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# Synthesis, NMR and Vibrational Spectroscopic Characterization, and Computational Study of the *cis*-IO<sub>2</sub>F<sub>3</sub><sup>2-</sup> Anion (PREPRINT)

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## Abstract

The  $\text{N}(\text{CH}_3)_4^+$  salt of the *cis*- $\text{IO}_2\text{F}_3^{2-}$  anion was synthesized from  $[\text{N}(\text{CH}_3)_4][\text{IO}_2\text{F}_2]$  and excess  $[\text{N}(\text{CH}_3)_4][\text{F}]$  in  $\text{CH}_3\text{CN}$  solvent. The  $[\text{N}(\text{CH}_3)_4]_2[\text{IO}_2\text{F}_3]$  salt was characterized by Raman, infrared, and  $^{19}\text{F}$  solid-state MAS NMR spectroscopy. Geometry optimization and calculation of the vibrational frequencies at the DFT level of theory corroborated the experimental finding that the  $\text{IO}_2\text{F}_3^{2-}$  anion exists as a single isomer with a *cis*-dioxo and *mer*-trifluoro arrangement. The fluorine atom in  $\text{IO}_2\text{F}_3^{2-}$  that is *trans* to one of the oxygen atoms is very weakly bound with a calculated bond length of 228.1 pm. The  $\text{IO}_2\text{F}_3^{2-}$  anion is only the second example of an  $\text{AEO}_2\text{F}_3$  species after  $\text{XeO}_2\text{F}_3^-$ .

**Keywords:** Iodine; Oxide fluorides; Vibrational spectroscopy; Solid-state NMR spectroscopy; Density functional theory calculations

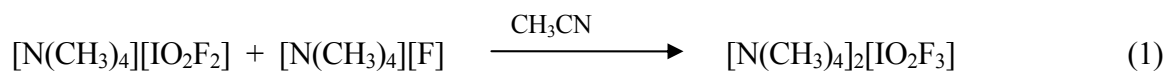
## Introduction

Iodine fluorides and oxide fluorides have been extensively investigated to study the relative repulsive effects of single-bond domains of fluorines, double-bond domains of oxygens, and lone pairs, in order to verify geometry predictions using the VSEPR model.<sup>1</sup> Three octahedral iodine(VII) fluorides and oxide fluorides have been prepared,  $\text{IF}_6^+$ ,<sup>2</sup>  $\text{IOF}_5$ ,<sup>3</sup> and  $\text{IO}_2\text{F}_4^-$ ,<sup>4</sup> being  $\text{AX}_6$ ,  $\text{AYX}_5$ , and  $\text{AY}_2\text{X}_4$  molecules, respectively. Interestingly, the  $\text{IO}_2\text{F}_4^-$  anion was found to exist as a mixture of the *cis*- and *trans*-isomer, with the *cis*-isomer being an exception to the VSEPR rules. Prior to this study only two pseudo-octahedral iodine(V) fluorides and oxide fluorides were known, i.e.,  $\text{IF}_5$ <sup>5</sup> and  $\text{IOF}_4^-$ ,<sup>6</sup> being  $\text{AEX}_5$  and  $\text{AEYX}_4$  VSEPR molecules, respectively. Iodine(V) oxide fluorides make possible the comparison between the repulsive effects of lone-pair and bonding pair domains. The repulsion caused by a lone-pair domain can be very similar to that of a double-bond domain.

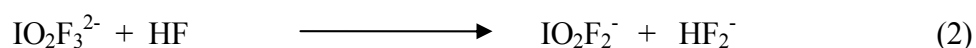
The availability of anhydrous  $[\text{N}(\text{CH}_3)_4][\text{F}]$ <sup>7</sup> has resulted in the preparation of a number of iodine fluoride and oxide fluoride dianions, such as the  $\text{IO}_2\text{F}_5^{2-}$ ,<sup>8</sup>  $\text{IOF}_5^{2-}$ ,<sup>9</sup> and  $\text{IF}_5^{2-}$ <sup>10</sup> anions. The lack of any report of an iodine  $\text{AEO}_2\text{X}_3$  species sparked interest in the synthesis of the  $\text{IO}_2\text{F}_3^{2-}$  anion and investigation of its geometry and possible isomerism. Prior to this study,  $\text{XeO}_2\text{F}_3^{2-}$  was the only  $\text{AEO}_2\text{F}_3$  species that has been synthesized,<sup>11,12</sup> which was shown to have a *cis*-dioxo arrangement based on the vibrational spectroscopy of its  $\text{Cs}^+$  salt.<sup>12</sup>

## Results and Discussion

**Synthesis of  $[\text{N}(\text{CH}_3)_4]_2[\text{IO}_2\text{F}_3]$ .** The  $\text{N}(\text{CH}_3)_4^+$  salt of the  $\text{IO}_2\text{F}_2^-$  anion reacts with a four-fold molar excess of  $[\text{N}(\text{CH}_3)_4][\text{F}]$  in  $\text{CH}_3\text{CN}$  at  $-32\text{ }^\circ\text{C}$  for ca. 100 h yielding the colourless  $[\text{N}(\text{CH}_3)_4]_2[\text{IO}_2\text{F}_3]$  salt in admixture with  $[\text{N}(\text{CH}_3)_4][\text{F}]$  according to eq. (1).

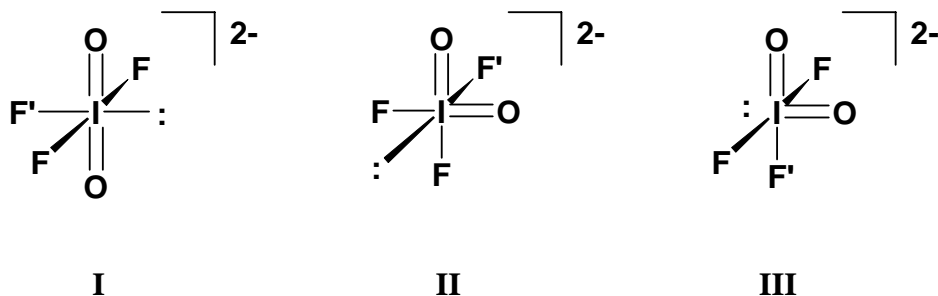


The use of stoichiometric amounts of  $[\text{N}(\text{CH}_3)_4][\text{F}]$  resulted in initial formation of small amounts of  $[\text{N}(\text{CH}_3)_4]_2[\text{IO}_2\text{F}_3]$  and its subsequent solvent attack to form  $[\text{N}(\text{CH}_3)_4]_2[\text{HF}_2][\text{IO}_2\text{F}_2]$ , which was identified by vibrational spectroscopy.<sup>13</sup> The solvent attack of anhydrous  $[\text{N}(\text{CH}_3)_4][\text{F}]$  in  $\text{CH}_3\text{CN}$  at temperatures higher than  $-20^\circ\text{C}$  is well documented,<sup>7</sup> however, the formation of bifluoride at temperatures below  $-30^\circ\text{C}$  is unprecedented. Extraction of  $[\text{N}(\text{CH}_3)_4][\text{F}]$  from the  $[\text{N}(\text{CH}_3)_4]_2[\text{IO}_2\text{F}_3]$ - $[\text{N}(\text{CH}_3)_4][\text{F}]$  mixture at low temperature also led to formation of  $[\text{N}(\text{CH}_3)_4]_2[\text{HF}_2][\text{IO}_2\text{F}_2]$ . In the absence of a sufficient excess of  $[\text{N}(\text{CH}_3)_4][\text{F}]$ , the  $\text{IO}_2\text{F}_3^{2-}$  anion apparently promotes proton abstraction from  $\text{CH}_3\text{CN}$ , even at  $-30^\circ\text{C}$ . The generated HF acts as a better fluoride-ion acceptor than the  $\text{IO}_2\text{F}_2^-$  anion (eq. 2), preventing the isolation of  $\text{IO}_2\text{F}_3^{2-}$  salts under stoichiometric conditions.



**Vibrational Spectroscopy.** The Raman and infrared spectra of  $[\text{N}(\text{CH}_3)_4]_2[\text{IO}_2\text{F}_3]$  containing about 3-fold molar excess of  $[\text{N}(\text{CH}_3)_4][\text{F}]$  are shown in Figure 1. The observed vibrational frequencies for  $\text{IO}_2\text{F}_3^{2-}$  and their assignments based on the theoretical calculations are summarized in Table 1. In addition to the vibrational bands attributable to unreacted  $[\text{N}(\text{CH}_3)_4][\text{F}]$  and to the  $\text{N}(\text{CH}_3)_4^+$  cation of the  $[\text{N}(\text{CH}_3)_4]_2[\text{IO}_2\text{F}_3]$  salt, eight and five anion bands were observed in the Raman and infrared spectra, respectively.

Three structures are conceivable for the  $\text{IO}_2\text{F}_3^{2-}$  anion; a *trans*- $\text{IO}_2\text{F}_3^{2-}$  (I) isomer of  $\text{C}_{2v}$  symmetry and two *cis*- $\text{IO}_2\text{F}_3^{2-}$  isomers (II) and (III), both having  $\text{C}_s$  symmetry.



The lone pair in a *trans*-dioxo arrangement would result in a slight deviation from linearity of the O-I-O moiety. Nevertheless, close to mutual exclusive behaviour of the Raman and infrared bands is expected, as is a large separation of the two I-O stretching modes due to maximum coupling of

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these modes. Strict mutual exclusion has been observed in vibrational spectra of *trans*-IO<sub>2</sub>F<sub>5</sub><sup>2-</sup><sup>8</sup> and *trans*-IO<sub>2</sub>F<sub>4</sub><sup>-4</sup> anions, in which both anions contain linear IO<sub>2</sub> moieties. In the Raman and infrared spectra of [N(CH<sub>3</sub>)<sub>4</sub>]<sub>2</sub>[IO<sub>2</sub>F<sub>3</sub>], two intense I-O stretching bands were observed at 832 (Raman)/834(infrared) and 798(Raman)/802(infrared) cm<sup>-1</sup>, consistent with a *cis*-dioxo arrangement in the IO<sub>2</sub>F<sub>3</sub><sup>2-</sup> anion. Furthermore, it was found by computational means that the *trans*-IO<sub>2</sub>F<sub>3</sub><sup>2-</sup> (I) isomer is not a local minimum on the ground-state potential energy surface (see **Computational Results**). The presence of a mixture of isomers was excluded based on the number of observed I-O stretching bands and on the solid-state NMR spectroscopic results (see **Solid-State NMR Spectroscopy**).

A total of 12 vibrational modes are expected for isomers II and III of the *cis*-IO<sub>2</sub>F<sub>3</sub><sup>2-</sup> anion, which span the irreducible representations  $\Gamma = 7A' + 5A''$  and  $\Gamma = 8A' + 4A''$ , respectively, in the C<sub>s</sub> point group, with all modes being Raman and infrared active. Isomer II is predicted to be less stable than isomer III by 46 kJ/mol. Furthermore, the predicted infrared and Raman vibrational spectra of (III) are in better agreement with experiment than those of (II), which suggests that the former is the experimentally observed isomer. Examination of the potential energy distribution (PED, not shown) of isomer III reveals that the two I-O stretching bands at 832 and 798 cm<sup>-1</sup> are only weakly coupled with each other and are characteristic of the stretching of the I-O bonds *cis*,  $\nu(\text{IO}_{\text{cis}})$ , and *trans*,  $\nu(\text{IO}_{\text{trans}})$ , to the I-F' bond, respectively. The lower frequency of  $\nu(\text{I-O}_{\text{trans}})$  compared to that of  $\nu(\text{I-O}_{\text{cis}})$  is a consequence of the *trans*-effect of the I-F' bond, rendering the I-O<sub>trans</sub> bond more ionic than I-O<sub>cis</sub>. Three I-F stretching bands were observed at 432, 405, and 358 cm<sup>-1</sup>. The latter band primarily involves the stretching of the weak I-F' bond, combined in an out-of-phase fashion with the symmetric IF<sub>2</sub> stretch. Compared with the I-O stretching (849 and 818 cm<sup>-1</sup>) and I-F stretching (468 and 445 cm<sup>-1</sup>) frequencies of the IO<sub>2</sub>F<sub>2</sub><sup>-</sup> anion, the lower stretching frequencies for the *cis*-IO<sub>2</sub>F<sub>3</sub><sup>2-</sup> anion are consistent with an increase of ionic character of the bonds in the dianion. As observed for iodine *trans*-dioxo species, the increased bond ionicity upon increasing the ionic charge is more pronounced for the I-F bonds than for the I-O bonds.<sup>8</sup> This is a direct consequence of the higher electronegativity of fluorine versus oxygen. The comparison of the stretching frequencies of *cis*-IO<sub>2</sub>F<sub>3</sub><sup>2-</sup> with *cis*-IO<sub>2</sub>F<sub>4</sub><sup>-</sup>, which are related by formal replacement of

a fluorine atom by a lone pair, reveals an even larger increase in ionicity of the I-O and I-F bonds when decreasing the oxidation state on iodine from +VII to +V. Such an effect has been correlated with the decrease of the effective electronegativity on iodine.<sup>8</sup>

**Solid-state NMR spectroscopy** The insolubility of  $[\text{N}(\text{CH}_3)_4]_2[\text{cis-IO}_2\text{F}_3]$  precludes its solution-phase NMR spectroscopic characterization. Fluorine-19 solid-state magic-angle spinning (MAS) NMR spectra were recorded of a  $[\text{N}(\text{CH}_3)_4]_2[\text{cis-IO}_2\text{F}_3]$ - $[\text{N}(\text{CH}_3)_4][\text{F}]$  mixture, sealed inside an FEP insert. Three resonances were observed with isotropic chemical shifts of 16.1, -4.7 ppm (approximately 2:1 ratio) and -91.9 ppm. The resonance at -91.9 ppm is attributable to  $[\text{N}(\text{CH}_3)_4][\text{F}]$ . The chemical shifts at 16.1 and -4.7 ppm can be assigned to the  $\text{IF}_2$  and  $\text{IF}'$  groups of the  $\text{IO}_2\text{F}_3^{2-}$  anion. The shift of the more covalently bonded  $\text{IF}_2$  moiety is close to  $\delta(^{19}\text{F})$  of  $[\text{N}(\text{CH}_3)_4][\text{IO}_2\text{F}_2]$  in  $\text{CH}_3\text{CN}$  solvent (13.7 ppm).<sup>13</sup> A lower chemical shift of the  $\text{F}'$  is consistent with a more polar, weaker I- $\text{F}'$  bond shifting  $\delta(^{19}\text{F})$  to the direction of  $\text{F}^-$  (-91.9 ppm). Proton-decoupling resulted in line widths of  $\Delta\nu_{1/2} = 150$  Hz (16.1 ppm) and  $\Delta\nu_{1/2} = 245$  Hz (-4.7 ppm) which did not allow for the observation of a resolved  $^2J(^{19}\text{F}\text{-}^{19}\text{F})$  coupling pattern. The difference in line widths is in agreement with an unresolved doublet and triplet pattern, suggesting a maximum value of 80 Hz for the  $^2J(^{19}\text{F}\text{-}^{19}\text{F})$  coupling constant. Such a value for the  $^2J(^{19}\text{F}\text{-}^{19}\text{F})$  coupling constant in an iodine(V) oxide fluoride is in line with the reported coupling value for  $\text{IF}_5$  of 85 Hz.<sup>15</sup>

The observation of relatively narrow resonances in the solid-state  $^{19}\text{F}$  NMR spectrum of  $\text{cis-IO}_2\text{F}_3^{2-}$  anion is in stark contrast to the broad lines observed in the solid-state NMR spectrum of the  $[\text{N}(\text{CH}_3)_4][\text{IO}_2\text{F}_2]$ .<sup>16</sup> While  $^{127}\text{I}$  relaxes slowly in the  $[\text{N}(\text{CH}_3)_4][\text{IO}_2\text{F}_2]$  salt, fast quadrupolar relaxation is observed for the  $\text{cis-IO}_2\text{F}_3^{2-}$  anion, resulting in self-decoupling of the  $^{19}\text{F}$  nucleus.

## Theoretical Calculations

### (a) Geometry

The geometries of the three isomers of the  $\text{IO}_2\text{F}_3^{2-}$  anion were calculated using density functional theory at the SVWN5/DZVP level of theory. The  $\text{C}_{2v}$ -symmetry *trans* isomer was found to have a single imaginary vibrational frequency, and therefore is not a local minimum. The  $\text{C}_s$ -symmetry isomers II and III were found to be local minima, with the former isomer less stable than the latter by 46 kJ/mol. The predicted gas-phase geometries of isomers II and III are summarized in Table 2,

as are the calculated and experimental gas-phase geometries of the  $\text{IO}_2\text{F}_2^-$  precursor. The lower energy of isomer III is in line with larger ligand repulsion caused by the lone pair compared to that of the I-O bonds. Having one I-O bond trans and one cis to the lone pair in isomer III is favoured versus both I-O bonds being cis to the lone pair as in isomer II. Comparison with calculated gas-phase and experimental geometry of the parent compound,  $\text{IO}_2\text{F}_2^-$ , showed that the I-F and I-O bonds elongate upon addition of  $\text{F}^-$  to form  $\text{IO}_2\text{F}_3^{2-}$ , which is consistent with increased ionicity of the IO and IF bonds. The I-F' bond in isomer III is weak, with a calculated bond length of 228.1 pm. The weakness of this IF' bond reflects the difficulty in forming the  $\text{IO}_2\text{F}_3^{2-}$  anion and is in agreement with vibrational frequencies (see **Vibrational Spectroscopy**). As expected, the O-I-O and F-I-F angles in  $\text{IO}_2\text{F}_2^-$  contract upon addition of  $\text{F}^-$ . The F-I-F angle in  $\text{IO}_2\text{F}_3^{2-}$  isomer III significantly deviates from  $180^\circ$ .

**(b) Vibrational Frequencies.** The calculated vibrational frequencies of the two *cis*-isomers (II) and (III) of the  $\text{IO}_2\text{F}_3^{2-}$  anion are listed in Table 1. The agreement between the unscaled calculated frequencies of isomer III and the experimental vibrational frequencies is reasonably good. However, the sequence of calculated  $\nu_{\text{as}}(\text{IF}_2)$  and  $\nu_{\text{s}}(\text{IF}_3)$  is opposite that of the experimental values. This reversed frequency sequence can be attributed to an overemphasis of I-F' involvement in  $\nu_{\text{s}}(\text{IF}_3)$  stretch, which results in lowering the calculation frequency. Calculations showed that the IO stretching modes are only weakly coupled, while coupling between the IF stretching modes is more pronounced.

## Conclusions

The fluoride-ion acceptor properties of  $\text{IO}_2\text{F}_2^-$  have been studied. The  $[\text{N}(\text{CH}_3)_4]_2[\text{IO}_2\text{F}_3]$  salt has been prepared and characterized by solid-state  $^{19}\text{F}$  MAS NMR and vibrational spectroscopy in conjunction with theoretical calculations. Of the three possible isomers of the  $\text{IO}_2\text{F}_3^{2-}$  anion, only the *cis*- $\text{IO}_2\text{F}_3^{2-}$  anion with a *mer*-trifluoro arrangement was observed as the exclusive product, which is a result of the repulsion caused by the lone pair. The resulting *cis*- $\text{IO}_2\text{F}_3^{2-}$  anion is presently only the second known  $\text{AO}_2\text{F}_3^{n-}$  species, beside the isoelectronic  $\text{XeO}_2\text{F}_3^-$ .



## Experimental

**Materials and Apparatus.** All volatile materials were handled on a Pyrex vacuum line equipped with glass/Teflon J. Young valves. Nonvolatile materials were handled in the dry nitrogen atmosphere of a dry box (Omni Lab, Vacuum Atmospheres).

Acetonitrile solvent (Baker, HPLC Grade) was purified according to the standard literature method.<sup>17</sup> The syntheses of  $[\text{N}(\text{CH}_3)_4][\text{F}]$ <sup>7</sup> and  $[\text{N}(\text{CH}_3)_4][\text{IO}_2\text{F}_2]$ <sup>13</sup> have been described previously.

**Preparation of  $[\text{N}(\text{CH}_3)_4]_2[\text{IO}_2\text{F}_3]$ .** Inside a drybox,  $[\text{N}(\text{CH}_3)_4][\text{IO}_2\text{F}_2]$  (0.189 mmol) and  $[\text{N}(\text{CH}_3)_4][\text{F}]$  (0.754 mmol) were loaded into a 3/4-in. o.d. FEP reactor equipped with a Swagelok ORM2 stainless-steel valve and a Teflon-coated stirring bar. Approximately 4.7 mL anhydrous  $\text{CH}_3\text{CN}$  was condensed at  $-196\text{ }^\circ\text{C}$  onto the solid mixture and allowed to warm to  $-30\text{ }^\circ\text{C}$ . The reaction mixture was stirred while maintained between  $-35$  and  $30\text{ }^\circ\text{C}$  using an ethanol bath cooled by a Thermo NESLAB CC-100 immersion cooler for 100 h. The  $\text{CH}_3\text{CN}$  solvent was pumped off while slowly warming from  $-30$  to  $0\text{ }^\circ\text{C}$ , yielding a fine, white powder consisting of  $[\text{N}(\text{CH}_3)_4]_2[\text{IO}_2\text{F}_3]$  and  $[\text{N}(\text{CH}_3)_4][\text{F}]$ .

**Vibrational Spectroscopy.** The Raman spectrum of  $[\text{N}(\text{CH}_3)_4]_2[\text{IO}_2\text{F}_3]$  was recorded on a Bruker RFS 100 FT Raman spectrometer with a quartz beam splitter, a liquid-nitrogen-cooled Ge detector, and a low-temperature accessory. The backscattered ( $180^\circ$ ) radiation was sampled. The actual usable Stokes range was  $50$  to  $3500\text{ cm}^{-1}$  with a spectral resolution of  $2\text{ cm}^{-1}$ . The  $1064\text{-nm}$  line of an Nd:YAG laser was used for excitation of the sample. The low-temperature spectrum of  $[\text{N}(\text{CH}_3)_4]_2[\text{IO}_2\text{F}_3]$  was recorded on a powdered sample in a melting point capillary using a laser power of  $200\text{ mW}$ . The FT-infrared spectrum of  $[\text{N}(\text{CH}_3)_4]_2[\text{IO}_2\text{F}_3]$  was recorded on a Nicolet Avatar 360 FTIR spectrometer at ambient temperature. An AgCl pellet was formed in a Wilks minipress inside the dry box by sandwiching the sample between two layers of AgCl disks. The spectra were acquired in 64 scans at a resolution of  $2\text{ cm}^{-1}$ .

**Solid-state NMR Spectroscopy.** Inserts were fabricated from FEP (a copolymer of perfluorinated polypropylene and polyethylene) as previously described.<sup>18</sup> Solid-state NMR spectra were recorded unlocked on a Varian INOVA 500 (11.744 T) spectrometer equipped with a Sun workstation. The <sup>19</sup>F NMR spectra were obtained using a Varian 4-mm HFX MAS T3 probe tuned to 469.756 MHz. Free induction decays for the <sup>19</sup>F spectra were accumulated with spectral width settings of 400 kHz. The number of transients accumulated for <sup>19</sup>F spectra were 128 using pulse widths of 1 μs; relaxation delay of 2 s were applied. Proton-decoupled <sup>19</sup>F NMR spectra were recorded using the TPPM decoupling mode. The <sup>19</sup>F spectra were referenced to external neat CFCl<sub>3</sub> at room temperature.

**Theoretical Calculations.** The geometries, harmonic vibrational frequencies, and infrared and Raman vibrational intensities of the isomers of the IO<sub>2</sub>F<sub>3</sub><sup>2-</sup> anion were calculated using density functional theory methods. Specifically, the SVWN5 functional<sup>19</sup> (Slater exchange plus Volkow-Wilk-Nusair formula 5 correlation) was used in conjunction with the double-zeta valence polarized (DZVP) basis set.<sup>20</sup> All calculations were performed using the GAMESS<sup>21</sup> quantum chemistry program.

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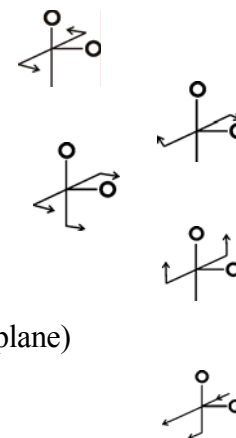
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Table 1. Observed and Calculated Vibrational Frequencies of isomers II and III of *cis*-IO<sub>2</sub>F<sub>3</sub><sup>2-</sup> and their assignment in point group C<sub>s</sub>

Frequencies, <sup>a</sup> cm <sup>-1</sup>					
[N(CH <sub>3</sub> ) <sub>4</sub> ][IO <sub>2</sub> F <sub>3</sub> ]		IO <sub>2</sub> F <sub>3</sub> <sup>2-</sup> , isomer II		IO <sub>2</sub> F <sub>3</sub> <sup>2-</sup> , isomer III	
Raman <sup>b</sup>	infrared <sup>c</sup>	calcd <sup>d</sup>	assignments	calcd <sup>d</sup>	assignments
832 [86]	834 s	720 (214) [14]	$\nu_8(A'')$ , $\nu_{as}(IO)$	764 (120) [19]	$\nu_1(A')$ , $\nu(IO_{cis})$
798 [100]	802 s	718 (122) [36]	$\nu_1(A')$ , $\nu_a(IO)$	722 (184) [31]	$\nu_2(A')$ , $\nu(IO_{trans})$
432 [18]		446 (155) [13]	$\nu_2(A')$ , $\nu_a(IF')$	382 (48) [15]	$\nu_3(A')$ , $\nu_s(IF_3)$
-	405 s	366 (127) [4]	$\nu_3(A')$ , $\nu_a(IF)$	417 (318) [0]	$\nu_9(A'')$ , $\nu_{as}(IF_2)$
358 [11]	358 m	336 (109) [6]	$\nu_9(A'')$ , $\nu_{as}(IF)$	328 (106) [5]	$\nu_4(A')$ , $\nu_{as}(IF_3)$
320 [9]	-	316 (12) [5]	$\nu_4(A')$ , $\delta_{scissoring}(IO_2)$	301 (17) [5]	$\nu_5(A')$ , $\delta_{scissoring}(IO_2)$
284 [18]	-	248 (22) [4]	$\nu_5(A')$ , $\delta_s(OIF')$	245 (0.1) [3]	$\nu_{10}(A'')$ , $\delta_{as}(IF_2)$
210 [2]	-	241 (0.2) [2]	$\nu_{10}(A'')$ , $\delta_{as}(OIF')$	215 (0) [4]	$\nu_{11}(A'')$ , $\delta_{as}(IF_2)$
180 [3]	-	176 (17) [2]	$\nu_6(A')$ , $\delta_s(FIF')$	186 (33) [1]	$\nu_6(A')$ , $\delta_{scissoring}(IF_2)$
-	-	174 (1.1) [1]	$\nu_{11}(A'')$ , $\delta_{scissoring}(OIF)$	148 (1) [0.3]	$\nu_7(A')$ , $\delta_{scissoring}(IF_2)$
-	-	140 (2.8) [1]	$\nu_7(A')$ , $\delta_{scissoring}(FIF)$	114 (0.2) [0]	$\nu_8(A')$ , $\delta_{puckering}(IOF_3 \text{ plane})$
108 [10]	-	108 (0.57) [0.3]	$\nu_{12}(A'')$ , $\delta_{puckering}(IO_2F_2 \text{ plane})$	94 (1) [1]	$\nu_{12}(A'')$ , $\delta(F_2IF')$



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<sup>a</sup> Abbreviations denote shoulder (sh), very strong (vs), strong (s), medium (m), weak (w), and very weak (vw). <sup>b</sup> The  $\text{N}(\text{CH}_3)_4^+$  cation modes were observed in the Raman spectrum (-100 °C) at 377 (9), 385 (11),  $\nu_8(\text{E})$ ; 464 (22),  $\nu_{19}(\text{F}_2)$ ; 758sh, 766 (91) ( $\text{N}(\text{CH}_3)_4\text{F}$ ),  $\nu_3(\text{A}_1)$ ; 955 (25), 966 (66) ( $\text{N}(\text{CH}_3)_4\text{F}$ ), 972sh,  $\nu_{18}(\text{F}_2)$ ; 1196 (5), 1208 (22),  $\nu_7(\text{E})$ ; 1296 (4), 1310 (5),  $\nu_{17}(\text{F}_2)$ ; 1409(8), 1420 (11),  $\nu_{16}(\text{F}_2)$ ; 1465(34), 1477(66) ( $\text{N}(\text{CH}_3)_4\text{F}$ ),  $\nu_2(\text{A}_1)$ ; 1487 (32), 1491sh, 1514 (14),  $\nu_6(\text{E})$ ; 2619(3), 2728(4), 2816 (51), 2826sh, 2841 (39), 2885(70), 2906sh, 2920sh, 2973 (84), 3009 (103), 3029 (114)  $\text{cm}^{-1}$ ,  $\nu_{\text{CH}_3}$  and binary bands (see refs 7 and 14). <sup>c</sup> The  $\text{N}(\text{CH}_3)_4^+$  cation modes were observed in the infrared spectrum at 463w,  $\nu_{19}(\text{F}_2)$ ; 741sh, 760m, 783w,  $\nu_3(\text{A}_1)$ ; 926 w,  $2\nu_{19}$ ; 949vs, 957vs, 967s ( $\text{N}(\text{CH}_3)_4\text{F}$ ),  $\nu_{18}(\text{F}_2)$ ; 1257 s,  $\nu_{17}(\text{F}_2)$ ; 1406 m,  $\nu_{16}(\text{F}_2)$ ; 1488vs, 1503vs, 1522 vs,  $\nu_{15}(\text{F}_2)$ ; 2100m, 2357w, 2513w, 2617 w, 2784w, 2831w, 2917sh, 2965w, 3020s  $\text{cm}^{-1}$ ,  $\nu_{\text{CH}_3}$  and binary bands (see refs 7 and 14). <sup>d</sup> SVWN5/DZVP. Infrared intensities, in  $\text{km mol}^{-1}$ , are given in parentheses, Raman intensities, in  $\text{\AA}^4 \text{amu}^{-1}$ , are given in square brackets.

**Table 2.** Calculated geometries of (II) and (III) isomers of  $\text{IO}_2\text{F}_3^{2-}$  and calculated and experimental geometries for  $\text{IO}_2\text{F}_2^-$

	$\text{IO}_2\text{F}_3^{2-}$ <sup>a</sup>		$\text{IO}_2\text{F}_2^-$ <sup>b</sup>	
	isomer II	isomer III	Calc.	Obs.
R(I-F), pm	222.4	216.0	207.7	200.84(15)
R(I-F'), pm	206.8	228.1		
R(I-O), pm	187.8	184.3, 187.9	182.5	177.7(2), 178.0(2)
∠ O-I-O, deg	97.9	100.5	109.84	106.00(12)
∠ F-I-F, deg	83.9	171.9	169.26	178.39(9)

<sup>a</sup> Calculated at the SVWN5/DZVP level of theory. <sup>b</sup> Data from ref. 13.

### Figure Captions

- Figure 1.** The vibrational spectra of  $[\text{N}(\text{CH}_3)_4]_2[\text{IO}_2\text{F}_3]$  containing about 75 mol-% of  $[\text{N}(\text{CH}_3)_4][\text{F}]$ : Raman spectrum (lower trace) recorded at  $-100\text{ }^\circ\text{C}$  using 1064-nm excitation and the infrared spectrum recorded at room temperature in an AgCl pellet. Asterisks (\*) and dagger (†) denote  $\text{N}(\text{CH}_3)_4^+$  bands and an artifact, respectively.
- Figure 2.** Solid-state  $^{19}\text{F}$  MAS NMR spectrum of  $[\text{N}(\text{CH}_3)_4]_2[\text{IO}_2\text{F}_3]$  containing about 75 mol-% of  $[\text{N}(\text{CH}_3)_4][\text{F}]$  at 15 kHz spinning rate recorded at  $-3^\circ\text{C}$ . Asterisks (\*) denote the spinning-sideband manifold from the FEP insert material.



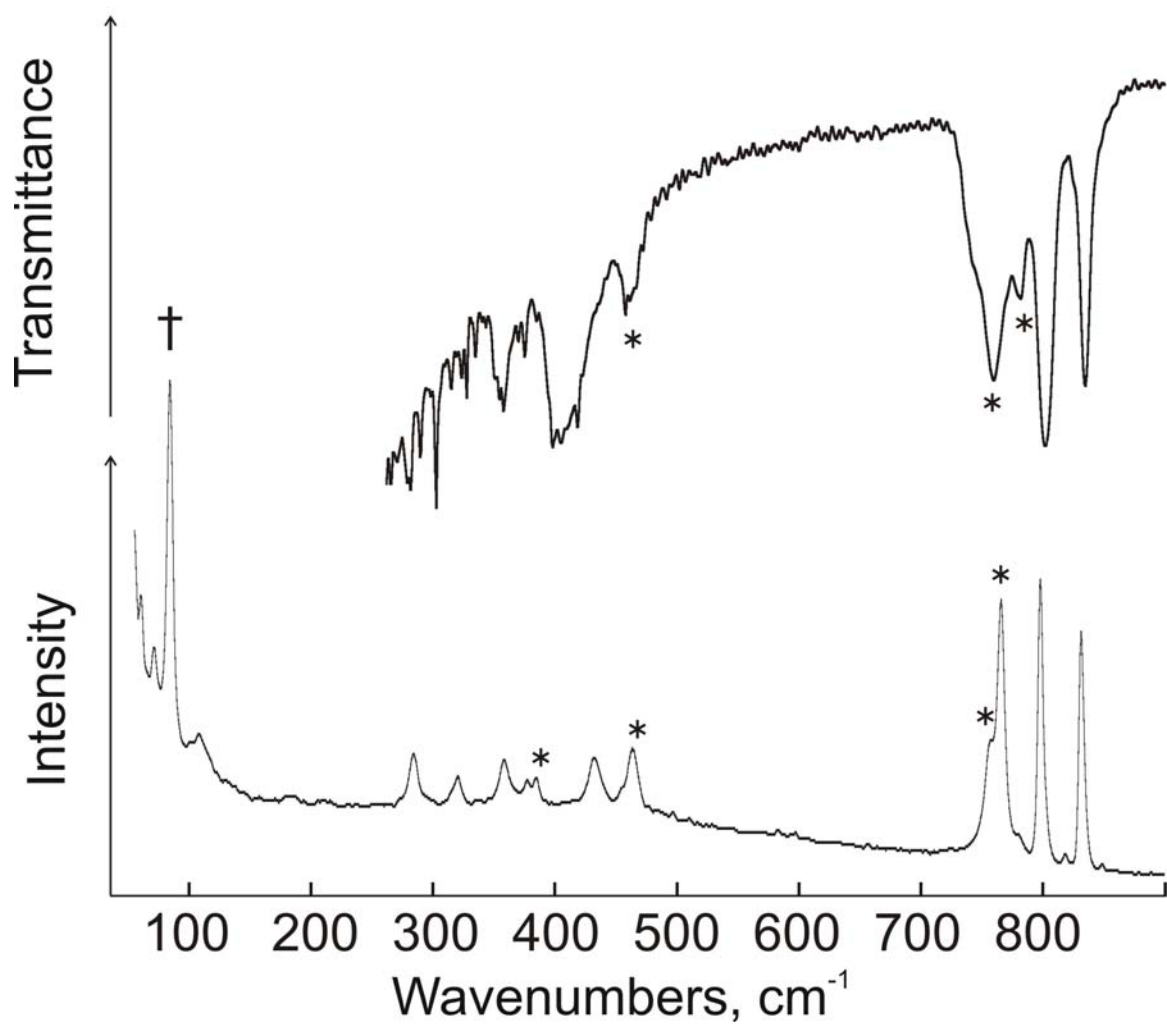


Figure 1

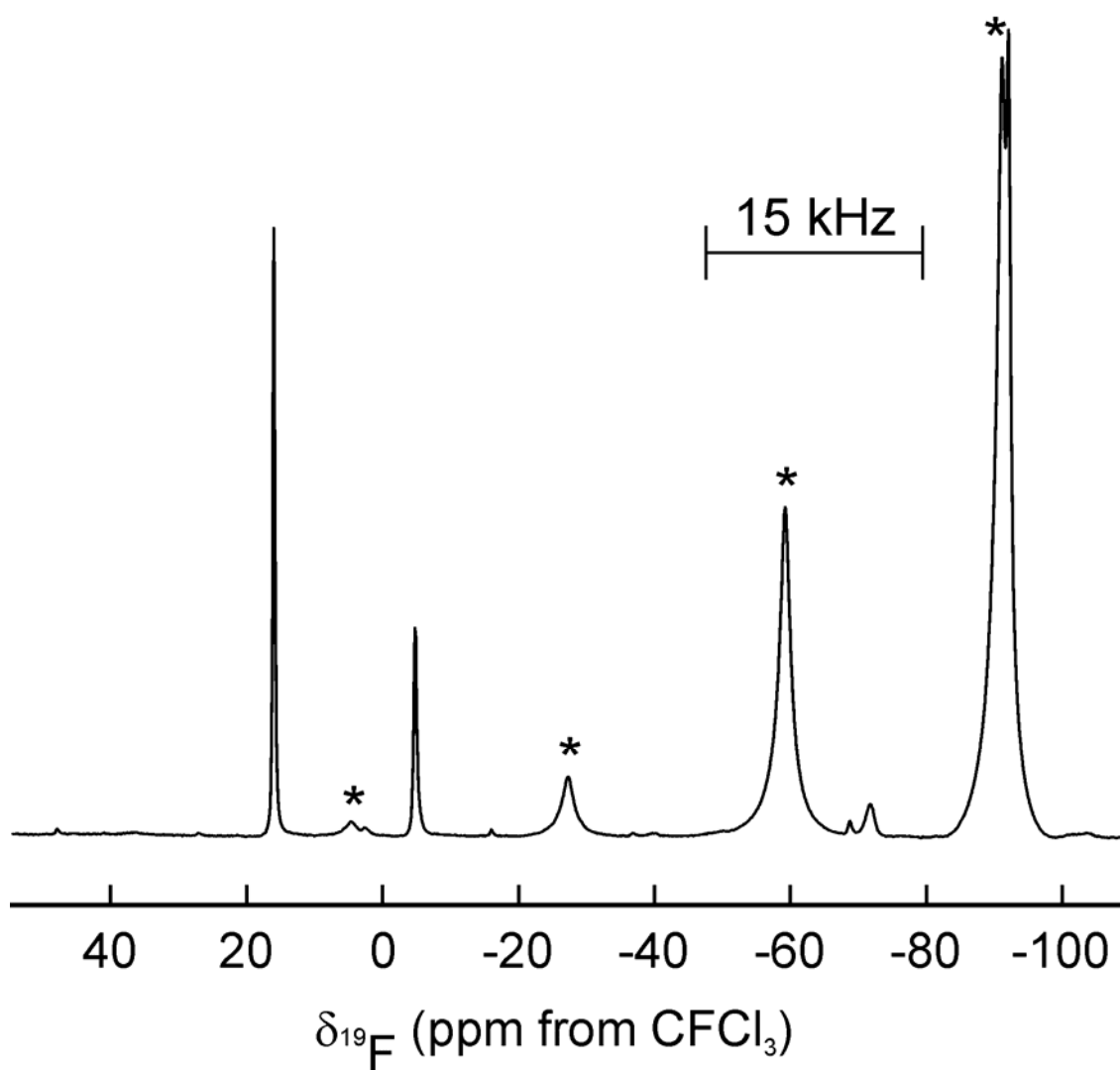


Figure 2

## Synopsis

### Synthesis, NMR and Vibrational Spectroscopic Characterization, and Computational Study of the *cis*-IO<sub>2</sub>F<sub>3</sub><sup>2-</sup> Anion

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The *cis*-IO<sub>2</sub>F<sub>3</sub><sup>2-</sup> anion, only the second example of a pseudo-octahedral AEO<sub>2</sub>F<sub>3</sub> species has been prepared and characterized by vibrational spectroscopy, solid-state NMR spectroscopy, and theoretical calculations. It is shown that the IO<sub>2</sub>F<sub>3</sub><sup>2-</sup> anion exists exclusively as the *cis*-dioxo isomer with a meridional trifluoro arrangement. The repulsion of the lone-pair and the I-O bond domains forces the lone pair into a *trans*-position to one I-O bonds.

