

Mean amplitudes of vibration of the trifluorosulfite anion

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Abstract

Mean amplitudes of vibration of the recently reported SOF_3^- anion were calculated from vibrational spectroscopic data, in the temperature range between 0 and 1000 K. The results are briefly discussed and some comparisons with isoelectronic molecules and ions are made. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The use of anhydrous tetramethylammonium fluoride as a source of “naked fluoride” [1] has allowed the recent synthesis of a considerable number of new and interesting fluoroanions [2–4]. The $\text{N}(\text{CH}_3)_4\text{F}$ is a valuable source of soluble fluoride ion combined with a large and relatively inert counter cation. Owing to its high solubility, $\text{N}(\text{CH}_3)_4^+\text{F}^-$ readily reacts with molecules of low fluoride ion affinity.

Using this fluoride ion source it was recently possible to prepare, for the first time, a salt of the fluorosulfite anion, SOF_3^- . It was stabilized as the tetramethylammonium salt, in an almost quantitative yield, by reaction of $\text{N}(\text{CH}_3)_4\text{F}$ with an excess of SOF_2 [5].

The spectroscopic study of the new anion, complemented with theoretical ab initio calculations, confirms the presence of a pseudo-trigonal bipyramidal structure with two long axial S–F bonds. The remaining fluorine atom, the oxygen atom and a sterically active electron lone pair occupy the equatorial plane.

As a continuation of our studies on the vibrational and bond properties of new simple inorganic species (cf. [6] and references therein), we have now undertaken the calculation of the mean amplitudes of vibration of this novel anion in a wide temperature range. The calculations were performed with the so-called “method of the characteristic vibrations” of Müller and coworkers [7–9].

The following structural parameters were used: $d(\text{S}-\text{F}_{\text{ax}})=1.79 \text{ \AA}$; $d(\text{S}-\text{F}_{\text{eq}})=1.60 \text{ \AA}$; $d(\text{S}-\text{O})=1.43 \text{ \AA}$; $\text{angle}(\text{O}-\text{S}-\text{F}_{\text{eq}})=106.7^\circ$ and $\text{angle}(\text{F}_{\text{ax}}-\text{S}-\text{F}_{\text{ax}})=166.5^\circ$ [5]. The necessary vibrational frequencies were also taken from the same literature source [5].

2. Results and discussion

The calculated mean amplitudes of vibration, in the temperature range between 0 and 1000 K, are shown in Table 1.

A first analysis of these values immediately confirms that the S–O bonds are particularly strong and that the S– F_{eq} bonds are appreciably stronger than the axial ones in agreement with the estimated bond distances [5]. As it can also be seen, the S– F_{ax} bonds display significant temperature dependencies, a behavior that is also characteristic for relatively long and weak chemical bonds.

In order to advance to a better characterization of the bonding, a comparison with the isoelectronic and isostructural ClOF_3 oxofluoride [10,11] appears interesting. In general, one expects that equivalent bonds will be stronger for a molecule than for an isoelectronic anion, generating somewhat lower mean amplitude values for the bonds in the neutral molecule.

In the case of ClOF_3 , mean amplitude values have been experimentally obtained from a gas phase electron diffraction study and where compared with those calculated from spectroscopic data [10]. We have recalculated these values, using the same procedure as for fluorosulfite, and found excellent agreement with the previously published data. Our

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Table 1
Mean amplitudes of vibration (\AA) for SOF_3^-

T (K)	$u_{\text{S-O}}$	$u_{\text{S-F}_{\text{ax}}}$	$u_{\text{S-F}_{\text{eq}}}$	$u_{\text{F}_{\text{ax}}\text{F}_{\text{ax}}}$	$u_{\text{O-F}_{\text{eq}}}$
0	0.0365	0.0488	0.0441	0.060	0.055
100	0.0365	0.0488	0.0441	0.060	0.056
200	0.0365	0.0496	0.0443	0.062	0.062
298.16	0.0366	0.0519	0.0454	0.067	0.070
300	0.0366	0.0520	0.0454	0.067	0.070
400	0.0370	0.0553	0.0474	0.072	0.078
500	0.0377	0.0591	0.0499	0.078	0.086
600	0.0387	0.0629	0.0526	0.084	0.093
700	0.0398	0.0667	0.0554	0.090	0.099
800	0.0411	0.0705	0.0581	0.095	0.106
900	0.0425	0.0741	0.0609	0.100	0.112
1000	0.0439	0.0776	0.0636	0.105	0.118

results, for some selected temperatures, are presented in Table 2 in order to facilitate the comparative discussions.

A comparison of the results for both species confirms the above mentioned expectations. The strong Cl–O bond of ClOF_3 presents slightly lower values than the S–O bond of SOF_3^- over the entire temperature range. The same behavior is observed when comparing the respective X–F_{ax} bonds. Interestingly, this trend is not maintained in the case of the X–F_{eq} bonds for which the amplitude values suggest a slightly stronger bond in the case of the fluorosulfite anion. At low temperatures the amplitude values for both species are comparable, but at higher temperatures, the anion shows slightly lower values. A comparison of the respective vibrational stretching energies and bond distances also shows a higher frequency and a slightly shorter bond for the anion [5,11].

The different characteristics of the S–F_{ax} and S–F_{eq} bonds, evidenced by significant differences in their mean vibrational amplitudes (cf. Table 1) and supported by the different bond lengths (1.79 and 1.60 \AA , respectively [5]), points again, to the existence of two clearly different S–F bonds, as it is also the case in ClOF_3 [10,11]. In both cases, the X–F_{eq} bonds can be considered as mainly covalent, whereas the axial ones can be rationalized in terms of semi-ionic (3c-4e) bonds.

Finally, also the two analyzed non-bonded, F_{ax}F_{ax} and F_{eq}O pairs, show differences. For the anion, $u_{\text{F}_{\text{ax}}\text{F}_{\text{ax}}} > u_{\text{O-F}_{\text{eq}}}$ at the lowest temperatures, but an inversion of this trend becomes apparent at room temperature. In the oxofluoride, $u_{\text{F}_{\text{ax}}\text{F}_{\text{ax}}}$ remains higher in the full temperature range. Between room temperature and 1000 K, the temperature dependencies of both pairs are comparable.

Table 2
Mean amplitudes of vibration (\AA) for ClOF_3 at selected temperatures

T (K)	$u_{\text{Cl-O}}$	$u_{\text{Cl-F}_{\text{ax}}}$	$u_{\text{Cl-F}_{\text{eq}}}$	$u_{\text{F}_{\text{ax}}\text{F}_{\text{ax}}}$	$u_{\text{O-F}_{\text{eq}}}$
0	0.0353	0.0483	0.0442	0.061	0.052
298.16	0.0354	0.0515	0.0445	0.067	0.062
500	0.0364	0.0588	0.0506	0.079	0.074
1000	0.0421	0.0774	0.0650	0.106	0.101

Table 3
Comparison of mean amplitudes of vibration (\AA) at 298 K, of SOF_3^- and isoelectronic species

Species	$u_{\text{X-O}}$	$u_{\text{X-F}_{\text{ax}}}$	$u_{\text{X-F}_{\text{eq}}}$	Reference
PF_4^-		0.0603	0.0442	[12]
SOF_3^-	0.0366	0.0519	0.0454	This work
ClO_2F_2^-	0.0366	0.0622		[13]
SF_4		0.050	0.044	[14]
ClOF_3	0.0354	0.0515	0.0445	This work
ClF_4^+		0.0458	0.0417	[15]

A great number of molecules and ions that are isoelectronic with SOF_3^- are known [5]. Therefore, it also seems valuable to make comparisons among all of them in order to obtain a general picture for the mean amplitudes of vibration of these types of systems. A comparison of values is presented in Table 3. From the tabulated data, some general trends become evident:

- The mean amplitudes of vibration for the X–O bonds lie in a very restricted range. For strong bonds, like those included in the table, the amplitude values are, as expected [8], very characteristic. They can be compared with values calculated for SO_3F^- , SOF_2 , SOF_4 , ClO_2 , ClO_4^- and similar species [8].
- In all cases, the mean amplitude values for the equatorial X–F bonds are lower than those of the corresponding axial bonds. The amplitude values of these last mentioned semi-ionic bonds cover a relatively broad range and are rather uncharacteristic.
- The amplitude values for the equatorial bonds, on the other hand, appear to be very characteristic. They are comparable, for example, to values calculated for PF_3 and for the PFX_2 and PF_2X mixed halides [8] as well as with those of ClF [16] and ClF_2^+ [17], in which strong covalent interhalogen bonds are present.

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