

Mean amplitude of vibration and Bastiansen–Morino shrinkage effect of some linear XF_2 species

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Abstract

Mean amplitudes of vibration of the linear XF_2^- difluorohalogenate (I) anions were calculated, using a recently reported set of consistent vibrational–spectroscopic data, in the temperature range between 0 and 1000 K. The study was complemented with similar calculations for KrF_2 and XeF_2 and with comparisons with other related species. Values of the Bastiansen–Morino shrinkage effect for these species were also estimated. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

The recent synthesis of the new $\text{N}(\text{CH}_3)_4\text{IF}_2$ salt, containing the linear IF_2^- anion [1], allowed a definitive assignment of its vibrational spectrum and to present a consistent set of vibrational frequencies for the related BrF_2^- and ClF_2^- species.

Using this set of vibrational data, we have calculated the mean amplitudes of vibration of the three mentioned interhalogen anions. For comparative purposes, we have also made a similar calculation for the related noble gas compounds KrF_2 and XeF_2 . Using results of these calculations we have also made an estimation of the Bastiansen–Morino shrinkage effect for all the mentioned species.

The calculations of the mean amplitudes of vibration were performed with the so-called ‘method of the characteristic vibrations’ of Müller et al. [2–4].

In the case of linear XY_2 species the Bastiansen–Morino shrinkage effect (δ) depends only on the value of the bending vibration [5] and can be estimated directly from the \sum_{22} matrix element, using the following relation [5]:

$$\delta = \frac{1}{2} \cdot R^{-1} \sum_{22} (R \text{ being the interatomic distance})$$

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2. Results and discussion

2.1. Mean amplitudes of vibration

The calculated mean amplitudes of vibration for the three interhalogen anions are presented in Table 1, whereas those for KrF_2 and XeF_2 are shown in Table 2.

As can be seen from Table 1, all the interhalogen bonds present very high mean amplitude values and an important temperature dependence. This behaviour may be considered as typical for very weak halogen–halogen bonds and for bonds which present important ionic contributions. The only interhalogen species which also shows mean amplitude values of similar magnitude are the D_{4h} species ClF_4^- , BrF_4^- and IF_4^- [6]. In all these cases this behaviour can be rationalized in terms of the semi-ionic three center-four electron bond model [7–9], which in the case of the XF_2^- species is apparently enhanced by the antisymmetric stretching motions [1], generating the unusual inversion of the two stretching modes (i.e., in these anions is $\nu_s > \nu_{as}$).

On the other hand, these effects are evidently lowered in the neutral noble gas fluorides, which shows lower mean amplitudes of vibration and temperature dependence (cf. Table 2). In the case of XeF_2 , the amplitude values are similar to that found for the Xe–F bonds in XeF_4 [10] and XeO_2F_2 [11], but lower as those calculated for the anions XeOF_5^- [12] and XeF_5^- [13].

Table 1
Mean amplitudes of vibration (\AA) for the three interhalogen anions

T (K)	ClF_2^-		BrF_2^-		IF_2^-	
	$u_{\text{Cl-F}}$	$u_{\text{F}\cdots\text{F}}$	$u_{\text{Br-F}}$	$u_{\text{F}\cdots\text{F}}$	$u_{\text{I-F}}$	$u_{\text{F}\cdots\text{F}}$
0	0.0537	0.061	0.0492	0.062	0.0495	0.063
100	0.0538	0.061	0.0492	0.062	0.0496	0.063
200	0.0556	0.063	0.0511	0.064	0.0520	0.066
298.16	0.0595	0.067	0.0550	0.069	0.0566	0.071
300	0.0596	0.067	0.0551	0.069	0.0567	0.071
400	0.0647	0.073	0.0599	0.075	0.0621	0.077
500	0.0699	0.079	0.0649	0.081	0.0676	0.084
600	0.0751	0.085	0.0698	0.088	0.0729	0.090
700	0.0801	0.091	0.0745	0.093	0.0779	0.096
800	0.0849	0.096	0.0791	0.099	0.0828	0.102
900	0.0895	0.101	0.0834	0.105	0.0874	0.108
1000	0.0940	0.106	0.0876	0.110	0.0918	0.113

Table 2
Mean amplitudes of vibration (\AA) for KrF_2 and XeF_2

T (K)	KrF_2		XeF_2	
	$u_{\text{Kr-F}}$	$u_{\text{F}\cdots\text{F}}$	$u_{\text{Xe-F}}$	$u_{\text{F}\cdots\text{F}}$
0	0.0453	0.062	0.0438	0.060
100	0.0454	0.062	0.0438	0.060
200	0.0465	0.064	0.0448	0.061
298.16	0.0492	0.069	0.0474	0.065
300	0.0493	0.069	0.0475	0.065
400	0.0530	0.075	0.0510	0.071
500	0.0569	0.081	0.0548	0.076
600	0.0609	0.087	0.0586	0.082
700	0.0648	0.093	0.0624	0.087
800	0.0686	0.099	0.0660	0.092
900	0.0722	0.104	0.0695	0.097
1000	0.0757	0.109	0.0729	0.102

Furthermore, a comparison of the values for the iso-electronic pairs $\text{BrF}_2^-/\text{KrF}_2$ and $\text{IF}_2^-/\text{XeF}_2$ clearly shows the expected bond re-inforcement on going from the anions to the neutral molecules, confirming again that the effect of semi-ionic bonds is less important in the second case [1].

The values presented in Table 1 also show that at room temperature the Cl–F bond is substantially weaker than the other two ones whereas the Br–F and I–F bonds are of similar strengths. This trend does not follow that of the respective stretching force constants ($f_r(\text{BrF}_2^-) > f_r(\text{ClF}_2^-) > f_r(\text{IF}_2^-)$ [1]), suggesting an additional mass effect which influences the mean amplitude values, as supported by the fact that with increasing temperatures the I–F bond becomes weaker than the Br–F bond.

On the other hand, the values for the non-bonded $\text{F}\cdots\text{F}$ distances follow the order $\text{IF}_2^- > \text{BrF}_2^- > \text{ClF}_2^-$ in the full temperature range.

In the case of KrF_2 and XeF_2 , the mean amplitudes of vibration follow the same trends as the force constants [1], pointing to somewhat stronger bonds in the case of the xenon fluoride.

Table 3
Values for the Bastiansen–Morino shrinkage effect (\AA)

T (K)	ClF_2^-	BrF_2^-	IF_2^-	KrF_2	XeF_2
0	0.0035	0.0027	0.0028	0.0030	0.0027
100	0.0037	0.0030	0.0033	0.0032	0.0030
200	0.0047	0.0041	0.0048	0.0043	0.0042
298.16	0.0061	0.0054	0.0067	0.0058	0.0057
300	0.0061	0.0054	0.0067	0.0058	0.0057
400	0.0078	0.0069	0.0087	0.0075	0.0074
500	0.0095	0.0085	0.0107	0.0092	0.0091
600	0.0112	0.0101	0.0127	0.0109	0.0108
700	0.0130	0.0117	0.0148	0.0126	0.0126
800	0.0147	0.0133	0.0169	0.0144	0.0143
900	0.0165	0.0149	0.0189	0.0161	0.0161
1000	0.0183	0.0166	0.0210	0.0179	0.0178

The present results for the ClF_2^- and BrF_2^- anions correct those of our previous calculations [14,15], based on the incorrect experimental spectroscopic data previously reported. Values calculated for XeF_2 and KrF_2 are in reasonably good agreement with the former results [16,17].

2.2. Bastiansen–Morino shrinkage effect

For the calculation of the Bastiansen–Morino shrinkage effect, the following internuclear distances were used: $d(\text{Cl–F}) = 1.90 \text{\AA}$, $d(\text{Br–F}) = 1.99 \text{\AA}$, $d(\text{I–F}) = 2.08 \text{\AA}$, $d(\text{Kr–F}) = 1.88 \text{\AA}$ and $d(\text{Xe–F}) = 1.98 \text{\AA}$ [1]. The obtained values, in the temperature range between 0 and 1000 K, as shown in Table 3. The results obtained for XeF_2 are in good agreement with those of a former calculation [18].

Interestingly, in the case of the XF_2^- species these values follow exactly the trend of the respective stretching force constant [1] in the full temperature range, that is, greater f_r -values generate a lower shrinkage effect.

In the case of the noble gas difluorides, although the values are very close, they are somewhat lower for XeF_2 , also in agreement with the trends shown by the force constants and mean amplitude values.

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