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Research Letter

Mean Amplitudes of Vibration of the IF_8^- Anion

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The mean amplitudes of vibration of the interesting IF_8^- anion (D_{4d} -symmetry), containing iodine (VII), were calculated from known spectroscopic and structural data in the temperature range between 0 and 1000 K. The results are discussed in comparison with those of related species.

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1. Introduction

Mean amplitudes of vibration are very useful and valuable parameters for the analysis of molecular structures and their vibrational behavior. In a similar way to vibrational frequencies and force constants, they can be very characteristic values for both bonded and nonbonded atoms [1, 2].

During years we have calculated mean amplitudes of vibration for a large series of molecules and ions containing halogen-halogen or halogen-oxygen bonds (for a recent review cf. [3]) and in this paper we present the results of our calculations for the interesting IF_8^- anion, which vibrational-spectroscopic behavior was only very recently definitely clarified [4].

As it is well known, the structure of this anion is a practically perfect Archimedean square antiprism [5], constituting the unique example of an interhalogen species presenting this geometry, which structural peculiarities are similar to those of the few other known examples of homoleptic species of this type, namely, ReF_8^{2-} , ReF_8^- , WF_8^{2-} , UF_8^{2-} , and XeF_8^{2-} [6, 7].

2. Calculations

The mean amplitudes of vibration were calculated with the method of the “characteristic vibrations” of Müller et al. [8] (cf. also [2, 9]). The necessary vibrational-spectroscopic data were taken from the recent paper of Dixon et al. [4] and

the geometrical parameters from the paper of Mahjoub and Seppelt [5].

3. Results and Discussion

The obtained results, in the temperature range between 0 and 1000 K, are shown in Table 1. Regarding the nonbonded $\text{F} \cdots \text{F}$ pairs, $\text{F} \cdots \text{F}$ (in plane) refers to the pairs within one hemisphere of the anion, whereas $\text{F} \cdots \text{F}$ (betw. planes) refers to neighboring pairs belonging to different hemispheres.

The analysis of the so far available data of mean amplitude values for I–F bonds has shown that the extreme values lie between 0.0377 Å (for IF_6^+) and 0.0602 Å (for IF_5^{2-}) [3, 10], in agreement with the fact that in the first case iodine presents the oxidation state +7 and a positive charge whereas in the other one the iodine is in the oxidation state +3 and not only presents two negative charges but also an important congestion effect on the molecular plane, in which the fluorine atoms are practically in contact [3, 10, 11]. Besides, these two species present also the greatest differences in bond lengths found in I/F species (1.75 Å for IF_6^+ , 2.095 Å for IF_5^{2-}) [3, 12]. Furthermore, the specially high mean amplitude value of IF_5^{2-} is in good agreement with the very low force constant calculated for the I–F bonds in this anion (1.53 mdyne/Å [11]).

The values of the mean amplitudes of vibration calculated for the I–F bonds of IF_8^- fall clearly into the mentioned

TABLE 1: Mean amplitudes of vibration (in Å) for the IF_8^- anion in the temperature range between 0 and 1000 K.

T (K)	$u_{\text{I-F}}$	$u_{\text{F...F}}$ (in plane)	$u_{\text{F...F}}$ (betw. planes)
0	0.0426	0.062	0.072
100	0.0426	0.062	0.072
200	0.0433	0.064	0.079
298.16	0.0455	0.069	0.089
300	0.0456	0.069	0.089
400	0.0487	0.075	0.099
500	0.0521	0.082	0.109
600	0.0556	0.088	0.118
700	0.0590	0.094	0.127
800	0.0624	0.100	0.135
900	0.0656	0.105	0.143
1000	0.0688	0.110	0.150

TABLE 2: Mean amplitudes of vibration (in Å) of some iodine (VII) species at three different temperatures ((eq): equatorial I–F bonds; (ax): axial I–F bonds).

Species	0 K	298.16 K	600 K	Reference
IF_6^+	0.0367	0.0377	0.0433	[13]
IF_7 (eq)	0.0408	0.0430	0.0516	[14]
IF_7 (ax)	0.0378	0.0390	0.0454	[14]
IOF_6^- (eq)	0.0418	0.0444	0.0537	[15]
IOF_6^- (ax)	0.0396	0.0414	0.0491	[15]
$\text{IO}_2\text{F}_5^{2-}$	0.0455	0.0499	0.0625	[16]
IO_2F_4^-	0.0421	0.0448	0.0544	[17]
IF_8^-	0.0426	0.0455	0.0556	this work

range as it can also be seen from the comparative data presented in Table 2. This comparison shows that the values for IF_8^- are appreciably higher than those found for IF_6^+ showing again the effect of the geometry and of the negative charge over bond weakening [3]. Besides, these amplitude values are only somewhat higher than those calculated for the equatorial IF_7 bonds.

On the other hand, the values calculated for IF_8^- lie relatively close to those of the equatorial I–F-bonds of IOF_6^- . In comparison with the interhalogen bonds of the other two fluorooxoanions containing iodine (VII), IF_8^- presents lower mean amplitudes of vibration (i.e., stronger I–F bonds) than $\text{IO}_2\text{F}_5^{2-}$ but weaker I–F bonds than IO_2F_4^- , in the full temperature range.

Concerning the amplitude values of the nonbonded pairs, those of the same hemispheres are always lower and show a smaller temperature dependence than those between F-atoms belonging to the different hemispheres.

Conclusions

Mean amplitudes of vibration of the IF_8^- anion clearly lie in the expected range determined for I–F bonds. These values point to relatively weak bonds, when compared with iodine fluorine bonds present in other simple iodine (VII)

species, such as IF_7 or IF_6^+ , in agreement with the higher coordination number and with the presence of a negative charge in the case of the IF_8^- anion.

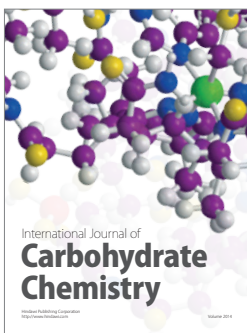
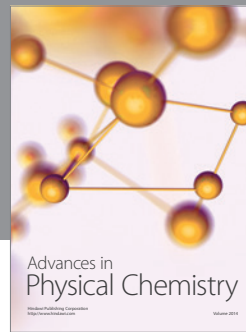
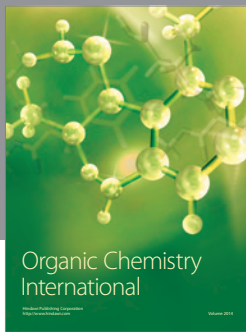
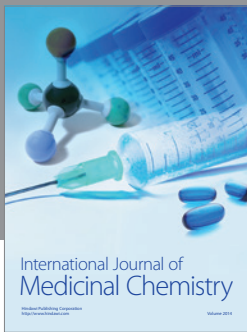
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