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From strong to weak NF bonds: on the design of a new class of fluorinating agents†

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A set of 50 molecules with NF bonds was investigated to determine the factors that influence the strength of a NF bond, with the aim of designing a new class of fluorinating agents. The intrinsic bond strength of the NF bonds was used as bond strength measure, derived from local stretching NF force constants obtained at the CCSD(T)/aug-cc-pVTZ and ω B97XD/aug-cc-pVTZ levels of theory. The investigation showed that the NF bond is a tunable covalent bond, with bond strength orders ranging from 2.5 (very strong) to 0.1 (very weak). NF bond strengthening is caused by a combination of different factors and can be achieved by e.g. ionization. Whereas, the NF bond weakening can be achieved by hypervalency on the N atom, using a N→Ch (Ch: O, S, Se) donor–acceptor type bond with different electron-withdrawing groups. These new insights into the nature of the NF bond were used to propose and design a new class of fluorinating agents. Hypervalent amine-chalcogenides turned out as most promising candidates for efficient electrophilic fluorinating agents.

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1 Introduction

The field of fluorination chemistry is an active area of research.¹ Due to the favorable properties of fluorinated compounds, especially with respect to metabolic degradation and thermal stability, fluorinated molecules have found many applications as pharmaceuticals, agrochemicals, and materials.^{2–5} More than 25 percent of pharmaceuticals and 40 percent of agrochemicals on the market contain fluorine atoms.^{6,7} The fluorinated drug molecules bind stronger to the target active sites through possible halogen bond formation and improve metabolic stability in living cells.^{8–17}

The development of fluorination chemistry has been a long journey, from one century ago with the first examples of electrophilic and nucleophilic fluorination to the more recent fluoromethylation, difluoromethylation and trifluoromethylation.¹ While the source for nucleophilic fluorine is abundantly available, the source for electrophilic fluorine is limited.^{9,18} Initially, radical fluorination with gaseous molecular fluorine F₂ (BDH(F–F) = 37.9 kcal mol^{–1})^{19,20} was the only option for electrophilic reactions. However its toxicity and the risks associated with its handling, brings forward the effort to look for another

source of electrophilic fluorinating agents, starting from the 1960s, from the O–F bonds,^{8,21–24} and recently in late 1980s and early 1990s with NF bonds.^{25–30}

Recently, Togni's reagents have become well known trifluoromethylating reagents in organic synthesis^{31–33} as the CF₃ group can dramatically enhance chemical and metabolic stability, lipophilicity, and binding selectivity.^{34–36} The discovery of new fluorination agents in the last two decades, such as SelectFluor^{28,30} and DAST (diethylaminosulfur trifluoride),³⁷ has provoked increasing interest in the development of fluorinating agents.^{1,38}

Fluorination chemistry faces many challenges, such as lacking generality, practicality, and predictability, making this an active field of research. Many of the fluorinating agents on the market contain NF bonds. Thus, it is important to understand the key factors that influence the strength of the NF bond. The efforts to relate bond lengths and bond strengths can be traced to the works initiated in the 1920s by Kratzer³⁹ and later by Badger,^{40,41} where they found an empirical relationship between bond lengths and stretching frequencies. This empirical relationship was the basis for the tenet relating bond lengths and bond strengths: “the shorter bond is always the stronger bond”.^{42–46} In the last three decades, it has been proved that this tenet is not always true. A reverse bond length–bond strength (BLBS) relationship were observed, for example: in the fluoro amines H_nNF_{3–n} and methyl fluoro amines (CH₃)_nNF_{3–n} with (n = 0–2),^{47–56} the fluorine bonds in substituted ethane homologues,^{57–59} the O–F bonds in HOF, OF₂, and FNO₂,^{60–64} and the S–F bonds in the SF₂ dimer.^{65,66}

Vibrational spectroscopy is a powerful tool to identify and characterize a molecule with the help of its vibrational modes.

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‡ In memoriam.

However, on a routine basis, the amount of information contained in a measured vibrational spectra is not explored to its full extent. Konkoli and Cremer^{67,68} developed the extended use of vibrational spectroscopy by empowering the theory of local modes for a dynamical model of the bond strength. They demonstrated that the local mode analysis gives a direct way of determining the intrinsic strength of a bond,^{56,69–71} which has successfully been applied to both covalent bonds^{71–74} and weak chemical interactions.^{14,15,75–85} In this work, we systematically studied the strength of the NF bonds in a set of 50 representative molecules and in the commercial fluorinating agent, SelectFluor.^{9,13,86–88} SelectFluor is one of the most economical, stable (in various solvents), and safe fluorinating agents¹³ which are used in pharmaceuticals, agrochemicals, and advanced materials.^{11,12,89–91} SelectFluor has an electrophilic fluorine which can be donated to other compounds. Thus, the knowledge of the key factors that influence the strength of the NF bonds can be a guide to design a new class of fluorinating agents.

The main objectives of this paper are: (i) to evaluate why the NF bond becomes stronger upon ionization of the fluoroamine molecules; (ii) to evaluate why the NF bond becomes weaker in the case of hypervalent fluoroamine chalcogenides, and how an additional electron withdrawing group (EWG) or electron donating group (EDG) affect the NF bond strength; (iii) to investigate the interplay of electronic effects causing the strengthening or weakening of NF bonds in general; (iv) to investigate the NF bond strength in connection with the electrophilic fluorinating agent, SelectFluor, and to show that upon ionization, the NF bond in the SelectFluor radical becomes much weaker; and (v) to propose a new class of electrophilic fluorinating agents which are based on hypervalent fluoroamine chalcogenides.

To fulfill the objectives, a large number of quantum chemical calculations were carried out on 50 fluoroamine molecules (see Fig. 1). The computational methods that were used in this work are discussed in Section 2. In the Results and discussion section (Section 3), we introduce the factors that influence the strength of the NF bonds of the molecules investigated in this work, followed by discussing the criteria for the design of a new type of NF fluorinating agents. The concluding remarks of this work are made in Section 4.

2 Computational methods

Equilibrium geometries and normal vibrational modes of molecules **1–26** and reference molecules **R1–R2** were obtained using coupled cluster theory with singles, doubles, and perturbative triples (CCSD(T))^{92,93} and Dunning's aug-cc-pVTZ basis sets.^{94–96} For radical systems, unrestricted HF wavefunctions were used as reference. These results were compared with the fluoroamines (**N1–N24**) published previously (see ESI†).⁵⁵ Molecules **21–26** and **N16–N24** were re-calculated at DFT level to verify that the chosen ω B97XD functional reproduces the CCSD(T) results. The results of molecules **N16–N24**⁵⁶ can be found in Table S1 ESI.† We resort to DFT due to the size of our molecules of interest: the commercial fluorinating agents (SelectFluor). The SelectFluor compounds and its tetrafluoroborate

counteranions **27–32**, substituted chalcogenides **33–50**, and corresponding bond strength order (BSO) references **R1–R2** were optimized using the ω B97XD⁹⁷ with Dunning's aug-cc-pVTZ basis set.^{94–96} For radical systems, unrestricted U- ω B97XD was used.

The normal vibrational modes of a molecule are coupled *via* electronic and kinematic (mass) coupling.⁶⁷ Electronic decoupled modes are obtained by solving the Wilson equation,⁹⁸ where the resulting normal modes are delocalized in the molecular framework as a result of kinematic (mass) coupling. Previously, Konkoli and Cremer demonstrated that a mass-decoupled equivalent of the Wilson equation leads to local vibrational modes which are associated with a given internal coordinate, q_n , (bond length, bond angle, and dihedral angle), solving the mass-decoupled Euler–Lagrange equations.^{67,68} Furthermore, Zou and Cremer showed that there is a one to one relationship between the local and the normal vibrational modes, which can be verified with the Adiabatic Connection Scheme (ACS).⁷⁰ Therefore, the local (NF) vibrational force constant $k^a(\text{NF})$ is the appropriate tool for the description of the NF bond strength *via* vibrational spectroscopy.

2.1 BSO scaling

The conversion of local mode force constants, k^a , of NF bonds into bond strength order, BSO(NF), were determined with using the power relationship:

$$\text{BSO}(\text{NF}) = a(k^a)^b \quad (1)$$

As reference molecules, H₂NOH (**R1**) and HNO (**R2**) were used: the k^a associated with the N–O bond in H₂NOH (**R1**) was set to have BSO = 1 and the k^a associated with N=O bond in HNO (**R2**), was set to have BSO = 2. It was also assumed that $k^a = 0$ equals to BSO $n = 0$. At the CCSD(T)/aug-cc-pVTZ level of theory: $a = 0.402$ and $b = 0.669$, while at ω B97XD/aug-cc-pVTZ: $a = 0.369$ and $b = 0.654$ were obtained.

2.2 NF BSO scaling

Further scaling was done to scale the NF bond in H₂N–F (**R3**) to have BSO = 1. As a result, the scaling factor $f_{\text{CCSD(T)}} = 0.962$ was applied for BSO obtained from CCSD(T) and $f_{\omega\text{B97XD}} = 0.992$ for BSO obtained from DFT leading to

$$\text{BSO}(\text{NF})^{\text{scaled}} = f_n \times \text{BSO}(\text{NF})^{\text{unscaled}}$$

where n : ω B97XD, CCSD(T).

The CCSD(T) calculations were performed using the CFOUR^{99,100} program, while DFT calculations were done with the Gaussian09¹⁰¹ package. All CCSD(T) calculations were carried out using a convergence criterion of 10^{-7} Hartree Bohr⁻¹ for geometry and for the self-consistent field (SCF) iterations, and a threshold of 10^{-9} for the CC amplitudes. All DFT calculations were carried out with an ultrafine integration grid¹⁰² and a tight convergence criterion for the forces (10^{-5}) and displacements in the geometry optimizations. Each equilibrium geometry obtained by either CCSD(T) or DFT corresponds to a geometry minimum. NF bond dissociation energies and enthalpies were calculated using the G4 method.¹⁰³ The calculated charge distribution was obtained *via* the natural population analysis within the natural bond orbital (NBO) scheme,^{104,105} where

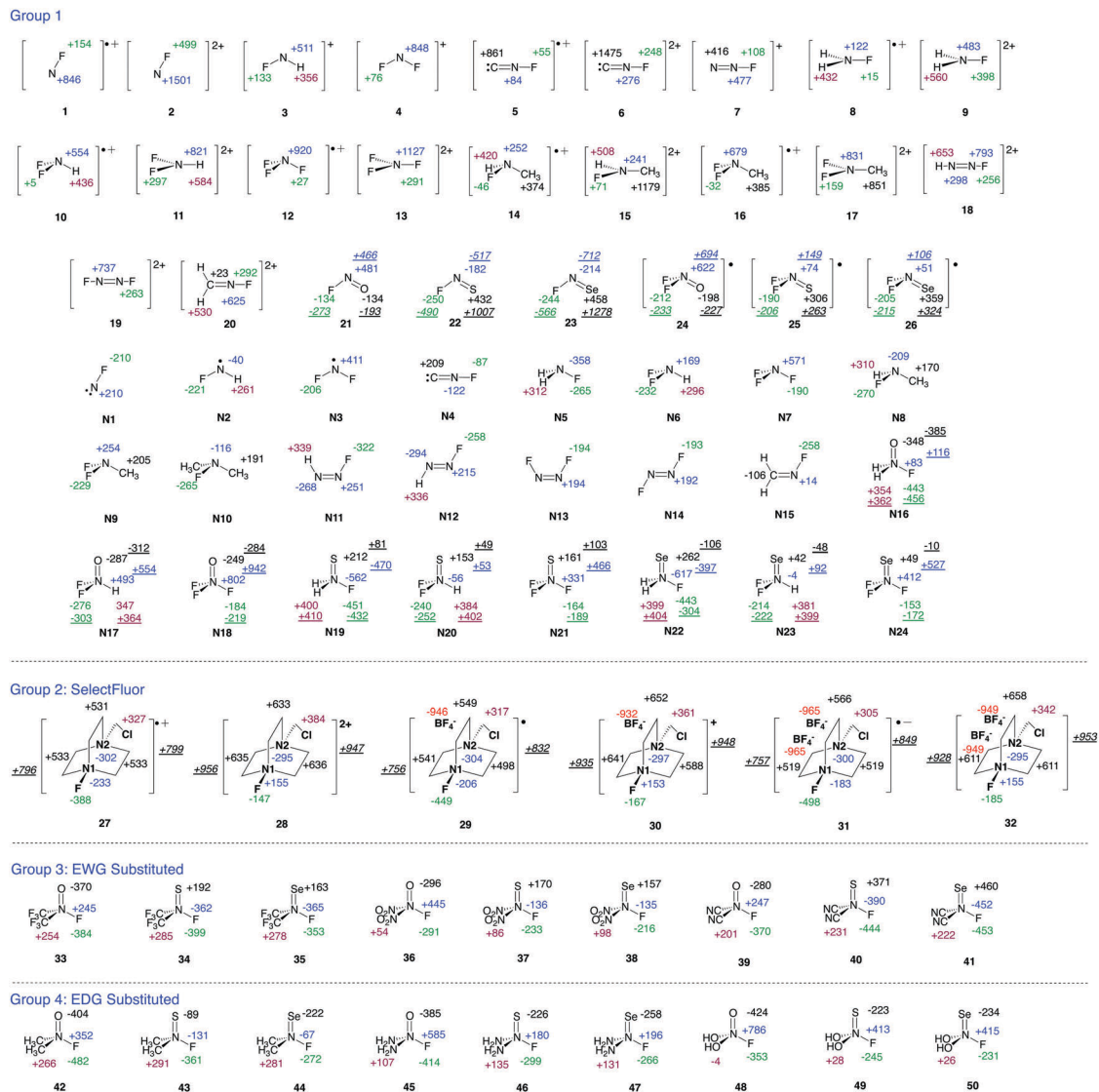


Fig. 1 NBO charges of molecules **1–50** and **N1–N24** in me. The numbers represent the partial atomic charges on N atoms (blue) and F atoms (green) (for Group 1: H atoms (magenta) and other atoms or functional groups (black), while for Group 2: CH₂Cl functional group (magenta), the –CH₂–CH₂– group (black), and the tetrafluoroborate counteranions (red), and for group 3 and 4: functional group (magenta) and atoms O, S, and Se (black)). For Group 1 (molecules **1–26** and **N1–N24**), NBO charges were calculated at the U/R-CCSD(T)/aug-cc-pVTZ level of theory; (underlined numbers for molecules **21–26** and **N16–N24**: U/R- ω B97XD/aug-cc-pVTZ NBO charges for comparison). For Group 2–Group 4 (molecules **27–50**) NBO charges were calculated at the U/R- ω B97XD/aug-cc-pVTZ level of theory. The underlined numbers for Group 2 molecules reflect the charge of methyl group attached to **N1** (left) and that of the methyl group attached to **N2** (right).

response densities were used for CCSD(T). The electron density and the energy density^{106–108} at the NF bond critical points^{109–111} were calculated using the AIMAll program.¹¹² Local mode force constants and frequencies⁶⁷ were calculated using COLOGNE2017.¹¹³ The pyramidalization angle of the NR₃ amines were determined according to the scheme proposed by Haddon.¹¹⁴

3 Results and discussion

The results are organized in the following way: first, the use of local mode analysis as a measure of intrinsic bond strength is discussed (Section 3.1). Second, the strength of the NF bonds

from strong to weak, which can be tuned by ionization or hypervalency, is discussed, followed by factors affecting the strength of NF bond in fluoroamines (Section 3.2). Third, the NF bond in SelectFluor is discussed (Section 3.3), followed by the discussion of the designing of a new class of fluorinating agents (Section 3.4).

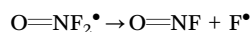
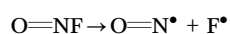
3.1 Local mode analysis as a predictive tool

3.1.1 Intrinsic vs. thermodynamic bond strength parameter.

Bond dissociation energy (BDE) and bond dissociation enthalpy (BDH) are important parameters for the description of chemical reactions. They are also widely used as a measure of chemical bond strength, where values are calculated by taking the energy (enthalpy) difference between the molecule at its equilibrium

and the dissociated molecular fragments in their ground state. However, BDE and BDH are of limited value for the description of the intrinsic bond strength, because they include geometry relaxation and electron density reorganization of the fragments, as pointed out by Cremer *et al.*^{55,56,115} Therefore, the local force constant k^a and the related BSO are the most suitable measure of the intrinsic bond strength for covalent bonds^{71–74} and weak chemical interactions.^{14,15,75–85}

The correlation of k^a (BSO) with BDE for many molecules has shown that a chemical bond may have a large value of k^a but low BDE, or the inverse.^{55,56,82} A low BDH value is a consequence of a large relaxation energy of the one or both dissociated fragments, while a high BDH value implies there is only little reorganization of the electronic structure and geometry upon dissociation. One striking example is with nitrosyl fluorides **21** ($k^a = 1.832$ mdyne \AA^{-1} ; $\text{BDH}(\text{NF}) = 61.41$ kcal mol^{-1}) and difluoroamine oxide radical **24** ($k^a = 2.180$ mdyne \AA^{-1} ; $\text{BDH}(\text{NF}) = 6.12$ kcal mol^{-1}) (see Fig. 2), which fluorine dissociates through the following reactions:



The $k^a(\text{NF})$ increases in values for about 18%, while the $\text{BDH}(\text{NF})$ increases 10 times higher, which is due to large differences in geometry and electronic structures between the two radical fragments and the nitrosyl fluoride molecules, while for the difluoroamine oxide radical, both the dissociated radical fluorine and nitrosyl fluoride have similar geometries and/or electronic structures with the undissociated molecules.^{55,56,73,82,115}

We found for molecules **1–26** and **N1–N24** no obvious correlation between local mode force constants k^a and BDE or BDH. For EWG- and EDG-substituted fluoroamine chalcogenides, the low $k^a(\text{NF})$ values for both groups of molecules do not necessarily reflect the $\text{BDE}(\text{NF})$: EWG-substituted have low $\text{BDE}(\text{NF})$ values while EDG-substituted $\text{BDE}(\text{NF})$ are larger (Fig. 2). While both groups have similar NF bond strength, it

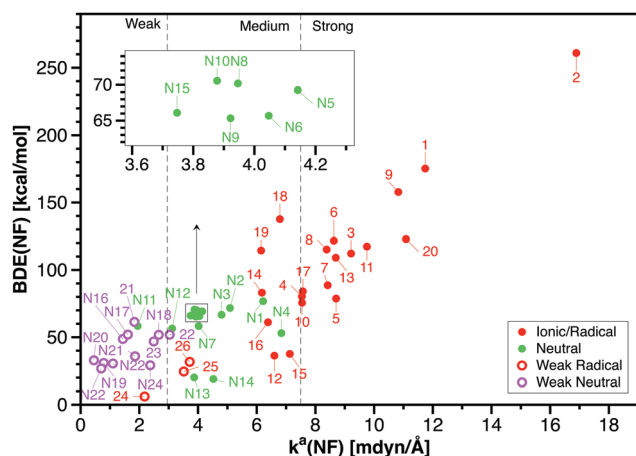


Fig. 2 The NF bond dissociation enthalpy BDE and the corresponding local mode force constant $k^a(\text{NF})$ of the molecules **1–26** and **N1–N24** calculated at U/R-CCSD(T)/aug-cc-pVTZ level of theory.

seems that the dissociation products of the EWG-substituted fluoroamine chalcogenides have larger resemblance in terms of the relaxed geometries and importantly the electronic structure of the chalcogenides with the dissociated fragments: *i.e.* the EWG-substituted fluoroamine chalcogenides have already some (di-)radicaloid characters due to large negative charges in both of N and F atoms.

3.2 NF bonds: from strong to weak

3.2.1 Strong NF bonds. Table 1 and Fig. 1 summarize molecular geometries, NBO charges, and NF bond properties of molecules **1–26** with strong NF bonds. The different effects that influence the NF strength are discussed in this section.

Ionization effect. The first ionization energy from $[\text{N-F}]$ (**N1**) to $[\text{N-F}]^{\bullet+}$ (**1**) is 12.16 eV (exp. 12.26 eV,¹¹⁶ Table S4, ESI†). The resulting NF bond in $[\text{N-F}]^{\bullet+}({}^2\Sigma^-)$ **1** is a shortened NF bond from 1.318 to 1.184 \AA (exp. 1.180 \AA)¹⁹ with NF stretching force constant $k^a(\text{NF}) = 11.742$ mdyne \AA^{-1} (bond strength order, BSO $n(\text{NF})$, 2.008) (see Fig. 3). This is stronger than the CC bond in ethene C_2H_4 ($k^a(\text{CC}) = 9.201$ mdyne \AA^{-1})¹¹⁷ with predicted $\text{BDH}(\text{NF})$ of 175.22 kcal mol^{-1} (*i.e.* a 2.281 BSO ratio with respect to the neutral NF).

NF bonds become very strong upon second ionization. Through second ionization, the NF bond in $[\text{N-F}]^{2+}({}^1\Sigma^+)$ **2**, which is isoelectronic to the molecular nitrogen N_2 , is shortened from 1.184 to 1.099 \AA with an NF stretching force constant of 16.890 mdyne \AA^{-1} . This means that the NF bonds are about the same strength as the CC bond in ethyne C_2H_2 ($k^a(\text{CC}) = 16.191$ mdyne \AA^{-1})¹¹⁷ but weaker than the NN bond in N_2 ($k^a(\text{NN}) = 22.409$ mdyne \AA^{-1}).⁷³ The double ionization energy from $[\text{N-F}]$ to $[\text{N-F}]^{2+}$ is 35.85 eV (CCSD(T), Table S4, ESI†). The corresponding NF in $[\text{N-F}]^{2+}({}^1\Sigma^+)$ **2** has a bond strength order of 2.561 (BSO $n(\text{NF}) = 2.561$). Based on the composite G4 method, the two-and-half NF bond order is predicted to have bond dissociation enthalpy BDH of 260.96 kcal mol^{-1} , which is higher than triple ratio (3.39) of the corresponding BDH of the neutral NF molecule, 76.83 kcal mol^{-1} . Furthermore, from a high level B3LYP//CCSD(T)/CBS calculation, the enthalpy of formation of $[\text{N-F}]^{\bullet+}$ is predicted to be 340.6 kcal mol^{-1} (ref. 118) and the results from large multireference calculations show that **2** is kinetically stable,^{119–121} with a barrier of about 106 kcal mol^{-1} .¹²⁰ The formation of $[\text{N-F}]^{2+}$ has been experimentally detected by mass spectroscopy, from electron impact ionization of NF_3 .¹²²

The ionization of the NF molecule increases the natural bond orbital (NBO) charges of each N and F atom. In neutral NF **N1**, as F is a more electronegative than N (Pauling electronegativity $\chi_{\text{F}} = 3.98$ and $\chi_{\text{N}} = 3.04$), F has a negative charge of -210 millielectron (me) while N has a positive charge of $+210$ me (see Table S5, ESI†). Upon single and double ionization of **N1**, F become positive, *i.e.* $+154$ (**1**) and $+499$ me (**2**), while less electronic shielding leads to a larger positive charge on the N atoms:¹²³ $+846$ (**1**) and $+1501$ me (**2**) (see Fig. 1).

The strengthening of the NF bond is caused by increasing the covalent characters. From the electron density analysis of

Table 1 NF bond distances $R(\text{NF})$, local mode frequencies $\omega^a(\text{NF})$, force constant $k^a(\text{NF})$, bond strength order BSO $n(\text{NF})$, electron densities ρ_c , energy densities H_c , the energy density ratio $\frac{H_c}{\rho_c}$, NF bond dissociation energy BDE and enthalpy BDH for molecule **1–26** and reference molecules **R1–R2**, calculated at U/R-CCSD(T)/aug-cc-pVTZ level of theory

#	Molecule (state), sym.	$R(\text{NF})$ (Å)	$\omega^a(\text{NF})$ (cm^{-1})	$k^a(\text{NF})$ ($\text{mdyn } \text{Å}^{-1}$)	BSO $n(\text{NF})$	$\rho_c(\text{NF})$ ($\text{e}/\text{Å}^3$)	$H_c(\text{NF})$ ($\text{h}/\text{Å}^3$)	$\frac{H_c}{\rho_c}(\text{NF})$ (h/e)	BDE ^a (kcal mol^{-1})	BDH ^a (kcal mol^{-1})
N-F in cations										
1	$[\text{N-F}]^{+\bullet}(^2\Sigma^-)$, $C_{\infty v}$	1.184	1572	11.742	2.008	3.436	-6.901	-2.008	177.49	175.22
2	$[\text{N-F}]^{2+}(^1\Sigma^+)$, $C_{\infty v}$	1.099	1886	16.890	2.561	4.370	-10.591	-2.424	263.73	260.96
3	$[\text{HN-F}]^+(^1A')$, C_s	1.237	1393	9.215	1.708	3.030	-5.021	-1.657	116.20	112.23
4	$[\text{FN-F}]^+(^1A_1)$, C_{2v}	1.245	1260	7.539	1.493	3.090	-4.697	-1.520	82.52	80.32
5	$[\text{C=N-F}]^{+\bullet}(^2\Pi)$, $C_{\infty v}$	1.256	1354	8.705	1.644	2.939	-3.943	-1.341	81.82	78.75
6	$[\text{C=N-F}]^{2+}(^1\Pi)$, $C_{\infty v}$	1.222	1348	8.628	1.634	3.225	-4.522	-1.403	123.48	121.71
7	$[\text{N=N-F}]^+(^1\Pi)$, $C_{\infty v}$	1.246	1331	8.418	1.607	3.022	-4.080	-1.350	91.52	88.65
8	$[\text{H}_2\text{N-F}]^+(^2A')$, C_s	1.280	1329	8.384	1.603	2.763	-3.772	-1.365	120.02	115.21
9	$[\text{H}_2\text{N-F}]^{2+}(^1A')$, C_s	1.202	1510	10.826	1.902	3.388	-5.950	-1.756	164.69	157.79
10	$[\text{H(F)N-F}]^{+\bullet}(^2A')$, C_s	1.276	1260	7.545	1.494	2.846	-3.773	-1.326	78.72	75.61
11	$[\text{H(F)N-F}]^{2+}(^1A_2)$, C_{2v}	1.211	1433	9.756	1.774	3.427	-5.408	-1.578	123.00	117.38
12	$[\text{F}_2\text{N-F}]^{+\bullet}(^2A_1)$, C_{3v}	1.281	1179	6.602	1.366	2.859	-3.591	-1.256	38.70	36.29
13	$[\text{F}_2\text{N-F}]^{2+}(^1E)$, C_{3v}	1.221	1353	8.693	1.642	3.379	-4.829	-1.429	112.30	109.13
14	$[\text{H}_3\text{C(H)N-F}]^{+\bullet}(^2A)$, C_1	1.301	1140	6.177	1.307	2.613	-3.348	-1.281	88.34	83.14
15	$[\text{H}_3\text{C(H)N-F}]^{2+}(^1A)$, C_1	1.282	1225	7.127	1.438	2.817	-3.586	-1.273	40.45	37.59
16	$[\text{H}_3\text{C(F)N-F}]^{+\bullet}(^2A')$, C_s	1.294	1189	6.714	1.382	2.718	-3.442	-1.266	65.01	61.13
17	$[\text{H}_3\text{C(F)N-F}]^{2+}(^1A')$, C_s	1.250	1263	7.573	1.497	3.121	-4.322	-1.385	89.52	84.14
18	$[\text{HN=N-F}]^{2+}(^1\Pi)$, $C_{\infty v}$	1.214	1196	6.789	1.392	3.310	-4.674	-1.412	141.48	137.62
19	$[\text{FN=N-F}]^{2+}(^1\Pi_u)$, $D_{\infty h}$	1.230	1138	6.150	1.303	3.158	-4.177	-1.323	117.95	114.43
20	$[\text{H}_2\text{C=N-F}]^{2+}(^1B_2)$, C_{2v}	1.197	1528	11.087	1.932	3.443	-5.588	-1.623	127.69	122.89
Ch=NF (Ch = O, S, Se)										
21	$[\text{O=N-F}]^{+\bullet}(^2A')$, C_s	1.514	623	1.832	0.580	1.513	-1.016	-0.671	63.14	61.41
22	$[\text{S=N-F}]^{+\bullet}(^2A')$, C_s	1.436	719	2.490	0.712	1.816	-1.559	-0.858	48.32	46.82
23	$[\text{Se=N-F}]^{+\bullet}(^2A')$, C_s	1.413	798	3.034	0.812	1.921	-1.785	-0.929	53.44	51.86
Ch=NF ₂ ⁺										
24	$[\text{O=N(F)-F}]^{+\bullet}(^2B_2)$, C_{2v}	1.436	678	2.180	0.651	1.879	-1.543	-0.821	7.95	6.12
25	$[\text{S=N(F)-F}]^{+\bullet}(^2B_2)$, C_{2v}	1.390	860	3.515	0.896	2.095	-2.036	-0.972	26.48	24.49
26	$[\text{Se=N(F)-F}]^{+\bullet}(^2B_2)$, C_{2v}	1.390	882	3.693	0.926	2.086	-2.051	-0.983	33.65	31.67
References: NO bonds										
R1	$\text{H}_2\text{N-OH}(^1A')$, C_s	1.443	942	3.905	0.962	1.924	-1.562	-0.812	69.08	62.98
R2	$\text{HN=O}(^1A')$, C_s	1.210	1582	11.007	1.923	3.505	-5.496	-1.568	167.50	164.71

^a BDE and BDH are calculated with the G4 method.

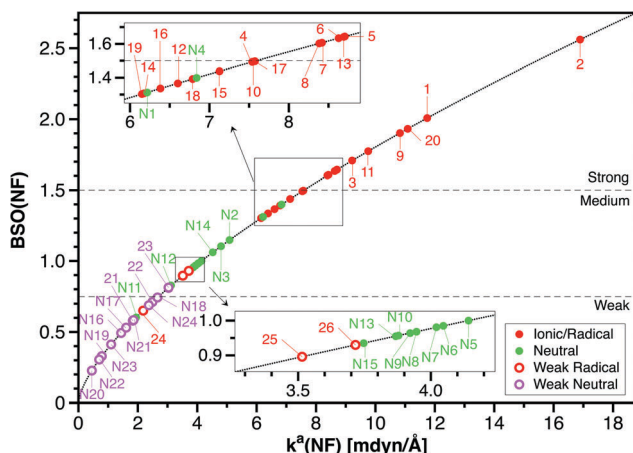


Fig. 3 The NF bond strength order (BSO) $n(\text{NF})$ of molecules **1–26** and **N1–N24** calculated at U/R-CCSD(T)/aug-cc-pVTZ level of theory.

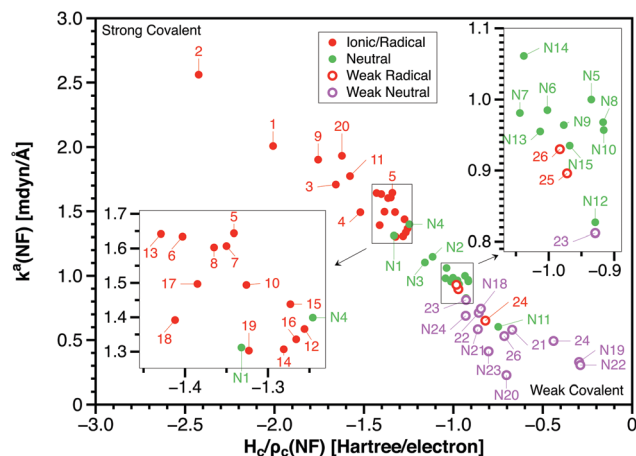


Fig. 4 The energy density $\frac{H_c}{\rho_c}$ at the N-F bond critical point for molecules **1–26** and **N1–N24** calculated at U/R-CCSD(T)/aug-cc-pVTZ level of theory.

the NF bond at bond critical point ρ_c , there is a significant increase from 2.391 (**N1**), to 3.436 (**1**) and 4.370 $\text{e}/\text{Å}^3$ (**2**), and an increase of covalent character as indicated by the more negative

values of the energy density ratio $\frac{H_c}{\rho_c}$: -1.332 (**N1**), -2.008 (**1**) and -2.424 h/e (**2**) (see Fig. 4). These results are in line with the

trend shown by the (multi)-cation of diatomic molecules.^{73,120} The strong electronegativity of the $[\text{N-F}]^{\bullet+}$ is considered an important factor in the plasma etching of the Si/SiO₂, where it may strongly bind to the O atom through the N atom.¹²⁴ Moreover, the less steric hindrance due to the missing (lone pair) electrons from the non-bonded region also leads to a shorter N–F bond distance, *i.e.* the exchange repulsion between lone pairs of N and F become smaller in **1** and **2** compared to the neutral compound **N1**.

Protonation and fluorination of NF bond. The protonation and fluorination of the N atom in **1** decreases NF bond strength order from 2.008 to 1.708 (**3**) and 1.493 (**4**) respectively, and also decreases the covalent character of the NF bonds. The additional electropositive H (**3**) decreases the charge of the central N atom to +511 me, while the electronegative F (**4**) just slightly increases the N charge to +848 me (compared to +846 me in **1**). The fact that the charge on the F atoms decreases from +154 (**1**) to +133 (**3**) and +76 me (**4**), indicates that the bond weakening is due to the electrons being more attracted to the F atoms' domain than to the NF bond region, which is also confirmed by the electron density analysis (0.406 (**3**) and 0.346 e/Å³ (**4**) decrease). With respect to their neutral counterpart **N2** and **N3**, the NF bonds in **3** and **4** are significantly stronger (Table 1 and Fig. 1).

NF bonds in **N2** and **N3** were shown to have a reverse bond length–bond strength (BLBS) relationship,⁵⁵ contrary to their cationic counterparts **3** and **4**. The NF bond in **N3** is shorter but weaker than the one in **N2**, while NF in **4** is longer ($R(\text{NF}) = 1.245 \text{ \AA}$) and weaker (BSO $n = 1.493$) than the one in **3** ($R(\text{NF}) = 1.237 \text{ \AA}$; BSO $n = 1.708$). The NF bond in **N3** is weakened by the lone pair–lone pair (lp(F)–lp(F)) repulsion,⁵⁵ which cease to exist in **4** due to reduced electron densities at F (NBO charges of +76 me, compared to –206 me in **N3**). The NF bond in **4** is due to the (mutual) anomeric delocalization of one of the in-phase (ip) lp(F) to the vicinal $\sigma^*(\text{NF})$, which is missing in **3**. From the second order perturbative analysis of donor–acceptor in NBO basis, it shows that the anomeric delocalization in **N3** (2e-stabilization $\Delta E_{ij} 6.05 \text{ kcal mol}^{-1}$) is not as strong as in **4** ($\Delta E_{ij} 15.84 \text{ kcal mol}^{-1}$) due to lower electronegativity of its F substituents compared to the positively charged F atoms in **4**.

Carbene- and nitrene-fluoroamines. The single ionization of carbene-fluoroamine **5** increases the NF bond strength order from 1.399 in neutral **N4** to 1.644. As in the previous case, the NF bond strengthening is due to an increased in the electron densities at the NF bond critical point (Table 1). Surprisingly, the further ionization of **5** to **6**, slightly decreases the bond strength order to 1.634, while the electron density at NF bond critical point are slightly increased by 0.286 e/Å³ due to a mutual increase of charges on both N and F (Fig. 1). However the BDH(NF) of **6** is 1.5 times higher than **5** due to the lower stabilization-energy of the dissociated fragment $[\text{CN}]^{2+}$ compared to $[\text{CN}]^+$.

The weaker NF bond in **6** (BSO $n = 1.634$; $R(\text{NF}) = 1.222 \text{ \AA}$) is also a shorter bond than in **5** (BSO $n = 1.644$; $R(\text{NF}) = 1.256 \text{ \AA}$),

thus a reverse BLBS anomaly. This is also observed for the cationic nitrene-fluoroamine **7**, which is isoelectronic with **6**, and has a shorter ($R(\text{NF}) = 1.246$) but weaker NF bond (BSO $n = 1.607$) than **5**. The anomaly can be explained as follows: (i) the NF bond shortening is due to the increase of the bond polarization, *i.e.* the charge of C atom **6** is significantly larger than the one in **5**, while in **7** it is due to electronegativity (N is more electronegative than C), which leads to a shortening of 0.010 Å; (ii) The NF bond weakening is due to the lp(F) and $\pi(\text{CN})$ (**6**)/ $\pi(\text{NN})$ (**7**) repulsion.

Fluoroamines. The reverse BLBS anomaly in neutral fluoroamines **N5–N7**,⁵⁵ are generally lost upon ionization, except for one: the shorter NF in cationic difluoroamine **10** ($R(\text{NF}) = 1.276 \text{ \AA}$; BSO $n = 1.494$) is weaker than the NF in cationic **8** ($R(\text{NF}) = 1.280 \text{ \AA}$; BSO $n = 1.603$). There is a significant hyperconjugation ($\Delta E_{ij} 56.86 \text{ kcal mol}^{-1}$) from lp(F) to partially filled lp(N) (*i.e.* **N(10)**: +554 me) which shorten the NF bond, and due to the lp(F)–lp(F) repulsion ($\angle \text{FNF} = 114.1^\circ$). In the fluoroamine **8**, there is only a small anomeric delocalization of lp(F) to the $\sigma^*(\text{NH})$.

The bond elongation and subsequent weakening in trifluoroamine cationic radical **12** is due to the large hyperconjugative effect (ΔE_{ij} between 17.90–133.03 kcal mol^{–1}) of mutual delocalization from $\sigma^*(\text{NF})$ to $\sigma^*(\text{NF})$, which was previously very small ($\Delta E_{ij} = 1.40 \text{ kcal mol}^{-1}$) in the neutral counterpart **N7** and is overridden by the stronger anomeric delocalization effect of 7.15 kcal mol^{–1}. Thus, there is a direct BLBS relationship for **12** compared to **8** and **10**. The cationic trifluoroamine **12**, for which the study of its inversion barrier was of main interest for spectroscopists and theorists in the late 1980s,^{125–135} is an important intermediates for plasma etching and cleaning of semiconductors.¹³⁶

For dicationic species **9**, **11**, and **13**, the normal BLBS relationship is also observed: The NF bond lengthening in **11** and **13** are due to bond polarity and anomeric effect lp(F) → $\sigma^*(\text{NH})$ which consequently weakens the NF bond. The dicationic fluoro- **9** ($k^a = 10.826 \text{ mdyne \AA}^{-1}$; BSO $n = 1.902$) and difluoro-amine **11** ($k^a = 9.756 \text{ mdyne \AA}^{-1}$; BSO $n = 1.774$) are among the strongest NF bonds in the series. The strength of the NF bond in **9** is enhanced through the strong inductive effect of positively charged N (+483 me) and F (+398 me). The roughly equal positive charge of both atoms means that electrons delocalized into the NF bond region will be distributed equally between the two, giving more covalent character ($H_{\text{c}}/\rho_{\text{c}} = -1.756 \text{ h e}^{-1}$). From the NBO analysis of **11**, through the bond delocalization of ip lp(F) → $\sigma^*(\text{NH})$ ($\Delta E_{ij} 6.82 \text{ kcal mol}^{-1}$), N become more positively charged (+821 me) than the F atoms (+297), reducing the covalent character of NF bond ($H_{\text{c}}/\rho_{\text{c}} = -1.578 \text{ h e}^{-1}$), and consequently weaken the NF bond, which is worsened by the delocalization of ip lp(F) → $\sigma^*(\text{NF})$. For **13**, the charge imbalance between N (+1127) and F (+291) with ip lp(F) → $\sigma^*(\text{NF})$ is still present. The increase of charge in N atoms has also been experimentally shown by Olah and coworkers to be due to the inductive effects; the higher number of fluorine substituents in NR₂F gives higher ¹⁵N NMR chemical shifts (deshielding) which thus increase the positive charge on the central N atom.¹²³

Methyl fluoroamines. Comparing **9** with **15** and **11** with **17**, in which one H atom is substituted with a methyl group that has a stronger electron-donating capability, the NF bonds are weakened for both **15** ($k^a = 7.127$ mdyn \AA^{-1} ; BSO $n = 1.438$) and **17** ($k^a = 7.573$ mdyn \AA^{-1} ; BSO $n = 1.497$). The electron delocalization from the methyl unequally decreases the positive charge at N (+241 (**15**)) and F (+71 (**15**), +159 me (**17**)) while slightly increasing the charge at N in **17** (+831 me), giving a the weaker NF bond with less covalent character.

The diazene- and methene-fluoroamines. The NF bond strength in diazenes **18–19** can be analyzed against the nitrene **7**: the additional proton (**18**), or fluorine cation (**19**) on the terminal N atom at nitrene, cause further imbalance of positive N and F charges, thus NF bond in diazenes are weaker than NF in nitrene. However, interestingly the methene fluoroamines **20**, for which the NF bond has a local force constant k^a 11.087 mdyn \AA^{-1} and a bond strength order BSO n 1.932, which is only slightly weaker from the second strongest NF bond in the series, the $[\text{N-F}]^+ (\mathbf{1})$. The imbalance of charges between N and F in methene fluoroamine **20** is much less than in **1**. However, due to lack of surrounding chemical environment in **1**, its NF bond has more covalent character ($H_c/\rho_c = -2.008$ h/e) than the NF bond in **20** ($H_c/\rho_c = -1.623$ h/e). Looking into the second-order perturbative NBO donor-acceptor analysis reveals that the strong NF **20** is due to the strong delocalization of both in-phase (ip) (ΔE_{ij} 27.81 kcal mol $^{-1}$) and out-of-phase (oop) (ΔE_{ij} 10.48 kcal mol $^{-1}$) lp(F) $\rightarrow \pi(\text{CN})$.

Effect of the electron ionization on molecular geometry. Double ionization of pyramidal (bent) structures leads to a planarization (linearization) of the molecule. Planarization occurs in $[\text{NH}_2\text{F}]^{2+}$ (**9**), $[\text{NF}_2\text{H}]^{2+}$ (**11**), $[\text{NF}_3]^{2+}$ (**13**), $[\text{MeHNF}]^{2+}$ (**15**), $[\text{MeNF}_2]^{2+}$ (**17**), $[\text{HNNF}]^{2+}$ (**18**), $[\text{FNNF}]^{2+}$ (**19**), and $[\text{H}_2\text{C}=\text{NF}]^{2+}$ (**20**), while linearization is apparent in the *cis*- or *trans*-diazene **N11–N14** which become linear diazene **18** and **19**. The planarization/linearization of geometries plays some role in the NF bond strengthening in cationic species, as has been described previously.^{55,56,82}

In fluoroamine $[\text{H}_2\text{NF}]^+ (\mathbf{8})$, loss of a single electron results in a C_{2v} planar structure due to the small size of the hydrogens. For other pyramidal structures, a single ionization tends to decrease the pyramidalization θ_p angle,¹³⁷ while for a bent structure like **N2** and **N3**, it enlarges the bond angle, *i.e.* 100.0° (**N2**) and 103.1° (**N3**) to become 104.8° (**3**) and 107.9° (**4**) respectively (Fig. S1, ESI†).

It is also noteworthy that upon an electron pair ionization from $[\text{FN-F}]^+ (\mathbf{3})$, the resulting $[\text{FN-F}]^{3+} ({}^1\Sigma_u^+, D_{\infty h})$ is linear, while upon the $[\text{HN-F}]^+ (\mathbf{2})$, the resulting $[\text{HN-F}]^{3+}$ is dissociated into NF^{2+} and H^+ . The $[\text{FN-F}]^{3+} ({}^1\Sigma_u^+, D_{\infty h})$ has $R(\text{NF}) = 1.144$ \AA with $k^a(\text{NF}) = 12.161$ mdyn \AA^{-1} $n(\text{NF}) = 2.056$, $\omega(\text{NF}) = 1600$ cm $^{-1}$ and energy density ratio at bond critical point of -1.775 Hartree per electron. However, $[\text{FN-F}]^{3+}$ is an exotic species, and is higher in energy than $[\text{FN-F}]^+$ by 58.77 eV and $[\text{FN-F}]$ by 70.28 eV.

U/R-CCSD(T)/aug-cc-pVTZ vs. U/R- ω B97XD/aug-cc-pVTZ. Fig. 5 compares the NF bond strength order (BSO $n(\text{NF})$) of molecules **21–26** and **N16–N24** calculated at U/R-CCSD(T)/aug-cc-pVTZ and at U/R- ω B97XD/aug-cc-pVTZ levels of theory. ω B97XD and

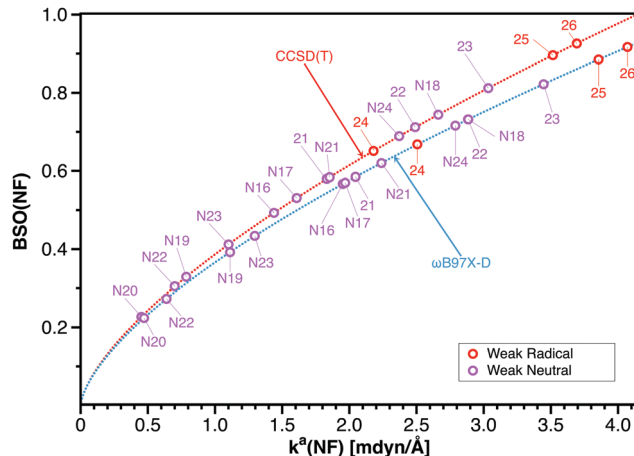


Fig. 5 Comparison of the NF bond strength order (BSO $n(\text{NF})$) of molecules **21–26** and **N16–N24** calculated at U/R-CCSD(T)/aug-cc-pVTZ and U/R- ω B97XD/aug-cc-pVTZ levels of theory.

CCSD(T) results show similar trends. Therefore, the restriction to ω B97XD for the remaining molecules **27–50**, including the SelectFlour series, is justified.

3.2.2 Weak NF bonds. Table 2 and Fig. 1 show the molecular geometries, NBO charges, and the NF bond properties of weak NF bonds, molecules **21–50**. Different types of weak NF bonds will be discussed in this section.

In a previous study,⁵⁶ we have found weak NF bonds, with intrinsic BSO $n < 0.500$, when we tried to investigate the nature of hidden bond strength anomaly, *i.e.* the shorter the NF bonds are not necessarily the stronger, in the fluoroamine-chalcogenide compounds. In this paper, we would like to extend this knowledge by investigating the nature behind these, by systematically showing how hypervalency and EDG or EWG substitution to these moiety leads to weaker NF bond. We compared how the NF bond strength changes upon series of $\text{Ch}=\text{N-F}_n$ ($\text{Ch} = \text{O}, \text{S}, \text{Se}; n = 1-3$) molecules/radicals. The interesting properties of the weak NF bonds are that they may have an efficient source for electrophilic fluorine, which is an important tool for synthesis of many molecules.^{9,18,138}

Ch=NF molecules. Fluoroamine oxide (or nitrosyl fluoride) **21** has a weak intrinsic NF bond strength ($k^a = 2.046$ mdyn \AA^{-1} ; BSO $n = 0.585$), while stronger NF bonds in fluoroamine sulfide **22** ($k^a = 2.883$ mdyn \AA^{-1} ; BSO $n = 0.732$), and selenide **23** ($k^a = 3.446$ mdyn \AA^{-1} ; BSO $n = 0.822$) have lower BDH(NF) than 61.41 kcal mol $^{-1}$ (**21**); 46.82 (**22**) and 51.86 kcal mol $^{-1}$ (**23**) (Fig. 6 and Table 2). With heavier chalcogenides, which are more electropositive in nature, the stronger NF bond is due to stronger inductive effect which gives higher electron occupation of N atom: +466 (**21**), -517 (**22**), and -712 me (**23**). The most covalent character is in the NF bond of **23** due to a balanced distribution of electrons in the bonding region $H_c/\rho_c = -0.952$ h e $^{-1}$, while NF in **21** is weakened due to electrons that are more localized at the F atoms giving a weaker covalent bond ($H_c/\rho_c = -0.671$ h e $^{-1}$) (see Fig. 7). Also from the NBO analysis, there is some extent of anomeric delocalization of lp(Ch)

Table 2 NF bond distances $R(\text{NF})$, local mode frequencies $\omega^a(\text{NF})$, force constant $k^a(\text{NF})$, bond strength order BSO $n(\text{NF})$, electron densities ρ_c , energy densities H_c , the energy density ratio $\frac{H_c}{\rho_c}$, NF bond dissociation energy BDE and enthalpy BDH for molecule **21–50** and reference molecules **R1–R3**, calculated at U/R- ω B97XD/aug-cc-pVTZ level of theory

#	Molecule (state), sym.	$R(\text{NF})$ (Å)	$\omega^a(\text{NF})$ (cm^{-1})	$k^a(\text{NF})$ ($\text{mdyn } \text{Å}^{-1}$)	BSO $n(\text{NF})$	$\rho_c(\text{NF})$ ($\text{e}/\text{Å}^3$)	$H_c(\text{NF})$ ($\text{h}/\text{Å}^3$)	$\frac{H_c}{\rho_c}(\text{NF})$ (h/e)	BDE ^a (kcal mol^{-1})	BDH ^a (kcal mol^{-1})
Ch=NF (Ch = O, S, Se)										
21	[O=N-F] ^(2A') , C _s	1.492	656	2.046	0.585	1.605	-1.077	-0.671	63.14	61.41
22	[S=N-F] ^(2A') , C _s	1.409	779	2.883	0.732	1.950	-1.728	-0.886	48.32	46.82
23	[Se=N-F] ^(2A') , C _s	1.390	852	3.446	0.822	2.040	-1.942	-0.952	53.44	51.86
Ch=NF ₂ ^{•+}										
24	[O=N(F)-F] ^(2B₂) , C _{2v}	1.419	726	2.506	0.668	1.963	-1.598	-0.814	7.95	6.12
25	[S=N(F)-F] ^(2B₂) , C _{2v}	1.375	901	3.855	0.885	2.173	-2.090	-0.962	26.48	24.49
26	[Se=N(F)-F] ^(2B₂) , C _{2v}	1.374	926	4.070	0.917	2.176	-2.133	-0.980	33.65	31.67
SelectFluor										
27	[(F-TEDA)] ^{•+} , C ₁	1.954	493	1.154	0.402	0.535	-0.060	-0.113	18.92	16.62
28	[(F-TEDA)] ²⁺ , C ₁	1.367	1077	5.511	1.117	2.246	-2.196	-0.978	64.85	60.81
29	[(F-TEDA)(BF ₄)] ^{•+} , C ₁	1.960	493	1.155	0.402	0.529	-0.058	-0.109	25.06	22.82
30	[(F-TEDA)(BF ₄)] ⁺ , C ₁	1.374	1055	5.282	1.087	2.196	-2.129	-0.969	64.69	60.69
31	[(F-TEDA)(BF ₄) ₂] ^{•+} , C ₁	1.976	471	1.053	0.379	0.510	-0.050	-0.097	30.44	28.30
32	[(F-TEDA)(BF ₄) ₂], C ₁	1.381	1033	5.072	1.058	2.152	-2.066	-0.960	64.96	61.31
Subst. chalcogenides										
33	O=N((CF ₃) ₂)-F ^(1A'') , C _s	1.579	580	1.598	0.497	1.316	-0.677	-0.515	40.91	38.15
34	S=N((CF ₃) ₂)-F ^(1A'') , C _s	1.668	368	0.643	0.274	1.049	-0.394	-0.376	20.20	17.48
35	Se=N((CF ₃) ₂)-F ^(1A'') , C _s	1.615	169	0.135	0.099	1.197	-0.537	-0.448	14.27	12.24
36	O=N((NO ₂) ₂)-F ^(1A) , C ₁	1.465	656	2.044	0.584	1.745	-1.248	-0.715	47.77	43.44
37	S=N((NO ₂) ₂)-F ^(1A) , C ₁	1.408	707	2.377	0.645	1.995	-1.711	-0.858	33.96	32.28
38	Se=N((NO ₂) ₂)-F ^(1A) , C ₁	1.381	814	3.146	0.775	2.131	-2.004	-0.940	28.97	27.00
39	O=N((CN) ₂)-F ^(1A'') , C _s	1.632	487	1.125	0.395	1.156	-0.502	-0.434	25.44	23.64
40	S=N((CN) ₂)-F ^(1A'') , C _s	1.807	381	0.688	0.287	0.739	-0.160	-0.217	12.88	11.58
41	Se=N((CN) ₂)-F ^(1A'') , C _s	1.835	329	0.514	0.237	0.689	-0.130	-0.189	10.51	9.28
42	O=N((CH ₃) ₂)-F ^(1A'') , C _s	1.669	453	0.974	0.360	1.037	-0.401	-0.386	57.49	54.89
43	S=N((CH ₃) ₂)-F ^(1A'') , C _s	1.572	303	0.435	0.212	1.319	-0.695	-0.527	39.02	36.97
44	Se=N((CH ₃) ₂)-F ^(1A'') , C _s	1.451	652	2.017	0.579	1.782	-1.386	-0.778	38.15	35.98
45	O=N((NH ₂) ₂)-F ^(1A) , C ₁	1.594	479	1.090	0.387	1.280	-0.639	-0.499	56.89	53.68
46	S=N((NH ₂) ₂)-F ^(1A) , C ₁	1.497	375	0.668	0.281	1.623	-1.076	-0.663	42.07	40.06
47	Se=N((NH ₂) ₂)-F ^(1A) , C ₁	1.450	594	1.678	0.514	1.822	-1.400	-0.768	39.03	37.00
48	O=N((OH) ₂)-F ^(1A'') , C _s	1.532	530	1.332	0.442	1.515	-0.902	-0.595	56.15	53.67
49	S=N((OH) ₂)-F ^(1A'') , C _s	1.442	604	1.735	0.525	1.889	-1.455	-0.770	43.70	41.81
50	Se=N((OH) ₂)-F ^(1A'') , C _s	1.419	700	2.324	0.635	1.998	-1.661	-0.832	46.50	44.48
References: NO bonds										
R1	H ₂ N-OH ^(1A) , C _s	1.427	1022	4.594	0.992	2.007	-1.594	-0.794	69.08	62.98
R2	HN=O ^(1A') , C _s	1.202	1736	13.264	1.984	3.662	-5.819	-1.589	167.50	164.71
NF bonds, H ₂ N-F										
R3	H ₂ N-F ^(1A') , C _s	1.420	990	4.652	1.000	1.907	-1.765	-0.926	73.10	69.27

^a BDE and BDH are calculated with the G4 method.

(Ch = O, S, or Se) to the $\sigma^*(\text{NF})$, which weakens the NF bond: strong delocalization is observed for **21** (ΔE_{ij} 94.56 kcal mol⁻¹) but weaker for **22** (ΔE_{ij} 45.18 kcal mol⁻¹) and **23** (ΔE_{ij} 30.80 kcal mol⁻¹).

Ch=NF₂ radicals. Upon fluorination of the fluoroamine chalcogenides **21–23**, the resulting radical species **24–26** have a stronger NF bond strength. The reason for this is the significantly smaller weakening effect of lp(Ch) (Ch = O, S, or Se) → $\sigma^*(\text{NF})$ for **24** (ΔE_{ij} 30.26 kcal mol⁻¹), **25** (ΔE_{ij} 12.72 kcal mol⁻¹), and **26** (ΔE_{ij} 7.48 kcal mol⁻¹). The other weakening effect of the lp(F) → $\sigma^*(\text{NF})$ are very small (less than 1.00 kcal mol⁻¹).

Ch=NF₃ molecules. Fluorination of **24–26** results in hypervalent fluoroamine oxides **N18**, sulfides **N21**, and selenides **N24**. This fluorination strengthens the intrinsic NF bond strength in **N18** but

weakens the NF bond in **N21**, and **N24**. The addition of an extra fluorine significantly increases the positive charge of the central N atom for all chalcogenides (Δ = +180 (**N18**), +257 (**N21**), +361 (**N24**) me), while slightly reducing the negative charges among the fluorines (Δ = +36 (**N18**), +26 (**N21**), +62 (**N24**) me). This increases the inductive effect in NF bonds and thus weakening the covalent bond. Another weakening factor is the stronger lp(Ch) (Ch = O, S, or Se) → $\sigma^*(\text{NF})$ delocalization as the additional fluorine lower the $\sigma^*(\text{NF})$ energy. However the strengthening of NF bond in **N18** is an exception which might be caused by the smaller magnitude of induction compared to the one in **N21** or **N24**.

Ch=NH_{(3-n)F_n} molecules. The substitution of one or two fluorines with hydrogens, weakens the NF bonds

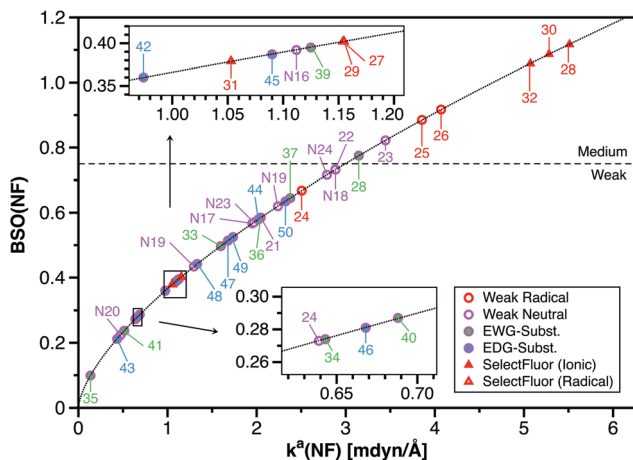


Fig. 6 The NF bond strength order (BSO) $n(\text{NF})$ of molecules **21–50** and **N16–N24** calculated at U/R- ω B97XD/aug-cc-pVTZ level of theory.

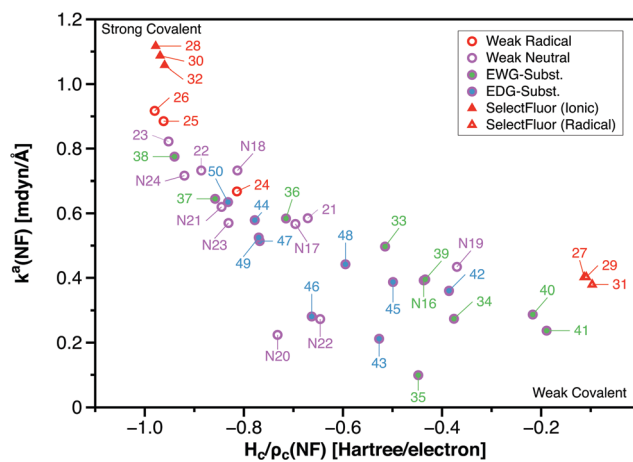


Fig. 7 The energy density $\frac{H_c}{\rho_c}$ at the N–F bond critical points of molecules **21–50** and **N16–N24** calculated at U/R- ω B97XD/aug-cc-pVTZ level of theory.

(**N16–N17**, **N19–N20**, **N22–N23**), due to smaller induction compared to the trifluoroamine chalcogenides. The inductive effects seems to play the major role of weakening the NF bond, as in these hydrogen-substituted molecules the anomeric delocalization $\text{lp}(\text{Ch}) \rightarrow \sigma^*(\text{NH})$ (Ch = O, S, or Se) is preferable to that of $\sigma^*(\text{NF})$. With two substituted fluorines, the extra mutual $\text{lp}(\text{F}) \rightarrow \sigma^*(\text{NF})$ will further weaken the NF bonds.

EWG-substituted fluoramine chalcogenides. Except for the nitro-substituted **36–38**, EWG weaken the NF bonds in trifluoromethyl- **33–35** and nitril-substituted **39–41** with respect to the trifluoro oxides **N18**, sulfides **N21**, and selenides **N24** counterparts, with the weakening effect more significant for the sulfides and selenides. Electropositive S and Se cause large negative charge at the central N atoms, the magnitude of which are large and comparable to the negative charges at the F atoms, thus resulting in the low electronic density at NF bond critical point. This consequently decreases the covalent character of the NF bonds. The oxides **33** and **39** are the least weakened for

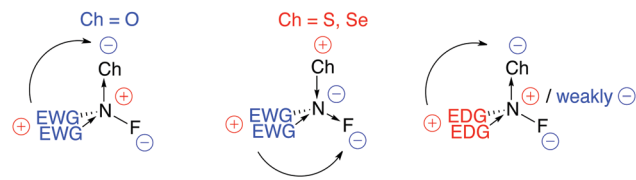


Fig. 8 The effect of EWG or EDG to the fluoramine chalcogenides **33–50**.

the opposite reason: the electronegative O draws some at the electronic densities from N domain, which in turn causes the positive charge at N. These positive charges at N are however smaller than those in trifluoroamine chalcogenides.

Polarized NF bonds due to the positive N and negative F, also decrease the covalent character of the bond. However, thanks to the higher electronegativity of N, the electronic densities at the NF bonds are not as low as those in the sulfides or selenides, which gives the oxides higher covalency degree thus stronger bonds than the latter. With the EWG, the BDH(NF) also decreases significantly if compared to the unsubstituted **N16–N24**.

In summary, Fig. 8 shows that electropositive S or Se induce back donation to the N resulting in cumulative electronic charges at N atom. These additional electronic densities are further stabilized by the EWGs and fluorine atoms, keeping the negative charges at N atoms, thus localized negative charges at both end of the NF bond weaken the bond.

For the nitro-substituted, only the oxide **36** give NF bond weakening, which magnitude is smaller if compared to the trifluoromethyl- **33** and nitril-substituted oxides **39** due to the existence of competing anomeric delocalization between $\text{lp}(\text{O}) \rightarrow \sigma^*(\text{NN})$ and $\text{lp}(\text{O}) \rightarrow \sigma^*(\text{NF})$. The former causes the weakening of the NN bond, resulting in a peculiarly long NN bonds for species **36–38** (1.632–1.873 Å, Fig. S3, ESI†). The sulfide **37** and selenide **38** has NF bond strengthening due to the larger anomeric delocalization to the antibonding NN.

EDG-substituted fluoramine chalcogenides. Surprisingly, EDG seems to have the same NF intrinsic bond weakening effects as the EWG, but to a lesser extent (Table 2). This is due to the EDG tending to give stronger delocalization to the $\text{N}=\text{Ch}$ bonds, thus giving negative charges at the chalcogens, even for the electropositive S and Se (Fig. 8). The weakening mechanism with the EDG is similar with the weakening mechanism of EWG of the oxides. However, different from EWGs, the EDGs somewhat increase the BDH(NF). The discrepancy between the $k^a(\text{NF})$ and BDH(NF) is discussed previously in Section 3.1.

3.2.3 Factors affecting the strength of NF bonds in fluoramines

Strong bonds. From the trends, we discussed previously, NF intrinsic bonds strengthening are caused by a combination of multiple factors and can be achieved by: (i) increasing the electron density in the NF bond region by taking density from $\text{lp}(\text{N})$ and decreasing $\text{lp}(\text{N})\text{--lp}(\text{F})$ exchange repulsion *via* ionization. For obtaining strong NF bonds, it is preferable to have equal positive charges between N and F, especially if there exists an additional electron-donating group (EDG) or an electron-withdrawing group (EWG) attached to the N atom.

(ii) The strong electronegativity of F means that electrons from other less electronegative atoms will be taken out upon ionization in fluoroamines. The lone pair electrons of F then may become the source for the “bonding” of electrons *via* induction. (iii) By attaching an EDG or EWG, delocalization of electron from EDG *via* hyperconjugation or anomeric delocalization to N–F may increase electron density at the NF bond region, if there is equalization of positive charge between N and F, thus strengthening it. On the contrary, with the EWG, electrons from N or F may delocalize to the EWG which reduces the inductive power of the NF domain. (iv) Keeping the number of substituent as low as possible, which allows one to have the opportunity to utilize non-bonding electrons by the inductive effect. (v) Two or more geminal fluorines attached to the same atom, which may have NF bond weakening effect due to mutual anomeric delocalization of $\text{lp}(\text{F}) \rightarrow \sigma^*(\text{NF})$. (vi) Avoiding the through-space $\text{lp}(\text{F})\text{--lp}(\text{F})$, through-bond $\text{lp}(\text{F})\text{--lp}(\text{N})$, or through-bond $\text{lp}(\text{F})\text{--}\pi(\text{AX})$ electron–electron repulsions. (vii) Strong electronegative atoms like N and O, which are good candidates for making strong fluorine bond. With the O, strong fluorine bonds may also be achieved by *e.g.* OF^+ . CCSD(T)/aug-cc-pVTZ results gives the OF bond distance $R(\text{OF}) = 1.243 \text{ \AA}$; local mode force constant $k^a = 8.243$; and bond order BSO $n = 1.585$.

The weak bonds. Conversely, the NF bond weakening in fluoroamine is caused by: (i) the hypervalency of NR_2F , in which the lone pair electrons at N are exhausted by forming a new donor–acceptor type bond $\text{N} \rightarrow \text{Ch}$ (Ch: O, S, Se). Anomeric delocalization and larger inductive effects introduced by the chalcogens weaken the NF bonds. (ii) Geminal fluorine atoms, which may further weaken the NF bonds which due to additional $\text{lp}(\text{F}) \rightarrow \sigma^*(\text{NF})$. (iii) Electron withdrawing groups EWG in fluoroamine chalcogenides can interact with (especially electro-positive) chalcogenes stabilizing negative charge at both N and F atoms, thus weakening the NF bond by reducing the electron density along the NF bond path. (iv) Electron donating groups EDG may also weaken the intrinsic NF bond, with a similar mechanism as found for the EWG in the fluoroamine oxides.

3.3 NF bonding in SelectFluor

In this study, we focus on the simple model of SelectFluor ($\text{R} = -\text{CH}_2\text{Cl}$; $\text{X} = \text{BF}_4^-$), and investigate the NF bonds in closed-shell (28, 30, 32) and radical form (27, 29, 31), with (29–32) or without the presence of the tetrafluoroborate salts (27–28). We conducted all calculations in the gas phase, as preliminary calculations using continuum solvation model with water, acetonitrile, and dimethylformamide (DMF), shows only infinitesimal changes (see Table S6, ESI†).

3.3.1 NF bonds. The radical form of SelectFluor ((27, 29, 31), Table 2) has significantly weaker intrinsic NF bonds strength than the closed-shell counterparts (28, 30, 32), with longer NF bonds, have very low electron density at the bond critical points and are indicated to have a very low covalent character from the low energy density values. The BDH(NF) of the radicals are also significantly lower than the BDH(NF) in closed-shell molecules. With the presence of counterions, the

NF bond become somewhat stronger while the BDH(NF) values slightly decrease.

3.3.2 Electron affinity. The fact that the radicals have weaker NF bonds, which is an important factor for the efficient fluorination capability of SelectFluor, can be rationalized in the following way. We may see that the radical forms of SelectFluor are the counterpart of the closed-shell system upon receiving one extra electron. The electron affinities of the closed shell molecules are large and exothermic: 243.39 (28), 169.66 (30), and 100.17 kcal mol^{-1} (32, Table 3), indicating that radical forms are favored and will easily be formed if there is an available source for single electron transfer.

Upon fluorination, the captured electron is predominantly shared among the N1 atom, adjacent F atom, and the six methylene groups of the TEDA (Fig. 1), *e.g.* the electron gains for each are: N1 –388; F: –241; 6Me –308 me (27); N1: –359; F: –282; Me: –295 me (29); and N1: –338, F: –313, Me: –275 me (31). Upon presence of the BF_4^- ions, the distribution of electrons in the six methylene groups are disrupted, the three atoms which are attached to N1 atom gain more electronic charges than those attached to N2: –160 *vs.* –148 me (27); –179 *vs.* –116 me (29); –171 *vs.* –104 me (31).

The electron gain by the N1 atom changes its charge from positive to negative for 27, 29 and 31, which seems to be stabilized by the positive charges of adjacent methylene groups. The negative charges at both N and F atoms considerably weaken the NF bond, which is in conjunction with our previous analysis with the substituted fluoroamine chalcogenides (Fig. 1).

Also, differing from the previous analysis which suggests that the chloromethylene may have partial double-bond character,⁹ the CCl bond seems to have only “nearly-single-bond” character. The MO itself shows that the HOMO has a $\pi^*(\text{CCl})$ antibonding character, while the [HOMO–1] is predominantly $\sigma^*(\text{CCl})$. From the NBO analysis, the Cl atom is close to neutral (either weakly positive or negative by a few milli-electrons (me)), while the large positive charges are due to the hydrogens of the methylene.

3.3.3 Effect of $\text{R} = \text{ClCH}_2^-$ *vs.* $\text{X} = \text{BF}_4^-$. The effect of the counterions BF_4^- seems to be stronger than the effect of the chloromethylene ClCH_2^- at the N2 position. We can see from the charge analysis that there is an unequal distribution of electron between the three methylene groups on N1 and the other three groups at N2. While it has been reported that different R- or X-groups can affect the fluorinating strength of the SelectFluor,⁹ it seems that by changing the counterions, greater effect may be obtained.

3.3.4 Frontier orbitals. From molecular orbital analysis, the LUMO of closed shells shows an σ^* antibonding character on the NF bond (Fig. 9, Fig. S7 and S8, ESI†). This means the capture of one electron by these molecules will put an extra electron in the LUMO orbital (which becomes the HOMO of the radical SelectFluor). This weakens the NF bond and gives already some radical character to the N and F atoms as confirmed by the difference spin density analysis.

The weak NF bond, in relation to the highly-efficient SelectFluor (F-TEDA) compounds, acts as electrophilic fluorine

Table 3 The electron affinities EA (kcal mol⁻¹) upon capture of one electron, calculated at U/R- ω B97XD/6-31++G(d,p) level of theory^a

Reaction	Molecule	EA ^b	EA ^c	EA ^d
SelectFluor				
28 → 27	[(F-TEDA)] ²⁺ → [(F-TEDA)] ^{•+}	-243.39		
30 → 29	[(F-TEDA)(BF ₄)] ⁺ → [(F-TEDA)(BF ₄)] ^{•+}	-169.66		
32 → 31	[(F-TEDA)(BF ₄) ₂] → [(F-TEDA)(BF ₄) ₂] ^{•-}	-100.17		
EWG-substituted				
33	O=N((CF ₃) ₂)-F(¹ A''), C _s	-10.98	-41.86	-30.88
34	S=N((CF ₃) ₂)-F(¹ A''), C _s	-46.79	-66.41	-19.51
35	Se=N((CF ₃) ₂)-F(¹ A''), C _s	-54.93	-71.59	-16.41
36	O=N((NO ₂) ₂)-F(¹ A), C ₁	-38.77	-39.98	-1.21
37	S=N((NO ₂) ₂)-F(¹ A), C ₁	-44.34	-49.34	-5
38	Se=N((NO ₂) ₂)-F(¹ A), C ₁	-52.24	-55.34	-3.1
39	O=N((CN) ₂)-F(¹ A''), C _s	-52.47	-61.71	-9.24
40	S=N((CN) ₂)-F(¹ A''), C _s	-80.29	-79.94	0.36
41	Se=N((CN) ₂)-F(¹ A''), C _s	-84.95	-83.61	1.34
EDG-substituted				
42	O=N((CH ₃) ₂)-F(¹ A'), C _s	47.72	-26.3	-74.02
43	S=N((CH ₃) ₂)-F(¹ A''), C _s	7.84	-44.92	-52.76
44	Se=N((CH ₃) ₂)-F(¹ A''), C _s	2.98	-44.48	-47.46
45	O=N((NH ₂) ₂)-F(¹ A), C ₁	33.05	-34.74	-67.79
46	S=N((NH ₂) ₂)-F(¹ A), C ₁	6.01	-45.64	-51.65
47	Se=N((NH ₂) ₂)-F(¹ A), C ₁	3.38	-43.41	-46.78
48	O=N((OH) ₂)-F(¹ A''), C _s	12.07	-25.24	-37.31
49	S=N((OH) ₂)-F(¹ A), C _s	-12.06	-38.01	-25.95
50	Se=N((OH) ₂)-F(¹ A), C _s	-13.12	-35.82	-22.7

^a We use here reaction energies, thus negative (positive) EA means energy is released (needed) upon capture of one electron. ^b Undergo the subsequent reaction: Ch = NR₂F $\xrightarrow{e^-}$ [Ch = NR₂]^{•-} + F[•]. ^c Undergo the reaction: Ch = NR₂F $\xrightarrow{e^-}$ [Ch = NR₂]^{•+} + F⁻. ^d Enthalpy difference between homolytic bond dissociation (EA) and heterolytic bond dissociation (EA).

source for fluorination reactions. The radical species of the SelectFluor, have significantly lower BDH(N-F) than its respective closed shell analogues, which may explain the ease of forming the radical species. This may indirectly confirm the results of the computational study done by Zhang and coworkers that also shows single electron transfer is energetically favored over the two-electron transfer of SN₂-type mechanism.¹³⁹ The efficiency of SelectFluor might be due to relatively low BDH(N-F) of the radical species (Table 2). The anionic tetrafluoroborate salts add some stability to the N-F bond strength by about 6 kcal per mol per salt molecule.

3.4 Fluoroamine chalcogenides: a new class of fluorinating agents?

3.4.1 The design of new efficient fluorinating agent. Based on this investigation, we suggest some possible hypervalent NF compounds that might be used as a catalyst for fluorination reactions. The unsubstituted hypervalent amine chalcogenides 39–47 have relatively weak N-F bonds, if compared to the closed shell SelectFluor molecules, either stabilized by counterions (49) or not (50 and 28). The BDH(N-F) are decreased further with the introduction of EWG.

The dicyano-fluoroamine-selenides Se=N(CN)₂F 41 give the lowest BDH(N-F) of 9.28 kcal mol⁻¹, but not necessarily the weakest N-F bond strength (BSO $n_{(NF)}$ = 0.237). The weakest N-F bond strength happens to present in Se=N(CF₃)₂F 35 which have BSO $n_{(NF)}$ 0.099 but higher BDH(N-F) 12.24 kcal mol⁻¹.

This shows the tunability of NF bond strength by different EWG or EDG functional group substitutions. EDGs increases the

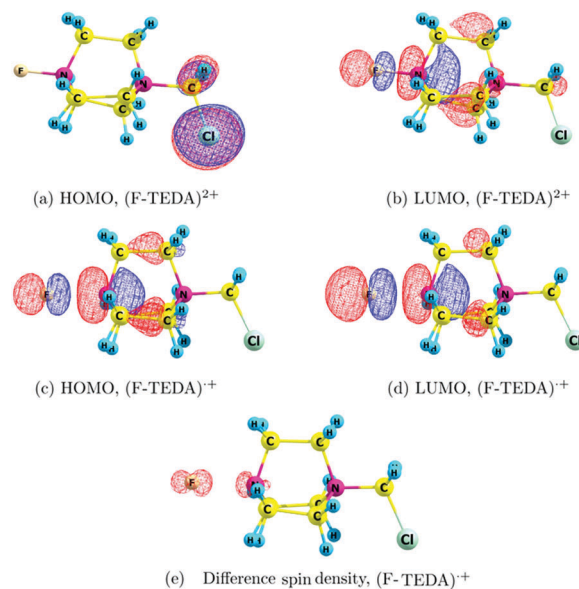


Fig. 9 Frontier orbitals of F-TEDA 27–28 calculated at the ω B97XD/aug-cc-pVTZ level of theory. The difference electron spin density, red denotes positive alpha over beta spin density difference.

BDH(N-F), while EWG decreases the BDH(N-F), which confirms the postulates that EWG substitution to these moieties leads to more electrophilic N-F fluorinating reagents resulting from the decrease of the electron density on the NF bonding region.

3.4.2 LUMO of the substituted fluoroamine chalcogenides. The LUMOs of the substituted fluoroamine chalcogenides also

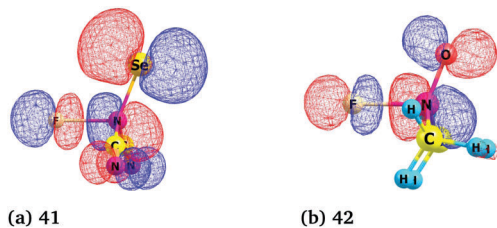


Fig. 10 LUMOs of EWG- (41) and EDG-substituted (42) fluoroamine chalcogenides, calculated at the ω B97XD/aug-cc-pVTZ level of theory.

have NF antibonding character (Fig. 10 and Fig. S9, ESI[†]), which upon capturing of an electron, will break the NF bond, *i.e.* the F will dissociate from the chalcogenides. We follow here two possibilities of NF bond breaking:



It seems that the EWG-substituted fluoroamine chalcogenides, the oxides 39–41, energetically favor the creation of electrophilic fluorine, with possible competition with the forming of nucleophilic one.

3.4.3 Possible H-bond interactions. Although for the past 25 years, there have been unsuccessful efforts on the search for pentavalent nitrogen molecules, *i.e.* NF_5 ,^{140–147} the hypervalent amine chalcogenides, namely trifluoroamine oxide, F_3NO , have been synthesized in 1966 by Stewart and coworkers.^{148,149} This perfluorinated amine oxides has a boiling point of -85° and a melting point of -160° . It is a strong oxidizing agent but is immune to hydrolysis even by strong aqueous bases. This particular compound has been studied rigorously, both experimentally^{150–161} and computationally.^{162–167} It is considered as a both oxidizing and fluorinating agent.^{151,156,157,160} It can also be used as a source for preparing nitrosyl fluoride¹⁵⁵ and recently, proposed to be used as substitute gases for semiconductor CVD chamber cleaning.¹⁶¹ Again however, the unpopularity of trifluoroamine oxide F_3NO as a fluorinating agent might be due to the same reason nitrosyl fluoride was unpopular: It is in the gas phase at the room temperature, thus is difficult to handle.

Hypervalent amine-chalcogenides 33–50, which have never been synthesized, contain atoms H, N, O, and F which means they have a good chance of forming stabilizing hydrogen or halogen bonds between themselves, or with water or polar organic solvent molecules.

4 Conclusions

In this work, we investigated a set of 50 NF molecules with the aim of finding the factors that influence the strength of NF bonds and designing a new class of fluorinating agents. The NF bonds are a tunable covalent bonds, with BSO values varying from very strong 2.5 to merely 0.1, which can be achieved by ionization or hypervalency on N, using a $\text{N} \rightarrow \text{Ch}$ (Ch: O, S, se) donor-acceptor type bond with different substitution of EWG.

The intrinsic bond strength of the NF bond is caused by a combination of multiple factors, and can be increased by: increasing the electron density in the NF bond region by taking density from $\text{lp}(\text{N})$ and decreasing $\text{lp}(\text{N})$ – $\text{lp}(\text{F})$ exchange repulsion *via* ionization. A positive charge balance between N and F is important for obtaining a strong NF bond, especially in the presence of an additional electron-donating group (EDG) or an electron-withdrawing group (EWG) attached to the N atom. Delocalization of electrons from EDG *via* hyperconjugation or anomeric delocalization to N–F, may increase electron density at the NF bond region. On the contrary, with the EWG, electrons from N or F may delocalize to the EWG which reduces the inductive power of the NF domain. Strong electronegative atoms like N and O are good candidates for making strong fluorine bond. With oxygen, a strong fluorine bond may also be achieved by *e.g.* OF^+ , which CCSD(T)/aug-cc-pVTZ results give OF bond distance $R(\text{OF}) = 1.243 \text{ \AA}$; local mode force constant $k^a = 8.243$; and BSO $n = 1.585$.

The NF bond weakening in fluoroamine is caused by the $\text{Ch}=\text{NR}_2\text{F}$ hypervalency, in which the lone pair electrons at N are exhausted by forming a new donor-acceptor type bond $\text{N} \rightarrow \text{Ch}$ (Ch: O, S, Se). The anomeric delocalizations and larger inductive effects introduced by the chalcogens weaken the NF bonds. Geminal fluorine atoms, may further weaken the NF bonds which due to additional $\text{lp}(\text{F})$, two or more geminal fluorine attached to the same atom may have NF bond weakening effect due to mutual anomeric delocalization of $\text{lp}(\text{F}) \rightarrow \sigma^*(\text{NF})$. EWGs in fluoroamine chalcogenides, may have interact with (electropositive) chalcogens, for stabilizing negative charges at both N and F atoms, thus weakening the bond by reducing electron densities along the NF bond path, while EDG, may also weaken the intrinsic NF bond, with similar mechanism of the EWG in the fluoroamine oxides. The understanding of the nature of the strength of the NF bonds is the key to design a new class of fluorinating agents. While BDE and BDH are important parameters for synthesis and chemical reactions, they have the limitation of describing the intrinsic strength of a bond, thus dismiss the possibility of the understanding of the nature of the bond. On the other hand, bond strength order based on the intrinsic strength obtained from the local stretching force constant is valuable to enlighten the electronic nature of a chemical bond. It is predicted that the EWG ($-\text{CF}_3$ and $-\text{CN}$) substituted hypervalent fluoroamines chalcogenides: the oxides 39 and especially sulfides 34, 40 and selenides 35, 41 may be used as efficient electrophilic fluorinating agents. These proposed hypervalent amine-chalcogenides can form stabilizing hydrogen or halogen bonds between themselves, or with the solvent molecules, resulting in reagents that are easy to handle, and may become an alternative to other electrophilic fluorinating agents such as SelectFluor (F-TEDA) compounds, which is indicated also to have a weak NF bonds for the ease of forming radical F for fluorination.

Conflicts of interest

There are no conflicts to declare.

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