

## Mean Amplitudes of Vibration of the *trans*-IO<sub>2</sub>F<sub>5</sub><sup>2-</sup> Anion

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The mean amplitudes of vibration of the *trans*-IO<sub>2</sub>F<sub>5</sub><sup>2-</sup> anion have been calculated from recently reported spectroscopic and structural data between 0 and 1000 K. Bond peculiarities are discussed in comparison with those of related species.

**Key words:** IO<sub>2</sub>F<sub>5</sub><sup>2-</sup>; Mean Amplitudes of Vibration; Bond Properties.

The *trans*-IO<sub>2</sub>F<sub>5</sub><sup>2-</sup> anion, representing the first example of a heptacoordinated main group AO<sub>2</sub>X<sub>5</sub> species, has been recently obtained in the form of its tetramethylammonium salt and characterized by infrared and Raman spectroscopy and theoretical calculations [1]. It has a pentagonal-bipyramidal geometry with the two oxygen atoms occupying the axial positions and completes the series of pentagonal-bipyramidal iodine fluoride and oxide fluoride species.

In previous papers we have calculated the mean amplitudes of vibration of some of these species, formally derived from an sp<sup>3</sup>d<sup>3</sup> hybridization of the central atom, i.e.: IF<sub>5</sub><sup>2-</sup> [2], IOF<sub>5</sub><sup>2-</sup> [3], IOF<sub>6</sub><sup>-</sup> [4] and IF<sub>7</sub> [5] and of certain related xenon compounds [3, 5–7]. In order to complement and extend these studies we have now performed similar calculations for the new *trans*-IO<sub>2</sub>F<sub>5</sub><sup>2-</sup> anion.

The calculations were performed with the method of characteristic vibrations of Müller et al. [8] (cf. also [9, 10]). The necessary vibrational data were taken from [1], and the following geometrical parameters were used:  $R(I-O) = 1.78 \text{ \AA}$ ,  $R(I-F) = 1.97 \text{ \AA}$ ,  $\angle O-I-F = 90^\circ$ ,  $\angle F-I-F = 72^\circ$  [1].

The obtained results, in the temperature range between 0 and 1000 K, are shown in Table 1.

Table 1. Calculated mean amplitudes of vibration (in Å) of *trans*-IO<sub>2</sub>F<sub>5</sub><sup>2-</sup>.

T (K)	$u_{I-O}$	$u_{I-F}$	$u_{O...O}$	$u_{F...F}$	$u_{O...F}$
0	0.0380	0.0455	0.052	0.078	0.060
100	0.0380	0.0455	0.052	0.079	0.060
200	0.0381	0.0468	0.052	0.090	0.065
298.16	0.0388	0.0499	0.053	0.103	0.071
300	0.0388	0.0500	0.053	0.103	0.071
400	0.0401	0.0541	0.055	0.115	0.079
500	0.0418	0.0582	0.057	0.127	0.086
600	0.0438	0.0625	0.060	0.138	0.093
700	0.0459	0.0666	0.063	0.149	0.099
800	0.0480	0.0705	0.066	0.158	0.105
900	0.0501	0.0743	0.069	0.168	0.111
1000	0.0523	0.0780	0.072	0.177	0.117

Table 2. Comparison of the mean amplitudes of vibration (in Å and at 298.16 K) of *trans*-IO<sub>2</sub>F<sub>5</sub><sup>2-</sup> with those of structurally related species

Species	$u_{I-O}$	$u_{I-F(\text{eq})}$	$u_{F...F(\text{eq})}$	Refer.
IO <sub>2</sub> F <sub>5</sub> <sup>2-</sup>	0.0388	0.0499	0.103	this paper
IOF <sub>5</sub> <sup>2-</sup>	0.0379	0.0551	0.084	[3]
IOF <sub>6</sub> <sup>-</sup>	0.0375	0.0490	0.076	[4]
IF <sub>5</sub> <sup>2-</sup>		0.0602	0.105	[2]
IF <sub>7</sub>		0.0430	0.062	[5]

From this Table it can immediately be seen that, as expected, and also in agreement with the respective force constants ( $f(I-O) = 5.62$  and  $f(I-F) = 2.42 \text{ mdyn/\AA}$  [1]) the I-O bonds are appreciably stronger than the I-F bonds, the former showing lower mean amplitudes in the whole temperature range. A comparison with the previously investigated related species shows that the  $u_{I-O}$ -values are comparable to those calculated in the cases of IOF<sub>5</sub><sup>2-</sup> and IOF<sub>6</sub><sup>-</sup> (cf. Table 2). The important strength of the I-O linkages, reflected in the low mean amplitude values, is additionally evidenced by the fact that these values are even lower than in IO<sub>3</sub><sup>-</sup> and IO<sub>4</sub><sup>-</sup> [9]. These results agree also with the usually accepted bonding model for this type of species [1, 3, 11, 12], which in this case suggests that the two axial oxygen atoms are covalently bonded to the central atom through an sp<sub>z</sub> hybrid orbital, whereas the bonding of the five equatorial fluorine atoms involves a highly ionic 6-center 10-electron bond (6c-10e) originated by the interaction of these atoms with a  $p_x$ ,  $p_y$  hybrid orbital of iodine.

The larger mean amplitudes and big temperature dependences calculated for these bonds also confirm the formation of relatively weak I-F bonds, suggested by this model. Additionally, an analysis of the data pre-

sented in Table 2 shows that the mean amplitudes for the I-F bonds show a greater dispersion than that of the I-O bonds. This also agrees with the recent finding that the equatorial I-F bonds in these species are strongly influenced by the ionic charges and by the oxidation state of iodine [1]. Notwithstanding, the values calculated for  $\text{IO}_2\text{F}_5^{2-}$  and their temperature dependence are comparable to those of  $\text{IOF}_6^-$  [3]. The enhancement of the I-F bond polarity and concomitant bond weakening is particularly important in the case of  $\text{IF}_5^{2-}$ , as can be seen from the high mean amplitude of vibration of this bond. Besides, in this case congestion effects in the  $\text{IF}_5$  plane are also important, contributing to bond lengthening and weakening [2, 13].

Regarding the mean amplitude values for the non-bonded atom pairs of *trans*- $\text{IO}_2\text{F}_5^{2-}$ , they are found in the order  $u_{\text{O}\dots\text{O}} < u_{\text{O}\dots\text{F}} < u_{\text{F}\dots\text{F}}$ . The values for the last pair show the greatest temperature dependence, a

fact also probably related to the ionicity of these bonds and to a certain contribution of congestion effects. This contribution is also evidenced by the fact that the values found here are totally comparable, also in their strong temperature dependence, to those calculated for  $\text{IF}_5^{2-}$  [2] (cf. again Table 2).

It is also interesting that the  $u_{\text{O}\dots\text{F}}$ -values found here are comparable to those of  $\text{XeOF}_5^-$  (0.070 Å at 298.16 K) and are only slightly lower than those found for  $\text{IOF}_5^{2-}$  (0.076 Å at 298.16 K), showing a similar temperature dependence as in the two mentioned anions [3].

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