

Review

# An Overview of the Understanding of Ions Containing Solely Fluorine Atoms

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This paper is dedicated to Prof. Boris Žemva on the occasion of his receiving Zois' lifetime achievement award.

## Abstract

We discuss in the current paper ions containing solely fluorine atoms,  $F^-$ ,  $F_2^-$  and  $F_3^-$ , their corresponding cationic and/or multiply charged counterparts. While the emphasis of the paper is on gas phase species, their energetics and reactions, aqueous solutions are also discussed. In particular, biomedical and analytical aspects of  $F^-$  are also considered. The new trichotomy of convenience, anthropocentrism and folksonomy is also applied to the understanding of our fluorine-containing ions.

**Keywords:** Ions, both anions and cations / ionization potential (ionization energy) and electron affinity / energetics and reactions / gas phase and aqueous solutions / anomalous properties / biomedical and analytical aspects / per and  $\pi$ -fluoro effects / convenience, anthropocentrism and folksonomy

## 1. Introduction – Species to be Discussed

Forms of neutral elemental fluorine are the fluorine atom, the difluorine molecule and species composed of three and four fluorine atoms. Among all of the elements fluorine is the most reactive, which results in the chemistry of its species being very extensive and so, the first two of these species,  $F^\bullet$  and  $F_2$  respectively, will not in the name of brevity be further discussed in this paper. The third species, the radical  $F_3^\bullet$ , has been suggested as an alternative to the radical ion  $(F_3)^{2+\bullet}$  formed by radiolysis of a variety of solid alkali metal fluorides.<sup>1</sup> The last species is best described as the dimer of difluorine,  $(F_2)_2$ , and experimentally demonstrated to be polar, i.e., the species does not have a square, rectangular nor tetrahedral geometry.<sup>2</sup> On the other hand, it may be understood as a “very weak dispersion donor-acceptor complex” of two  $F_2$  molecules, one *en route* to  $F_2^{+\bullet}$  and the other to  $F_2^{-\bullet}$ .<sup>3</sup>

The current paper limits the discussion of ions that are composed only of fluorine; both anions and cations

will be discussed. We clearly mean by this anions such as the well-studied fluoride ion,  $F^-$ . Both  $F^{2+\bullet}$  and  $F_2^{-\bullet}$  also qualify for discussion. We also mean by such ions the cation  $F^{+\bullet}$  where we are fully aware of controversies on species that contain “positive fluorine”.<sup>4-6</sup> The study of the ions  $F^{2+\bullet}$ ,  $F_2^{+\bullet}$  and the numerous other ions containing only fluorine seemingly lack controversy – we believe this state of quiet is most probably due to the incorrect perception of the lack of chemistry to discuss them. Among ions to be discussed, only  $F^-$  anion has been proven to be existent in aqueous solution and ionic salts while the other ions were found primarily in the gaseous phase but occasionally in nonaqueous media.

A sample of the variety of other ions of interest to fluorine community that contain fluorine bonded to other atoms can be found elsewhere in this special issue and will not be discussed in the current study. Central atoms of polyatomic ions and clusters are known to span A to Z, e.g.,  $Na_3AlF_6$  and  $KZrF_5$ . However, even if only species with measured enthalpies, Gibbs energies and entropies of formation<sup>7</sup> were to be presented here, there are still too many data and so, exhaustive or comprehensive discussions of

even just one of the three quantities could prove tiring, if not exhausting. (We recall that the more restricted topic of entropies of fluoroanions in aqueous solution was discussed.<sup>8</sup>) Likewise, if only those ions of significant utility were to be discussed, we still would have an excess of subject matter. And so, we consider only ions that contain just fluorine. We will also present an understanding of the chemistry of these ions being more detailed in discussing fluoride within the context of human health, biomedical chemistry and analytical chemistry. In addition the recently enunciated three-fold criteria of “convenience, anthropocentrism and folksonomy” will be defined and discussed<sup>9–11</sup>. This trichotomy will be presented in the final section of our paper.

## 2. Monoatomic Fluorine Species

### 2. 1. The Fluorine Anion F<sup>-</sup>

We start our discussion with the aforementioned ion F<sup>-</sup>, the monoatomic anion fluoride, as it is the most extensively studied of the fluorine containing ions. Indeed, F<sup>-</sup> is among the most extensively studied ions of any composition at all. As such, we cannot hope to discuss all of its interesting and important features in our current study. We start with the gaseous species and discussion of its ionization energy (IE, also called ionization potential and likewise abbreviated IP), that is, the energy (or occasionally enthalpy) associated with the process (eq. 1)



This quantity is more commonly known as the electron affinity (EA) of the neutral atom fluorine. It is entirely reasonable that the electron affinity of fluorine would be higher than any other atom. After all, atomic fluorine is small and is to be found on the right side and high up in the periodic table. Fluoride ion is a closed shell species and has a complete octet of valence electrons, or more precisely, we know its electron configuration is the same as the “inert gas” neon, 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>. Fluoride ion is isoelectronic to the atom neon, also notable for its tightly bound electrons and high ionization energy.<sup>12</sup> Possible contenders of atomic high electron affinities, helium, neon and argon, nominated because of their periodic table location and size are plausibly disqualified because these neutrals are already closed shell, filled octet species. Their anions would necessarily have the “extra” electron in the “next” higher shell and so the electron would be but weakly bound as is the case for the isoelectronic alkali metals, Li, Na and K respectively.

Taking the values for all of the halogens we find that the electron affinity of fluorine is high, (3.399 ± 0.003) eV but that of chlorine is higher, (3.617 ± 0.003) eV (1 eV ≈ 96.5 kJ mol<sup>-1</sup>).<sup>13</sup> (See the appendix of this paper for a collection of these and of all other electron affinities, and ionization energies, that appear in the current study.)

The values for bromine and iodine are also high,<sup>13</sup> (3.365 ± 0.003) eV and (3.0591 ± 0.0004) eV and the order Cl > Br > I follows the expected periodic trend of decreasing electron affinities proceeding down a column in the periodic table. It appears that fluorine has “an aversion” of having 8 valence electrons as found in its most common and important ion. Indeed, this aversion is shared by compounds of fluorine including the diatomic halogen itself, and this “anomalous property of fluorine” when comparison is made with the heavier halogens is found to be shared by adjoining columns that begin with oxygen and nitrogen.<sup>14–15</sup> At least within the context of ionization energies and electron affinities, this pattern was also shown to transcend the nonmetals to be applicable to multiply charged metallic ions (indeed, cations) isoelectronic to F<sup>-</sup> and also to multiply charged ions isoelectronic to O<sup>-</sup> and N<sup>-</sup> anions as well.<sup>16</sup>

The energetics of well over 200 gas phase reactions of F<sup>-</sup> have been reported and chronicled. Many of these include proton transfer and complexation.<sup>17–18</sup> There are numerous related reactions with the other halide ions.<sup>17–18</sup> We now mention but a single reaction of F<sup>-</sup> and that of the other halide ions, protonation, for which we will make a comparison. It is well-established that the protonation becomes increasingly exothermic in the gas phase in the order I<sup>-</sup> < Br<sup>-</sup> < Cl<sup>-</sup> < F<sup>-</sup>.<sup>19–20</sup> This relative exothermicity contributes to HF being the weakest acid of the hydrogen halides, or equivalently, F<sup>-</sup> being the strongest base among the aqueous halides.<sup>21</sup> However, the dominant reason for this acidity order has been convincingly shown to be the exceptional negative entropy of solvation of F<sup>-</sup> that is ameliorated upon protonation to form HF.<sup>22</sup> The standard entropy S<sup>o</sup> of aqueous F<sup>-</sup> is -13.8 J mol<sup>-1</sup> K<sup>-1</sup> while that of the isoelectronic aqueous Ne is 66.1 J mol<sup>-1</sup> K<sup>-1</sup>. The difference is 80 J mol<sup>-1</sup> K<sup>-1</sup>. The absolute entropies of F<sup>-</sup> and Ne as gases are almost identical, an immediate corollary of the fact they have nearly the same mass: in fact, the evaluated values are 145.6 and 146.3 J mol<sup>-1</sup> K<sup>-1</sup>.<sup>7,23</sup> A difference of 80 J mol<sup>-1</sup> K<sup>-1</sup> between the pairwise entropy differences of the gaseous and aqueous species is noted – should this be ascribed to the charge on the F<sup>-</sup>? Consider Cl<sup>-</sup>, Ar and the related analysis. The standard entropy of aqueous Cl<sup>-</sup> is 56.5 J mol<sup>-1</sup> K<sup>-1</sup>, while that of the isoelectronic aqueous Ar is 59.4 J mol<sup>-1</sup> K<sup>-1</sup>.<sup>7</sup> The values of S<sup>o</sup> are nearly the same, the difference is but 3 J mol<sup>-1</sup> K<sup>-1</sup>. The corresponding values of S<sup>o</sup> of Cl<sup>-</sup> and Ar as gases should be almost identical given they have nearly the same mass: in fact the evaluated values are 153.4 and 154.8 J mol<sup>-1</sup> K<sup>-1</sup>, nearly the same.<sup>7,23</sup> So, the value of S<sup>o</sup> of Cl<sup>-</sup> and Ar are nearly the same regardless of the phase. The difference of 80 J mol<sup>-1</sup> K<sup>-1</sup> found for F<sup>-</sup> and Ne is not just due to the negative charge of the F<sup>-</sup> and its absence in Ne, i.e., there is no additive constant correcting for the contribution of the charge of the solute.

F<sup>-</sup>, in fact, is special. Among all ions discussed in the current study, F<sup>-</sup> anion verily alone occurs in aqueous solution and has an extensive, and human-centered, analy-

tical and biomedical chemistry. As not to dominate the discussion in this paper with but one species, and only two of many aspects of its chemistry at that, as acknowledged in the introduction, we defer these attributes until later. At that time we will also discuss the concepts of “convenience, anthropocentrism and folksonomy” that populate the title of the current study as they are relatively humanistic in their mode of understanding and expressions.

### 2. 1. 1. An Example of Biomedical and Analytical Aspects of Aqueous Fluoride Ion

Among the ions reviewed in the present article, the free fluoride ion  $F^-$  in aqueous solution is not only the sole ion with application in human medicine, it is the only ion with such applications at all. One human-centered application will be discussed, another briefly mentioned. To avoid any conflict in using the terms “fluorine” or “fluoride” elsewhere, the term »fluorine« will be used in this article to denote the element in any of its forms and »fluoride« to denote free inorganic fluoride to which a fluoride ion selective electrode responds.

### 2. 1. 2. How Essential is Fluorine and the Use of $F^-$

Fluorine is regarded as an essential element, since resistance to dental caries was/is considered as a physiologically important function.<sup>24</sup> In addition  $F^-$  has been used in treatment of postmenopausal osteoporosis.<sup>25</sup>

### 2. 1. 3. Possible Side Effects of $F^-$

$F^-$  is a cumulative toxin accumulated in mineralized tissues, notably tooth crystals and the lattice of bone.<sup>24</sup> Excessive intake of  $F^-$  over the long term may lead to the development of dental fluorosis in children up to the age of 7–8 years or even to the development of skeletal fluorosis in both children and adults. Thresholds of 0.05–0.07 and 0.03–0.04 mg/day/kg body weight of  $F^-$  have both been suggested for the appearance of dental fluorosis.<sup>26–28</sup> The clinical features of mild dental fluorosis vary from thin white striations across the tooth’s enamel surface to white flecks or small pits on the enamel of the teeth. With increasing severity, the white areas merge and loss of enamel surface can occur. Skeletal fluorosis is characterized by immobilization of joints of the axial skeleton and of the major joints of the extremities.<sup>29</sup> A combination of osteosclerosis, osteomalacia and osteoporosis of varying degrees as well as exostosis formation characterizes the bone lesions related to skeletal fluorosis.

### 2. 1. 4. $F^-$ Controversy

It has been established that: (1) the majority of the benefit from  $F^-$  in protection against dental caries can be

attributed to its topical, rather than systemic, effects and (2) the long-term benefit of  $F^-$  in the treatment of postmenopausal osteoporosis remains questionable. It is therefore not surprising that “fluorine” is regarded as one of the most controversial elements, or more precisely, dietary species. A typical example of the  $F^-$  controversy is illustrated by the facts that: (1) more than two-thirds of the U.S. population receives fluoridated drinking water and that fluoridation is on the increase<sup>30</sup>, (2) water fluoridation, is among other organizations is supported by the World Health Organization (WHO)<sup>31</sup>, but (3) water fluoridation is banned in most of Europe<sup>32</sup>.

### 2. 1. 5. $F^-$ Requirements and Their Estimation

The estimation of the optimal concentration of  $F^-$  in drinking water is based on the pioneering research of Dean<sup>33</sup> from 1942, based on which Hodge<sup>34</sup> in 1950, plotted the average community index of dental fluorosis and the average caries incidence against the concentration of  $F^-$  in community water supplies. Reduction of the average occurrence of dental caries per child was nearly maximal in communities having concentrations of  $F^-$  in water close to 1.0 mg/L. In this way, 1 mg/L became the “optimal” concentration for  $F^-$  in drinking water – it was associated with a high degree of protection against dental caries and low prevalence of the milder forms of dental fluorosis.

### 2. 1. 6. Adequate Intake of $F^-$

The adequate intake (AI) of  $F^-$  from all sources is set at 0.05 mg/day/kg body weight; this intake is recommended for all ages greater than 6 months, because it confers a high level of protection against dental caries and is not associated with any known unwanted health effects.<sup>25</sup> The Estimated Average Requirement (EAR) serves as the basis for setting the Recommended Dietary Allowances (RDA).<sup>25</sup> If adequate scientific documentation for calculating an EAR is not available, as is the case of  $F^-$ , the AI is set instead of the RDA, which has however rather uncertain origin.<sup>35</sup> Empirical evidence however suggests that 0.05–0.07 mg  $F^-$ /kg body weight/day can be considered as a useful upper limit for  $F^-$  intake in children. This dietary recommendation has also been applied to adults.

### 2. 1. 7. Fluorine Intake

Drinking water, beverages (such as tea), food and  $F^-$ -containing dentifrices are regarded as the main dietary contributors to human  $F^-$  intake.<sup>36</sup> A literature review<sup>35</sup> of  $F^-$  intake in humans revealed that the range of average daily  $F^-$  intake in children (without considering possible intake of  $F^-$  supplements) is between 0.008 and 0.060 with an average of 0.030 mg/kg body weight in nonfluoridated

ridated areas. The average daily intake of  $F^-$  in fluoridated areas generally exceeds the recommended intake: it ranges between 0.016 and 0.147, with an average of 0.062 mg/kg body weight. With the use of  $F^-$  containing supplements the intakes of  $F^-$  in children from nonfluoridated and fluoridated areas, the total intake is almost similar to what the dosage schedule recommends, depending on age, from 0.5 to 1.0 mg/day of  $F^-$ . Children in fluoridated areas and those in nonfluoridated areas to whom the  $F^-$  supplements are provided are therefore at risk for the development of dental fluorosis. The average daily total  $F^-$  intake in adults in nonfluoridated areas was estimated to range from 0.008–0.021 (average 0.016) mg/kg body weight and in fluoridated areas to range from 0.013–0.054 (average 0.030) mg/kg body weight for a 70 kg man which is almost 2-fold higher. In addition, it is worth mentioning that the daily intake of  $F^-$  with daily consumption of five cups of tea (1 L) of any of the most commonly consumed types of tea can represent 9–101% of the AI for a 70 kg man.<sup>37</sup>

## 2. 1. 8. Fluorin(d)e Analytical Methods

Analytical techniques used for the determination of fluorine usually rely on the “direct” determination of free  $F^-$  ion as present in an aqueous solution of the sample. Total fluorine ( $F_t$ ) can generally be determined only after total decomposition of the sample. The difference between  $F_t$  and  $F_f^-$  leads to the amount of bound fluorine ( $F_b$ ).<sup>38</sup> Basic requirements for accurate and precise determination of the amount of  $F_f^-$  (or  $F_t$ ) in any type of the sample are: (1) the sample has to be appropriately pre-treated so that the required form of fluorine can be determined; (2) interfering reactions have to be effectively suppressed; (3) the final concentration of fluorine must be above the detection limit of the method; and (4) if possible, method should be validated using certified reference material (CRM), or the results of analyses compared to the results obtained by an independent method.

Total decomposition of the sample is generally required for the purpose of determination of  $F_t$ . Commonly used procedures involve oxygen bomb combustion in a closed bomb, open ashing, alkali hydroxide or alkali carbonate fusion, pyrohydrolysis, acid extraction and microwave acid digestion.

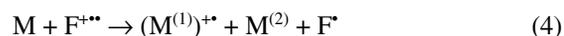
Among the methods used for the determination of  $F_t$  or  $F_f^-$  are fluoride ion selective electrodes, ion and gas chromatography, aluminium monofluoride (AlF) molecular absorption spectrometry,<sup>19</sup>F NMR spectroscopy, helium microwave-induced or inductively coupled plasma atomic emission spectrometry, electrothermal atomic absorption spectrometry, inductively coupled plasma–mass spectrometry, enzymatic, catalytic, polarographic/voltammetric methods, radioactivation, proton induced gamma emission, near infrared spectroscopy, neutron activation analysis should all be mentioned.<sup>35</sup>

## 2. 1. 9. An Observation Regarding Research on one Aspect of $F^-$ in Medicine and Human Health

Reiterating,  $F^-$  is with no doubt the most studied fluorine species. The majority of  $F^-$  research results in medicine and human health are of older date and the newer ones rather scattered. This implies that for a definitive answer on possible beneficial or deleterious effects of  $F^-$  on human health further studies are recommended.

## 2. 2. The Fluorine Cation $F^{***}$

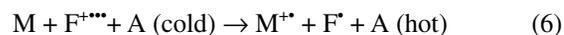
Let us now leave fluorine in monoatomic and anionic form. The next species discussed is the monoatomic cation  $F^{***}$ . The ionization energy of fluorine ( $F^*$ ) is 17.422 eV. This quantity is higher than that of any other element except that of Ne, 21.564 eV and of He, 24.587 eV. It is not surprising that the ionization energy of F is so exceptionally high because of the high effective nuclear charge (actually  $Z_{\text{eff}}/n$ ) and small size of this element, a feature shared with these two light noble gases. The value for neon is still higher than fluorine because it is further to the right in the periodic table and, as normally presented, helium is found above neon and so even more possessive of its valence electrons. Accordingly, because of the strong attraction of  $F^{***}$  and electrons, the chemistry of  $F^{***}$  is plausibly dominated by electron transfer (eq. 2); sometimes the newly formed cation is generated in a vibrationally, rotationally and/or electronically excited state (eq. 3) and sometimes this new cation immediately fragments (eq. 4).<sup>39–41</sup>



Nonetheless, despite this ambiguity in possible reactions of  $F^{***}$ , a cation affinity scale has been generated corresponding to the exothermicity of the reaction of a set of Lewis bases, ( $L_b$ ), with  $F^{***}$  to form the corresponding covalent complexes, eq. (5)



This reaction is rarely directly experimentally realized even in the presence of cooling additives, as opposed to eq. (6)



Nonetheless, this so-called “ $F^+$  detachment scale”<sup>42</sup> has found considerable use in understanding the energetics of diverse fluorinated species, e.g., nitrogen and oxygen fluorides.<sup>43</sup> Indeed, the study of the energetics of reac-

tion (5), now relabeled as “F<sup>+</sup> affinity” together with the parallel concept of “F<sup>-</sup> affinity” of Lewis acids (L<sub>a</sub>) (reaction (7)) provide considerable insight for both the practitioners of synthetic and thermo-chemistry of inorganic fluorine compounds, e.g., Christe et al.<sup>44</sup> and Grant et al.<sup>45</sup>



Among the numerous interesting features of these association reactions (5) and (7), we choose but one. Consistent with Hund’s rule, F<sup>3+</sup> with its 1s<sup>2</sup>2s<sup>2</sup>2p<sup>4</sup> electron configuration is a ground state triplet because of its two unpaired electrons found in degenerate orbitals. As such, were (L<sub>b</sub>F)<sup>+</sup> to be observed from direct or cooled reactions, by spin conservation this species should be considered in its triplet state. Indeed, both (HeF)<sup>+</sup> and (NeF)<sup>+</sup> are found to be ground state triplets according to high level computational chemistry;<sup>46</sup> earlier theoretical studies optimistically suggested singlets<sup>47</sup> encouraged by analogies to the isoelectronic HF and F<sub>2</sub> respectively. Many other (L<sub>b</sub>F)<sup>+</sup> species, however, may be formed *via* other more experimentally realizable synthetic routes, and are ground state singlets formally arising from a bond between L<sub>b</sub><sup>+</sup> and F with their sole unpaired valence electron apiece. For example, (XeF)<sup>+</sup> has all of its electrons paired and its salts (and/or fluorine-bridged derivatives) are readily prepared from XeF<sub>2</sub> on reaction with suitable fluorine and fluoride (F<sup>-</sup>) acceptors, generically Lewis acids (L<sub>a</sub>) (see formal reaction 8).<sup>48–50</sup>



### 2. 3. Fluorine Dianion, F<sup>2-</sup>

In that fluorine binds a single electron less tightly than we might have expected, we should not be surprised that F<sup>2-</sup> is even a less favorable species energetically than is the monoanion F<sup>-</sup>. Indeed, despite its occasional appearance in discussions in the literature<sup>51–52</sup> the free anion F<sup>2-</sup> is no doubt unstable relative to the loss of an electron to form F<sup>-</sup>, e.g., see Chattaraj and Duley.<sup>53</sup> F<sup>2-</sup> is not a common component of salts, of minerals or of ores: it is tempting to say that its possible presence is notable for its absence. For example, the major fluorine-containing ore is fluorspar (fluorite), i.e., calcium fluoride, is not Ca<sup>2+</sup> F<sup>2-</sup> but rather Ca<sup>2+</sup> (F<sup>-</sup>)<sub>2</sub>. This material absence does not mean that F<sup>2-</sup> is conceptually irrelevant – after all, oxide ion O<sup>2-</sup> is most assuredly a highly important species in the research and pedagogical literature even though the gaseous ion is likewise unstable relative to the loss of an electron to form O<sup>-</sup>. For example of importance, using estimated energies using Glockler’s approach<sup>54</sup> for all four halogen dianions F<sup>2-</sup>, Cl<sup>2-</sup>, Br<sup>2-</sup> and I<sup>2-</sup> as input information, an explanation<sup>55</sup> was given for the general reluctance of fluorine to be the central atom for nucleophilic displacement, i.e., S<sub>N</sub>2(F) reactions (eq. 9) compared to those S<sub>N</sub>2(Hal)

reactions involving the heavier halogens Hal = Cl, Br and I (eq. 10).



### 2. 4. Fluorine Dication, F<sup>2+</sup>

Removal of two electrons from atomic fluorine in a chemical context seems unlikely. The ionization energy of F<sup>3+</sup> is 34.970 eV and exceeds that of any neutral species.<sup>12,56</sup> This value also exceeds that of any singly charged atomic ion save those of He, Li, O, Ne and Na. As such, F<sup>2+</sup> is not expected to be a “gentle reagent”, either for chemical combination or even electron transfer. Among other processes, in the gas phase low energy F<sup>2+</sup> has been shown to react<sup>57</sup> with C<sub>60</sub> to form F<sup>-</sup> and excited (C<sub>60</sub>)<sup>3+</sup> ions by three electron transfer. The resulting fullerene “cations decay following a variety of channels, such as thermal electronic ionization, evaporation of C<sub>2</sub> units, asymmetric fission, and multifragmentation”. Relatedly, adenine with a somewhat higher ionization energy than C<sub>60</sub> also reacts<sup>58</sup> with F<sup>2+</sup> to form singly and doubly charged molecular ions with accompanying fragmentation. The ionization energies of adenine and C<sub>60</sub> are (8.20 ± 0.03) and (7.58 ± 0.04) eV respectively.<sup>59–60</sup>

### 2. 5. Fluorine Trication, F<sup>3+</sup> and Even More Positively Charged Species

If F<sup>2+</sup> is avariciously hungry for electrons, F<sup>3+</sup> is even more so. The ionization energy of F<sup>2+</sup> is 62.707 eV.<sup>12</sup> It is thus not surprising that gas phase F<sup>3+</sup> reactions are accompanied by multiple electron transfer from any, and so presumably all, species with lower ionization energy than F<sup>2+</sup>. F<sup>3+</sup> so reacts with C<sub>60</sub> by this process and F<sup>-</sup> is among the observed products, albeit in lower yield than with positive and less charged fluorine cations.<sup>61</sup> Fluorine ions with charges exceeding +3 have also been studied. Whether the interaction of these ions with neutral species are called reactions or collisions, the products from these neutrals are multiply charged resulting from electron transfer. For example, F<sup>7+</sup> and F<sup>8+</sup> react with the noble gases Ar and Kr to result in ions up to Ar<sup>10+</sup> and Kr<sup>14+</sup>.<sup>62</sup> We hesitate to discuss any of these processes in terms of multiply charged noble gas molecular ions – for example, should we (or even can we?) really conceptually interrelate ArF<sup>8+</sup> with the isoelectronic ArH<sup>+</sup> which is unbound and the fragile, very weakly bound ArHe<sup>+</sup>?<sup>63</sup> Likewise, F<sup>8+</sup> and F<sup>9+</sup> react with one-, two- and three-carbon alkanes and alkenes<sup>64</sup> for which the cross section of single electron transfer from these molecules is indistinguishable from the sum of the atomic cross section contributions, i.e., the molecules behave like a collection of atoms – chemistry, as a study of molecules, has seemingly disappea-

red. As such, we now end the discussion of atomic fluorine ions.

### 3. Diatomic Fluorine Species

#### 3. 1. Difluorine Dianion, $F_2^{2-}$

The first species we will discuss is  $F_2^{2-}$  to which we append the plausible name of “difluorine dianion”. This is the conjugate base of bifluoride ion,  $HF_2^-$ . While gas phase  $HF_2^-$  is strongly bound ( $192 \pm 7$ )  $\text{kJ mol}^{-1}$ , there is no evidence for  $F_2^{2-}$  in the gas phase.<sup>65</sup> We are not surprised as we recall the general observation that in the absence of solvation or counterions, multiply charged molecular ions are rarely stable relative to the loss of an electron and/or bond cleavage. The presence of  $F_2^{2-}$  ion in the condensed phase has been suggested as part of discussions of terms of the NMR spectra of concentrated fluoride ion solutions<sup>66</sup> and explicit quantum chemical calculations of  $F_2^{2-}$  hydrates.<sup>67</sup>

#### 3. 2. Difluorine Anion, $F_2^{-}$

There have been many measurements of the electron affinity of diatomic fluorine.<sup>17</sup> We choose  $(3.10 \pm 0.01)$  eV, a consensus of the nearly identical values,<sup>68–69</sup> the former source<sup>68</sup> we take to be the most reliable and the latter<sup>69</sup> because of other measurements reported therein that we will soon discuss in this article. With what quantities of other species can this be related? This value is somewhat less than that of the aforementioned atomic fluorine,  $(3.448 \pm 0.005)$  eV.<sup>13</sup> That the molecular electron affinity is less than the atomic electron affinity is consistent with

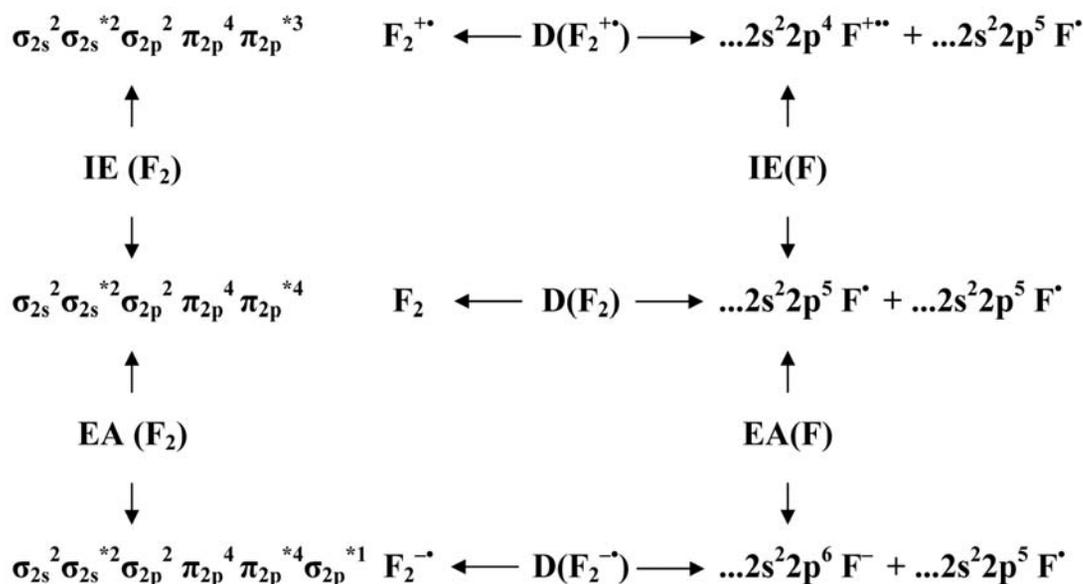
the presence of an electron in an antibonding orbital of  $F_2$ . (See Figure 1 that summarizes some thermochemical and quantum chemical relations between  $F_2^{-}$ ,  $F_2$ ,  $F_2^{+}$  and  $F^-$ ,  $F^+$ ,  $F^{+*}$ .)

The same trend is seen for the electron affinities of  $Cl_2$ ,  $Br_2$  and  $I_2$  compared to the monoatomic halogens. Taking an average of the value from Chupka and Berkowitz<sup>69</sup> and Hughes, Lifschitz and Tiernan<sup>70</sup> we derive values of 2.35, 2.57 and 2.50 eV with plausible error bars for each value of  $\pm 0.15$  eV. Regardless of experimental uncertainties, it is unequivocal that the electron affinity of  $F_2$  is considerably larger than that of  $Cl_2$  and that of the heavier halogen diatomics. This is consistent with the suggestion that  $F^-$  is destabilized because of its 8 valence electrons while  $F_2^{-}$ , now written as  $F^{-1/2}-F^{-1/2}$ , is stabilized with fewer electrons.<sup>14</sup> Indeed, we may suggest stabilization of some 0.6 eV as a plot of either  $EA(X_2)$  vs.  $EA(X)$ , or of  $EA(X_2)$  vs.  $IE(X_2)$  would have suggested an EA an electron affinity of ca. 2.5 eV (i.e., roughly the same as that of the other diatomic halogens).

Another comparison follows from simple recollection of the definition and values of electronegativity, i.e., that  $D(AB)$  is larger than the average of  $D(A_2)$  and  $D(B_2)$  where  $D$  where  $D$  is the bond dissociation energy. As an example, it is readily concluded (eq. 11) that

$$\frac{1}{2}[D(Na_2) + D(F_2)] < D(NaF) \quad (11)$$

Accordingly, from the definitions of bond energy and enthalpy of formation, that the (gas phase) enthalpy of formation of  $AB$  is smaller, more negative, than the average of those of  $A_2$  and  $B_2$ . In the particular, the simple inequality (eq. 12) may be suggested as well



**Figure 1.** Some thermochemical and quantum chemical relationships between  $F_2^{-}$ ,  $F_2$ ,  $F_2^{+}$  and  $F^-$ ,  $F^+$ ,  $F^{+*}$ . For the three molecular species, the ... means we have omitted the lowest lying  $\sigma_{1s}^2$  and  $\sigma_{1s}^{*2}$  orbitals while for the atomic species we have omitted the lowest lying  $1s^2$  orbitals. D stands for homolytic bond dissociation energy, IE for ionization energy and EA for electron affinity.

$$1/2[\Delta H_f^\circ(\text{g, Na}_2) + \Delta H_f^\circ(\text{g, F}_2)] > \Delta H_f^\circ(\text{g, NaF}) \quad (12)$$

Using the enthalpy of formation of Na<sub>2</sub> and gaseous NaF, we find that gaseous NaF, per mole, is more stable than Na<sub>2</sub> and F<sub>2</sub> by 362 kJ mol<sup>-1</sup>.<sup>7</sup> We now ask: is it also true (eq. 13) that

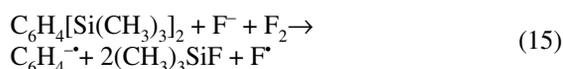
$$1/2[\Delta H_f^\circ(\text{g, Na}_2^-) + \Delta H_f^\circ(\text{g, F}_2^-)] > \Delta H_f^\circ(\text{g, NaF}^-) \quad (13)$$

or equivalently from the definition of electron affinity (eq. 14)

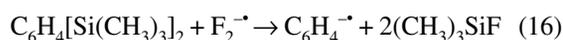
$$1/2[\Delta H_f^\circ(\text{g, Na}_2) - \text{EA}(\text{Na}_2) + \Delta H_f^\circ(\text{g, F}_2) - \text{EA}(\text{F}_2)] > [\Delta H_f^\circ(\text{g, NaF}) + \text{EA}(\text{NaF})] \quad (14)$$

Using the enthalpies of formation of Na<sub>2</sub> and NaF(g)<sup>7</sup>, the electron affinities of Na<sub>2</sub> and NaF of (0.52 ± 0.10) and (0.43 ± 0.15) eV<sup>71–72</sup> we find that the inequality for neutrals in eq. 12 remains affirmed by the inequality for anions in eq. 14. Numerically, gaseous NaF<sup>-</sup>, per mole, is more stable than Na<sub>2</sub><sup>-</sup> and F<sub>2</sub><sup>-</sup> by 240 kJ mol<sup>-1</sup>. We admit our surprise at the magnitude of this relative stability because NaF<sup>-</sup>, like the homonuclear anions, is not a Coulombically stabilized ion pair that explains the strong binding of the atoms in neutral NaF.

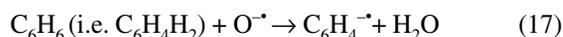
The chemistry of F<sub>2</sub><sup>-</sup> is surprisingly sparse.<sup>73</sup> Plausible gas phase reactions of F<sub>2</sub><sup>-</sup> either are dominated by those of F<sub>2</sub> and/or those of F<sup>-</sup>. Many others do not proceed at all.<sup>74</sup> For example, consider the reaction of *o*-, *m*- and *p*-bis(trimethylsilyl)benzene with F<sup>-</sup> and F<sub>2</sub> to form the radical anions of *o*-, *m*- and *p*-benzyne respectively, (eq. 15)



This reaction (eq. 16) does not proceed through



By analogy to the general dehydrogenation of benzene and other aromatics with O<sup>-</sup> to form the corresponding *o*-aryne radical anion, e.g. (eq. 17).<sup>75–76</sup>



To the extent that thermochemistry and kinetics parallel, we may directly contrast the dehydrogenating (and thus other reactions) of F<sub>2</sub><sup>-</sup> and O<sup>-</sup> by looking at the exothermicity of the reaction (eq. 18)



The HF bond is strong, presumably stronger than the O–H bond as found in H<sub>2</sub>O. O is electron hungry” but F is more so, and two polar H–O bonds are traded for two even

more polar H–F bonds. The F–F bond in F<sub>2</sub> is weak, and even weaker in F<sub>2</sub><sup>-</sup>. Taking the enthalpies of formation of H<sub>2</sub>O, O<sup>-</sup> and HF (all from [7]), and that of F<sub>2</sub><sup>-</sup> from that of the neutral diatomic and its electron affinity, we derive eq. 18 to be *endothermic* by nearly 150 kJ mol<sup>-1</sup>. No wonder that F<sub>2</sub><sup>-</sup> is so unreactive.

### 3. 3. Difluorine cation, F<sub>2</sub><sup>+</sup>

There have been many measurements of the ionization energy of diatomic fluorine. Following Lias’ suggestion and evaluation<sup>56</sup>, we choose the measurements of Van Lonkhuyzen and De Lange<sup>77</sup>, namely (15.697 ± 0.003) eV. With what other quantities can this be related? This value is significantly less than that of atomic fluorine, 17.422 eV, a result consistent with the molecular orbital analysis that suggests loss of an antibonding electron upon ionization.<sup>12</sup> Taking the average of the nearly identical values from Van Lonkhuyzen and De Lange<sup>77</sup> and Yench et al.<sup>78</sup>, we find the ionization energy of Cl<sub>2</sub> and Br<sub>2</sub> as (11.480 ± 0.005) and (10.517 ± 0.005) eV; Lias<sup>56</sup> is surprisingly silent on the former quantity but recommends values of (10.517 ± 0.003) and (9.3074 ± 0.0002) eV for Br<sub>2</sub> and I<sub>2</sub>. Reminding the reader, values of 12.967, 11.814 and 10.451 eV for atomic chlorine, bromine and iodine, respectively are given<sup>12</sup>, again, the diatomic halogens have ionization energies rather much less than that of the atoms, all presumably for the same molecular orbital based reason. It is interesting to note that while the difference of the diatomic and atomic values monotonically decrease as we go from F to I, ca. 1.7, 1.5, 1.3 and 1.2 eV, these four differences are not that different given the over 6 eV spread in individual ionization energy values.

Another relevant comparison is that of F<sub>2</sub> with HF, with recommended values (15.697 ± 0.003) vs. (16.03 ± 0.04) eV.<sup>56</sup> These two values are quite similar, as befits “the perfluoro effect” – i.e., the ionization energy of a perfluorinated species corresponding to the loss of a π electron is very similar to that of the parent species upon the loss of a π electron while that corresponding to the loss of a σ electron is much higher in the perfluorinated case.<sup>79–80</sup> (For completeness now, we note that the π-ionization of partially fluorinated species is rather much the same as the perfluorinated and parent species, the so-called “π-fluoro effect”.<sup>81</sup> As such, the ionization energy of F<sub>2</sub> is to be compared with that of HF, but neither is meaningfully compared with H<sub>2</sub> which totally lacks π electrons although its recommended ionization energy is numerically very similar as well, (15.42593 ± 0.00005) eV.<sup>56</sup>

A third comparison follows from simple recollection of the definition and values of electronegativity, i.e., that D(AB) is larger than the average of D(A<sub>2</sub>) and D(B<sub>2</sub>). As an example, we recall (eq. 19)

$$1/2[\text{D}(\text{Na}_2) + \text{D}(\text{F}_2)] < \text{D}(\text{NaF}) \quad (19)$$

Accordingly, from the definitions of bond energy and enthalpy of formation, that the (gas phase) enthalpy of formation of AB is smaller, more negative than the average of A<sub>2</sub> and B<sub>2</sub>. In the particular, remember the simple inequality, already written as eq. 12.

We now may ask: is it also true (eq. 20) that

$$\frac{1}{2}[\Delta H_f^\circ(\text{g}, \text{Na}_2^{++}) + \Delta H_f^\circ(\text{g}, \text{F}_2^{++})] > \Delta H_f^\circ(\text{g}, \text{NaF}^{++}) \quad (20)$$

or equivalently from the definition of ionization energy (eq. 21)

$$\frac{1}{2}[\Delta H_f^\circ(\text{g}, \text{Na}_2) + \text{IE}(\text{Na}_2) + \Delta H_f^\circ(\text{g}, \text{F}_2) + \text{IE}(\text{F}_2)] > [\Delta H_f^\circ(\text{g}, \text{NaF}) + \text{IE}(\text{NaF})] \quad (21)$$

The ionization energy of NaF is at most 10.41 eV, i.e., the reported quantity<sup>82</sup> corresponds to the vertical process wherein by definition, the cation has the same geometry as the precursor neutral. As such, the right hand side is an upper bound to the adiabatic ionization energy. Using the enthalpies of formation of Na<sub>2</sub> and NaF(g) from ref. [7], we deduce the right hand side of the last inequality is no less than 350 kJ mol<sup>-1</sup> less than the right hand side – the inequality for cations is affirmed as it is for neutrals. Indeed, the difference of the left and right side in eq. 17 is very much the same value as for that of the neutrals in eq. 12. From the logic enunciated by Jolly<sup>83</sup>, the electronegativity difference of Na<sup>+</sup> and F<sup>+++</sup> may be expected to be about the same as between Na and F. The inequalities are thus plausible and all is good. Then it is remembered that:

1. we have some unknown correction to make for the difference of vertical and adiabatic ionization energies for NaF, the latter resulting in the most stable form of NaF<sup>++</sup>;
2. the bond energy of F<sub>2</sub><sup>++</sup> is larger than that of F<sub>2</sub> because an antibonding electron is lost upon ionization of F<sub>2</sub> and
3. despite the loss of an electron from a bonding orbital upon ionization of Na<sub>2</sub>, the bond energy of Na<sub>2</sub><sup>++</sup> is unequivocally larger than that of Na<sub>2</sub>,
4. but in contradistinction,
5. the bond energy of the ion NaF<sup>++</sup> is expected to be much less than that of the neutral NaF because the former species lacks Coulombic stabilization found in the latter. More precisely, NaF is recognized here as the ion pair Na<sup>+</sup> and F<sup>-</sup> which is strongly electrostatically bound because the component ions are oppositely charged while in NaF<sup>++</sup>, the component Na<sup>+</sup> is expected to but weakly stick to F by ion induced dipole attraction.

The fourth interrelationship involves ClF, F<sub>2</sub> and Cl<sub>2</sub> and has conceptual features reminiscent of the preceding discussions. However, in the current case here we discuss only adiabatic ionization energies of nonionic compounds. The recommended ionization energy of ClF is

(12.66 ± 0.01) eV while that of HCl is (12.744 ± 0.009) eV; we remember the value of the ionization energy of Cl<sub>2</sub> is (11.480 ± 0.005) eV.<sup>56,77</sup> The perfluoro and π-fluoro effects are shown to be valid again, i.e., IE(ClF) ~ IE(HCl). It is readily deduced (eq. 22) that

$$\frac{1}{2}[\text{D}(\text{Cl}_2) + \text{D}(\text{F}_2)] < \text{D}(\text{ClF}) \quad (22)$$

Accordingly, from the definitions of bond energy and enthalpy of formation, the simple inequality (eq. 23) may be suggested as well

$$\frac{1}{2}[\Delta H_f^\circ(\text{g}, \text{Cl}_2) + \Delta H_f^\circ(\text{g}, \text{F}_2)] > \Delta H_f^\circ(\text{g}, \text{ClF}) \quad (23)$$

The enthalpy of formation values affirms this.<sup>7</sup> We now ask: is it also true (eq. 24) that

$$\frac{1}{2}[\Delta H_f^\circ(\text{g}, \text{Cl}_2^{++}) + \Delta H_f^\circ(\text{g}, \text{F}_2^{++})] > \Delta H_f^\circ(\text{g}, \text{ClF}^{++}) \quad (24)$$

or equivalently from the definition of ionization energy (eq. 25)

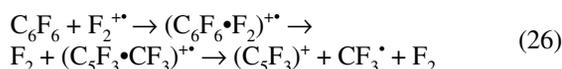
$$\frac{1}{2}[\Delta H_f^\circ(\text{g}, \text{Cl}_2) + \text{IE}(\text{Cl}_2) + \Delta H_f^\circ(\text{g}, \text{F}_2) + \text{IE}(\text{F}_2)] > [\Delta H_f^\circ(\text{g}, \text{ClF}) + \text{IE}(\text{ClF})] \quad (25)$$

This, too, is affirmed – the left hand side of eq. 25 is more positive than the right by ca. 100 kJ mol<sup>-1</sup>. We are encouraged. Dare we conclude that the (gas phase) enthalpy of formation of AB<sup>+</sup> may be assumed in general to be smaller, more negative, less positive than the average of those of A<sub>2</sub><sup>+</sup> and B<sub>2</sub><sup>+</sup>?

As noted above, both F<sup>•</sup> and F<sup>+++</sup> strongly bind electrons, they are markedly electron-deficient. This makes both species highly reactive as 1-electron oxidants. Consider now the reaction chemistry of F<sub>2</sub><sup>++</sup>. It is entirely reasonable that F<sub>2</sub><sup>++</sup> reacts with most neutral species M to form the corresponding M<sup>+</sup> ion by electron transfer. Then again, we recall that the F–F bond in F<sub>2</sub><sup>++</sup> is relatively weak. This suggests that F<sub>2</sub><sup>++</sup> would be a powerful fluorinating agent, or more properly F<sup>+++</sup>– transferring reagent rather than F–transferring reagent since F<sup>+++</sup> is a less-likely byproduct than F<sup>•</sup> (After all, F<sup>+++</sup> would be expected to oxidize MF to form MF<sup>+</sup> and F<sup>•</sup>.) In a pioneering gas phase ion-molecule reaction study by Berkowitz and Chupka,<sup>84</sup> F<sub>2</sub><sup>++</sup> was reacted with Ar (and likewise F<sub>2</sub> with Ar<sup>+</sup>) and ArF<sup>+</sup> was the observed product, the neutral F presumably undetected (indeed undetectable by these experiments). From this reaction chemistry and already known ionization of F<sup>•</sup> and F<sub>2</sub> alike, and bond energies of F<sub>2</sub> and therefore F<sub>2</sub><sup>++</sup>, a lower bound for the bond energy of ArF<sup>+</sup> of 1.655 eV (160 kJ mol<sup>-1</sup>) was deduced. Neither HeF<sup>+</sup> nor NeF<sup>+</sup> were observed by these authors in related reactions involving He and Ne, in contradistinction to the mass spectrometric claims for HeF<sup>+</sup>, HeF<sub>2</sub><sup>+</sup> and HeF<sub>2</sub><sup>2+</sup> reported from a mixture of He and F<sub>2</sub>.<sup>85</sup> Turning now to the more reactive hea-

vier noble gases Kr and Xe,  $F_2^{2+}$  reacts with Kr to form  $Kr^{2+}$  (with traces of  $KrF^+$ ) and also reacts with Xe to form  $Xe^+$  as the sole ionic product.<sup>86</sup>

Cipollini, Crestoni, and Fornarini<sup>86</sup> also showed that  $F_2^{2+}$  reacts with many other neutrals by related processes as well as forming ions recognizable as arising from bond cleavage of the neutral. Among the more thermochemically evocative reactions was that with  $H_2$  which formed  $F_2H^+$ , thereby allowing the proton affinity of  $F_2$  to be determined to be  $(260 \pm 20) \text{ kJ mol}^{-1}$ , which we recognize as one of the lowest values of all neutral molecular or even atomic species ever observed.<sup>87</sup> A surprising reaction is that of  $F_2^{2+}$  with hexafluorobenzene,  $C_6F_6$ , in which  $C_6F_6^{+}$  and  $C_5F_3^+$  are the dominant products. The former presumably results from electron transfer from  $C_6F_6$ . The latter is a long-known fragment ion of  $C_6F_6$  with an appearance potential almost the same as the ionization energy of  $F_2$ .<sup>88–89</sup> That is, one may formulate the following sequential reactions (eq. 26) involving a long-lived complex



The ionization energy of hexafluorobenzene and benzene are close, cf. the “perfluoro effect”,<sup>79–80</sup> with the evaluated values of  $(9.90 \pm 0.04)$  and  $(9.24378 \pm 0.00007)$  eV, respectively. The values for perfluorinated and the parent cyclohexane are  $(13.2 \pm 0.1)$  and  $(9.88 \pm 0.03)$  eV.<sup>58,90</sup> The appearance potential for  $C_5H_3^+$  formed from  $C_6H_6^{+}$  is close to that of  $C_5F_3^+$  from  $C_6F_6^{+}$ .<sup>91</sup> So, what is the major ionic product from the reaction of  $C_6H_6 + F_2^{2+}$  – plausibly it would be  $C_5H_3^+$  or maybe some mono or difluorinated derivative? Or, maybe it would be  $C_6H_6^{+}$  or its mono or difluorinated derivative? In fact, while ionized benzene is an important product, the dominant resulting species is protonated difluorobenzene,  $C_6H_5F_2^+$  formed with unknown regioselectivity.<sup>92</sup> A set of substituted benzenes was also studied<sup>92</sup> resulting in the corresponding radical cation, the corresponding protonated difluorobenzene derivative and, by fragmentation and loss of the substituent, protonated difluorobenzene itself. This last fragmentation is of negligible importance for the powerfully electron donating methoxy substituent, and becomes the dominant process for the powerfully electron withdrawing nitro substituent. No data are available for any fluorinated benzenes for which the consequences of the perfluoro and  $\pi$ -fluoro effects could be directly tested.<sup>81</sup>

### 3. 4. Multiply Charged Cations of Difluorine

We know of no chemistry associated with any of these species, neither  $F_2^{2+}$  nor any even more positively charged cations of difluorine. This is perhaps surprising because both  $F_2^{2+}$ <sup>93–94</sup> and  $F_2^{4+}$ <sup>95–96</sup> are both metastable relative to dissociation according to calculational theory;

these multiply charged ions may be recognized as isoelectronic to the strongly bound  $O_2$  and  $N_2$  respectively.

## 4. Ions From $F_3$ and $F_4$

By analogy to the other halogens and the related interhalogen species, many such ions look plausible. However, among the diverse anions, only trifluoride ion,  $F_3^-$ , has been observed and characterized experimentally as having a  $F^-F_2$  bond energy of  $(98 \pm 11 \text{ kJ mol}^{-1})$  in the gas phase<sup>68</sup> (also see Tuinman et al.<sup>97</sup>). This is a respectable quantity, nearly identical to that of  $Cl_3^-$ , and just  $30 \text{ kJ mol}^{-1}$  less than the likewise nearly identical well-established  $Br_3^-$  and even better known  $I_3^-$ .  $F_3^-$  is well-established in cryogenic matrices, found therein both as ion pairs<sup>98–99</sup> and as a free, symmetric triatomic ion<sup>100</sup>. No binary salts are known for  $F_3^-$ .<sup>97, 100</sup> Except for  $F_4^-$  (accompanying  $F_n^-$ ,  $n = 1, 2$  and  $3$ ) as a sputtering product from LiF surfaces<sup>102</sup>, no evidence is known for any larger polyfluoroanion,  $F_n^-$  in any phase, or for any of these ions in the condensed phase, neither solution nor solid salt.

Despite quantum chemical calculations showing bound  $F_3^{+103–104}$  and metastable  $F_4^{2+}$  cations,<sup>103</sup> no tri or tetrafluorine cations appear in the experimental literature.

## 5. Considerations of Convenience, Anthropocentrism And Folksonomy

In discussing the ions containing only fluorine, the current study also draws attention to the structures (conceptual more than molecular) that support the distinctions as to why and how categories or taxonomies (of concepts, ideas and integrative components) are differentiated from and also work with each other much as the various species are differentiated from each other and related ions and neutrals.

One such set of categories is that of the trichotomy of convenience, anthropocentrism and folksonomy. Earlier discussed in relation to the understanding of acids, bases and salts<sup>9</sup>, aromaticity and antiaromaticity<sup>10</sup>, and the periodic table<sup>11</sup> gives optimism that these three concepts are likewise relevant to the current discussion.

### 5. 1. Definition of Convenience

From a contemporary, continuously updated electronic dictionary<sup>105</sup> we find “fitness or suitability for performing an action or fulfilling a requirement”. Nearly all of the ions we have discussed are fit and suitable species for the understanding of ions composed solely of fluorine. That  $F_2^-$  and  $F_2^{2-}$  are unbound and strictly speaking do not exist may disqualify them to many readers; nonexistent species are hardly convenient substances for experimental studies. Then again  $F^-$  with but 10 electrons, spherical ( $^1S$ ) symmetry has long made it an appealing species

for the practitioners of quantum chemical computational theory.<sup>106–107</sup> The multiply charged positive atomic ions such as  $F_2^{+***}$  are neither synthesized nor reacted under conventional chemical conditions. Then again, neither are  $F^{+**}$ ,  $F_2^{+*}$  and  $F_2^{-*}$  and so are scarcely convenient reagents. By contrast,  $F^-$  as found as an aqueous ion (with associated cation and solvent to be assured) has diverse and well-defined analytical protocols and important biomedical applications. Aqueous fluoride is an important species that is convenient to research, to study, and to use. That fluoride is often strongly associated with the cation in this aqueous medium introduces the complication of free and total ion concentration, and these must be determined separately. However, this is a distinction that provides powerful insights even about well-studied species such as the hexafluoropnictate ions ( $PnF_6^-$ ,  $Pn = P, As, Sb, Bi$ ) and their salts.<sup>38,108–110</sup> An inconvenience has become an asset. In much the same way, distinctions can be made between the above ions that contain only fluorine from related species containing the other halogens such as the ambisaline  $ICl_2^+$  and  $ICl_2^-$ , where we use the neologism ambisaline introduced<sup>9</sup> to convey a pair of ions both of which are found in salts albeit often not with commonplace counterions. That these other species were but briefly mentioned, if at all, in the current study is an invitation to a far more complete discussion of current research as well as a prelude to future investigations.

## 5. 2. Definition of Anthropocentric

From the earlier cited e-dictionary,<sup>105</sup> we find a definition of anthropocentric as “interpreting or regarding the world in terms of human values and experiences”. Most assuredly, the concern about the biomedical application of fluoride ion qualifies. So does the preference of considering aqueous solutions as opposed to the gas phase. However, this brings up the inconvenient confusion as to the meaning of “free” in the connection of “free fluoride”. The meaning of this depends on the context of whether aqueous solutions are intended, in which case “free” means uncomplexed by some metal ion or the gas phase is chosen in which case “free” means unsolvated. The latter adjectives “uncomplexed” and “unsolvated” are more correct, but “free” with its human connotations and therefore ambiguity is a common word in our scientific vocabulary.

## 5. 3. Definition and Discussion of Folksonomy

Our e-dictionary<sup>105</sup> does not include this word. It is a rather new concept used to date more by information and computer scientists<sup>111</sup> rather than by they who study atoms and molecules, whether as inorganic or organic neutrals, ions, discrete molecules and salts.<sup>9–11</sup> Allen<sup>112</sup> described folksonomy as: “...a term coined by information architect Thomas Vander Wal to describe a collection of metadata created by users, which is developed in a col-

laborative žbotttom-up’ fashion rather than the žtop-down’ fashion of a controlled vocabulary.” Mathes<sup>113</sup> writes about users of documents, media and metadata which were “created for ...individual use that is also shared throughout a community.” Mathes<sup>113</sup> offers additional explanation of folksonomies, writing that they are not “...a predetermined set of classification terms or labels” The examination of folksonomies is not strongly justifiable just to see the “tags” used, but that the community of users sharing information is an incipient value of folksonomies concluding that what to some may seem a chaotic and ambiguous system may in fact be the start of deeper meaning sharing and the communication of those meanings.

Within the current context, folksonomy speaks to words used by the community of interest, here chemical researchers in general, and those interested in the chemistry of fluorinated species in the particular. We have taken words and concepts from the often non-interacting communities of analytical, biomedical and physical chemistry, among others. Species include the classical and long-discussed, if not long-understood,  $F^-$ . There are other species that might be deemed worthy of a grade of “F+” if not an “F-“ such as  $F^{+**}$ ,  $F_2^{+*}$ ,  $F_2^{-*}$  were a student mentioning these species on examinations or homework assignments. Serious and seasoned practitioners of our discipline(s) also need to acknowledge the reasonableness of the existence of these species. Although we are mixing the condensed and gaseous phases, dare we say that the set of fluorine-containing ions compose “The stone that the builders rejected has become [a] cornerstone”.<sup>114</sup>

## 6. Acknowledgement

One of the authors (M.P.S.) gratefully acknowledges the Slovenian Research Agency (ARRS) for the financial support of the present study within the research program: P1-0045 Inorganic Chemistry and Technology.

## 7. Appendix

**Table 1.** The collected electron affinities and ionization energies cited in the current study. All values are in electron volts, where  $1 \text{ eV} \approx 96.5 \text{ kJ mol}^{-1}$ .)

Species	Quantity	Value	Reference <sup>a</sup>
$F^*$	EA	$3.399 \pm 0.003$	13
$Cl^*$	EA	$3.617 \pm 0.003$	13
$Br^*$	EA	$3.365 \pm 0.003$	13
$I^*$	EA	$3.0591 \pm 0.0004$	13
$F^*$	IE	17.422	12
	IE	17.42282	56 <sup>b</sup>
Ne	IE	21.564	12
	IE	$21.56454 \pm 0.00001$	56 <sup>b</sup>
He	IE	24.587	12
	IE	24.58741	56 <sup>b</sup>

F <sup>+</sup>	IE	34.970	12
Adenine	IE	8.20 ± 0.03	59
C <sub>60</sub>	IE	7.58 ± 0.04	60
F <sup>2+</sup>	IE	62.707	12
F <sub>2</sub>	EA	3.10 ± 0.01	68,69
Cl <sub>2</sub>	EA	2.35 ± 0.15	69,70
Br <sub>2</sub>	EA	2.57 ± 0.15	69,70
I <sub>2</sub>	EA	2.50 ± 0.15	69,70
Na <sub>2</sub>	EA	0.52 ± 0.10	71
NaF	EA	0.43 ± 0.15	72
F <sub>2</sub>	IE	15.697 ± 0.003	56,77
Br <sub>2</sub>	IE	11.480 ± 0.005	77,78
Br <sub>2</sub>	IE	10.517 ± 0.005	56,77,78
I <sub>2</sub>	IE	9.3074 ± 0.0002	56
HF	IE	16.03 ± 0.04	56
H <sub>2</sub>	IE	15.42593 ± 0.00005	56
NaF	IE	≤ 10.41 <sup>c</sup>	82
Na	IE	5.139	12
		5.13908	56
Na <sub>2</sub>	IE	4.892 ± 0.002	56
ClF	IE	12.66 ± 0.01	56,77
HCl	IE	12.744 ± 0.009	56,77
Hexafluoro- benzene	IE	9.90 ± 0.04	56
Benzene	IE	9.24378 ± 0.00007	56
Perfluorocyclohexane	IE	13.2 ± 0.1	56
Cyclohexane	IE	9.88 ± 0.03	90

<sup>a</sup> Reference citations in brackets indicate sources used to derive a consensus value.

<sup>b</sup> We did not use these more numerically precise (but otherwise effectively indistinguishable) as to make comparisons with other atomic species more facile.

<sup>c</sup> This value is for the vertical quantity and so is an upper bound to the adiabatic value we always prefer to use.

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## Povzetek

V članku predstavlja razpravo o ionih, ki so sestavljeni zgolj iz atomov fluora, to je  $F^-$ ,  $F_2^-$  in  $F_3^-$  ionih oziroma njihovih ustreznih kationskih in/ali večkrat nabitih oblikah. Poudarek je na energetiki in reakcijah zvrsti v plinasti fazi, omenjene pa so tudi zvrsti v vodni fazi. Posebej sta obravnavana še biomedicinski in analizni vidik fluoridnega iona. Za razumevanje omenjenih ionov je uporabljen tudi na novo uveden princip trihotomije prikladnosti, antropocentrizma in folksonomije.