
**Fig. 7** The optimized structures of three (NaF)<sub>4</sub> isomers form I, form II, and form III**Table 3** The Gibbs free energy changes ( $\Delta G$ , in kcal/mol) for the adsorption of HF on NaF, the generation of (NaF)<sub>4</sub>, and the adsorption of HF on (NaF)<sub>4</sub>

Reaction	$\Delta G$
4NaF $\rightarrow$ (NaF) <sub>4</sub> (I)	-141.15
4NaF $\rightarrow$ (NaF) <sub>4</sub> (II)	-125.90
4NaF $\rightarrow$ (NaF) <sub>4</sub> (III)	-125.03
HF + NaF $\rightarrow$ NaF...HF	-12.93
HF + (NaF) <sub>4</sub> (I) $\rightarrow$ (NaF) <sub>4</sub> (I-1)...HF	-8.29
HF + (NaF) <sub>4</sub> (I) $\rightarrow$ (NaF) <sub>4</sub> (I-2)...HF	-12.70
HF + (NaF) <sub>4</sub> (II) $\rightarrow$ (NaF) <sub>4</sub> (II-1)...HF	-12.08
HF + (NaF) <sub>4</sub> (II) $\rightarrow$ (NaF) <sub>4</sub> (II-2)...HF	-15.28
HF + (NaF) <sub>4</sub> (III) $\rightarrow$ (NaF) <sub>4</sub> (III)...HF	-12.22

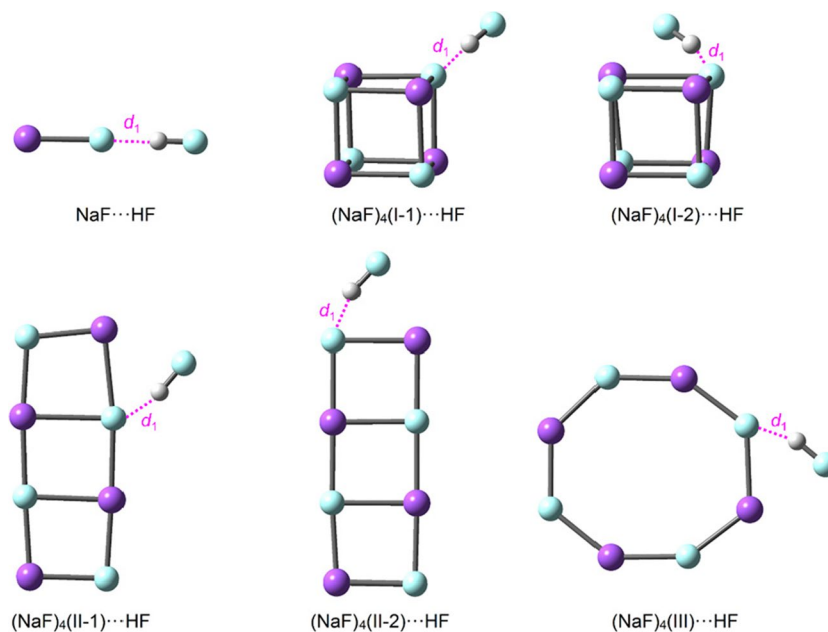
The resultant NaF can further form larger cluster [33], for instance, the (NaF)<sub>4</sub> tetramer (Fig. 7) [35]. As outlined in Table 3, the generation of (NaF)<sub>4</sub> tetramer including forms I, II, and III from NaF is exothermic. The resultant NaF as well as the (NaF)<sub>4</sub> tetramer has the capability of adsorbing HF, as revealed by the MSEP results (Fig. 8) in which the F atom in NaF or (NaF)<sub>4</sub> possessing the negative MSEP region can donate electrons to H atom of HF, so the interaction of NaF as well as the (NaF)<sub>4</sub> tetramer with HF was further investigated.

As depicted in Fig. 9, the interaction of NaF with HF leads to the complex NaF...HF; the form I as well as II of (NaF)<sub>4</sub> can interact with HF to produce two complexes (i.e., (NaF)<sub>4</sub>(I-1)...HF, (NaF)<sub>4</sub>(I-2)...HF, (NaF)<sub>4</sub>(II-1)...HF and

**Fig. 8** The MSEP maps for NaF, (NaF)<sub>4</sub> form I, form II, and form III mapped on the surface of molecular electron density



**Fig. 9** The optimized structures of the complexes NaF...HF, (NaF)<sub>4</sub>(I-1)...HF, (NaF)<sub>4</sub>(I-2)...HF, (NaF)<sub>4</sub>(II-1)...HF, (NaF)<sub>4</sub>(II-2)...HF, and (NaF)<sub>4</sub>(III)...HF



(NaF)<sub>4</sub>(II-2)...HF), but the form III of (NaF)<sub>4</sub> can interact with HF to produce only one complex (NaF)<sub>4</sub>(III)...HF. These processes are exothermic, as can be seen from the

Gibbs free energy changes in Table 3. These complexes have strong interaction energies which can be seen from the  $\Delta E_{\text{int},1}$  values in Table 4. The interaction energy of

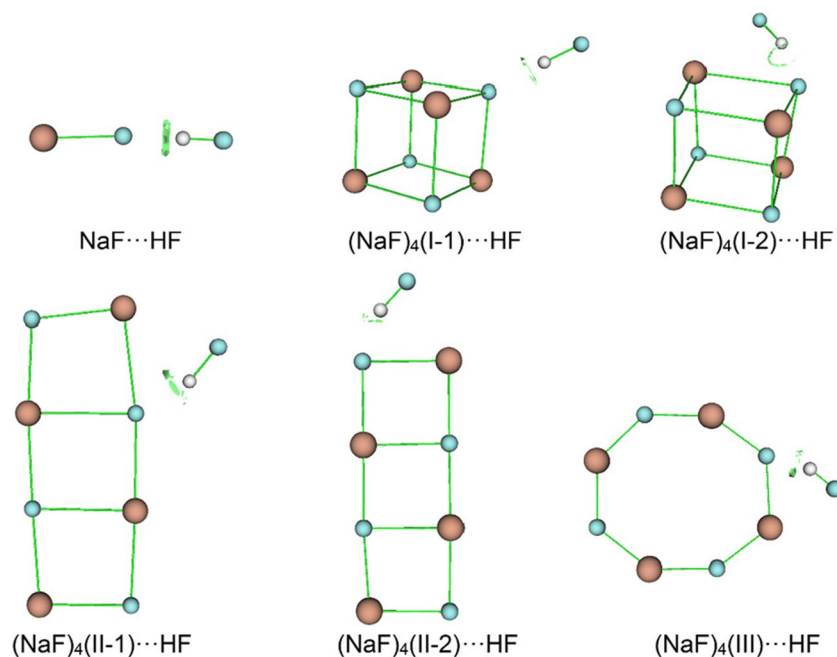
**Table 4** The F...H distance ( $d_1$ , in Å) and interaction energy ( $\Delta E_{\text{int},1}$ , in kcal/mol) for the complexes NaF...HF, (NaF)<sub>4</sub>(I-1)...HF, (NaF)<sub>4</sub>(I-2)...HF, (NaF)<sub>4</sub>(II-1)...HF and (NaF)<sub>4</sub>(II-2)...HF, and (NaF)<sub>4</sub>(III)...HF, and the electron density ( $\rho$ ) and Laplacian ( $\nabla^2\rho$ ), the electronic potential energy density ( $V$ ), the electronic kinetic energy density ( $G$ ), and

the electronic energy density ( $H$ ) at the intermolecular F...H BCPs for the complexes NaF...HF, (NaF)<sub>4</sub>(I-1)...HF, (NaF)<sub>4</sub>(I-2)...HF, (NaF)<sub>4</sub>(II-1)...HF and (NaF)<sub>4</sub>(II-2)...HF, and (NaF)<sub>4</sub>(III)...HF. Units are in a.u.<sup>a</sup>

Complex	$d_1$	$\Delta E_{\text{int},1}$	$\rho$	$\nabla^2\rho$	$V$	$G$	$H$
NaF...HF	1.4654	-22.07	0.06612	0.19756	-0.06781	0.05860	-0.00921
(NaF) <sub>4</sub> (I-1)...HF	1.4865	-18.45	0.06366	0.19176	-0.06462	0.05628	-0.00834
(NaF) <sub>4</sub> (I-2)...HF	1.3981	-22.64	0.01813	0.11827	-0.02051	0.02504	0.00453
(NaF) <sub>4</sub> (II-1)...HF	1.3935	-20.12	0.08526	0.20466	-0.09592	0.07354	-0.02238
(NaF) <sub>4</sub> (II-2)...HF	1.3691	-25.42	0.09132	0.20000	-0.10599	0.07800	-0.02799
(NaF) <sub>4</sub> (III)...HF	1.4136	-21.47	0.01739	0.11128	-0.01960	0.02371	0.00411

<sup>a</sup>The intermolecular F...H BCPs for the complexes NaF...HF, (NaF)<sub>4</sub>(I-1)...HF, (NaF)<sub>4</sub>(I-2)...HF, (NaF)<sub>4</sub>(II-1)...HF and (NaF)<sub>4</sub>(II-2)...HF, and (NaF)<sub>4</sub>(III)...HF are shown in Fig. 11

**Fig. 10** The RDG isosurfaces for the complexes NaF...HF, (NaF)<sub>4</sub>(I-1)...HF, (NaF)<sub>4</sub>(I-2)...HF, (NaF)<sub>4</sub>(II-1)...HF, (NaF)<sub>4</sub>(II-2)...HF, and (NaF)<sub>4</sub>(III)...HF. The surfaces are colored on a blue-green-red scale

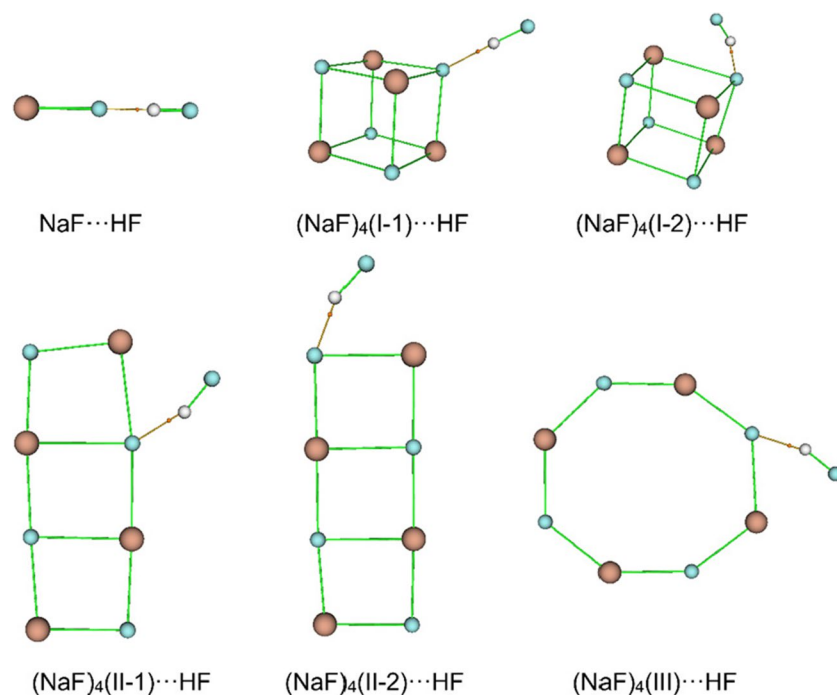


(NaF)<sub>4</sub>(I-2)...HF (or (NaF)<sub>4</sub>(II-2)...HF) is much stronger than that of (NaF)<sub>4</sub>(I-1)...HF (or (NaF)<sub>4</sub>(II-1)...HF).

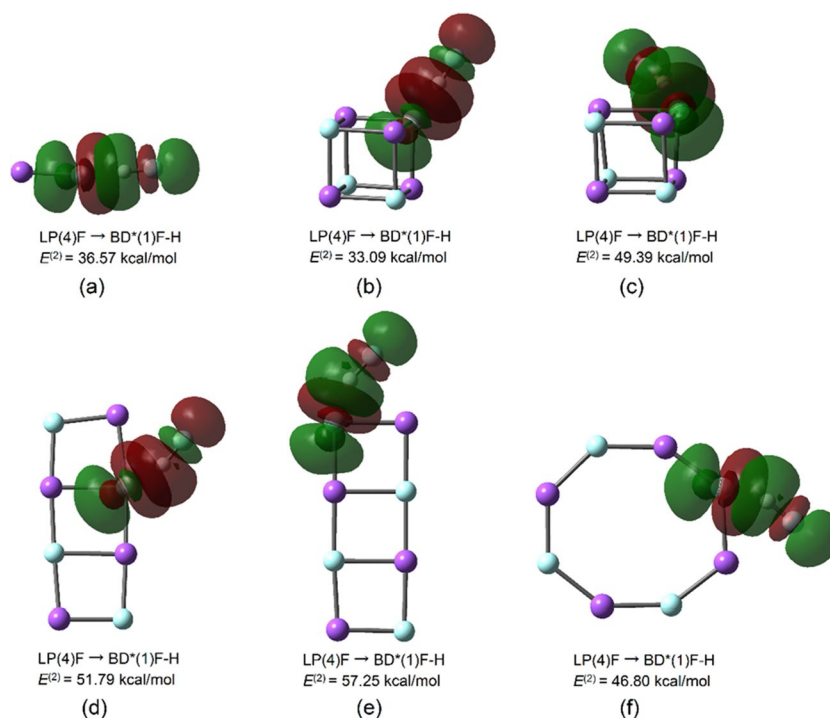
NCI analysis shows that the green circle appears between F atom of NaF (or (NaF)<sub>4</sub>(I-1), (NaF)<sub>4</sub>(I-2), (NaF)<sub>4</sub>(II-1), (NaF)<sub>4</sub>(II-2), (NaF)<sub>4</sub>(III)), and H atom of HF in the RDG isosurface (Fig. 10), suggesting that the attractive interaction forms between them. As displayed in Fig. 11, the intermolecular BCP between F atom of NaF

(or (NaF)<sub>4</sub>(I-1), (NaF)<sub>4</sub>(I-2), (NaF)<sub>4</sub>(II-1), (NaF)<sub>4</sub>(II-2), (NaF)<sub>4</sub>(III)), and H atom of HF appears in the complex NaF...HF (or (NaF)<sub>4</sub>(I-1)...HF, (NaF)<sub>4</sub>(I-2)...HF, (NaF)<sub>4</sub>(II-1)...HF, (NaF)<sub>4</sub>(II-2)...HF, and (NaF)<sub>4</sub>(III)...HF), meaning the formation of F...H interaction. The *H* values for F...H interactions in the complexes NaF...HF, (NaF)<sub>4</sub>(I-1)...HF, (NaF)<sub>4</sub>(II-1)...HF, and (NaF)<sub>4</sub>(II-2)...HF are negative (Table 4), indicating that these F...H interactions

**Fig. 11** The intermolecular BCPs for the complexes NaF...HF, (NaF)<sub>4</sub>(I-1)...HF, (NaF)<sub>4</sub>(I-2)...HF, (NaF)<sub>4</sub>(II-1)...HF, (NaF)<sub>4</sub>(II-2)...HF, and (NaF)<sub>4</sub>(III)...HF



**Fig. 12** The intermolecular donor-acceptor orbital interactions for the complexes (a) NaF...HF, (b) (NaF)<sub>4</sub>(I-1)...HF, (c) (NaF)<sub>4</sub>(I-2)...HF, (d) (NaF)<sub>4</sub>(II-1)...HF, (e) (NaF)<sub>4</sub>(II-2)...HF, and (f) (NaF)<sub>4</sub>(III)...HF



are covalent dominant, while the F...H interactions in (NaF)<sub>4</sub>(I-2)...HF and (NaF)<sub>4</sub>(III)...HF are electrostatic dominant due to their positive  $H$  values.

The intermolecular donor-acceptor orbital interactions (i.e.,  $E^{(2)}$ ) for the complexes NaF...HF, (NaF)<sub>4</sub>(I-1)...HF, (NaF)<sub>4</sub>(I-2)...HF, (NaF)<sub>4</sub>(II-1)...HF and (NaF)<sub>4</sub>(II-2)...HF, and (NaF)<sub>4</sub>(III)...HF are depicted in Fig. 12. It can be seen that the  $E^{(2)}$  values for the intermolecular donor-acceptor orbital interactions between the lone pair orbital of F and antibonding orbital of HF are very large for these complexes, indicating the strong electron transfer from F atom to HF during the formation of F...HF hydrogen bond.

## Conclusions

In this work, the reaction of sodium (Na) with hydrogen fluoride (HF) was theoretically investigated, and the detailed mechanism was explored. At first, Na interacts with HF to form a complex HF...Na, and then the approaching of F atom of HF to Na results in a transition state H...F...Na. Accompanied by the broken of H-F bond, the bond forms between F and Na atoms as NaF, then the product NaF is yielded due to the removal of H atom. The resultant NaF can further form (NaF)<sub>4</sub> tetramer, and NaF as well as (NaF)<sub>4</sub> tetramer can further adsorb HF to form a strong complex. These results would provide valuable insight into the chemical reaction of Na and HF and the adsorption interaction between sodium fluoride salt and HF.

**Supplementary Information** The online version contains supplementary material available at <https://doi.org/10.1007/s00894-023-05821-z>.

**Author contribution** QY, JY, and P-PZ: data analysis, writing—review and editing; H-RZ, P-YL, GG, YY, and WD: data analysis and discussion; P-YL and H-RZ: calculations and data collection

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## Declarations

**Conflict of interest** The authors declare no competing interests.

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## Authors and Affiliations

Qinwei Yu<sup>1</sup> · Jianming Yang<sup>1</sup> · Hai-Rong Zhang<sup>2</sup> · Peng-Yu Liang<sup>2</sup> · Ge Gao<sup>2</sup> · Yongna Yuan<sup>3</sup> · Wei Dou<sup>2</sup> · Pan-Pan Zhou<sup>2</sup>

✉ Qinwei Yu  
qinweiyu2014@163.com

✉ Jianming Yang  
yangjm204@163.com

✉ Pan-Pan Zhou  
zhoupp@lzu.edu.cn

Yongna Yuan  
yuanyan@lzu.edu.cn

<sup>1</sup> State Key Laboratory of Fluorine & Nitrogen Chemicals, Xi'an Modern Chemistry Research Institute, Xi'an 710065, People's Republic of China

<sup>2</sup> Key Laboratory of Advanced Catalysis of Gansu Province, Advanced Catalysis Center, College of Chemistry and Chemical Engineering, Lanzhou University, 222 South Tianshui Road, 730000 Lanzhou, People's Republic of China

<sup>3</sup> School of Information Science & Engineering, Lanzhou University, Lanzhou, Gansu 730000, People's Republic of China