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## Pentagonal Planar $AX_5$ Species: Synthesis and Characterization of the Iodine (III) Pentafluoride Dianion, $IF_5^{2-}$

Karl O. Christe,<sup>\*,§</sup> William W. Wilson,<sup>†</sup> Greg W. Drake,<sup>#</sup> David A. Dixon,<sup>||</sup> Jerry A. Boatz,<sup>#</sup> and Robert Z. Gnann<sup>§</sup>

*Hughes STX, Propulsion Directorate, Air Force Research Laboratory, Edwards Air Force Base, California 93524, Loker Hydrocarbon Research Institute, University of Southern California, Los Angeles, California 90089, and Pacific Northwest National Laboratory, Richland, Washington 99352.*

**Abstract:** The new  $IF_5^{2-}$  dianion, which is only the second known example of a pentagonal planar  $AX_5$  species, was prepared as its  $N(CH_3)_4^+$  salt from  $N(CH_3)_4IF_4$  and  $N(CH_3)_4F$  in  $CH_3CN$  solution. Its structure was established by infrared and Raman spectroscopy, *ab initio* calculations and a comparison to isoelectronic  $XeF_5^-$ . Furthermore, vibrational spectroscopy and x-ray powder diffraction data show that the previously reported composition " $Cs_3IF_6$ " is actually a mixture of  $Cs_2IF_5$  and  $CsF$ . *Ab initio* calculations also show that the most probable geometries for  $IF_6^{3-}$  are vibrationally unstable and undergo spontaneous  $F^-$  ion loss with formation of either pentagonal planar  $IF_5^{2-}$  or square planar  $IF_4^-$ . The synthesis and some properties of the new  $N(CH_3)_4IF_4$  salt and a revised normal coordinate analysis of  $XeF_5^-$  are also presented.

## Introduction

In 1991, the synthesis and characterization of the  $XeF_5^-$  anion was reported.<sup>1</sup> This anion is highly unusual as it is the only known example of a pentagonal planar  $AX_5$  species. In our search for additional representatives of this class, it was noted that the Raman spectrum of a sample<sup>2</sup> having the analytical composition  $Cs_3IF_6$  closely resembled that of  $CsXeF_5$ . As the unknown  $IF_5^{2-}$  is isoelectronic with  $XeF_5^-$  and is likely to be isostructural, we suspected that the previously reported " $Cs_3IF_6$ " composition might actually be a mixture of  $CsF$  and  $Cs_2IF_5$ . Fortunately, the original sample of " $Cs_3IF_6$ " had been preserved in our laboratory for 25 years and showed no signs of deterioration. Therefore, this sample was reinvestigated as it could possibly contain a pentagonal planar  $IF_5^{2-}$  dianion. Unfortunately, both  $CsF$  and the cesium salt of the multiply

charged anion present in the " $\text{Cs}_3\text{IF}_6$ " sample were found to be insoluble in all available chemically inert solvents, thus preempting either their separation by extraction methods or the identification of the multiply charged anion by methods such as multinuclear NMR spectroscopy or growing of a single crystal for x-ray diffraction. It was therefore interesting to synthesize soluble  $\text{IF}_4^-$  and  $\text{F}^-$  salts containing a common cation, which would allow the determination of the true combining ratio of  $\text{IF}_4^-$  with  $\text{F}^-$ . A comparison of the vibrational spectra of the resulting product with those of " $\text{Cs}_3\text{IF}_6$ " should then also permit a positive identification of the anion present in " $\text{Cs}_3\text{IF}_6$ ".

## Experimental

The original  $^2\text{Cs}_3\text{IF}_6$  sample, prepared by the combination of  $\text{CsF}$  and  $\text{IF}_3$  in a 3:1 mol ratio in a  $\text{CFCl}_3$  suspension at  $-78^\circ\text{C}$ ,<sup>3,4</sup> was used in this study. The preparation of  $\text{IF}_3$ ,<sup>3</sup> anhydrous  $\text{N}(\text{CH}_3)_4\text{F}^5$  and  $\text{XeF}_2$ <sup>6</sup> have previously been described. The purity of the  $\text{IF}_3$  was checked by its low temperature Raman spectrum which was in excellent agreement with a previous report.<sup>7</sup> The  $\text{N}(\text{CH}_3)_4\text{I}$  (K & K Laboratories, Inc.) was used as received. The  $\text{CH}_3\text{CN}$  (J.T. Baker, bioanalyzed, low water) was dried over  $\text{P}_2\text{O}_5$  prior to its use. The volatile fluorine compounds were handled in a stainless-steel Teflon-FEP vacuum line, similar to one previously described.<sup>8</sup> The  $\text{CH}_3\text{CN}$  was handled in a flamed out Pyrex glass vacuum line equipped with Kontes Teflon valves and a Heise pressure gauge.

Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer using  $\text{AgCl}$  disks prepared by pressing the finely powdered sample between two thin  $\text{AgCl}$  plates in a Barnes Engineering minipress inside the glove box. An  $\text{AgCl}$  blank was placed into the reference beam to compensate for the absorption of the window material. Raman spectra were recorded on either a Cary Model 83GT, a Spex Model 1403 or a Bruker Equinox 55 spectrophotometer using the 488 nm exciting line of an Ar ion laser, the 647.1 nm line of a Kr ion laser or the 1064 nm line of a neodymium yag laser, respectively.  $^{19}\text{F}$  NMR spectra were recorded at 84.24 MHz on a Jeol FX902 multinuclear instrument between  $+30$  and  $-30^\circ\text{C}$ , using  $\text{CH}_3\text{CN}$  as a solvent and  $\text{d}_6$ -

acetone/ $\text{CFCl}_3$  as an external lock substance and standard. The DSC data were recorded using a DuPont Model 910 DSC. A DuPont Model 2000 Thermal Analyst was used for recording and analyzing the data. The samples were crimp sealed in aluminum pans inside the drybox and heated at a rate of  $2\text{ }^\circ\text{C}/\text{min}$ .

**Synthesis of  $\text{N}(\text{CH}_3)_4\text{IF}_4$ .** Inside the dry box,  $\text{N}(\text{CH}_3)_4\text{I}$  (2.163 mmol) and  $\text{XeF}_2$  (4.327 mmol) were combined in a prepassivated (with  $\text{ClF}_3$ ) Teflon FEP, 0.75 inch o.d. Teflon FEP U-tube which was closed with two stainless steel valves. On the glass vacuum line,  $\text{CH}_3\text{CN}$  (10 mL liquid) was added at  $-196\text{ }^\circ\text{C}$ , and the mixture was warmed to  $-31\text{ }^\circ\text{C}$ . After 8 hr, all gas evolution had ceased, and the amount of gas volatile at  $-78\text{ }^\circ\text{C}$  (2.1 mmol of Xe) was measured. A white solid had formed in the bottom of the tube which was identified as  $\text{N}(\text{CH}_3)_4\text{IF}_2$ .<sup>9</sup> Upon warming of the mixture to room temperature, the yellowish  $\text{CH}_3\text{CN}$  solution turned more orange and additional gas evolved. After 1.5 hr at  $20\text{ }^\circ\text{C}$ , the gas evolution (2.13 mmol of Xe) was complete, resulting in a white solid and clear orange-yellow solution. All volatile material was pumped off at room temperature leaving behind 602 mg of a white solid (weight calcd for 2.163 mmol of  $\text{N}(\text{CH}_3)_4\text{IF}_4 = 599.4\text{ mg}$ ) which was identified by vibrational and NMR spectroscopy as  $\text{N}(\text{CH}_3)_4\text{IF}_4$ .

$\text{N}(\text{CH}_3)_4\text{IF}_4$  was also prepared by the reaction of stoichiometric amounts of  $\text{N}(\text{CH}_3)_4\text{F}$  and  $\text{IF}_3$  in  $\text{CH}_3\text{CN}$  solution of  $-31\text{ }^\circ\text{C}$ . However, this synthesis is inferior to the one described above.

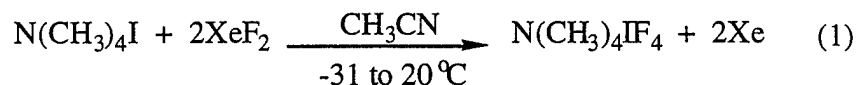
**Synthesis of  $[\text{N}(\text{CH}_3)_4]_2\text{IF}_5$ .** Inside the dry box,  $\text{N}(\text{CH}_3)_4\text{IF}_4$  (0.58 mmol) and  $\text{N}(\text{CH}_3)_4\text{F}$  (0.72 mmol) were loaded into a prepassivated, 0.75 inch o.d., Teflon-FEP ampoule which contained a Teflon coated magnetic stirring bar and was closed by a stainless steel valve. On the glass line, dry  $\text{CH}_3\text{CN}$  (7.2 mL) was added at  $-196\text{ }^\circ\text{C}$  and the mixture was stirred for 18 hr at  $-31\text{ }^\circ\text{C}$ . The solvent was pumped off for 14 hr, first at  $-31\text{ }^\circ\text{C}$  and during the last stages at room temperature, resulting in a white dry solid (227 mg, weight calcd for 0.58 mmol

$[\text{N}(\text{CH}_3)_4]_2\text{IF}_5$  plus 0.14 mmol  $\text{N}(\text{CH}_3)_4\text{F}$  = 228 mg) which was shown by vibrational spectroscopy to consist mainly of  $[\text{N}(\text{CH}_3)_4]_2\text{IF}_5$ , containing a small amount of unreacted  $\text{N}(\text{CH}_3)_4\text{IF}_4$  and the excess of  $\text{N}(\text{CH}_3)_4\text{F}$  used in the reaction.

**Theoretical Calculations.** Electronic structure calculations were done at the local density functional theory (LDFT) level<sup>10,11</sup> with a polarized valence double zeta basis set (DZVP)<sup>12</sup>, and at the Hartree-Fock (HF) level<sup>13</sup> with an effective core potential (ECP)<sup>14</sup> on I for the core electrons and with a polarized double zeta basis set for the valence electrons, and with an all electron polarized double zeta valence set on F.<sup>15</sup> Geometries were optimized using analytical methods.<sup>16</sup> Analytic second derivatives were calculated at the optimized LDFT geometries.<sup>17</sup> Numerical second derivatives were calculated at the Hartree-Fock level by using a two-point differencing scheme. The LDF calculations were done with DGAUSS<sup>18</sup>, and the HF calculations were done with Gaussian 94.<sup>19</sup> The calculated Hessian matrices (second derivatives of the energy with respect to Cartesian coordinates) were converted to symmetry-adapted internal coordinates for further analysis using the program systems GAMESS<sup>20</sup> and Bmtrx.<sup>21</sup>

## Results and Discussion

**Synthesis and Properties of  $\text{N}(\text{CH}_3)_4\text{IF}_4$ .** As already pointed out in the Introduction, the determination of the combining ratio of  $\text{IF}_4^-$  with  $\text{F}^-$  required the availability of soluble salts of these two anions with a common counterion. Since  $\text{N}(\text{CH}_3)_4\text{F}^5$  and  $\text{N}(\text{CH}_3)_4\text{XF}_4$  ( $x = \text{Br}$  or  $\text{Cl}$ )<sup>22</sup> were known to have good solubility in  $\text{CH}_3\text{CN}$ , the  $\text{N}(\text{CH}_3)_4\text{IF}_4$  salt appeared to be an ideal candidate for our reactions. Our first attempts to prepare this salt from  $\text{N}(\text{CH}_3)_4\text{F}$  and  $\text{IF}_3$  in  $\text{CH}_3\text{CN}$  solution at  $-31^\circ\text{C}$  produced only impure products. Subsequently, the following improved synthesis (1) gave very pure  $\text{N}(\text{CH}_3)_4\text{IF}_4$ , eliminated the need for the thermally unstable  $\text{IF}_3$ , which is difficult to purify,<sup>3,4</sup> and utilized only commercially available starting materials. It is



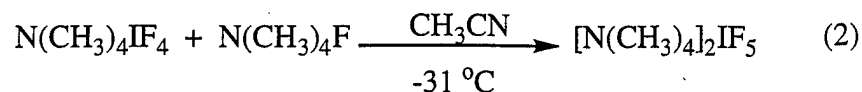
similar to the one previously reported<sup>23</sup> for 1,1,3,3,5,5 hexamethylpiperidinium ( $\text{pip}^+$ ) $\text{IF}_4^-$  from  $\text{pip}^+\text{F}^-$ , iodine and  $\text{XeF}_2$ , but offers the advantages of avoiding a 7 step, 14% yield synthesis of  $\text{pip}^+\text{F}^-$  and the handling of volatile elemental iodine.

$\text{N}(\text{CH}_3)_4\text{IF}_4$  is a white crystalline solid which, based on DSC data and vibrational spectra, undergoes a reversible endothermic phase change of 21.8 J/g at 73.8 °C and irreversible exothermic decomposition at 284 °C. The surprisingly high thermal stability of this compound is in marked contrast to that of  $\text{pip}^+\text{IF}_4^-$  which was reported<sup>23</sup> to be unstable above 0 °C.

The  $^{19}\text{F}$  NMR spectra of  $\text{N}(\text{CH}_3)_4\text{IF}_4$  in  $\text{CH}_3\text{CN}$  solution were recorded at -30 and 30 °C and consisted of broad singlets at  $\delta = -106.5$  with half widths of 385 and 1061 Hz, respectively. The observed chemical shift is in excellent agreement with the value of -106 ppm, previously reported<sup>23</sup> for  $\text{pip}^+\text{IF}_4^-$  in  $\text{CH}_3\text{CN}$  at -20 °C. The chemical shift of  $\text{IF}_4^-$  fits nicely the trends observed for other halogen fluoride anions,<sup>25,26</sup> i.e., the shielding of the fluorine ligands decreases with increasing oxidation state and electronegativity of the central atom (see Table 1). Pronounced line broadening with increasing temperature was also observed for  $\text{BrF}_4^-$  and  $\text{ClF}_4^-$ .<sup>26</sup>

The infrared and Raman spectra of  $\text{N}(\text{CH}_3)_4\text{IF}_4$  are summarized in Table 2. The bands observed for the  $\text{IF}_4^-$  part of  $\text{N}(\text{CH}_3)_4\text{IF}_4$  agree well with those previously reported for  $\text{CsIF}_4$ ,<sup>2</sup> but not with those (Ra: 573.5, 461 and 213  $\text{cm}^{-1}$ ) previously listed<sup>23</sup> for  $\text{pip}^+\text{IF}_4^-$ . Particularly, the value of 573.5  $\text{cm}^{-1}$ , reported for  $\nu_1(\text{A}_{1g})$  of  $\text{pip}^+\text{IF}_4^-$ , is outside the expected (see Computational Results below) range and is likely incorrect. The bands due to the  $\text{N}(\text{CH}_3)_4^+$  cation have been summarized in a footnote of Table 2. They are in excellent agreement with those previously reported for other  $\text{N}(\text{CH}_3)_4^+$  salts<sup>1,5,9</sup> and, therefore, do not require further discussion.

**Synthesis and Properties of  $[\text{N}(\text{CH}_3)_4]_2\text{IF}_5$ .** The combination of  $\text{N}(\text{CH}_3)_4\text{IF}_4$  with a slight excess of  $\text{N}(\text{CH}_3)_4\text{F}$  in  $\text{CH}_3\text{CN}$  solution at -31 °C produced the desired  $[\text{N}(\text{CH}_3)_4]_2\text{IF}_5$  (2).



Prolonged reaction times (about 20 hr) and stirring resulted in an almost quantitative conversion of  $\text{IF}_4^-$  to  $\text{IF}_5^{2-}$  thus establishing the 1:1 combining ratio between  $\text{IF}_4^-$  and  $\text{F}^-$ . In the presence of a large excess of  $\text{F}^-$  ions, no further fluoride ion uptake and, hence, no formation of  $\text{IF}_6^{3-}$  were observed. Attempts to carry out reaction (2) in  $\text{CHF}_3$  solution at  $-78\text{ }^\circ\text{C}$  were unsuccessful and only unreacted  $\text{N(CH}_3)_4\text{IF}_4$  was recovered.

The  $[\text{N(CH}_3)_4]_2\text{IF}_5$  salt is a white solid which is stable at room temperature. It has very little solubility in solvents, such as  $\text{CH}_3\text{CN}$ , which precluded its characterization by NMR spectroscopy and the growing of single crystals for a crystal structure determination. Infrared and Raman spectra of the solid were used for its characterization. They are given in Figure 1 and Table 3, and their assignments are discussed below in more detail.

**Characterization of  $\text{Cs}_2\text{IF}_5$ .** In the original report<sup>2</sup> on " $\text{Cs}_3\text{IF}_6$ ", the true combining ratio of  $\text{IF}_3$  with  $\text{CsF}$  had not been established. An arbitrary 1:3 ratio of the starting materials had been used and, since both,  $\text{CsF}$  and  $\text{Cs}_2\text{IF}_5$ , are insoluble, the products could not be separated and, therefore, by necessity had the analytical composition  $\text{Cs}_3\text{IF}_6$ .

In the reaction of  $\text{IF}_4^-$  with an excess of fluoride ions, the logical first step is the addition of one fluoride ion with formation of  $\text{IF}_5^{2-}$ . The addition of a second fluoride ion with formation of an  $\text{IF}_6^{3-}$  trianion becomes less likely since the Lewis acidity of the parent anion decreases with the addition of each  $\text{F}^-$  ion. Although, based on these arguments, the formation of  $\text{IF}_5^{2-}$  is clearly favored over that of  $\text{IF}_6^{3-}$ , it previously had not been given much consideration due to the absence of any other  $\text{AX}_5\text{E}_2$  species containing two free valence electron pairs (E) on A. This picture, however, has changed recently with the synthesis of surprisingly stable  $\text{XeF}_5^-$  salts.<sup>1</sup>

Our reinvestigation of the original<sup>2</sup> " $\text{Cs}_3\text{IF}_6$ " sample, which had been preserved in our laboratory for 25 years without noticeable decomposition, showed that it is indeed a mixture of  $\text{Cs}_2\text{IF}_5$  and  $\text{CsF}$ , based on the following evidence:



- (i) X-ray powder data: The previously published powder pattern of “Cs<sub>3</sub>IF<sub>6</sub>” (Table II of reference 2) shows all the lines characteristic<sup>27</sup> for CsF (d(Å), intens: 3.4 ms, 3.03 mw, 2.106 mw, 1.801 mw, 1.735 vw, 1.496 w, 1.370w, 1.336 mw, 1.223 w, 1.153w) and leaves no doubt that “Cs<sub>3</sub>IF<sub>6</sub>” contains a very significant amount of free CsF.
- (ii) Infrared spectrum: The infrared spectrum of “Cs<sub>3</sub>IF<sub>6</sub>” was rerecorded and compared to that of CsF taken under the same conditions. It was found that the major absorption in both spectra was a very intense and broad band at 298 cm<sup>-1</sup> due to CsF which in the “Cs<sub>3</sub>IF<sub>6</sub>” case confirms the presence of free CsF but obscures the less intense IF<sub>5</sub><sup>2-</sup> bands.
- (iii) Raman spectrum: A higher quality Raman spectrum, which did not suffer from fluorescence,<sup>2</sup> was obtained by means of 1064 nm excitation with a neodymium yag laser and is shown in Figure 2. The dominant Raman bands at 478, 396, 339 and 325 cm<sup>-1</sup> are in excellent agreement with those of IF<sub>5</sub><sup>2-</sup> in [N(CH<sub>3</sub>)<sub>4</sub>]<sub>2</sub>IF<sub>5</sub> (see Table 3) and leave no doubt that the dominant anion in “Cs<sub>3</sub>IF<sub>6</sub>” is IF<sub>5</sub><sup>2-</sup>. For a hypothetical IF<sub>6</sub><sup>3-</sup> anion, the additional fluoride ligand and extra formal negative charge should cause a different band pattern and significant shifts to lower frequencies. In addition to the intense IF<sub>5</sub><sup>2-</sup> bands, the “Cs<sub>3</sub>IF<sub>6</sub>” spectrum showed several very weak bands which can be assigned to likely impurities, such as IF<sub>7</sub><sup>2-</sup> (556 and 454 cm<sup>-1</sup>) or IOF<sub>5</sub><sup>2-</sup> (865 cm<sup>-1</sup>)<sup>28</sup> and lattice vibrations (140 and 110 cm<sup>-1</sup>). The formation of IF<sub>7</sub><sup>2-</sup> and IOF<sub>5</sub><sup>2-</sup> can be easily rationalized. Iodine trifluoride has a tendency to disproportionate to I<sub>2</sub> and IF<sub>5</sub>,<sup>3</sup> and IF<sub>5</sub> is known<sup>28</sup> to react with excess F<sup>-</sup> to give IF<sub>7</sub><sup>2-</sup>. Similarly, a trace of moisture will result in partial hydrolysis of IF<sub>6</sub><sup>-</sup> to give IOF<sub>4</sub><sup>-</sup>, which in turn is known to give with excess F<sup>-</sup> the IOF<sub>5</sub><sup>2-</sup> dianion.<sup>28</sup> These impurities had been formed already during the original preparation<sup>4</sup> and were not generated during sample storage.

**Vibrational Spectra and Electronic Structure Calculations.** The vibrational spectra of IF<sub>5</sub><sup>2-</sup> are summarized in Table 3 and were assigned by analogy with those established for the isoelectronic XeF<sub>5</sub><sup>-</sup> anion.<sup>1,29</sup> The only difference is the reversal of the identity of  $\nu_3$  and  $\nu_6$  in the E<sub>2</sub> block, based on the results of the potential energy distribution (see below). The spectra of IF<sub>5</sub><sup>2-</sup> and

$\text{XeF}_5^-$  are very similar. They exhibit the expected frequency decreases for  $\text{IF}_5^{2-}$  due to the additional negative charge which enhances the  $\text{X}(\delta^+)-\text{F}(\delta^-)$  polarity of the bonds. Analogous general frequency and bond weakening effects are also observed on going from  $\text{IF}_4^-$  (see Table 2) to  $\text{IF}_5^{2-}$  (see Table 3).

The geometry and the vibrational spectra of  $\text{IF}_5^{2-}$  and  $\text{XeF}_5^-$  were studied by electronic structure calculations at the HF and LDFT levels. To evaluate the reliability of our computational methods, the well known  $\text{IF}_4^-$  geometry<sup>23</sup> and spectra<sup>2</sup> were calculated first. As can be seen from Tables 2 and 4, the HF/ECP/DZP method gave the better results. For  $\text{IF}_4^-$ , the bond length, calculated at the HF/EDP/DZP level is only 0.013 Å shorter than the observed one.<sup>23</sup> For  $\text{IF}_5^{2-}$ , the minimum energy structure at both the HF and LDFT levels was pentagonal planar with  $D_{5h}$  symmetry. Assuming a similar correction as for  $\text{IF}_4^-$ , the bond length of  $\text{IF}_5^{2-}$  is predicted to be 2.11 Å. This bond length increase of 0.09 Å relative to  $\text{IF}_4^-$  can be explained by the increased polarity of the bonds (see above) and increased ligand-ligand repulsion due to a decrease of the F-I-F bond angle from 90° in  $\text{IF}_4^-$  to 72° in  $\text{IF}_5^{2-}$ .

The symmetry force constants and potential energy distributions (PED) were calculated for  $\text{IF}_5^{2-}$  and  $\text{XeF}_5^-$  using the scaled HF/ECP/DZP frequencies (see Table 5). Since we were unable to duplicate with our computer calculations the previously published, hand calculated, out of plane deformation force constants,<sup>1,29</sup> the originally given<sup>1</sup> G matrix was reexamined and found to contain incorrect multiplicity factors for  $G_{22}$  and  $G_{77}$ . The corrected G matrix for  $\text{XeF}_5^-$  is given in Table 6 and was verified by the machine methods. A typographical error for a sign in one of the originally published<sup>1</sup> symmetry coordinates, i.e.,  $(S_{5b})$  should read  $(2/5)^{1/2} [\sin 2\alpha(\Delta r_2 - \Delta r_5) - \sin \alpha(\Delta r_3 - \Delta r_4)]$  has already been corrected elsewhere.<sup>29</sup> The revised force constant,  $F_{22} = 0.480 \text{ m dyn } \text{Å}/\text{rad}^2$ , for the symmetric out of plane deformation of  $\text{XeF}_5^-$  is now in much better agreement with our expectation. The deformations out of the highly crowded pentagonal plane should possess significantly smaller force constants than the corresponding in plane deformations.

As can be seen from Tables 3 and 5, the results from the normal coordinate analyses confirm the identities of these pentagonal planar anions. The general fit between the calculated and observed frequencies is very good. The only remaining minor ambiguities in the normal coordinate analyses are: (i) for  $\text{XeF}_5^-$ , the exact location of the infrared active, in plane deformation mode,  $\nu_4$ , is somewhat uncertain. Based on the calculations, its frequency is similar to, but its infrared intensity is much lower than those of the out of plane umbrella deformation mode,  $\nu_2$ . Therefore, we assume that  $\nu_4$  is hidden under the  $\nu_2$  band; (ii) for  $\text{IF}_5^{2-}$ , the location of the infrared active, out of plane umbrella deformation mode was obscured. In the  $\text{Cs}_2\text{IF}_5$  spectrum, the strong absorption due to free  $\text{CsF}$  obscured this region, and in the  $[\text{N}(\text{CH}_3)_4]_2\text{IF}_5$  spectrum, the presence of an  $\text{IF}_4^-$  impurity and the broadness of the  $\nu_3$  mode of  $\text{IF}_5^{2-}$  interfered. In the Raman spectrum of  $\text{Cs}_2\text{IF}_5$ , one of the two  $E_2'$  bands exhibits a splitting, similar to those observed for these modes in  $\text{XeF}_5^-$ . In Table 3, this splitting was tentatively assigned to  $\nu_5$  because this requires a smaller splitting. However, if one assumes  $\nu_6$  to be split instead of  $\nu_5$ , the average of the 396 and 339  $\text{cm}^{-1}$  components would result in much better agreement with the calculated frequency of 366  $\text{cm}^{-1}$  and the  $[\text{N}(\text{CH}_3)_4]_2\text{IF}_5$  spectrum, in which  $\nu_6$  of  $\text{IF}_5^{2-}$  probably coincides with a cation band at 366  $\text{cm}^{-1}$ .

An inspection of the potential energy distributions for  $\text{IF}_5^{2-}$  and  $\text{XeF}_5^-$  (see Table 5) shows that the E modes of  $\text{XeF}_5^-$  are considerably more characteristic than those of  $\text{IF}_5^{2-}$ . This is due to the increased bond polarity in  $\text{IF}_5^{2-}$ , which lowers preferably the stretching force constant and makes its value more similar to those of the deformation constants. This enhances the mixing of the normal modes in  $\text{IF}_5^{2-}$  and, in its  $E_2'$  block, results in the higher frequency mode becoming mainly the bending motion. A further consequence of the larger bond polarity in  $\text{IF}_5^{2-}$  is the increased coupling of the stretching motions involving opposite bonds ( $\text{frr}' = 0.42 \text{ m dyn} / \text{\AA}$ ). This large  $\text{frr}'$  value is responsible for the low frequency of the antisymmetric stretching mode,  $\nu_3(E_1')$ , which represents

the reaction coordinate for the loss of an F<sup>-</sup> ion. This finding is in accord with the observation that IF<sub>5</sub><sup>2-</sup> readily loses an F<sup>-</sup> ion to give IF<sub>4</sub><sup>-</sup>.

The stability of the hypothetical IF<sub>6</sub><sup>3-</sup> anion was also examined by ab initio methods. The four most likely geometries of IF<sub>6</sub><sup>3-</sup> are shown in Figure 3. Like IF<sub>5</sub><sup>2-</sup>, this anion contains two free valence electron pairs on iodine. If both electron pairs are sterically active, the most likely structure is the one with D<sub>3d</sub> symmetry, in which the two more repulsive free pairs avoid each other as much as possible by occupying the axial trans positions of a bicapped octahedron. If, on the other hand, one of the two free valence electron pairs on iodine is sterically inactive, i.e., occupies an A<sub>1g</sub> or s-orbital, only *p* and *d*-orbitals of iodine are involved in the bonding and, therefore, the resulting structures are governed by repulsion effects, and, as in transition metal heptafluorides,<sup>30</sup> the energetically most favored structures become the monocapped octahedron of C<sub>3v</sub> symmetry and the monocapped trigonal prism of C<sub>2v</sub> symmetry. The pentagonal bipyramid of C<sub>5v</sub> symmetry is slightly higher in energy, but was also considered.<sup>31-33</sup>

The structures of all four geometries of IF<sub>6</sub><sup>3-</sup> were calculated at the restricted Hartree-Fock (RHF) self-consistent field level, using effective core potentials<sup>34</sup> and the corresponding valence basis sets of Stevens, Basch, Krauss, and Jasien.<sup>35</sup> The basis set was augmented with a diffuse s+p shell<sup>36</sup> and a *d* polarization function<sup>37</sup> on each atom. All calculations were performed using the GAMESS quantum chemistry package.<sup>20</sup> Since the HOMO of the D<sub>3d</sub> and C<sub>3v</sub> structures is a half-filled degenerate orbital pair, Jahn-Teller distortion to lower symmetry is anticipated. Therefore, the initial geometries of these conformations were distorted to C<sub>s</sub> symmetry by slight elongation of one pair of trans fluorine ligands. For each of the four conformations, geometry optimization led to the dissociative loss of one or two fluoride ligands. Specifically, optimization of the C<sub>2v</sub> conformation and the distorted D<sub>3d</sub> and C<sub>3v</sub> structures led to formation of square planar [IF<sub>4</sub>]<sup>-</sup> and 2 fluoride anions, whereas optimization of the C<sub>5v</sub> structure led to formation of pentagonal planar [IF<sub>5</sub>]<sup>2-</sup> and one fluoride anion. Thus, none of the four conformations were found to be a local minimum. Although more extensive calculations are desirable to definitively rule out the stability of the [IF<sub>6</sub>]<sup>3-</sup>, the present results strongly indicate that this anion is not a stable species.

## Conclusions

The successful synthesis of a second example of a pentagonal planar  $AX_5$  species demonstrates that  $XeF_5^-$  is not a unique case, and that other examples of  $AX_5$  molecules of  $D_{5h}$  symmetry, such as  $TeF_5^{3-}$ ,  $AuF_5^{2-}$  or  $PtF_5^{3-}$ , might also exist. Although  $IF_5^{2-}$  had been prepared 30 years ago,<sup>3</sup> its nature had not been recognized until now. The greatly delayed recognition of this unusual anion parallels the discovery<sup>1</sup> of  $XeF_5^-$  which had originally been mistaken for octahedral  $XeF_6^{2-}$ .<sup>38-40</sup>

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## References

- ♥ Dedicated to Professor Neil Bartlett on the occasion of his 65th birthday
- ‡ Hughes STX
- § University of Southern California
- || Pacific Northwest National Laboratory
- # Propulsion Directorate, Air Force Research Laboratory
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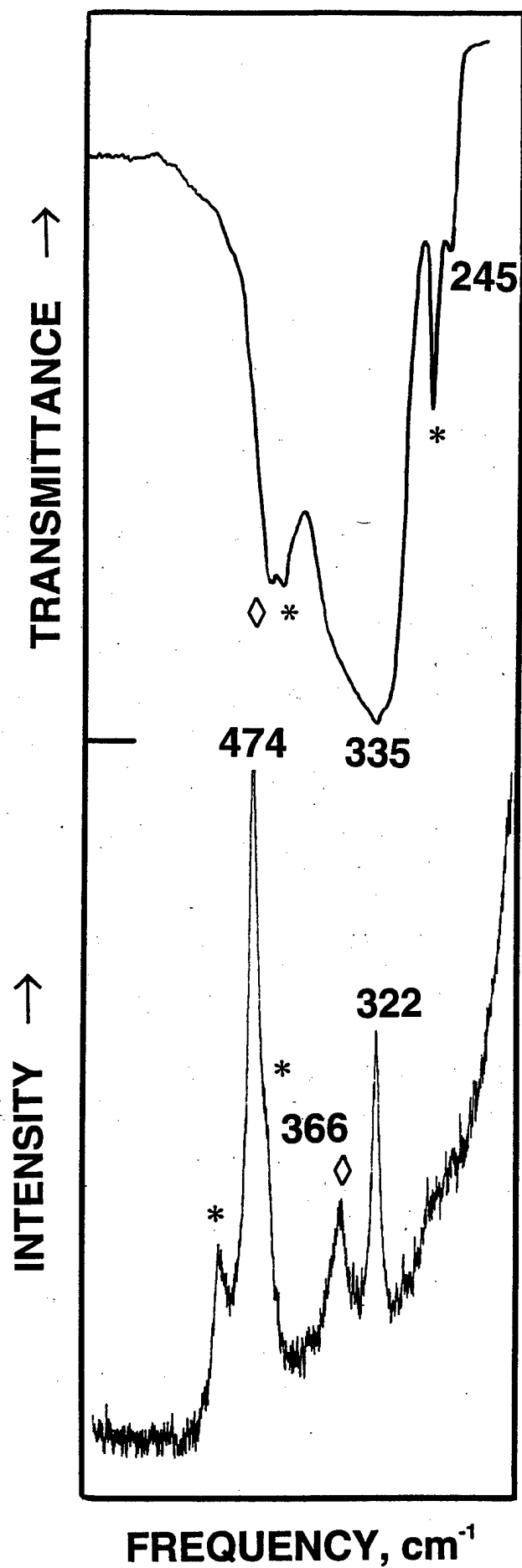
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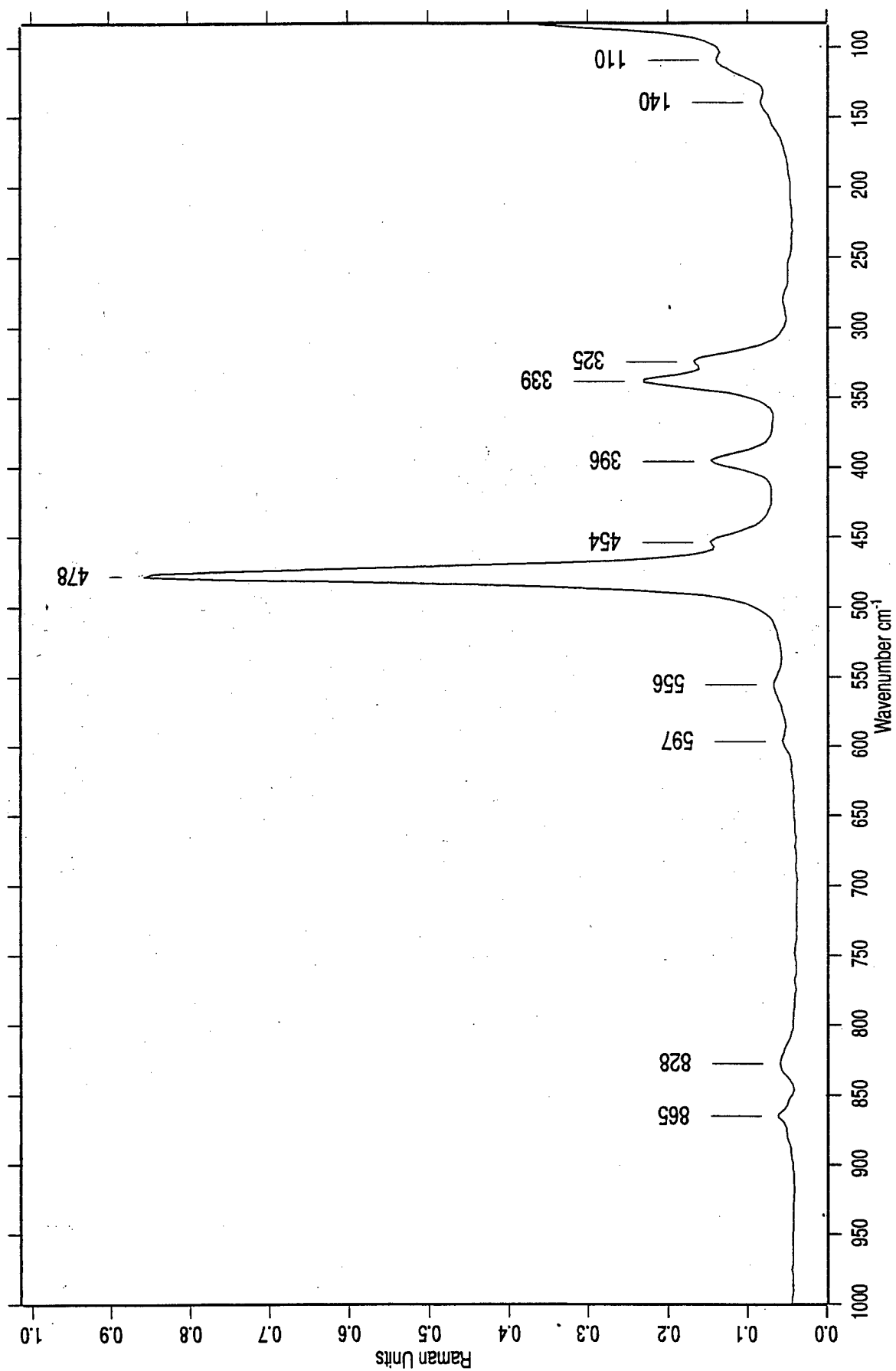


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## Diagram Captions

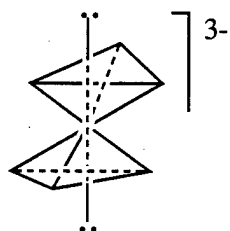
- Figure 1 Infrared and Raman spectra of solid  $[\text{N}(\text{CH}_3)_4]_2\text{IF}_5$ . The bands masked by asterisks and diamonds are due to  $\text{IF}_4^-$  and  $\text{N}(\text{CH}_3)_4^+$ , respectively, while those marked by frequency values belong to  $\text{IF}_5^{2-}$ .
- Figure 2 Raman spectrum of  $\text{Cs}_2\text{IF}_5$ .
- Figure 3 Most likely geometries of the  $\text{IF}_6^{3-}$  trianion and their spontaneous decomposition modes.



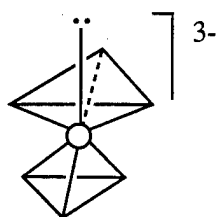


Two sterically active  
free valence  
electron pairs

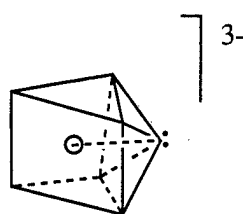
One sterically active and one sterically inactive free valence electron pair



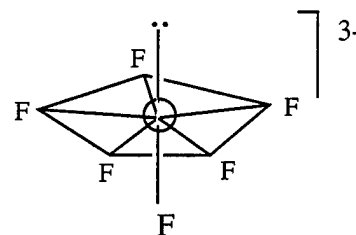
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BICAPPED  
OCTAHEDRON



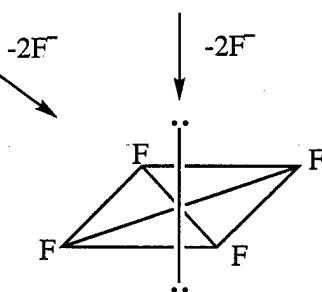
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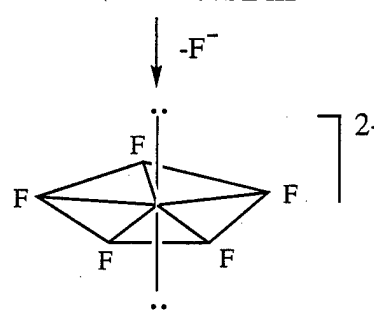
$C_{2v}$   
MONOCAPPED  
TRIGONAL PRISM



$C_{5v}$   
PENTAGONAL  
BIPYRAMID



$D_{4h}$   
SQUARE  
PLANAR



$D_{5h}$   
PENTAGONAL  
PLANAR

Table 1.  $^{19}\text{F}$  Chemical Shifts for Binary Halogen Fluoride Anions

oxidation state of central atom			
+I	$\text{IF}_2^-$ -282 <sup>a</sup>		
+III	$\text{IF}_4^-$ -106 <sup>b</sup>	$\text{BrF}_4^-$ -37 <sup>c</sup>	$\text{ClF}_4^-$ 67 <sup>c</sup>
+V	$\text{IF}_6^-$ 13 <sup>c</sup>	$\text{BrF}_6^-$ 94 <sup>c</sup>	
+VII	$\text{IF}_8^-$ 249 <sup>d</sup>		

<sup>a</sup>: ref 9. <sup>b</sup> this work and ref 23. <sup>c</sup> ref 25. <sup>d</sup> ref 26. <sup>e</sup> ref 22.

Table 2. Observed and Calculated Vibrational Spectra of  $\text{IF}_4^-$

assgnts and approx mode descriptions in point group D <sub>4h</sub>		obsd freq, cm <sup>-1</sup> (rel int) <sup>a</sup>				calcd freq, cm <sup>-1</sup> (IR int) <sup>b</sup>			
		CsIF <sub>4</sub>		N(CH <sub>3</sub> ) <sub>4</sub> IF <sub>4</sub> <sup>d</sup>		HF/ECP/DZP		LDFT/DZVP	
		IR		RA		IR		RA	
						unscaled		scaled	
Ra	A <sub>1g</sub> ν <sub>1</sub> ν sym in phase	—	522(10)	—	515(10)	559(0)	520	495(0)	
IR	A <sub>2u</sub> ν <sub>2</sub> δ umbrella	271ms	—	267ms	—	326(78)	277	255(40)	
Ra	B <sub>1g</sub> ν <sub>3</sub> ν sym out of phase	—	455(7.2)	—	457(5.6)	493(0)	458	449(0)	
Ra	B <sub>2g</sub> ν <sub>4</sub> δ scissor	—	195(0+)	—	197(0.5)	225(0)	191	167(0)	
—	B <sub>2u</sub> ν <sub>5</sub> δ pucker	—	—	—	—	185(0)	157	140(0)	
IR	E <sub>u</sub> ν <sub>6</sub> ν asym	448vs	—	449 vs	—	481(951)	447	501(544)	
	ν <sub>7</sub> δ asym	n. obsd	—	n. obsd	—	139(3)	118	115(3)	

<sup>a</sup>Data for CsIF<sub>4</sub> from ref 2, for N(CH<sub>3</sub>)<sub>4</sub> IF<sub>4</sub> from this study. <sup>b</sup>Infrared intensities in km/mol. <sup>c</sup>Empirical scaling factors of 0.9294 and 0.8490 for the stretching and deformation modes, respectively, were used to maximize the fit between the observed and calculated frequencies. <sup>d</sup>In addition to the above listed IF<sub>4</sub><sup>-</sup> bands, the following bands due to N(CH<sub>3</sub>)<sub>4</sub><sup>+</sup> were observed: IR: 3118sh, 3040w, 2969vw, 1490 mw, 1444w, 1416mw, 1287w, 952m, 922w, 462m; Ra: 3021(0.7), 2969(0.2), 2942(0.4), 2907(0.1), 2800(0.1), 1471(0.6), 1461(0.7), 1413(0.3), 1284(0.1), 1175(0.15), 1168(0.1), 947(1.5), 754(1.5), 450 sh on the intense 457 IF<sub>4</sub><sup>-</sup> band, 369(0.2).

Table 3. Observed and Calculated Vibrational Spectra of  $\text{IF}_5^{2-}$  Compared to Those Observed for  $\text{XeF}_5^-$

assgnts and approx mode descriptions in point group $D_{3h}$		$\text{IF}_5^{2-}$			$\text{XeF}_5^-$		
		obsd freq, $\text{cm}^{-1}$ (rel int)		scaled <sup>a</sup>	caled freq, $\text{cm}^{-1}$ (IR int) <sup>f</sup>		obsd freq, $\text{cm}^{-1}$ (rel int)
		$\text{Cs}_2\text{IF}_5$	$[\text{N}(\text{CH}_3)_4]\text{IF}_5^b$		HF/ECPP/DZP	$\text{CsXeF}_5$	$\text{N}(\text{CH}_3)_4\text{XeF}_5$
		Ra	IR	RA	unscaled	IR	Ra
Ra	$A_1'$ $\nu_1$ $\nu$ sym	478(10)		474(10)	487(0)	468	504(10)
IR	$A_2''$ $\nu_2$ $\delta$ umbrella		(—) <sup>c</sup>		320(97)	307	274s
IR	$E_1'$ $\nu_3$ $\nu$ asym		335vs, br		356(588)	342	509sh 465vs 420sh
	$\nu_4$ $\delta$ asym in plane		245w		259(14)	249	288sh
Ra	$E_2'$ $\nu_5$ $\nu$ asym	339(2)		322(3.8)	349(0)	335	432(1.5)
		325(1.6)					422(1.6)
	$\nu_6$ $\delta$ asym in plane	396(0.9)		(366) <sup>d</sup>	381(0)	366	380(2.2) 369(2.3)
Ra	$E_2''$ $\nu_7$ $\delta$ pucker				104(0)	100	377(3.3)

<sup>a</sup>Data from ref 1. <sup>b</sup>In addition to the above listed  $\text{IF}_5^{2-}$  bands, the following bands due to  $\text{N}(\text{CH}_3)_4^+$  were observed: IR: 3034ms, 1507ms, 1415w, 1255m, 963s, 467m; Ra: 3010(1.3), 2943(0.8), 2810(0.4), 1478(1.8), 952(1.8), 751(3.0), 460(sh), 366(1.0). <sup>c</sup>This band is masked by the very intense broad band at 335  $\text{cm}^{-1}$ . <sup>d</sup>This band is obscured by the relatively intense 366  $\text{cm}^{-1}$   $\text{N}(\text{CH}_3)_4^+$  band. <sup>e</sup>An empirical scaling factor of 0.9606 was used to maximize the fit between observed and calculated frequencies. <sup>f</sup>Ir intensities in  $\text{km/mol}$ .



Table 4. Calculated, Observed and Predicted Bond Lengths for  $\text{IF}_4^-$  and  $\text{IF}_5^{2-}$

	bond distances (Å)		
	observed	calculated	predicted
$\text{IF}_4^-(\text{D}_{4h})$	2.007 <sup>a</sup>	HF/ECP/DZP	LDFT/DZVP
		1.994	2.069
$\text{IF}_5^{2-}(\text{D}_{5h})$	—	2.094	2.163
			2.11

<sup>a</sup> Ref. 23.

Table 5. Symmetry Force Constants and Potential Energy Distribution of  $D_{3h}$   $IF_5^2$  and  $XeF_5$ . Calculated from the Scaled HF/ECP/DZP Second Derivatives

freq, $cm^{-1}$	$IF_5^{2-a}$		$XeF_5^b$	
	sym force consts <sup>c</sup>		sym force consts <sup>c</sup>	
	obsd	calcd	obsd	calcd
$A_1'$	474	468	502	503
$A_2''$		307	278	305
$E_1'$	335	342	455	454
$E_2'$	245	249	278	276
	322/339	335	423	425
$E_2''$	366/396	366	377	378
		100		107
internal force constants				
	fr	1.529		2.043
	frr	0.035		0.137
	frr'	0.423		0.260

<sup>a</sup>Empirical scaling factors of 0.9606 and (0.9606)<sup>2</sup> were used for the frequencies and force constants, respectively. <sup>b</sup>Scaling factors: 0.87322 and (0.87322)<sup>2</sup>. <sup>c</sup>Stretching constants in mdyn/Å, deformation constants in mdyn/Å, and stretch-bend interaction constants in mdyn/rad.

Table 6. G Matrix<sup>a</sup> for Pentagonal Planar XeF<sub>5</sub><sup>-</sup> of Symmetry D<sub>5h</sub>

A <sub>1</sub> '	G <sub>11</sub> = μ <sub>y</sub> = 5.2637 x 10 <sup>-2</sup>
A <sub>2</sub> ''	G <sub>22</sub> = (5/r <sup>2</sup> )(μ <sub>y</sub> + 5μ <sub>x</sub> ) = 1.1201 x 10 <sup>-1</sup>
E <sub>1</sub> '	G <sub>33</sub> = μ <sub>y</sub> + 5μ <sub>x</sub> /2 = 7.1679 x 10 <sup>-2</sup>
	G <sub>34</sub> = (5 <sup>3/2</sup> μ <sub>x</sub> )/(4r sin α) = 1.1123 x 10 <sup>-2</sup>
	G <sub>44</sub> = (1/r <sup>2</sup> )(5μ <sub>y</sub> sin <sup>2</sup> 2α + μ <sub>x</sub> ) = 2.4334 x 10 <sup>-2</sup>
E <sub>2</sub> '	G <sub>55</sub> = μ <sub>y</sub> = 5.2637 x 10 <sup>-2</sup>
	G <sub>56</sub> = 0
	G <sub>66</sub> = (1/r <sup>2</sup> )(4μ <sub>y</sub> sin <sup>2</sup> α) = 4.7026 x 10 <sup>-2</sup>
E <sub>2</sub> ''	G <sub>77</sub> = (3·5 <sup>1/2</sup> )(5/2r <sup>2</sup> )μ <sub>y</sub> = 2.4823 x 10 <sup>-2</sup>

<sup>a</sup>The following geometry and masses were used for the calculation of the G matrix:  
r = 2.0124 Å and α = 72°; m<sub>x</sub> = 131.292; m<sub>y</sub> = 18.998.