VIP **Polyfluoride Anions** *Very Important Paper*

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Fluorine-Rich Fluorides: New Insights into the Chemistry of Polyfluoride Anions**

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Abstract: *Polyfluoride anions have been investigated by matrix-isolation spectroscopy and quantum-chemical methods. For the first time the higher polyfluoride anion $[F_5]^-$ has been observed under cryogenic conditions in neon matrices at 850 cm^{-1}. In addition, a new band for the $Cs^+[F_3]^-$ complex in neon is reported.*

In the recent years several new polyhalogen anions have been predicted and experimentally characterized.[1] These anions are dominated by the heavier halogens iodine and bromine with a decreasing number of compounds involving chlorine and fluorine.[2] Recent discoveries are reported in Ref. [1a,3]. To date only one polyfluoride anion has been experimentally detected. First under cryogenic conditions in argon matrices as $[M]^+[F_3]^-$ (M = K, Rb, Cs) ion pairs[4] and later in the gas phase by mass spectrometry.[5] It has also recently been shown that free $[F_3]^-$ ions can be generated by IR laser-ablation of metals together with excess fluorine (see Figure 1 and Ref. [6]).

Free $[F_3]^-$ ions are of synthetic and theoretical interest. Numerous quantum-chemical investigations have been reported in the recent years on its chemical bonding, stability, and properties.[5,7] As a result of the special bonding situation of fluorine and polyfluorides with many electrons localized in a relatively small space, which leads to stretched bonds based on coulomb repulsion,[8] their quantum-chemical treatment requires a so-called non-dynamical correlation which can be adequately treated by coupled-cluster calculations.[9]

In a recently published investigation by Miao polyfluorides of cesium with Cs in higher oxidation states have been addressed.[10] These DFT calculations have shown that at standard pressure the ion pair $Cs^+[F_3]^-$ is the preferred minimum, while it will rearrange at pressures above 30 GPa to yield cesium in the formal oxidation state III, CsF_3. In addition to this interesting species, Hoffmann et al. report in a Communication in this issue that a computed star-like CsF_5 species is found to be a minimum.[11]

Our knowledge about the experimentally known and predicted polyfluorides has increased over the last years. However, some elementary questions regarding the molecular structure of simple ion pairs or salts involving the $[F_3]^-$ ion, such as $Cs^+[F_3]^-$, or the possible existence of higher polyfluoride anions, such as $[F_5]^-$ ions, remained unsolved. Herein we report experimental and quantum-chemical attempts to provide a deeper understanding of this special group of polyhalogen anions, namely the polyfluorides.

Several matrix-isolation experiments have been carried out in our groups, such as the laser-ablation technique, evaporation of cesium fluoride, the reaction of evaporated potassium with fluorine, as well as microwave and electric discharge experiments. In all the experiments the reaction products have been trapped in neon and argon matrices condensed at 4 K. The fluorine employed was carefully purified and blank spectra have been recorded to avoid misinterpretations. For more details see the Experimental Section in the Supporting Information.

It has recently been shown that the free linear $[F_3]^-$ ion can be obtained by laser-ablation of metals with a few percent of fluorine in noble-gases. The mechanism to generate this anion under such conditions is proposed as follows (Figure 1, top. Laser-ablation (Nd:YAG laser) of metals generates a metal plasma, free electrons, and UV radiation. The UV radiation causes F–F bond breaking in F_2 ($\lambda \approx 365$ nm). F atoms will be able to capture free electrons and form fluoride anions, which are trapped in inert noble-gas matrices. By reaction with molecular fluorine the formation of $[F_3]^-$ was finally obtained according to Figure 1, top, Reactions a, b, c, and d. Reaction d has been computed at the coupled-cluster level (CCSD(T)/aug-cc-pV5Z) to be exothermic by 96.9 kJ mol^{-1}.[6]

The computed anharmonic antisymmetric stretching mode for linear $[F_3]^-$ is 523.4 cm^{-1} at the CCSD(T)/aug-cc-pVQZ level. This result is in very good agreement with the metal-independent band position observed at 524.7 cm^{-1} in solid neon.[6] A significant shift to 510.6 cm^{-1} measured in the

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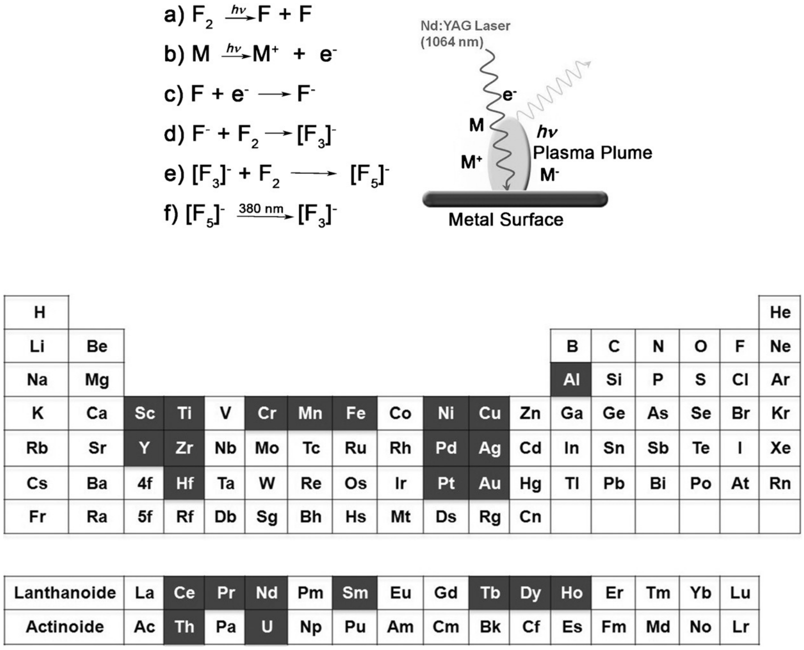

Figure 1. Laser-ablation of a metal into an argon or neon stream containing a few percent of fluorine leads to the formation and trapping of the isolated $[F_3]^-$ upon condensation at 4 K. Top: proposed mechanism for the formation of polyfluoride anions in the gas phase. Bottom: Fluorine experiments with the metals on black backgrounds have been performed to date: see Ref. [6] for earlier studies.

argon matrix is due to stronger host/guest interactions. There is a larger discrepancy between the computed frequency of the linear $[F_3]^-$ mode and a band for the $M^+[F_3]^-$ (M = Cs, Rb, K) ion-pair complex in argon matrices[4] of $\Delta\tilde{\nu} = 27\ \mathrm{cm}^{-1}$. Matrix-isolation experiments using alkali-metal fluorides in neon matrices to explore possible matrix effects on these bands have not been performed up to now.

Therefore we evaporated dry CsF at 900–940 K from a self-constructed furnace into the matrix compartment together with F_2 in neon where the reaction mixture was immediately deposited at 4 K. The IR spectra show one intense band at 561.3 cm^{-1} which increases slightly on annealing to 10 K but decomposes almost completely during irradiation using unfiltered light of $\lambda > 220$ nm (Figure 2). In analogy with its argon-matrix counterpart at 550.5 cm^{-1} this band is assigned to the $Cs^+[F_3]^-$ complex. A further band of neat CsF has been detected as well at 336.6 cm^{-1} in solid neon. This is in good agreement with a published band at 313 cm^{-1} in solid argon[4] and the gas-phase value of 352.6 cm^{-1} taking into account the large matrix shift for a strongly interacting ionic diatomic molecule.[12] Our far-IR (FIR) spectra are shown in Figure S1 (Supporting Information).

In an attempt to generate free $[F_3]^-$ by a "dark method", neat potassium was evaporated at 410–440 K and co-condensed with fluorine in excess neon. The weakly bonded valence electron at potassium should be transferred to fluorine without the formation of an ion-pair complex. Unfortunately, the experiment shows that it is not possible to generate free $[F_3]^-$ ion by this way. The spectra in Figure 3 show that $K^+[F_3]^-$ is formed under these conditions. The reported wave number for $K^+[F_3]^-$ in solid argon is 549.6 cm^{-1}. We measured a band for this ion pair in solid neon at 557 cm^{-1} and a matrix site at 561 cm^{-1}, which accounts for a blue shift of approximately 8 cm^{-1} from argon to neon. This is in good agreement with the shift observed for the corresponding $Cs^+[F_3]^-$ ion pair.

These $Cs^+[F_3]^-$ and $K^+[F_3]^-$ ion pairs have also been explored computationally at various levels of theory. Density functional theory failed to reproduce the experimental frequencies, demonstrating the necessity to perform high-level coupled-cluster calculations (Tables S1–S3 in the Supporting Information). At the CCSD(T)/def2-TZVPP level we found a slightly bent C_{2v} structure of the $[F_3]^-$ ion with the metal cation located above the middle fluorine atom where the F–F bonds are slightly elongated (174.9 or 175.4 ppm)

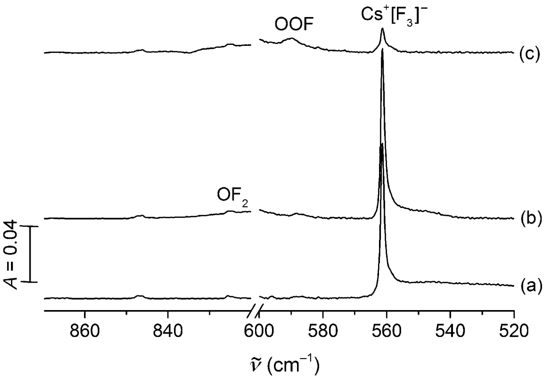

Figure 2. Matrix-isolation IR spectra of the reaction product of thermally evaporated CsF and F_2 in solid neon at 4 K. a) Spectra of CsF and 1.5% F_2 after deposition in neon, b) after annealing to 10 K, c) after 20 min of photolysis at $\lambda > 220$ nm.

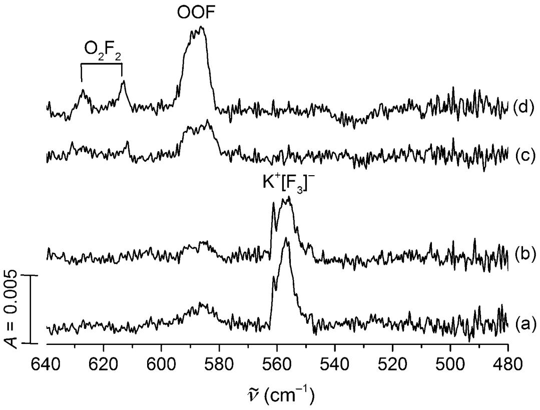

Figure 3. Matrix-isolation IR spectra of the major reaction product of thermally evaporated K and F_2 in solid neon at 4 K. a) Spectra of K and 2% F_2 after deposition in neon, b) after annealing to 10 K, c) after 20 min of photolysis at > 220 nm. d) after annealing to 12 K

compared to those of free $[F_3]^-$ (173.7 pm; Figure 4 and Table S2). The optimization was carried out in C_s symmetry to avoid misleading structures at a shallow hypersurface. The computed structure is in agreement with the qualitative structure suggested for a $M^+[F_3]^-$ ion pair published by one of us in 1977.[4]

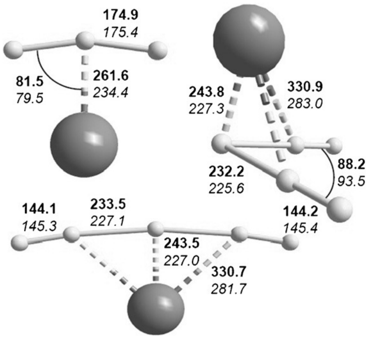

Figure 4. Optimized structure of the $M^+[F_3]^-$ and $M^+[F_5]^-$ ion pairs (M = K, Cs) at the CCSD(T)/def2-TZVPP level. Bond lengths [pm], angle [°]. Bold values belong to the cesium ion pair, italic values belong to the potassium compound.

For the $Cs^+[F_3]^-$ complex the antisymmetric stretching band is computed (CCSD(T)/def2-TZVPP) at 590.2 cm^{-1} (with 213 $km\,mol^{-1}$ intensity) and at 552.0 cm^{-1} (with 98 km mol^{-1} intensity) including anharmonic corrections. A better agreement with the value of 561.3 cm^{-1} observed in solid neon is achieved using the higher CCSD(T)/def2-QZVPP level (568.2 cm^{-1} with 262 $km\,mol^{-1}$), see also Table S3. These results show that for an accurate description, anharmonic corrections and at least a triple-zeta basis set should be used. Compared to the value of the isolated $[F_3]^-$ ion of 524.7 cm^{-1} our results show that in solid neon the cation/anion interactions in $M^+[F_3]^-$ lead to blue-shifts of 36.6 cm^{-1} for M = cesium and approximately 32 cm^{-1} for M = potassium, and to an elongation of the F–F bonds compared to those in the free $[F_3]^-$. In contrast the corresponding symmetric stretching mode of $Cs^+[F_3]^-$ is computed at a lower frequency (388.2 cm^{-1}, CCSD(T)/def2-QZVPP, anharmonic correction) than the Raman band measured in solid argon at 461 cm^{-1}.[4]

Results of the computed thermochemistry of the free and complexed anions are shown in Table 1 and Table S1–S3 in the Supporting Information. They revealed that the formation of $[F_3]^-$ is far less favored starting from the CsF and KF ion pairs (−13.2 $kJ\,mol^{-1}$ and −23.1 $kJ\,mol^{-1}$) than the reaction of free F^- and F_2 (−104.1 $kJ\,mol^{-1}$). This difference is of course due to the relatively strong Coulombic bonding interaction in M^+F^-. Test calculations using a small core ECP of the Stuttgart/Cologne group (denoted as SDD)[13] for both, Cs and K, show that the more exothermic reaction of KF with F_2 is due to the use of an all-electron basis set for K while the Cs atom reveals a 46 electron pseudo potential, see Table 1, right column.

Table 1: Calculated reaction energies for the formation of polyfluorides and alkali-metal ion pairs.[a]

Reaction		CCSD(T)	
	def2-ZVPP	def2-QZVPP	SDD/def2-TZVPP
$F^- + F_2 \rightarrow [F_3]^-$	−116.6	−104.1	
$CsF + F_2 \rightarrow Cs^+[F_3]^-$	−14.6	−13.2	−52.7
$KF + F_2 \rightarrow K^+[F_3]^-$	−24.2	−23.1	−46.3
$F^- + 2\,F_2 \rightarrow [F_5]^-$	−131.9		
$[F_3]^- + F_2 \rightarrow [F_5]^-$	−15.3		
$CsF + 2\,F_2 \rightarrow Cs^+[F_5]^-$	−27.2		
$Cs^+[F_3]^- + F_2 \rightarrow Cs^+[F_5]^-$	−12.5		
$KF + 2\,F_2 \rightarrow K^+[F_5]^-$	−29.9		
$K^+[F_3]^- + F_2 \rightarrow K^+[F_5]^-$	−5.7		

[a] Values in $kJ\,mol^{-1}$. All values are ZPE corrected expect those at the SDD/def2-TZVPP level.

In addition to the observation of the 524.7 cm^{-1} band for free $[F_3]^-$ in solid neon, a second band located at 850.7 cm^{-1} (see Figure 5) has been repeatedly observed in various laser-ablation experiments using different metals and F_2. The assignment of this second band is puzzling. Herein we report our attempts to identify the carrier of this absorption and to discuss preliminary assignments.

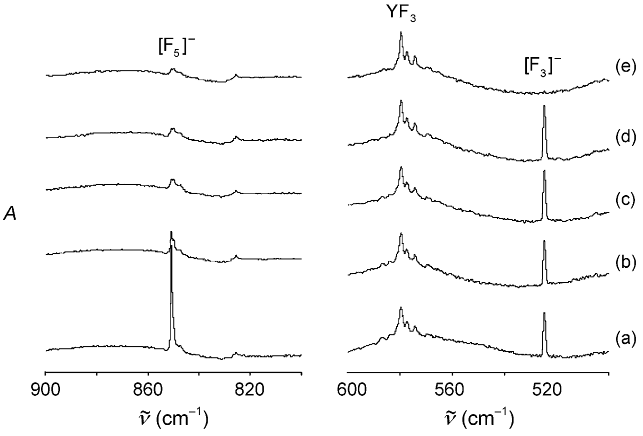

Figure 5. IR spectra for laser-ablated Y and F_2 reaction products in solid neon at 6 K. a) Y + F_2 (0.5 % in neon) deposition for 60 min, b) after λ > 530 nm irradiation for 15 min, c) after λ > 380 nm irradiation for 15 min, d) after λ > 290 nm irradiation for 15 min, e) after λ > 220 nm irradiation for 15 min.

We tentatively assign the 850.7 cm^{-1} absorption to a free $[F_5]^-$ ion isolated in solid neon for the following reasons: 1) like the band of free $[F_3]^-$ at 524.7 cm^{-1} also the band at 850.7 cm^{-1} is found to be metal independent; 2) the extreme photosensitivity of the 850.7 cm^{-1} absorption is suggestive of a charged carrier formed by electron capture or removal; note, that laser-ablation of metals produces electrons and photons, which are capable of ionization, see Figure 1, top Reactions b,c;[14] and 3) the absorption at 850.7 cm^{-1} in the neon matrix is favored at higher fluorine concentration relative to the 524.7 cm^{-1} absorption for isolated $[F_3]^-$, which supports its assignment to a higher polyfluoride anion species.

Figure 5 illustrates representative spectra in solid neon for the high yielding $M + F_2$ system where $M =$ yttrium in which the new 850.7 cm^{-1} absorption is three-times stronger than the 524.7 cm^{-1} band. The 580 cm^{-1} band is assigned to YF_3 from the metal atom reaction with F. Irradiation at $\lambda > 530$ nm decreases the 850.7 cm^{-1} band by 90% with no effect on the 580 or 524.7 cm^{-1} bands (Figure 5b). Continued irradiation at $\lambda > 380$ nm decreased the intensity of the sharp 850.7 cm^{-1} band by another 80% and increased the 524.7 cm^{-1} band by 10% intensity, and further irradiation at $\lambda > 290$ nm halved the 850.7 cm^{-1} band and increased the 524.7 cm^{-1} band by another 5% (Figure 5d).

The $[F_3]^-$ absorptions at 510.6 cm^{-1} in argon matrix and 524.7 cm^{-1} in neon matrix are destroyed upon irradiation at $\lambda > 220$ nm, which is consistent with the photo-decomposition of $[F_3]^-$ into F^- and F_2, both these products are IR inactive.[15] This observation is in line with CCSD(T)/aug-cc-pVQZ calculations, which confirm the existence of only a single minimum for the linear $[F_3]^-$ ion on the potential energy hypersurface (see Figure S2).

Note, that no counterpart of the 850.7 cm^{-1} band was observed in solid argon. This observation holds for all 24 laser-ablation experiments using different metallic elements for which the formation of free $[F_3]^-$ has been observed (Figure 1, bottom). Because the neon matrix environment supports the stabilization of cations better than an argon matrix,[16] and laser ablation is accompanied by vacuum UV light capable of producing high-electron-affinity cations,[17] we have also considered various fluorinated cations as well as oxygen- or nitrogen-containing carriers for the 850.7 cm^{-1} absorption. However, such species can safely be excluded, since neither was any isotopic shift observed in experiments in which $^{18}O_2$ or $^{15}N_2$ were added to the noble gas/fluorine sample, nor do the computed spectra of possible cationic species (see Figure S3 and Table S4) fit to the observed band position.

State-of-the-art quantum-chemical calculations have recently shown that the formation of a $[F_5]^-$ ion is in line with the formation of its heavier homologues of chlorine, bromine, and iodine.[6] It is effectively a $[F_3]^-$ ion at which a F_2 molecule is coordinated in an end-on fashion, a so-called hockey-stick structure (Figure S4). This structural motive is similar to a crystal structure of a $[Cl_5]^-$ ion.[18] The thermochemical stability of $[F_5]^-$ against F_2 elimination was predicted to be 17.4 kJ mol^{-1} at the CCSD(T)/aug-cc-pVQZ level and is therefore similar to that of the $Cs^+[F_3]^-$ complex (Table S1).

There are, however, two intriguing observations which prompted us to refuse the computed hockey-stick structure for the $[F_5]^-$ ion isolated in solid neon. The first is an unusually large disagreement between the experimental frequency of 850 cm^{-1} and the computed value of 807.7 cm^{-1} at the CCSD(T)/aug-cc-pVQZ level, a level which was found to account very well for similar species.[6] Secondly, the presence of a single, strong mid-IR band indicates a C_{2v} symmetric V-shaped structure of the Ne-matrix isolated $[F_5]^-$ ion rather than a hockey-stick structure for which two strong F–F stretching bands are predicted at 807.7 and 527.5 cm^{-1} corresponding to the F_2 and the F_3 moieties, respectively. The V-shaped structure of $[F_5]^-$ was calculated in the gas phase to be 6.2 kJ mol^{-1} higher in energy than the hockey-stick structure.[6] For the hockey-stick structure we found a very shallow potential energy surface along the bending angle $A1$ at the central F atom, see Figure 6, left. Closing the bending angle $A1$ by 20° requires energetically only around 1.5 kJ mol^{-1} but leads to a significant increase in the frequency of the coordinated F_2 moiety, approaching the value of the observed 850 cm^{-1} band (Figure 6, right). Thus, in the neon matrix the symmetric V-shaped structure might be stabilized by neighboring cationic species. Unfortunately, an adequate quantum-chemical investigation simulating the neon matrix with the embedded $[F_5]^-$ ion treated at the necessary coupled-cluster level, is to our knowledge, not feasible to date.

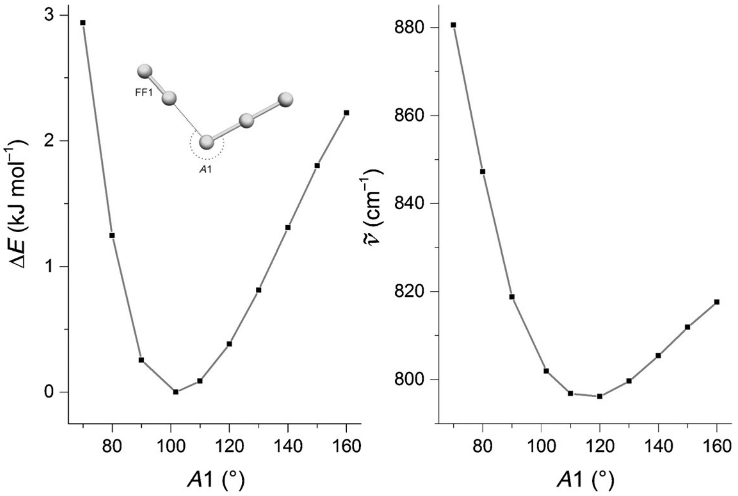

Figure 6. Computed relaxed potential energy surface at CCSD(T)/aug-cc-pVTZ level along the fixed bending angle and its influence at the F_2 stretching mode (FF1) in $[F_2{\cdots}F_3]^-$.

A similar competition between V-shaped and hockey-stick structures has also been observed for other polyhalogen $[X_5]^-$ ions. For the $[Cl_5]^-$ ion quantum-chemical calculations at the CCSD(T)/aug-cc-pVTZ level predict a C_{2v} minimum structure, formally composed of a $[Cl]^-$ ion symmetrically coordinated by two Cl_2 units.[2c,19] However, Raman spectra of $[Cl_5]^-$ salts in solution are more consistent with a hockey-stick $[Cl_3\text{-}Cl_2]^-$ structure, which more recently has been confirmed by an X-ray structure analysis of yellow crystals of $[PPh_2Cl_2][Cl_5]^-$.[18]

The observation that the carrier of the 850.7 cm^{-1} band has never been observed in solid argon is in accord with previous CCSD(T) results, which revealed that in contrast to neon, argon atoms interacts relatively strongly with the anions in question and may therefore protect the $[F_3]^-$ ion from being coordinated by F_2.[6] As a proof of principle the stronger cation/anion interaction in the $Cs^+[F_3]^-$ ion pair may also prevent the formation of a $Cs^+[F_5]^-$ complex in argon matrices. This conclusion is in agreement with our experiments (see Figure 2), as well as with our CCSD(T) calculations, see Figure 4. The $M^+[F_5]^-$ ion pairs are best described as M^+F^- with two coordinated F_2 units. Two isomers of these complexes have been considered. The C_s symmetric complex is a true minimum, while the C_{2v} symmetric complex, although having the same total energy, revealed a small imaginary frequency for the out of plane mode at the coupled-cluster level. The calculated thermochemistry shows that these complexes are less favored than the free $[F_5]^-$ ion (see Table 1 and Tables S1–S3 in the Supporting Information). For more details of CsF_5 complexes see the work of Hoffmann et al.[11]

These and previous experiments show that IR laser ablation of metals gives access to anions in the gas phase. Other experimental attempts, such as microwave or electrical discharge experiments or the evaporation of potassium in the presence of fluorine, have failed to generate the $[F_5]^-$ ion. Only one alternative experimental attempt using mass spectrometry has perhaps lead into the formation of a free $[F_5]^-$ ion. It has been reported that a corresponding $[F_5]^-$ peak at m/z 95 was observed in the gas phase in a flowing afterglow source of a tandem mass spectrometer.[5b] Unfortunately the signal was too weak for an unambiguous assignment.

In conclusion, herein we report the observation of the $Cs^+[F_3]^-$ ion pair as well a so-far unknown higher polyfluoride free anion, $[F_5]^-$, isolated in neon matrices. Based on state-of-the-art quantum-chemical calculations at the CCSD(T) level we have shown that the new 561.3 cm^{-1} band observed in neon matrices is due to an almost T-shaped structured $Cs^+[F_3]^-$ complex (Figure 3). An intriguing band obtained at 850.7 cm^{-1} in solid neon by IR laser ablation of several metals in the presence of elemental fluorine in many experiments carried put in Virginia and Freiburg/Berlin is assigned to a novel V-shaped $[F_5]^-$ anion.

Keywords: cesium fluorides · coupled-cluster calculations · fluorides · matrix-isolation spectroscopy · polyfluoride anions

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