Mean Amplitudes of Vibration of the Novel IF_5^{2-} Anion

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Mean amplitudes of vibration for the recently described planar pentagonal IF_5^{2-} anion have been calculated, from vibrational spectroscopic data over a wide temperature range. The results are briefly discussed and some comparisons with related species are made.

Key words: Pentafluoroiodate(III); Mean Amplitudes of Vibration; Bond Properties.

The first example of a chemical species adopting the unusual pentagonal planar geometry was the anion XeF_5^-, reported in 1991 [1]. Recently, Christe *et al.* [2] reported the existence of the IF_5^{2-} dianion, which is only the second known example of such a molecular geometry.

In order to advance in the characterization of this very interesting species, we have now undertaken a calculation of its mean amplitudes of vibration and compared the results with those obtained for some related molecules and ions.

The calculations were performed using the method of characteristic vibrations of Müller and co-workers [3–5]. The vibrational frequencies were taken from [2] and an F–I–F angle of 72° was assumed.

The mean amplitudes of vibration calculated for IF_5^{2-}, in the temperature range between 0 and 1000 K, are presented in Table 1. For comparative purposes, Table 2 shows the corresponding values for the isoelectronic XeF_5^- anion [6] and other closely related species.

The amplitude value for the I–F bond in IF_5^{2-} is, as expected, appreciably higher than that of the Xe–F bond in XeF_5^-, in agreement with the additional negative charge present over the iodine species and its lower nuclear charge. These two factors evidently produce an enhancement of the I–F bond polarity, generating a weakening of these bonds [2], which can also be visualized from the strong temperature dependence of its amplitude values (see Table 1), which in this case is yet more important than in XeF_5^- [6].

On the other hand, the very strong temperature dependence also observed for the non-bonded in-plane F···F distances suggests that the congestion effect on the plane, admitted in the case of XeF_5^- [1, 6] has a still higher impact in the case of the IF_5^{2-} structure, contributing additionally to the I–F bond polarity and lengthening.

Interestingly, the values calculated for the out-of-plane F···F mean amplitudes are similar to those found in XeF_5^-, showing a similar temperature dependence [6].

The u_{I-F} amplitude values are also higher than those calculated for the square planar IF_4^- anion [7], in which iodine presents the same nuclear charge, reflecting again the bond weakening produced after the addition of the fifth fluorine atom. Obviously, all other iodine containing species included in Table 2 show appreciably lower I–F mean amplitude values, in agreement with the higher charge of the halogen in all these examples. A comparison with the three related tellurium species, also included in this Table, shows the same trend.

Table 1. Calculated mean amplitudes of vibration (in Å) for IF_5^{2-}.

T (K)	u_{Xe-F}	$u_{F\cdots F}$ (in-plane)	$u_{F\cdots F}$ (out-of-plane)
0	0.0511	0.079	0.061
100	0.0513	0.081	0.061
200	0.0547	0.092	0.063
298.16	0.0602	0.105	0.068
300	0.0603	0.105	0.068
400	0.0665	0.118	0.073
500	0.0725	0.130	0.079
600	0.0784	0.142	0.085
700	0.0839	0.152	0.091
800	0.0892	0.162	0.096
900	0.0942	0.172	0.102
1000	0.0991	0.181	0.107

Table 2. Mean amplitudes of vibration (in Å) for selected species related to IF_5^{2-} (T=298 K).

Species	u_{X-F}	$u_{F\cdots F}$ (in-plane)	$u_{F\cdots F}$ (out-of-plane)	Ref.
XeF_5^-	0.0515	0.083	0.065	[6]
IF_4^-	0.0520	0.139	0.066	[7]
IF_5^{2-}	0.0602	0.105	0.068	this work
IF_7	0.0430 (eq)	0.062		[8]
IOF_6^-	0.0444 (eq)	0.064		[9]
IOF_5	0.0397 (eq)	0.075		[10]
TeF_7^-	0.0452 (eq)	0.074		[8]
$TeOF_6^{2-}$	0.0475 (eq)	0.070		[9]
TeF_5^-	0.0509 (eq)	0.121	0.069	[11]

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Besides, the mean amplitudes for the non bonded, in plane, F···F pairs, are larger than in all the related species, except those of IF_4^- and TeF_5^-. But, on the other hand, the out-of-plane values for the non-bonded pairs are practically identical in these three cases.

To conclude, this study allows a wider insight into the bond and vibrational properties of the interesting IF_5^{2-} anion. Its mean amplitudes of vibration confirm the existence of larger, weaker and somewhat more polar bonds than in IF_4^- and important similarities with the isoelectronic XeF_5^- anion.

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