Mean Amplitudes of Vibration of $BrO_2F_2^-$ and $IO_2F_2^-$

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Mean amplitudes of vibration of the anions $BrO_2F_2^-$ and $IO_2F_2^-$ have been calculated from vibrational spectroscopic data in the temperature range between 0 and 1000 K. Bond properties of these species are discussed on the basis of the obtained results and by comparison with known data for related molecules and ions.

Key words: $BrO_2F_2^-$; $IO_2F_2^-$; Mean Amplitudes of Vibration; Bond Properties.

A great number of oxohalogen fluorides of the type F_nXO_m (with X = Cl, Br, I) are known, including neutral molecules as well as anionic and cationic species [1, 2]. Chlorine [1, 3] and bromine [1, 4] compounds are especially abundant and have been thoroughly investigated during the last decades.

As part of a long-term research project devoted to the characterization of bond properties of species containing interhalogen bonds, we have investigated different molecules and anions of this type [5–14]. As a continuation of these studies we have now performed an analysis of the bond properties of the $BrO_2F_2^-$ and $IO_2F_2^-$; through a calculation of their mean amplitudes of vibration from spectroscopic data.

The structure of these anions can formally be derived from an sp^3d hybridization of the central halogen atom, i.e., this atom is located at the center of a trigonal bipyramid, the two fluorine atoms at the apices and the oxygen atoms, together with a lone electronic pair, at the basis of the bipyramid.

A partial assignment of the Raman spectrum of $KBrO_2F_2$ was firstly reported by Bougon and Tantot [15] and by Gillespie and Spekkens [16]. A complete assignment of the full vibrational (Raman and IR) spectrum, based on the C_{2v}-symmetry of the $BrO_2F_2^-$ anion, was published by Bougon et al. [17]. The vibrational spectrum of the isostructural $IO_2F_2^-$ anion was investigated and assigned by Carter and Aubke [18].

Table 1. Calculated mean amplitudes of vibration (in Å) for $BrO_2F_2^-$.

T(K)	u_{Br-O}	u_{Br-F}	u_{OO}	u_{FF}	u_{OF}
0	0.0375	0.0514	0.056	0.069	0.057
100	0.0375	0.0516	0.056	0.069	0.057
200	0.0375	0.0542	0.058	0.074	0.061
298.16	0.0380	0.0591	0.060	0.081	0.068
300	0.0380	0.0592	0.061	0.081	0.068
400	0.0390	0.0649	0.065	0.090	0.075
500	0.0404	0.0706	0.069	0.098	0.082
600	0.0421	0.0761	0.073	0.106	0.089
700	0.0439	0.0814	0.077	0.114	0.095
800	0.0458	0.0865	0.082	0.121	0.102
900	0.0477	0.0913	0.086	0.128	0.107
1000	0.0497	0.0959	0.090	0.134	0.113

Table 2. Calculated mean amplitudes of vibration (in Å) for $IO_2F_2^-$.

T(K)	u_{I-O}	u_{I-F}	u_{OO}	u_{FF}	u_{OF}
0	0.0379	0.0476	0.059	0.061	0.062
100	0.0379	0.0477	0.060	0.061	0.062
200	0.0380	0.0495	0.062	0.063	0.066
298.16	0.0386	0.0534	0.066	0.068	0.073
300	0.0387	0.0534	0.066	0.068	0.073
400	0.0399	0.0582	0.071	0.073	0.081
500	0.0416	0.0630	0.076	0.079	0.088
600	0.0436	0.0678	0.082	0.085	0.095
700	0.0457	0.0724	0.087	0.091	0.101
800	0.0478	0.0768	0.092	0.096	0.108
900	0.0499	0.0810	0.097	0.102	0.114
1000	0.0520	0.0851	0.101	0.107	0.120

The mean amplitudes of vibration were calculated by the method of the characteristic vibrations of Müller et al. [19] (cf. also [20, 21]). The necessary vibrational frequencies were taken from the papers of Bougon et al. ($BrO_2F_2^-$) [17] and of Carter and Aubke ($IO_2F_2^-$) [18]. The following geometrical parameters were used: d(Br–O) = 1.60 Å; d(Br–F) = 1.85 Å; d(I–O) = 1.93 Å; d(I–F) 2.0 Å, and the bond angles were considered as those of a perfect trigonal bipyramid (< OXF = 90°, < OXO = 120° and < FXF = 180°) [1, 17].

The results of the calculations, in the temperature range between 0 and 1000 K are shown in Tables 1 and 2.

As it can be seen, the mean amplitudes of vibration for the Br–O and I–O bonds show comparable values in the whole temperature range, the latter being only slightly higher, indicating comparable strengths of the halogen-oxygen bonds in both species. On the other hand, these mean amplitudes are, as expected, very characteristic and

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Table 3. Comparison of the mean amplitudes of vibration (in Å) for the bonded atoms in the three isostructural $XO_2F_2^-$ species.

T(K)	$ClO_2F_2^-$		$BrO_2F_2^-$		$IO_2F_2^-$	
	u_{Cl-O}	u_{Cl-F}	u_{Br-O}	u_{Br-F}	u_{I-O}	u_{I-F}
0	0.0364	0.0550	0.0375	0.0514	0.0379	0.0476
298.16	0.0366	0.0622	0.0380	0.0591	0.0386	0.0534
500	0.0378	0.0737	0.0404	0.0706	0.0416	0.0630
1000	0.0443	0.0996	0.0497	0.0959	0.0520	0.0851

practically coincide with those calculated in other similar species, for example in the corresponding XO_4^- tetraoxoanions [20], in BrO_3F [5], BrO_2F [7], IOF_5 [10] and in the corresponding XF_4O^- anions [9].

In the case of the interhalogen bonds, the I–F bond seems to be somewhat stronger than the respective Br–F bond. The same trend has been observed in the case of the XF_4O^- species [9], but it is not found systematically in the case of other pairs of structurally related bromine and iodine species (cf., e.g. [13, 22, 23]). On the other hand, these amplitude values are relatively high in comparison with those found in other similar X–F bonds [5, 7, 9, 10, 23], suggesting the presence of relatively weak interhalogen bonds with important ionic contributions. This weakness becomes also evident from the important temperature dependence of these bonds.

Regarding the mean amplitudes of the three non-bonded pairs they also show a strong temperature dependence. Values for the u_{OO} and u_{OF} pairs lie higher in the iodine species, whereas those for the u_{FF} pair lie higher in the bromine compound.

Finally, a comparison of the calculated values with those of the isostructural chlorine species [8] seems interesting. This comparison is presented in Table 3, at four temperatures.

As it can be seen, the values of the X–O bonds, even though comparable at the lowest temperature, show increasing differences in the order $ClO_2F_2^- < BrO_2F_2^- < IO_2F_2^-$, with increasing temperatures. This order follows the decrease of electronegativity of the halogen atoms, showing a reinforcement of the halogen-oxygen bond that parallels the electronegativity of the halogen atom. A different trend is observed for the interhalogen bonds. In this case, bond reinforcement occurs in the same direction as the increase in electronegativity difference between the two halogen atoms, i.e., the I–F bond is the strongest whereas the Cl–F bond is the weakest one.

As discussed earlier [8], in all these cases the presence of very strong halogen-oxygen bonds contributes to the enhancement of the ionic character of the halogen-fluoride bonds. Therefore, as an extreme description, the two axial X–F bonds may be considered as semi ionic p–σ bonds, with four electrons over the three centers [8, 24].

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