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New insight into the electronic structure of SiF₄: synergistic back-donation and the eighteen-electron rule†

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SiF₄ demonstrated high thermal stability in dry air or vacuum, and a Si–F bond length of 1.554 Å is close to the second period element C–C bond length (1.54 Å) of C₂H₆. To determine which factors confer this property of SiF₄, here we conduct a comparative study of a series of molecules SiH_nF_{4–n} (*n* = 0, 1, 2, 3), SiX₄ (X = Cl, Br, I), CF₄ and TiF₄ in terms of bond length and energy, molecular orbitals, and adaptive natural density partitioning (AdNDP) analysis. The AdNDP analysis shows that there are five 5c–2c bonds in SiF₄, here named synergistic back-donation (SBD) bonds. These SBD bonds together with the Si–F σ bonds and the eighteen-electron rule are demonstrated as the main factors contributing to the short Si–F bond length and the high thermal stability of SiF₄ in dry air or vacuum. Moreover, the SBD bonds exist widely in other isoelectronic species of SiF₄ such as ClO₄[–], SO₄^{2–}, PO₄^{3–} and XeO₄.

1. Introduction

As a material widely used in chemical production, SiF₄ has attracted the attention of researchers. For decades, researchers have studied the structure and IR and Raman spectra of SiF₄.^{1–7} Different from other silicon tetrahalides (SiCl₄, SiBr₄, and SiI₄), SiF₄ is gaseous, while other silicon tetrahalides are liquids or solids.⁸ Moreover, SiF₄ has higher thermal stability than SiCl₄, SiBr₄ and SiI₄.⁹ Such a high thermal stability of SiF₄ originates from its short Si–F bond length (1.554 Å),¹⁰ which is very close to the C–C bond length (1.54 Å) of C₂H₆.¹¹ The short C–C bond length is well understood as C is the second period element with a small atomic radius. However, Si is the third period element with a bigger atomic radius. Moreover, the Si–F bond length of SiH_nF_{4–n} (*n* = 1, 2, 3) is not usually as short as that of SiF₄.^{10,12–14} So, what confers the short Si–F bond length and unusual thermal stability of SiF₄?

In fact, this question has troubled scientists since the length of the Si–F bond of SiF₄ was first determined by Natta and Brockway.¹⁵ The Si–F bond length measured by Natta was 1.56 ± 0.01 Å. Then, in 1934, the Si–F bond length measured by Brockway and Wall¹⁶ was 1.54 ± 0.01 Å. They found that the Si–F bond length deviates from the addition of covalent radii

(1.81 Å), so they proposed that there are double electron pair bonds in SiF₄. A few years later, Schomaker and Stevenson¹⁷ proposed that the bond length should be corrected by the addition of atomic radii and suggested that the normal Si–F single bond length of SiF₄ should be 1.68 ± 0.01 Å. In 1952, Pauling¹⁸ supposed that there exists a compensatory mechanism, and the central atom of SiF₄ forms several bonds with a large number of ionic features. The formation of π bonds would reduce the charge on Si atoms. Moreover, he supposed that the unusual thermal stability of SiF₄ was due to its resonant structure, and the bond order of Si–F is 1.5 which is between single and double bonds.¹⁹ After decades in 1983, Takami¹⁰ *et al.* studied the infrared–microwave double resonance spectroscopy of SiF₄ and the measured Si–F bond length was 1.554 Å. Above all, these results still remain in the stage of experiment and conjecture that do not give a direct physical description. In 2004, Lindner and coworkers²⁰ theoretically studied the structures of halosilanes and halogermanes, and found it is typical for E–X bonds (E = Si, Ge; X = F, Cl, Br) to contract as more X atoms are substituted on the central E atom. They also found that there exist electrostatic interactions in MH_{4–n}X_n (*n* = 1–4, M = Si, Ge; X = F, Cl, Br).

In this article, we further study the high thermal stability of SiF₄ in theory to explain why SiF₄ has a short Si–F bond length. A comparative study of bond length, bond energy, and molecular orbitals and chemical bonding analysis were conducted for molecules SiH_nF_{4–n} (*n* = 0, 1, 2, 3), SiX₄ (X = Cl, Br, I), CF₄ and TiF₄. As we know, CF₄, SiF₄ and TiF₄ are isoelectronic species because the elements C, Si and Ti all have four valence electrons. The adaptive natural density partitioning (AdNDP)²¹

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analysis shows that there are five 5c–2e bonds in SiF₄. We named this kind of 5c–2e bond as a synergistic back-donation (SBD) bond. Moreover, SiF₄ also satisfies the eighteen-electron (18e) rule²² perfectly from the AdNDP results. Thus, we suppose that the SBD and 18e rule lead to the high thermal stability of SiF₄ in dry air or vacuum. We also calculate other isoelectronic species of SiF₄ like ClO₄[–], SO₄^{2–}, PO₄^{3–} and XeO₄. As we expected, the SBD and 18e rule exist widely in pentatomic tetrahedral molecules or ions.

2. Computational methods

The pentatomic molecules SiH_nF_{4–n} (*n* = 0–3), SiX₄ (X = Cl, Br and I), CF₄, TiF₄, ClO₄[–], SO₄^{2–}, PO₄^{3–} and XeO₄ were optimized at the M06-2X²³/def2-TZVPP²⁴ level of theory. The geometric structures are all Td symmetry, except SiH_nF_{4–n} (*n* = 1–3). The frequencies were calculated to confirm that the molecular geometries are local minimum. To study the thermal stability of SiF₄, the bond energies (BEs) were calculated using formula (1) at the M06-2X/def2-TZVPP level of theory. All the calculations were performed using the Gaussian09 software package.²⁵

$$BE = E_X + E_{SiH_nX_{3-n}} - E_{SiH_nX_{4-n}} \quad (X = F, Cl, Br, I; n = 0, 1, 2, 3) \quad (1)$$

Further, adaptive natural density partitioning (AdNDP) was chosen for chemical bonding analysis using the M06-2X functional and ANO-RCC²⁶ all-electron basis set. The natural bond orbital (NBO)²⁷ analysis was also performed at the M06-2X/def2-TZVPP level of theory. The NBO analysis contains Wiberg bond indices (WBIs)²⁸ and natural population analysis (NPA) charges.²⁹ The NBO and AdNDP analyses were performed using Multiwfn3.8.³⁰ Moreover, the results of canonical molecular orbitals (CMOs) and AdNDP analysis were visualized using VMD1.9.3.³¹

3. Results and discussion

3.1. The high thermal stability of SiF₄

A benchmark was performed on SiX₄ (X = F, Cl, Br and I) molecules to find an appropriate method and basis set. The calculated Si–X bond lengths of SiX₄ using different theoretical methods at the same basis set of def2-TZVPP are listed in Table 1. Compared with the experimental values, the methods CCSD, M06-2X, MP2 and wB97X can be chosen. The Si–F bond length of SiF₄ calculated by CCSD and M06-2X accords well with

Table 2 The calculated and experimental Si–F bond lengths (Å) of SiH_nF_{4–n} (*n* = 0–3)

Molecules	Theory	Experiment
SiH ₃ F	1.597	1.595 ¹²
SiH ₂ F ₂	1.582	1.576 ¹³
SiHF ₃	1.570	1.563 ¹⁴
SiF ₄	1.558	1.554 ¹⁰

the experimental results. But for SiCl₄, SiBr₄ and SiI₄, CCSD and M06-2X are not appropriate methods. Considering that the factual states of SiCl₄ (l), SiBr₄ (s) and SiI₄ (s) totally differ from our calculation conditions in vacuum, these differences between the calculated and experimental values are acceptable. Moreover, because the CCSD method is very time-consuming and the results calculated by CCSD and M06-2X are quite similar, the more economical method M06-2X was chosen for geometry optimization.

A series of Si–F bond lengths and bond energies of SiH_nF_{4–n} (*n* = 0–3) molecules were studied to see whether the most stable Si–F bond only exists in SiF₄. The structures of SiH_nF_{4–n} (*n* = 0–3) were optimized at the M06-2X/def2-TZVPP level of theory, and the results are listed in Table 2. The calculated bond lengths accord well with the experimentally determined values. The Si–F bond length becomes shorter as the number of F atoms increases, for example, 1.597 Å in SiH₃F > 1.582 Å in SiH₂F₂. The trend of the calculated Si–F bond length also agrees well with the experimental observations. These results further confirm that the theoretical methods used here are appropriate. SiF₄ possesses the shortest Si–F bond length among these molecules, which is related to its special electronic structure (*vide infra*).

It is well known that the larger the bond energy, the more stable the molecule, so the Si–X bond energies of SiX_n (X = Cl, Br, I) and SiH_nF_{4–n} (*n* = 0–3) were calculated using formula (1). The calculated and experimental bond energies are listed in Table 3. It shows that the differences between the calculated and experimental values are very small (less than 5 kcal mol^{–1}), namely, the theoretical values calculated at the M06-2X/def2-TZVPP level of theory match the experimental ones very well. The trend of bond energies observed in experiments is also reproduced in theory. It can be observed that the bond energies decrease in the order of SiF₄ > SiCl₄ > SiBr₄ > SiI₄. In addition, the Si–F bond energies of SiH_nF_{4–n} (*n* = 0–3) increase with the increase in the number of F atoms, for example,

Table 1 The experimental and calculated Si–X (X = F, Cl, Br, I) bond lengths (Å) of SiX₄

	SiF ₄	SiCl ₄	SiBr ₄	SiI ₄
Experiment	1.554 ¹⁰	2.019 ³²	2.283 ³³	2.432 ³⁴
CCSD	1.559	2.024	2.193	2.428
M06-2X	1.558	2.021	2.195	2.426
B3LYP	1.568	2.036	2.213	2.458
wB97X	1.565	2.019	2.189	2.427
CAM-B3LYP	1.561	2.023	2.195	2.435
LC-wPBE	1.565	2.012	2.178	2.408
MP2	1.566	2.020	2.185	2.411

Table 3 The calculated and experimental Si–X bond energies (kcal mol^{–1}) of SiX_n (X = Cl, Br, I) and SiH_nF_{4–n} (*n* = 0–3)

Molecules	Theory	Experiment
SiF ₄	163.40	166.60 ⁹
SiCl ₄	107.66	110.20 ⁹
SiBr ₄	85.34	88.10 ⁹
SiI ₄	62.94	67.90 ⁹
SiH ₃ F	149.47	152.50 ⁹
SiH ₂ F ₂	158.63	
SiHF ₃	163.09	

Table 4 Wiberg bond indices (WBIs) of the Si–F bond, the total electron number of the F → Si back-donation (N_{d}), the NBO population of the 3d orbitals of Si and NBO based atomic charges of Si for molecules $\text{SiH}_n\text{F}_{4-n}$ ($n = 0-3$)

Molecules	SiF_4	SiHF_3	SiH_2F_2	SiH_3F
WBIs	1.81	1.80	1.77	1.74
N_{d}	0.45	0.28	0.13	0.07
NBO population	$3\text{d}^{0.1}$	$3\text{d}^{0.09}$	$3\text{d}^{0.07}$	$3\text{d}^{0.05}$
Charge	2.57	2.24	1.83	1.31

158.63 kcal mol^{−1} in SiH_2F_2 > 149.47 kcal mol^{−1} in SiH_3F , consistent with the shorter Si–F bond length in SiH_2F_2 . Because SiF_4 has the shortest Si–F bond length, its bond energy is the largest. These results are consistent with the calculated WBIs of the Si–F bond which are shown in Table 4. The values of WBIs are 1.81 (SiF_4) > 1.80 (SiHF_3) > 1.77 (SiH_2F_2) > 1.74 (SiH_3F), showing a decrease in the stability from SiF_4 to SiH_3F . Moreover, the WBIs also support that these Si–F bonds are between single and double bonds. In short, the values of bond length, bond energies and WBIs demonstrate that SiF_4 has high thermal stability.

3.2. Molecular orbitals (MOs) and chemical bonding analysis

To explain the high thermal stability of SiF_4 in dry air or vacuum, a comparative study of the MOs and chemical bonding analysis were performed for the molecules $\text{SiH}_n\text{F}_{4-n}$ ($n = 0-3$), CF_4 and TiF_4 . As we know, CF_4 , SiF_4 and TiF_4 are isoelectronic species because the elements C, Si and Ti all have four valence electrons.

The MOs were calculated using the M06-2X functional and ANO-RCC all-electron basis set based on the geometries optimized at the M06-2X/def2-TZVPP level of theory. The canonical MOs (CMOs) of SiF_4 and SiHF_3 were plotted at the surface of isovalue = 0.03 and are shown in Fig. 1. In addition, the CMOs of other molecules are shown in Fig. S1 in the ESI.† SiF_4 has 32

valence electrons (four electrons from the Si atom and twenty-eight electrons from four F atoms), so there are 16 occupied valence MOs in Fig. 1A. The lowest four orbitals (one-fold degenerate orbital at −38.49 eV and three-fold degenerate orbitals at −37.50 eV) contribute to Si–F σ bonds. The remaining MOs are lone pairs of F atoms. Fig. 1B shows the CMOs of SiHF_3 . SiHF_3 has 26 valence electrons and 13 occupied valence MOs. The lowest three orbitals at −37.74 eV and −36.98 eV still correspond to Si–F σ bonds. The orbital at −19.06 eV contributes to Si–H σ bonds. Obviously, the orbital energy of the Si–H σ bond is much higher than that of the Si–F σ bond because the 2p orbital energy of F is more close to the 3s or 3p orbital energy of Si. Thus, the Si–F bond is more favorable for the molecular thermal stability than the Si–H bond. The average orbital energies of Si–F σ bonds decrease with the increase in the number of F atoms, i.e. −36.23 eV (SiH_3F) > −36.74 eV (SiH_2F_2) > −37.23 eV (SiHF_3) > −37.75 eV (SiF_4). This corresponds well with the bond energies, namely, a lower average orbital energy of the Si–F σ bond means a larger Si–F bond energy. Therefore, the molecule becomes more stable as the number of F atoms increases.

Compared with SiF_4 , the orbital energy of the C–F σ bond of CF_4 is the lowest, whereas that of the Ti–F σ bond of TiF_4 is the highest (see Fig. S1C and D, ESI†), because the 2p orbital energy of the F atom approaches the 2s or 2p orbital energy of the C atom but is far away from the 3d or 4s orbital energy of the Ti atom. From this respect, the trend of bond energies should be C–F (in CF_4) > Si–F (in SiF_4) > Ti–F (in TiF_4). However, a factual trend of Si–F (in SiF_4) > Ti–F (in TiF_4) > C–F (in CF_4) is observed both in theory and in the experiment (Table S1, ESI†). This difference implies that other bonding actions may be involved in Si–F and Ti–F bonds (*vide infra*).

To give a straightforward physical view of bonding formation, the adaptive natural density partitioning (AdNDP) analysis was performed. The AdNDP method is developed from the natural bond orbital (NBO) analysis and can be used to

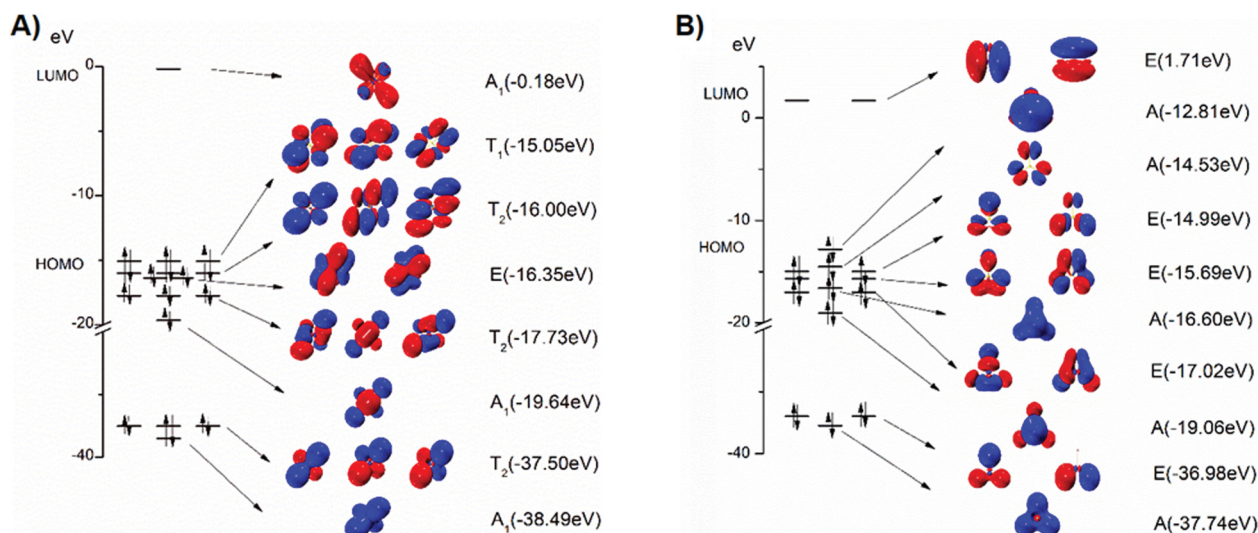


Fig. 1 The canonical molecular orbitals (CMOs) of (A) SiF_4 with T_d symmetry and (B) SiHF_3 with C_{3v} symmetry. The isovalue is 0.03.

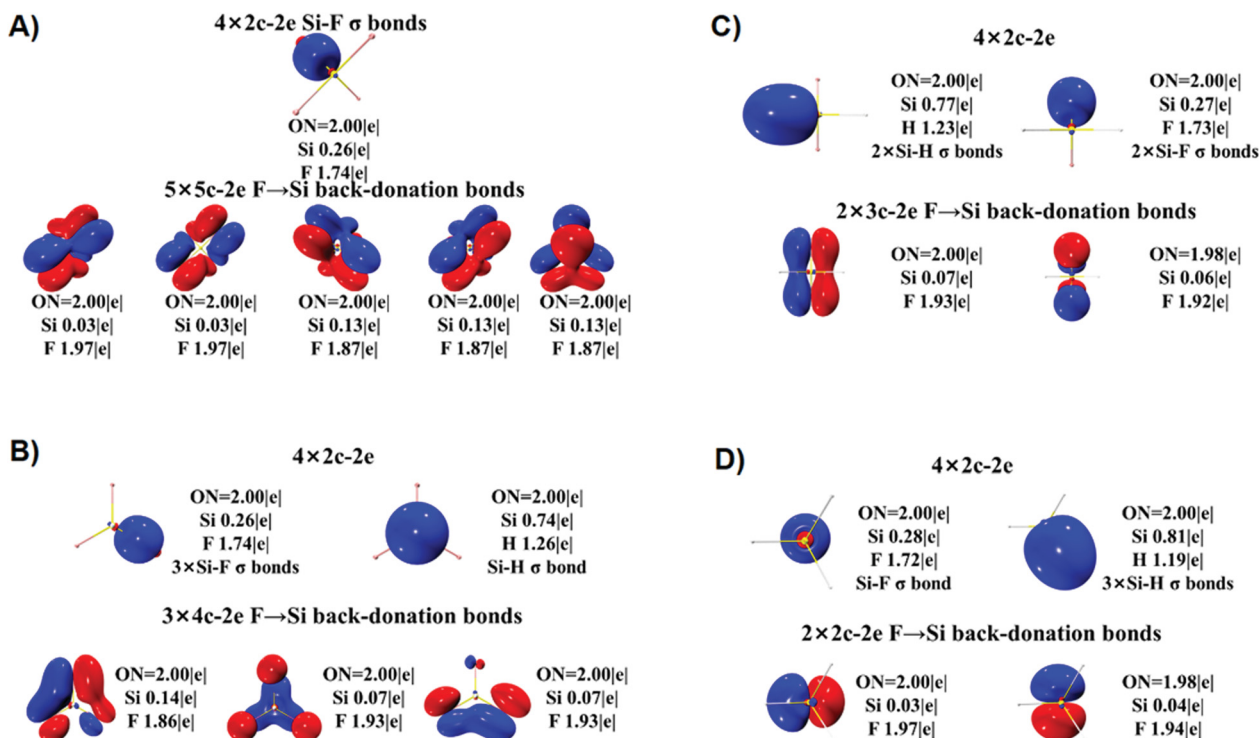


Fig. 2 AdNDP localized natural bonding orbitals of different molecules: (A) SiF_4 , (B) SiHF_3 , (C) SiH_2F_2 , and (D) SiH_3F . ON denotes the occupation number.

study $nc-2e$ bonds; here $1 \leq n \leq N_{\text{atoms}}$, where N_{atoms} represents the total atom number of the molecule. The AdNDP localized natural bonding orbitals of $\text{SiH}_n\text{F}_{4-n}$ ($n = 0-3$), CF_4 and TiF_4 are plotted in Fig. 2 and Fig. S2 in the ESI,[†] respectively. The occupation numbers (ONs) of these orbitals are all about $2.00|e|$. The occupation number means the number of electrons in a bond. It proves that our results are reliable. Here, we just show the orbitals contributing to the Si-F or Si-H bond, and the orbitals just composed by the electrons of F atoms are neglected. Taking SiF_4 as an example, there are 16 occupied orbitals by MO analysis and 16 bonds by AdNDP analysis. Through AdNDP analysis, there are four $1c-2e$ bonds (lone pairs of F atoms), four $2c-2e$ bonds (Si-F σ bonds), three $4c-2e$ bonds (linear combinations of lone pairs of F atoms) and five $5c-2e$ bonds (F-Si back-donation bonds). These $1c-2e$ and $4c-2e$ bonds are only related to F atoms and do not get any contribution from the Si atom, so we neglect these bonds and only plot the other nine bonds (four $2c-2e$ bonds and five $5c-2e$ bonds).

As shown in Fig. 2A, the AdNDP analysis of SiF_4 presents four $2c-2e$ Si-F σ bonds contributing to the bond order about 1. Because of the higher electronegativity of the F atom, there are more electrons on F ($1.74|e|$) and less electrons on Si ($0.26|e|$), so the four $2c-2e$ bonds are characterized by $\text{Si} \rightarrow \text{F}$ σ donation bonds. Significantly, there exist five $5c-2e$ bonds delocalized on the whole molecule, making extra contribution to the Si-F bonding. The five $5c-2e$ bonds are characterized by $\text{F} \rightarrow \text{Si}$ back-donation bonds. Obviously, in the five $5c-2e$ bonds the four F atoms as a whole feedback 0.45 electrons

($0.03 \times 2 + 0.13 \times 3 = 0.45|e|$) to somewhere of the Si atom, so the contribution of $5c-2e$ bonds to the Si-F bond order is less than 1. Which parts of Si are used to accept the electrons from F atoms? The NBO analysis results listed in Table 4 show that the 3d orbitals of the Si atom accept a few electrons back-donated from F atoms, because there are $0.1e$ on the 3d orbitals of Si, while there are still $0.35e$ left. Thus, we assume that the electrons of F atoms are mainly back-donated to σ -holes³⁵ on Si. The term “ σ -hole” means the regions with positive potential, on the extensions of covalent bonds of Group IV–VII atoms. In recent years, the concept of σ -holes has been studied extensively. Alvaro Muñoz-Castro and coworkers³⁶ found that σ -holes result in the interaction of $[(\text{NHC})\text{M}]^+$ ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$) with Et_2O and H_2O ; Nie and coworkers³⁷ found that SnI_4 can interact with fullerene (C_{60}) via σ -holes. The σ -hole characteristics of $\text{SiH}_n\text{F}_{4-n}$ ($n = 0-3$) are plotted in Fig. S3 (ESI[†]) by using an electrostatic potential surface over a 0.001 a.u. electron density. Here, the σ -holes are located on the extensions of Si-F bonds. We assume the σ -holes around the Si atom interact with the electrons of F atoms. This assumption is also supported by Lindner’s work.²⁰ Lindner and coworkers found that the Si atom becomes more positive as the number of F atoms increases, and there exists an electrostatic interaction between Si and F atoms. Essentially, the interactions of σ -holes with the electrons of F atoms are electrostatic. These interactions result in the formation of five $5c-2e$ bonds. The AdNDP localized natural bonding orbitals of SiCl_4 , SiBr_4 and SiI_4 are similar to those of SiF_4 , as shown in Fig. S4 (ESI[†]), and the total feedback electron number in these $5c-2e$ bonds is shown in Table S2 (ESI[†]). In SiX_4 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) molecules, $\text{Cl} \rightarrow \text{Si}$ back-donation electrons (0.49)

in SiCl_4 are most. Thus, the feedback electron number depends not only on the electronegativity of the X atom, but also on the polarity of lone pairs of X atoms. Here, we named this kind of 5c-2e bond as a synergistic back-donation (SBD) bond, which contributes to the high thermal stability of SiX_4 .

Moreover, in addition to the SBD bond, the 18e rule is another important factor to enhance the stability of SiF_4 . For many years, SiF_4 is traditionally considered as a perfect molecule which follows the octet rule³⁸ well. Both Si and F atoms have eight electrons in their valence shell like the noble gas Ne. Besides the octet rule, AdNDP localized natural bonding orbitals show that SiF_4 also accords well with the 18e rule. The 18 electrons come from the four 2c-2e bonds and five 5c-2e bonds. Above all, the Si-F σ bonds and SBD bond together with the 18e rule result in a higher WBI value (1.81) and the unusual thermal stability of SiF_4 .

Compared with SiF_4 , SiHF_3 lacking one F atom has three 2c-2e Si $\rightarrow$ F σ donation bonds, one 2c-2e Si-H σ bond, and three 4c-2e F $\rightarrow$ Si back-donation bonds (Fig. 2B). Similarly, Fig. 2C shows that SiH_2F_2 has two 2c-2e Si $\rightarrow$ F σ donation bonds, two 2c-2e Si-H σ bonds, and two 3c-2e F $\rightarrow$ Si back-donation bonds. The AdNDP orbitals of SiH_3F shown in Fig. 2D are one 2c-2e Si $\rightarrow$ F σ donation bond, three 2c-2e Si-H σ bonds, and two 2c-2e F $\rightarrow$ Si back-donation bonds. Obviously, 2c-2e Si $\rightarrow$ F σ donation bonds and nc-2e F $\rightarrow$ Si back-donation bonds contribute to the Si-F bond order more than 1, but the three molecules SiHF_3 , SiH_2F_2 and SiH_3F do not follow the 18 electron rule. SiHF_3 is fourteen electron count

(four 2c-2e bonds and three 4c-2e bonds as shown in Fig. 2B), and SiH_2F_2 and SiH_3F are twelve electron count (four 2c-2e bonds and two 3c-2e bonds as shown in Fig. 2C and 2D).

The results in Table 4 show that the ratio of 3d(Si) population to N_e (the total electron number of the F $\rightarrow$ Si back-donation) increases with the decrease in the number of F atoms ($0.05/0.07 > 0.07/0.13 > 0.09/0.28 > 0.1/0.45$), which means that the dominant back-donation was changed from F $\rightarrow \sigma$ -holes to F $\rightarrow$ 3d orbitals of Si with the decrease in the number of F atoms. Therefore, for SiH_3F , the two 2c-2e F $\rightarrow$ Si back-donation bonds mainly originate from the electrons back-donated from F to the 3d orbitals of Si and the contribution from σ -holes is very little, whereas, for SiF_4 , the five 5c-2e F $\rightarrow$ Si back-donation bonds mainly originate from the electrons back-donated from F to the σ -hole and the contribution from the 3d orbitals of Si is very little. Thus, with the decrease of the number of F atoms, the interaction of the σ -hole with the electrons of F atoms decreases, because the Si atom becomes less positive with the decrease in the number of F atoms as shown in Table 4 (the NBO based atomic charges on Si). However, the total electron number of the F $\rightarrow$ Si back-donation (N_e) for molecules $\text{SiH}_n\text{F}_{4-n}$ ($n = 0-3$) increases sharply with the increase in the number of F atoms (from 0.07 to 0.45), resulting in increased values of WBIs from SiH_3F (1.74) to SiF_4 (1.81). SiF_4 has the strongest feedback and the biggest WBI value among $\text{SiH}_n\text{F}_{4-n}$ molecules.

The total feedback of CF_4 in the 5c-2e bond (Fig. S2A and Table S2, ESI†) is about $0.002 \times 2 + 0.11 \times 3 = 0.334|e|$, which is

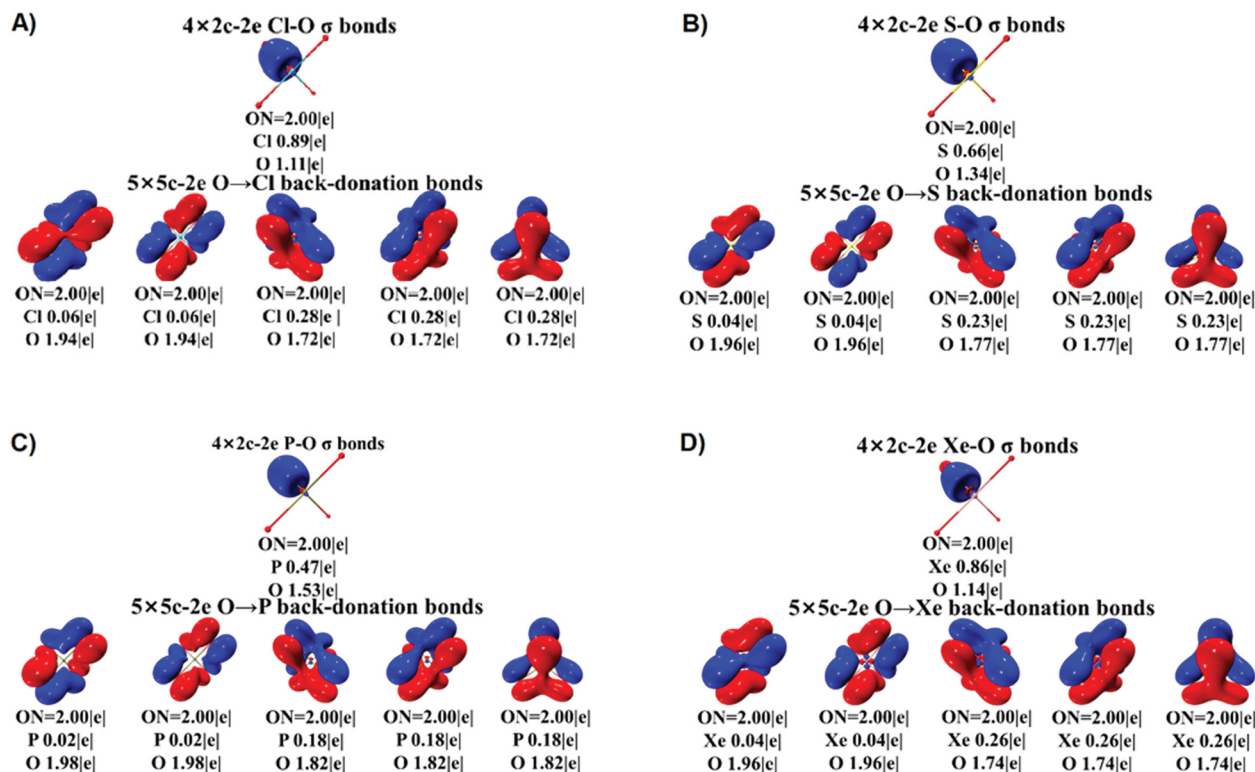


Fig. 3 AdNDP localized natural bonding orbitals of different molecules: (A) ClO_4^- , (B) SO_4^{2-} , (C) PO_4^{3-} , and (D) XeO_4 . ON denotes the occupation number.

Table 5 NPA charges of the isoelectronic species of SiF₄ (ClO₄[−], SO₄^{2−}, PO₄^{3−} and XeO₄)

	Cl, S, P or Xe	O
ClO ₄ [−]	2.59	−0.90
SO ₄ ^{2−}	2.59	−1.15
PO ₄ ^{3−}	2.51	−1.38
XeO ₄	3.85	−0.96

less than that of SiF₄, because the shorter radius of the C atom makes its electron density larger, leading to a stronger repulsion for the electrons from F atoms. TiF₄ is a coordination compound, and the total feedback electron number is increased to $0.29 \times 2 + 0.15 \times 3 = 1.03|e|$ (Fig. S2B and Table S2, ESI†). The electrons on F atoms are mainly back-donated to two 3d orbitals and three 4p orbitals of the Ti atom. As we know, the more the electrons back-donated from the F atoms to the central atom, the stronger the back-donation bond. Thus, the SBD bond energy should follow the order of TiF₄ > SiF₄ > CF₄. As stated in the section of Molecular orbitals, the trend of σ bond energy is C–F > Si–F > Ti–F. Both of these factors make the average bond energy follow the order of Si–F (in SiF₄) > Ti–F (in TiF₄) > C–F (in CF₄) as shown in Table S1 (ESI†).

3.3. SBD bonds in other isoelectronic species of SiF₄

AdNDP analysis proves that SiX₄, CF₄ and TiF₄ have five 5c–2e bonds, *i.e.* SBD bonds. Here a new question emerges. Whether do the SBD bonds exist in other isoelectronic species? We take four isoelectronic species ClO₄[−], SO₄^{2−}, PO₄^{3−} and XeO₄ as examples to perform AdNDP bonding analysis, and the results are plotted in Fig. 3. Obviously, there are also five SBD bonds in the four isoelectronic species just like the case in SiF₄. The feedback electrons of the four O atoms to the central atom (Cl, S, P or Xe) were calculated. The results show that the degree of back-donation decreased in the order of ClO₄[−] (0.96|e|) > XeO₄ (0.86|e|) > SO₄^{2−} (0.77|e|) > PO₄^{3−} (0.58|e|). Moreover, the natural population analysis (NPA) was also performed on these four species. NPA charge analysis is a part of natural bond orbital (NBO) analysis and can be used to calculate the charge of atoms. The results of NPA charge analysis are listed in Table 5. The O atoms are negatively charged, and the negative charges on O atoms increase in the order of ClO₄[−] < XeO₄ < SO₄^{2−} < PO₄^{3−}, which is opposite to the degree of back-donation in SBD bonds (ClO₄[−] > XeO₄ > SO₄^{2−} > PO₄^{3−}). This is reasonable because the negative charges on O atoms are mutually exclusive, and the more the negative charges, the stronger the exclusiveness, leading to fewer electrons back-donated from O atoms to the central atom.

4. Conclusion

By a comparative study of a series of molecules SiH_nF_{4−n} ($n = 0-3$), SiX₄ (X = Cl, Br, I), CF₄ and TiF₄ in terms of bond lengths, energies, MOs and AdNDP analysis, we found that the Si–F σ bonds, SBD bonds and the eighteen-electron rule are three main factors contributing to the short Si–F bond length,

the large bond energy and the high thermal stability of SiF₄. In molecules SiH_nF_{4−n} ($n = 0-3$), the Si–F bond length decreases and bond energies increase as the number of F atoms increases. SiF₄ has the shortest Si–F bond length and the largest bond energy and WBI value, because it has the most electrons back-donated from F atoms to the central atom, and meanwhile it follows the eighteen-electron rule. The AdNDP analysis also shows that SBD bonds widely exist in other isoelectronic species of SiF₄ like SiX₄, ClO₄[−], SO₄^{2−}, PO₄^{3−} and XeO₄. As reported previously, SnI₄ can interact with C₆₀ *via* σ -holes. The species we studied in this work, as the isoelectronic species of SnI₄, may interact with C₆₀ *via* σ -holes as well. It provided a new direction for further study.

Conflicts of interest

There are no conflicts of interest to declare.

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